

Concentration of trace metals in sediments and soils from protected lands in south Florida: background levels and risk evaluation

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Abstract A comprehensive environmental evaluation was completed on 20 metals: two reference metals (Fe, Al) and several minor trace metals (As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn) for surface soils and sediments collected from 50 sites in Everglades National Park (ENP), the coastal fringes of Biscayne National Park (BNP), and Big Cypress National Preserve. Samples were prepared by acid digestion (EPA3050) and analyzed by ICP/MS detection (EPA6020). Although no widespread contamination was detected across the two parks and one preserve, there were some specific areas where metal concentrations exceeded Florida's ecological thresholds, suggesting that some metals were of concern. A screening-level evaluation based on a proposed effect index grouped trace metals by their potential for causing negligible, possible, and probable effects on the biota. For example, Cu in BNP and Cr and Pb in ENP were considered of concern because their adverse

effect likelihood to biota was assessed as probable; consequently, these trace metals were selected for further risk characterization. Also, stations were ranked based on a proposed overall contamination index that showed that: site BB10 in BNP and sites E3 and E5 in ENP had the highest scores. The first site was located in a marina in BNP, and the other two sites were along the eastern boundary of ENP adjacent to current or former agricultural lands. An assessment tool for south Florida protected lands was developed for evaluating impacts from on-going Everglades restoration projects and to assist State and Federal agencies with resource management. The tool consists of enrichment plots and statistically derived background concentrations based on soil/sediment data collected from the two national parks and one preserve. Finally, an equally accurate but much simplified approach is offered for developing enrichment plots for other environmental settings.

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Introduction

The Florida Everglades is one of the largest freshwater marshes in the world. A century ago, it encompassed more than 10,000 km² (4,000 mi²), extending 160 km (100 miles) in length from Lake Okeechobee to Florida Bay and 64 km (40 miles) in width from the

eastern Coastal Pineland Ridge to the western Flatwoods. This extensive freshwater ecosystem comprises wet prairies, sawgrass marshes, cypress and mangrove forests, and coastal lagoons and bays, which provide a mosaic of wildlife habitats. Early Florida settlers recognized the farming potential of peat-rich marshland in the northern Everglades and tried unsuccessfully to drain them by digging drainage canals. These early canals altered the natural drainage system and exacerbated south Florida's droughts and flooding problems, especially during the devastating hurricanes of the 1920s and 1940s. In the late 1940s, the federal government developed a major water control project to provide water supply and flood protection for south Florida. This project helped to spur an unprecedented urban and agricultural growth in south Florida, and like the early drainage efforts, this project substantially changed the hydrology and ecology of the Everglades. Currently, one half of the historic Everglades has been lost to agriculture and urban areas; nearly three fourths of the water that flowed through Everglades has been lost to tide, and the quality of the remaining water is often degraded; and the upper three fourths of the historic Everglades system has been compartmentalized by levees and canals. These changes have caused significant losses of natural habitat that have been manifested in a 90–95 % decline in wading bird populations and also a decline in fishery resources in estuaries and bays (U.S. Army Corps of Engineers (USACE) 1999).

The federal government and the state of Florida, in an unprecedented effort of cooperation, drafted a plan known as "The Comprehensive Everglades Restoration Plan (CERP)," which was approved by the United States Congress in the Water Resources Development Act of 2000, to restore, protect, and preserve the natural resources of central and southern Florida. The CERP includes 60+ key projects that will be implemented in the next 30 years at an estimated cost (2004) of \$10.9 billion dollars (National Research Council (NRC) 2008). A key element of CERP is to recover natural patterns of water quantity and quality and their timing and distribution characteristics (U.S. Army Corps of Engineers (USACE) 2003). To properly assess benefits from these projects, baseline hydrologic, biogeochemical, and ecological conditions of the Everglades ecosystem first must be established.

While trace metals are ubiquitous in the environment and some are essential micronutrients, all are

toxic to biota above some threshold concentration. Trace metals are introduced into the environment by weathering of rocks and from anthropogenic sources. In the Everglades, urban and agricultural runoff is mostly responsible for the degradation of water and soil/sediment quality (Anderson and Flaig 1995; Goodman et al. 1999; Walker 1999; Miller et al. 2004; Fulton et al. 2004; Li et al. 2011). Trace metal water concentrations in the Everglades ecosystems, although very low and often below thresholds and method detection levels (MDLs) (Miller et al. 2004; Shinde 2007; Arroyo et al. 2009), could concentrate to elevated and toxic levels as they partition to sediments and soils under anoxic conditions. These low trace-metal water concentrations provide a false perception suggesting that impacts on the ecosystems are either nonexistent or small and negligible. A closer analysis suggests otherwise. In the Everglades, for example, mercury contamination of the biota has been extensively documented (Axelrad et al. 2010), yet mercury in surface water samples has seldom exceeded the State's Class III standard in a decade-long monitoring of inflow structures (Rumbold 2005; Rumbold et al. 2006; Gabriel et al. 2008, 2009). Soil/sediment concentrations appear to be better indicators of anthropogenic pollution and ecosystem contamination than water concentrations, especially when soil/sediment concentrations are normalized to reference elements from non-anthropogenic sources (Schropp and Windom 1988; Windom et al. 1989; Schropp et al. 1990; Carvalho et al. 2002).

The purposes of this study were to conduct a screening level evaluation of potential trace metal contamination in protected federal parklands in south Florida, to identify areas and metals of concern, and to develop a management tool for distinguishing natural, and yet regional, background concentrations from other low level anthropogenic-derived inputs that may increase the local trace metal storage in soils and sediments.

Materials and methods

Study area

Everglades National Park (ENP) is located at the south end of the Florida peninsula and is characterized by a low, flat, wet plain covered by a wide grassy river with alternating ridges and sloughs, covering an area of 6,110 km² (2,400 mi²). Biscayne National Park (BNP)

is located at the southern end of Biscayne Bay and a few miles east of ENP. The park covers an area of 700 km² (270 mi²) of which 95 % is water. Biscayne Bay is mainly a shallow saltwater lagoon where salinity is controlled by point releases of freshwater from canals and groundwater discharges. Big Cypress National Preserve (BICY) is located northwest of ENP and BNP—and about 72 km (45 miles) west of Miami. The preserve is dominated by a wet cypress forest that supports numerous and varied habitats covering an area of 2,900 km² (1,100 mi²). All three units are adjacent to or in close proximity to large metropolitan areas and subject to heavily managed water regimes (Fig. 1).

Sample collection and analysis

Both soil and sediment samples were collected at 28 stations in ENP, 9 stations in BICY, 11 stations in BNP, and 2 in other special interest areas outside the parks (OTH; Fig. 1) in 2006 and 2007. Surface soils/sediment samples were collected from shallow marsh areas, 30 to 100 cm deep, using a 6.25-cm-diameter, 50-cm-long acrylic coring tube. Samplers were pushed into soft soils/sediments and recovered by capping the top to create a slight vacuum. Water was carefully drained from the top of the core, and only the top 10 cm of undisturbed soils/sediments was retained for analysis. Estuarine and canal sediments, or samples deeper than 100 cm, were collected with a 22.9-cm (9-inch) Eckman dredge. A clean Teflon or plastic spatula was used to remove the undisturbed material from the center of the dredge to prevent contamination. At each site, a total of five cores/casts collected within a 20-m (65.6 ft) radius were taken and combined into a composite sample. Station locations and ancillary bulk sediment parameters are listed in Table 1. Samples were stored in pre-cleaned 125-ml polypropylene containers which were pre-rinsed with 10 % trace metal grade hydrochloric acid and double-deionized water. All samples were chilled at the collection site and kept at or below 4 °C after collection and during transport. Additional samples were collected for analysis of ancillary parameters. Upon arrival to the laboratory, samples were frozen at or below -10 °C until the time of analysis.

Precautions were taken to minimize possible metal contamination throughout all sampling and analytical procedures. Bottles and material used for collection and analysis were cleaned and immersed for at least 1 week in a soap solution, 2 % Micro-90 (International

Products Corporation, NJ, USA); during the second week, they were immersed in a 10 % HCl solution, rinsed with ultrapure water (Milli-Q), dried in a clean laminar flowing bench (Class 100), and stored in zip-lock bags. All reagents and containers were tested to assess for the potential introduction of contaminants during sampling and analytical laboratory procedures.

Only Optima-grade acids were used to prepare samples and standards. Procedural blanks and QA/QC samples were analyzed in each sample batch to assess precision (duplicates) and accuracy (fortified blanks and/or standard reference materials).

Soil/sediment samples were defrosted in the laboratory and air dried for up to 2 days in a plastic desiccator and kept under a clean laminar flow hood (Class 100). Dry samples (~0.2 g) were digested in a hot block at 95 °C with concentrated nitric acid (Optima-grade, Fisher Scientific A509-212) and hydrogen peroxide (Optima-grade, Fisher Scientific P-17-0500), following an adaptation of EPA method 3050B. Samples were processed in duplicate, and a strict QA/QC protocol was followed, which included: blanks, blank spikes (LBS), matrix spikes, and reference material. Recoveries for QC samples were: blanks <3 MDL, LBS ±15 %, matrix spikes and reference material ±30 %, and duplicates <20 % RPD.

Concentrations of 20 metals (Ag, Al, As, Ba, Be, Cd, Co, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, and Zn) were determined directly or by using a sample dilution by ICP-MS (nebulization method) on a Agilent 4500A ICP-MS system. Three levels of sample dilution were necessary: 5 times for trace metals (most analytes), 10 times for minor elements (Ba, Cu, Mn, and Zn), and 1,000 times for major elements (Al and Fe). Bismuth (Bi), Ge, and In were used as internal standards. Because in most samples concentrations of several trace metals (Ag, Be, Cd, Hg, Mo, Sb, and Sn) were extremely low or below detection limits, they were excluded from the analyses. Selenium (Se) was also excluded from analysis because of potential isobaric interferences. The analyses and results of this study are based on As, Cr, Cu, Ni, Pb, and Zn, which are of potential concern in south Florida (MacDonald 1994; MacDonald et al. 2003). In addition, a selected group of metals (Al, Ba, Co, Fe, Mn, and V) were also included in the study because of their biogeochemical implications or their use as reference elements.

Carbon content was measured in duplicate using a LECO CN 2000 analyzer. Two subsamples of 100 mg

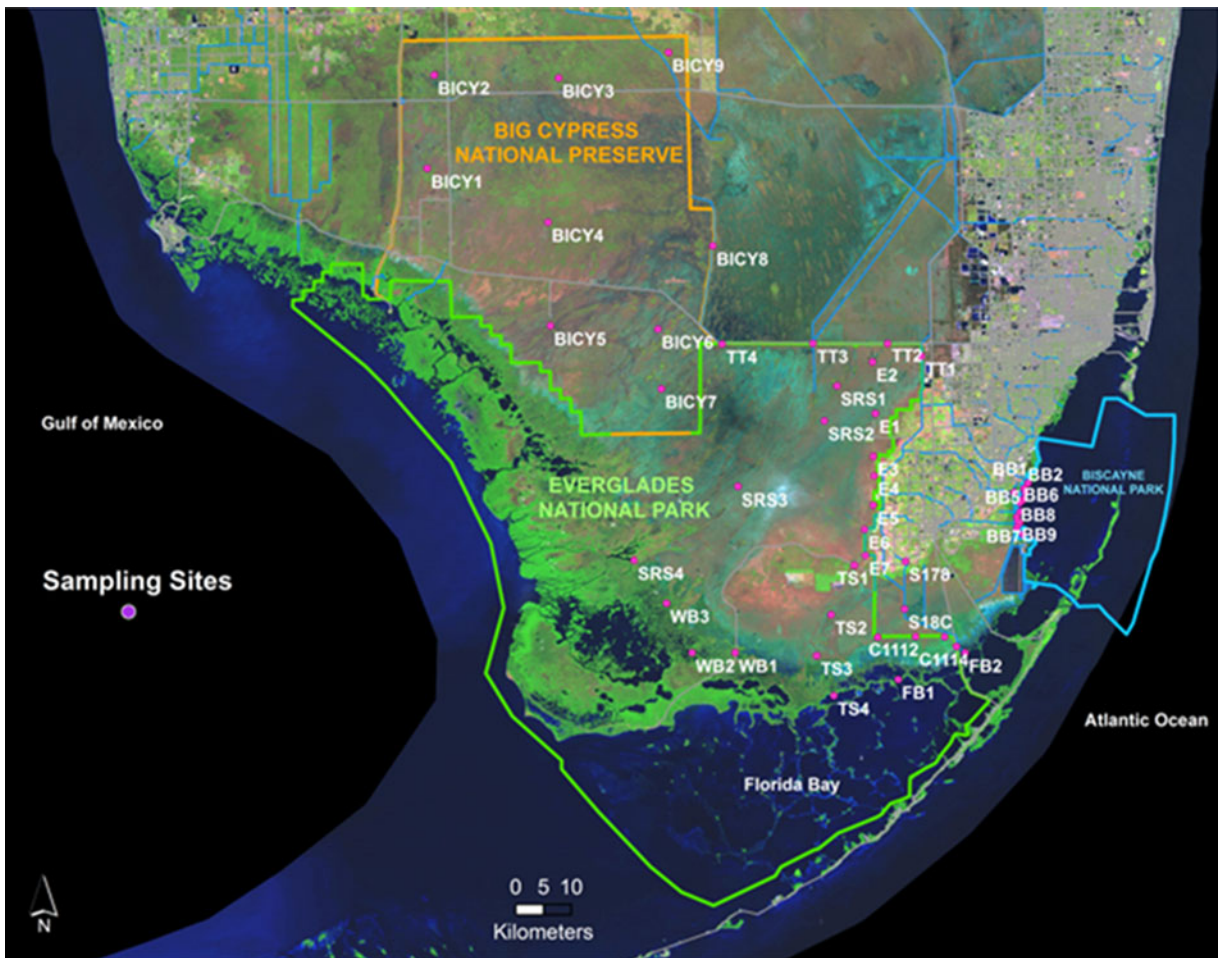


Fig. 1 Geographical location of the soil/sediment collection sites in ENP, BNP, and BICY

were used to determine the total carbon percentage (%TC) after combustion at 1,050 °C. Another two subsamples of 100 mg were digested with HCl in a LECO CC 100 digester, and the resulting CO₂ was measured by the same LECO CN 2000 analyzer to estimate the inorganic carbon content (%IC). The difference between the %TC and the %IC was the organic carbon (%OC). The calcium carbonate percentage was estimated by multiplying the %IC by a conversion factor equal to 8.33.

Effect and contamination indices (EI and CI)

Sample concentrations and the Florida’s Sediment Quality Assessment Guidelines (SQAGs), for both inland and coastal waters, were used to compute indices to perform a screening-level evaluation of potential

biological effects (MacDonald 1994; MacDonald et al. 2003). The purpose of this screening-level evaluation was to identify those trace metals whose concentrations were above specific thresholds and that may require further risk analyses. The indices also provided a mean for ranking the monitored sites based on their overall trace metal contamination.

The screening-level evaluation of effects on the biota from exposure to soil/sediment trace metals was performed considering three effect levels: negligible, possible, and probable. The analysis consisted of the following three steps:

1. An EI_Po (possible) index was estimated for each metal using the SQAG’s possible effect level, for freshwater (TEC) and marine water (TEL). If the EI_Po was:

Table 1 Site descriptors, locations, and ancillary parameters describing bulk soil/sediment characteristics

Station	Latitude (N)	Longitude (W)	Area	% TC	% IC	% OC
C111-1	25.2850	-80.5700	C111 Basin	14.35	11.55	2.80
C111-2	25.2860	-80.5097	C111 Basin	15.38	11.87	3.51
C111-3	25.2900	-80.4520	C111 Basin	14.81	10.98	3.83
C111-4	25.2700	-80.4430	C111 Basin	12.61	0.48	12.13
E1	25.6430	-80.5770	East boundary	13.69	3.55	10.14
E2	25.7310	-80.5770	East boundary	41.16	3.39	37.76
E3	25.5790	-80.5750	East boundary	16.75	6.18	10.57
E4	25.5460	-80.5750	East boundary	17.01	7.53	9.48
E5	25.4990	-80.5750	East boundary	15.58	5.37	10.21
E6	25.4630	-80.5900	East boundary	13.58	11.72	1.86
E7	25.4180	-80.5890	East boundary	14.05	11.44	2.61
FB1	25.2164	-80.5354	Florida Bay	12.02	8.21	3.81
FB2	25.2600	-80.4260	Florida Bay	13.80	9.13	4.67
SRS1	25.6890	-80.6350	Shark River Slough	24.64	9.81	14.84
SRS2	25.6350	-80.6550	Shark River Slough	25.37	1.15	24.22
SRS3	25.5510	-80.7850	Shark River Slough	45.41	1.97	43.44
SRS4	25.4150	-80.9630	Shark River Slough	21.83	5.08	16.75
S178	25.4084	-80.5237	Lower C-111 Basin	14.19	10.46	3.73
S18C	25.3300	-80.5250	Lower C-111 Basin	12.43	10.58	1.85
TT1	25.7400	-80.4980	Tamiami Trail	15.92	11.46	4.46
TT2	25.7530	-80.5530	Tamiami Trail	18.78	9.96	8.83
TT3	25.7620	-80.6820	Tamiami Trail	20.05	7.22	12.83
TT4	25.7610	-80.8210	Tamiami Trail	14.74	7.16	7.58
TS1	25.4021	-80.6070	Taylor Slough	15.85	10.62	5.23
TS2	25.3220	-80.6440	Taylor Slough	43.02	NA	NA
TS3	25.2570	-80.6670	Taylor Slough	16.87	11.22	5.65
TS4	25.1905	-80.6400	Taylor Slough	13.37	9.06	4.31
WB1	25.4420	-80.7840	Southwest boundary	16.02	11.69	4.32
WB2	25.2470	-80.8960	Southwest boundary	17.19	6.67	10.52
WB3	25.3420	-80.9020	Southwest boundary	34.83	1.15	33.67
BICY1	26.0450	-81.3000	Big Cypress	13.73	9.64	4.09
BICY2	26.1850	-81.2670	Big Cypress	8.19	0.15	8.04
BICY3	26.1920	-81.0860	Big Cypress	7.03	0.17	6.86
BICY4	25.9580	-81.1030	Big Cypress	14.62	0.20	14.42
BICY5	25.7880	-81.1000	Big Cypress	10.88	0.13	10.75
BICY6	25.7612	-80.9360	Big Cypress	11.34	0.53	10.80
BICY7	25.6880	-80.9200	Big Cypress	14.66	10.16	4.51
BICY8	25.9191	-80.8387	Big Cypress	40.59	2.34	38.25
BICY9	26.2310	-80.9150	Big Cypress	1.12	0.34	0.78
BB1	25.5350	-80.3250	Biscayne Bay	12.91	8.49	4.43
BB2	25.5260	-80.3320	Biscayne Bay	11.96	7.99	3.97
BB3	25.5200	-80.3300	Biscayne Bay	13.18	8.88	4.29
BB4	25.5080	-80.3334	Biscayne Bay	9.11	4.46	4.65
BB5	25.4880	-80.3400	Biscayne Bay	9.70	5.15	4.55

Table 1 (continued)

Station	Latitude (N)	Longitude (W)	Area	% TC	% IC	% OC
BB6	25.5050	-80.3380	Biscayne Bay	11.22	5.57	5.65
BB7	25.4686	-80.3400	Biscayne Bay	15.42	4.25	11.17
BB8	25.4800	-80.3450	Biscayne Bay	13.63	11.09	2.54
BB9	25.4740	-80.3470	Biscayne Bay	14.69	10.83	3.87
BB10	25.4630	-80.3420	Biscayne Bay	14.58	8.80	5.78
BB11	25.4510	-80.3340	Biscayne Bay	11.65	3.52	8.13
BB12	25.5190	-80.3470	Biscayne Bay	13.64	11.21	2.43
BB13	25.6110	-80.3060	Biscayne Bay	11.76	8.14	3.62
BB14	25.5840	-80.3070	Biscayne Bay	12.67	3.33	9.34
BB15	25.5650	-80.3060	Biscayne Bay	5.97	1.24	4.73
BB16	25.5470	-80.3120	Biscayne Bay	2.36	0.22	2.14

%TC percent total carbon, %IC inorganic carbon, %OC organic carbon

- (a) less than zero, the effect level on the biota was considered to be negligible and the evaluation process ended,
 - (b) greater than zero, the effect level on the biota was either possible or probable, the evaluation continued with step 2;
2. An EI_Pr (probable) index was estimated for each metal using the SQAG's probable effect level, for freshwater (PEC) and marine water (PEL). If the EI_Pr was:
- (a) less than zero, the effect level on the biota was considered to be possible, no additional risk analysis is required but continued monitoring is recommended,
 - (b) greater than zero, the effect level on the biota was considered to be probable and a probabilistic risk characterization was strongly recommended;
3. A contamination index (CI) was estimated for each site by aggregating all of the metals' EI_Po. Continuing with the screening level assessment, stations were ranked on their level of contamination by the CI, which is an overall index for all trace metals present in soils/sediments at a station. The CI was computed by aggregating the EI_Po, which uses the SQAG's possible effect level, for freshwater (TEC) and marine water (TEL). The EI_Po could be positive or negative, but only positive values (concentration > SQAG) were summed to compute the CI.

The indices were computed as follows:

$$EI_{Px_j} = \frac{C_j - SQAG_{x_j}}{SQAG_{x_j}} \quad (1)$$

$$\begin{cases} x = o \text{ (possible), use TEC or TEL} \\ x = r \text{ (probable), use PEC or PEL} \\ j = \text{for each trace metal, } 1 \text{ to } n \end{cases}$$

$$CI_j = \sum_{i=1}^n EI_{Po_j} \quad , \text{ for } EI_{Po_j} > 0 \text{ and } j = 1 \text{ to } n \quad (2)$$

In computing the EI_Po, the SQAG is substituted by the threshold effect level TEC (freshwater) or TEL (coastal waters), and the index is only indicative of possible effects. An EI_Po below or equal to zero suggests that the soil/sediment concentration, which is below the threshold, is unlikely to cause adverse biological effects; however, if the EI_Po is above zero, adverse effects are possible. To find the level of these effects, an EI_Pr is computed by substituting the SQAG by the probable effect level PEC (freshwater) or PEL (coastal waters). An EI_Pr below or equal to zero implies possible biological effects, but an EI_Pr above zero suggests probable adverse effects. The threshold levels for freshwater soil/sediments were obtained from MacDonald et al. (2003) and for marine sediments from MacDonald (1994).

Statistical analyses

Statistical analyses were computed with MINITAB (Minitab Inc., State College, PA) and XLSTAT (Addinsoft Inc., New York, NY). For constituents with concentrations below the MDLs, Helsel’s MR (multiple-limit regression) method was used to estimate descriptive statistics and Kendall’s tau correlation coefficient (Helsel 2005). The statistical significance (α) of the tests was evaluated at 5 %.

Background

Background soil/sediment concentrations were estimated by park from the statistical characteristics of each trace metal distribution. A k-means cluster analysis was used to group stations on the basis of their trace metal concentrations. The number of groups was fixed to five, for convenience, after several iterations with more (six and seven) and fewer (four and three) groups were considered. Changing the number of groups mostly affected stations with the highest concentrations, but results were not significantly different for stations in the lower tiers (low concentrations). Once stations were catalogued into groups, the lowest two concentration brackets were selected to estimate natural background concentrations for trace metals within the study area.

Enrichment plots

Enrichment plots were developed based on a linear regression between concentrations of a trace metal from the stations catalogued as background and that of a reference element, in this case Al, with upper and lower prediction intervals (PIs). To develop these plots, first, the parameters of the regressions were estimated using the natural log transformed data, and then the PIs were estimated in the natural log space according to the equations below (Helsel and Hirsch 1992). Finally, the PIs were converted back to the original space by taking their antilog and were plotted in a log–log graph with the predictive values of the regression. Regression residuals were tested for normality at $\alpha=5$ %.

A predictive line in the plot takes the form of

$$\bar{y} = m \times x + b \tag{3}$$

while the predictive intervals are defined as

$$\ln(\text{PI}) = \bar{y} \pm c \tag{4}$$

the upper and lower boundaries are calculated using c from

$$c = t_{(1-\frac{\alpha}{2})\%} \times S \times \sqrt{1 + \frac{1}{n} + \frac{(x - \bar{x})^2}{SSx}} \tag{5}$$

where

$$SSx = \sum_{i=1}^n x_i^2 + n \times (\bar{x})^2 \tag{6}$$

To aid in the reconstruction of the enrichment plots, these equations were rearranged to estimate the upper and lower 95th PIs, in the original units (milligrams per kilogram). The linear fit was transformed to a power function, as follows:

$$\bar{y} = b \times x^m \tag{7}$$

and the predictive intervals were transformed accordingly,

$$\text{PI(U)} = \text{EXP}(b + c) \times x^m \tag{8}$$

$$\text{PI(L)} = \text{EXP}(b - c) \times x^m \tag{9}$$

where,

- z trace metal concentration, milligrams per kilogram
- y $\ln(z)$
- \bar{y} predictive (PRE) value of y , from regression analysis
- X natural log of aluminum, milligrams per kilogram
- \bar{x} average (x)
- m slope from linear regression
- b intercept from linear regression
- PI Predictive intervals: PI(U) upper and PI(L) lower
- $t_{(1-\alpha/2)\%}$ t -statistics at $(1-\alpha/2)$ and $n-1$ degrees of freedom
- α 10 %
- s standard deviation of residuals, $(y - \bar{y})$

Simplified approach

The value of c is not a constant, but its variance was small for the range of concentrations of Al (>100 and

<50,000) in this study. By substituting c for the average of the c 's values, $c1$, a much simpler set of equations, was possible. The PIs in the original units could then be predicted by the following equations:

$$PI(U) = \text{Exp}(b + c1) \times x^m \quad (10)$$

$$PI(L) = \text{Exp}(b - c1) \times x^m \quad (11)$$

where Exp is the anti-logarithm.

Results and discussion

Trace metal concentrations

The concentrations of the ten selected trace metals, including six metals of concern, and the two reference metals are shown in Tables 2 and 3, their ecological reference thresholds in Table 4, and their summary statistics by park in Table 5. The statistics include number of records, number of samples with values below the MDL (nondetects), mean, standard deviation (StDev), minimum (Min), first quartile (Q1), second quartile or median, third quartile (Q3), and maximum (Max). For Ba and Cr, a distinction was made between carbonate-rich coastal (C) and terrestrial (T) sediment samples because they were statistically different ($P < 0.05$) based on a Kruskal–Wallis test.

The analysis shows that ENP had the highest mean concentrations, except for Cu and Zn which were the highest in BNP and V in BICY. This apparently higher level of contamination in ENP than in the other two parks may be a reflection not only of elevated concentration inputs from anthropogenic sources but also from a site selection bias. More samples were collected in ENP to account for its larger size, and a large fraction of these stations were located along boundaries adjacent to urban or agricultural areas, where pollution was expected.

The data distribution was not always normal and varied by trace metal and by park. The number of nondetects was low, except for Mn in BNP. Most trace metal concentrations exhibited right skewness and had few but very large outliers. Maximum to median and StDev to mean ratios showed that Pb, Zn, and Cr in ENP and Cu and Zn in BNP have observations that were uncharacteristically large and potentially of concern. These outliers exceeded the medians by factors

ranging from 23 for Cu to 10 for Zn in BNP and from 57 for Pb to 23 for Zn in ENP; suggesting that contamination comes mainly from local anthropogenic sources. Cross-correlation analysis (Kendall's tau, $\alpha = 5\%$) for the three parks combined dataset, using averages, shows that Co, Ni, and Pb were frequently correlated (91 %, calculated as significant/total number correlations) to other trace metals and that Mn was the least frequently correlated (36 %). For the reference elements, Fe was more frequently correlated (80 %) than Al (60 %). The OC% was not correlated to any trace metal, and the IC% was correlated to As and Fe only. The type, degree, and frequency of correlation changed drastically when the data were analyzed by park.

The degree of correlations was less frequent (18 %) in BICY, where correlations extended to two or less trace metals, except for Fe and Cr, which had a slightly higher number of correlations; by contrast, the degree of correlation was most frequent in BNP, where trace metals were correlated to at least nine other trace metals, except for Ba and Mn, which were less frequently correlated. When the carbon fractions were included, Ni was significantly correlated to OC% in BICY; Mn, Co, and Ba were significantly correlated to IC% and As to OC% in BNP; but no trace metals were correlated to either IC% or OC% in ENP. Of all the trace metals, only Mn was inversely correlated, more frequently in ENP and less frequently in BICY. These correlations suggest that the sources of contamination vary by park and that they may include natural and anthropogenic sources. In BICY, V, Cr, Ni and As, which are strongly correlated to Fe, appear to come from natural sources; Pb, Co, and Zn from atmospheric deposition (Landing et al. 1995); and Cu, which is inversely correlated to Mn, from agricultural runoff. In BNP, Cu, which is strongly correlated to V, Cr, Co, Ni, Zn, As, Ba, and Pb, might have more than one source, but antifouling paint appears to be the main source. Two marinas within the park boundary show elevated concentrations for these metals. Other potential metal sources are urban and agricultural runoff, leachate from a nearby landfill, and runoff from a partially closed military airbase. In ENP, Pb, which is strongly correlated to several metals, except Mn, As, Fe and Al, appears to come from spent ammunition; and Cu, which is also related to most metals, except As and Ba, appears to come from agricultural and urban runoff (Gupta 1997).

Table 2 Trace metal concentrations (milligrams per kilogram dry weight, DW) in soils and sediments collected in 2006

Station	As	Ba	Co	Cr	Cu	Mn	Ni	Pb	V	Zn	Al	Fe
MDL TERRESTRIAL	0.21	1.34	0.05	1.88	0.48	6.4	0.47	0.97	0.57	3.6	901	515
MDL CARBONATE	0.09	0.59	0.02	0.66	0.17	37.6	0.24	0.16	0.19	2.6	718	703
C111-1	3.2	14.0	0.3	1.5	0.5	117.5	0.5	0.7	1.2	1.2	559	3,637
C111-2	1.2	13.3	0.5	0.8	0.7	74.4	0.7	3.0	1.5	3.6	352	3,204
C111-3	8.7	33.7	2.9	6.9	4.0	139.3	2.3	5.4	12.2	15.8	1,793	13,448
C111-4	3.4	18.5	0.5	10.2	4.1	14.0	4.0	22.6	9.1	6.0	4,575	4,056
E1	1.0	32.2	0.7	22.9	7.6	18.8	3.7	175.9	8.3	12.7	8,100	5,497
E2	8.2	40.0	1.4	5.2	2.6	38.2	3.0	7.6	6.1	5.8	2,736	9,710
E3	1.3	55.5	1.8	48.3	22.2	46.1	8.5	377.3	18.5	204.8	18,108	6,755
E4	1.6	55.6	1.0	35.7	8.7	42.9	6.8	25.2	20.6	25.7	17,397	8,024
E5	1.7	37.5	1.2	41.0	9.2	37.9	5.9	127.2	26.1	17.2	21,877	20,200
E6	0.9	27.6	0.5	3.6	1.4	115.9	1.0	4.8	9.0	2.6	1,784	7,145
E7	2.0	26.0	0.7	4.7	2.3	97.5	1.5	5.0	9.8	42.5	1,664	4,149
FB1	3.0	14.1	0.9	24.5	1.9	108.5	5.5	5.9	8.2	4.7	8,955	10,212
FB2	4.1	11.6	0.5	8.4	5.4	63.4	2.0	4.1	6.5	7.9	2,058	7,355
SRS1	9.6	48.4	1.2	2.9	1.8	207.2	2.6	9.6	4.5	17.1	1,582	16,731
SRS2	2.2	50.5	0.8	23.3	2.0	26.4	3.7	9.4	14.8	4.2	12,936	13,572
SRS3	9.3	18.3	0.8	4.5	2.0	47.9	1.9	6.6	6.2	6.6	1,929	17,327
SRS4	2.2	18.4	0.7	6.3	2.8	86.5	1.9	4.9	5.8	9.4	1,236	20,379
S178	2.0	19.6	0.9	11.8	19.0	43.8	3.7	14.2	4.6	51.4	2,397	3,957
S18C	3.8	7.4	0.9	11.5	1.2	25.6	3.0	1.8	7.5	1.9	6,715	8,826
TT1	2.6	37.8	0.6	3.0	2.4	59.0	2.2	14.0	4.6	9.2	4,322	16,335
TT2	1.8	16.6	0.4	3.3	3.0	33.7	1.4	12.3	2.2	19.4	1,464	5,771
TT3	2.5	29.1	0.9	7.4	6.9	53.6	3.2	6.5	4.4	17.1	6,211	15,144
TT4	2.6	21.4	1.1	10.7	3.6	27.5	3.6	14.4	6.1	24.2	10,401	8,980
TS1	1.2	13.6	0.4	7.2	1.2	38.5	1.7	3.8	6.3	3.4	5,941	7,580
TS2	1.8	5.8	0.3	0.8	1.6	2.8	1.3	6.2	3.6	3.4	738	3,663
TS3	1.4	17.6	0.3	2.9	0.8	53.0	0.8	2.4	2.5	2.8	1,204	2,644
TS4	1.4	10.1	0.5	11.1	1.6	54.0	2.3	3.1	3.8	4.2	3,537	5,627
WB1	1.0	26.9	0.6	4.0	1.0	130.7	1.3	4.2	4.9	3.0	1,628	4,083
WB2	1.5	12.6	0.6	12.5	1.4	64.3	2.4	5.4	4.9	3.5	4,120	6,730
WB3	2.7	11.1	0.7	20.7	4.2	53.2	4.9	12.1	8.0	9.9	5,743	8,870
BICY1	1.0	25.9	0.4	12.6	0.6	46.8	1.9	3.6	9.0	3.2	4,200	2,328
BICY2	0.8	30.8	0.5	18.7	2.8	7.9	3.0	6.7	12.3	5.6	8,945	2,783
BICY3	0.6	18.3	0.5	9.3	0.8	10.6	3.0	5.1	5.4	4.8	6,238	2,211
BICY4	1.2	7.8	0.4	16.8	2.8	4.2	2.6	3.9	11.2	3.8	3,759	1,902
BICY5	1.1	24.5	0.8	58.1	1.6	14.9	5.6	9.9	12.0	6.9	13,349	4,007
BICY6	2.9	16.8	0.7	22.8	1.0	14.5	4.0	8.8	20.2	32.6	10,212	8,728
BICY7	3.0	20.0	0.5	13.8	2.8	60.6	2.5	4.0	14.2	4.7	5,698	5,248
BICY8	3.6	18.8	0.8	8.3	2.6	13.7	3.2	12.2	9.4	6.4	3,118	3,655
BICY9	<i>0.1</i>	1.4	<i>0.02</i>	<i>0.2</i>	<i>0.1</i>	<i>2.4</i>	<i>0.1</i>	<i>0.6</i>	<i>0.2</i>	<i>2.7</i>	<i>102</i>	<i>79</i>
BB1	3.6	9.9	0.7	11.9	21.8	41.4	3.6	14.9	10.5	50.7	2,713	8,800
BB2	1.9	9.7	0.3	5.2	5.6	35.0	1.8	5.5	6.3	15.8	1,442	3,005
BB3	1.8	10.1	0.4	4.7	10.5	<i>34.1</i>	2.0	8.5	7.4	18.2	1,139	2,749

Table 2 (continued)

Station	As	Ba	Co	Cr	Cu	Mn	Ni	Pb	V	Zn	Al	Fe
BB4	2.0	6.5	0.4	5.4	5.9	25.9	1.9	3.6	4.9	11.0	1,574	2,781
BB5	2.8	6.0	0.4	6.4	8.9	27.7	2.9	6.4	12.3	17.6	1,815	3,084
BB6	2.4	8.5	0.4	5.1	16.3	32.7	2.1	3.9	6.4	13.3	1,778	3,091
BB7	4.3	7.9	0.9	9.9	16.4	24.6	7.5	8.9	10.2	26.4	2,993	4,417
BB8	2.1	11.9	0.6	7.3	4.4	36.3	2.3	3.9	4.9	12.3	1,987	2,861
BB9	2.0	10.3	0.4	7.7	0.8	67.9	1.8	3.1	5.3	3.7	3,258	2,780
BB10	5.7	10.8	0.7	18.3	194.1	28.9	5.3	19.7	7.5	156.0	4,241	5,056
BB11	3.2	11.0	0.5	9.0	10.4	27.4	3.8	11.4	9.0	21.7	2,901	4,090
BB12	2.5	18.3	2.0	10.4	11.7	56.0	3.1	11.2	8.0	56.5	2,740	2,974
BB13	1.6	3.2	0.2	4.2	7.9	7.1	1.3	7.5	3.8	15.9	2,753	2,929
BB14	2.1	3.7	0.1	2.4	6.3	7.9	1.1	6.5	3.0	10.0	732	1,978
BB15	2.2	2.0	0.1	2.4	4.7	5.4	1.3	2.7	3.2	6.1	532	1,210
BB16	0.8	0.9	0.02	1.2	1.2	2.6	0.5	1.0	1.5	2.7	251	471
Average	2.6	18.9	0.7	11.4	8.5	46.5	2.8	19.4	7.8	19.1	4,555	6,415
Median	2.1	16.6	0.6	7.7	2.8	37.9	2.4	6.4	6.4	9.2	2,753	4,149
Minimum	0.1	0.9	0.0	0.2	0.1	2.4	0.1	0.6	0.2	1.2	102	79
Maximum	9.6	55.6	2.9	58.1	194.1	207.2	8.5	377.3	26.1	204.8	21,877	20,379

Terrestrial samples are in bold to distinguish from marine carbonate samples. Numbers in italic font are below the MDL

The 90th percentile concentration, in milligrams per kilogram, and the spatial distribution of other even higher concentrations were as follows: As (6.4), in ENP it was particularly high along the Shark River Slough stations (SRS1 and SRS3), E2, and C111-3; Ba (51.2), in ENP it was mostly high along the eastern boundary sites (E1 through E6, except E2) and in BICY at BIGY6; Co (1.5), in ENP it was high at the lower eastern boundary stations (E3, E5, and E6) and C111-3 and in BICY at BICY6; Cr (33.5), in ENP it was high along the eastern boundary sites (E1 through E6, except E2) and in BICY at BICY5 and BICY6; Cu (16.3), in BNP it was high at BB1, BB3, BB5, and BB7 and very high at BB10; Mn (115.9), in ENP it was high along the Shark River Slough stations (SRS1 and SRS 2) and in the C111 canal stations; Ni (6.8), in ENP it was high along the eastern boundary sites (E1 through E6, except E2) and in BIGY at BIGY6; Pb (22.6), in ENP it was high along the eastern boundary sites (E1, E3, and E5), in OTH at S178, and in BICY at BICY6; V (18.2), in ENP it was high along the eastern boundary (E2, E3, and E5) and in BIGY at BIGY6; and Zn (35.4), in ENP it was high in E3 and TT4, in OTH at S178, and in BNP at BB1, BB12, and BB10. The two reference metals, Al (13,339) and Fe (15,144), were the highest in ENP at the eastern boundary sites for Al and at

the eastern boundary sites and lower Shark River Slough sites for Fe.

Possible and probable effects

The trace metal soil/sediment quality indices, which were derived from sample concentrations and the Florida's threshold levels (SQAG), were used to carry out a screening-level classification of stations into three groups according to their soil/sediment potential for causing biological adverse effects: (a) minimal adverse effects, (b) possible adverse effects, and (c) probable adverse effects (MacDonald 1994). The advantage of the EIs indices (EI_Po and EI_Pr) over conventional ratios (hazard quotient) is that the EIs are independent of the SQAG and could be summed into a single overall index for contamination and, therefore, of toxicity. The disadvantage of the CI index is that it indirectly assumes equal toxicity for all metals. This index could be improved if a weighted sum of the EI_Po indices is made by assigning toxicity potencies to each trace metal (Hakanson 1980).

Seven of the ten trace metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) have probable (TEC and TEL) effect level thresholds; thus, only these metals were used to compute the indices. The EI_Po index, which indicates possible

Table 3 Trace metal concentrations (milligrams per kilogram DW) in soils and sediments collected in 2007

Station	As	Ba	Co	Cr	Cu	Mn	Ni	Pb	V	Zn	Al	Fe
MDL TERRESTRIAL	0.21	1.34	0.05	1.88	0.48	6.4	0.47	0.97	0.57	3.6	901	515
MDL CARBONATE	0.09	0.59	0.02	0.66	0.17	37.6	0.24	0.16	0.19	2.6	718	703
C111-1	3.8	16.0	0.4	0.7	0.8	146.2	0.7	3.5	1.9	3.2	260	4,953
C111-2	1.0	19.3	0.3	0.4	0.9	68.9	0.6	2.7	1.2	3.3	115	3,632
C111-3	9.8	36.7	2.9	6.5	4.1	137.9	2.3	6.4	13.0	14.7	1,785	15,386
E1	1.3	76.8	1.5	58.0	4.6	22.7	9.5	32.8	18.2	8.3	23,858	7,765
E2	9.3	38.7	0.9	9.7	2.8	34.1	4.3	3.5	10.8	3.7	4,167	14,432
E3	1.3	65.7	1.5	64.5	7.7	69.5	10.2	65.9	28.5	24.7	23,578	10,417
E4	1.4	52.1	1.1	44.9	5.0	59.5	6.9	11.8	19.8	12.3	15,739	6,820
E5	3.7	83.9	3.5	154.6	8.4	71.8	18.5	44.7	77.5	16.0	47,238	46,150
E6	1.8	63.7	2.1	77.4	1.6	136.1	10.9	15.5	22.9	5.3	26,071	21,472
E7	1.3	28.1	0.5	8.0	1.9	112.0	2.1	3.7	7.3	7.1	2,908	3,911
FB1	3.7	11.9	0.8	18.3	1.6	86.6	4.0	4.7	6.3	3.9	6,809	9,591
FB2	4.2	13.2	0.7	12.5	5.3	77.1	3.4	5.4	8.7	11.2	4,250	8,717
SRS1	9.5	51.2	1.8	1.6	1.7	233.6	1.5	6.8	3.2	9.7	924	12,018
SRS2	4.7	47.2	0.9	6.1	3.6	162.8	2.7	12.1	9.2	10.7	2,474	11,555
SRS3	10.8	22.6	1.9	5.9	3.9	75.9	3.7	15.0	9.5	12.7	2,299	14,090
SRS4	3.6	9.8	0.8	21.2	5.5	107.6	4.3	9.7	15.1	11.8	3,602	27,641
S178	1.9	19.6	1.1	13.7	23.6	54.7	3.8	48.1	5.9	73.7	3,559	5,196
S18C	8.9	15.1	1.5	9.4	3.9	40.4	2.1	11.2	12.9	9.1	1,736	11,569
TT1	2.9	80.6	0.8	3.7	6.8	138.2	2.5	17.0	5.3	14.9	1,708	7,082
TT2	6.4	56.6	1.0	7.1	3.4	114.7	3.0	20.4	5.6	21.3	2,739	9,754
TT3	0.8	8.2	0.2	5.3	4.0	17.7	1.3	9.8	3.7	8.9	720	971
TT4	5.2	46.1	2.0	19.9	7.1	65.1	7.0	23.8	12.0	47.2	9,825	9,953
TS2	1.3	22.6	0.4	0.8	0.9	51.9	1.0	3.6	2.8	3.4	307	2,658
TS3	2.7	18.3	0.3	1.1	0.4	84.9	0.6	2.3	2.2	2.0	418	6,257
TS4	1.9	11.1	0.6	14.9	2.0	70.4	3.2	4.1	4.5	6.4	4,815	7,804
WB2	3.9	11.6	1.1	33.5	2.3	26.8	7.8	11.5	19.3	8.1	13,339	8,225
WB3	2.7	7.9	0.6	15.2	9.2	11.9	5.9	6.5	11.4	9.1	5,596	9,237
BICY1	0.7	22.1	0.4	10.5	0.6	36.5	1.5	3.9	7.9	2.0	2,195	1,272
BICY2	1.3	14.7	0.4	6.6	1.6	28.5	1.3	3.9	7.1	35.4	2,459	1,838
BICY3	1.0	10.6	0.4	2.1	1.2	27.6	1.4	5.0	1.1	4.8	930	624
BICY4	<i><0.21</i>	<i>0.9</i>	0.05	<i>1.3</i>	<i>0.2</i>	<i>0.6</i>	<i>0.2</i>	<i>0.5</i>	<i>0.7</i>	<i>1.2</i>	<i>323</i>	<i>156</i>
BICY5	0.7	9.4	0.4	21.0	2.6	11.1	2.1	5.3	7.9	4.4	4,375	1,746
BICY6	3.5	77.5	2.6	54.1	3.4	26.1	13.2	33.4	40.4	30.2	35,441	17,446
BICY7	1.9	10.1	0.4	14.1	0.6	9.7	2.1	3.3	16.7	1.9	5,119	3,881
BICY8	4.5	21.3	1.1	5.5	5.3	15.5	3.3	7.8	11.5	17.0	1,894	3,233
BICY9	1.0	18.3	0.5	5.0	5.7	11.8	2.1	7.2	11.1	7.4	2,540	910
BB1	4.0	10.2	0.7	12.2	27.7	40.6	3.5	18.1	11.3	44.8	2,933	9,571
BB2	2.1	10.5	0.4	5.0	9.7	37.1	2.1	5.7	9.3	21.9	1,515	2,821
BB3	1.9	8.0	0.4	4.6	26.0	31.6	1.9	9.9	5.4	18.5	1,121	2,373
BB4	3.5	7.8	0.4	5.0	2.6	31.3	1.5	1.5	5.4	2.9	1,707	3,606
BB5	3.5	8.5	0.5	10.8	20.3	38.7	4.1	10.3	14.5	27.4	3,050	3,401
BB6	4.0	10.7	0.7	10.6	13.7	40.9	4.2	6.4	10.8	15.3	3,809	4,798

Table 3 (continued)

Station	As	Ba	Co	Cr	Cu	Mn	Ni	Pb	V	Zn	Al	Fe
BB7	2.5	7.4	0.4	6.2	13.3	22.7	2.1	7.0	4.5	11.7	1,640	2,291
BB9	2.0	12.7	0.5	6.8	7.0	32.7	2.3	4.0	4.7	14.1	1,897	2,277
BB10	6.6	12.4	0.7	18.9	230.3	30.8	5.8	21.6	6.9	182.1	4,769	5,067
BB11	5.1	7.8	0.6	9.2	10.8	28.2	4.3	7.7	10.2	18.4	3,177	4,401
Average	3.5	26.4	0.9	17.9	11.0	60.5	4.0	12.3	11.4	17.9	6,342	8,021
Median	2.8	15.5	0.7	9.3	4.0	40.5	2.9	7.1	9.0	11.0	2,823	5,727
Minimum	0.0	0.9	0.0	0.4	0.2	0.6	0.2	0.5	0.7	1.2	115	156
Maximum	10.8	83.9	3.5	154.6	230.3	233.6	18.5	65.9	77.5	182.1	47,238	46,150

Terrestrial samples are in bold to distinguish from marine carbonate samples. Numbers in italic font are below the MDL

effects, showed that five trace metals (As, Cr, Cu, Pb, and Zn) were of concern and merited additional consideration. These trace metals, segregated by station and park, are listed in Table 6 and included As in ENP; Cr in ENP and BICY; Cu and Zn in BNP; Pb in ENP and OTH. Of these five trace metals, Cu, Cr, and Pb had also an EI_Pr index greater than zero and, consequently, were associated with probable adverse effects. Table 7 lists these trace metals and their corresponding sites: Cu in BB10, BNP; Cr in E5 and Pb in E3 and E1, all in ENP.

The level of contamination, by site, according to the CIs is listed in Table 8. The last column in this table shows an overall ranking from 1, indicating the most contaminated, to 13, indicating the least contaminated. Considering the 13 sites with a CI >0 only, ENP had the greater fraction of sites (46 %, 6/13) showing a greater level of contamination than BNP (31 %) and BICY (15 %); however, when the percentage of sites with a CI >0 to total number of sites per park is calculated, BNP has the largest fraction of sites (36 %, 4/11) than BICY (22 %) and ENP (20 %). The geographical distribution of the CIs is shown in Fig. 2.

In ENP, sites with a CI >0 were mostly located along the eastern boundary of the park (E1 through E6, except E2) and in Shark River Slough (SRS3). Stations along the eastern boundary of the park appeared to be most

heavily affected by anthropogenic inputs associated with spent ammunition (Pb) and agricultural and urban runoff (Cu). Some of these stations were located in or near former agricultural lands, which were part of the Homestead agricultural area and had been known to be a source of pesticides and nutrients to nearby marshes and coastal basins (Scott et al. 2002; Harman-Fetcho et al. 2005; Carriger et al. 2006; Sappington et al. 2007; Carriger and Rand 2008a, b). In BNP, sites with a CI >0 are located within the Bay Front Marina (BB10), Black Creek Marina (BB1), the Princeton Canal (BB1), which drains several nurseries, agricultural fields, and urban areas and may collect leachate from a nearby landfill (Long et al. 1999; O'Donnell et al. 2005), and the Military Canal (BB5), which collects runoff from partially closed military airbase (Superfund Site). In BICY, the sites with CI >0 were located within two major flow ways in the southern half of the preserve (BICY5 and BICY6). At these stations, Cr appears to be of concern. Because Cr is strongly correlated to Fe and Al, it is inferred that the high Cr observed at these stations may have come from soil erosion (Guertin et al. 2004) caused by past or on-going construction projects upstream of these stations. In OTH, the site with CI >0 is S178, which drains agricultural fields from the Loveland Slough basin. Although Pb was the only trace metal of concern

Table 4 Florida's Sediment Quality Assessment Guidelines (SQAG), in milligrams per kilogram

Effect level	Environment	As	Cr	Cu	Ni	Pb	Zn
Possible	TEC (freshwater)	9.8	43.4	31.6	22.7	35.8	121.0
	TEL (marine waters)	7.2	52.3	18.7	15.9	30.2	124.0
Probable	PEC (freshwater)	33.0	111.0	149.0	48.6	128.0	459.0
	PEL (marine waters)	41.6	160.0	108.0	42.8	112.0	271.0

Table 5 Summary statistics for soil/sediment trace metal concentrations, in milligrams per kilogram, by park

ENP	Al	As	Ba		Co	Cr		Cu	Fe	Mn	Ni	Pb	V	Zn
			T	C		T	C							
Records	53	53	42	11	53	42	11	53	53	53	53	53	53	53
Nondetects	8	0	0	0	0	7	0	1	0	3	0	0	0	11
Mean	6,777	3.5	35.3	12.3	1.0	17.7	16.7	3.8	10,138	76.6	3.7	23.1	10.2	14.4
StDev	8,827	2.8	20.4	2.4	0.7	28.9	7.9	3.6	7,469	48.7	3.3	57.8	11.5	28.3
Min	213	0.8	5.8	9.8	0.2	0.3	6.3	0.3	971	12.3	0.5	1.0	1.2	1.0
Q1	1,605	1.4	18.3	11.1	0.5	3.0	11.1	1.6	5,562	38.4	1.5	4.2	4.5	3.8
Median	3,537	2.6	30.7	11.6	0.8	6.3	14.9	2.8	8,225	65.1	2.7	6.6	6.5	8.9
Q3	8,528	4.0	50.7	13.2	1.2	20.7	21.2	5.2	13,510	110.3	4.6	14.7	12.1	15.4
Max	47,238	10.8	83.9	18.4	3.5	154.6	33.5	22.2	46,150	233.6	18.5	377.3	77.5	204.8
BNP														
Records	26	26	26	26	26	26	26	26	26	26	26	26	26	26
Nondetects	2	0	0	1	0	0	1	20	0	0	0	0	0	0
Mean	2,276	2.9	8.7	0.5	7.7	26.5	3599	25.6	2.9	8.1	7.2	30.6		
StDev	1,089	1.4	3.7	0.4	4.4	55.4	1,941	14.7	1.6	5.4	3.224	43.1		
Min	681	0.8	0.9	0.1	1.2	0.8	1,155	7.7	0.5	1.0	1.5	2.7		
Q1	1,497	2.0	7.2	0.4	4.9	5.8	2,655	14.7	1.8	3.9	4.85	11.5		
Median	1,942	2.5	9.1	0.4	6.6	10.4	2,990	21.9	2.2	6.8	6.65	16.8		
Q3	3,007	3.7	10.7	0.7	10.5	17.4	4,405	33.5	3.9	10.5	10.2	26.7		
Max	4,769	6.6	18.3	2.0	18.9	230.3	9,571	67.9	7.5	21.6	14.5	182.1		
BICY														
Records	18	18	18	18	18	18	18	18	18	18	18	18	18	18
Nondetects	2	2	1	2	2	2	2	2	2	2	1	5		
Mean	6,204	1.6	19.5	0.62	15.7	2.0	3,478	19.4	3.0	7.1	11.1	9.5		
StDev	8,067	1.3	16.5	0.54	16.0	1.6	4,033	15.6	2.8	7.1	9.0	11.3		
Min	488	0.3	1.4	0.17	1.4	0.3	328	3.3	0.7	1.4	0.7	0.6		
Q1	2,120	0.7	9.9	0.40	5.4	0.6	1,182	9.3	1.5	3.8	6.7	2.0		
Median	3,980	1.1	18.3	0.45	11.6	1.6	2,270	14.1	2.3	5.1	10.3	4.8		
Q3	6,915	2.9	22.7	0.73	19.3	2.8	3,913	27.8	3.2	8.1	12.8	9.8		
Max	35,441	4.5	77.5	2.60	58.1	5.7	17,446	60.6	13.2	33.4	40.4	35.4		

T terrestrial sediments, C coastal sediments

identified in this study, this site had received a great deal of attention for its high levels of pesticide contamination (Miles and Pfeuffer 1997; Fulton et al. 2004; Carriger et al. 2006; Carriger and Rand 2008a, b).

Background concentrations

One of the key goals of this study was to establish a set of background trace metal concentrations that describe

the regional soil/sediment composition in the absence of anthropogenic inputs. These levels are considered to represent baseline conditions and could be used to evaluate soil chemical changes from restoration projects (Jones et al. 1997). This is the first study to provide region-specific background concentration ranges for trace metals in south Florida in areas relevant to the National Park Service, which have never been surveyed or included in the baseline calculation

Table 6 Soil/sediment trace metal possible effect index

Possible effect index			
Park	Trace metal	Station	EI_Po
BICY	Cr	BICY5	0.34
		BICY6	0.25
BNP	Cu	BB10	11.32
		BB1	0.48
		BB3	0.39
		BB5	0.09
		BB10	0.47
ENP	Zn	BB10	0.47
	As	SRS3	0.10
		Cr	E5
	E6		0.78
	E3		0.49
	E1		0.34
	Pb	E4	0.03
		E3	9.54
		E1	3.91
	Zn	E5	2.55
E3		0.69	
OTH	Pb	S178	0.34

Higher values indicate higher potential for adverse effects

reports available in the literature (Schropp and Windom 1988; Windom et al. 1989; Schropp et al. 1990; Chen et al. 1999; Carvalho et al. 2002; Department of Environmental Resource Management (DERM) 2002).

From cluster analysis

From the k-means cluster analysis, concentrations from the lowest two tiers were selected to compute background concentrations. The summary statistics are

Table 7 Probable effect index of individual trace metals present in the soil/sediment samples

Probable effect index				
Park	Trace metal	Station	EI_Pr	
BNP	Cu	BB10	1.13	
ENP	Cr	E5	0.39	
		Pb	E3	1.95
			E1	0.37

Higher values indicate higher potential for adverse effects

Table 8 Overall station ranking based on the trace metal-derived contamination index (CI)

Contamination index (ci)			Overall Rank
Park	Station	CI	
BICY	BICY5	0.42	7
	BICY6	0.25	10
BNP	BB10	11.78	1
	BB1	0.48	6
	BB3	0.39	8
	BB5	0.09	12
	ENP	E3	10.72
E5		5.12	3
E1		4.25	4
E6		0.78	5
SRS3		0.10	11
E4		0.03	13
OTH	S178	0.34	9

presented in Table 9. These average concentrations, which were computed across each park to account for natural spatial variability, are assumed to represent current conditions without influences from anthropogenic sources. These background concentrations were not the same in all three parks. For example, ENP had the highest background concentrations (shown in parentheses in milligrams per kilogram): Al (4,177), As (2.07), Ba (12.5), Co (0.65), Cr (11.6), Fe (3,939), Ni (2.15), Pb (9.20), V (6.30), and from these, the coastal sediment samples were higher than the terrestrial sediment samples, except for Fe, Ba, and Pb; BNP had the highest concentrations for Cu (4.28), Mn (36.1), and Zn (12.2); by contrast, BICY had the lowest concentrations for As (1.07), Cu (2.03), Fe (2,296), Mn (17.0), Pb (5.58), and Zn (5.11). Several background calculations are available in the literature for other regions in Florida. For example, Chen et al. (1999) reported background concentrations for selected Florida soils while the predictive tool provided by Carvalho et al. (2002) is the basis for assessing enrichment plots using the natural variability of minerals, soils, and sediments for the State of Florida. Two smaller but more relevant studies have reported regional background concentrations of Miami-Dade County (DERM 2002) and for areas near Homestead (Scarlatos and Scarlatos 1997). A summarized comparison of the available background levels is shown in Table 10. In general, the park-specific background concentrations reported in this study are lower than those

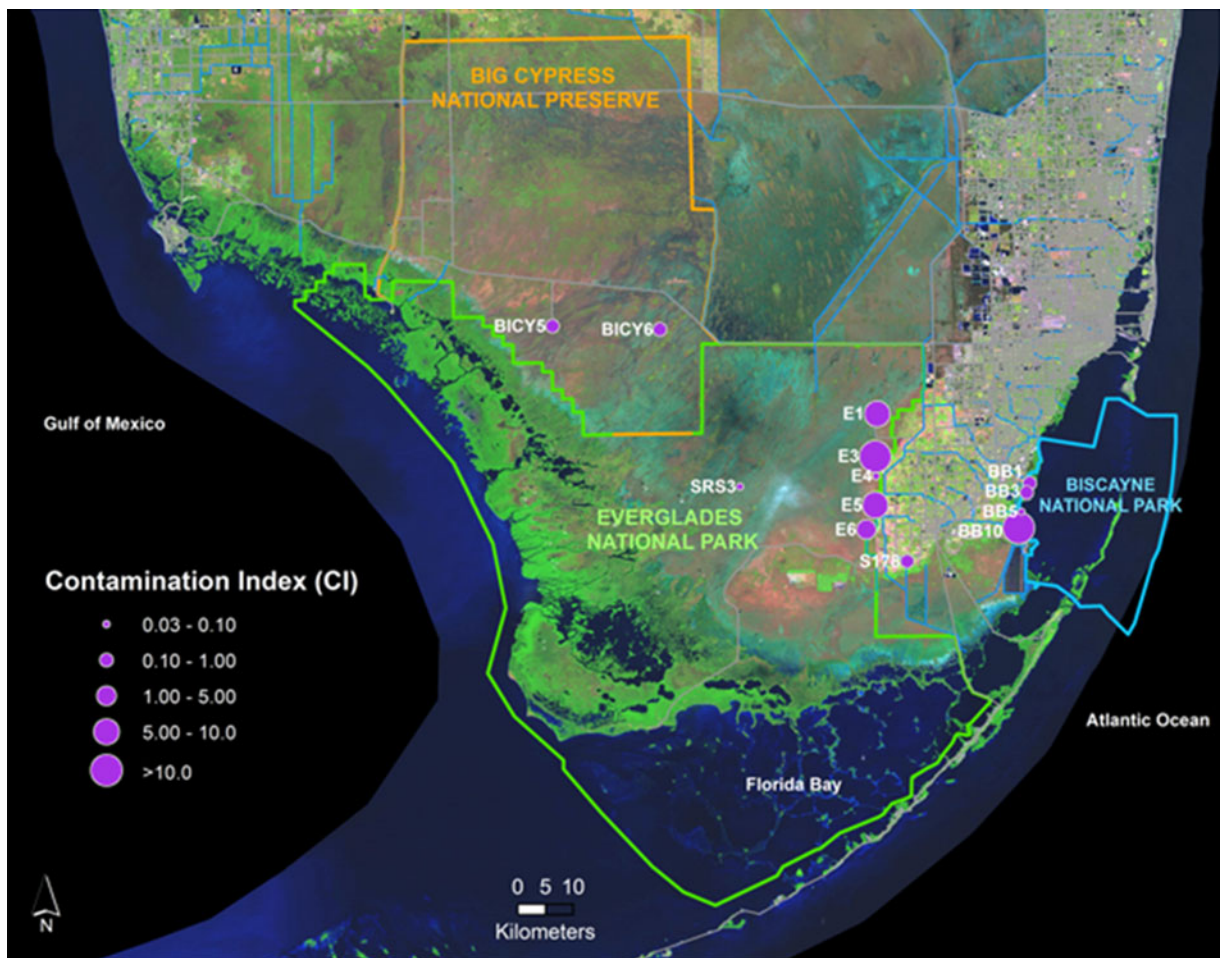


Fig. 2 Geographical distribution of sample sites based on their contamination index (CI) ranking. The size of the symbol is arbitrary but denotes differences in the trace metal concentrations

and their contribution to the sediment quality assessment guidelines (SQAGs) as described in Eq. 2

reported for other Florida environments. This local uniqueness (ENP, BNP, and BICY) is likely due to a lower mineralogical complexity with a rather low anthropogenic signature when compared with larger areas of the state. One deviation from this trend is the background concentrations of Cu and Zn for BNP that suggest that local boating activities may be influencing and surpassing the natural distributions.

Enrichment plots

Sediment and soil concentrations from ENP, BNP, and BICY were used in a management-decision process to assess whether or not sediments or soils have been affected by anthropogenic inputs. A similar tool, presented as enrichment plots (Schropp and Windom

1988; Windom et al, 1989; Schropp et al. 1990; Carvalho et al. 2002), has been widely used in the state of Florida—where statistically sound data are available for a wide variety of soils and sediments. Considering that these enrichment plots were based on an analysis of a state-wide sediment data sets, this tool may not be able to provide an adequate characterization of pristine environments such as the protected Florida Everglades, which is at the southern portion of the Florida peninsula and is dominated by natural biogeochemical cycles containing a rather small variety of mineral phases, like carbonate marls and peats.

A new set of enrichment plots was developed for south Florida’s protected lands from sediment and soil samples collected at ENP, BNP, and BICY. The average sample concentrations from the cluster analysis’ two

Table 9 Region-specific trace-metal background concentrations (milligrams per kilogram) as calculated from the cluster analysis

Background concentration, mg/kg, Park									
Analyte	Park	<i>N</i>	Avg	StDev	Min	Q1	Median	Q3	Max
Al	BNP	26	2,276	1,089	681	1,497	1,942	3,007	4,769
	BICY	14	3,168	1,780	792	1,678	2,829	4,561	6,238
	ENP-T	29	2,117	1,563	385	909	1,708	2,738	6,211
	ENP-C	10	4,177	1,689	1,236	3,167	4,185	5,633	6,809
As	BNP	16	2.04	0.45	0.80	1.90	2.05	2.35	2.80
	BICY	14	1.07	0.66	0.34	0.68	1.00	1.23	2.90
	ENP-T	26	1.64	0.61	0.80	1.20	1.40	2.05	2.90
	ENP-C	6	2.07	0.57	1.40	1.48	2.05	2.70	2.70
Ba	BNP	25	8.34	3.17	0.90	6.95	8.50	10.60	12.70
	BICY	8	9.04	5.51	1.40	3.07	9.75	13.67	16.80
	ENP-T	7	12.50	4.01	5.80	8.20	13.60	16.00	16.60
	ENP-C	11	11.36	1.70	7.90	10.10	11.60	12.60	14.10
Co	BNP	24	0.43	0.21	0.02	0.33	0.40	0.60	0.70
	BICY	16	0.45	0.21	0.05	0.40	0.40	0.50	0.80
	ENP-T	21	0.49	0.19	0.20	0.30	0.50	0.65	0.80
	ENP-C	10	0.65	0.11	0.50	0.58	0.65	0.73	0.80
Cr	BNP	24	6.82	3.10	1.20	4.93	6.30	9.38	12.20
	BICY	12	7.67	4.48	1.79	3.05	7.45	12.07	14.10
	ENP-T	30	4.85	2.65	1.32	2.65	4.25	6.95	10.70
	ENP-C	7	11.56	3.27	6.30	8.40	12.50	14.90	15.20
Cu	BNP	9	4.28	2.25	0.80	1.90	4.70	6.10	7.00
	BICY	18	2.03	1.61	0.25	0.60	1.60	2.80	5.70
	ENP-T	35	2.73	1.84	0.37	1.20	2.30	4.00	7.10
	ENP-C	11	3.09	1.67	1.40	1.60	2.30	5.30	5.50
Fe	BNP	24	3,143	1,052	1,210	2,467	2,952	3,969	5,067
	BICY	16	2,296	1,406	477	1,001	2,057	3,550	5,248
	ENP-T	15	3,939	1,341	971	3,204	3,911	4,953	6,257
	ENP-C ¹								
Mn	BNP	24	36.07	2.74	31.17	34.01	35.92	37.92	41.40
	BICY	17	17.03	12.01	3.68	8.80	13.70	26.85	46.80
	ENP-T	14	29.31	11.05	11.83	18.53	30.60	38.28	46.10
	ENP-C ¹								
Ni	BNP	15	1.73	0.50	0.50	1.30	1.90	2.10	2.30
	BICY	11	1.78	0.55	0.98	1.30	1.90	2.10	2.60
	ENP-T	23	1.50	0.71	0.50	0.80	1.40	2.20	2.70
	ENP-C	4	2.15	0.24	0.90	1.93	2.15	2.38	2.40
Pb	BNP	26	8.11	5.42	1.00	3.90	6.75	10.53	21.60
	BICY	17	5.58	2.81	1.92	3.75	5.00	7.50	12.20
	ENP-T	35	9.20	6.63	1.23	3.70	6.60	14.00	25.20
	ENP-C	12	6.45	2.99	3.10	4.25	5.40	8.90	12.10
V	BNP	19	5.65	2.06	1.50	4.50	5.40	7.40	9.30
	BICY	9	5.45	3.69	0.52	0.90	7.10	8.45	9.40
	ENP-T	27	4.90	2.62	1.20	2.50	4.60	6.30	9.50
	ENP-C	9	6.30	1.73	3.80	4.70	6.30	8.10	8.70

Table 9 (continued)

Background concentration, mg/kg, Park

Analyte	Park	N	Avg	StDev	Min	Q1	Median	Q3	Max
Zn	BNP	17	12.21	5.46	2.70	8.05	13.30	16.75	18.50
	BICY	15	5.11	3.76	1.45	2.53	4.70	6.40	17.00
	ENP-T	34	8.50	5.49	1.57	3.68	6.85	13.20	19.40
	ENP-C	12	7.51	2.92	3.50	4.33	8.00	9.78	11.80

T = terrestrial sediments

C = Coastal sediments

¹ not enough values to compute statistics

lower tiers were regressed against Al and potted on a log–log graph. These plots were prepared for Co, Cr, Cu, Ni, Pb, and V (Fig. 3). The other constituents, Mn and Zn, did not pass the normality test at $\alpha=5\%$, and As was not correlated with Al. In a few instances, outliers were removed to meet the normality requirement.

The Schropp plots commonly are used as a predictive tool to determine sample enrichment (Schropp and Windom 1988; Windom et al. 1989; Schropp et al. 1990; Carvalho et al. 2002). In an enrichment plot, a sample that

plots above the upper 95th PI is considered enriched; a sample that plots between the upper and lower 95th PIs is not considered enriched; and a sample that plots below the lower 95th PI may be considered unusual, unreliable, or possibly contaminated by the normalizing element.

Simplified approach

A simplified approach to the original derivation of the trace metal-to-aluminum regression is possible, if the *c*

Table 10 Background concentration of trace metals from three national parks, the State of Florida, Miami-Dade County, and the town of Homestead, Florida, in milligrams per kilogram

Trace Metal	National Park Lands				State of Florida		Dade County	Homestead
	BICY	BNP	ENP		Chen ^a 1999	Carvalho ^b 2002	DERM ^c 2002	Scarlatos ^d 1997
			T	C				
Al	3,168	2,276	2,117	4,177		10,793		
As	1.07	2.04	1.64	2.07	1.34	1.57	1.20	5.10
Ba	9.04	8.34	12.50	11.36	30.70	53.17		
Co	0.45	0.43	0.49	0.65				
Cr	7.67	6.82	4.85	11.56	15.90	23.25	6.80	33.50
Cu	2.03	4.28	2.73	3.09	6.10	4.69	4.10	
Fe	2,296	3,143	3,939			3,953		
Mn	17.03	36.07	29.31		48.80		55.00	
Ni	1.78	1.73	1.50	2.15	13.00	5.62	2.10	
Pb	5.58	8.11	9.20	6.45	11.20	6.33	26.00	29.90
V	5.45	5.65	4.90	6.30		19.17		
Zn	5.11	12.2	8.50	7.51	8.35	14.19	12.00	

^a Data from Chen et al. 1999

^b Data from Carvalho et al. 2002

^c Data from DERM 2002

^d Data from Scarlatos and Scarlatos 1997

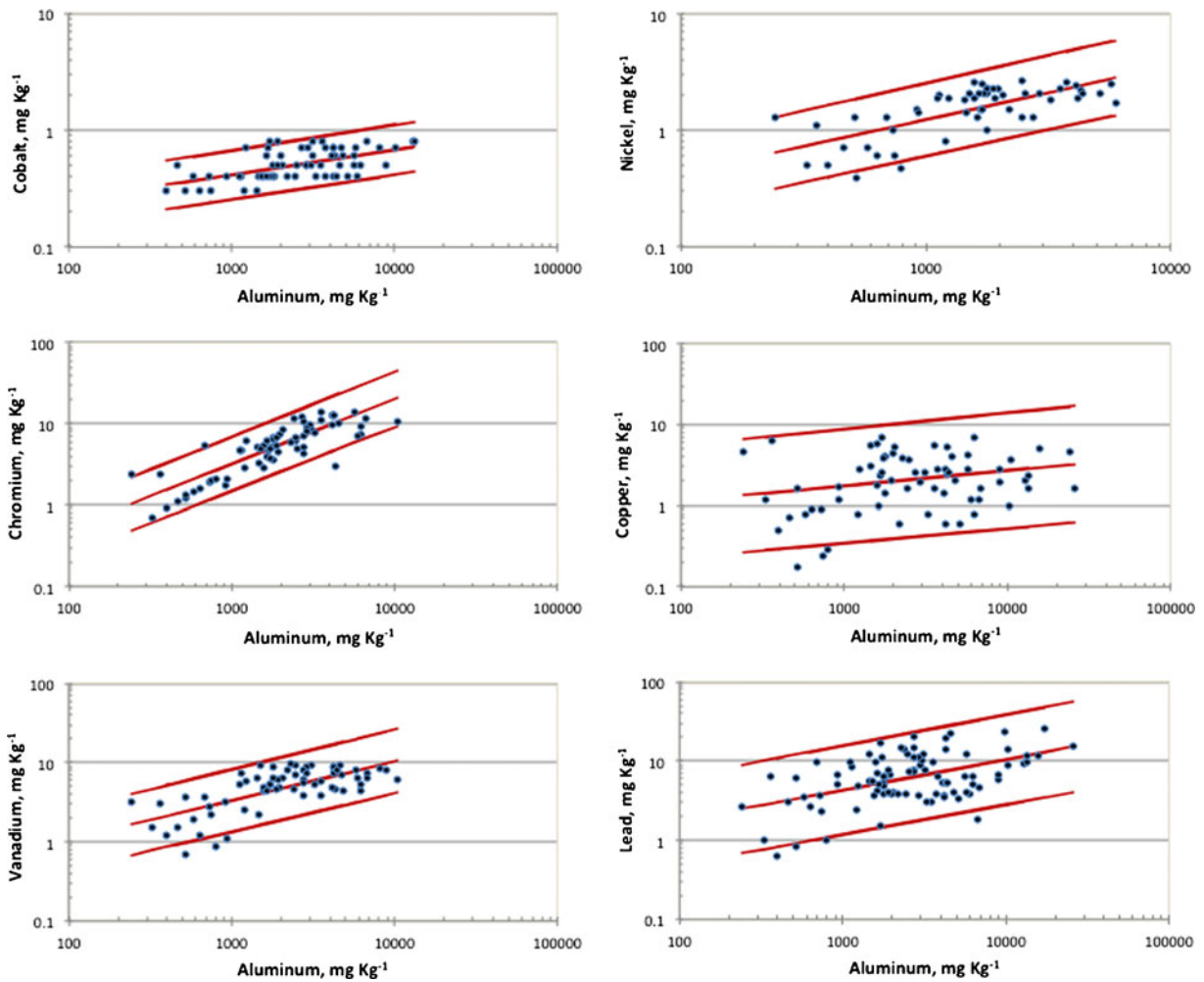


Fig. 3 Region-specific (Everglades and Biscayne National Parks and Big Cypress National Preserve) enrichment plots and their prediction intervals for Co, Ni, Cr, Cu, V, and Pb with respect to Al

as a normalizer. Only data from the two lowest tiers identified in the cluster analysis were used to generate the graphs

value of Eqs. 8 and 9 does not vary greatly over the range of Al values. In this study, this simplified

approach had a negligible effect on the accuracy of the PIs and allowed the estimation of PIs from only

Fig. 4 The 95th predictive intervals for Cu in ENP, BNP, and BICY. *Black markers* are the copper background values, *red solid line* and *red markers* are the regression line and PIs, respectively, without the simplified approach. *Dotted blue lines* are the PIs with the simplified approach

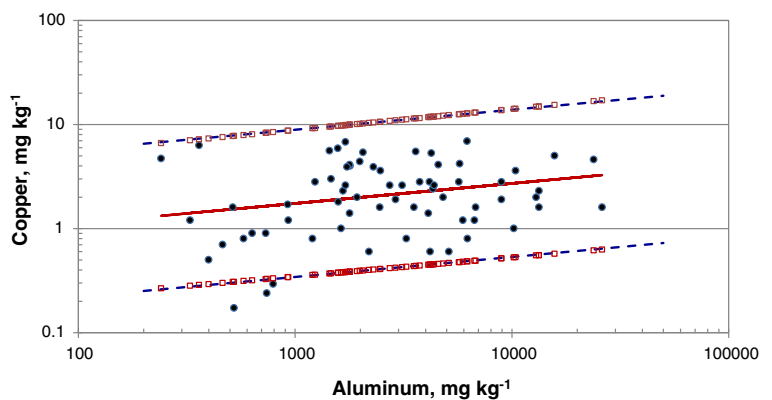


Table 11 Parameters used to construct the region-specific enrichment plots for trace metals with significant correlation with the normalizer (Al) using the simplified approach

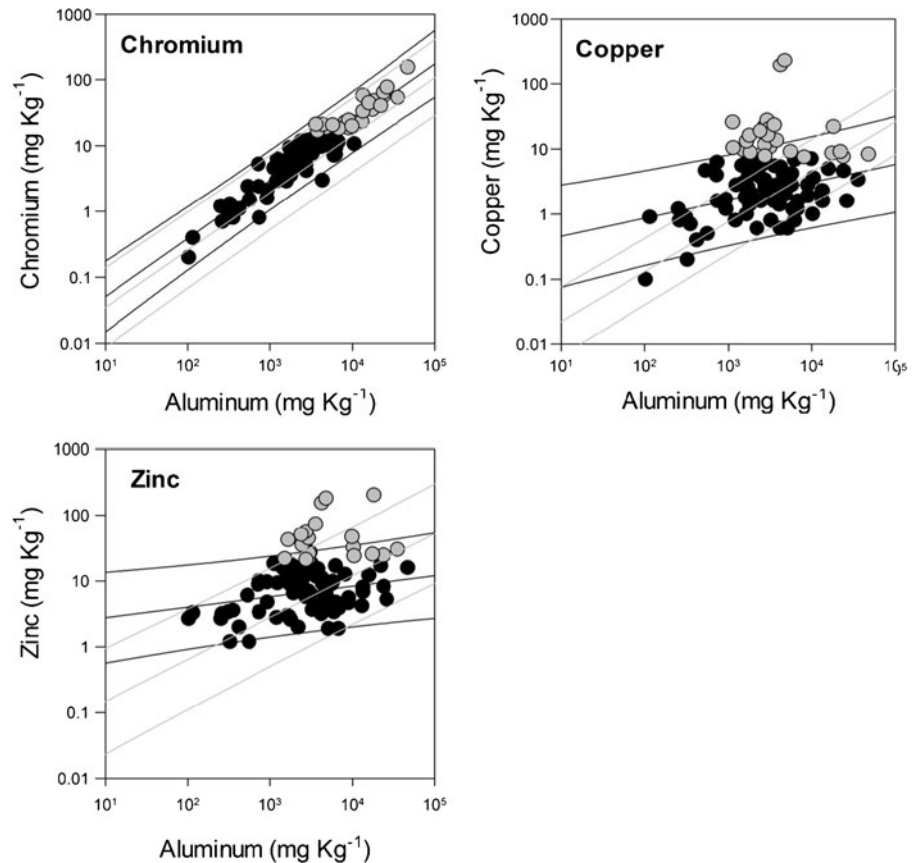
Trace Metal	Slope	Intercept		
		PRE	U	L
Co	0.2153	0.09360	0.15232	0.05752
Ni	0.4642	0.05001	0.10339	0.02419
Cr	0.7978	0.01297	0.02806	0.00599
Cu	0.1920	0.46348	2.36298	0.09091
V	0.4935	0.11004	0.27456	0.04411
Pb	0.3857	0.29884	1.09231	0.08176
Ba	0.5007	0.20307	0.60907	0.06770

The table provides the slope and intercepts for the predictive line (PRE) and the upper (U) and lower (L) 95 % prediction intervals

two Al concentrations. PIs with and without the simplified approach are shown in Fig. 4—red markers are the calculated values without simplification and the dotted lines are plotted with the four endpoints estimated with the simplified approach. The PIs presented

in the report were calculated using all of the *c* values, but a list of simplified parameters is offered in Table 11 to help interpret additional datasets. All the predictive lines shown in the enrichment plots in Fig. 3 can be generated using the slope and intercepts for the mean (PRE), upper (U), and lower (L) intervals provided in Table 11 based on Eqs. 5, 8, and 9. Plots are constructed by using four extreme values of Al and the element in question and the parameters provided in the table. Background soil/sediment concentrations and the enrichment plots are typically used to assess the onset of anthropogenic signatures well before biological effects are observed. Because specific SQAGs are available for both inland soils/sediments and marine sediments, enrichment plots are commonly used in the state of Florida to compare the concentration of a trace metal in a given soil/sediment sample against the typical background levels observed in a number of naturally occurring minerals based on two statewide assessments (Schropp and Windom 1988; Windom et al. 1989; Schropp et al. 1990; Carvalho et al. 2002).

Fig. 5 Comparative enrichment plots for chromium, copper, and zinc. Schropp (gray lines) and region-specific (black solid lines) for all soil/sediment data from ENP, BNP, and BICY produced for this study. All concentrations are in milligrams per kilogram. Samples described by black circles were used to compute background levels; samples with grey circles represent sites with higher concentrations



Samples showing concentrations above the upper confidence limit line are considered enriched, and the results are typically indicative of anthropogenic inputs. The plots are useful to guide the interpretation, but they do not provide a link to biological effects so they are used in combination with the SQAGs as presented in previous sections. One of the major drawbacks of the Schropp plots is that they are based on data from a rather large region, and thus, the plots are less appropriate for localized interconnected environments such as the lower Florida Everglades and its associated estuaries. In order to adapt this assessment tool to the local environments, the data for all background samples identified in the cluster analysis were used to calculate new predictive intervals. The lines described in Table 11 combine the background data for each trace metal using the two lowest tiers of the cluster analysis normalized to the concentration of aluminum (Table 9). To assess the correlation of the proposed background concentrations to the traditional Schropp plots, a simple comparison of the whole dataset generated from this study is presented in Fig. 5 for selected trace metals. The data points (black circles), including all results for all sites, are plotted against the traditional Schropp plot (gray lines) and the region-specific predictive intervals (black lines).

As seen in the graph, Cr shows a good correlation between the two predictive models with no substantial difference between the slopes. On the other hand, metals like Cu and Zn produced a distinctively lower background range for ENP, BNP, and BICY with respect to the rest of the state. In our opinion, this is likely representative of the mineral composition (mainly peat and carbonate marls) and the biogeochemical cycles in the area and indicative of a rather pristine and undisturbed environmental setting with very limited anthropogenic signatures. Because of these differences and similarities, the use of region-specific enrichment plots may be the best way to develop a simple management tool used for early detection of future contamination trends.

Conclusions

This is the first study that has developed a comprehensive assessment of trace metal in soils/sediments from three protected areas in south Florida: ENP, BNP, and BICY. Although no widespread contamination

was found, the study identified specific localized areas of potential concern where concentration levels exceeded Florida ecological thresholds. Out of the 12 trace metals studied, ENP consistently had the largest proportion (67 %) of the highest average concentrations compared to BNP (25 %) and BICY (8 %). By contrast, BICY had the largest proportion (50 %) of the lowest average concentrations compared to ENP (25 %) and BNP (25 %). Noteworthy were the concentrations of Pb in ENP and Cu and Zn in BNP, which were much higher than elsewhere in the study area. The analysis of the EI_Po indicated that potential adverse effects on the biota from exposure to elevated concentrations of Cu, Cr, and Zn were probable in some sites. Furthermore, the CI index identified stations E3, E5, E1, E6, SRS3, and E4, in descending order, to be the most contaminated in ENP; BB10, BB1, BB3, and BB5 in BNP; BICY5 and BICY6 in BICY; and S178 in OTH. Background concentrations estimated for the two parks and one preserve, which are representative of existing baseline conditions, were lower than those reported for the town of Homestead, FL, for Miami-Dade County, FL, and for the State of Florida. Finally, a region-specific set of enrichment plots for protected DOI lands in south Florida was developed. These plots, in combination with the background concentrations, could be easily used as a rapid assessment tool to predict whether the levels of trace metals in soil/sediment samples have been affected by anthropogenic inputs caused by changes in land use or by modifications to water delivery operations during the implementation of restoration projects. This study also provides clear evidence of the value and need for region-specific management tools in support of early intervention actions to protect valuable resources.

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