

# **Trace metals in the soils of Water Conservation Area of Florida Everglades: Considerations for ecosystem restoration**

Salwinder S. Dhaliwal<sup>1</sup> · Gurpal S. Toor<sup>2</sup> · Ignacio A. Rodriguez-Jorquera<sup>3</sup> · Todd Z. Osborne<sup>4</sup> · Susan Newman<sup>5</sup>

Received: 31 December 2015 / Accepted: 17 May 2016 / Published online: 26 May 2016 © Springer-Verlag Berlin Heidelberg 2016

#### Abstract

*Purpose* Inorganic contaminants present a major challenge for the restoration of aquatic ecosystems. The objectives of this study were to determine the extent of trace metal contamination and investigate the influence of different plant communities on trace metal accumulation in the soils of the Florida Everglades.

*Materials and methods* Soil samples (n = 117) were collected from 0 to 10-cm depth using a stainless steel coring device from sites with three dominant plant communities—cattail, sawgrass, and slough—of Water Conservation Area-2A (43, 281 ha) of Florida Everglades.

*Results and discussion* The mean pH in soils collected from three plant communities was 6.75–6.82, whereas electrical conductivity was slightly greater in the sawgrass (0.69 dS m<sup>-1</sup>) than cattail (0.58 dS m<sup>-1</sup>) and slough (0.40 dS m<sup>-1</sup>). Mean reduction–oxidation potential was greatest in cattail (–113 mV) than sawgrass (–85.3 mV) and

Responsible editor: Paulo Pereira	
Currel & Tear	

Gurpal S. Toor gstoor@ufl.edu

- <sup>1</sup> Department of Soils, Punjab Agricultural University, Ludhiana, Punjab, India
- <sup>2</sup> Soil and Water Quality Laboratory, Gulf Coast Research and Education Center, University of Florida, 14625 C.R. 672, Wimauma, FL 33598, USA
- <sup>3</sup> Department of Wildlife Ecology and Conservation, University of Florida, Gainesville, FL, USA
- <sup>4</sup> Whitney Laboratory for Marine Bioscience, University of Florida, St. Augustine, FL 32080, USA
- <sup>5</sup> Everglades Systems Assessment, South Florida Water Management District, West Palm Beach, FL, USA

slough (-48.3 mV) soils. Among 11 trace metals (As, B, Co, Cr, Cu, Mn, Mo, Na, Ni, Pb, Zn) found in soil samples, Na had the greatest contents and was greater in cattail (2070 mg kg<sup>-1</sup>) and sawgrass (1735 mg kg<sup>-1</sup>) than slough (1297 mg kg<sup>-1</sup>). Four trace metals (B, Cu, Mo, Ni) were significantly greater in cattail than sawgrass and slough. Whereas, Mn was significantly lower in cattail (31 mg kg<sup>-1</sup>) than both sawgrass (84 mg kg<sup>-1</sup>) and slough (51 mg kg<sup>-1</sup>). Cattail also had significantly lower Cr (1.97 mg kg<sup>-1</sup>) and Pb (10 mg kg<sup>-1</sup>) than sawgrass (Cr 2.5 mg kg<sup>-1</sup>; Pb 20.8 mg kg<sup>-1</sup>). As (<6.9 mg kg<sup>-1</sup>), Co (<1.3 mg kg<sup>-1</sup>), and Zn (<17.2 mg kg<sup>-1</sup>) were not significantly different among soils collected from three plant community-dominant sites. Contents of Cd and Se were below the method detection limits (Cd 0.01 mg L<sup>-1</sup>; Se 0.2 mg L<sup>-1</sup>) and are not reported.

*Conclusions* None of the trace metals in the soils exceeded the US Environmental Protection Agency sediment toxicity thresholds. Results from this study provided baseline concentrations of trace metals, which can be used to measure the success of restoration efforts in Florida Everglades.

Keywords Contamination  $\cdot$  Ecotypes  $\cdot$  Everglades  $\cdot$  Soils  $\cdot$  Trace metals

#### **1** Introduction

Soil contamination research is fundamental to protect water quality and can contribute to effective ongoing restoration efforts in the Florida Everglades. Human intervention has altered the hydrology and ecology of the south Florida ecosystem, which, in turn, has impacted the water quantity and quality in the Everglades (Markel and Hickey-Vargas 2000). Restoration and preservation of the ecology and water quality in the Everglades are a continuing challenge, whereby



sediments are the ultimate sink of pollutants transported from the landscape via multiple pathways such as surface runoff, leaching, and atmospheric deposition. Much of the previous soil contamination research in the Everglades ecosystem has been focused on the fate and transport of P (e.g., Osborne et al. 2011). Recently, Rand and Schuler (2009) reported that levels of seven trace metals (As, Cd, Cr, Cu, Pb, Ni, and Zn) at 32 soil sampling sites in south Florida canals exceeded the Florida Department of Environmental Protection (FDEP) soil quality guideline values. Long-term inputs of trace metals to aquatic systems from upland and/or atmospheric deposition sources can result in the bioaccumulation and biomagnification of pollutants in soils and cause toxicity to aquatic organisms (Belzunce et al. 2001). Further, these soils can be a long-term source of pollutants in the water column and expose aquatic and terrestrial organisms in the entire food web to pollutants (Lange et al. 1998; Herring et al. 2014).

Trace metals in the aquatic sediments can originate from both natural, such as parent rocks and minerals, and anthropogenic sources such as industrial and mining activities, atmospheric deposition, and runoff from urban and agricultural areas (Adriano 2001). It is known that runoff from the agricultural areas results in increased amounts of Cu, Fe, and Zn in the sediments (Han et al. 2007). In South Florida, the citrus industry uses Cu as a fertilizer and fungicide (Alva et al. 1995) with estimated use of 500 kg per year (Hoang et al. 2008). In addition, many trace metals (Cr, Pb Zn, Mn, and Ni) are present in fertilizers used in agriculture and constitute a potential source (Caccia et al. 2003). Atmospheric deposition of trace metals such as As, Al, and Hg has been reported to occur in the Everglades. For example, one of the most interesting features of atmospheric deposition of trace metals such as As and Al in the Southeast USA is their connection with the African soils (Garrison et al. 2003). Nevertheless, these extra continental fluxes of metals are minor for As in comparison to background concentrations in South Florida soils, which are important to consider when interpreting potential As contamination (Chen et al. 2002). In contrast to As, Cohen et al. (2008) reported atmospheric deposition as an important source of Hg in the Everglades soils due to the existence of point sources such as waste incineration sites in Miami (Dvonch et al. 1995).

Trace metals exhibit tremendous spatial and temporal variability in the aquatic systems (Bellucci et al. 2002; Bruland et al. 2006; Rivero et al. 2007) due to the variability in the deposition rate and complex sediment geochemistry that results in the formation of soluble and insoluble complexes. For example, in some parts of Everglades National Park such as Taylor slough (the southern-most extent of the Everglades), concentrations of Pb and Zn showed enrichment in the top 10– 15 cm of soils, whereas Al, Cu, Ni, and Fe increased with depth (Kotra et al. 2000). The distribution, accumulation, and release of trace metals in the sediments are influenced by the chemical properties such as pH; reduction-oxidation (Eh) potential; natural organic matter; texture; and oxides of Fe, Al, and Mn (Adriano 2001). In the Everglades, peat soils in the Water Conservation Area-2A (WCA-2A) contain up to 75 % natural organic matter with high content of humic acids (Duan 2012). King et al. (2006) reported that a decrease in sediment pH from 6.7 to 3.7 resulted in release of As, Cd, Cr, Cu, Pb, and Zn to the solution phase. An increase in electrical conductivity (EC) has been shown to increase the accumulation of trace metals in the soils. For example, the higher contents of Cu and Fe at the sites with higher EC were attributed to tidally induced resuspension (Fernandez et al. 2008; Tack and Vandecasteele 2008). Otero et al. (2000) reported that an increase in sediment Eh resulted in higher concentrations of Cu, Fe, Mn, and Zn in solution and uptake by small cordgrass (Spartina maritima). Thus, chemical properties can control how wetland plants distribute trace metals and hence alter their distribution in the sediments.

Moreover, different types of plant communities present in the water bodies differentially take up trace metals and can affect the concentrations of metals in the water column and soils. For example, Otero et al. (2000) reported that three trace metals (Fe, Mn, Zn) were greatest in the leaves than the stems of small cordgrass. In contrast, Fe was lower and Mn and Zn were higher in the soil than leaves and stems. Weis and Weis (2004) showed that different plant species have a variable capacity to accumulate metals as they found that Pb content was 40 % higher in the stem of smooth cordgrass (Spartina alterniflora) than common reed (Phragmites australis). Accumulation of Cd, Cu, Pb, and Zn in the roots of cattail (Typha angustifolia) reduced their availability in the sediments (Bose et al. 2008). Among 12 wetland grass species, Deng et al. (2004) observed that cattail (Typha latifolia) accumulated highest amounts of Pb ( $3256 \text{ mg kg}^{-1}$ ), followed by Zn (3089 mg kg<sup>-1</sup>), Cu (26 mg kg<sup>-1</sup>), and Cd (22 mg kg<sup>-1</sup>) in a wetland located near the Pb-Zn and Cu mines. The greater accumulation of metals in root and rhizomes of wetland plants was attributed to the presence of cortex parenchyma with large intercellular air spaces, suggesting that aquatic plants can be used as biological indicators to determine environmental pressures (Hozhina et al. 2001).

Quantifying trace metal contamination in the soils can be useful to protect aquatic systems since trace metal toxicity in the water column and sediments can severely affect the aquatic organisms. Various plant communities such as ridge, slough, and cattail are reported to be present in the Everglades. It is likely that these plant communities may affect the accumulation of trace metals in the soils. For example, cattail is known to accumulate a greater amount of P than slough and ridge (Deng et al. 2004; Bose et al. 2008). The contaminant runoff from the agricultural land is a big challenge in the Everglades restoration (Davis and Ogdon 1994); however, little emphasis has been placed on the trace metals in the restoration efforts. Therefore, the objective of this study was to determine the extent of trace metal contamination and investigate the impact of different plant communities (ridge, slough, cattail) on the trace metal accumulation in the soils of WCA-2A of the Florida Everglades.

#### 2 Materials and methods

#### 2.1 Study site

The subtropical Everglades aquatic ecosystem originates in the Kissimmee River-Lake Okeechobee watershed. The sheet flow of surface water from Lake Okeechobee passes in its way to the south throughout the Everglades Agricultural Area, parts of Big Cypress National Preserve, the WCA-1, 2, and 3 to finally reach the Everglades National Park. WCA-2A is a 43,281-ha peat-based wetland located in the northern portion of Everglades ecosystem, FL, USA (Fig. 1) and was established for flood protection, water supply, and other environmental benefits such as wildlife habitat. Surface hydrology of the area is controlled by an extensive system of levees and water control structures along the perimeter with inputs on the northern levee and outfalls along the east and west of the southernmost levee. Soils in WCA-2A are Histosols consisting of three recognized suborders-Fibrists, Hemists, and Saprists (Rivero et al. 2007). The low elevation gradient from northeast to southwest promotes gradual sheet flow across the area. Rainfall is a significant source of water in WCA-2A; nevertheless, significant volumes of P-enriched waters from Lake Okeechobee and the Everglades Agriculture Area enter WCA-2A via the Hillsboro Canal (Osborne et al. 2011). Nutrient enrichment of water and subsequently soil has impacted this naturally oligotrophic wetland, with the most visible observed change being the shift of vegetation community structure (Davis and Ogdon 1994; Osborne et al. 2011). For example, vegetation in oligotrophic portions of WCA-2A consists of short stature sawgrass (Cladium jamaicense Crantz) and species such as white waterlily (Nymphaea odorata) are dominant in open water areas. In P-enriched areas, cattail (Typha domingensis) creates monodominant stands, in particular in proximity to inflow points (Rivero et al. 2007). Thus, the area in WCA-2A can be tentatively separated into three distinct dominant plant communities such as (1) cattail, (2) mix of sawgrass and cattail in enriched ridges, and (3) white waterlily and sawgrass in the slough and ridge.

#### 2.2 Soil sample collection

Soil samples (n = 117) were collected in the 2008 winter (November–December), using a 10-cm-diameter stainless steel coring device following the methods described in

Osborne and DeLaune (2013). The core samples were sectioned in the field into floc (loose, unconsolidated soil material overlying the soil surface—a common feature of the Everglades) and 0–10-cm increments of consolidated soils. Samples were placed in plastic bags and stored in coolers on ice and transported to the laboratory for analysis. A floc sample was not present at every sampling site. As described above, these collected soils samples in the WCA-2A were distributed in three dominant plant communities, hereafter referred to as cattail (n=61), sawgrass (n=38), and slough (n=18).

#### 2.3 Sample processing and analyses

The moisture content determined in the laboratory using the gravimetric method (105 °C for 24 h) was >85 % in all the samples. Thus, the samples could not be digested for trace metals in a typical manner for soil and sediments using a method such as EPA 3050B. Therefore, the samples were digested using a dry ash procedure often used for the digestion of plant material. In brief, the wet samples were thoroughly mixed, and then, using the pre-determined moisture content, an amount of wet sample equal to 1.0-g dry weight was weighed into a high-form, glazed, porcelain crucible. The samples were placed into a programmable muffle furnace (Fisher Scientific Isotemp Programmable Muffle Furnace, 650 series, Pittsburg, Pennsylvania) by slowly raising the temperature to 160 °C and then holding it there for 4 h. This was followed by an increase in the temperature to 500 °C where the samples were allowed to ash for 5 h. Once the samples were removed from the furnace and allowed to cool to room temperature, the ash was moistened by adding approximately five drops of nanopure water (Barnstead/Thermolyne Corporation Series 896, Dubuque, Iowa) followed by the addition of 5 mL of 6 M HCl (Fisher Trace Metal Grade). The ash solution was allowed to stand for 30 min before quantitatively transferring to a 50-mL volumetric flask by pouring through a funnel containing a Whatman No. 41 filter paper and bringing volume to 50 mL using nanopure water.

The concentrations of the various metals (As, B, Co, Cr, Cu, Mn, Mo, Na, Ni, Pb, and Zn) were determined with inductively coupled plasma–optical emission spectrometry (ICP–OES) using a PerkinElmer Optima 2100 DV (Perkin Elmer, MA). The ICP–OES was calibrated using National Institute of Standards and Technology (NIST) traceable standards for all of the analyzed elements (multi-trace metal mix containing As, B, Co, Cr, Cu, Mn, Mo, Na, Ni, Pb, and Zn), which were diluted to the appropriate concentration ranges for each metal, and Yttrium was used as an internal standard. The precision of the trace element measurements was checked by analysis of the duplicate samples, and the accuracy was checked by analysis of 4 % of the samples, spiked at a

Fig. 1 Location map showing Water Conservation Area-2A (WCA-2A) of Florida Everglades. Note the three dominant plant communities: cattail (*Typha domingensis*), mix of sawgrass (*Cladium jamaicense*) and cattail in ridge, and white waterlily (*Nymphaea odorata*) and sawgrass in the slough



250 mg kg<sup>-1</sup> level for each metal. The precision ranged from 1.9 to 17.5 %, and the accuracy was 70–86 %. Soil pH, EC, and *E*h were measured after equilibrating 10 g of soil with 20 mL of deionized water (1:2) for 1 h with a multi-parameter water quality probe (HI 9828, Hanna Instruments Inc.).

#### 2.4 Statistical methods

Correlation analysis was performed to determine the strength of the relationship among trace metals and basic parameters. Significance was determined at P < 0.05. Least coefficient of variation was used to determine differences in basic parameters such as pH, EC, and *E*h among the three plant communities (cattail, sawgrass, slough). The significance of trace metal differences across plant communities was determined at P < 0.05 using SAS GLM Procedure, least square means.

#### **3 Results and discussion**

#### 3.1 Basic properties of soils

The pH, EC, and *E*h are important properties that influence the fate of trace metals in the water column and soils. The mean values (n = 117) of pH, EC, and *E*h in soils collected from plant communities (cattail, sawgrass, slough) were 6.79, 0.59 dS m<sup>-1</sup>, and –94.3 mV, respectively (Table 1). The soils from cattail, sawgrass, and slough did not have significantly different pH, EC, and *E*h. The pH had a least coefficient of variation (CV) values from 3 to 4 %, while CV was 84–100 % for EC and 147–262 % for *E*h across plant communities. Mean EC was greater in the sawgrass (0.74 dS m<sup>-1</sup>) than cattail (0.51 dS m<sup>-1</sup>) and slough (0.46 dS m<sup>-1</sup>). The mean *E*h in the soils was greatest in the cattail (–113 mV) followed by sawgrass (–85.3 mV) and slough (–48.3 mV).

**Table 1** Distribution of pH, EC (dS  $m^{-1}$ ), and *E*h (mV) in soil samples

Parameter	Plant community	Number of samples	Mean $\pm$ SE	Coefficient of variation (%)
pН	Sawgrass	38	6.75±0.04 a	3
	Slough	18	$6.81 \pm 0.06$ a	4
	Cattail	61	$6.82 \pm 0.03$ a	4
EC	Sawgrass	38	$0.69 \pm 0.09$ a	84
	Slough	18	$0.40 \pm 0.13$ a	89
	Cattail	61	$0.58 \pm 0.07$ a	100
<i>E</i> h	Sawgrass	38	$-85.3 \pm 24.8$ a	164
	Slough	18	$-48.3 \pm 36.0$ a	262
	Cattail	61	$-113.4 \pm 19.6$ a	147

Values followed by different letters for the same metal are significantly different at P < 0.05 using SAS GLM Procedure, least square means

SE standard error

Soil EC and Eh were significantly negatively correlated (r=-0.319). This is because as soils are reduced, dissolved oxygen decreases, and when all dissolved oxygen is consumed, anaerobic microbes use the electron accepters in the order of NO<sub>3</sub><sup>-</sup>, Fe<sup>3+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and HCO<sub>3</sub><sup>-</sup> and produce CO<sub>2</sub>, NH<sub>3</sub>, SO<sub>2</sub>, and CH<sub>4</sub>. This, in turn, induces several biogeochemical reactions, which affect trace metal fate in the aquatic systems (Fernandez et al. 2008). Across all plant communities, pH had a significant correlation with B, Mn, Na, and Ni (Table 2). Similarly, EC was significantly positively correlated with B, Cu, and Na and negatively correlated with Co. Soil Eh was significantly negatively correlated with Cu and Na and positively correlated with Co. The correlation of pH, EC, and Eh with trace metals suggests that these basic parameters affect accumulation of trace metals in the soils along with microorganisms and plant communities (Weis and Weis 2004; Deng et al. 2004; King et al. 2006; Bose et al. 2008).

#### 3.2 Influence of plant communities on trace metals in soils

In general, soils collected from the cattail showed the greatest mean concentrations of trace metals with the exception of Cr, Mn, and Pb (Table 3). However, the differences were only significant for selected trace metals among three plant communities. Overall, the highest trace metal concentrations were as follows: Na > Mn > B > Pb. Among these four trace metals, Pb is a concern because of its known high toxicity (Rechtschaffen 1997) and Pb was found in significantly

higher concentrations in the sawgrass and slough than cattail. Another trace metal determined in the sediments investigated here, Cu, is known to have moderately to high toxicity in aquatic biota, mainly in invertebrates (Hoang et al. 2008). Cu, Mn, and Zn are known to be carried with runoff from agricultural areas (Han et al. 2007), which could explain why the occurrence of these trace metals is correlated. Lastly, As (a highly toxic metalloid) has been linked with water quality issues in South Florida (Arthur et al. 2002; Perry 2008).

None of the trace metals in the soils across plant communities investigated here exceeded the US Environmental Protection Agency sediment toxicity thresholds (USEPA 2004). Nevertheless, some toxic trace elements (i.e., As) were closer to the toxicity thresholds. The bioaccumulation of metals in aquatic organisms and biomagnification in terrestrial organisms is known, and thus, it is important to analyze this information in a broader context as a precautionary principle when low levels are present in soils. Below, we first present a brief summary on each of the determined trace metals and then discuss the implications of these findings in the Everglades restoration efforts.

#### 3.2.1 Arsenic

Of the 117 samples, As was only detected in 66 samples. Mean total As across all plant community soils was 6.68 mg kg<sup>-1</sup> (CV 10–23 %), with a higher but non-

Table 2 Correlation coefficient between pH, EC, and Eh and trace metals in soil samples

	As	В	Со	Cr	Cu	Mn	Мо	Na	Ni	Pb	Zn
pH EC	0.108 0.096	0.459 0.199	0.009 - <i>0.477</i>	-0.078 -0.057	0.172 0.190	0.194 0.094	-0.061 -0.095	0.319 0.503	0.457 0.166	-0.033 0.054	0.052 0.005
Eh	-0.103	-0.143	0.231	-0.138	-0.411	-0.072	-0.072	-0.105	-0.316	0.118	-0.167

Italicized values in the table are statistical significant at P < 0.05

 
 Table 3
 Concentration of trace
metals (mg  $kg^{-1}$ ) in soil samples collected from three plant communities

Trace metal	Plant community	Number of samples	Mean±standard error	Coefficient of variation (%)		
As	Sawgrass	12	$5.88 \pm 0.41$ a			
	Slough	8	$6.41 \pm 0.50$ a	10		
	Cattail	46	$6.94 \pm 0.21$ a	23		
В	Sawgrass	38	$37.6 \pm 1.85$ a	30		
	Slough	18	$37.3 \pm 2.68$ a	30		
	Cattail	61	$48.7 \pm 1.46 \text{ b}$	23		
Со	Sawgrass	5	$1.14 \pm 0.10$ a	8		
	Slough	4	$1.33 \pm 0.11$ a	29		
	Cattail	9	$1.18 \pm 0.07$ a	14		
Cr	Sawgrass	38	$2.49 \pm 0.11$ a	23		
	Slough	17	$2.41 \pm 0.17 \text{ ab}$	26		
	Cattail	61	$1.97 \pm 0.09 \text{ b}$	38		
Cu	Sawgrass	38	$7.3 \pm 0.53$ a	31		
	Slough	18	$7.0 \pm 0.76$ a	28		
	Cattail	61	$10.3 \pm 0.41 \text{ b}$	38		
Mn	Sawgrass	38	$84.4 \pm 9.5 \text{ b}$	111		
	Slough	18	$50.7 \pm 13.8$ b	78		
	Cattail	61	$31.0 \pm 7.5$ a	82		
Mo	Sawgrass	37	$2.2 \pm 0.21$ a	28		
	Slough	17	$2.8 \pm 0.30$ a	63		
	Cattail	60	$3.7\pm0.16\ b$	37		
Na	Sawgrass	38	1735±216 a	113		
	Slough	18	$1297 \pm 314$ a	24		
	Cattail	61	$2070 \pm 171$ a	48		
Ni	Sawgrass	2	$5.1 \pm 0.05 \text{ a}$	1		
	Slough	1	$5.5 \pm 0.0$ a	0		
	Cattail	11	$6.5 \pm 0.2 \text{ b}$	11		
Pb	Sawgrass	38	$20.8\pm1.39\ b$	47		
	Slough	17	$20.2 \pm 2.08 \text{ b}$	53		
	Cattail	56	$10.0 \pm 1.15$ a	69		
Zn	Sawgrass	38	15.1±1.11 a	37		
	Slough	18	$16.7 \pm 1.62$ a	37		
	Cattail	61	$17.2 \pm 0.88$ a	45		

Values followed by different letters for the same metal are significantly different at P < 0.05 using SAS GLM Procedure, least square means

significant value in cattail than sawgrass and slough (Table 3). In Florida Histosols (wetland soils), Chen et al. (2002) reported As content of 2.35 mg kg<sup>-1</sup>, which is about sixfold above the USEPA screening limit of 0.40 mg kg<sup>-1</sup> (USEPA 2004). Comparing our data with the literature showed that As in the soils was elevated but was below the 7.26 mg kg<sup>-1</sup> of threshold effect level (TEL) as suggested by Jaagumagi (1990). Arsenic in the soils may have originated from natural (soil weathering) as well as anthropogenic sources, such as runoff from land. Soil As was significantly correlated with Cu, Mo, and Na (Table 4) suggesting a common source. In a comprehensive study of As in Marl soils of south Florida, Chen et al. (1999) also observed correlation of As with Cu (r=0.81).

## 3.2.2 Boron

Among all trace metals, B had the third highest content and was detected in all samples. The mean B across all soils was 43.3 mg kg<sup>-1</sup>. A significantly greater amount of B was observed in cattail (48.7 mg  $kg^{-1}$ ) than both sawgrass and slough (~37 mg kg<sup>-1</sup>), with a CV of 23-30 % (Table 3). The accumulation of B in the soils may be due to the natural and anthropogenic (atmospheric and

Table 4	Correlation coefficient among trace metals in soil samples collected from three plant communities									
	As	В	Со	Cr	Cu	Mn	Мо	Na	Ni	Pb
В	0.065									
Co	-0.028	-0.486								
Cr	-0.138	-0.287	0.382							
Cu	0.305	0.528	-0.100	0.005						
Mn	-0.086	-0.035	0.567	0.173	-0.255					
Mo	0.482	0.304	-0.040	-0.287	0.493	-0.364				
Na	0.330	0.418	-0.369	-0.260	0.193	0.082	0.104			
Ni	0.023	0.216	0.819	-0.013	0.348	-0.421	0.137	0.065		
Pb	-0.131	-0.225	-0.278	0.507	-0.270	0.229	-0.375	-0.156	-0.240	
Zn	0.011	0.089	0.401	0.357	0.447	-0.058	0.167	-0.111	0.577	0.017

Italicized values in the table are statistical significant at P < 0.05

terrestrial) sources. Rose-Koga et al. (2006) reported B concentration of  $0.1-3.0 \ \mu g \ L^{-1}$  in the atmosphere due to the seawater aerosol evaporation and volcanic emission, which was deposited back on earth with rainfall (Reimann et al. 2007). A significant positive correlation of B with Cu, Mo, Na, and Ni and a negative correlation with Co, Cr, and Pb were observed (Table 4).

#### 3.2.3 Cobalt

Among 117 soil samples, Co was detected in only 18 samples spread across three plant communities. The frequency of detection was 15 %, with 50 % samples in cattail. The mean Co in the soils was 1.2 mg kg<sup>-1</sup>, with a higher but non-significant value in slough than sawgrass and cattail (Table 3). Co in the soils has natural (soil weathering) as well as anthropogenic sources, such as runoff from agricultural land. Continuous submergence in Everglades may affect Co behavior in soils. For example, Fling et al. (2004) reported higher Co  $(1.33 \text{ mg kg}^{-1})$  in slough as compared to sawgrass and cattail, which may have been due to reduced conditions in which the soils remain under water for more than 9 months in a year. In this study, Co in the soils had significant positive correlation with Cr, Mn, Na, and Zn and negative correlation with B. Na, and Pb (Table 4).

#### 3.2.4 Chromium

In 117 soil samples, Cr was detected in 116 samples. The mean Cr across all soils was 2.2 mg kg<sup>-1</sup>, with a higher and significant value in sawgrass than cattail (Table 3). The Cr in the present study soils is >25-fold below TEL of 52.3 mg kg<sup>-1</sup>. Chen et al. (2002) reported Cr content of 15.9 mg kg<sup>-1</sup> in >95 % of South Florida soils. Soil Cr was

significantly positively correlated with Pb and Zn and negatively correlated with B, Mo, and Na (Table 4).

#### 3.2.5 Copper

Copper was detected in all the samples, with mean content of 8.8 mg kg<sup>-1</sup> and significantly greater values in cattail than sawgrass and slough (Table 3). In Florida Histosols (surface soils) with 51 g kg<sup>-1</sup> of organic C, Chen et al. (1999) observed Cu content of 6.1 mg kg<sup>-1</sup> in >95 % samples. In this study, soil Cu was significantly positively correlated with As, Mo, Na, Ni, and Zn and negatively correlated with Mn and Pb (Table 4). Chen et al. (1999) in surface soils of south Florida observed correlation of Cu with As (r=0.15), Mn (r=0.39), Mo (r=0.37), and Zn (r=0.70).

#### 3.2.6 Manganese

Manganese was detected in 100 % of samples. Among 11 trace metals, Mn had the second highest contents (after B), with mean value of 51.35 mg kg<sup>-1</sup> across all the plant community soils and a higher and significant value in slough and sawgrass than cattail (Table 3). In Florida Histosols, Mn in >95 % soil samples was 48.8 mg kg<sup>-1</sup> (Chen et al. 1999), which was similar to our study. Many research studies have suggested that Mn may have a phytotoxic effect on various littoral salt marsh species (Rozema et al. 1985; Singer and Havill 1993). In this study, Mn was only significantly positively correlated with Co and Pb and negatively correlated with Cu, Mo, and Ni (Table 4). In 24 Marl soils in south Florida, Chen et al. (1999) observed correlation of Mn with As (r=0.23), Cu (r=0.25), Fe (r=0.36), and Zn (r=0.36).

#### 3.2.7 Molybdenum

Of the 117 samples, Mo was detected in 114 samples. Mean Mo content in all soils was  $3.05 \text{ mg kg}^{-1}$ , with a

higher and a significant value in cattail than sawgrass and slough (Table 3). Chen et al. (1999) observed that the content of Mo in >95 % soil samples was 1.0 mg kg<sup>-1</sup>. The accumulation of Mo in the soils was attributed to sorption on Mn oxyhydroxides under oxic conditions (Tribovillard et al. 2006) and Mo scavenging by sulfide minerals or sulfidized organic matter under sub-oxic and anoxic conditions (Vorlicek et al. 2004). Mo was significantly positively correlated with As, B, and Cu and negatively correlated with Cr, Mn, and Pb (Table 4). In surface soils of south Florida, Chen et al. (1999) observed correlation of Mo with As (r=0.23) and Ag (r=0.67).

#### 3.2.8 Sodium

Sodium was detected in all the samples and had the greatest contents among 11 trace metals. The mean Na content across all plant community soils was 1843 mg kg<sup>-1</sup>, with a higher and non-significant value in cattail as compared to sawgrass and slough (Table 3). Costa et al. (2003) in the Gualaxo River basin and Mandovi Estuary reported Na content from 10 to 396 mg kg<sup>-1</sup> due to the presence of Fe ore mines in the vicinity of the river. Moral et al. (2008) found higher content of Na in the sediments from southeast Spain due to the widespread use of phosphatic fertilizers. In our study soils, Na probably originated from anthropogenic sources, such as runoff from agricultural land particularly due to the use of phosphatic fertilizers that contain Na (DeCarlo et al. 2005). Soil Na was significantly positively correlated with As, B, and Cu and negatively correlated with Co and Cr (Table 4).

#### 3.2.9 Nickel

Across the 117 soil samples, only 14 samples had detectable Ni, 80 % of which were collected from cattail. The mean Ni content across all soils was 5.6 mg kg<sup>-1</sup>, with a significant higher value in cattail than sawgrass and slough (Table 3). Ni in our soils is much below the TEL toxicity limits suggesting less risk of Ni contamination in WCA-2A of Everglades. In the present study, Ni was significantly positively correlated with B, Co, Cu, and Zn and negatively correlated with Mn and Pb (Table 4).

#### 3.2.10 Lead

Lead was detected in 111 of 117 samples. The mean Pb content across all soils was 15.27 mg kg<sup>-1</sup>, with a significantly higher value in sawgrass and slough than cattail (Table 3). The Pb contents in the soils are much the 30.2 mg kg<sup>-1</sup> of TEL as suggested by Jaagumagi (1990). This suggests that the level of Pb in the soils is below threshold risk values. Chen et al. (1999) found that the content of Pb in >95 % of Florida soils was 4.89 mg kg<sup>-1</sup>, which was below the USEPA screening

limit (USEPA 2004). A large number of studies have reported both atmospheric and anthropogenic depositions of Pb in the soils under different conditions (Shotyk et al. 2003; Filgueriras et al. 2004; Morillo et al. 2005; Cuong and Obbard 2006). Soil Pb was significantly positively correlated with Cr and Mn and negatively correlated with B, Co, Cu, Mo, and Ni (Table 4). Chen et al. (1999) in surface soils of south Florida observed correlation of Pb with Ag (r=0.15), As (r=0.45), Cd (r=0.34), Cu (r=0.12), Mo (r=0.07), and Zn (r=0.20).

#### 3.2.11 Zinc

Zn was detected in all the samples, with mean content of 16.44 mg kg<sup>-1</sup> across all soils and a higher and nonsignificant value in cattail than sawgrass and slough (Table 3). Chen et al. (1999) observed Zn content of 8.35 mg kg<sup>-1</sup> in Florida histosols, which was below the USEPA screening limit. The contents in our soils are much below the 124 mg kg<sup>-1</sup> of TEL. The Zn in the WCA-2A soils likely originated from natural (soil weathering) as well as anthropogenic sources, such as runoff from agricultural land particularly with the use of phosphatic fertilizers that contain Zn (DeCarlo et al. 2005). Berg and Steinnes (1997) observed a mean Zn content of 45 mg kg<sup>-1</sup> due to the atmospheric and anthropogenic sources. In this study, Zn was only significantly and positively correlated with Co, Cr, Cu, and Ni (Table 4). Chen et al. (1999) in surface soils of south Florida observed correlation of Zn with Ag (r=0.39), As (r=0.21), Cd (r=0.37), Cu (r=0.70), Cr (r=0.31), Mn (r=0.53), and Pb (r=0.20).

#### 3.3 Considerations for Everglades ecosystem restoration

Though none of the trace metals determined in the soils collected from three dominant plant communities (cattail, sawgrass, slough) exceeded the US Environmental Protection Agency sediment toxicity thresholds (USEPA 2004), some values are high enough to raise concerns (e.g., Cu). These can be toxic and bioaccumulate in key species present in the Everglades ecosystem for which conservation efforts and funds have been in place. For instance, Cu can be toxic to apple snail (Alva et al. 1995; Hoang et al. 2008), which is key prey for the endangered Snail Kite (Sykes 1987). Other trace metals such as As have implications in groundwater pollution, which is also a target in Everglades restoration efforts (Perry 2008). On the other hand, chemical properties of soils in Everglades such as high organic matter (and thus humic acids) can bind trace metals and serve as a protective barrier to metal toxicity (Drexel et al. 2002; Buschmann et al. 2006). Therefore, our data should be considered in the context of a natural system, and thus, more research on the toxicity of trace metals to the most sensitive organisms inhabiting the Everglades ecosystem is necessary to better understand the real impacts of trace metal pollution. Interestingly, sediments collected from the soils dominated by cattail showed the overall highest trace metal concentrations. This may be related with the runoff from agricultural areas, since cattail is dominant where P is plentiful, as nutrient enrichment stimulates its growth (Urban et al. 1993). Thus, it is logical to assume that within WCA-2A, the sites that receive greater runoff from the agricultural areas also receive greater loads of trace metals.

# 4 Conclusions

Quantification of trace metal contents in the soils is important to address environmental and scientific issues in the Greater Everglades. As the WCA-2A receives inflow water from the surrounding agricultural areas, the main source of trace metals in the soils is probably due to the anthropogenic inputs and discharge of runoff waters. Atmospheric deposition of trace metals such as Hg and As has been reported in the literature. The present study presents useful information and an index for the evaluation of soil contamination in Florida Everglades. The data showed that several trace metals such as Na, Mn, B, Pb, Zn, Cu, As, Ni, Mo, Cr, and Co are deposited in the soils. The baseline knowledge about the existence of metals in the aquatic systems can be a powerful way to convey environmental information for decision making and management involving natural resources conservation. The correlation analysis used in this study provided understanding of the complex dynamics of trace metals in soils with three dominant plant communities. The correlations indicated that many metals such as Mn, Cu, and Zn have common sources. The results of this study would significantly fill the knowledge gap about contents of trace metals in the soils, which can be used to measure the success of comprehensive restoration in terms of trace metal accumulation and evaluate the potential risks of trace metals to aquatic organisms in the Florida Everglades.

## References

- Adriano DL (2001) Trace elements in terrestrial environments: biogeochemistry, bioavailability and risks of metals, 2nd edn. Springer, New York
- Alva AK, Graham J, Anderson CA (1995) Soil pH and copper effects on young 'Hamlin' orange trees. Soil Sci Soc Am J 59:481–487
- Arthur JD, Dabous AA, Cowart JB (2002) Mobilization of arsenic and other trace elements during aquifer storage and recovery, southwest Florida. In US Geological survey artificial recharge workshop proceedings, pp 47-50
- Bellucci LG, Frignani M, Paolucci D, Ravanelli M (2002) Distribution of heavy metals in sediments of Venice Lagoon: the role of industrial area. Sci Total Environ 295:35–49

- Belzunce MJ, Solaun O, Franco J, Valencia V, Borja A (2001) Accumulation of organic matter, heavy metals and organic compounds in surface sediments along the Nervion Estuary (Northern Spain). Mar Pollut Bull 42:1407–1411
- Berg T, Steinnes E (1997) Recent trends in atmospheric depositions of trace elements in Norway as evident from 1995 moss survey. Sci Total Environ 208:197–206
- Bose S, Vedamati J, Rai V, Ramanathan AL (2008) Metal uptake and transport by *Tyaha angustata* L. grown on metal contaminated waste amended soil: an implication of phytoremediation. Geoderma 145: 136–142
- Bruland GL, Grunwald S, Osborne TZ, Reddy KR, Newman S (2006) Spatial distribution of soil properties in Water Conservation Area 3 of the Everglades. Soil Sci Soc Am J 70:1662–1676
- Buschmann J, Kappeler A, Lindauer U, Kistler D, Berg M, Sigg L (2006) Arsenite and arsenate binding to dissolved humic acids: influence of pH, type of humic acid, and aluminum. Environ Sci Technol 40: 6015–6020
- Caccia VG, Millero FJ, Palanques A (2003) The distribution of trace metals in Florida Bay sediments. Mar Pollut Bull 46:1420–1433
- Chen M, Ma LQ, Harris WG (1999) Baseline concentrations of 15 trace elements in Florida surface soils. J Environ Qual 28:1173–1181
- Chen M, Ma LQ, Harris WG (2002) Arsenic concentrations in Florida surface soils: influence of soil type and properties. Soil Sci Soc Am J 66:632–640
- Cohen MJ, Lamsal S, Osborne TZ, Bonzongo JC, Newman S, Reddy KR (2008) Soil total mercury concentrations across the Greater Everglades. Soil Sci Soc Am J 73:675–685
- Costa AT, Arias NH, Carvalho LJ, Friese K, Mages M (2003) Surface water quality and sediment geochemistry in the Gualaxo do Norte basin, eastern Quadrilatero Ferrifero, Minas Gerais, Brazil. Environ Geol 45:226–235
- Cuong DT, Obbard JP (2006) Metal speciation in coastal marine sediments from Singapore using a modified BCR-sequential extraction procedure. Appl Geochem 21:1335–1346
- Davis SM, Ogdon J (1994) Everglades: the ecosystem and its restoration. St. Lucie Press, Delray Beach
- DeCarlo EH, Tomlinson MS, Anthony SS (2005) Trace elements in streambed sediments of small subtropical streams on O'ahu Hawaii: results from the USGS NAWQA program. Appl Geochem 20:2157–2188
- Deng H, Ye ZH, Wong MH (2004) Accumulation of lead, zinc, copper and cadmium by 12 wetland plant species thriving in metalcontaminated sites in China. Environ Pollut 132:29–40
- Drexel RT, Haitzer M, Ryan JN, Aiken GR, Nagy KL (2002) Mercury (II) sorption to two Florida Everglades peats: evidence for strong and weak binding and competition by dissolved organic matter released from the peat. Environ Sci Technol 36:4058–4064
- Duan Z (2012) The distribution of toxic and essential metals in the Florida Everglades. FIU Electronic Theses and Dissertations. Paper 684. http://digitalcommons.fiu.edu/etd/684
- Dvonch JT, Vette AF, Keeler GJ, Evans G, Stevens R (1995) An intensive multi-site pilot study investigating atmospheric mercury in Broward County, Florida. Mercury as a Global Pollutant. Springer Netherlands, In, pp 169–178
- Fernandez S, Villanueva U, de Diego A, Arana G, Madariaga JM (2008) Monitoring trace elements (Al, As, Cr, Cu, Fe, Mn, Ni and Zn) in deep and surface waters of the estuary of the Nerbioi-Ibaizabal Iver (Bay of Biscay, Basque Country). J Mar Syst 72:332–341
- Filgueriras AV, Lavilla I, Bendicho C (2004) Evaluation of distribution, mobility and binding behavior of heavy metals in surficial sediments of Louro River (Galicia, Spain) using chemometric analysis. Sci Total Environ 330:115–129
- Fling H, Aumen N, Armentano T, Mazzotti F (2004) The role of flow in the Everglades landscape. Wildlife ecology and conservation

department, University of Florida Cooperative Extension Service, IFAS, FL, CIR 1452, pp 1-7

- Garrison VH, Shinn EA, Foreman WT, Griffin DW, Holmes CW, Kellogg CA, Majewski MS, Richardson LL, Ritchie KB, Smith GW (2003) African and Asian dust: from desert soils to coral reefs. BioScience 53:469–480
- Han FX, Kingery WL, Hargreaves JE, Walker TW (2007) Effects of land uses on solid-phase distribution of micronutrients in selected vertisols of Mississippi River Delta. Geoderma 142:96–103
- Herring G, Eagles-Smith CA, Gawlik DE, Beerens JM, Ackerman JT (2014) Physiological condition of juvenile wading birds in relation to multiple landscape stressors in the Florida Everglades: effects of hydrology, prey availability, and mercury bioaccumulation. PLoS ONE 9:1–10
- Hoang TC, Rogevich EC, Rand GM, Gardinali PR, Frakes RA, Bargar TA (2008) Copper desorption in flooded agricultural soils and toxicity to the Florida apple snail (Pomacea paludosa): implications in Everglades restoration. Environ Pollut 154:338–347
- Hozhina EI, Khramov AA, Gerasimov PA, Kumarkov AA (2001) Uptake of heavy metals, arsenic, and antimony by aquatic plants in the vicinity of ore mining and processing industries. J Geochem Explor 74:153–162
- Jaagumagi R (1990) Development of Ontario provincial sediment quality guidelines for As, Cd, Cr, Cu, Fe, Pb, Mn, Hg, Ni, and Zn. Water Resource Branch. Environment Ontario, Toronto, p 10
- King RF, Royle A, Putwain PD, Dickinson NM (2006) Changing contaminant mobility in a dredged canal sediment during a three-year phytoremediation trial. Environ Pollut 143:318–326
- Kotra RK, Colmes CW, Orem WH, Hageman PL, Briggs PH, Meier AL, Brown ZA (2000) Regional geochemistry of metals in organic-rich sediments, sawgrass and surface water, from Taylor Slough, Florida. US Department of the Interior, US Geological Survey
- Lange TR, Richard DA, Royals HE (1998) Trophic relationships of mercury bioaccumulation in fish from the Florida Everglades. Report to the Florida Department of Environmental Protection, Tallahassee.
- Markel RS, Hickey-Vargas R (2000) Element and sediments accumulation rates in the Florida Everglades. Water Air Soil Pollut 122:327–349
- Moral R, Perez-Murcia MD, Perez-Espinosa A, Moreno-Caselles J, Paredes C, Rufete B (2008) Salinity, organic content, micronutrients and heavy metals in pig slurries from southeastern Spain. Waste Manage 28:367–371
- Morillo J, Usero J, Garcia A (2005) Biomonitoring of trace metals in a minepolluted estuarine system (Spain). Chemosphere 58:1421–1430
- Osborne TZ, DeLaune RD (2013) Soil and sediment sampling of inundated environments. In: DeLaune RD, Reddy KR, Richardson CJ, Megonigal JP (eds) Methods in wetland science. Soil Science Society of America, Madison WI, pp 21–40
- Osborne TZ, Bruland GL, Newman S, Reddy KR, Grunwald S (2011) Spatial distributions and eco-partitioning of soil biogeochemical properties in the Everglades National Park. Environ Monit Assess 183:395–408

- Otero XL, Sanchez JM, Macias F (2000) Nutrient status in tall and short forms of Spartina maritima in the salt marshes of ortigueira (NW Iberian Peninsula) as related to physicochemical properties of the soils. Wetlands 20:461–469
- Perry WB (2008) Everglades restoration and water quality challenges in south Florida. Ecotoxicology 17:569–578
- Rand GM, Schuler LJ (2009) Aquatic risk assessment of metals in sediment from south Florida canals. Soil Sediment Contam 18:155–172
- Rechtschaffen CL (1997) Lead poisoning challenge: an approach for California and other states. Harvard Environ Law Rev 21:387
- Reimann C, Arnoldussen A, Boyd R, Finne TE, Koller F, Nordgulen O, Englaier P (2007) Elements contents in leaves of four plant species (birch, mountain ash, fern and spruce) along anthropogenic and geogenic concentration gradient. Sci Total Environ 377:416–453
- Rivero RG, Grunwald S, Osborne TZ, Reddy KR, Newman S (2007) Characterization of the spatial distribution of soil properties in Water Conservation Area 2A, Everglades, Florida. Soil Sci 172: 149–166
- Rose-Koga EF, Sheppard SMF, Chaussidon M, Carigan J (2006) Boron isotopic composition of atmospheric precipitations and liquid–vapour fractionation. Geochim Cosmochim Acta 70:1603–1615
- Rozema J, Luppes E, Broekman R (1985) Differential response of saltmarsh species to variations of iron and manganese. Vegetation 62: 293–301
- Shotyk W, Goodsite ME, Roos-Barraclough F, Frei R, Heinemeier J, Asmund G, Lohse C, Hansen TS (2003) Anthropogenic contributions to atmospheric Hg, Pb and As accumulation recorded by peat cores from southern Greenland and Denmark dated using the <sup>14</sup>C bomb pulse curve. Geochim Cosmochim Acta 67:3991–4011
- Singer CE, Havill DC (1993) Resistance to divalent manganese of saltmarsh plants. J Ecol 81:797–806
- Sykes PW Jr (1987) The feeding habits of the snail kite in Florida. Colonial Waterbirds, USA, pp 84–92
- Tack FMG, Vandecasteele D (2008) Cycling and ecosystem impact of contaminated calcareous dredged sediment-derived soils (Flanders, Belgium). Sci Total Environ 400:283–289
- Tribovillard N, Algeo TJ, Lyons T, Riboulleau A (2006) Trace metals and paleodox and paleoproductivity proxies: an update. Chem Geol 232: 12–32
- Urban NH, Davis SM, Aumen NG (1993) Fluctuations in sawgrass and cattail densities in Everglades Water Conservation Area 2A under varying nutrient, hydrologic and fire regimes. Aquat Bot 46:203–223
- USEPA (2004) Framework for inorganic metals risk assessment. Risk Assessment Forum, United States Environmental Protection Agency, Washington
- Vorlicek TP, Khan MD, Kasuya Y, Helz GR (2004) Capture of Mo in pyrite forming sediments: role of ligand-induced reduction by polysulphides. Geochim Cosmochim Acta 68:547–556
- Weis JS, Weis P (2004) Metal uptake, transport and release by wetland plants: implications for phytoremediation and restoration. Environ Int 30:685–700