

Concentrations of P, K, Al, Fe, Mn, Cu, Zn, and As in Marl Soils from South Florida

M. Chen, L. Q. Ma*, and Y. C. Li

ABSTRACT

Enrichment of nutrients (P) and trace elements (As, Fe, Cu, Mn, and Zn) in soils has contributed to the degradation of the Everglades ecosystem. Better understanding of elemental concentrations in soils is important for restoration and conservation of this fragile ecosystem. In this study, concentrations of P, K, Al, Fe, Cu, Mn, Zn, and As in 13 archived disturbed and undisturbed marl soils and five recently-collected undisturbed marl soil profiles from south Florida were determined using EPA Method 3051a (microwave, $\text{HNO}_3/\text{HCl} = 3:1$, v/v). Geometric mean (GM) concentrations of P, K, Al, Fe, Mn, Cu, Zn, and As in surface marl soils were 256, 212, 5100, 2800, 60.3, 3.81, 13.9, and 4.31 mg kg⁻¹, respectively, which were 2.6 to 15.8 times greater than those of Florida soils. No significant differences in elemental concentrations were found between the archived and the newly-collected soils, or between disturbed and undisturbed soils. Based on factorial analysis and spatial distribution similarities, these elements were divided into three groups: Group 1 (As, Fe, Cu, Al, and P), Group 2 (K and Zn), and Group 3 (Mn). Elevated elemental concentrations in marl soils may not all originate from anthropogenic sources and may attribute to elemental accumulation during formation of calcite.

The Florida Everglades is the most protected ecosystem since it is the largest remaining subtropical wilderness in the continental United States. It encompasses more than 600 000 ha of predominately wet prairie and mangrove forests. The unique geographic position of south Florida during the Pleistocene produced a terrain significantly different from the rest of the peninsula. Calcium carbonate, in the form of broken shell fragments and chemically-precipitated particles, was the main source of sediments (Lane, 1994). Marl soils or marl-forming wetland soils occur primarily within Everglades National Park and are usually poorly drained. These soils appear to experience a much greater natural range of variability in elemental concentrations. The vegetation in the Everglades has a limited capacity for nutrient uptake and is sensitive to enrichment of nutrients. Historically, the Everglades is a low-nutrient system and receives nutrients directly from atmospheric deposition and from upstream floodwaters. Much of the latter originated as overflow from Lake Okeechobee, passed through a continuous expanse of shallow freshwater wetlands and discharged to the tidal estuaries of the Florida Bay. This water was low in plant nutrients (particularly P), and the Everglades has been an oligotrophic ecosystem for the last 5000 yr. However, during the 20th century, drainage and development have eliminated or severely stressed the natural system of south Florida.

Changes in supply of nutrients and heavy metals to the Everglades have become significant. The concentration of N and P in Everglades National Park surface water inflow increased at an average rate of 5% yr⁻¹ from 1978 to 1989 (Walker, 1991). Nutrient-enriched waters from agricultural runoff have changed vegetation patterns in the Everglades. High levels of Hg are identified in all levels of the food chain, from fish to raccoon and alligator (McPherson and Halley, 1996). The understanding of the changes in these elements is important for restoration and conservation of this fragile wetland system. Background concentrations of P and trace elements in Florida surface soils (Ma et al., 1997; Chen et al., 1999a, 1999b) and enrichment of soil P and other elements in north Everglades (Reddy et al., 1998) have been well documented. However, little information is available on concentrations of P, K, Al, Fe, Mn, Cu, Zn, and As in marl soils from south Florida.

The purposes of this study were to: 1) establish background concentrations of P, K, Zn, Cu, Fe, Mn, Al, and As in marl soils from south Florida; 2) determine distribution patterns of elemental concentrations in marl soil profiles from south Florida; and 3) discuss anthropogenic influence on elemental concentrations in marl soils from south Florida. Among these elements, P, K, Fe, Mn, Cu, and Zn are essential plant nutrients, As is a Class A human carcinogen, Al is a reference element (Schropp et al., 1990; Windom et al., 1989).

MATERIAL AND METHODS

Thirteen archived marl soil samples (Aquents) were previously collected and characterized during the soil survey program (Chen et al., 1999a). The 13 soil samples can be divided into disturbed (N = 7) and undisturbed (N = 6) soils for assessing possible anthropogenic influence on elemental concentrations in soils. The disturbed soils were identified either by plowing or clearing ("p" subordinate horizon designation). These were compared to five soil profiles that were recently collected from an area in the Everglades National Park (loamy, carbonic, hypothermic Topic Fluvaquents). Samples were collected in 5-cm increments from top of the soil profile to bedrock. A total of 24 samples were collected which include five bedrock samples for comparison of the weathering effect on elemental concentrations in soils. Samples were air-dried and ground to pass a 2-mm sieve.

Approximately 1 g of soil or ground rock was weighed into a 120-mL Teflon pressure digestion vessel (CEM, Matthews, NC), and 9 mL concentrated HNO_3 and 3 mL concentrated HCl were then added. Samples and reagents were well mixed, sealed, and digested in a CEM-2000 digestion microwave oven (CEM, Matthews, NC) for 5.5 min at 3.94×10^5 Pa. The digestion solution was brought to a final volume of 100 mL with deionized

Ming Chen, Inst. Geography and Nat. Resources, Chinese Acad. Sci., Beijing 100101, China; L. Q. Ma, Soil and Water Science Dep., Univ. of Florida, Gainesville, FL 32611-0290; Y.C. Li, Tropical Res. and Educ. Center, Homestead, FL 33031-3314. Florida Agric. Exp. Stn. Journal Series No. R-07481.

*Corresponding author (lqma@ufl.edu).

Contribution published in

Soil Crop Sci. Soc. Florida Proc. 59:124-129 (2000).

distilled water following filtration (Whatman 42). Concentrations of P, K, Al, Fe, Mn, Cu, and Zn were determined using a multi-channel inductively coupled plasma spectrophotometer (Thermo Jarrell Ash ICAP 61-E, Franklin, MA). Arsenic concentrations were analyzed on a Perkin-Elmer SIMAA 6000 graphite furnace atomic absorption spectrophotometer unit (Norwalk, CT) using EPA method 7060A (USEPA, 1995).

All statistical analyses were performed using SAS program (SAS Institute, 1987). Simple correlation analysis and R-mode factorial analysis were used to associate elemental concentrations. Since most of the data were log-normally distributed, geometric means (GM) were used to describe the central tendency of the data. Arithmetic means (AM) were used to compare the data with data reported in literature. The following methods were used to calculate the upper one-sided 95% confidence limit ($UCL_{0.95}$) and the lower one-sided 5% confidence limit ($LCL_{0.05}$) for the true mean.

$$UCL_{0.95} = \exp\left(\mu_y + 0.5\delta^2 + \delta \times \frac{H_{0.95}}{\sqrt{n-1}}\right)$$

$$LCL_{0.05} = \exp\left(\mu_y + 0.5\delta^2 + \delta \times \frac{H_{0.05}}{\sqrt{n-1}}\right)$$

where, μ_y is the AM of log-transformed data, δ is the standard deviation of log-transformed data, n is the number of samples, $H_{0.95}$ and $H_{0.05}$ are the H-statistic tabulated constants for the upper and lower confidence limits, respectively (Gilbert, 1987).

Quality Control of Soil Analysis

EPA Method 3051a is a total-recoverable method, and an alternative for the conventional hot-plate EPA Method 3050. It was proved to be better than EPA Method 3051 for analyzing both certified and Florida surface soils (Chen and Ma, 1998). In this study, standard reference material 2709, a sand soil from the National Institute of Standards and Technology was digested in triplicate and analyzed using EPA Method 3051a (Table 1). Satisfactory recoveries (87% to 105%) were found for P, Zn, Cu, Mn, and Fe. However, only partial decomposition was found for Al (59.6%), K

Table 1. Elemental concentrations and method recovery of NIST† standard reference material 2709.

Element	Measured	Certified	Recovery
	----- mg kg ⁻¹ -----		---- % ----
Al	44 700	75 000	59.6
As	11.5	17.7	65.2
Cu	36.2	34.6	105
Fe	31 000	35 600	87.1
K	6 670	20 300	32.8
Mn	501	538	93.2
P	620	620	100
Zn	109	102	102

†National Institute of Standards and Technology.

(32.8%), and As (65.2%). Lower recoveries have been reported for Al and K, and especially for As, using total-recoverable methods (Chen and Ma, 1998; Kane, 1995).

RESULTS AND DISCUSSION

Concentrations of P, K, Al, Fe, Mn, Cu, Zn, and As in Surface Marl Soils

Concentrations (GM) of P, K, Al, Fe, Mn, Cu, Zn, and As in surface marl soils from south Florida were compared with results of 448 Florida surface soils (Table 2), which were determined in a previous study (Chen et al., 1999a). There were no significant differences ($P = 0.05$) in concentrations for most elements, except for Fe, between recently-collected soils and archived soils. However, GM concentrations of all elements in soils from south Florida overall were significantly greater ($P = 0.05$) than those of Florida surface soils with ratios varying from 2.6 for P to as high as 15.8 for Fe (Table 2). This is expected since marl soils analyzed were wet soils, which is consistent with our recent investigation, in which the greatest As concentrations in Florida surface soils were associated with wet soil suborders such as Hemists, Sapristis, Aquepts, Aquolls, and Aquepts.

Elemental concentrations in soils vary greatly which may lead to erroneous conclusion that an area is contaminated due to high elemental concentration. Establishment of background concentrations based on adequate site-specific sampling and comparison to normal background ranges for a specific area and land use can help resolve the confusion (Breckenridge and Crockett, 1995). A scientific estimation of the degree of elemental contamination in soils requires the establishment of reference values (background values) for the same soil types in the area. Anthropogenic influences on As, Cd, Cu, Pb, and Zn concentrations in sediments from Biscayne National Park and Collier County in south Florida had been mentioned by other researchers (Strom et al., 1992; Grabe, 1996). In this study, however, no significant differences ($P = 0.05$) were found in elemental concentrations between disturbed and undisturbed soils, though GM concentrations of P, Zn, and Cu in disturbed soil were slightly greater than in undisturbed soils (Fig. 1). Thus, the two data sets could be

Table 2. Geometric mean concentrations of eight elements in surface marl soils (0-16 cm) compared with data from literature.

Element	Newly collected marl soils (N = 5)	Archived marl soils (N = 13)	Florida surface soils (N = 448)†
	----- mg kg ⁻¹ -----		
Al	11 500	3 700	1 300
As	4.00	4.44	0.27
Cu	4.14	3.70	0.73
Fe	9 800	1 700	620
K	271	193	55.6
Mn	124	45.7	11.3
P	219	273	84.8
Zn	16.4	13.1	4.52

†From Chen et al., 1999a, 1999b.

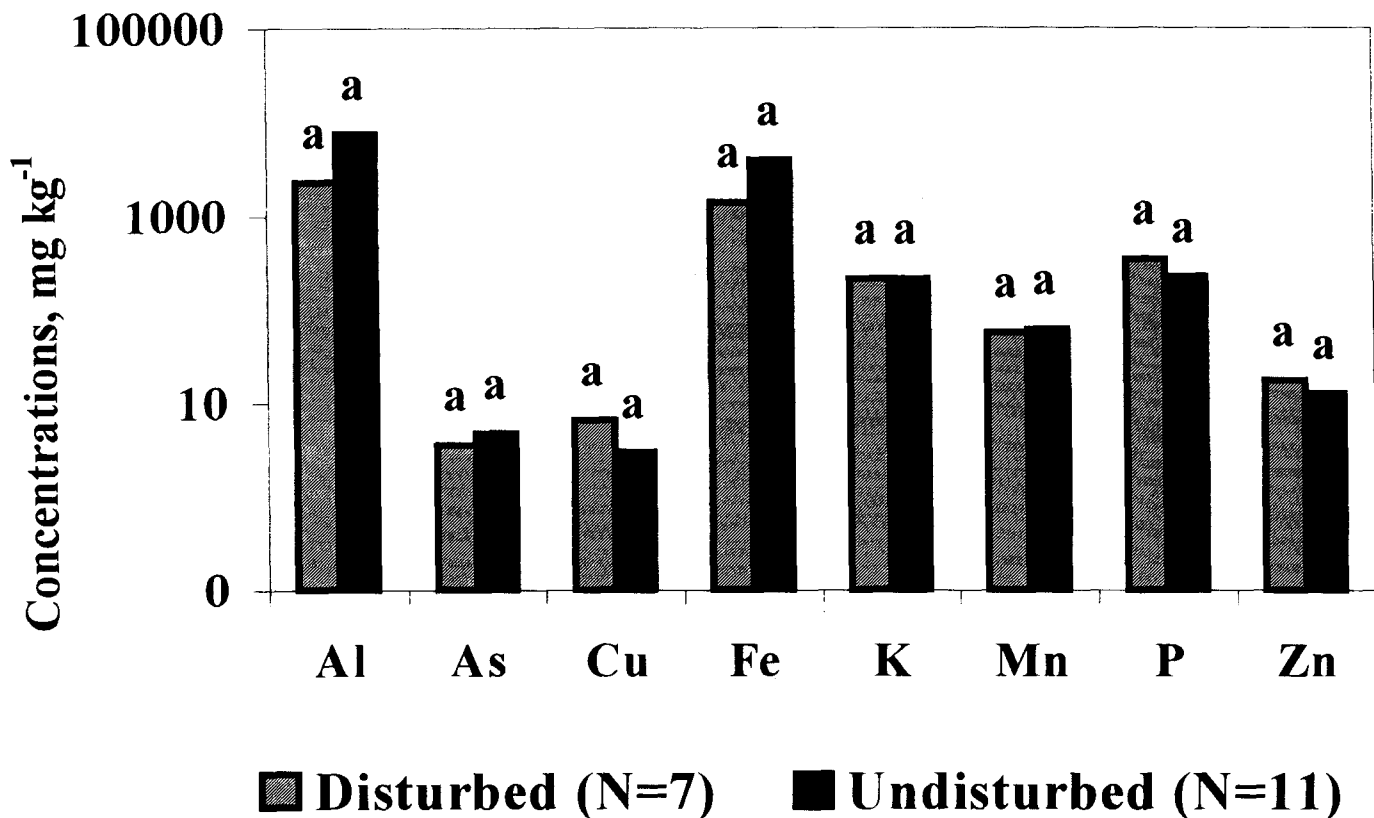


Fig. 1. Geometric mean concentrations of eight elements in disturbed and undisturbed surface marl soils from south Florida. Values with same letters for a given element are not significantly different at $\alpha = 0.05$.

merged to define elemental background concentrations for marl soils in south Florida (Table 3).

A 95% confidence interval for the mean describes an interval in which the true mean will fall within a specified level of certainty, 95%. For a one-tailed distribution and environmental applications, UCL is usually the upper tail not exceeding a regulatory action level. Logan and Miller (1983) stated that values greater than 2 to 3 times the mean background levels should be indicative of metal contamination. In this study, values of the UCL for the means of these eight elements in marl soils from

south Florida varied from ~4 to ~140 times greater than GM concentrations of these elements. It has been reported that GM is an underestimate of the true mean (Gilbert, 1987). However, UCL for most of the elements studied, except for Al, Fe, and Mn, were around 2 times higher than AM concentrations of these elements (Table 3). High elemental concentrations in these soils may not be anthropogenic in nature which is consistent with our recent investigation that certain Florida soil types had natural high As background-concentrations.

Table 3. Concentrations of P, K, Al, Fe, Mn, Cu, Zn and As in surface marl soils from south Florida (N = 18).

Element	Range	GM†	AM‡	UCL _{95%} §	LCL _{5%} ¶
-----mg kg ⁻¹ -----					
Al	400-101 000	5 100	15 000	66 500	8 400
As	0.81-61.1	4.31	9.18	18.1	5.04
Cu	0.02-244	3.81	23.6	45.1	12.9
Fe	200-34 200	2 800	6 600	26 600	4 200
K	43.0-1 065	212	315	560	221
Mn	4.20-476	60.3	121	552	88.9
P	52.5-5 215	256	515	1038	300
Zn	1.90-121	13.9	23.2	49.3	15.8

†GM = Geometric mean.

‡AM = Arithmetic mean.

§UCL_{95%} = 95% upper confidence limit for geometric mean.

¶LCL_{5%} = 5% lower confidence limit for geometric mean.

Distribution of P, K, Al, Fe, Mn, Cu, Zn, and As in Marl Soil profiles

Table 4 lists concentration distributions of these eight elements at different depths for the 5 soil profiles collected from the Everglades National Park. Bedrock here refers to the weathering raw material immediately on top of the rock. It was reasoned that if the ratio of an element in topsoil/bedrock was appreciably >1, then enrichment of the element may have occurred (Fig. 2).

Element enrichment in top soils was statistically significant ($P < 0.05$) for all eight elements except for As when compared to the bedrock (Fig. 2 and Table 4). Phosphorus, K, Cu, Zn, and As are elements applied in fertilizers, bactericides, and fungicides used in agriculture. Underground flow and atmospheric deposition from nearby agricultural area could be sources for those chemicals. However, extremely high concentrations of Al and Fe in the 15 to 20-cm layer on Site 3 showed actually strong geological control rather than surface enrichment (Table 4). This is especially true for As, which had the highest concentration distribution in either the bedrock (Sites 1, 2, and 4) or the subsurface layers (Sites 3 and 5). Arsenic probably originated from the bedrock

rather than from anthropogenic sources in these soils. This is consistent with results of the U.S. Geological Survey (1996), which reported that nonessential trace elements (such as Cr, Co, Pb, and Hg) were generally not being cycled but were instead being concentrated in organic-rich sediments at the sawgrass (*Cladium jamaicense* Crantz) prairie wetlands in south Florida.

Factors Controlling P, K, Al, Fe, Mn, Cu, Zn, and As in Marl Soils from South Florida

Correlation analysis is a useful tool for analyzing similarities between paired data (Ma et al., 1997; Chen et al., 1999a). In this study, significant positive correlation ($r > 0.5$) was found among As, Fe, Cu, Al, P (Table 5). Manganese showed no significant positive correlation with any other element. The highest correlation coefficient between As and Fe indicates that Fe is the major control factor for As distribution in soils. Chen et al. (1999a) found that total Fe and/or Al are highly correlated to concentrations of As and other trace elements in Florida surface soils. Doyle and Otte (1997) suggested that it is the oxidation of Fe, rather than the

Table 4. Concentrations of P, K, Al, Fe, Mn, Cu, Zn and As in different soil layers and bedrock on five sites from the Everglades National Park.

Layers	Al	As	Cu	Fe	K	Mn	P	Zn
----- cm ----- mg kg ⁻¹ -----								
Site 1								
0-5	2 936	0.9	2.1	3 737	144	99	246	8.2
6-10	3 352	3.1	1.9	4 633	94	137	188	7.5
11-15	2 126	1.4	2.1	4 316	63	194	84	21.1
16-20	4 374	3.8	2.0	5 646	119	219	80	17.9
21-25	10 752	1.4	3.3	8 954	212	170	98	16.3
Bedrock	8 881	13.0	3.4	10 373	169	114	68	3.4
Site 2								
0-5	3 213	0.6	2.0	1 880	141	131	161	12.0
6-10	2 793	1.4	1.8	1 295	108	92	126	18.0
11-15	9 343	1.0	2.3	4 225	188	122	235	14.1
16-20	9 229	2.2	2.0	3 935	183	97	162	8.1
Bedrock	4 938	10.3	1.8	9 153	53	53	71	7.1
Site 3								
0-5	8 222	12.0	6.9	9 677	300	81	416	16.2
6-10	4 550	2.4	2.4	4 668	118	128	284	14.2
11-15	22 794	29.8	5.5	22 059	239	101	404	14.7
16-20	74 759	74.1	15.4	100 385	636	185	655	23.1
Bedrock	3 674	6.4	1.6	4 909	49	51	66	4.9
Site 4								
0-5	43 401	2.5	7.6	15 051	1 041	122	355	33.0
6-10	47 321	2.8	7.1	15 464	1 089	75	304	26.8
Bedrock	9 531	3.3	1.8	7 202	217	60	126	7.2
Site 5								
0-5	2 321	1.4	4.5	2 701	89	116	112	15.6
6-10	2 144	1.5	3.5	2 109	105	86	105	5.3
11-15	6 989	2.4	4.3	5 935	194	108	129	10.8
16-20	29 783	13.5	6.5	33 696	478	230	239	17.4
Bedrock	7 762	6.9	2.6	7 685	128	142	77	3.8

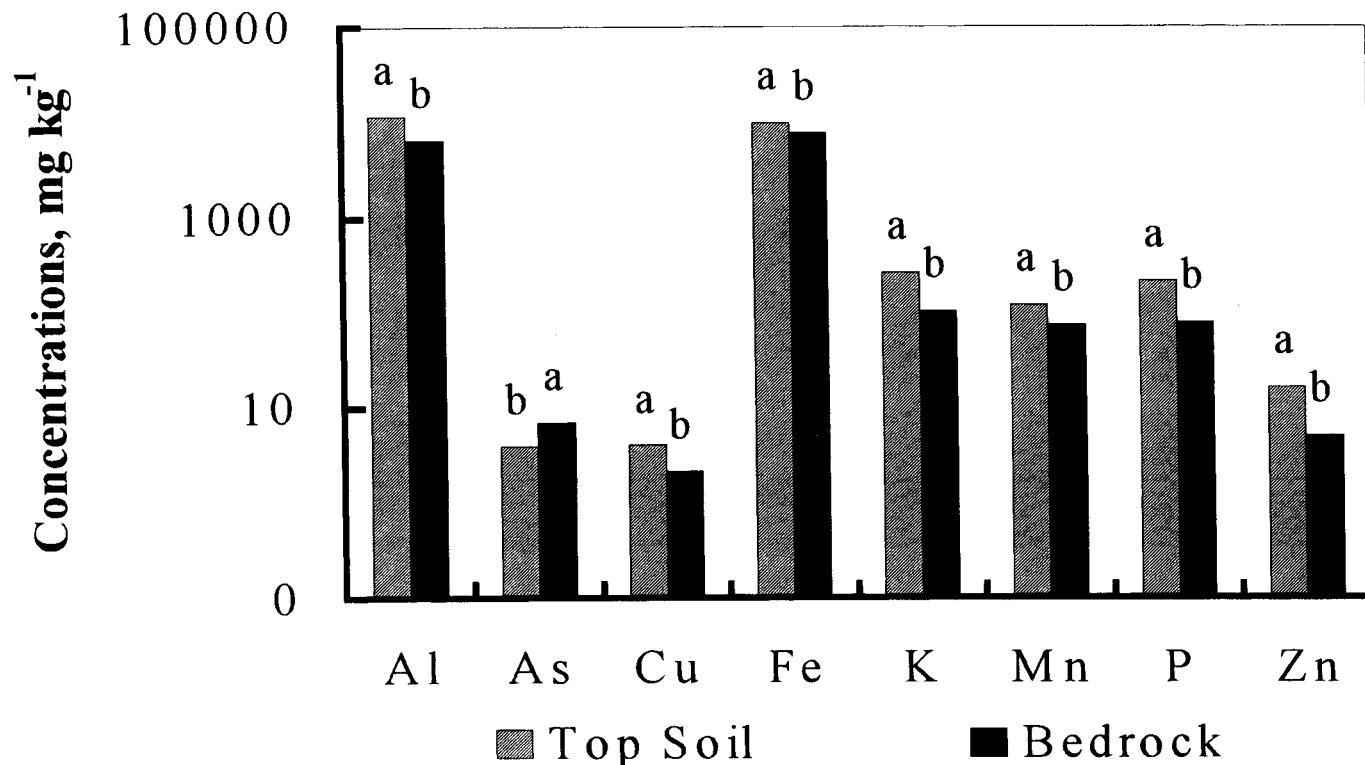


Fig. 2. Geometric mean concentrations of eight elements in topsoil and bedrock on five sites from Everglades National Park. Values with same letters for a given element are not significantly different at $\alpha = 0.05$.

binding to organic matter, that controls the accumulation of Zn and As in wetland soils.

Factorial analysis is an extension of correlation analysis. It can divide variables into groups that are consistent with anthropogenic or pedogenic processes (Dudka, 1992). In this study, an R-mode factor analysis separated the soil analysis data into three subcategories of Factor I (As-Fe-Cu-P-Al), Factor II (K-Zn), and Factor III (Mn) (Table 6). These factors explained 93% of the total variance using the eight elements as variables in the analysis. The resulting varimax factors were not correlated, and different variables generally had different loadings on different factors. Factor I explained 47% of the total variance and was the most important factor, which was consistent with correlation data in Table 5. It had large loadings from concentrations of As, Fe, Cu, P, and Al

(>50%). Factor II explained 32% of the total variance and had large loadings from concentrations of K and Zn (>80%), as well as moderate loadings from concentrations of Al, Cu, and P (26-41%). Factor III explained 14% of the total variance. It had very large loadings from concentrations of Mn (96%) and may represent the oxidation-reduction status of the soils.

This study indicates that concentrations of P, K, Al, Fe, Mn, Cu, Zn, and As in marl soils were higher than concentrations in Florida soils overall. The 95% upper confidence level could be used as a reference criterion to quantify background concentrations of these elements. Elevated elemental concentrations in marl soils may not all originate from anthropogenic sources and may attribute to elemental accumulation during formation of calcite.

Table 5. Correlation coefficients between elemental concentrations (mg kg⁻¹) in different soil layers and bedrock on five sites from the Everglades National Park (N = 24).

r	Fe	Cu	Al	P	K	Zn	Mn
As	0.95***	0.81***	0.73***	0.73***	0.27	0.20	0.23
Fe	1.00	0.88***	0.85***	0.75***	0.45*	0.37*	0.36
Cu	0.88***	1.00	0.91***	0.84***	0.69**	0.58**	0.25
Al	0.85***	0.91***	1.00	0.78***	0.84***	0.64**	0.23
P	0.75***	0.84***	0.78***	1.00	0.59**	0.54**	0.11
K	0.45*	0.69***	0.84***	0.59**	1.00	0.75***	0.06
Zn	0.37*	0.58**	0.64***	0.54**	0.75***	1.00	0.36

*, **, ***Significant different at levels of $\alpha = 0.05$, 0.01, and 0.001, respectively.

Table 6. Results of R-mode factorial analysis for elemental concentrations (mg kg⁻¹) in five soil profiles from the Everglades National Park showing percentage of the total variance explained by different factors derived by varimax rotation.

Element	Variance explained by factor number			Variance explained by all factors
	I	II	III	
As	97	0	1	98
Fe	88	4	5	97
Cu	67	26	1	94
P	58	24	0	82
Al	53	41	0	94
K	8	84	1	93
Zn	2	80	9	90
Mn	2	1	96	99
Total	47	32	14	93

ACKNOWLEDGEMENT

This research was sponsored in part by the Florida Center for Solid and Hazardous Waste Management (Contract No. 96011017). The authors would like to thank Dr. G. W. Hurt for providing several soil samples from south Florida. The helpful suggestions made by Drs. W. G. Harris, R. D. Rhue, J. B. Sartain and two anonymous reviewers are gratefully acknowledged.

REFERENCES

Breckenridge, R. P., and A. B. Crockett. 1995. Determination of background concentrations of inorganics in soils and sediments at hazardous waste sites. USEPA Engineering Forum Issue. EPA/540/S-96/600. U.S. Gov. Print. Office, Washington, DC.

Chen, M., and L. Q. Ma. 1998. Comparison of four USEPA digestion methods for trace metal analysis using certified and Florida soils. *J. Environ. Qual.* 27:1294-1300.

Chen, M., L. Q. Ma, and W. G. Harris. 1999a. Baseline concentrations of 15 trace elements in Florida surface soils. *J. Environ. Qual.* 28: 1173-1181.

Chen, M., L. Q. Ma, and W. G. Harris. 1999b. Assessment of P concentrations in different types of Florida surface soils. *Soil Crop Sci. Soc. Florida Proc.* 58: 58-62.

Doyle, M. O., and M. L. Otte. 1997. Organism-induced accumulation of iron, zinc and arsenic in wetland soils. *Environ. Pollut. Ser. A* 96:1-11.

Dudka, S. 1992. Factor analysis of total element concentrations in surface soils of Poland. *Sci. Total Environ.* 121:39-52.

Gilbert, R. O. 1987. *Statistical methods for environmental pollution monitoring.* John Wiley & Sons, Inc., New York, NY.

Kane, J. S. 1995. Leach data vs total: which is relevant for SRMs? *Fresenius Z. Anal. Chem.* 352:209-213.

Lane, E. 1994. Florida's geological history and geological resources. Florida Geological Survey Spec. Publ. 35. Tallahassee.

Logan, T. L., and R. H. Miller. 1983. Background levels of heavy metals in Ohio farm soils. p. 3-15. *In* Soil contamination analysis. Res. Circ. 275. Ohio Agri. Res. Dev. Ctr. Wooster.

Ma, Q. L., F. Tan, and W. G. Harris. 1997. Concentrations and distributions of eleven elements in Florida soils. *J. Environ. Qual.* 26:769-775.

McPherson B. F., and R. Halley. 1996. The south Florida environment—a region under stress. National Water—Quality Assessment Program. U.S. Geological Survey Circ. 1134. U.S. Gov. Print. Office, Washington, DC.

Reddy, K. P., G. A. O'Connor, and P. M. Gale. 1998. Phosphorus sorption capacities of wetland soils and stream sediments impacted by dairy effluent. *J. Environ. Qual.* 27:438-447.

SAS Institute. 1987. *SAS user's guide: Statistics.* ASA Inst., Cary, NC.

Schropp, S. J., F. G. Lewis, H. L. Windom, and J. D. Ryan. 1990. Interpretation of metal concentrations in Estuarine sediments of Florida using Aluminum as a reference element. *Estuarine* 13: 227-235.

Strom, R. N., R. S. Braman, W. C. Jaap, P. Dalan, K. B. Donnelly, and D. F. Martin. 1992. Analysis of selected trace metals and pesticides offshore of the Florida Keys. *Fla. Sci.* 55:1-13.

Walker, W. W. 1991. Water quality trends at inflows to Everglades National Park. *Water Resour. Bull.*, 27:59-72.

Windom, H. L., S. J. Schropp, F. D. Calder, J. D. Ryan, R. G. Smith, Jr., L. C. Burney, F. G. Lewis, and C. H. Rawlinson. 1989. Natural trace metal concentrations in estuarine and coastal marine sediments of the southeastern United States. *Environ. Sci. Technol.* 23:314-420.

U.S. Environmental Protection Agency. 1995. *Test Methods for Evaluating Solid Waste; Vol. IA: Laboratory Manual Physical/Chemical Methods.* U.S. Gov. Print. Office, Washington, DC.

U.S. Geological Survey. 1996. *South Florida Ecosystems: The Role of Peat in the Cycling of Metals.* U.S. Geological Survey Fact Sheet, FS-161-96. U.S. Gov. Print. Office, Washington, DC.