Prediction of Extractable Metals in Retention Pond Sediments at Surface Coal Mines

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ABSTRACT / Fifty-two grab samples of bottom sediment in settling ponds were obtained at 17 surface coal mines in the eastern and midwestern U.S. A series of laboratory extraction procedures were designed to simulate a wide range of possible natural conditions. The three types of laboratory extraction procedures were (1) a low-pH buffered extract; (2) a series of low-pH, near-neutral-pH, and high-pH nonbuffered extracts; and (3) a DTPA extract. For the transition metals examined (Fe, Mn, Ni, Zn, Co, Cu, Cr, Fe, Al), higher percentages were extracted by the low-pH buffered extract than by the low-pH nonbuffered extract and the DTPA extract. Within the nonbuffered series, higher percentages of individual metals were extracted at lower pH levels. There was generally a consistent order of "extractability" for all the extracts performed. At the mines using a chemical treatment to neutralize acid mine drainage, Mn was the most mobile and Fe and Al the least mobile of the metals considered; at the mines not using a chemical treatment, Ni, Zn, and Co were among the most mobile and Fe, Al, and Cr the least mobile of the metals studied.

Two stepwise regression procedures (maximum R^2 improvement and backward elimination) were used to suggest a ranking of independent variables that influence extractable metals. Statistically significant independent variables differed for the various metals. In general, the total amount of metal present was most important in determining metal extractability in the buffered extract at the mines using chemical treatment, and variables related to the natural acidity or alkalinity of the sediment and element interrelationships were important in the other extracts. A detailed examination of regression equations for the buffered extract suggests that it is possible to predict extractable metals using simple regression models based on the total amount of metals present, metals interrelationships, and sediment acidity or alkalinity.

Background and Introduction

Previous work on sediments and sediment-water interactions in coal-mining related systems has focused on physical, chemical, or mineralogical aspects of sediments and sediment-water systems (Gang and Langmuir 1974; Nesbit 1980; Barnhisel and Massey 1969; Massey 1972; Smith and Sobek 1978; Iverson and others, 1978; Krothe and others, 1980; Moran and others, 1978); laboratory studies on dominant reactions in mine drainage and chemistry of sediment-water systems (Singer and Stumm 1968; Lenda and Gast 1973; Stumm and Morgan 1970; Farrah and others 1980; Kerndorff and Schnitzer 1980); simulated weathering studies of specific rock units (Caruccio 1968); and column leaching studies (Infanger and Hood 1980). In this study, which focuses on preliminary work on sediments contained in coal strip mine settling ponds, a more empirical approach based on a series of laboratory extraction techniques was adopted to examine extractable metals over a range of pH conditions in this mixed natural system. Two major reasons for this approach are

(1) To provide guidance for experimental design for more detailed work on strip mine settling pond sediments and

(2) To begin to develop simple analytical techniques which give meaningful information on sediment toxicity to mine operators and regulatory agencies.

Grab samples of the sediments retained in settling ponds were obtained at 17 eastern and midwestern U.S. strip mines. The pond sediments included transported suspended solids as well as precipitates that were formed mainly as a result of chemical neutralization treatment processes for acid mine drainage. These precipitates can include hydrated ferrous and/or ferric oxides, gypsum, hydrated aluminum oxide, varying amounts of sulfates, carbonates, bicarbonates, and trace amounts of phosphate and metals (Lovell 1970). Seven of the mines used chemical neutralization treatment(s); the treatments involved the use of hydrated lime, soda ash, sodium hydroxide, and anhydrous ammonia. These reagents were mixed with the raw mine water prior to flow into settling ponds; in some cases, mixing occurred in the settling pond itself. Approximately one-half of the samples (28 of 52) were obtained at these seven mines. At both these mines and those that did not use chemical treatment(s), mine drainage was retained in one or more settling ponds in order to reduce concentrations of suspended solids before discharge.

This study was initiated after a comparison of metals concentrations in mine waters before and after chemical treatment indicated significant reductions following treatment. Total analyses of metals concentrations in sediment samples had indicated higher concentrations in the pond sediments of those mines where chemical treatment was used; this occurred due to removal of the metals from mine drainage as a result of the chemical treatment to raise the pH. In effect, the ponds at mines with chemical treatment appear to concentrate metals removed from mine drainage. At most mines, the last solid materials contacted by the mine effluent before discharge offsite are the settling-pond sediments. The natural potential for remobilization may be high due to variations in influent water quality.

In particular, a major purpose of this study was to contrast

Environ Geol 4, 223–238

extractable metals in pond sediments at various pH levels at mines with chemical treatment to those at mines without treatment. The techniques used to investigate extractable metals in the sediments consisted of three types of laboratory extractions, including a buffered system (sodium acetate–acetic acid) to simulate maximum extractable metals under long-term equilibrium conditions of contact with mine waters, a nonbuffered system of water extracts at extreme pH variations to investigate short-term contact of mine waters with sediments, and a chelate system to examine extractable metals available for plant uptake. The chelate chosen was diethylene triaminepentaacetic acid (DTPA), which in previous soils work (Council on Soil Testing and Plant Analysis 1974) has been demonstrated to be correlatable to available Zn, Mn, Fe, and Cu. The metals examined were Fe, Mn, Al, Cu, Co, Cd, Zn, and Cr. The selection of laboratory extraction techniques—as opposed to sequential extractions, leaching columns, modifications of soxhlet extraction apparatus, or various types of simulated weathering experiments—was based on two factors:

(1) Good reproducibility of results based on simple procedures and

(2) As indicated previously, the eventual goal of developing meaningful standardized procedures useful to both the coal industry and regulatory personnel.

Methods

Fig. 1 shows the regional distribution of study sites. The selection of sites was designed to maximize climatologic and geologic diversity in the Appalachian and Interior Coal Provinces. Because the study was restricted to surface mines, sites were generally limited to settings near coal basin margins.

Grab samples were taken as close as possible to the centerline of ponds, generally both in the influent "delta" and at the point of discharge. In a few cases, the drainage channel between a chemical treatment facility and a pond was lined with sediment; such channel sediment was also sampled. Samples were retained in plastic bags and kept refrigerated until they could be air-dried prior to analysis. The samples obtained included a mixture of (1) transported overburden materials (both weathered and unweathered) broken down by the mining process and pumped with mine drainage from the active pit; (2) natural sediments and soil eroded from the pond perimeter; (3) poorly crystalline precipitates mainly from chemical treatment processes (the precipitates generally included iron, manganese, and aluminum oxyhydroxides and calcium sulfates); and (4) unreacted solid neutralizing reagents, such as hydrated lime or soda ash, resulting from overtreatment.

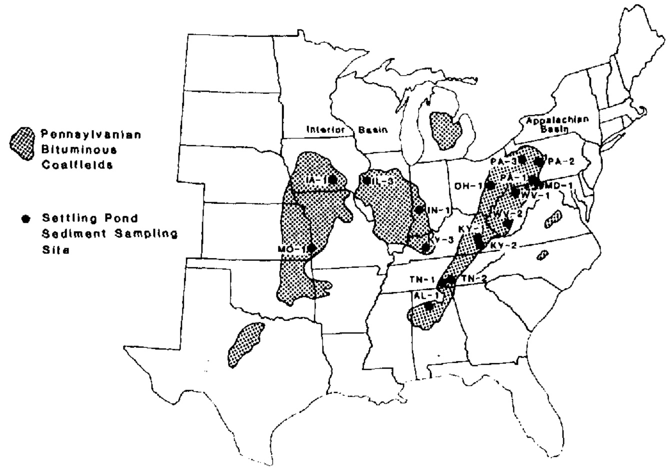

Figure 1. Regional distribution of study sites.

Extraction techniques were chosen to simulate a wide range of possible pH conditions in the pond environment so that variations in metals remobilization could be described in terms of potential natural settings that might occur over time in a single pond. All methods are described or referenced in Fig. 2; all analyses were done at Argonne National Laboratory. Analyses were subject to appropriate laboratory quality control, including replicates and inclusion of U.S. Geological Survey standard rock samples. All metals analysed were done on a Perkin-Elmer Model 603 Atomic Absorption Spectrophotometer. Complementary analytical work to characterize basic physical and chemical properties of the sediments included determinations of total carbon, total sulfur, sulfate sulfur, neutralization potential, pH, and Munsell color. The carbon and sulfur analyses were done on a Leco furnace. Sulfide sulfur values reported in this paper consist of "(total sulfur minus sulfate sulfur)." In addition, X-ray diffraction work to characterize the mineralogy of the sediments was performed by Dr. Robert Doehler of Northeastern Illinois University, Chicago. Standard X-ray techniques were utilized, including use of corundum as an internal standard and comparative runs with commercially available standard clays to obtain a semiquantitative estimate (±5 to 10%) of "percent clay minerals" present in each sample.

A statistical analysis approach to data interpretation was advised due to the physical and chemical diversity of the sediments. Two Statistical Analysis System (SAS 1979) stepwise regression procedures were chosen in an effort to determine the relative statistical significance of several system variables. The variables under consideration include that those might be expected to influence extractable metals, namely, the total amount of a given metal present, various measures of sample acidity–alkalinity, and elemental interrelationships.

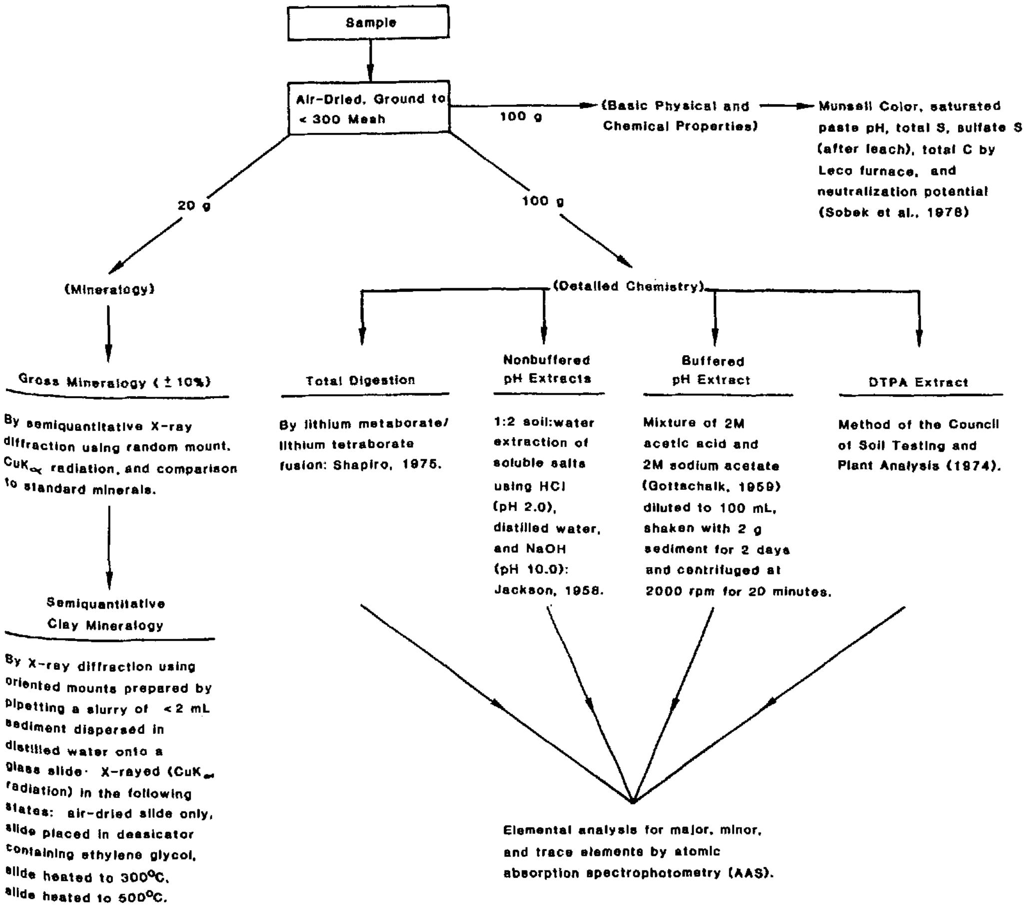

Figure 2. Schematic diagram for analysis of sediments.

The two procedures chosen were the maximum R^2 improvement method (MAXR) and the backward elimination (BACKWARD) technique, both of which are discussed in detail later in this paper.

Results

Table 1 indicates basic physical/chemical properties of the various sediment samples; samples were designated by mine number (using state abbreviations) and sample number. Note that the range of properties was extreme. The mines using a chemical neutralization treatment for mine drainage and the various treatments were as follows:

Mine KY-3	20% solution of sodium hydroxide
Mine MD-1	Hydrated lime [$Ca(OH)_2$], soda ash (Na_2CO_3), and an alkaline paper mill waste
Mine MO-1	Anhydrous ammonia (NH_3)
Mine PA-1	Hydrated lime
Mine PA-3	Soda ash (or hydrated lime)
Mine WV-1	Hydrated lime and soda ash
Mine WV-2	Soda ash

At those sites using hydrated lime, especially MD-1 and WV-1, the high values for neutralization potential, pH, total carbon, and percent calcium (not reported in Table 1) were good indicators of overtreatment, thus confirming previous field observations. At some sites, for example PA-3, the pond sediments included a substantial percentage of coal fines and pyritic black shale, which was reflected in high total carbon, high sulfide sulfur, low neutralization potential, and low pH. Mineralogically, all the sediment samples were dominated by quartz and nonexpandable clay minerals (mainly kaolinite and illite). However, at mines with chemical neutralization treatment, variable portions of the resulting sediment samples consisted of precipitates and severely weathered minerals that resulted in high background scattering of X-radiation and,

Table 1. Basic physical/chemical properties of sediments.

Mine #/sample #	Munsell color	pH	Neutralization potential T. $CaCO_3$/1000 T.	% C	% S	% SO_4^{-2}
MO-1/1	2.5Y4/2	7.2	164	4.7	0.33	0.29
MD-1/1	10YR6/4	9.1	405	4.7	4.6	0.00
MD-1/2	2.5Y5/4	2.7	−2.1	6.1	1.6	0.05
MD-1/3	2.5Y6/4	6.6	8.4	2.2	0.15	0.05
MD-1/4	10YR6/2	12.1	370	8.7	7.6	0.20
MD-1/5	10YR6/2	9.1	310	3.8	8.0	0.00
MD-1/6	10YR5/3	8.5	332	4.7	2.4	0.10
MD-1/7	2.5Y7/4	5.4	5.0	0.77	0.14	0.02
MD-1/8	10YR5/4	8.2	136	6.7	7.0	0.10
AL-1/1	2.5Y6/4	5.4	0.77	4.3	0.38	0.08
IL-3/1	2.5Y4/0	8.2	124	11	15	15
IL-3/2	2.5Y5/4	5.4	30	2.9	0.08	0.06
IA-1/1	5Y4/2	6.9	29	3.1	0.13	0.05
PA-1/1	5Y5/3	7.3	15	5.1	0.03	0.02
PA-1/2	10YR6/2	7.3	13	3.5	0.05	0.04
PA-1/3	10YR3/1	8.3	94	32	0.70	0.55
PA-1/4	2.5Y5/2	7.4	22	4.0	0.06	0.04
PA-2/1	5Y5/2	6.7	4.4	21	0.43	0.35
PA-2/2	5Y5/2	6.5	5.3	17	0.40	0.35
PA-2/3	5Y4/1	6.7	2.3	2.4	0.04	0.01
PA-2/4	10Y6/4	6.7	9.9	8.8	0.33	0.33
PA-2/5	2.5Y5/2	6.3	6.6	37	0.65	0.60
PA-3/1	2.5Y6/4	5.7	1.5	5.5	0.06	0.06
PA-3/2	10YR5/1	3.0	−2.2	13	1.3	1.3
PA-3/3	5Y5/2	2.7	−4.0	8.3	2.1	1.9
PA-3/4	5Y5/2	3.5	0.98	18	1.1	0.93
PA-3/5	5Y6/4	4.1	3.5	3.0	0.28	0.15
OH-1/1	2.5Y3/2	3.5	11	9.1	1.1	0.85
OH-1/2	2.5Y5/2	4.7	4.5	6.0	0.83	0.45
IN-1/1	5Y6/4	7.9	54	1.4	0.08	0.06
IN-1/2	2.5Y6/2	7.9	233	3.8	0.09	0.06
IN-1/3	10YR5/1	5.5	31	6.3	1.1	0.93
IN-1/4	10YR6/3	8.0	246	2.7	0.06	0.05
IN-1/5	2.5Y6/4	7.6	58	2.5	0.20	0.18
TN-1/1	10YR5/1	3.2	−3.5	16	1.1	0.85
TN-1/2	5Y4/1	3.4	0.26	18	1.5	0.80
TN-1/3	2.5Y5/2	3.5	−2.0	7.9	0.50	0.30
TN-2/1	5Y6/3	6.2	2.7	2.3	0.07	0.03
TN-2/1	2.5Y6/4	6.3	2.2	1.2	0.07	0.04
TN-2/3	2.5Y6/4	4.0	2.4	0.05	0.02	—
TN-2/4	2.5Y6/4	4.0	0.46	1.5	0.05	0.03
TN-2/5	5Y6/3	5.5	2.0	1.4	0.01	0.01
TN-2/7	2.5Y6/4	4.3	−0.26	2.2	0.08	0.03
TN-2/8	2.5Y6/4	4.5	−0.98	1.3	0.07	0.04
KY-1/1	10YR5/2	7.7	22	5.0	0.05	0.05
KY-2/1	10YR6/4	6.7	6.1	1.5	0.01	0.01
KY-2/2	10YR6/3	6.7	5.4	1.9	0.13	0.08
KY-3/1	10YR4/4	8.4	156	2.9	0.60	0.05
KY-3/2	10YR6/3	7.3	18	2.6	0.07	0.04
KY-3/3	2.5Y6/2	6.8	4.3	2.2	0.13	0.02
KY-3/4	10YR5/1	7.5	71	1.7	0.08	0.04
WV-2/1	2.5Y5/4	6.2	3.5	3.6	0.04	0.05
WV-2/2	5Y5/3	5.0	1.2	5.4	0.08	0.05
WV-2/3	2.5Y6/4	5.0	1.2	2.6	0.01	0.01
WV-2/4	10YR5/2	5.8	2.0	4.2	0.08	0.04
WV-1/1	2.5Y5/4	7.2	12	2.3	0.01	0.01
WV-1/2	5Y5/4	7.3	89	5.7	0.38	0.27
WV-1/3	5Y6/3	7.5	134	3.8	0.31	0.17
WV-1/4	2.5Y7/4	7.1	23	2.7	0.07	0.03

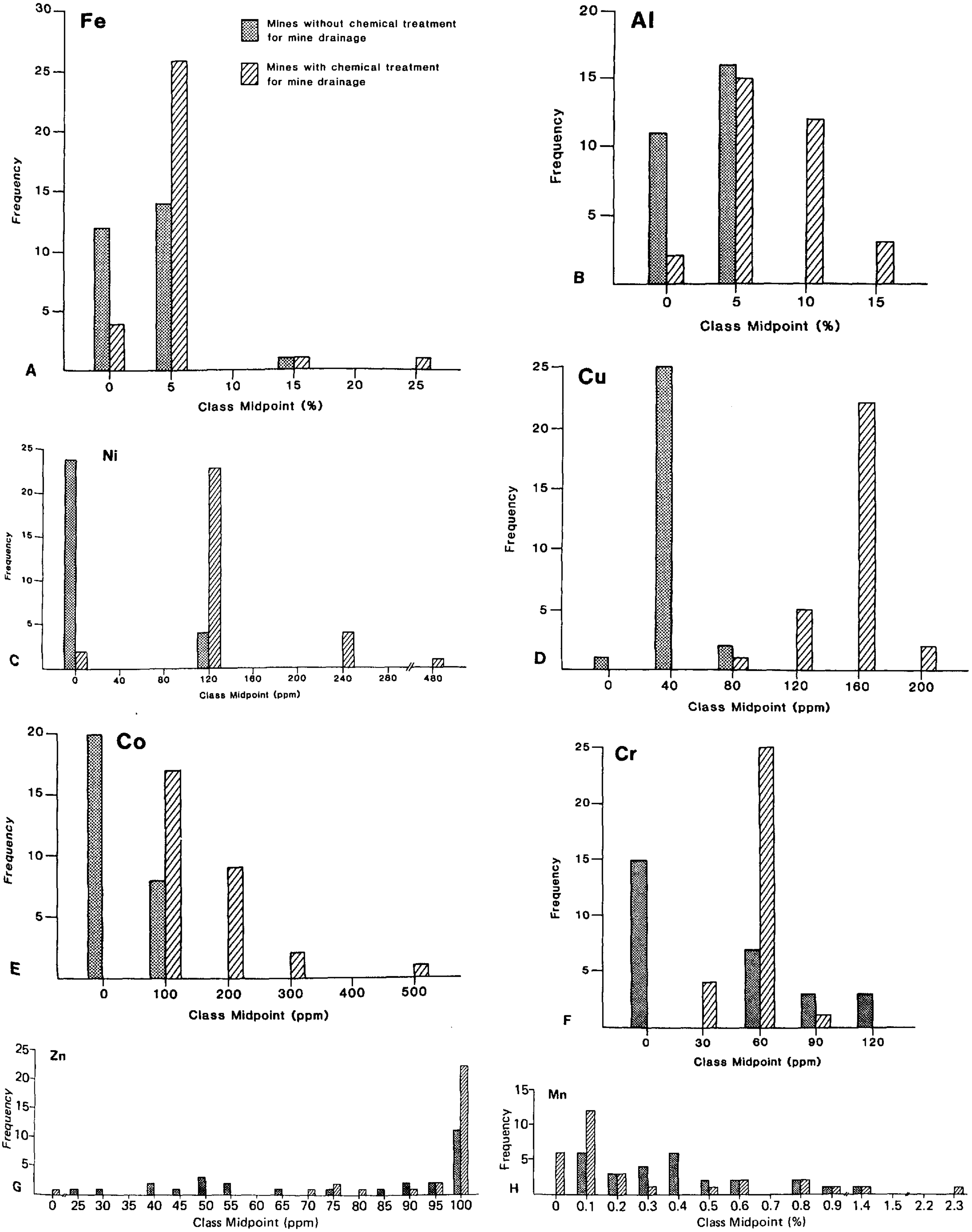

Figure 3. Histograms for total metals concentrations in sediments.

Table 2. Summary statistics for extractable metals in settling pond sediments, expressed as fraction of total metal present.[a] Mines with chemical treatment (For percent extractable, multiply mean value by 10^2.)

	pH 3.4			ph 2.0			Distilled water			pH 10.0			DTPA (pH 7.3)		
Metal	X	N	SD	X	N	SD	X	N	SD	X	N	SD	X	N	SD
Al	0.0093	29	0.013	0.00043	30	0.00069	0.00013	30	0.00041	0.000058	29	0.00020	0.000055	30	0.00015
	(R = 0.00046-0.056)			(R = 0-0.0023)			(R = 0.0000031-0.0022)			(R = 0-0.0011)			(R = 0-0.00075)		
Co	0.17	28	0.12	0.019	29	0.032	0.012	29	0.036	0.0058	28	0.019	0.027	29	0.027
	(R = 0.015-0.39)			(R = 0.00049-0.14)			(R = 0-0.18)			(R = 0-0.010)			(R = 0.0012-0.11)		
Cr	0.031	29	0.036	0.0013	30	0.0026	0.000016	30	0.000090	0.00076	29	0.0036	0.0022	30	0.0014
	(R = 0-0.146)			(R = 0-0.0098)			(R = 0-0.00049)			(R = 0-0.020)			(R = 0-0.0051)		
Cu	0.026	29	0.016	0.0052	30	0.012	0.0026	30	0.0079	0.00060	29	0.00071	0.0087	30	0.0064
	(R = 0.0064-0.63)			(R = 0-0.058)			(R = 0-0.38)			(R = 0.0033)			(R = 0.0012-0.031)		
Fe	0.0097	29	0.0086	0.0028	30	0.0047	0.00043	30	0.0011	0.00010	29	0.00021	0.0026	30	0.0022
	(R = 0-0.041)			(R = 0-0.18)			(R = 0.000018-0.0054)			(R = 0-0.00081)			(R = 0.00021-0.0079)		
Mn	0.50	26	0.18	0.15	29	0.19	0.051	29	0.11	0.019	28	0.050	0.12	29	0.099
	(R = 0.11-0.81)			(R = 0-0.59)			(R = 0.000014-0.41)			(R = 0-0.22)			(R = 0.000089-0.30)		
Ni	0.31	29	0.24	0.021	30	0.045	0.018	30	0.043	0.0061	29	0.019	0.034	30	0.038
	(0.039-0.83)			(R = 0-0.16)			(R = 0-0.21)			(R = 0-0.098)			(R = 0.0043-0.14)		
Zn	0.29	28	0.16	0.035	29	0.059	0.019	29	0.047	0.012	28	0.023	0.047	29	0.036
	(R = 0.075-0.68)			(R = 0.00015-0.22)			(R = 0.000080-0.22)			(R = 0.00097-0.11)			(R = 0.0023-0.15)		

[a] X = mean; N = number of samples; SD = standard deviation; and R = range.

Table 3. Summary statistics for extractable metals in settling pond sediments, expressed as fraction of total metal present. Mines without chemical treatment. (For percent extractable, multiply mean value by 10^2.)

	pH 3.4			ph 2.0			Distilled water			pH 10.0			DTPA (pH 7.3)		
Metal	X	N	SD	X	N	SD	X	N	SD	X	N	SD	X	N	SD
Al	.0059	28	.0055	.0023	28	.0036	.00029	28	.00054	.00031	28	.00062	.000090	28	.00016
	(R = .00071-.031)			(R = 0-.016)			(R = .000010-.0023)			(R = 0-.0023)			(R = 0-.00062)		
Co	.11	28	.085	.060	28	.12	.021	28	.040	.014	28	.031	.050	28	.046
	(R = 0-.29)			(R = .0018-.62)			(R = 0-.15)			(R = 0-.13)			(R = .0049-.14)		
Cr	.0075	14	.0084	.00034	13	.00074	0	13	0	.00007	13	.00018	.0018	13	.0015
	(R = 0-.026)			(R = 0-.0026)						(R = 0-.00063)			(R = 0-.0045)		
Cu	.083	28	.052	.024	28	.042	.0051	28	.013	.0017	28	.0014	.024	28	.015
	(R = 0-.22)			(R = 0-.18)			(R = 0-.063)			(R = 0-.0060)			(R = 0-.063)		
Fe	.023	28	.024	.0048	28	.0083	.0014	28	.0034	.00048	28	.00080	.0048	28	.0047
	(R = .0027-.12)			(R = 0-.032)			(R = 0-.015)			(R = 0-.0036)			(R = .00038-.018)		
Mn	.074	28	.043	.035	28	.033	.0011	28	.017	.0044	28	.017	.029	28	.027
	(R = .0056-.20)			(R = .00001-.11)			(R = .00001-.048)			(R = 0-.045)			(R = .00063-.15)		
Ni	.18	25	.097	.045	25	.11	.030	25	.039	.016	25	.029	.057	25	.066
	(R = 0-.47)			(R = 0-.51)			(R = 0-.11)			(R = 0-.092)			(R = 0-.30)		
Zn	.14	28	.075	.049	28	.055	.038	28	.10	.018	28	.017	.048	28	.074
	(R = .0058-.32)			(R = .00022-.23)			(R = .00049-.54)			(R = .00058-.066)			(R = .00015-.36)		

frequently, a lack of discernable peaks to which substantial portions of the sample could be assigned.

Fig. 3 indicates the differences in total metals concentrations at all 17 mines. The histograms in most cases indicate separate populations for total metals concentrations in the two groups of samples—the mines using treatment vs. the mines not using treatment. This is most apparent for copper and least apparent for iron, where the two subsets merge into a single population. Even for iron, however, the high values of the distribution are dominated by mines that use a chemical treatment. Thus, the settling-pond sediments at mines using treatment are generally characterized by higher total metals concentrations. Presumably, these higher concentrations are due to removal of dissolved metals from the treated mine effluent by one of several possible mechanisms: direct precipitation as discrete solid phases; co-precipitation with dominant iron, manganese, and aluminum solid phases; or adsorption onto clays and colloidal precipitates. Other possibilities for elevated total metals concentrations in pond sediments as a whole include regional geochemical variations and substitutions by trace metals in dominant mineral phases.

Tables 2 and 3 summarize extractable metals concentrations in the pond sediments by the various techniques used in this investigation. Table 2 includes only those mines using a chemical neutralization treatment; Table 3 includes those mines without treatment. The results are expressed as fraction of total metal present. Note that in the tables there is a relatively consistent order in the ease of extractability of the metals considered. Using the average values, the decreasing ease of extractability is as follows:

Mines with treatment (Table 2): Mn > Ni, Zn, Co > Cu, Cr > Fe, Al

Mines without treatment (Table 3): Ni, Zn, Co > Mn, Cu > Fe, Al, Cr

Several significant trends can be noted from Tables 2 and 3:

(1) Generally, higher percentages of metals were extracted at lower pH levels within the nonbuffered extract sequence. The buffered extracts were also performed on samples at pH 4.0, 5.0, and 5.9 (data not reported here), and the same is true within the buffered system.

(2) As expected, higher percentages of extractable metals were characteristic of the low-pH buffered extract (3.4) as opposed to the percentages in the low-pH (2.0) nonbuffered extract.

(3) The DTPA extract compared favorably with the pH-2.0 nonbuffered extract in terms of extractable metals. For mines with treatment, the average values of pH-2.0 extractable Zn, Ni, and Co were 60 to 75% of the average values for DTPA-extractable Zn, Ni, and Co. For mines without treatment, the average values for all elements except Al and Cr were extremely comparable.

(4) For mines with treatment, manganese was in all cases the most mobile of the metals examined, while iron and aluminum tended to be among the least mobile. Aluminum in the high-pH (10.0) nonbuffered extract might be expected to increase over that in the distilled water extract, but this was not the case. For mines without treatment, Ni, Co, and Zn were generally more extractable than the Mn.

Because of the large standard deviations indicated in Tables 2 and 3, however, the use of these average values to predict extractable metals for one element or to predict extractable metals for several elements based on relative averages is not advisable. A more suitable method is to utilize statistical techniques that will indicate the relative significance of various independent variables as predictors of extractable metals in this system. The ultimate goal in this study was to indicate which diagnostic parameters (total metals present, acidity—alkalinity variables, or element interrelationships) could be used in a regression model to predict extractable metals with a high degree of statistical significance. Two stepwise regression procedures (SAS 1979) were utilized: the maximum R^2 improvement technique (MAXR) and the backward elimination technique (BACKWARD). For both techniques, a regression model is evaluated in which the dependent variable Y (a particular metal extract) is described in terms of a number of independent variables (X1, X2, X3 . . . XM) which correspond to possible diagnostic parameters for extractable metals,

$$Y = f(X1, X2, \ldots, XM).$$

The two stepwise regression procedures differ in several ways. The MAXR technique first determines a one-variable model with the highest R^2.[1] Then MAXR successively determines the two-variable model, three-variable model, . . . M-variable model, each of which would produce the greatest increase in R^2 over the previous model. ($M \leq N$, N = total number of independent variables considered). The choice of variables for any size model is not limited by the variables included in the more limited models preceding it. That is, all variables are evaluated equally at each step, which is a superior technique to conventional stepwise procedures. The BACKWARD technique is highly complementary to the MAXR technique. The BACKWARD procedure first calculates regression statistics for a model that includes all of the independent variables, which would correspond to the N-variable model for the MAXR technique. Then, variables are successively deleted from the model on the basis of their increasing relative contribution to the regression model. In other words, the first variable deleted is the one that produced the smallest contribution to the model. The BACKWARD procedure terminates at the point where all the remaining variables produce F-statistics at a particular significance level (in this case, 0.10).[2] More information on the two procedures can be obtained in SAS 1979 and Hocking 1976. Because of the overall differences in concentrations of total and extractable metals discussed above, the data from the mines using chemical treatments and those with no chemical treatments were treated as separate populations and evaluated separately using the two regression procedures.

Table 4 indicates summary equations using MAXR for extractable metals in the pH (3.4) sodium acetate/acetic acid buffer solution. The y value is the amount of a given metal extracted by the pH-3.4 acetate buffer. It should be noted that the remainder of this paper will concentrate on specific results for the pH 3.4 acetate buffer extract. This extract was chosen to simulate *maximum* extractable metals under long-term contact with acid waters. This emphasis on acetate–buffer-extractable metals is not meant to imply that this is the most relevant procedure for predicting metals concentrations in mine

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[1] R^2 is the proportion of the variance of Y that can be attributed to its linear regression on X1, X2, . . . XM. That is, it measures how much variation in the dependent variable can be accounted for by the model (SAS 1979).

[2] F value is the ratio defined by dividing the mean square (MODEL) by the mean square (ERROR) as a measure of how well the model accounts for the behavior of the dependent variable.

Table 4. Summary equations for extractable metals using pH-3.4 sodium acetate/acetic acid buffer and stepwise maximum R^2 improvement regression technique. Includes equations for best one-, two-, three- and four-variable models. Independent variables considered include total metal present (tot), pH, NP, clay %, carbon % (C), and sulfide sulfur % (S^{-2}).[a]

Metal	Best one-var.	R^2;df	Best two-var.	R^2	Best three-var.	R^2	Best four-var.	R^2	R^2 for best six-var.
Mines with chemical treatment									
Fe	$y = 24.2(C) - 288$	0.26;28	$y = 38.5(\text{tot}) - 26.3(C) - 47$	0.36	$y = 47.0(\text{tot}) + 34.0(\text{pH}) - 27.5(C) - 220$	0.42	$y = 49.5(\text{tot}) + 40.5(\text{pH}) + 1.06(\text{clay}) + 26.8(C) - 315$	0.42	0.43
Mn	$y = 0.3430(\text{tot}) + 258$	0.85;27	$y = 3640(\text{tot}) - 84.7(\text{pH}) + 756$	0.86	$y = 3480(\text{tot}) - 108(\text{pH}) - 7.76(\text{clay}) + 1280$	0.86	$y = 3470(\text{tot}) - 110(\text{pH}) - 8.81(\text{clay}) + 12.2(C) + 1280$	0.87	0.87
Al	$y = 120(S^{-2}) + 488$	0.11;28	$y = 131(\text{tot}) + 208(S^{-2}) - 606$	0.30	$y = 155(\text{tot}) + 107(\text{pH}) + 170(S^{-2}) - 1450$	0.34	$y = 54.0(\text{pH}) + 31.7(\text{clay}) - 49.6(C) + 307(S^{-2}) - 1120$	0.41	0.43
Co	$y = 0.345(\text{tot}) - 24.7$	0.69;27	$y = 0.252(\text{tot}) - 4.28(S^{-2}) - 13.5$	0.72	$y = 0.271(\text{tot}) + 0.514(\text{clay}) + 6.94(S^{-2}) - 41.6$	0.77	$y = 0.249\ (\text{tot}) + 2.97(\text{pH}) + 565(\text{clay}) + 6.50(S^{-2}) - 59.1$	0.79	0.79
Cr	$y = 0.0107(\text{NP})\ 0.826$	0.41;28	$y = 0.0574(\text{tot}) + 0.0126(\text{NP}) - 2.60$	0.52	$y = 0.0635(\text{clay}) + 0.0129(\text{NP}) - 0.0584(C) - 2.54$	0.55	$y = 0.0687(\text{tot}) + 0.0117(\text{NP}) - 0.0597(C) + 0.0970(S^{-2}) - 2.92$	0.55	0.56
Cu	$y = 0.0567(\text{tot}) - 4.72$	0.21;28	$y = 0.0850(\text{clay}) +$	0.33	$y = 0.0635(\text{clay}) + 0.144(C) + 0.868(S^{-2}) - 0.433$	0.42	$y = 0.0424(\text{tot}) + 0.0591(\text{clay}) + 0.0119(C) + 0.750(S^{-2}) - 2.92$	0.44	0.47
Ni	$y = 0.701(\text{tot}) - 40.3$	0.85;28	$y = 0.783(\text{tot}) + 0.574(\text{clay}) - 75.6$	0.86	$y = 0.740(\text{tot}) + 4.84(\text{pH}) + 0.693(\text{clay}) - 107$	0.88	$y = 0.786(\text{tot}) + 6.69(\text{pH}) - 0.0807(\text{NP}) + 0.627(\text{clay}) - 116$	0.88	0.88
Zn	$y = 0.346(\text{tot}) - 8.30$	0.75;27	$y = 0.188(\text{tot}) + 17.9(S^{-2}) + 10.3\ 10.3$	0.79	$y = 0.263(\text{tot}) - 0.177(\text{NP}) + 18.1(S^{-2}) + 5.58$	0.82	$y = 0.233(\text{tot}) - 11.2(\text{pH}) - 0.285(\text{NP}) + 20.5(S^{-2}) - 54.5$	0.85	0.88
Mines without chemical treatment									
Fe	$y = 134(\text{tot}) - 250$	0.30;24	$y = 134(\text{tot}) + 43.7(C) - 80.4$	0.40	$y = 115(\text{tot}) - 333(\text{pH}) + 10.2(\text{NP}) + 1970$	0.55	$y = 110(\text{tot}) - 294(\text{pH}) + 10.9(\text{NP}) + 42.9(C) - 1420$	0.64	0.67
Mn	$y = 1.88(\text{NP}) - 217$	0.27;24	$y = 2.13(\text{NP}) + 11.8(C) + 122$	0.53	$y = 39.5(\text{pH}) + 1.74(\text{NP}) + 12.8(C) - 101$	0.61	$y = 35.2(\text{pH}) + 1.57(\text{NP}) - 2.65(\text{clay}) + 15.3(c) - 12.8$	0.63	0.64
Al	$y = -12.5(\text{pH}) + 210$	0.17;24	$y = -17.2(\text{pH}) + 0.373(\text{NP}) + 227$	0.33	$y = -22.1(\text{pH}) + 0.362(\text{NP}) - 93.3(S^{-2}) + 265$	0.39	$y = -22.1(\text{pH}) + 0.336(\text{NP}) - 0.357(\text{clay}) - 77.2(S^{-2}) + 274$	0.40	0.44
Co	$y = 0.0460(\text{NP}) + 4.29$	0.34;24	$y = 0.103(\text{tot}) + 0.0410(\text{NP}) - 0.660$	0.55	$y = 0.101(\text{tot}) + 0.0458(\text{NP}) + 0.219(C) - 2.35$	0.74	$y = 0.0100(\text{tot}) + 0.0419(\text{NP}) - 0.0474(\text{clay}) + 0.266(C) - 1.15$	0.76	0.76
Cr	$y = 0.0124(\text{NP}) + 0.302$	0.74;24	$y = 0.0112(\text{NP}) - 0.0115(\text{clay}) + 0.675$	0.78	$y = 0.00244(\text{tot}) + 0.0114(\text{NP}) - 0.00859(\text{clay}) - 0.677$	0.80	$y = -0.00296(\text{tot}) + 0.0115(\text{NP}) - 0.0123(\text{clay}) + 0.774(S^{-2}) + 0.728$	0.82	0.82
Cu	$y = 0.181(C) + 1.81$	0.50;24	$y = 0.0337(\text{tot}) + 0.153(C) + 0.699$	0.54	$y = 0.0390(\text{tot}) + 0.136(C) + 2.35(S^{-2}) + 0.385$	0.56	$y = 0.0350(\text{tot}) + 0.310(\text{pH}) + 0.141(C)\ 4.04(S^{-2}) - 1.43$	0.60	0.60
Ni	$y = 0.200(\text{tot}) - 0.597$	0.65;24	$y = 0.197(\text{tot}) + 0.309(C) - 2.81$	0.77	$y = 0.177(\text{tot}) + 0.0336(\text{NP}) + 0.340(C) - 2.88$	0.81	$y = 0.181(\text{tot}) - 1.05(\text{pH}) + 0.0429(\text{NP}) + 0.311(C) + 2.86$	0.85	0.86
Zn	$y = 0.00379(\text{tot}) - 15.0$	0.04;24	$y = 0.00430(\text{tot}) - 2.45(\text{pH}) + 0.842$	0.08	$y = 0.00631(\text{tot}) + 3.69(\text{pH}) - 0.0841(\text{NP}) - 4.75$	0.12	$y = 0.00602(\text{tot}) + 4.02(\text{pH}) - 0.0693(\text{NP}) + 0.157(\text{clay}) - 11.6$	0.13	0.13

[a] S^{-2} based on difference between total sulfur and sulfate sulfur.

effluents, but rather was intended to demonstrate a representative standardized procedure as a basis for development of empirical models for such mixed systems. In addition, the acetate buffer extractions yielded the highest relative metals concentrations, so it was possible to examine models for all metals of interest since they were all present in detectable quantities.

In the model chosen, six independent variables were evaluated (N = 6). The six variables were total metal present, pH, neutralization potential (NP), clay percent, carbon percent, and the difference between total sulfur and sulfate sulfur (an approximate measure of sulfide sulfur, assuming low organic sulfur). The goal was to evaluate the relative importance of the total analysis, the acidity–alkalinity variables (pH, NP, and sulfide sulfur), and the clay and carbon content as predictors of maximum extractable metals. As seen in Table 4, the acetate-buffer-extractable manganese, cobalt, nickel, and zinc at mines with chemical treatments can be predicted with a high degree of statistical significance from the respective total metal present. It can be recalled from Table 3 that these were the metals that were generally the most extractable by the various techniques utilized. For mines without chemical treatments, the acetate-buffer-extractable nickel could be predicted with an R^2 value of 0.65 from only the total nickel present; extractable chromium, on the other hand, was best predicted by NP.

Addition of successive variables in order to enlarge the models resulted in significant improvements in R^2 for certain metals extracted by the pH-3.4 acetate buffer. At the mines with chemical treatment, these metals and the four best independent variables were

Iron	Total, pH, clay, carbon	$R^2 = 0.42$
Aluminum	pH, clay, carbon, sulfide S	$R^2 = 0.41$
Chromium	NP, total, carbon, sulfide S	$R^2 = 0.55$
Copper	Total, clay, carbon, sulfide S	$R^2 = 0.44$

At the mines without chemical treatment, improvements in R^2 were noted for the following pH-3.4 (acetate buffer) extractable metals by inclusion of the four best independent variables listed below:

Iron	Total, pH, NP, carbon	$R^2 = 0.64$
Manganese	pH, NP, clay, carbon	$R^2 = 0.63$
Aluminum	pH, NP, clay, sulfide S	$R^2 = 0.40$
Cobalt	Total, NP, clay, carbon	$R^2 = 0.76$
Copper	Total, pH, carbon, sulfide S	$R^2 = 0.60$

In all cases, for both the mines with and without chemical treatments, the best six-variable model offered no substantial improvement in R^2 over the best four-variable model. Indeed, in most cases, the best four-variable model offered no substantial improvement in R^2 over the best two- or three-variable model, which strongly suggests that it is possible to describe acetate–buffer-extractable metals in terms of *simple* regression models.

Table 5 presents summary equations using BACKWARD for pH-3.4 acetate-buffer-extractable metals. The table is limited to the regression equations for the smallest number of independent variables in which all variables are significant at the 0.10 level. Note that, for most metals, the most limited model at this significance level is a simple two- or three-variable model, generally the same two- or three-variable model as that given in Table 4 using the MAXR technique.

Tables 4 and 5 thus indicate that, for most metals, the acetate–buffer-extractable metals in settling pond sediments can be predicted from a relatively limited number of independent variables. It is important to note that these variables and combinations of variables differ considerably for the different metals studied. At the mines with chemical treatment, which exhibited higher total metals concentrations in the pond sediments, the total amount of metal present is generally a good predictor for acetate–buffer-extractable metals; of secondary importance were clay, carbon, and sulfide sulfur. However, at the mines without chemical treatment, pH, NP, and carbon plus the total metal present were generally the best predictors for acetate–buffer-extractable metals, indicating the increasing importance of acidity–alkalinity factors where total metals concentrations were lower.

Table 6 summarizes the results of MAXR and BACKWARD using an enlarged model with a greater number of variables. One factor that has not yet been introduced in this discussion is the possibility of elemental interrelationships that influence extractable metals. In Table 6, for each extract, the independent variables considered included pH, neutralization potential, total carbon percent, sulfide sulfur percent (taken as the difference between total sulfur and sulfate sulfur), sulfate sulfur percent, the total amount of a given metal present in sediment, quartz percent, clay percent, and the two metal extracts which correlated highest (Pearson r) with each pH 3.4 extract under consideration. Comparing Table 6 to Tables 4 and 5, significant improvements in R^2 can be noted for the models for many of the pH 3.4 extractable metals.

Table 5. Summary equations extractable metals using pH-3.4 sodium acetate/acetic acid buffer and stepwise backward regression procedure. Includes equations for smallest number of independent variables where all variables significant at 0.100 level. Independent variables considered include total metal present (tot), pH, NP, clay %, carbon % (C), and sulfide sulfur % (S^{-2}).[a]

Metal	Mines with chemical treatment	R^2; Degrees of freedom	Mines without chemical treatment	R^2; Degrees of freedom
Fe	y = 38.5(totFe) + 26.3(C) + 47.1	0.36;28	y = 110(totFe) − 293(pH) + 10.9(NP) + 42.9(C) + 1420	0.64;24
Mn	y = 3430(totMn) + 258	0.85;27	y = 39.5(pH) + 1.74(NP) + 12.8(C) − 101	0.61;24
Al	y = 30.6(clay) − 49.9(C) + 327(S^{-2}) − 740	0.40;28	y = −17.2(pH) + 0.373(NP) + 227	0.33;24
Co	y = 0.271(totCo) + 0.514(clay) + 6.94(S^{-2}) − 41.6	0.77;27	y = 0.101(totCo) + 0.0458(NP) + 0.219(C) − 2.35	0.74;24
Cr	y = 0.0574(totCr) + 0.0126(NP) − 2.60	0.52;28	y = 0.0112(NP) − 0.0115(clay) + 0.675	0.78;24
Cu	y = 0.0634(clay) + 0.144(C) + 0.868(S^{-2}) − 0.433	0.42;28	y = 0.181(C) + 1.81	0.50;24
Ni	y = 0.783(totNi) + 0.574(clay) − 75.6	0.86;28	y = 0.181(totNi) − 1.05(pH) + 0.0429(NP) + 0.311(C) + 2.86	0.85;24
Zn	y = 0.235(totZn) + 12.7(pH) − 0.309(NP) + 2.12(C) + 20.9(S^{-2}) − 75.6	0.86;27	no significant variables	—

[a] S^{-2} based on difference between total sulfur and sulfate sulfur.

For the mines with chemical treatment, the largest percent improvements in R^2 (best four-variable model MAXR) were noted for the least extractable metals (aluminum, iron, chromium, copper). Similarly, the largest percent improvements in R^2 for the mines without chemical treatment were for zinc (most extractable) and, secondarily, for iron and aluminum (least extractable).

Finally, Fig. 4 presents plots of predicted vs. observed extractable metals using the best four-variable MAXR models for each metal from Table 6 in a general linear model (SAS 1979). (Table 7 includes the predictive equations utilized in Fig. 4). One should note from Table 6 that certain highly correlated metal extracts figured prominently in the best four variable models in Fig. 4, especially the models for Co 3.4, Mn 3.4 (mines without treatment), Cr 3.4 (mines with treatment), and Ni 3.4. This strongly suggests the similar behavior of the more easily extractable metals. Overall, Figure 4 demonstrates that simple models for acetate buffer extractable metals can be developed using stepwise regression techniques. In general, an R^2 of >0.75 is necessary to yield values of extractable metals that are useful predictors for the actual laboratory data.

Test of Best Four-Variable Models for pH 3.4 Extractable Metals Using Independent Data Set

In order to test the best four-variable models for pH 3.4 extractable metals, an independent data set was utilized. The new data set included samples taken on a 10-m grid at two previously unstudied retention ponds. The ponds were located in North Central Alabama and Northern West Virginia. The Alabama pond, designated PP, was located in an area which had been mined and abandoned; the pH of pond water and sediment were both approximately 2.5. The West Virginia pond, designated MR, was located on an active mine. The pH of untreated mine drainage at the MR site was approximately 2.0. After treatment with sodium hydroxide and hydrated lime, the pH of pond water and sediment were both above 11.0; strong pH gradients existed in the pond between its influent and effluent structures. Thus, the ponds were quite different chemically. Samples at both sites were air-dried and subjected to the same analytical procedures described previously, with one exception. The low pH nonbuffered extract was done at pH 2.5 rather than pH 2.0, largely because this was the measured pH at the PP site. Table 8 presents summary equations using the same four independent variables for the pH 3.4 extractable metals that were used in Figures 4(a)–(h) and Table 7. When Table 7 and Table 8 are compared, the R^2 values are somewhat less in Table 8; however, the derived "best" variables are reasonably good predictors for most of the more easily extractable metals, namely, cobalt, chromium, nickel, zinc, and manganese. The low R^2 value for iron may be partially explained by the substitution of the pH 2.5 extract for the pH 2.0 extract. If the stepwise regression for zinc, which

Table 6. Summary of significant variables using MAXR and BACKWARD with enlarged number of variables, including the two highest correlatable metal extracts.

	Al pH 3.4						Fe pH 3.4					
	T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
MAXR Best Model of x Variables where x = 1	Cr3.4	.39	SO_4	.29	Cr3.4	.41	C	.26	FeH_2O	.89	FeH_2O	.83
2	Cr3.4 TAl	.46	SO_4 pH	.38	Cr3.4 TAl	.49	C FeDTPA	.37	FeH_2O C	.93	FeH_2O C	.88
3	Cr3.4 NP Qtz	.63	pH Qtz Clay	.51	Cr3.4 S^{-2} NP	.63	C FeDTPA pH	.43	NP C Fe10	.96	FeH_2O C pH	.90
4	Cr3.4 NP Qtz SO_4	.72	pH SO_4 Qtz Clay	.53	Cr3.4 S^{-2} Clay NP	.69	C FeDTPA pH TFe	.50	NP C TFe Fe2.0	.97	FeH_2O C pH TFe	.90
BACKWARD	T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
Smallest Model	(x = 5)	.77	(x = 3)	.51	(x = 5)	.72	(x = 6)	.62	(x = 8)	.98	(x = 3)	.90
of x Variables where all Variables Significant at 0.10 level	NP pH Qtz Cr3.4 CdH_2O		pH Qtz Clay		NP C S^{-2} Clay Cr3.4		pH C TFe Qtz Cu3.4 FeDTPA		NP C SO_4 TFe Qtz Clay Fe2.0 FeH_2O		pH C FeH_2O	

	Cr pH 3.4						Cu pH 3.4					
	T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
MAXR Best Model of x Variables where x = 1	Cd3.4	.50	NP	.77	Cd3.4	.52	ZnDTPA	.38	C	.54	Qtz	.37
2	Cd3.4 CdH_2O	.57	NP Co3.4	.80	Cd3.4 CdH_2O	.57	SO_4 Qtz	.56	C TCu	.58	Qtz CuH_2O	.50
3	Cd3.4 CdH_2O S^{-2}	.66	NP Co3.4 Clay	.85	Cd3.4 CdH_2O S^{-2}	.59	SO_4 S^{-2} ZnDTPA	.66	C SO_4 TCu	.70	CuH_2O S^{-2} C	.60
4	Cd3.4 CdH_2O S^{-2} Qtz	.69	NP TCr Clay Co3.4	.86	Cd3.4 CdH_2O S^{-2} CdH_2O	.63	SO_4 S^{-2} ZnDTPA Clay	.70	NP C SO_4 TCu	.73	pH C Qtz CuH_2O	.63
BACKWARDS	T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
Smallest Model	(x = 3)	.66	(x = 3)	.83	(x = 6)	.68	(x = 4)	.70	(x = 5)	.78	(x = 5)	.66
of x Variables where all Variables Significant at 0.10 level	Cd3.4 CdH_2O S^{-2}		NP TCr Co3.4		NP SO_4 S^{-2} Clay Cd3.4 CdH_2O		S^{-2} Clay ZnDTPA CuH_2O		NP C SO_4 TCu CuH_2O		pH C SO_4 Qtz CuH_2O	

(Table continued on next page.)

Table 6 continued.

Mn pH 3.4						Co pH 3.4					
T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
TMn	.85	Co3.4	.53	Ni3.4	.78	Ni3.4	.86	Ni3.4	.78	Ni3.4	.87
TMn	.91	Co3.4	.66	Ni3.4	.88	Ni3.4	.86	Ni3.4	.90	Ni3.4	.88
Cr10		Ni3.4		Cr10		Mn3.4		Mn3.4		Mn3.4	
Qtz	.94	Co3.4	.70	Ni3.4	.89	Ni3.4	.87	Ni3.4	.94	Ni3.4	.89
Clay		Ni3.4		Cr10		Mn3.4		Mn3.4		Mn3.4	
Cr10		C		NP		Clay		pH		Clay	
Qtz	.95	Co3.4	.72	Ni3.4	.90	Ni3.4	.88	Ni3.4	.94	Ni3.4	.90
Clay		Ni3.4		Cr10		Mn3.4		Mn3.4		Mn3.4	
Cr10		C		NP		Clay		pH		Clay	
SO_4		NP		SO_4		S^{-2}		TCo		pH	
T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
(x = 6)	.96	(x = 2)	.66	(x = 5)	.92	(x = 1)	.86	(x = 5)	.95	(x = 4)	.90
SO_4		Co3.4		SO_4		Ni3.4		pH		pH	
S^{-2}		Ni3.4		Qtz				Qtz		Clay	
Qtz				Clay				Clay		Ni3.4	
Clay				Cr10				Ni3.4		Mn3.4	
Cr10				Ni3.4				Mn3.4			
Ni3.4											

Ni pH 3.4						Zn pH 3.4					
T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
Co3.4	.86	Co3.4	.78	Co3.4	.87	Ni3.4	.81	Zn2.0	.90	Ni3.4	.80
Co3.4	.92	Co3.4	.87	Co3.4	.91	S^{-2}	.88	Zn2.0	.94	Ni3.4	.85
TNi		pH		TNi		Ni3.4		TZn		S^{-2}	
Co3.4	.92	Co3.4	.95	Co3.4	.91	S^{-2}	.89	Zn2.0	.97	Ni3.4	.86
TNi		pH		TNi		Clay		TZn		S^{-2}	
Qtz		TNi		Mn3.4		Ni3.4		pH		pH	
Co3.4	.93	Co3.4	.96	Co3.4	.92	pH	.90	Zn2.0	.98	Ni3.4	.88
TNi		pH		TNi		NP		TZn		S^{-2}	
Qtz		Tni		Mn3.4		S^{-2}		pH		pH	
Zn3.4		Clay		S-2		Ni3.4		Qtz		Clay	
T	R^2	U	R^2	CM	R^2	T	R^2	U	R^2	CM	R^2
(x = 2)	.92	(x = 4)	.96	(x = 2)	.91	(x = 5)	.93	(x = 4)	.98	(x = 5)	.88
TNi		pH		TNi		pH		pH		pH	
Co3.4		TNi		Co3.4		NP		TZn		NP	
		Clay				S^{-2}		Qtz		S^{-2}	
		Co3.4				Qtz		Zn2.0		Clay	
						Ni3.4				Ni3.4	

Key to Abbreviations:

T = Mines with chemical treatment
U = Mines without chemical treatment
CM = Combined Mines
xx3.4 = metal (xx) extracted by pH 3.4 acetate buffer
xx2.0 = metal (xx) extracted by pH 2.0 water extract
xxH_2O = metal (xx) extracted by distilled water extract
xxDTPA = metal (xx) extracted by DTPA extract
xx10 = metal (xx) extracted by pH 10.0 water extract
C = percent total carbon
NP = neutralization potential (T $CaCO_3$/1000 T.)
S^{-2} = percent sulfide sulfur = [percent total sulfur − percent sulfate sulfur]
SO_4 = percent sulfate sulfur
Qtz = percent quartz
Txx = Total metal (xx) present in sediment

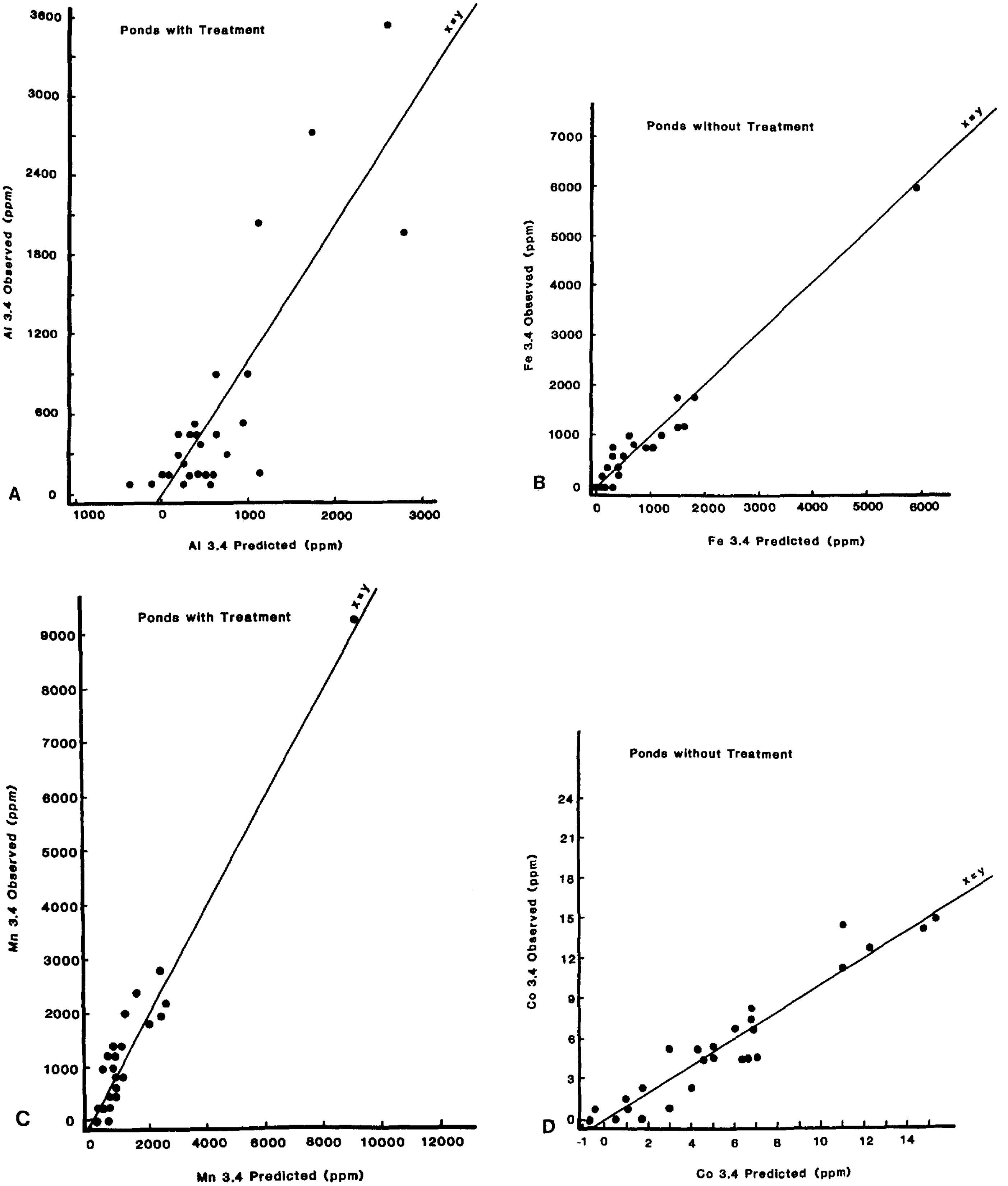

Figure 4. Predicted vs. observed acetate-buffer-extractable metals using best MAXR four variable models from Table 6 in a general linear model (SAS 1979). Extractable metals in ppm. Abbreviations same as Table 6. (Figure 4 continued on page 236.)

Figure 4. *continued*

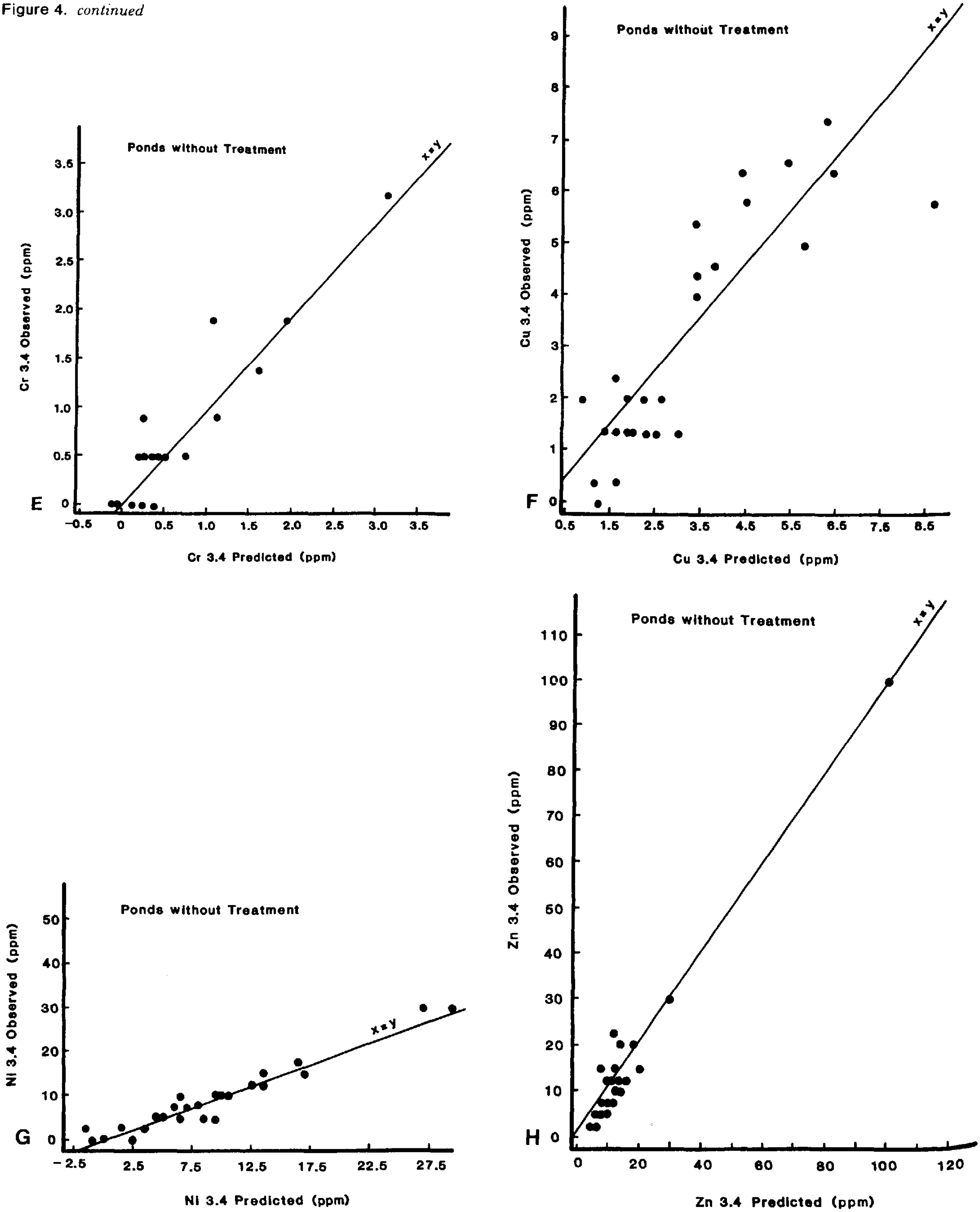

Table 7. Predictive equations for Figs. 4 A–H.

Figure 4	Equation	R^2
A	Al 3.4 Predicted = 336 (Cr 3.4) − 5.31(NP) − 26.1(qtz) − 631(SO_4) + 1600	.72
B	Fe 3.4 Predicted = 5.95(NP) + 27.7(C) + 0.00256(TFe) + 1.70(Fe2.0) − 30.9	.96
C	Mn 3.4 Predicted = −18.1 (qtz) − 432 (SO_4) − 17.3(clay) + 11400(Cr10.0) − 2425	.95
D	Co 3.4 Predicted = 0.476(Ni3.4) + 0.00435(Mn3.4) + 0.783(pH) − 0.027(TCo) − 3.06	.91
E	Cr 3.4 Predicted = −0.00178(TCr) + 0.00870(NP) − 0.0123(clay) + 0.0525(Co3.4) + 0.535	.86
F	Cu 3.4 Predicted = 0.171(C) + 0.0128(NP) − 0.363(SO_4) + 0.0563(TCu) − 0.409	.74
G	Ni 3.4 Predicted = 1.27(Co3.4) + 0.102(TNi) − 1.41(pH) + 0.0584(clay) + 3.51	.96
H	Zn 3.4 Predicted = 1.25(Zn2.0) + 0.00355(TZn) + 2.49(pH) − 0.0597(qtz) − 4.10	.96

Table 8. Predictive equations for pH 3.4 extractable metals at PP and MR ponds using best four variables from Table 7; stepwise regression MAXR procedure. N = 43.

Equation	R^2
Al 3.4 Predicted = 838(Cr3.4) + 9.09(NP) + 121(qtz) + 559(SO_4) − 1780	.52
Fe 3.4 Predicted = 5.68(NP) + 1230(C) + 0.000989(TFe) + 7.95(Fe2.5) − 2930	.45
Mn 3.4 Predicted = −36.8(qtz) + 17.2(SO_4) − 22.6(clay) − 304(Cr10) + 2342	.72
Co 3.4 Predicted = 0.830(Ni3.4) + 0.0570(Mn3.4) − 2.82(pH) − 0.0167(TCo) + 1.20	.97
Cr 3.4 Predicted = −0.000278(TCr) + 0.000975(NP) − 0.0206(clay) + 0.00905(Co3.4) + 1.77	.84
Cu 3.4 Predicted = 1.28(C) − 0.0375(NP) + 3.93(SO_4) + 0.00499(TCu) + 0.995	.44
Ni 3.4 Predicted = 0.513(Co3.4) + 0.0246(TNi) + 5.14(pH) + 0.186(clay) − 29.7	.86
Zn 3.4 Predicted = 1.02(Zn2.5) + 0.270(TZn) + 17.4(pH) − 5.80(qtz) + 39.1	.76

also includes the pH 2.5 term, is rerun using only the PP data, where the observed water and sediment pH's were 2.5, the R^2 value jumps to .96. In general, though, the R^2 values are reasonably good considering the limited number of variables included in the model.

Discussion and Conclusions

In this study, sediments were subjected to standardized laboratory extractions, and metals mobility was demonstrated to be related to gross sediment composition, elemental interrelationships, and acidity-alkalinity factors, as well as total metals concentrations. Since the purpose of this investigation was to examine this mixed natural system as the sum of its component parts and to develop tools for prediction of metals remobilization in such systems, the sediment samples were not fractionated by grain size or chemical components before total analysis or the various extraction procedures. For some metals, such as manganese, the total concentration of that metal was directly correlatable to the acetate extractable metal. In general, the more extractable the metal, the better predictor was the total concentration.

Statistical analysis of results obtained for laboratory extractions of settling pond sediments at coal strip mines suggests that it is possible to use simple regression models as general predictors of extractable metals. However, the independent variables that are the best predictors, as discussed above, are quite different for individual metals. Often, the variables that are the best predictors may require more analytical time to derive than the variable of interest. In addition, the reliability of the best possible regression models for predicting (acetate buffer) extractable metals differs for individual metals and also between the mines that use chemical neutralization treatments and those that do not. The results obtained to date suggest caution with regard to formulating broad statements regarding the environmental implications of total metals concentrations in mixed systems of natural sediments that are subject to highly acid or alkaline conditions. This study is a first step in understanding and predicting extractable metals in sediments retained in coal strip mine settling ponds.

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