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The Distribution of Toxic and Essential Metals in the Florida Everglades

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

THE DISTRIBUTION OF TOXIC AND ESSENTIAL METALS IN THE FLORIDA EVERGLADES

A thesis submitted in partial fulfillment of

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MASTER OF SCIENCE

in

CHEMISTRY

by

Zhiwei Duan

2012

To: Dean Kenneth G. Furton
College of Arts and Sciences

This thesis, written by Zhiwei Duan, and entitled The Distribution of Toxic and Essential Metals in the Florida Everglades, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

Yuan Liu

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Yong Cai, Major Professor

Date of Defense: July 2, 2012

The thesis of Zhiwei Duan is approved.

Dean Kenneth G. Furton
College of Arts and Sciences

Dean Lakshmi N. Reddi
University Graduate School

Florida International University, 2012

DEDICATION

I dedicate this thesis to my family, especially to my wife Xiaoduo and to my parents for their love and unconditional support.

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ABSTRACT OF THE THESIS

THE DISTRIBUTION OF TOXIC AND ESSENTIAL METALS IN THE FLORIDA EVERGLADES

by

Zhiwei Duan

Florida International University, 2012

Miami, Florida

Professor Yong Cai, Major Professor

Concentrations of 18 metals, including toxic metals (As, Cd, Cr, Ni and Pb) and essential metals (Al, Ba, Be, Co, Cu, Fe, Li, Mg, Mn, K, Sr, V and Zn) in various compartments (sediment, floc, and periphyton) were measured in the Florida Everglades to (i) establish the spatial distribution pattern of the metals in the Everglades and (ii) quantify the major sources of the 18 metals present in the Everglades. The highest mean concentrations of all metals analyzed in the Everglades were detected in soil, followed by floc and periphyton. Most metals exhibited random spatial distribution patterns. Risk assessment using Sediment Quality Guidelines (SQGs) concluded that all toxic metals (Cd, Cr, Pb, Ni, Cu, Zn and As) exhibited average concentrations that were well below FL guidelines as well as other domestic and international guidelines. On the basis of the current study, the Everglades can be considered a pristine environment.

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1.1 Metals in the environment

1.1.1 Sources of metals

Metals are an integral part of the earth and they can originate from both natural and anthropogenic sources (Nagajyoti et al. 2010). Some metals mainly originate from natural source, e.g., aluminum (Al), iron (Fe), calcium (Ca) and potassium (K). Geothermal sources, such as volcanic eruptions, are one of the major natural sources of metal (Nagajyoti et al. 2010). Volcanic eruptions have been known to release high levels of toxic metals into the environment by wind force (Nagajyoti et al. 2010). Other natural sources include marine aerosols, forest fires, and sea sprays (Florea and Busselberg 2006). Some metals, such as cadmium (Cd), arsenic (As), and chromium (Cr), are mostly attributed to anthropogenic sources although those metals can also be found in nature at trace levels (Nagajyoti et al. 2010). There are several types of major anthropogenic sources for metals, which include industry, agriculture, atmosphere, and others (Nagajyoti et al. 2010). Many potentially toxic metals, including Cd, Cr, lead (Pb), nickel (Ni), and zinc (Zn) can be generated from industrial activities. Lead was used in gasoline as an antiknock agent for almost a century before leaded gasoline was phased-out (Florea and Busselberg 2006). It is also used in the paint, radiation shields, car batteries, glass and soldering. Nickel is widely used in the metal-processing industry such as stainless steel makings, coinage and alloys (Florea and Busselberg 2006). Burning of fossil fuels have contributed to the elevated levels of Ni in the city soils (Raposo et al. 2001). Cadmium has been used in the manufacturing of batteries, plating, pigments and plastics. Agricultural sources of toxic metals result from use of inorganic fertilizers (Cd, Cr, Ni, Pb and Zn), animal manure (Manganese (Mn), Zn, copper

(Cu) and cobalt (Co)) and sewage sludge (Zn, Cr, Pb, Ni, Cd and Cu) (Verkleji 1993; Nagajyoti et al. 2010). Toxic metals can be distributed as results of atmospheric sources, such as rain and snowfall. Other possible sources include coal burning plants (Cd, mercury (Hg), Mn, Ni, Al, Fe and titanium (Ti)), vehicle emissions (Cd, Cr, Hg, Ni, Pb and Zn) and landfill pollutions (Zn, Pb, Al, tin (Sn), Fe and Cu) (Verkleji 1993; Nagajyoti et al. 2010). Agricultural run-offs and wastes from industry are also responsible for the contamination of metals in the aquatic ecosystems (Sharma and Sohn 2009).

1.1.2 Threat of toxic metals

Metal pollution has emerged as a worldwide problem that results from increased anthropogenic activities as well as natural processes (Florea and Busselberg 2006). Of all metals, Cadmium, Hg, Pb, Cr, As, Cu, Ni, and Zn are of greatest concern because of their high toxicities and threats to human and wildlife (Florea and Busselberg 2006). Toxic metals are detrimental not only to terrestrial animals and plants but also to fish, birds, and other organisms in aquatic environments. Heavy metal pollution from domestic water and sewage alone can cause long-lasting harm to both aquatic plants and animals (Nriagu 1988).

Toxic metals can affect plants via a variety of pathways. Zinc can cause chlorosis in young leaves and thus constrain the growth above and below ground (Lee et al. 1996). Chromium can significantly depress the capability of plants to carry out photosynthesis (Clijsters and Vanassche 1985). Lead is known as a non-essential metal for the growth of plants, and is considered detrimental to plants cells if accumulated (Kaznina et al. 2005). High level of Pb was found in algae in both short and long term exposure (Scheidegger et al. 2011). Long term exposure to Pb could cause damage to metabolism, decrease in the photosynthetic activity, and elevation in the production of reactive oxygen species which lead to the slow growth and development of plants (Kaznina et al. 2005). In addition, the excess of Pb may also inhibit enzyme activities and alter mineral nutrition (Sharma and Sohn 2009). Cadmium is another well-studied toxic metal (Tolley et al. 1992; Su et al. 2009). Cadmium along with Pb can cause lipid peroxidation, metabolite degradation, overproduction of H_2O_2, declination in the protein amount and DNA damage, and ultimately cell death (Piotrowska et al. 2010). Arsenite (As^{III}) is the most toxic inorganic As forms (Mass et al. 2001). Trivalent arsenic has high affinity for biomolecules such as glutathione (GSH) and cysteinyl residues of enzymes, and can affect the activity of a number of enzymes (Aposhian and Aposhian 2006). Toxic metals at high concentration not only threaten plants, but also pose serious dangers to animals. Arsenic is one of the most well-known environmental pollutants because of its prevalent existence, high toxicity and bioaccumulation potential. It widely exists in water and soil and poses great threats to humans. Acute effects of As poisoning range from irritation to the nose and throat to nausea, vomiting and diarrhea (Florea and Busselberg 2006). Chronic exposure of As leads to cancer, liver damage and dermatosis (Florea and Busselberg 2006). Arsenic is also known to be toxic to many aquatic organisms from daphnids (water fleas) to fish (zebrafish and rainbow trout) (Elnabarawy et al. 1986). Lead can induce damage to and the part of nervous systems (Florea and Busselberg 2006). Prolonged exposure to Pb could affect encoding as well as storage and retrieval of verbal information (Marchetti 2003). Excess Pb in the human body can lead to harmful effects on calcium dependent proteins and neurotransmitters receptors (Florea and Busselberg 2006). Lead also can act as a strong neurotoxin that causes brain damage and cognitive deficits in children (Huang and Schneider 2004). The target organs of chromium (VI) toxicity include skin, mucous and respiratory tract (Salem et al. 1994). Cancer induced by Cr has also been reported (Rossi and Wetterhahn 1989). Chronic inhalation exposure to Ni can cause respiratory problem and even death (Rendell et al. 1994). Cadmium can have adverse effects on calcium metabolism, food intake, and hardness of eggshells (Burger 2008). Acute Cd poisoning can cause severe irritation to the stomach, leading to diarrhea and even death.

1.1.3 Importance of essential metals

Essential metals provide some critical biochemical components to enzymatic reaction for organisms (Goyer 1997). Animals will not survive in the absence of essential metals, which support functions of vital organs. Nine metals (Co, Cr, Cu, Fe, Mg, Mn, molybdenum (Mo), selenium (Se) and Zn) are considered nutritionally essential to human (Florea and Busselberg 2006). Trace elements including Al, boron (B), Co, Cu, Fe, Mn, Mo, Ni, rubidium (Rb), Ti, vanadium (V) and Zn are considered essential to plants (Kabata-Pendias 2004). Although some of these essential metals can also be detrimental at high concentrations.

Essential metals are necessary for a variety of processes in animals and plants. Some essential metals (e.g., Zn, Fe and Ca) are involved in key metabolic processes such as respiration, photosynthesis, fixation and assimilation of some major nutrients such as nitrogen and sulfur. Others are known to be important for maintaining the activity of enzymes (e.g., Cu, Fe, Mn, and Zn). Some metals (e.g., Al, Cu, Co, Mo, Mn, and Zn) are known to be responsible for protection mechanisms of frost-hardy and drought–resistant plant (Kabata-Pendias 2004). In the aquatic ecosystem, Cu and Zn are essential micronutrients for maintaining normal functions of many enzyme systems in both algae and higher plants. Manganese oxidation is important for the growth of algae (Knauer et al. 1999).

Manganese also plays an important role in the photosynthesis of algae (Jahnke and Soulen 1978).

1.1.4 Cycling of metals in the aquatic system

Elevated metals have been increasingly observed in wildlife of many aquatic ecosystems as results of the increase in human activities, posing severe threat to both human and environmental health. Metals can enter aquatic ecosystems through various sources (e.g., atmosphere deposition, runoffs, and river). Once in the aquatic ecosystem, metals will go through a number of biogeochemical processes and be distributed into various compartments of aquatic systems (Warren and Haack 2001). These processes mainly include adsorption/desorption, transformation between different metal species, exchange of metals in the sediment-water interface (diffusion and suspension/precipitation), uptake of metals by microorganisms or plants, and bioaccumulation along food chain (Christensen et al. 2001; Warren and Haack 2001; Weng et al. 2002). The biogeochemical cycling of As is shown in Figure 1-1. In the aquatic system, adsorption/desorption is an important biogeochemical process as it is one of the controlling factors of concentrations of toxic metals in the aquatic environment (Sullivan and Aller 1996). Arsenic, Pb and Cd are commonly involved in the adsorption/desorption process with metal oxides (e.g., Fe and Mn) in soil. The process is strongly affected by pH and concentrations of adsorbents (Davis and Leckie 1978). Furthermore, sediment-water interface reactions are responsible for metal partitioning between the solid and solution phases (Warren and Haack 2001). Metal partitioning is affected by many factors, such as the system pH, ionic strength, and content of dissolved organic matter (DOM) as well as the characteristics and concentrations of solid sorbents and the kinetics of relevant reactions (Warren and Haack 2001). After partitioning process of metals in different phases, metals are initially taken up by either cyanobacteria or plants in the aquatic system. During the cycling processes, some metals are transformed under the influence of microorganisms, either by redox processes (e.g., Fe and Mn) or by akylation (e.g., Hg) (Ledin 2000). Bacteria can methylate arsenic to form both volatile (e.g., methylarsines) and nonvolatile (e.g., monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) compounds (Duester et al. 2005). Marine algae can also transform arsenate into MMAA and DMAA in seawater. Over time, accumulation of metals occur in two ways: sorption (passive) or intracellular, metabolism-dependent (active) uptake. Passive accumulation is affected by metal binding functional groups on the cell surface, as well as metal speciation in the aquatic phase. Active uptake of metals relies on an energy source (Ledin 2000). Fish and plants contaminated with heavy metals are consumed by larger organisms via digestions. The potentially toxic metals are then returned to the aquatic environment through excretion.

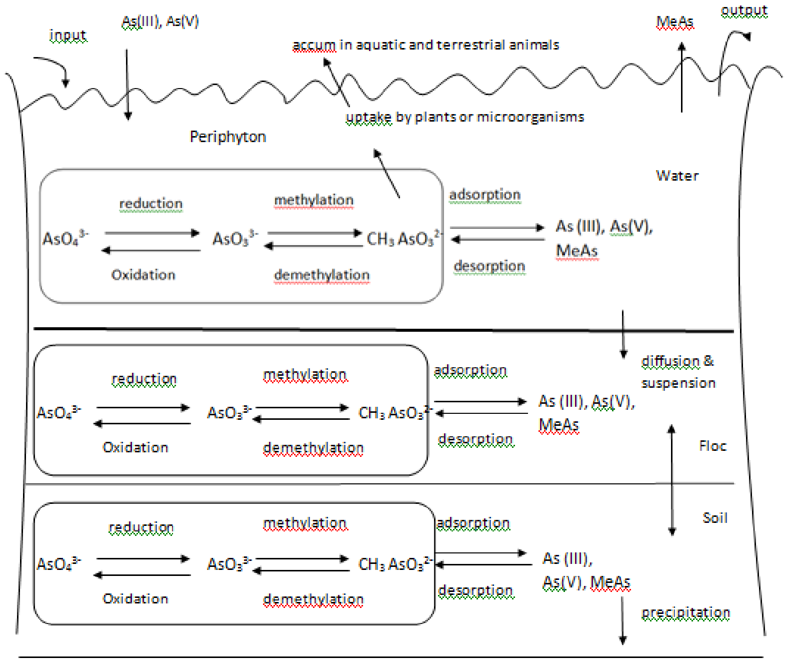

Figure 1-1 Diagram of As cycling in various matrices in an aquatic system

Cycling and fate of metals in aquatic systems are determined by many environmental factors, including DOM, pH, redox potentials, and metal-metal interactions. A heterogeneous complex of different molecular weight species with variety of water solubilities and reactivities makes up DOM (Aiken et al. 2011). DOM can form soluble complexes with toxic metals, increasing their solubility and altering their biogeochemical cycles (Hesterberg 1998). Because of high natural production of organic carbon in many aquatic ecosystems, Dissolved Organic Matter could have a strong influence on the behavior of metals (Aiken et al. 2011). Soil/sediment pH has a substantial impact on the solubilities of metals. For example, metal cations (Cu, Pb, Zn, Ni and Al) become more adsorbed under more basic condition (Adriano 1986), whereas metal anions tend to be less adsorbed under the same condition. In addition, redox potential affects the metal cycles in the aquatic environment by changing phases of metal species (solid Mn (IV) mineral, Fe (III) mineral reduced to aqueous Mn^{2+} and Fe^{2+}) (Hesterberg 1998). As a result, toxic metals (As, Cd and Pb) associated with Mn- and Fe- oxides minerals can change their solubilities. Metal-metal interactions may influence cycling of metals via several pathways, 1) formation of colloids which can influence the adsorption/desorption and bioavailability of metals, 2) formation of metal-metal complexes that enhance or inhibit the uptake of metal, and 3) competing for the binding sites on proteins or solids which can affect the adsorption/desorption or toxicity of metals. The metal-colloid complexes can be formed between toxic metals and metals that are considered micronutrients, such as Zn, Fe, and Ca (Peraza et al. 1998). Rahman and co-workers (2008) found a positive correlation between As and Fe concentrations in the same aquatic plant exposed to As solution suggesting the adsorption of As on ferric iron inhibited the mobility of As into the roots of duckweed. David Wright (1995) determined that an inversely correlation exists between Ca and Cd concentrations through experiments on perch eggs. Toxic metals can compete with essential metals for binding sites. Cadmium can potentially interfere with metabolism of four metals essential to nutrition (Fe, Zn, Ca and Cu). Furthermore, increased concentration of Cd decreases Fe and Cu absorption. Lead competes, with Ca for binding sites on intestinal mucosal proteins, with iron for transport systems of the intestine, and with Zn for Gastro-Intestinal uptake, respectively. Arsenic is known to interact with Se and Zn. Antagonistic effects are also discovered between As and Se. Arsenic also binds with Zn although the mechanism is unknown (Peraza et al. 1998). It was postulated that trace metals inhibit gill Ca ATPase in the order $Hg^{2+}>Pb^{2+}>Cu^{2+}>Cd^{2+}>Zn^{2+}$ (Viarengo and Nott 1993). In aquatic plants, Zn has been shown to reduce Cu toxicity by promoting antioxidant defense as well as increasing chlorophyll and carotenoid contents in the freshly grown aquatic plant, duckweed (Upadhyay and Panda 2010).

1.2 Metals in the Florida Everglades

1.2.1 Overlook of the Everglades

The Florida Everglades is a unique subtropical wetland environment (Fig 1-2), which varies seasonally in term of ecological conditions. Majorie Stoneman Douglas (1947) praises the uniqueness of the Everglades in her famous book "River of Grass". It is large (originally ~1.6×10^6 ha), near sea level (3 ± 3m elevation), wet in summer and dry in most of winters (Merkel and Hickey-Vargas 2000). Water used to flow freely through the Kissimmee chain of lakes in central Florida into the Kissimmee River and south into Lake Okeechobee (Clarke and Dalrymple 2003). Lake Okeechobee would overflow during the subtropical rainy season and send water to Florida Bay. As a result of the flat landscape, water used to proceed as a 30-mile wide sheet of flowing water (Clarke and Dalrymple 2003). South Florida is known for its diverse plants species as well as some endangered animal species (Scheidt and Kalla 2007). Cypress swamps, pine and mangrove forests are among major plants around the Everglades area (MePherson and Halley 1996). The suitable landscapes have supported animals including snail kite, wood stork, Florida black bear and Florida alligator. Among animal species living in the Everglades area, the Florida panther, alligators and manatees are on the endangered species list. Flooding has become a major issue for the early human settlers with agricultural interests. In order to minimize the damage flooding would cause on the crops, more than 400 miles of canals, levees and dams were constructed to drain the wetland in the south Florida by the early 1900s (Sklar et al. 1999). Even longer canals and levees, along with water control structures and pump stations, were installed in an effort to further drain the area. Fresh water (1.7 billion gallons/day on average) was to be routed directly to the sea to avoid flooding upon storm events. The excessive drainage dramatically altered the fragile balance of fresh to salt water in the south Florida area (Clarke and Dalrymple 2003). As a result of regulating overland flow of water, natural resources within the Everglades area (LNWR, WCA-2, WCA-3, ENP) were significantly degraded (SFWMD 1999). Drained peat soils were oxidized because of the lowered water table (EAA), resulting in the sink of the land surface by 3-10 feet (Perry 2008). The increased nutrient level in the Everglades soil, from nearby agricultural and urban development, has shifted vegetation community dynamics (Davis 1991; Merkel and Hickey-Vargas 2000). Other adverse impacts include enhancement of organic matter decomposition and microbial activity leading to the increase of nutrient concentrations in floodwater (Wright and Reddy 2001).

Today, the great Florida Everglades are dramatically different in terms of ecology and hydrology. The excessive drainage caused by water management results in increased highly productive algal-phytoplankton blooms, declines in sea grass beds and coral communities (MePherson and Halley 1996). Population of wading birds have been mitigated by a staggering 85-90% for those that nest their young in the Everglades (Clarke and Dalrymple 2003). The change in the water distribution has alternated habitat for both plants and animals in addition to the salinity changes (Horrocks and Ogden 1994). The hydrological alternation is blamed for the dramatic declines of fish and wildlife populations.

In an effort to restore conditions in the Everglades back to the pre-development state where landscape can support abundant wildlife and plants, the Comprehensive Everglades Restoration plan (CERP) was created. In 2000, the legislation regulating CERP was signed into law By President Clinton with an estimated funding of $7.8 billion for a 30-year project.

The goal of the plan was to restore the ecological beauty in the Everglades area. However, the consideration for contribution by human activities to the pollution in the Everglades area has been largely neglected by CERP. A report prepared by the U.S. General Accounting office has called for the need to fill data gaps in the scientific information on potentially harmful contaminants and their risks to native aquatic organisms.

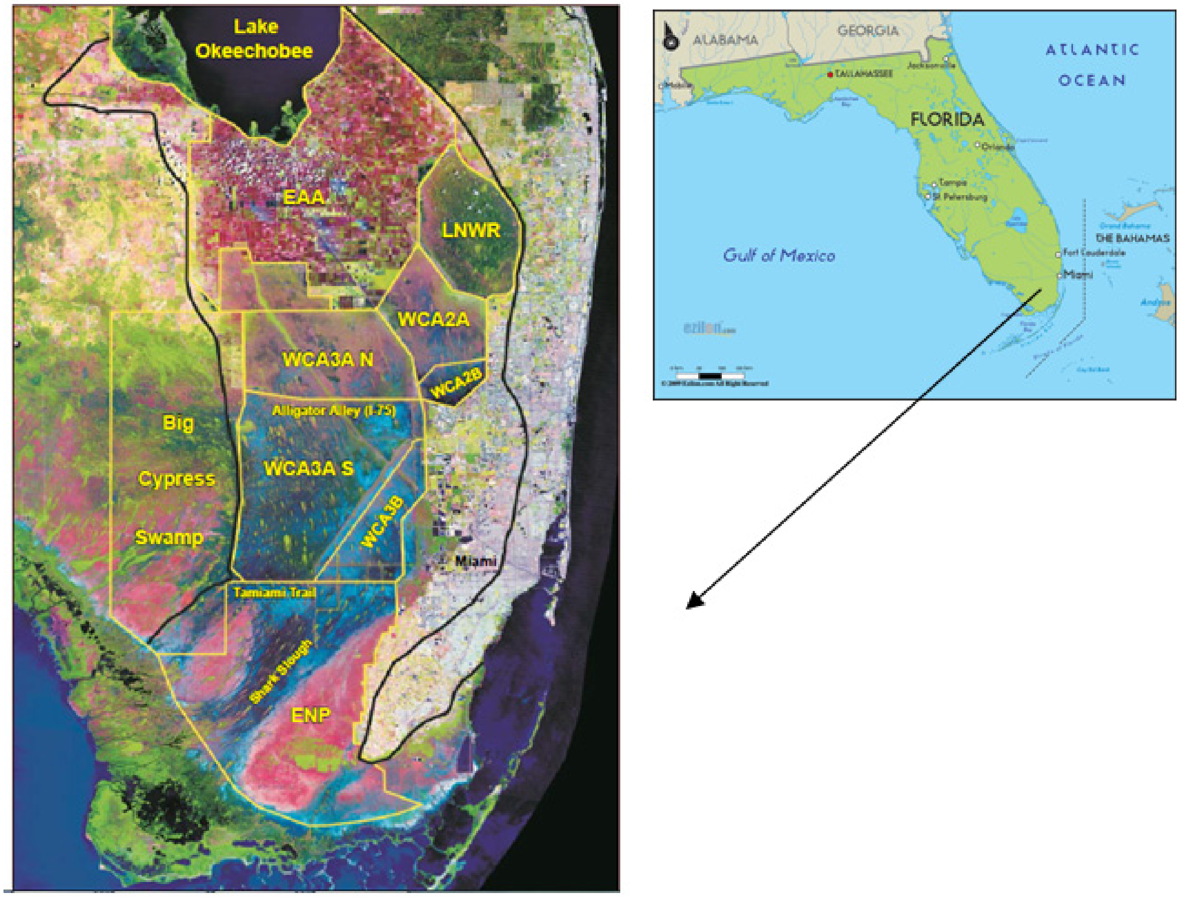

Figure 1-2 Satellite image of South Florida, including main components of the Florida Everglades: Everglades Agricultural Area (EAA); Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR); Everglades Water Conservation Area 2 (WCA 2); Everglades Water Conservation Area 3; the eastern portion of Big Cypress National Preserve, and the freshwater portion of Everglades National Park (ENP). Light areas on the east are urban development (Scheidt and Kalla 2007).

1.2.2 Possible sources of metals in the Everglades

Metal distributions in the Everglades are under influences from several sources, including agriculture, atmospheric deposition, road traffic, landfill, wastewater management, tourism (airboat), airport, cattle ranching and dairy farming (Chaney and Ryan 1993; Chen et al. 1997; Viard et al. 2004; Carriger et al. 2006; Dragovic et al. 2008) . With the flow of drainage water from Everglades Agriculture Area (EAA) into the Water Conservation Areas (WCAs), metals contained in pesticides and fertilizers (e.g., Mg, K, Al, Fe, Cr, Cd, As, Hg and Pb) can become inputs in the Everglades (Craft and Richardson 1997). Atmospheric inputs such as wind and rainfall can contribute to the metal distributions as well (Pironfrenet et al. 1994; Lu et al. 2003). Florida is one of the regional background locations with the highest rates of Hg deposition (Sillman et al. 2007). Atmospheric deposition of Cd and Pb from rains and aerosols originated in fertilizers (Pironfrenet et al. 1994; Dammgen et al. 2000) is another possible alternate source affecting metal distributions in the Everglades. Motor vehicle emissions on surrounding roads may also contribute to some metals (e.g., Zn, Pb, Cd) (Garcia et al. 1996; Othman et al. 1997; Viard et al. 2004; Calace et al. 2012). Waste water, including discharge from domestic and industrial treatment plant as well as runoff from landfill, can also contribute to aggravated levels of metals in the Everglades area (McPherson 1990). The Florida Everglades is a well- known tourist spot with airboat guided tour being one of the most popular activities. Kendall-Tamiami Airport (KTMB), one of the “busiest general aviation airports in Florida”, is located not too far from the southeastern region of Everglades National Park. They might contribute to Pb in the Everglades because Pb is an ingredient used in the jet fuel (EPA 2010). Cattle ranching and dairy farming are another prominent agriculture activity that affects the ecosystem. High densities of cattle can be seen in the surrounding areas of Everglades in Hendry, Palm Beach, Broward, Miami-Dade and Collier counties (MePherson and Halley 1996). Sewage biosolids that are applied to dairy farm lands surrounding the Everglades could contribute to the elevated levels of toxic metals (Cd, Cr, Ni, Pb) in underground water and runoffs (Richards et al. 2004).

1.2.3 Previous studies on metals in the Everglades and surrounding areas

Several previous studies have investigated levels of several metals in Biscayne Bay, the Florida Keys, Florida Bay, and surrounding estuaries (Windom et al. 1989; Strom et al. 1992). Lead and Zn contamination were found in Biscayne Bay and Pensacola Bay as determined from comparisons between sample data with metal-aluminum relationships designed for natural uncontaminated sediments collected from the same region (Windom et al. 1989). Carnahan and co-workers (2008) reported distributions of 11 heavy metals (Cu, Zn, Cr, Hg, Pb, Ni, Ag, As, Cd, Sb and Sn) in Biscayne Bay sediments in Florida. Silver, As, Sb, Sn, and Cd were rarely detected whereas Cu, Hg, Ni, Pb, and Zn were frequently detected using inductively coupled plasma-optical-emission spectrometry (ICP-OES) and a flow-injection mercury system (FIMS). Elevated levels of Pb were found in most samples, compared with establish criteria. The highest concentrations of Cu, Zn, Cr, Hg, Pb, and Ni were found closest to Miami and near the mouths of several canals along the western margin of the bay. Strom et al. (1992) investigated trace metal concentrations (As, Pb, Cu, and Cd) in the sediments and producer as well as consumer organisms in samples from Florida Keys. Concentrations of As (<0.2 ppm), Pb (0.8-4.5 ppm), Cd (0.2-1.2 ppm), Cu (0.8-3.8 ppm) were measured. The results showed that the Florida Keys had low metal pollutions with a few anthropogenic effects (human inputs). A few studies have been done on the distribution of metals and their implications in the surrounding areas of the Everglades (Caccia and Millero 2003; Carnahan et al. 2008; Rand and Schuler 2009). Caccia et al. (2003) studied distribution of trace metals (Sc, V, Ba, Cd, Cr, Co, Cu, Pb, Mn, Ni, Zn, Al, Mg, and Fe) in Florida Bay sediments and concluded all metals exhibited similar distribution pattern with except for Mn and Fe. The highest concentrations were influenced by the input and runoff from the Taylor Slough. Maximum concentrations of those metals in the Florida Bay were found to be lower than those in most estuarine systems in the United States. The organic material in the Florida Bay originated from detritus of sea grasses as determined using the ratio of the percentage of organic carbon and nitrogen in the sediments (Caccia and Millero 2003). The strong correlations were found between Al and metals (Ni, Cr, Pb, Ba, Fe, V, Cu and Zn) suggesting close association of those metals with fine fraction of the sediments (aluminosilicates).

Few studies conducted in the Everglades focused on source and fate of metals. Very little interest was given with regard to possible pollution associated with metals in the past century (Kushlan and Hunt 1979). A detailed study was conducted on major ions from a Big Cypress Swamp alligator pond during a dry season. High concentrations of Al, Fe, Mg, Hg, Pb and Zn were found. Kushlan and Hunt determined that the high values were as results of reduced water volumes, rapid decomposition of animal and plant material, and reduction of bound compounds in anaerobic conditions. Rand and Schuler (2009) conducted a two-tier aquatic screening-level ecological risk assessment for several metals (As, Cd, Cr, Cu, Pb, Ni, Zn) in sediment at 32 sites from the south Florida freshwater canals inside the Everglades. For tier 1, As, Cd, Cr, Cu, Pb, Ni and Zn were identified as the metals of potential ecological concern (COPECs) as their concentrations have exceeded Florida sediment quality assessment Guideline (SQAG) at 10 sites. For tier 2, a probabilistic risk assessment method was used to compare distributions of predicted pore water exposure concentrations of seven metal COPECs with distributions of species response data from laboratory toxicity tests to quantify the likelihood of risk. Arsenic and Cr at sites surrounding the Everglades National Park were found to be the most frequently detected COPECs in sediment. Potential risks associated with Pb and Cu were estimated to be high. However, this study only set up about 20 sites around Everglades, most of which were at the boundary of Everglades. However, only 7 toxic metals were studied in Rand's research with goals to conduct a screening-level ecological risk assessment. Most studies associated with metals in the Everglades have focused on mercury because of its high toxicity to humans and its relatively high concentrations found in the Everglades ecosystem (Cai et al. 1999; Evans and Crumley 2005; Cohen et al. 2009). Cai et al. (1999) studied the interaction between organic C and Hg species in natural water in the Florida Everglades, and concluded Total Hg (THg) and Methyl Hg (MeHg) shared different distribution pattern in different phases. Furthermore, colloidal forms were found to contain most of THg, while MeHg is present almost exclusively in the lower molecular weight fraction of the colloid and in the truly dissolved fraction. Using stable isotopes of carbon, nitrogen, and sulfur measured in fish from the Florida Bay, Evans and Crumley (2005) concluded that MeHg and nutrient elements shared pathways through the food web, and the accumulation of MeHg sustained in gamefish supported by epibenthic feeders. Cohen and co-workers (2009) mapped soil total Hg concentrations per mass (THg_M) and area (THg_A) across the Everglades and predicted its spatial pattern. Sources of elevated THg including canal water from EAA and subsidence or oxidation of peal soil were proposed by the same group.

Over the last two decades, several programs supported by federal and state agencies have been carried out to examine Hg pollution in the Everglades. For example, studies on Hg were conducted through the Regional Environmental Monitoring and Assessment Program (REMAP). Hg contamination was examined in terms of distribution among different matrices (water, mosquitofish, periphyton), and bioaccumulations (Scheidt and Kalla 2007). The goal of R-EMAP was to provide accurate and timely scientific information for management decisions on the restoration efforts in the Everglades (Scheidt and Kalla 2007). The Everglades R-EMAP area covers areas from north of Lake Okeechobee to the mangrove fringe on Florida Bay and from the ridge along the east coast to the west of Big Cypress National Preserve. The whole sample areas covers over 750 miles of canals and over 3,000 square miles of freshwater marsh. In May 2005 and November 2005, phase III of the program was conducted as samples were extracted from 228 Everglades marsh sites, covering marsh and canal locations throughout the freshwater Everglades and Big Cypress (Scheidt and Kalla 2007). Liu et al. (2008) analyzed samples from R-EMAP in 2005, and determined the concentrations for THg in the increasing order: periphyton < floc < soil. In addition, the same study concluded that condition for bioaccumulation of Hg is favored, on the basis of the distribution patterns of THg and MeHg (Liu et al. 2008). Bioaccumulation and spatial patterns in Hg cycling were then investigated, which lead to the identification of important factors (surface water dissolved organic matter (DOC_{sw}, pH, chloride, etc.) in controlling THg distribution (Liu et al. 2009). Using samples collected in both summer and winter seasons of 2005, mass inventories of THg and MeHg as well as mass budgets of Hg were constructed, in an effort to evaluate the magnitude of legacy Hg contamination and help predict the fate of new Hg in the Everglades area (Liu et al. 2011). Li and co-workers investigated the degradation of MeHg in the Everglades using stable isotope ($Me^{201}Hg$) addition method. The study demonstrated that the degradation of MeHg can be attenuated by sunlight, a controlling factor in the distribution of MeHg in Everglades' water.

1.3 Rationale and objectives of this study

Most of the previous work done on metals in the Everglades has focused on Hg, although other metals of environmental concerns deserve an equal share of the spotlight. The few studies that have been conducted for other metals rather than Hg in the Everglades have dealt with the assessment of eco-toxicity for a limited number of metals using data measured in Everglades' soil/sediment (Caccia et al. 2003; Carnahan et al. 2008; Rand and Schuler 2009). There is still a general lack of knowledge on the source, distribution, transport, and risk of metals in the Everglades.

Soil, flocculent materials (floc) and periphyton are three important components of the Everglades. Investigation of metal contamination in soil can help us assess the potential risk of metal pollution on aquatic organisms, and make efforts to prevent further deteriorations (Rand and Schuler 2009). Periphyton, an omnipresent feature of Everglades' marshes, is a community comprised of plants, algae and certain animals (MePherson and Halley 1996). It is responsible for almost half of primary production of the Everglades and serves as food source for small consumers like small fish, grass shrimp at the base of food chain (McCormick et al. 1996; Gaiser et al. 2006). Trace metals present in periphyton could enter higher trophic levels. Identification of metals in periphyton can help trace and estimate concentrations and source of metals in organisms higher up in the food chain. Flocculent material (floc), on the other hand, is composed of microorganisms, organic particles (detritus, cellular debris), inorganic particles (clays and silts) and pores (Neto et al. 2006). The important role played by floc in aquatic system lead to the belief that floc can dictate the fate and effect of particle-associated contaminates (Droppo 2001). In the Everglades, higher plant detritus, periphyton, carbonates, and remains of aquatic organisms in the freshwater and estuarine make up the floc (Neto et al. 2006). Floc also represents a significant part of food web for invertebrate and fish, and a thorough investigation of metal pollutions associated with it is essential to predict overall fate and source of trace metals in the Everglades ecosystem. A comprehensive study on metals in these important matrices (soil, periphyton and floc) is of great importance for a better understanding of the biogeochemical cycling of metals in the Everglades. Results of this study will also provide background information that is needed to aid the restoration effort set forth by the CERP.

The main objective of this research is to assess the current status of toxic and essential metals in the Florida Everglades. The following specific aims will be pursued in order to successfully accomplish this objective:

1. To determine the concentrations of 18 metals, including toxic metals (As, Cd, Cr, Ni and Pb) and essential metals (Al, Ba, Be, Co, Cu, Fe, Li, Mg, Mn, K, Sr, V and Zn) in various compartments (sediment, Floc, and periphyton) in the Florida Everglades.
2. To establish the spatial distribution pattern of the metals in the Everglades.
3. To quantify the major sources of the 18 metals present in the Everglades.

2. Methods

2.1 Experimental section

2.1.1 Sample collection

Sampling covered the entire freshwater Everglades, including Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR), water conservation area 2 (WCA-2), WCA-3, and Everglades National Park (ENP). Soil, floc and periphyton were collected at 195 random located stations during the REMAP project in 2005 (Scheidt and Kalla 2007). Probability-based sampling design, adopted by the REMAP project was selected.

Soil samples were extracted with a 3-inch diameter clean polycarbonate coring tube to sample the top 10 cm. The flocculent detrital material (floc) is the top layer of the soil is composed of suspended organic material containing mostly detritus from plants and algal inputs from periphyton (collected separately during soil sample collection. Three types of periphyton, floating mat (floating), soil mat (lying on the soil surface), and epiphytic (associating with macrophytes), were collected in the field. A layer of periphyton mat, if found on the top of the soil core, was separated and stored in a separate container. Samples in both dry and wet seasons (May and November 2005) were collected (Figure 2-1). All samples, soil, floc, and periphyton were stored in refrigerator at -20° C before sample processing and analysis.

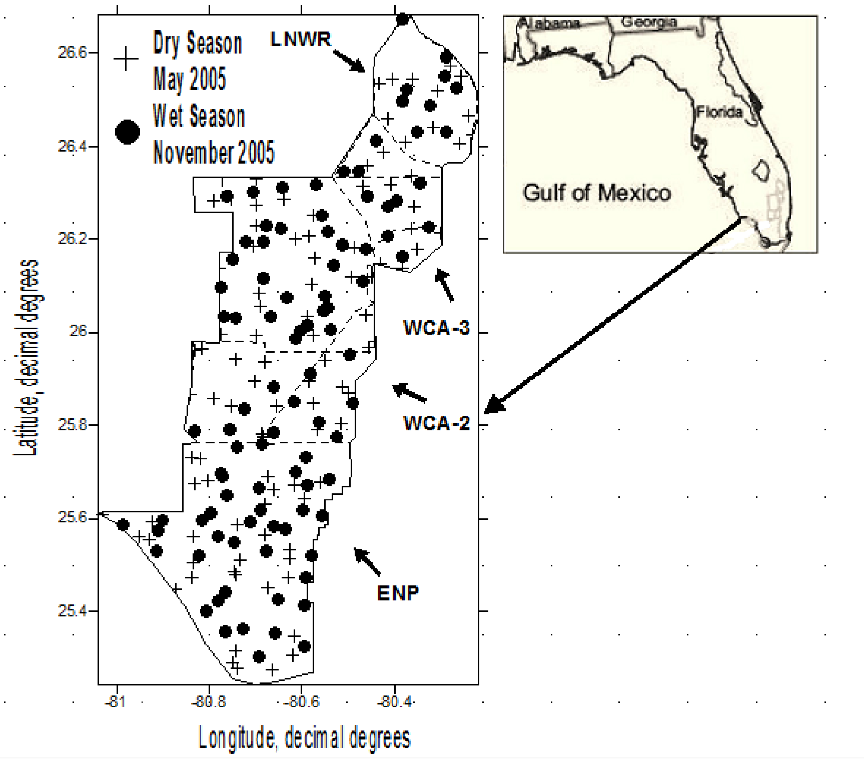

Figure 2-1 A map showing sampling sites in the Florida Everglades. Sites were sampled during the dry (May) and wet season (November). LNWR: Arthur R. Marshall Loxahatchee National Wildlife Refuge; WCA-2 and WCA-3: Water Conservation Areas; ENP: Everglades National Park

2.1.2 Sample preparation and analysis

Soil, floc, and periphyton samples were dried in the laboratory oven at 60C for four days, and then were homogenized using pestle and mortar. Approximately 0.5 g of each sample was transferred to a clean polypropylene digestion tube (50 ml). Five ml concentrated nitric acid (trace metal grade) was added to each sample and the mixture was heated at 95 ± 5˚C on a hot block for an hour. After samples cooled to the room temperature, one ml of 30% hydrogen peroxide was added and then the samples were heated again at 95 ± 5˚C for additional 20 minutes. The samples were diluted with deionized water to 50 ml. Prior to analysis, samples were filtered (0.2 μm filter size) and diluted on the basis of their concentrations (rough estimation for each metal analyzed). Twenty μL of yttrium was added to 10 ml of sample solution to serve as the internal standard.

Concentrations of metals were analyzed using an ELAN DRC-E inductively coupled plasma-mass spectrometry system (ICP-MS). Personal Computer-based data acquisition and analysis software (ELAN version 3.4) was used.

Quality assurance/quality control (QA/QC) was taken to ensure data duplicity and highest accuracy possible. For every 20 samples prepared, two additional aliquots of one selected sample were spiked at the level of 1-5 times estimated concentration of metals in samples to serve as matrix spike and matrix spike duplicate (MS/MSD), along with two method blanks (containing only 2% HNO_3 (v/v) and DIW) to assure quality and reliability of the analysis. For every 20 samples prepared, one sample was selected for triplicate analysis.

2.1.3 Data analysis

Concentrations of Li, Be, V, Mn, Co, Cu, Tl, Zn, Sr, Ba, Al, Fe, K, Mg, As, Cd, Cr, Ni and Pb from all matrices collected in both dry and wet seasons were calculated on the basis of dry weight. Total recoverable analytes (mg/kg, dry weight basis) in solid samples were calculated for each sample analyzed using the equation below:

$$C_{sample} = (C_{extract} \times V_{extract})/W_{dry} \qquad (1)$$

Where C_{sample} is the concentration for total recoverable analyte; $C_{extract}$ is the concentration of analyte in the extract (mg/L); $V_{extract}$ is the volume of extract (L); W_{dry} is the dry weight of sample aliquot extracted (Kg).

Parameters, including maximum, minimum, standard deviation, and median values were calculated as well. Contour maps of each metal from both dry and wet seasons were plotted using SURFER. Pearson's correlation analyses of all metals were conducted intra and inter all matrices using Statistical Package for the Social Sciences (SPSS). The detection limits of ICP-MS techniques for all metals analyzed are listed in Table 2-1.

Table 2-1 Detection Limits of trace metals by ICP-MS

Element	Detection Limit [mg/Kg]	Element	Detection Limit [mg/Kg]
Al	0.2	Li	0.01
As	0.02	Mg	0.06
Ba	0.01	Mn	0.004
Be	0.001	Ni	0.01
Cd	0.004	K	0.3
Cr	0.02	Sr	0.001
Co	0.003	Tl	0.001
Cu	0.05	V	0.05
Fe	0.2	Zn	0.2
Pb	0.005		

3. Results

3.1 Metal concentrations in Florida Everglades soil, floc, and periphyton

All three matrices, soil, floc and periphyton, had different trends in terms of average concentrations and concentration ranges (Table 3.1 and 3.2). For soil samples, some metals (Al, Cu, Ni and Pb) had higher concentrations in the dry season than in the wet season (Fig 3-1). Concentrations of Be, V, Co, Tl, Zn, Sr, Ba, Fe, Mg and Cd varied little during the year, while Cr and K was twice more concentrated in the wet season than in the dry season. The dry season also had a larger concentration ranges for most of metals than the wet season. Among all the metals, iron and Al had the highest concentrations in both dry and wet seasons. For floc samples, average concentrations varied significantly from dry season to wet season (Fig 3-2). Copper, Mg, Cr, Ni, Pb had higher concentrations in the dry season compared to the wet season; Li, Co, Tl, Cd and As had little concentration variations between seasons. Aluminum and K had higher mean concentrations in the wet season. Iron had the highest concentrations of all the metals analyzed. Mean concentration of almost all metals analyzed from periphyton varied little between seasons (Fig 3-3). Only Be, Al, Fe, Pb, Cd and Zn exhibited visible concentration changes. Aluminum and Pb had higher concentrations in the dry season while Be, Zn, Cd, and Fe were more concentrated in the wet season. Other metals (Li, V, Mn, Co, Cu, Tl, Sr, Ba, Cr, Cd, Ni and As) had few changes in terms of mean concentrations. Similar to the other two compartments, iron is the most concentrated metal in periphyton. As for the distribution of metals among different compartments, average concentrations of most metals follow the order of soil>floc>periphyton, except for Mn, Sr, Ba, K, Ni, Cu and Zn. Floc had the highest concentrations of Cu and Zn while periphyton had the most concentrated values for Mn, Sr, Ba, K and Ni. Aluminum and Fe had the highest concentrations among all metals from sediment samples in both dry season (May 2005) and wet season (November 2005), while Tl was the least concentrated metal.

Table 3-1 Average concentrations of metals in all matrices (soil, floc, and periphyton) in dry season (mg/kg for all metals except for Al, Fe and Mg given in (mg/g))

Metals	Soil		Floc		Periphyton	
	Mean	Range	Mean	Range	Mean	Range
Lithium	1.58±3.06	0.061-20.9	0.79±0.37	0.10-1.94	0.63±0.52	0.10-1.90
Beryllium	0.096±0.109	0.002-0.542	0.07±0.05	0.001-0.3	0.033±0.02	0.01-0.09
Vanadium	12.23±9.76	2.40-70.1	7.75±6.8	0.32-37.0	2.32±1.89	0.69-8.61
Manganese	92.0±72.1	1.40-363	138±94.7	16.9-411	586±570	83.2-1,883
Cobalt	0.675±0.340	0.013-1.72	1.13±0.41	0.45-2.16	0.68±0.26	0.24-1.19
Copper	6.10±10.8	0.161-71	17.8±22.4	2.76-120	4.07±6.02	0.56-24.0
Thallium	0.027±0.0230	0.001-0.166	0.013±0.012	0.001-0.087	0.006±0.01	0.001-0.02
Zinc	7.15±4.87	0.013-26	19.9±8.82	5.77-59.8	7.16±4.10	2.42-16.8
Strontium	360±224	13.1-1098	367±331	20.3-2301	602±480	150-1,890
Barium	42.9±15.8	12.6-87.5	49.1±12.4	26.7-84.7	65.0±50.1	26.1-215
Aluminum	4.12±5,26	.328-46.3	.706±.750	0.015-4.76	1.27±1,69	0.051-4,84
Iron	6,10±5,04	.602-25.9	5.50±5.31	0.037-27.1	4.27±4,11	.242-14.8
Potassium	157±86.2	2.17-368	395±326	39-2,25	522±338	186-1,251
Magnesium	2.11±1.86	.0676-17.2	2.24±1.43	.166-7.59	2.66±2,04	.240-7.28
Chromium	4.28±4.93	0.065-30.6	5.89±3.70	2.00-17.9	1.95±1.31	0.59-5.44
Nickel	4.87±3.83	0.383-19.6	9.35±7.71	3.51-39.1	16.5±8.63	4.05-33.7
Arsenic	2.82±1.97	0.142-8.41	4.41±2.45	0.84-13.7	1.26±1.00	0.22-4.06
Cadmium	0.118±0.127	0.004-1.07	0.114±0.108	0.01-0.78	0.03±0.02	0.01-0.08
Lead	18.5±38.5	0.122-280	2.67±4.12	0.05-19.3	0.87±1.29	0.02-4.74

Table 3-2 Average concentrations of metals in all matrices (soil, floc, and periphyton) in wet season (mg/kg for all metals except for Al, Fe and Mg given in (mg/g))

Metals	Soil		Floc		Periphyton	
	Mean	Range	Mean	Range	Mean	Range
Lithium	1.27±1.65	0.064-10.3	0.80±0.94	0.17-5.72	0.50±0.51	0.09-1.75
Beryllium	0.084±0.064	0.007-0.395	0.42±0.31	0.01-1.55	0.09±0.09	0.02-0.38
Vanadium	11.8±7.17	1.35-43.6	11.2±7.18	2.99-32.9	3.23±1.91	1.21-9.87
Manganese	67.7±46.5	7.09-197	371±412	17.8-2,278	532±484	86.9-1,881
Cobalt	0.82±1.1	0.14-8.96	1.07±0.40	0.43-2.70	0.86±0.36	0.43-1.67
Copper	2.89±2.02	0.127-9.97	7.39±4.91	2.54-30.8	4.36±4.95	0.68-20.3
Thallium	0.025±0.041	0.001-0.264	0.016±0.01	0.004-0.059	0.01±0.02	0.001-0.11
Zinc	7.29±4.95	0.404-20.9	16.7±6.62	6.05-35.2	12.6±7.79	3.06-30.4
Strontium	346±205	60.0-856	391±308	76.8-1,579	543±405	81.9-1,976
Barium	43.3±17.6	9.07-95	68.5±39.0	24.1-227	67.0±41.2	18.7-171
Aluminum	3.08±4.30	0.051-21.9	1.13±1.59	0.058-9.96	0.494±0.580	0.070-2.97
Iron	6.16±3.99	0.808-20.9	5.98±4.77	0.524-19.5	5.86±4.68	0.770-17.5
Potassium	335±225	1.9-958	570±591	97-4294	742±511	140-1,988
Magnesium	2.04±1.61	0.0071-13.4	0.961±0.864	0.127-4.26	2.07±1.61	0.340-7.04
Chromium	12.1±15.2	1.80-59.8	3.08±1.26	1.31-9.15	1.62±0.92	0.62-4.15
Nickel	3.423±2.03	1.06-13.0	3.37±1.63	1.31-11.12	17.7±10.9	4.82-46.8
Arsenic	3.13±2.77	0.074-14.9	3.39±1.91	0.49-8.74	2.12±1.79	0.38-7.17
Cadmium	0.12±0.12	0.007-0.83	0.092±0.033	0.022-0.186	0.07±0.15	0.01-0.99
Lead	1.27±1.65	0.24-146	0.80±0.94	0.37-21.6	0.50±2.88	0.02-12.2

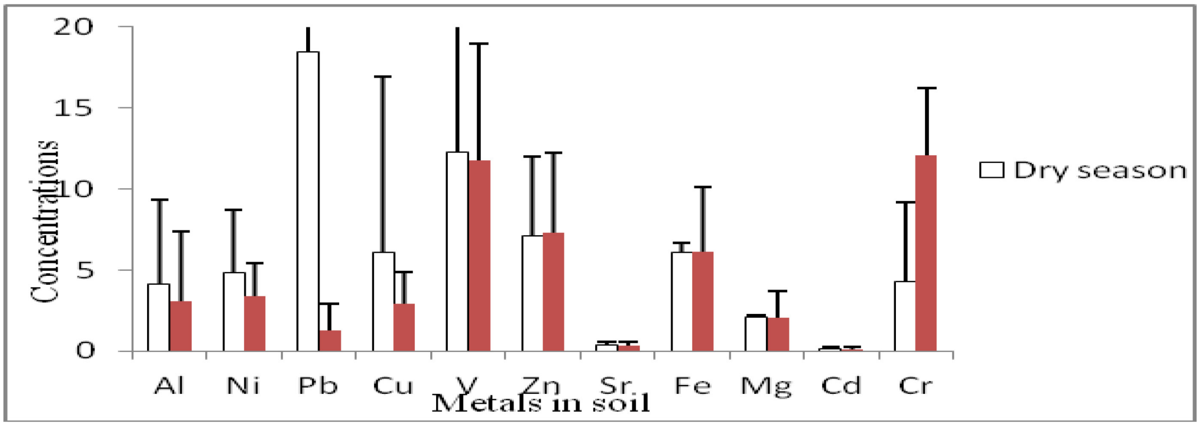

Figure 3-1 Comparison of metal concentrations from soil in dry and wet season

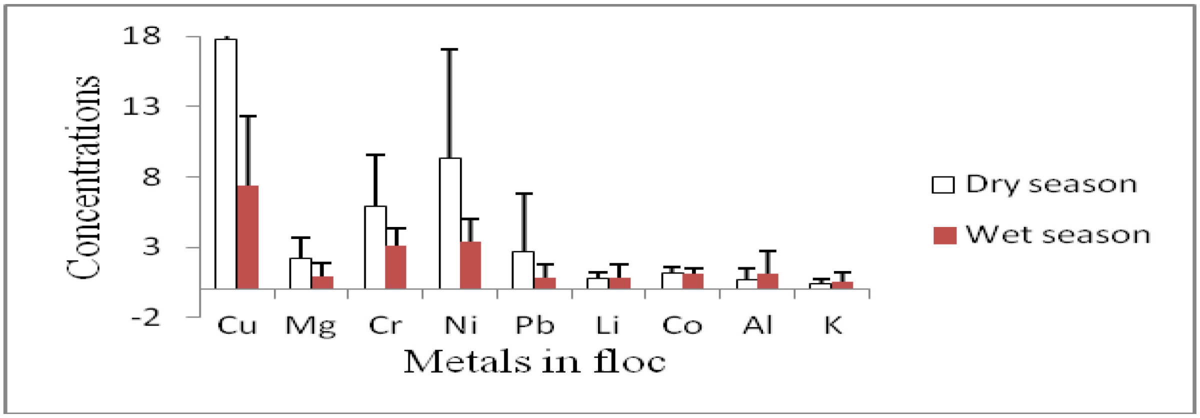

Figure 3-2 Comparison of metal concentrations from floc in dry and wet season

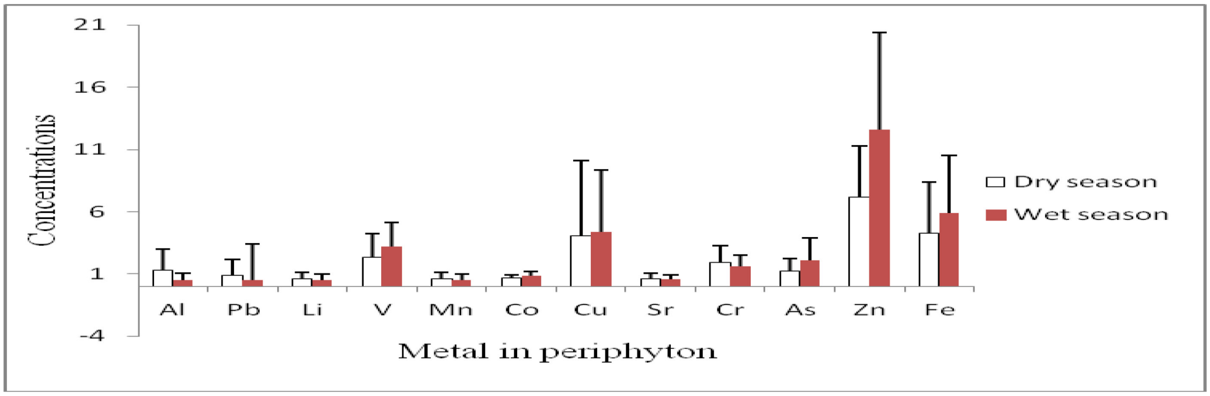

Figure 3-3 Comparison of metal concentrations from periphyton in dry and wet season

Correlation matrixes for metals present in the three compartments are shown in Tables 3.3, 3.4, and 3.5. Between soil and periphyton metals, soil metals (Mn, As, Cd and Zn) and periphyton metal (Zn) were significantly correlated. Periphyton Sr and Mg had strong correlation with soil metals (Co, Cu, Cd, Tl, Pb and Sr) (Table 3.3). Between soil and floc metals, Cr in soil correlated well with Tl and Pb in floc. Soil metals (Ni and As) correlated with floc metals (Sr and Fe), respectively (Table 3.4). Between floc and periphyton, periphyton metal Ni correlated well with floc metal Zn. Strontium in periphyton correlated significantly with Sr, Ba and Mg in floc (Table 3.5).

Table 3-3 correlation matrix of metals (soils, x axis) versus periphyton (y axis)

Metals in soil

Metals in periphyton

	Li	**Be**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**As**	**Cd**	**Tl**	**Zn**	**Pb**	**Sr**	**Ba**	**Al**	**Fe**	**K**	**Mg**
Li	+																		
Be	-	-																	
V	-	-	-																
Cr	-	-	-	-															
Mn	-	-	-	-	-														
Co	-	-	-	-	-	-													
Ni	-	-	-	-	++	-	-												
Cu	-	-	-	-	-	-	-	++											
As	-	+	-	-	++	-	+	-	+										
Cd	-	-	-	-	-	-	-	-	-	-									
Tl	-	-	-	-	-	-	+	-	-	-	-								
Zn	+	+	-	-	++	-	-	-	++	+	-	++							
Pb	-	-	-	-	-	-	-	+	+	-	-	+	-						
Sr	-	-	-	-	-	++	+	++	-	++	++	-	++	++					
Ba	-	-	-	-	-	-	-	-	-	-	-	-	+	-	-				
Al	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-			
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-		
K	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Mg	-	-	-	-	-	++	-	++	-	++	++	-	++	++	++	-	-	-	++

++ indicates p<0.01 level
+ indicates p<0.05 level
-indicates p>0.05 level

Table 3-4 Correlation matrix of metals (soils, x axis) versus floc (y axis)

metals in soil

Metals in floc

	Li	Be	V	Cr	Mn	Co	Ni	Cu	As	Cd	Tl	Zn	Pb	Sr	Ba	Al	Fe	K	Mg
Li	++																		
Be	-	-																	
V	-	-	++																
Cr	-	-	-	+															
Mn	-	-	-	-	-														
Co	-	-	-	-	+	-													
Ni	-	-	-	-	-	-	-												
Cu	-	-	++	-	+	-	-	-											
As	-	-	-	-	-	-	-	-	++										
Cd	-	-	-	-	-	-	-	-	-	-									
Tl	-	-	-	++	-	-	-	-	-	-	-								
Zn	-	+	-	-	+	-	-	+	-	-	-	+							
Pb	-	-	-	++	-	-	-	-	-	-	-	-	-						
Sr	-	-	-	-	+	-	++	-	-	-	-	-	-	++					
Ba	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-				
Al	+	-	+	+	-	-	-	-	-	-	++	-	-	-	-	+			
Fe	-	-	-	-	-	-	-	-	++	-	-	-	-	-	-	-	++		
K	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Mg	+	-	-	-	-	-	-	-	-	-	-	-	-	++	-	-	-	-	-

++ indicates p<0.01 level
+ indicates p<0.05 level
-indicates p>0.05 level

Table 3-5 correlation matrix of metals (floc, x axis) versus periphyton (y axis)

Metals in floc

Metals in periphyton

	Li	**Be**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**As**	**Cd**	**Tl**	**Zn**	**Pb**	**Sr**	**Ba**	**Al**	**Fe**	**K**	**Mg**
Li	-																		
Be	-	-																	
V	-	-	-																
Cr	-	-	-	-															
Mn	-	-	-	-	-														
Co	-	-	-	-	-	-													
Ni	-	-	-	-	-	-	-												
Cu	-	-	+	-	-	-	-	+											
As	-	-	-	-	-	-	-	-	++										
Cd	-	-	-	-	-	-	-	-	-	-									
Tl	-	-	-	-	-	-	-	-	-	-	-								
Zn	-	-	-	-	-	-	++	-	-	-	-	-							
Pb	-	-	-	-	-	-	-	-	-	-	-	-	-						
Sr	-	-	-	-	-	-	-	-	-	-	-	-	-	++					
Ba	-	-	-	-	-	-	+	-	-	-	-	-	-	++	-				
Al	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-			
Fe	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-		
K	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-	
Mg	-	-	-	-	-		-	-	-	-	-	-	-	++	-	-	+	-	-

++ indicates p<0.01 level
+ indicates p<0.05 level
-indicates p>0.05 level

3.2 Spatial distribution of metals in Everglades soil, floc and periphyton

3.2.1 Spatial distribution of metals in soil

Spatial distribution patterns of toxic metals (Cd, Cr, Ni, As and Pb) in soil were grouped together (Fig 3.4 -3.6). Although Cu and Zn are considered toxic at high concentrations, the two were mixed with essential metals because 1) those two metals are essential to plants and other organisms at low concentrations; 2) average concentrations of Cu and Zn from all matrices were low.

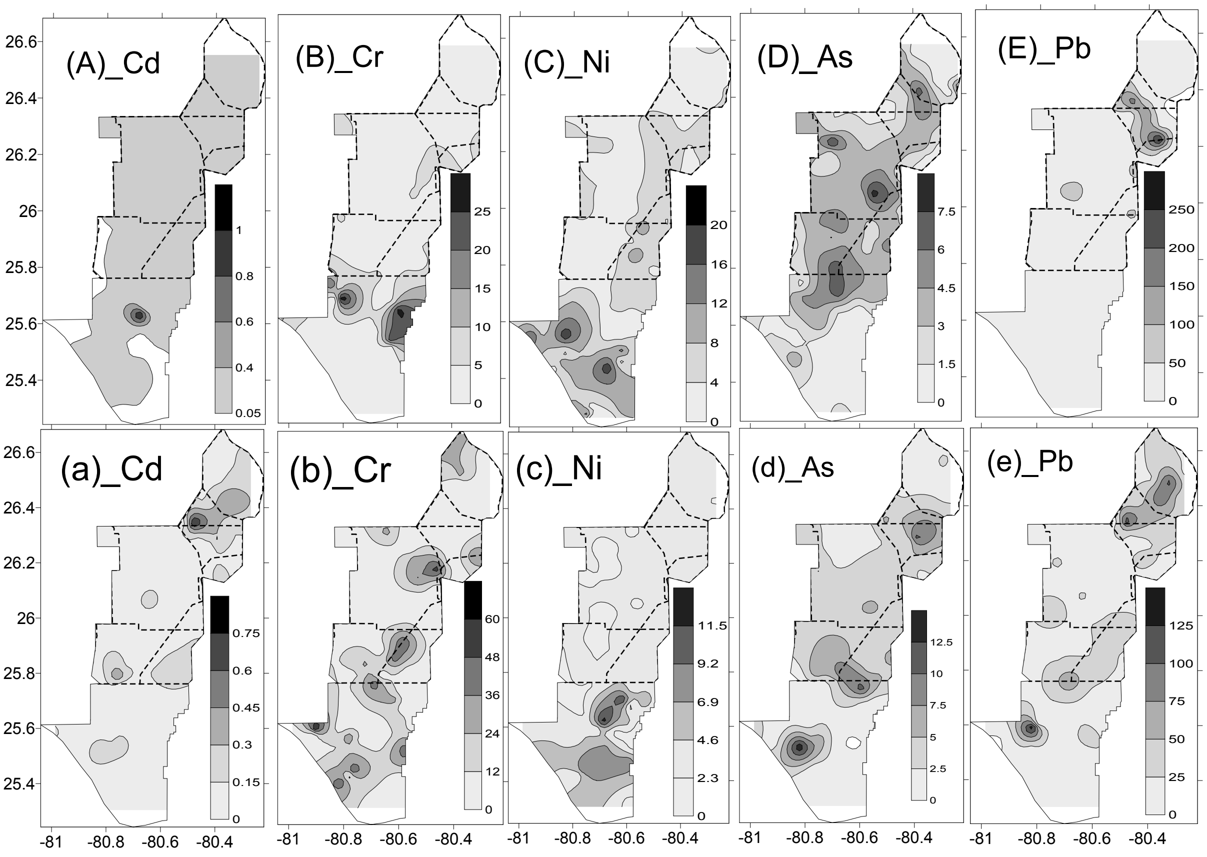

Figure 3-4 Spatial variation of toxic metals in soils of the Florida Everglades (A) Cd, (B) Cr, (C) Ni, (D) As, and (E) Pb during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

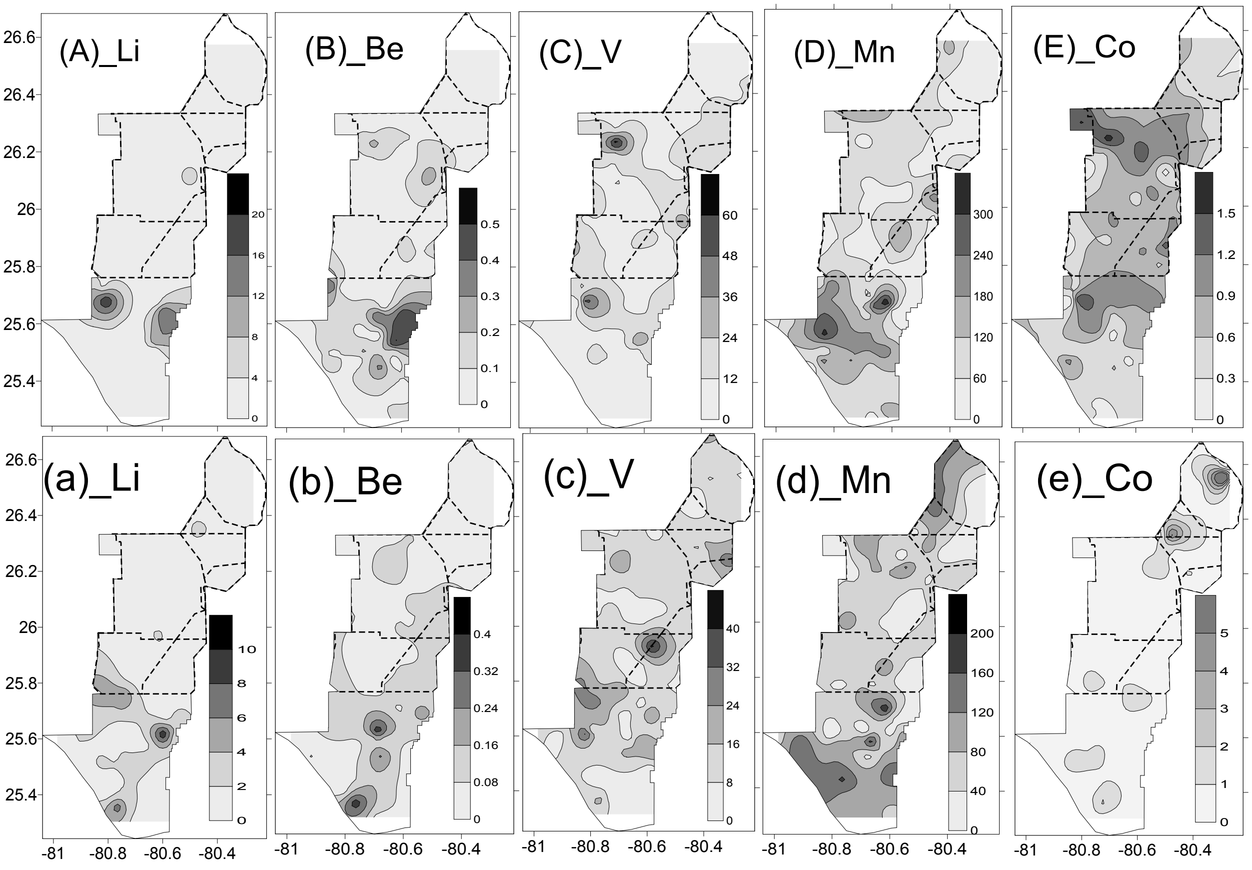

Figure 3-5 Spatial variation of essential metals in soils of the Florida Everglades (A) Li, (B) Be, (C) V, (D) Mn, and (E) Co during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

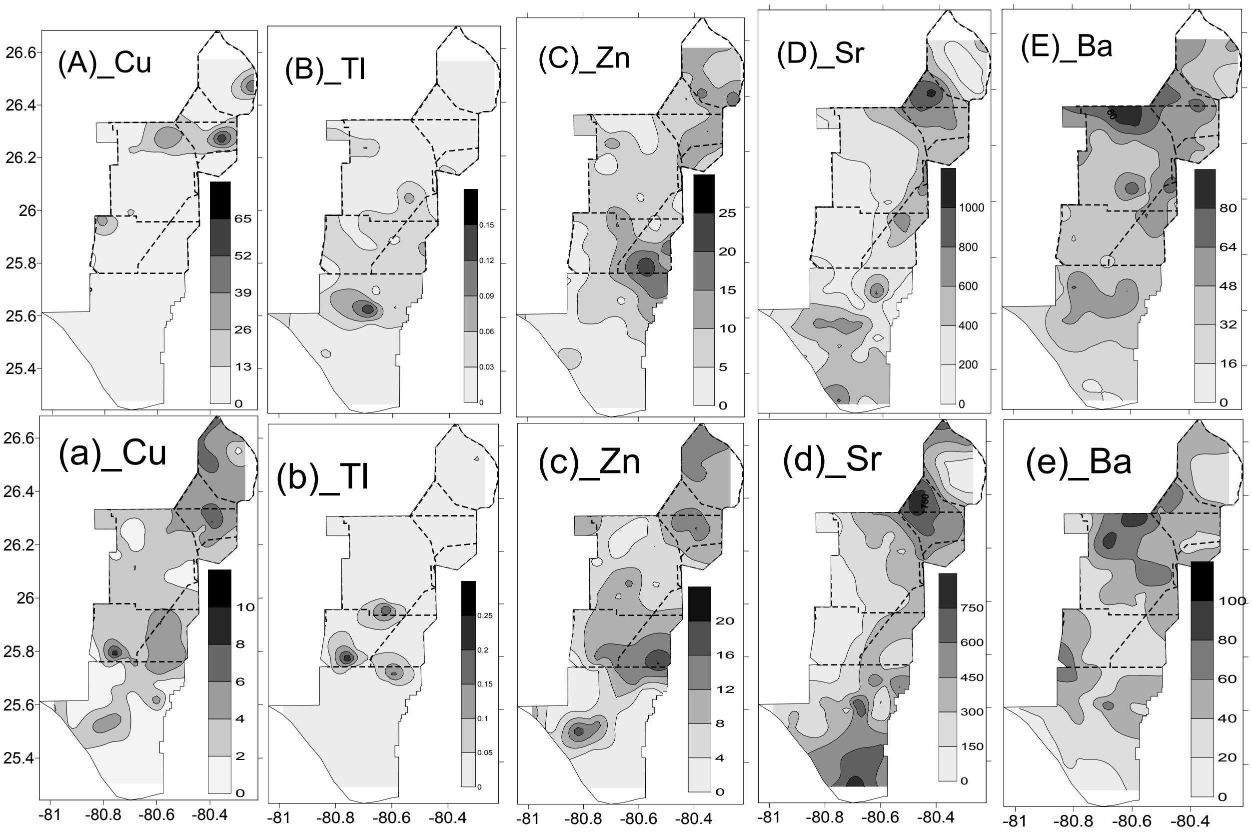

Figure 3-6 Spatial variation of essential metals in soils of the Florida Everglades (A) Cu, (B) Tl, (C) Zn, (D) Sr, and (E) Ba during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

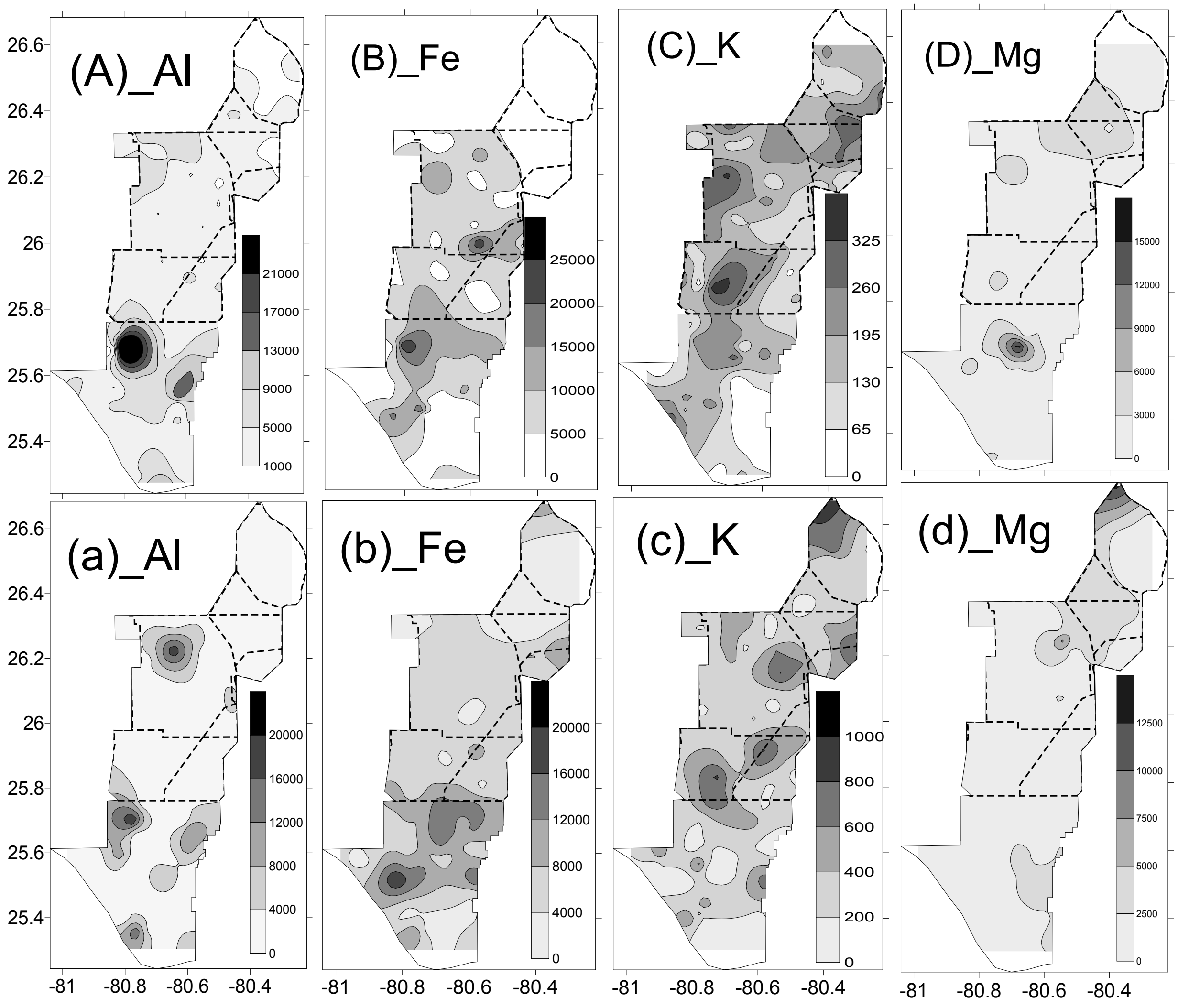

Figure 3-7 Spatial variation of essential metals in soils of Florida Everglades (A) Al, (B) Fe, (C) K and (D) Mg during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

Spatial distributions of metals in soils from both seasons are very complex. For example, Sr decreased in concentration from east to west, while Pb and Ba decreased in concentration from north to south (Fig 3-4). In the dry season, hot spots, defined as areas where significantly higher concentrations of metals are observed, were mainly observed in several distinctive areas of LNWR, WCA-2, WCA-3, and ENP (Fig 3-4 through Fig 3-7). Maximum concentrations were observed in the western area of ENP for Li, Be, V, Mn, Co, Tl, Al, Fe, Cd, Cr, and Ni; WCA-2 for Cu, Sr, Pb, and Ba; eastern area of ENP for Li, Be, V, Mn, and Zn; northern area of ENP for Mg. The highest concentration of As was found in the northern area of WCA-3 near the Tamiami Trail. There is no distinctive pattern presented for K. In terms of minimum concentrations, all metals except for Cu, Sr, Ba, and K had cold spots located in Loxahatchee National Wildlife Refuge. The least concentrated samples containing Cu and Ba were extracted from south of ENP, while least concentrated Sr samples came from western area of WCA-3.

The distribution patterns in the wet season were similar to those in the dry season. Some essential metals (Li, V, Tl, As, Pb, Al, and Fe) were observed to have hot spots and cold spots in the same locations where the maximum and minimum concentrations occurred in the dry season (Fig 3-4 through Fig 3-7). Hot spots were seen in the western area for Li, V, Cu, Tl, Ba, Al, and Fe, WCA-2 for Cu, Pb, Sr, and Ba, northeastern area of ENP for Be, Li and V, and Zn; LNWR for Cd, Cr, Pb, Mg and Co. The distribution pattern was ambiguous for K and Mn. Minimum concentrations were detected in LNWR for all metals except for Co, Cu, Zn, Sr, Ba, and Magnesium. Cobalt, Cu, Zn, Ba and Mg had the lowest concentrations in the southern part of ENP, whereas the lowest concentrated samples in Sr and Ba were spotted in the western area of Water Conservation Area-3.

3.2.2 Spatial distribution of metals in the Florida Everglades floc

Distributions of metals in floc were group in the same way as did the soil. Dry season and wet season had drastically different spatial patterns. In dry season, concentrations of Pb, Sr and Mg attenuated from north to south (Fig 3-8, 3-9 and 3-10). Other metals had more complex spatial distribution patterns. Several regions covered with highly concentrated metals in floc samples. The distribution of metals had hot spots in western area of WCA-3 for Li, Be, V, Cr, As, Mn, Co, Cu, Tl and Al and WCA-2 for Sr, Ba, Ni and Magnesium (Fig 3-7 through Fig 3-10). Zn and Ba had the lowest concentrations in the mid region of Water Conservation Area-3.

In wet season, concentrations of Mn, Sr, K and Mg decreased from north towards south (Fig 3-9, 3-10 and 3-11). Chromium, As, and Pb were similarly distributed as in the dry season. Several metals，including Li, Be, Mn, Sr, and Mg，had the highest concentration discovered in the eastern area of WCA-3, whereas western area of WCA-3 contained maximum concentrations of V, Co, Cu, Tl, Zn, Fe, and K (Fig 3-9 through Fig 3-11). On the other end of spectrum, the minimum concentrations of Li and Be were located in the western zone of Water Conservation Area-3. The south of ENP contained least concentrated of some metals including Mn, Cu, Zn, Sr, Mg and Barium. Western area of the ENP and eastern area of WCA-3 contained minimum concentrations of V, Cu, Tl, Al, Fe and Cobalt.

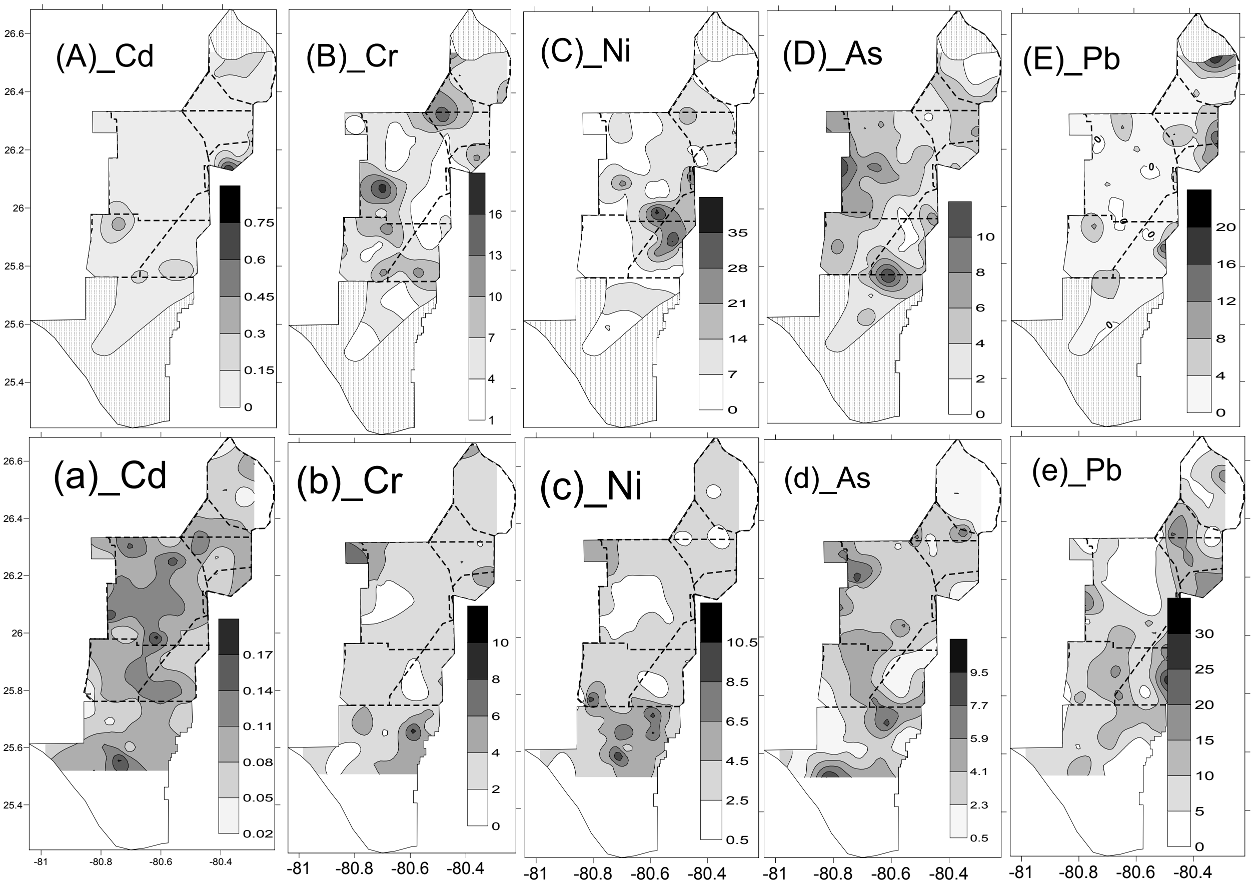

Figure 3-8 Spatial variation of toxic metals in floc of the Everglades (A) Cd, (B) Cr, (C) Ni, (D) As, and (E) Pb during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

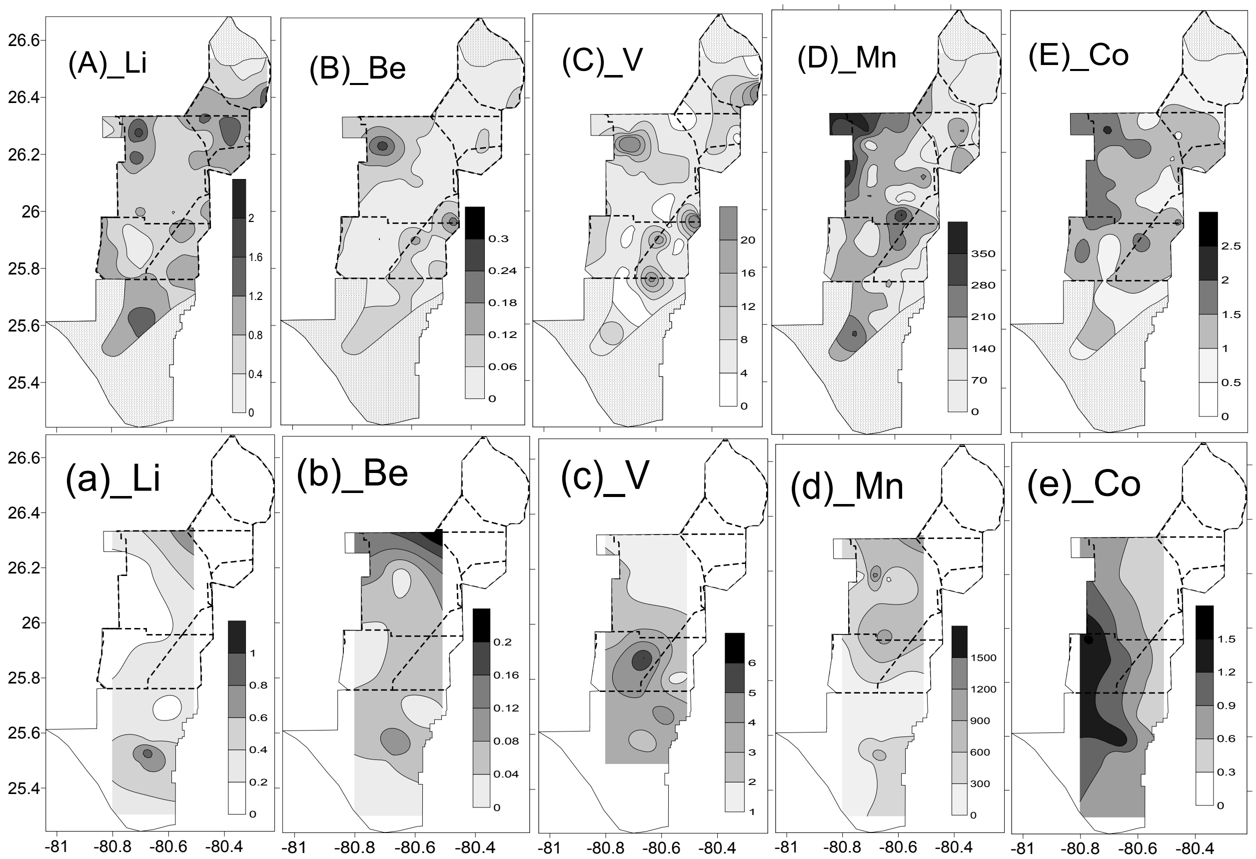

Figure 3-9 Spatial variation of essential metals in floc of Florida Everglades (A) Li, (B) Be, (C) V, (D) Mn, and (E) Co during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

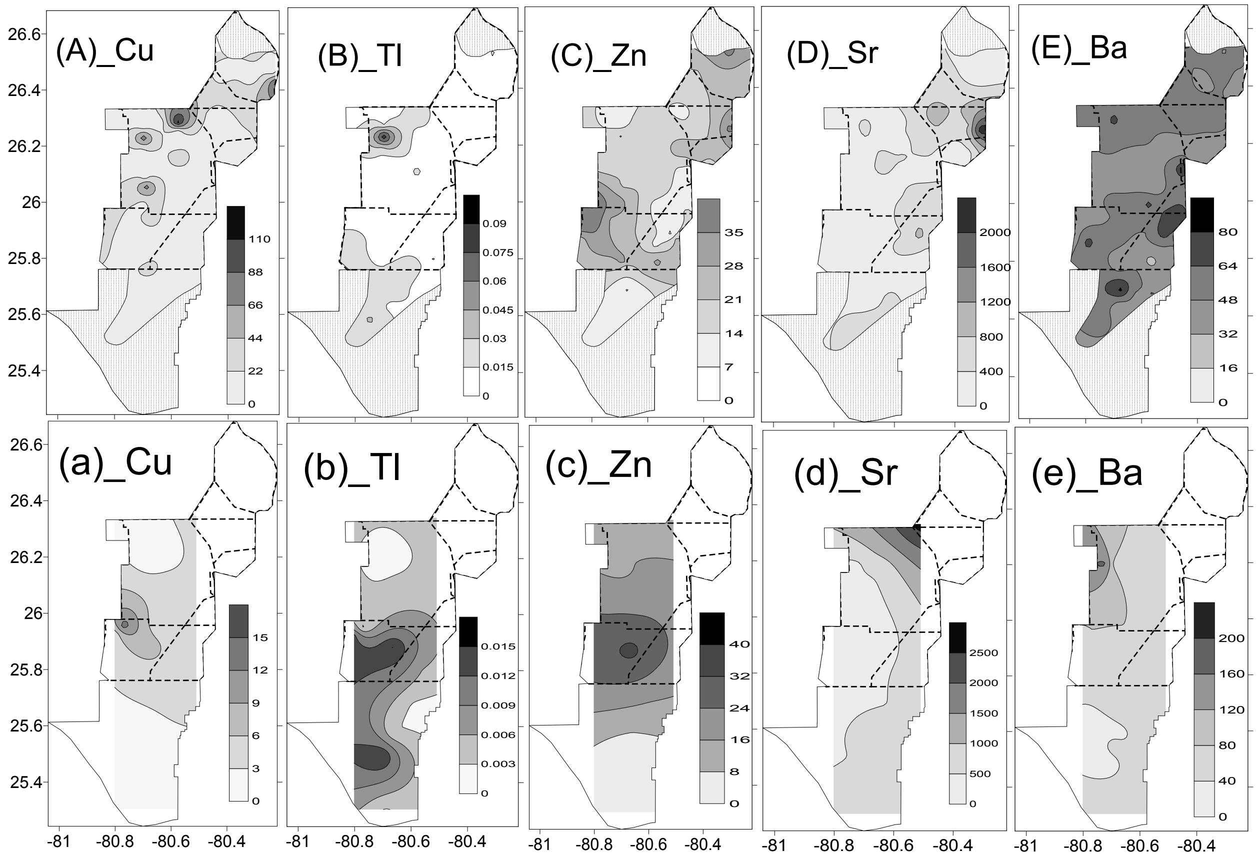

Figure 3-10 Spatial variation of essential metals in floc of Florida Everglades (A) Cu, (B) Th, (C) Zn, (D) Sr, and (E) Ba during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

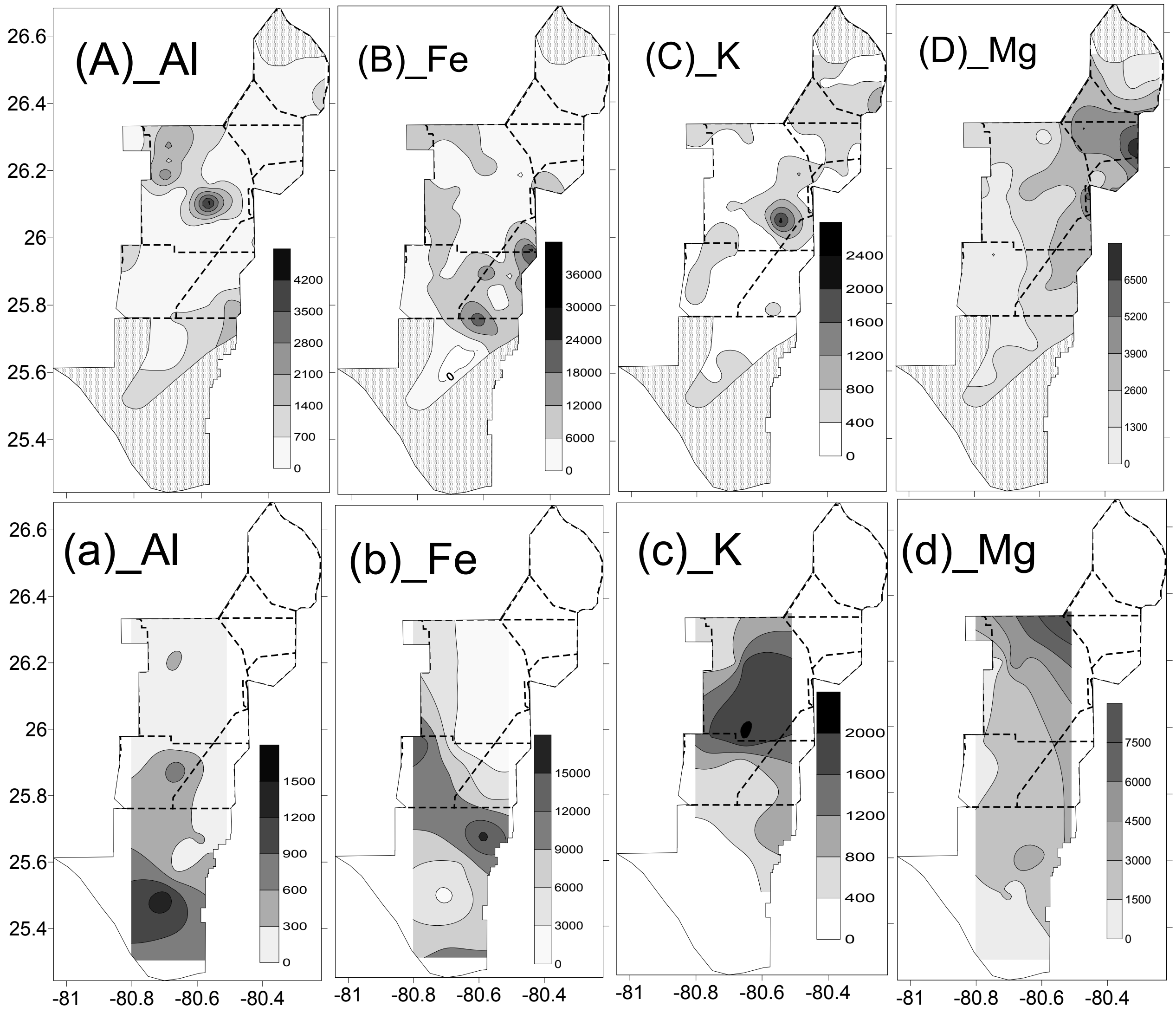

Figure 3-11 Spatial variation of essential metals in floc of Florida Everglades (A) Al, (B) Fe, (C) K, and (D) Mg during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

3.2.3 Spatial distribution of metals in periphyton

Spatial distribution patterns were plotted for benthic periphyton (Fig 3-12 through Fig 3-14), epiphytic periphyton (Fig 3-15 through 3-17) and floating periphyton (Fig 3-18through 3-20). Toxic and essential metals were categorized in the same way as soil and floc. Hot and cold spots were shown on each figure.

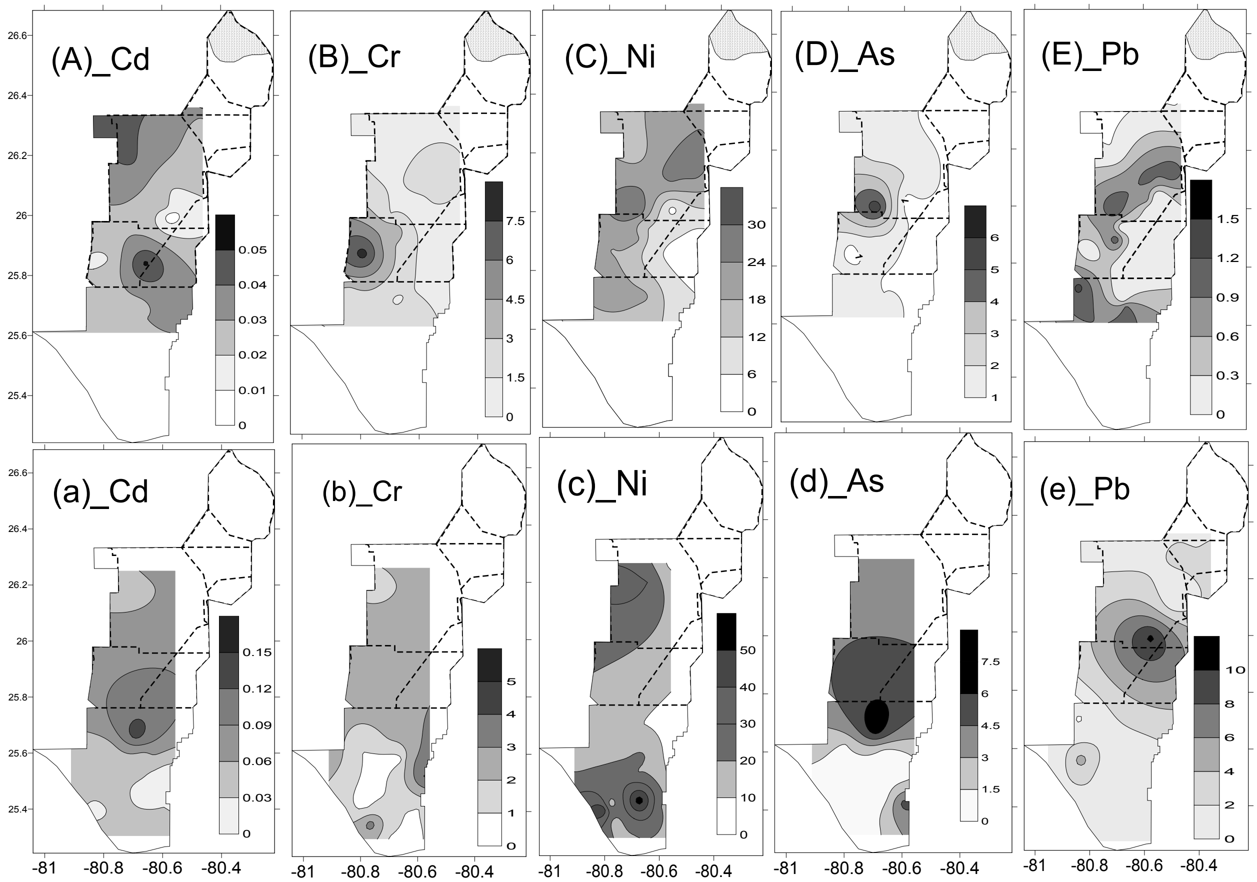

Figure 3-12 Spatial variation of toxic metals in Benthic Periphyton of Florida Everglades (A) Cd, (B) Cr, (C) Ni, (D) As, and (E) Pb during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

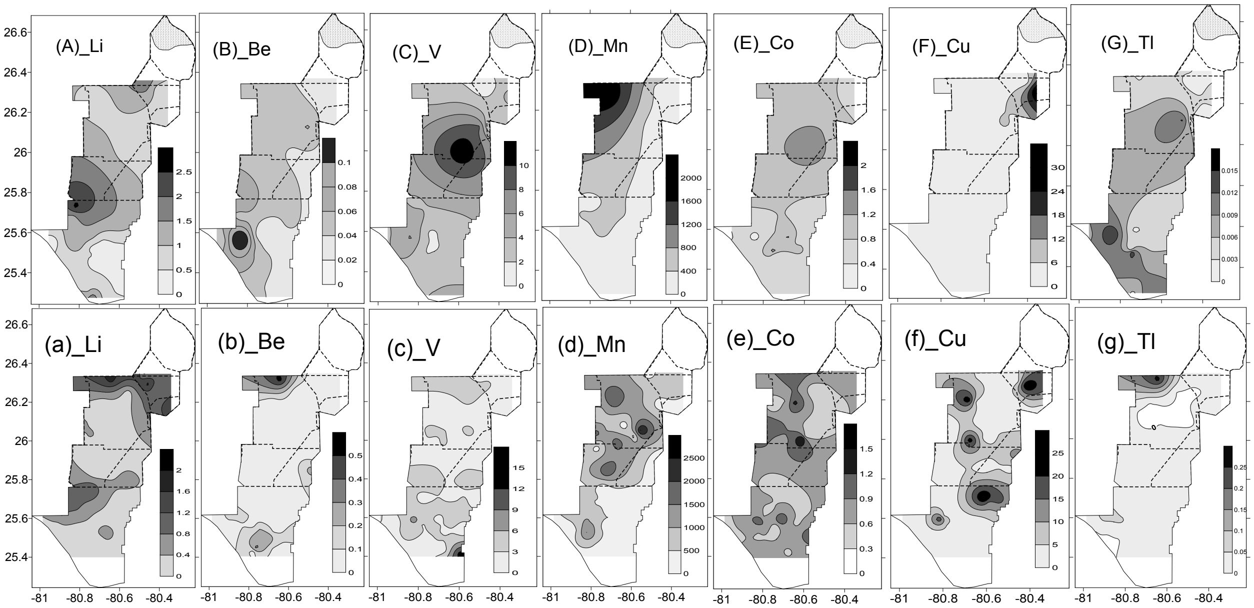

Figure 3-13 Spatial variation of essential metals in benthic periphyton of Florida Everglades (A) Li, (B) Be, (C) V, (D) Mn, (E) Co, (F) Cu (G) Tl during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

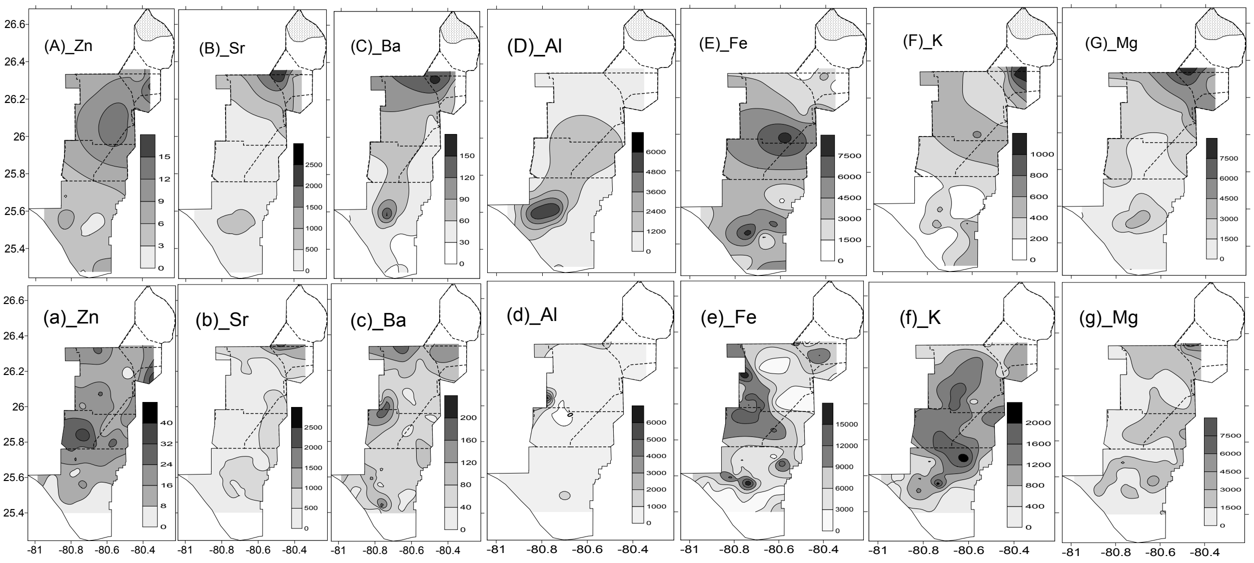

Figure 3-14 Spatial variation of essential metals in benthic periphyton of Florida Everglades (A) Zn, (B) Sr, (C) Ba, (D) Al, (E) Fe, (F) K, (G) Mg during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

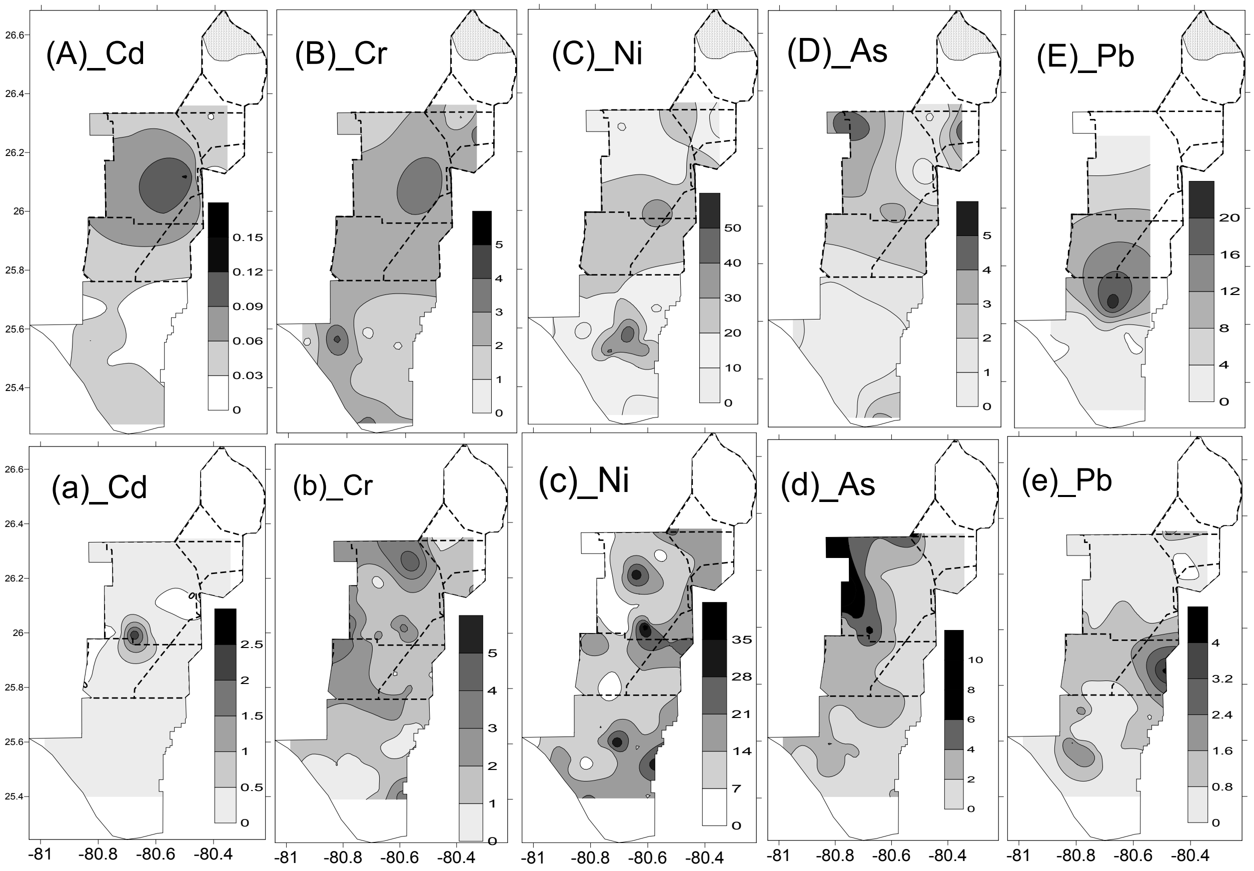

Figure 3-15 Spatial variation of toxic metals in Epiphytic periphyton of Florida Everglades (A) Cd, (B) Cr, (C) Ni, (D) As, and (E) Pb during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

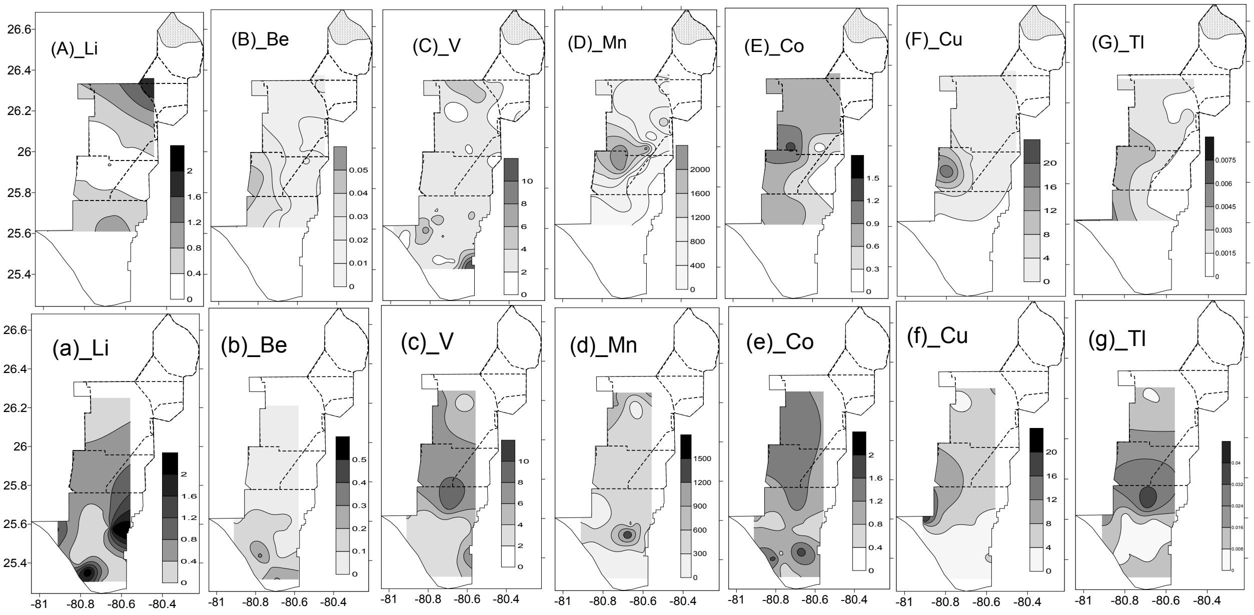

Figure 3-16 Spatial variation of essential metals in epiphytic periphyton of Florida Everglades (A) Li, (B) Be, (C) V, (D) Mn, (E) Co, (F) Cu (G) Tl during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

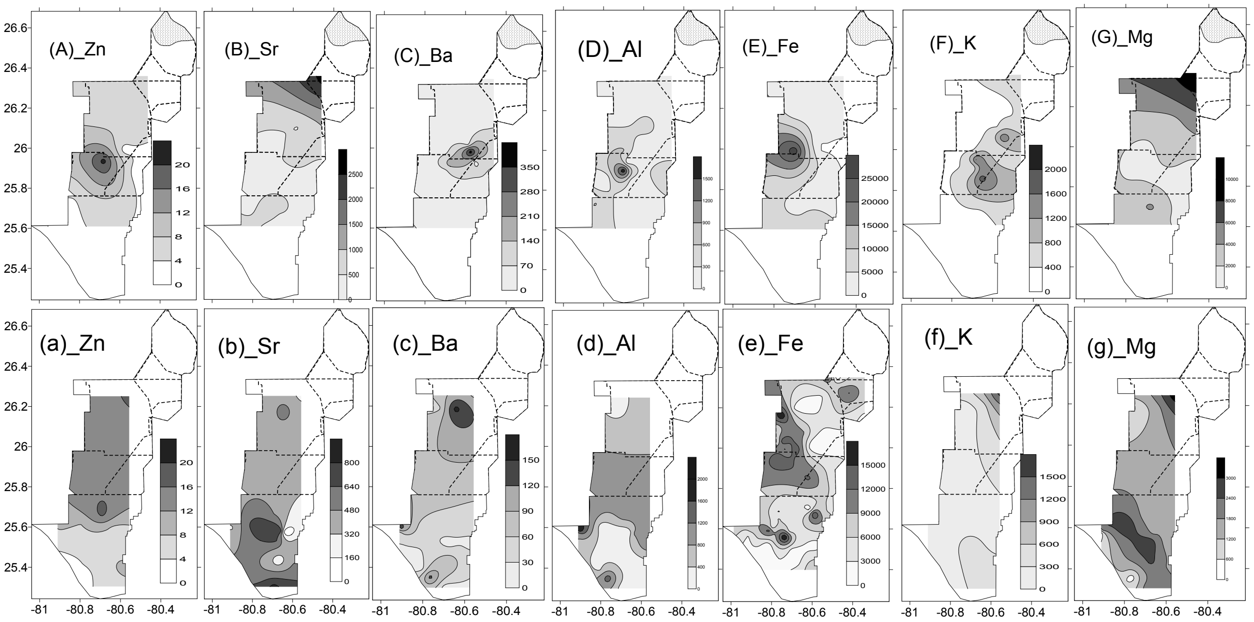

Figure 3-17 Spatial variation of essential metals in epiphytic periphyton of Florida Everglades (A) Zn, (B) Sr, (C) Ba, (D) Al, (E) Fe, (F) K, (G) Mg during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

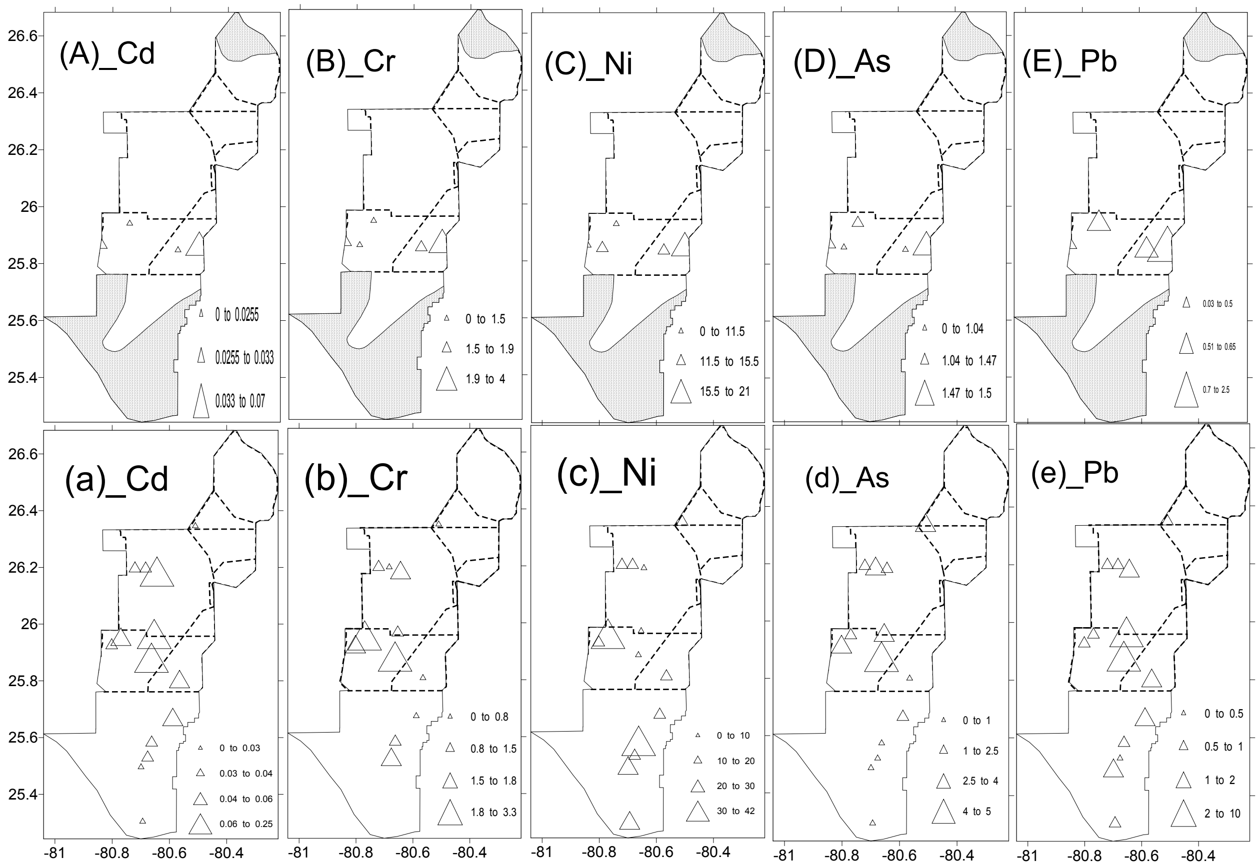

Figure 3-18 Spatial variation of toxic metals in floating periphyton of Florida Everglades (A) Cd, (B) Cr, (C) Ni, (D) As, and (E) Pb during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

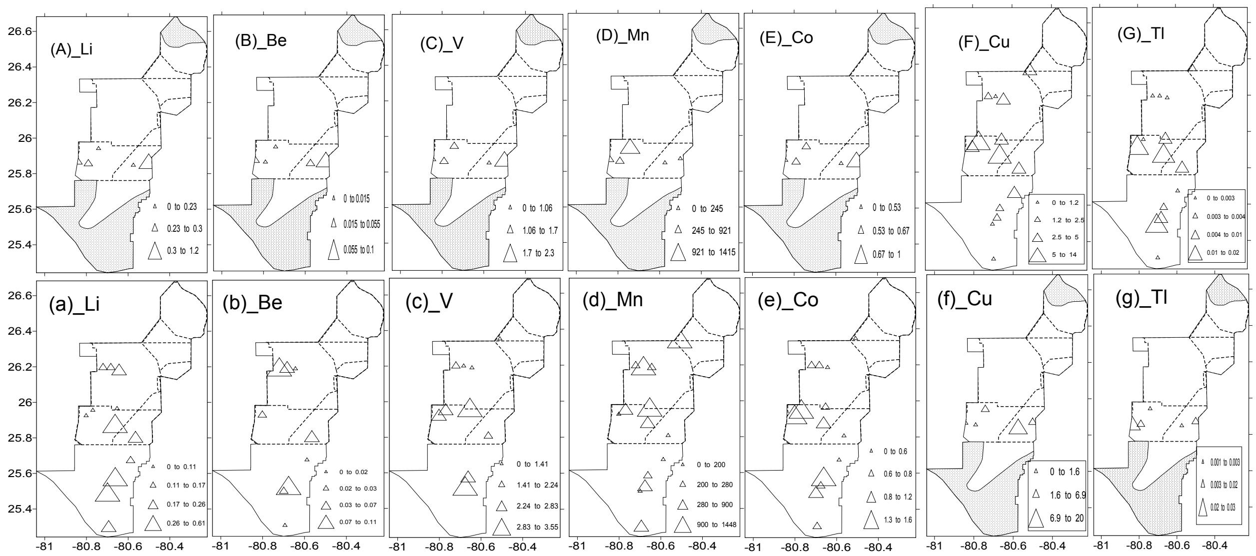

Figure 3-19 Spatial variation of essential metals in floating periphyton of Florida Everglades (A) Li, (B) Be, (C) V, (D) Mn, (E) Co, (F) Cu (G) Tl during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

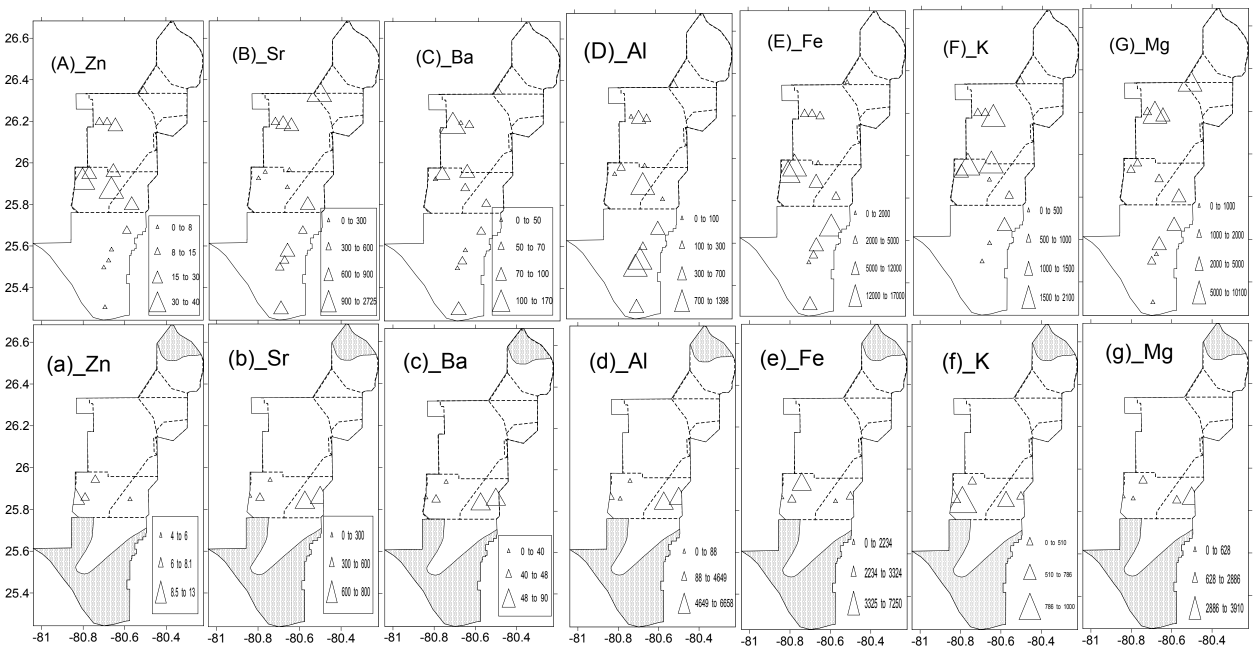

Figure 3-20 Spatial variation of essential metals in floating periphyton of Florida Everglades (A) Zn, (B) Sr, (C) Ba, (D) Al, (E) Fe, (F) K, (G) Mg during the dry season (Top, labeled with capital letters) and wet season (bottom, labeled with lowercase letters).

In the dry season, Ni, Sr and Mg exhibited clear spatial distribution pattern in which the concentration decreased from north to south for benthic periphyton (Fig 3-11 and 3-13). For epiphytic periphyton, concentrations of Sr and Mg decreased also from north to south. The distribution patterns were less clear for floating periphyton. The maximum concentrations were observed in several distinct locations in the dry season for all periphyton samples involved (Fig 3-12 though 3-14). In epiphytic periphyton, two locations, eastern and western area of WCA-3, contained hot spots for Li, V, Sr, Mg, Cd, Cr and Ni as well as Be, Mn, Co, Cu, Tl, Zn, Al, Fe and Pb, respectively (Fig 3-15 through 3-17). In benthic periphyton, the eastern area (Li, Cu, Sr, Ba, K, Mg, Pb, V, Co, Tl, Zn and Fe) of WCA-3 contained most of hot spots (Fig 3-12 through 3-14). Other hot spots were location in areas including western ENP (Be, Tl, Al, Fe), western WCA-3 (Mn, Cd, As) (Fig 3-13 and 3-14). In floating periphyton, west (Li, V, Mn, Co, Cu, Tl, Zn, AL, Fe and K) and east (Sr and Mg) of WCA-3 were home to most hot spots (Fig 3-19 and 3-20). Two metals, Be and Ba, were mostly concentrated in the western area of WCA-3 (Fig 3-19 and 3-20).

In the wet season, no clear trends of spatial distribution patterns of metals were observed for periphyton. The distribution patterns for the wet season varied significantly when compared with the dry season (Fig 3-12 through 3-20). For epiphytic periphyton, maximum concentrations of metals (Li, Be, Mn, Co, Al, Fe, Mg) were observed in the western corner of ENP (Fig 3-16 and 3-17). Other areas, such as mid ENP (V, Mn, Tl, Zn, Sr), west of ENP (Cu) as well as east of WCA-3 (Ba and K), were also home to hot spots (Fig 3-16 and 3-17). Toxic metals (Cr, Ni and As) had maximum concentrations near EAA (Fig 3-17). For benthic periphyton, the maximum concentrations were spotted in several places: west (Li, Be, Mn, Co, Tl, Ba and Cd) and east (Cu, Sr, Mg, Ni and Pb) of WCA-3 (Fig 3-13 and 3-14). For floating periphyton, hot spots were located in either east or west of WCA-3 under limited data (Fig 3-18 through 3-20).

4. Discussion

4.1 Factors influencing the spatial distribution of metals in the Florida Everglades

4.1.1 Effects of possible sources on metal distribution in the Everglades

Metals in the Everglades could originate from natural sources as well as anthropogenic sources. The Everglades is a 500,000 ha freshwater wetland mainly composed of sawgrass and open water slough (Craft and Richardson 1997). The soil matrix is composed of the most abundant metals in the earth's crust such as Al, Fe, Mg, K and Ca (Schulze 1989). Peat soils, primarily found in the central Everglades, and marl soils, found in the shallow peripheral marshes, are two major soil types in the Everglades (Scheidt and Kalla 2007). Peat soils are formed as results of plant matter decay while marl soils are more calcitic in composition in association with calcitic algae mat (periphyton) (MePherson and Halley 1996), which contributes to the natural concentrations of Cr, Mn, Co, Ni, Cu, Zn, Cd and Pb (Nagajyoti et al. 2010). Under the soils, a large volume of carbonate sediments composed exclusively of limestone dolomite and anhydrite serve as sources to minerals such as Fe, Al and Magnesium. Two major sloughs in the Everglades, Taylor and Shark Sloughs, carry surface water sheet flow from WCAs and EAA to Everglades National Park. They might serve as sinks for elements from erosion of soils and weathering of the underlain sediment rocks (Gough et al. 2000).

Anthropogenic sources could include farming activities in the EAA area, atmospheric deposition, road traffic, tourism (airboat), and the regional airport. The distribution of metals could partially be explained by the impact of these potential sources. Everglades Agricultural Area is about 7,000 acres (account for 27% of total historic Everglades) with major productions in sugarcanes (Light 2010). A large amount of fertilizer was used to enhance the growth of sugarcanes, snap beans, cabbage, and other crops in EAA area (Förstner and Wittmann 1981; MePherson and Halley 1996). Nitrogen and phosphate containing fertilizers are widely used in the agricultural production at the rate of 7 tons/mi^2 for nitrogen and 3 tons/mi^2 for phosphate. Average concentrations of toxic metals (Pb, As, Cd, Cr and Ni) presented in the phosphate (P) fertilizers in the U.S. are shown in Table 4.1. Since currently there are no data on the background concentrations of toxic metals in the Everglades area, toxic metals in the P fertilizers were compared with sediment quality guidelines (SQGs) designed for freshwater sediment assessment. All toxic metals from fertilizers exceeded limits of "no effect" category, and some metals surpassed limits set for "probable effect" category. Several major canals including Miami canal, North new river canal and Hillsboro canal, along with large capacity pump stations, were constructed in an effort to prevent flooding in EAA by diverting water into WCAs and LNWR (Figure 4-3). Toxic metals from fertilizers might be carried by the canals and enter WCAs and LNWR. Because of the absence of background concentrations of toxic metals in the Everglades, The concentrations of As, Pb, Cu and Zn from the current study were compared to Sediment Quality Guideline values. All metals compared exceeded no-effect category of SQGs. The high concentrations found in WCAs and LNWR varied for Cu (52-65 mg/Kg), As (7.5-10 mg/Kg) ,Pb (125-250 mg/Kg) and Zn (20-25 mg/Kg) for the dry season (Fig 4-1). The detected concentrations were well above FL SQGs in the no effect category which might be attributed to agricultural applications (e.g. fertilizers) in the Everglades Agricultural Area.

Table 4-1 Comparison of toxic metals in P fertilizers and in sediment quality guidelines (SQGs) LEL=Lowest Effect Levels; TEL= threshold effect levels; SEL=severe effect level; PEL=probable effect levels

SQGs	As (mg/Kg)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)
No effects					
LEL(Florida)	6	0.6	26	16	31
TEL(Florida)	5.9	0.6	37	18	35
Probable effects					
SEL(Florida)	33	10	110	75	250
PEL(Florida)	17	90	197	36	91.3
P fertilizers	12	11	109	37	12

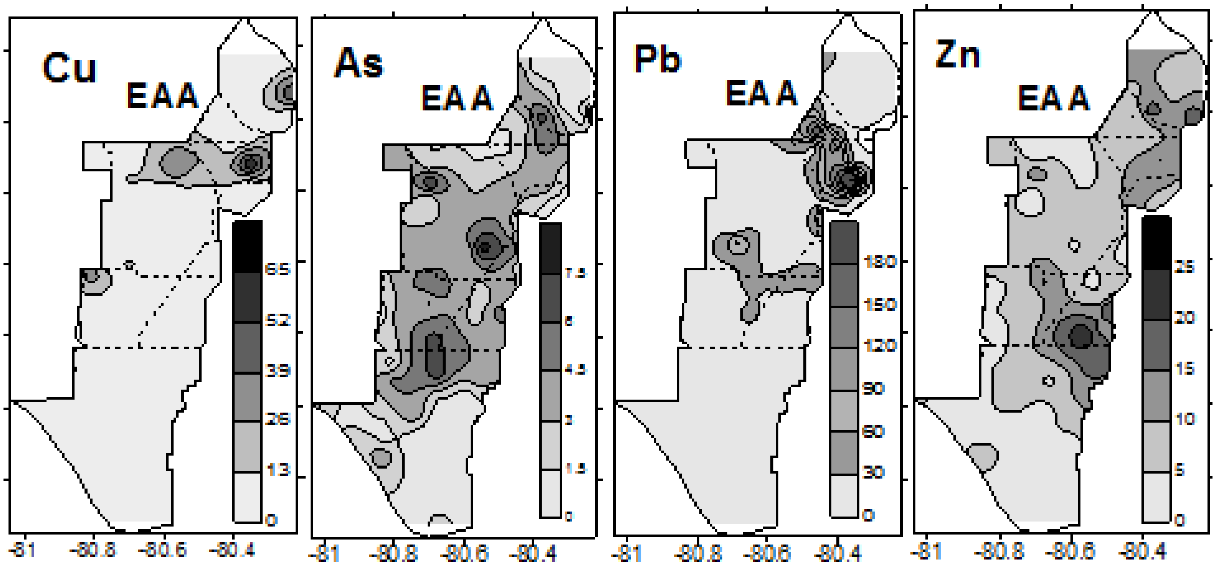

Figure 4-1 Metals with elevated concentrations (mg/Kg) for Cu, As, Pb and Zn in soils from the dry season that are possibly affected by fertilizers applied in EAA

Areas in the immediate vicinity of major roads could be under stress of metals that result from the elevated heavy metal concentrations from roadway emissions generated mainly from vehicle component and equipment (brakes, tires, parts wear and lubricant oil in engine) (Pagotto et al. 2001; Viard et al. 2004; Apeagyei et al. 2011). The deposited metals from roads might be accumulated on the road surface and eventually be transported via re-suspension or carried by runoff to the nearby soil (Turer et al. 2001). Schauer et al. (2006) studied metals in crushed brake pads and housing dust and confirmed Fe, Cu and Ba to be the most abundant elements. The tire analyses from the same study found that Zn concentrations were about 15 times higher than concentrations of Zn in brakes. Other parts of the motor vehicles such as rotor (made from cast iron) or drum against which the brake pad presses can contribute to the elevated concentrations of iron. In addition, Ba was found in a large amount in brake wear emissions. Zinc and Ba components are employed extensively in lubricant oils for diesel and other combustion engines (deMiguel et al. 1997). Exhaustive studies have shown correlations between metal concentrations and road side soils (Turer et al. 2001; Apeagyei et al. 2011; Mejia et al. 2011; Mikalajune and Jakucionyte 2011; Zafra et al. 2011). Lead and Zn originated from vehicular traffic were detected at high concentrations 26, 988 and 6,156 ug/g, which became the major components of metal pollutions to Sydney estuary catchment soils (Birch et al. 2011). Turer et al. (2001) determined that Pb sampled in the roadside soil could mainly originate from vehicle exhaust when leaded fuel was still used in Cincinnati, Ohio. Concentrations of Zn, Cu, K, Ti, Sr and Ca found in brake pads were found to correlate with elevated concentrations in road dust (Apeagyei et al. 2011). Previous studies indicated that road dusts associated with high traffic road could contain high concentrations of Cr, Fe, Cu, Pb, and Zn, in both urban and rural area (Pagotto et al. 2001; Viard et al. 2004; Apeagyei et al. 2011). Similar results of elevated metal concentrations were found in my study: several of toxic metals including Cr, As and Zn (Figure 4-2) showed several “hot spots” in soil samples near two major roadways, US I-75 and US Route 41. US Route 41 is a major road that extends from Miami in the east of South Florida to Naples in the west of South Florida, The highest Cr level varied between 48 to 60 mg/kg was found in the vicinity of I-75, a major interstate highway traveled from south of Florida to Michigan. Elevated concentration of Zn (20 mg/Kg) was also found near both roads, implying that road dusts might play an important role in the distributions of both Cr and Zn in the Everglades.

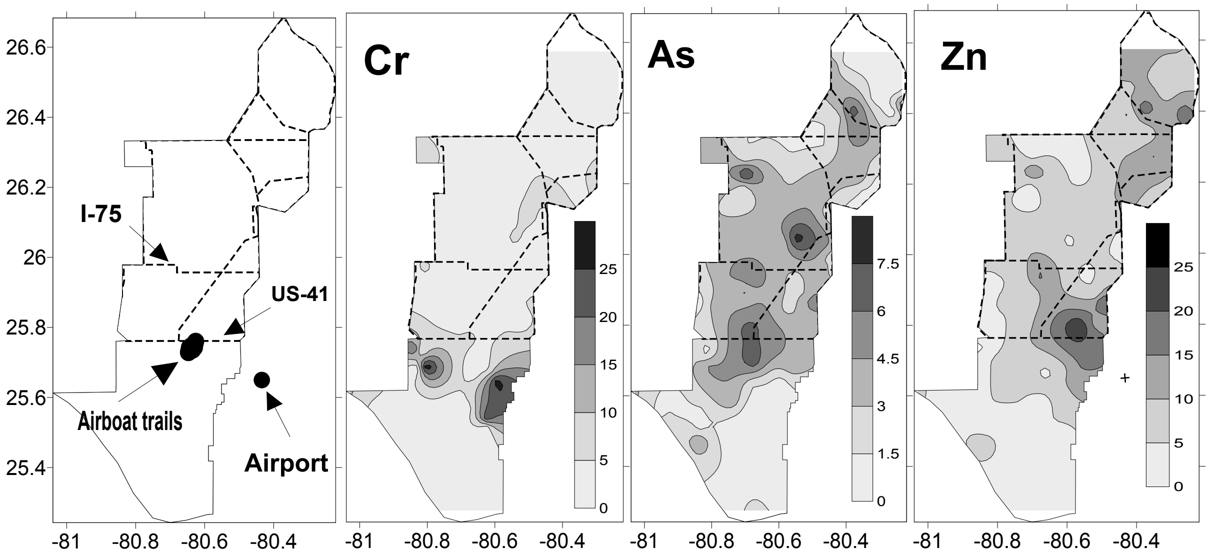

Figure 4-2 Distribution of metals (Cr, As and Zn) in soil (mg/kg) from the dry season possibly influenced by road traffic, airboat trails and airport

Airboats have been used extensively in the marshes of the Everglades. Numbers of airboats have been increased since the 80s of last century (Johnston 1984). Several studies have done on adverse impact of airboat activities on the hydrology (Weeks 1989), soils (Yamataki 1994) and vegetation (KcKee 1993). Alongside of U.S. Route 41, multiple businesses offer airboat tours with routes regulated under the state laws (FWC 2012). Routes taken by commercial airboats in the Everglades were indicated in Figure 4-2. Although few studies were conducted on the metal pollutions in the Everglades area in association with airboat activities, use of airboats would probably cause alterations of flow pattern, soil displacement (oxidation), and change in plant composition (Wright 2000; Rehage and Trexler 2006). The oxidation in the soil and change in vegetation communities might negatively impact the cycling of metals in different matrices (soil, floc and periphyton). Boat paint and parts involved in airboat operation and emission from gas burning could also contribute to the elevated levels of As and Zinc (Figure 4-2). Arsenic (>7.5 mg/kg) and Zn (>20 mg/kg) showed elevated concentrations in the immediate surrounding areas of the regulated airboat trails, suggesting potential correlations with airboat activities.

Aircraft emissions containing toxic metals can potentially harm both the environment and animal health (Lee et al. 2010). The main emitted species are generated from combustion of kerosene with ambient air in the engine combustion chamber. Some emitted species may contain metals (Cu and Zn) from fuel system (Lee et al. 2010), and from erosion of metal parts (Demirdjian et al. 2007). Chromium plating has been used in gas turbine engine maintenance operations to repair worn Darts and replace worn or damaged Cr used (Schell and Rechsteiner 2000). High emissions of Cr (VI) were found from aircraft engines (Agrawal et al. 2008). The elevated concentrations of Cr (>25 mg/Kg) and Zn (>25mg/Kg) were detected near Kendall-Tamiami Executive Airport (KTMB) located in the vicinity of northwestern region of Everglades National Park (Fig 4-2). As one of the busiest general aviation airports in Florida (KTMB 2012), the aviation activities from KTMB might contribute to the high concentrations of Cr and Zn in the nearby Everglades area.

The eastern panhandle of the ENP, along with Shark River slough, and Taylor River slough regularly receive water from canal constructed in the 70s as part of Central and South Florida (C&SF) project (Sklar et al. 1999). Shark River slough receives water from canal (L-67A) that was originated in Everglades Agricultural Area. Furthermore, canal S-332 was constructed to deliver water from north (EAA) into Taylor river slough (Figure 4-3). Manganese, K and Sr in soil all had high concentrations in the surrounding areas of EAA in the north and in the south of Everglades National Park (Figs 3.4 through 3.6). The elevated concentrations of Mn, K and Sr in the surrounding areas of EAA could be attributed to the terrestrial input and runoff from EAA, as water move from north of Everglades to the south carrying input influenced by agricultural and rural development area (EAA). The arid regions of North Africa are inordinate source of soil dust. Large amounts of soil containing toxic metals are taken during the dust storm and transported to other continents on the prevailing winds (Perry et al. 1997). Atmospheric deposit of African dust may contribute to the elevated concentrations of Pb, As, Cu and Fe in the Florida Bay area during the low tide flux (Thornberry 2008).

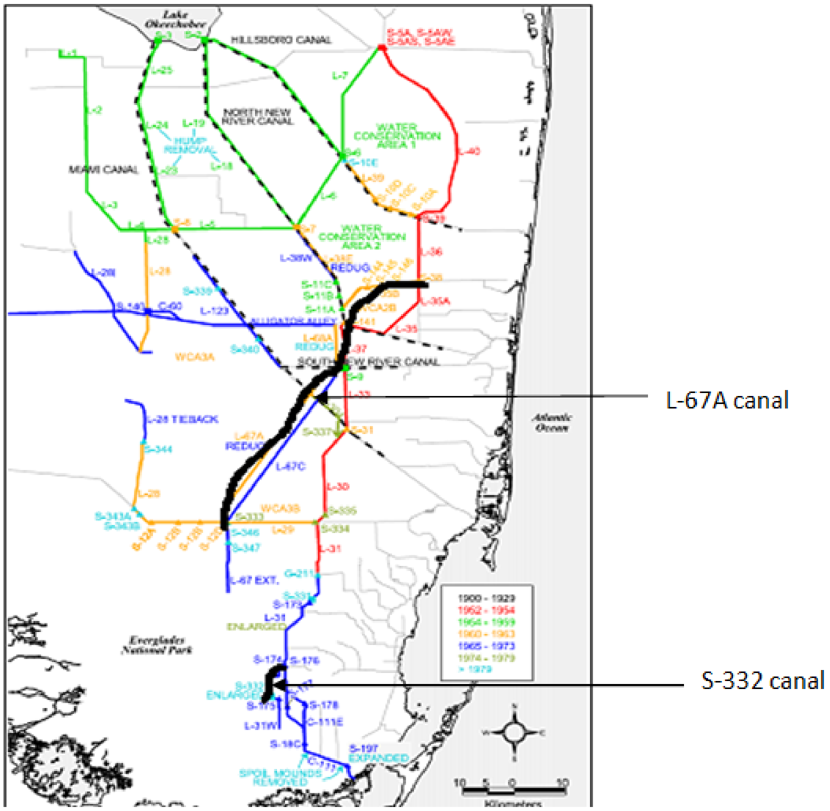

Figure 4-3 Diagram showing canals and levees in the Everglades (Light and Dineer 1994).

4.1.2 Effects of environmental parameters and metal-metal interactions on the distribution of metals in the Florida Everglades

In addition to the above-mentioned sources, some important environmental factors, such as soil natural organic matter (NOM), soil pH, oxidation-reduction potential (redox) and dissolved organic matter (DOM) could potentially impact on the distributions of metals. NOM is mainly composed of carbon, oxygen and small amount of N and P (EPA 2007). It is formed by all detrital organic matter in a natural system, making it an important component of the majority of freshwater environment (Warren and Haack 2001). Aquatic NOM could be categorized based on size: DOM and particular organic matter (POM). DOM is defined as the organic matter that passes through a 0.45 μm pore filter while POM does not. Organic matter is known to have strong binding ability to retain inorganic soil contaminants (metals) (Hesterberg 1998; Perkins et al. 2000). In the Everglades, the highest organic matter content was found in LNWR with median of 94%, followed by WCA-3 and WCA-2 with 75% organic matter. The peat soils in the north are generally rich in organic while the marl soils in the south are minerals (Scheidt and Kalla 2007). Humic substances are major parts of NOM in soil and water. (Frimmel 1998). Peat soils are also highly enriched in humic substances (Hajje and Jaffe 2006). Humic substances bind with metals either through forming soluble organic complexes to retain metals in soil or forming insoluble complexes resulting in reduction in bioavailability of metals (Logan et al. 1997). Mineral surface reaction with metals occurs mainly through sorption process (Brown et al. 1999). Variables controlling rate of sorption depend on several factors including pH, mineral surface charge, and type of sorption complex formed, among others (Brown et al. 1999). As pH increases, metals (such as Pb) existing as cations over a wide pH range have higher affinities for a mineral surface, while metals (such as As) behaving as anions have lower affinities. In contrast, NOM is always negatively charged under normal environmental conditions and show high affinity for cationic metal species (Warren and Haack 2001).

Dissolved organic matter has a strong influence on the fate of dissolved metal in metal-organic complexes (Sauve et al. 2000). DOM is known to strongly bind toxic metals such as Cu, Pb, Cd, Zn and Ni (Weng et al. 2002). In the aquatic environment, humic substance makes up majority of DOM (Weng et al. 2002). Humic-metal complexes can be categorized into two groups: outer sphere complexes, which are favored by alkali and alkaline (e.g., Be, Mg, Ca, Sr, Ba) earth metals that metal is held more loosely than inner sphere complexes, which is preferred by transition elements (e.g., Cu, Cd, Zn and Pb) based on formation of a covalent bond between ligands and metal ions (Logan et al. 1997). Metal cations (e.g., Mg^{2+}, Al^{3+}) that are compact and not very polarizable prefer reactions with ligands that are also less polarizable (e.g., O-containing ligands). These are known as hard acids and bases. Large and more polarizable metals (e.g., Cd^{2+}, Cu^{2+}) are likely to react with more polarizble ligands (e.g., S-, P- and N-containing ligands. Table 4-2 illustrated some examples of both hard and soft acids as well as bases. Significant correlation were observed between DOC and metals in soils (Ni, Cu, As, K and Mg) (Table 4.3) ($p<0.01$). The close correlation between DOM and Pb confirmed the statement that organic matter content plays an essential role in the Pb sorption by soil (Lee et al. 1998). Other study showed that Pb was preferably associated with soil organic fraction, as verified by the current study (Dragovic et al. 2008). Ash free weight represents the content of organic matter in soils. The significant correlations found between ash free weight (OM in soil) and transitional metals (Cu, As, Pb and Zn) were probably resulted from formation of inner sphere complexes of those two groups (Fig. 4-4). Most metals were significantly correlated with ash free weight of the soil (except for V, Cr, Fe, K and Mg), indicating the important role that NOM play in regulating metal distribution.

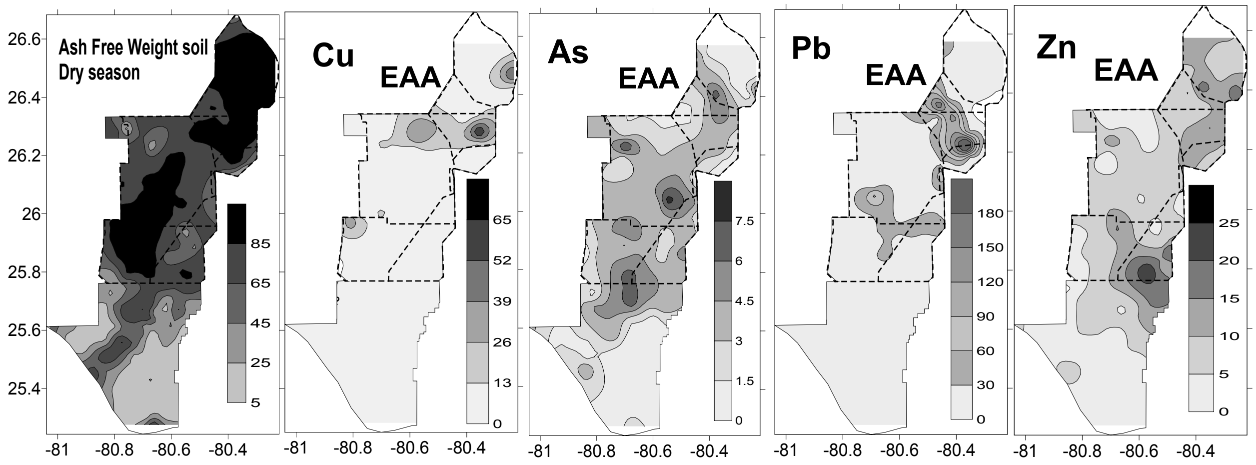

Figure 4-4 Distributions of Cu, As, Pb and Zn (mg/Kg) as well as ash free weight (%) from the dry season.

Table 4-2 Hard and soft acids (metal ions) and bases (ligands) (EPA 2007).

Hard acids	Al^{2+}, Ba^{2+}, Be^{2+}, Co^{3+}, Cr^{3+}, Fe^{3+}, Mn^{2+}, Sr^{2+}
Borderline acids (between hard and soft)	Cu^{2+}, Fe^{2+}, Ni^{2+}, Pb^{2+}, Zn^{2+}
Soft acids	Cd^{2+}, Cu^{+}, Tl^{3+}, Tl^{+}
Hard bases	F^{-}, H_2O, OH^{-}, $SO4^{2-}$, $HCO3^{-}$
Borderline bases (between hard and soft)	Cl^{-}, Br^{-}, NO_2^{-}, SO_3^{2-}
Soft bases	I^{-}, HS^{-}, S^{2-}, CN^{-}, SCN^{-}, Se^{2-}, $S_2O_3^{2-}$, 2-, -SH, $-SCH_3$, $-NH_2$, R-, C_2H_4, C_6H_6, RNC, CO, R_3P, $(RO)_3P$, R_3As, R_2S, RSH, RS-

Soil pH is probably the most important property regulating solubility of metals in soils (Hesterberg 1998). The soil pH influences virtually the solubility of all metals and their biogeochemical processes in soil, including complexation and acid-base reactions of metal species, dissolution and precipitation of metal solid phases as well as metal sorption. Furthermore, pH controls binding and speciation of metals by affecting distribution of dissolved ligands (e.g., phosphate, sulfate, carbonate, humic substances) as well as surface charge of binding sites on DOM and solid phases (EPA 2007). In the sediment, sorption to the solid phase controls the concentration of metals in the dissolved phase (common phase of metals exist in oxic sediment pore water). Metal cations (e.g. Mn, Al and Fe) usually increase in solubility (less adsorption) with decreasing in pH as the surface binding sites are protonated. Conversely, metal cations decrease in solubility (more adsorption) with increasing in pH (Adriano 1986). The sorption and dissolution patterns are opposite for anionic species such as oxyanions of As, Mo, Se, and Cr, since at high pH oxyanions competes with OH^{-} ions for sorption sites. In my study, the pH values in soil were around 5-6 in LNWR, 7-7.5 in WCA-3, 6.5-7 in WCA-2, and 7-7.5 in ENP (Scheidt and Kalla 2007). Cations, including Ni, Mn, Li and Be in soil, had elevated concentrations from dry season in ENP where the pH is the highest (Fig 4-5). The explanation was mentioned earlier. The correlation study showed significant correlations between pH and most of metals analyzed (Li, Be, Mn, Ni, Cu, As, Cd, Zn, Pb, Sr, Al and K) (p<0.01) in soil (Table 4.3).

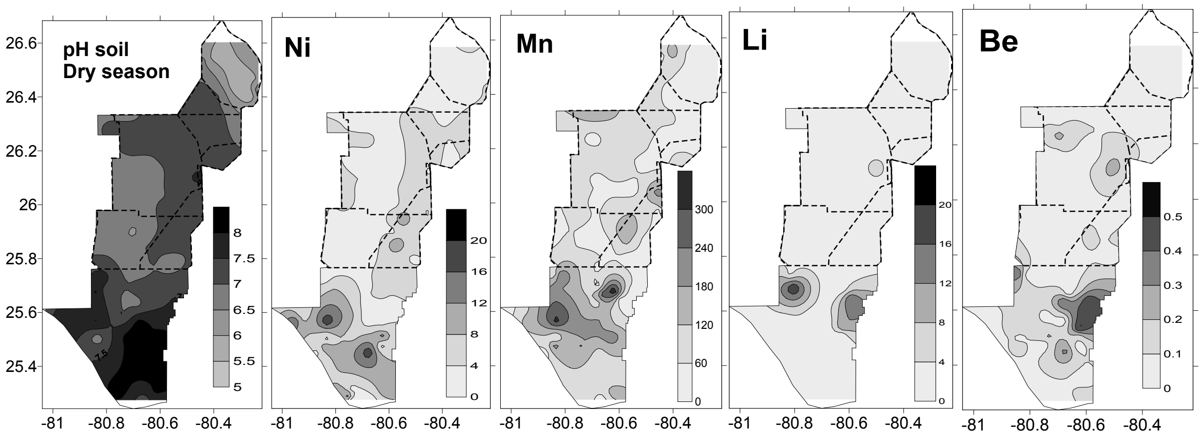

Figure 4-5 Distributions of Ni, Mn, Li and Be (mg/Kg) as well pH from the dry season.

Redox potential affects metal dynamics through metals redox species with more than one possible oxidation state (Warren and Haack 2001). Redox status can impact partitioning of elements between solution and solid phase, resulting in the changes of solubilities of associated toxic metals (Hesterberg 1998). For example, oxyhydroxides solid Fe (III) phase as a result of Fe^{3+} hydroxylation and precipitation could provide a highly reactive surface for trace metals in aqueous environment. Reduction of Fe and Mn, under reducing conditions, could release associated metals into the water or pore water. Ultimately, those dissolved metals probably would be carried upward by diffusion or downward by precipitation (EPA 2007). In the aquatic environment, oxidation/reduction potential (Eh) measures tendency of the solution to gain/lose electrons. High Eh values are maintained in oxidizing or aerobic conditions while low Eh values are maintained in reducing and anaerobic conditions (EPA 2007). Correlations between Eh and most of metals analyzed were not significant except for Sr ($p<0.01$). The weak correlations between metal concentrations in the Everglades and Eh are probably results of stronger influence from other environmental factors (NOM and pH).

Table 4-3 Correlations between metals in matrices (soil and floc) and environmental parameters (DOM, pH, ash free weight (AFW) and Eh)

Metals	pH (r value)	pH	Eh (r value)	Eh	Ash free weight(r)	Ash free weight
Li	0.216	++			-0.250	++
Be	0.301	++			-0.263	++
V						
Cr						
Mn	0.45	++			-0.548	++
Co					0.186	+
Ni	0.461	++			-0.476	++
Cu	-0.184	+			0.303	++
As	-0.197	++			0.489	++
Cd	-0.267	++			0.360	++
Tl					0.156	+
Zn	-0.419	++			0.556	++
Pb	-0.199	++			0.289	++
Sr	0.458	++	-0.256	++	-0.377	++
Ba			-0.169	+	0.187	+
Al	0.216	++			-0.216	++
Fe						
K	-0.302	++				
Mg			-0.159	+		

++ indicates $p<0.01$ level

+ indicates $p<0.05$ level

The key parameters affecting metal bioavailability in soils, besides organic matter, soil pH, Eh, are Fe and Mn oxyhydroxides (EPA 2007). Iron oxyhydroxides include oxides, hydroxides, and oxide hydroxide forms. All forms are very stable and exhibit high energies of crystallization. Fe^{3+} hydrolyzes and precipitates as oxyhydroxides solid Fe (III) phase which provides a very reactive surface for trace metals in aqueous environment (Warren and Haack 2001). Like Fe oxides, Mn oxides are very stable state with low solubility. Overall, Mn oxyhydroxides are considered more reactive than Fe oxides. Both Mn and Fe oxides have high affinities for trace metals, contributing to the variations in concentrations of those metals (Warren and Haack 2001). Both adsorption and co-precipitation (solid solution) might occur between metals and Fe hydroxides as well as Mn hydroxides under oxidizing conditions; then reduction and dissolution reactions under reducing conditions (EPA 2007) . My study showed strong correlations between metals (Ni, As, Cd, Tl, Zn and Sr) and Mn or Fe (Fig 4-4), which may be explained by the strong affinities of Mn or Fe oxides for those metals.

Concentrations of metals in periphyton might be strongly influenced by soil metals uptake by plants (Albers and Camardese 1993). The processes governing availability of trace metals to plants include complexation with organic and inorganic ligands and adsorptions, precipitation and dissolution of solids. Adsorption and precipitation could occur in the uptake of soil metals in roots and shoots (EPA 2007). In strongly acidic soils, plant uptake of Zn, Mn and Co increase, which might explain the elevated concentrations of those metals in epiphytic periphyton (typically associated with macrophyte) in my study. Manganese, Zn and Co in epiphytic periphyton all had the highest concentrations in soil with pH less than 7 (Fig

4-6). In the benthic periphyton, the distribution of metals might under strong influence of OM content because of its close association with soils. High concentrations of Cu, As, Pb and Zn were detected in the soil with highest OM content (Fig 4-7).

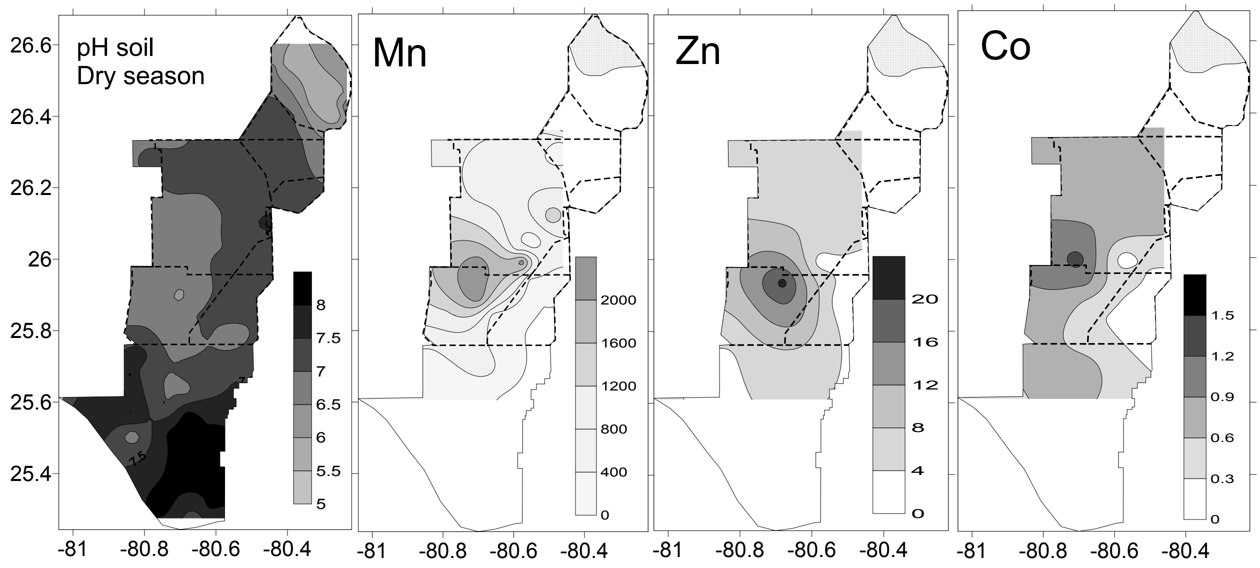

Figure 4-6 Distributions of Mn, Zn and Co (mg/Kg) in epiphytic periphyton from the dry season

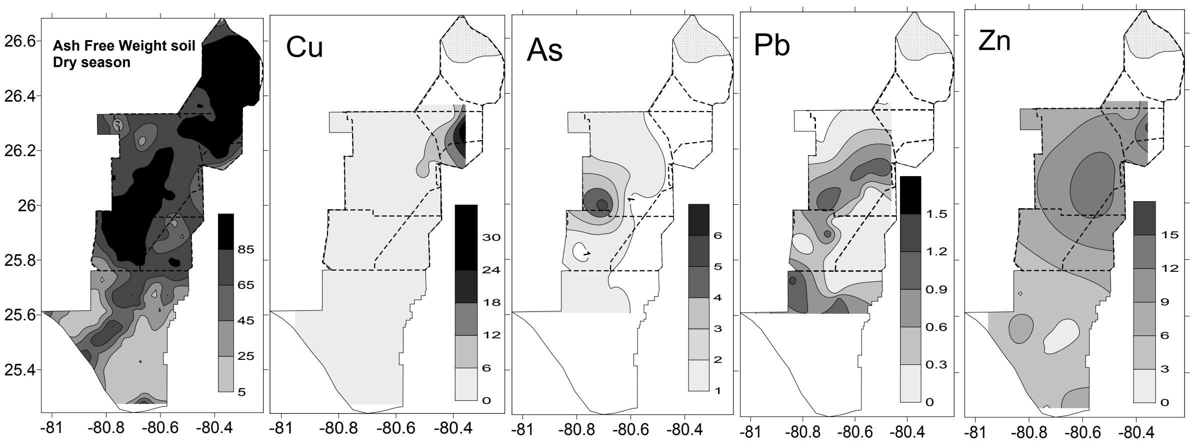

Figure 4-7 Distributions of Cu, As, Pb and Zn (mg/Kg) in benthic periphyton from the dry season

In soil (Table 4.4), Zn was significantly correlated with Mn, Co, Cu, As, Cd and Tl ($P<0.01$). Pb was correlated with Mn, Co, Cu, As, Cd, Tl and Zn ($p<0.05$). Iron had strong correlation with Cr and As ($P<0.01$). Copper, Zn, and As are all elements contained in fertilizers, bactericides, and fungicides used in the agriculture. It might explain the close associations among those metals. Underground flow as well as atmospheric deposition from nearby agriculture area might lead to the elevated levels of those metals (Chen et al. 2000). Manganese correlated well with Ni, As, Cd, Tl, Zn and Sr. Results imply that potentially toxic metals Pb, As, Ni, Cd and Zn maybe closely associated with Mn- and Fe- oxides minerals as reported in the literature (Hesterberg 1998). Toxic metals (Cd, Pb, Ni, As and Cu) correlated among themselves. The possible colloids formed between toxic metals (Cr, As, Cd) and micronutrients (Zn and Fe) might explain the indicative correlations between these two groups. In floc (Table 4.5), Zn was correlated well with Cu, As and Al ($P<0.01$). Iron had strong correlation with As. Manganese in floc only correlated with As ($P<0.05$), maybe as a result of low concentrations in surface peats in the Everglades (Craft and Richardson 1997). In periphyton (Table 4.6), zinc correlated strongly with Ni, Cu, As and Cd ($p<0.01$). Pb correlated significantly with As, Cd and Zn. Iron correlated with As, Cd, Zn and Al. It is probably because of strong affinity of Fe hydroxides for these metals. Living algae and other organism are part of floc and periphyton (Smith 2004). The close correlation among Zn, Fe, Cu, Pb might indicate that same origins exist for those metals.

Table 4-4 Correlation of metals among soil

	Li	Be	V	Cr	Mn	Co	Ni	Cu	As	Cd	Tl	Zn	Pb	Sr	Ba	Al	Fe	K	Mg
Li	1																		
Be	-	1																	
V	++	-	1																
Cr	++	+	++	1															
Mn	-	-	+	-	1														
Co	-	-	-	-	-	1													
Ni	-	-	-	-	++	++	1												
Cu	-	-	-	-	+	+	-	1											
As	-	-	-	-	++	++	-	+	1										
Cd	-	-	-	-	++	++	++	++	++	1									
Tl	-	-	-	-	++	++	++	++	++	++	1								
Zn	-	-	-	-	++	++	-	++	++	++	++	1							
Pb	-	-	-	-	+	++	-	+	+	+	+	++	1						
Sr	-	-	+	-	++	-	++	-	-	+	+	+	-	1					
Ba	-	+	++	-	-	-	-	-	-	-	-	-	-	++	1				
Al	++	-	++	-	-	-	-	-	-	-	-	++	-	-	+	1			
Fe	++	-	++	+	+	-	-	-	++	-	-	-	-	-	-	++	1		
K	-	+	++	++	-	-	++	-	-	-	+	-	-	-	+	++	-	1	
Mg	-	-	-	-	-	-	-	-	-	++	-	-	-	++	++	-	-	++	1

++ indicates $p<0.01$ level
+ indicates $p<0.05$ level
-indicates $p>0.05$ level

Table 4-5 Correlation of metals among floc

	Li	**Be**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**As**	**Cd**	**Tl**	**Zn**	**Pb**	**Sr**	**Ba**	**Al**	**Fe**	**K**	**Mg**
Li	1																		
Be	-	1																	
V	++	-	1																
Cr	-	++	-	1															
Mn	-	-	-	-	1														
Co	-	++	-	++	-	1													
Ni	-	-	+	-	-	+	1												
Cu	+	-	+	-	-	-	-	1											
As	-	-	-	-	+	++	-	-	1										
Cd	-	-	-	-	-	-	-	-	-	1									
Tl	-	++	-	++	-	++	-	-	-	-	1								
Zn	++	-	-	-	-	-	-	++	++	-	-	1							
Pb	-	++	-	++	-	++	-	-	-	-	++	-	1						
Sr	-	-	-	-	-	-	++	-	-	-	-	++	-	1					
Ba	-	++	-	++	-	++	-	-	-	-	++	-	++	-	1				
Al	++	-	++	-	-	-	-	-	-	-	-	++	-	-	-	1			
Fe	-	-	+	-	-	-	-	-	++	-	-	-	-	-	-	+	1		
K	-	-	++	-	-	-	+	-	-	-	-	-	-	-	-	-	-	1	
Mg	-	-	+	-	-	-	++	-	-	-	-	-	-	++	-	-	-	-	1

++ indicates $p<0.01$ level
+ indicates $p<0.05$ level
-indicates $p>0.05$ level

Table 4-6 Correlation of metals among periphyton

	Li	**Be**	**V**	**Cr**	**Mn**	**Co**	**Ni**	**Cu**	**As**	**Cd**	**Tl**	**Zn**	**Pb**	**Sr**	**Ba**	**Al**	**Fe**	**K**	**Mg**
Li	1																		
Be	+	1																	
V	-	-	1																
Cr	++	-	++	1															
Mn	-	-	-	-	1														
Co	-	-	-	-	-	1													
Ni	-	-	+	-	-	++	1												
Cu	-	-	-	-	-	-	+	1											
As	-	-	+	+	-	+	++	++	1										
Cd	-	++	++	++	-	+	++	-	++	1									
Tl	+	++	+	-	-	-	-	-	-	++	1								
Zn	-	+	-	++	-	-	++	++	++	++	+	1							
Pb	-	-	++	-	-	+	-	-	++	++	-	++	1						
Sr	++	-	++	-	-	-	+	-	-	-	-	-	-	1					
Ba	-	+	-	-	++	-	-	-	-	-	-	-	-	+	1				
Al	+	+	-	+	-	-	-	-	-	-	++	-	-	-	-	1			
Fe	-	++	+	-	-	+	-	-	++	++	++	++	-	-	-	++	1		
K	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	1	
Mg	-	-	+	-	-	-	++	-	-	-	-	-	-	++	-	-	-	-	1

++ indicates p<0.01 level

+ indicates p<0.05 level

-indicates p>0.05 level

4.2 Risk assessment of toxic metals in the Florida Everglades

Soil is an essential part of ecosystem as it serves as home to most of aquatic plants and animals (Dragovic et al. 2008). Furthermore, toxic metals existing in water at trace level can be accumulated in the sediment. Risk of metals in aquatic systems is commonly evaluated by measuring metal concentrations in soils (Lourino-Cabana et al. 2011). To assess the risk of metals, the background levels of trace metal have to be determined. One of the common ways for conducting risk assessment on metals in sediment is to compare experimental data in sediment with Sediment Quality Guidelines (SQGs). Sediment Quality Guidelines were originally derived using a database generated from studies conducted in both saltwater and freshwater, later better quality data were added to the database (Long et al. 1995). Sediment Quality Guidelines could be divided into two classes, mechanically and empirically based guidelines (Chapman et al. 1998). The mechanical approach accounts for bioavailability through monitoring the chemical and biological processes. Mechanistically based guidelines are derived from theoretical understanding of factors that control the bioavailability of sediment contaminants (Wenning and Ingersoll 2002), which addresses the sources of sediment toxicity, not whether or not the existence of toxic substances in the sediment. Empirical approach utilizes database of sediment chemistry and their biological effects. The most commonly used methods from this approach includes Effects Range-median (ERM), Apparent Effects Threshold (AET), Sediment Quality Guideline Quotient 1 (SQGQ1) and Logistic Regression Model (LRM) (Buchman 1999). Out of those methods, SQGQ1 was derived from less number of chemicals than other approaches. Logistic Regression Model approach is difficult to apply because of complex of regression must be utilized to determine probability of toxicity. All guidelines, which can be roughly categorized, are used as screening tools for the assessment of potential toxic metals. Table 4.7 listed SQGs used to compare with the current studies, including those derived from U.S., Australia, New Zealand, Italy and Netherland. The category includes: background (BK), which depicts background levels of a constituent in a region or nation; empirically derived (ED), which utilizes sediment chemistry and their biological effects; equilibrium partitioning (EP), which based on aquatic toxicity values; consensus based (CB), which was defined as the average of various SQGs from the same class (Apitz et al. 2007).

When compared average concentrations of potentially toxic metals from the current study (As, Cd, Cr, Ni, Pb, Cu, and Zn) with those of the background-based guidelines, the results from current study are closest to Flemish reference, a background-based guideline (Table 4.7). All results, except for Pb, were below the limit of Flemish reference. The average concentration of toxic metal, Pb, was still less than other background-based guideline. None of toxic metals had mean concentrations exceeded criteria set in the non-effects guidelines as well as probable-effects guidelines. In addition, the results of current study were on par with LEL and TEL values from similar studies conducted in Florida for each compound investigated (Table 4.7). Limited studies have been conducted on the risk assessment of metals in the Everglades.

Table 4-7 Summary of sediment quality guidelines (SQGs) summary SQG derivation: BK = background based; ED = empirically derived; CB = Consensus based. (Apitz et al. 2007)

SQGs	Type	As (mg/Kg)	Cd (mg/kg)	Cr (mg/kg)	Ni (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	Zn (mg/kg)
Background-based								
Flemish ref.	BK	11	0.4	17	11	14	8	67
No effects								
LEL(Florida)	ED	6	0.6	26	16	31	16	120
TEL(Florida)	ED	5.9	0.6	37	18	35	36	123
TEL	ED	7.2	0.7	52.3	15.9	30.2	18.7	124
ERL	ED	8.2	1.2	81	20.9	46.7	34	150
US TEC	CB	7.7	0.9	66.7	18.4	38.5	26.4	137
Probable effects								
ERM	ED	70	9.6	370	52	220	270	410
SEL(Florida)	ED	33	10	110	75	250	110	820
PEL(Florida)	ED	17	90	197	36	91.3	197	315
PEL	ED	41.6	4.2	160.4	42.8	112.2	108.2	271
AET	ED	35	3	62	110	400	390	410
PEC(I)	CB	54.3	5.8	268.5	58.3	296	214.6	396.2
US PEC	CB	56.2	5.5	208.8	68.1	253.4	256.1	363.7

Table 4-8 Percentages of toxic metals over the SQG's limit from sediment and floc samples

Soil (N=195)	**As**	**Cd**	**Cr**	**Ni**	**Pb**	**Cu**	**Zn**
LEL(FL)	8.2(16)	0.5(1)	10.1(20)	1.5(3)	16.9(33)	3.6(7)	None
US TEC	2.1(4)	none	none		6.7(13)	1.5(3)	None
TEC (I)	None	None	none		5.1(10)	1.5(3)	None
SEL(FL)	None	none	none		0.5(1)		None
floc (N=151)							
LEL(FL)	15.2(23)	0.7(1)	None	5.3(8)	None	11.3(17)	None
US TEC	2.6(4)	none	none	2.6(4)	none	9.3(14)	None
TEC (I)	None	None	none	1.3(2)	none	3.3(5)	None
SEL(FL)	None	none	none	none	none	0.7(1)	None

Although the mean values of the toxic metals did not exceed the no-effects SQGs, multiple samples had concentrations of toxic metals over several SQGs (LEL (FL), US TEC, TEC (I) and SEL (FL)) in the no-effect category (Table 4.8). Given relatively high background concentrations of As in the Everglades soils compared to rest of the state of Florida with 7.02 mg/Kg being the highest concentration in the state (Chen et al. 2001), both wet and dry seasons' As concentrations in soils didn't exceed the background value. Other toxic metals (Cd, Cr, Ni and Pb) have no known background concentrations information. Both LEL and SEL are guidelines made specifically based on sediment samples from state of Florida. Both TECs were average values of guidelines made in domestic and international respectively. Lead and Cr from sediments, as well as As and Cu from Floc, had concentrations over LEL level set in Florida in more than 10% of total sample. However, only one sample from each compartment contained concentrations of toxic metals (Pb and Cu) over criteria of probable-effects SQGs. The use of various SQGs, derived both domestically and internationally, has been utilized to evaluate the possibility of toxicity levels of COPECs in the Everglades. Even though most surveyed area contained samples with concentrations well under the limit set by SQGs from the probable-effects class, some areas, such as LNWR, northwestern part of WCA-3 in the surrounding area of EAA) should be subjected to site-specific risk assessment for carrying high concentration of toxic metals at several sites. Arsenic, Cr, and Pb from sediment contained concentration levels that pose dangers to ecological and human receptors as multiple samples exceeded background SQGs (Table 17) in the northern region in ENP and part of LNWR and Water Conservation Area-2. For floc, samples were found in the northern area of WCA-3 with elevated concentrations in As, Ni and Cu (Figure 4-8). The elevated level of those toxic metals (As, Pb and Ni) might affect aquatic plants and animals in the vicinity of contaminated area, causing biological harms such as metabolite degradation, enzyme activity inhibition, calcium metabolism problem, among others.

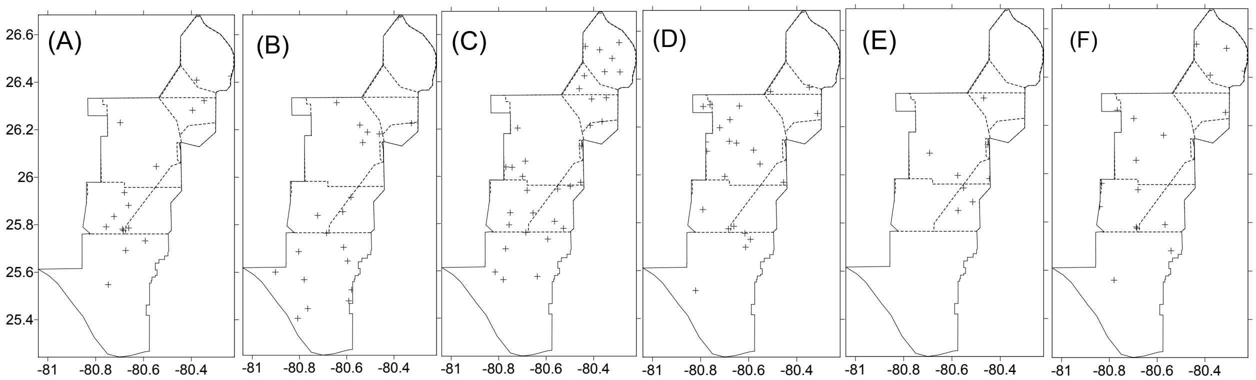

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Figure 4-8 Spatial distribution of selected toxic metals with concentrations exceeding SQGs in soils (A) As, (B) Cr, (C) Pb, and in floc of Florida Everglades (D) As, and (E) Ni, (F) Cu

5. Conclusions

The highest mean concentrations of all metals analyzed in the Everglades were detected in soil, followed by floc and periphyton. Most of metals in soil exhibited maximum concentrations in the dry season. The nearly opposite occurred for floc, where only Cr, Ni, and Cu were more concentrated in the dry season. Seasonal variation had little influence on the concentration in metals from periphyton. Most metals exhibited random spatial distribution patterns.

The distribution and concentration of dissolved metals in soils are possibly under the influence of major anthropogenic sources: agriculture and development activities (Cu, Pb, Zn, and As), road dusts and associated pollutions (Cr and Zn), air-boat tours (As and Zn) and air trafficking (Cr and Zn). The environmental parameters, including NOM and pH, are essential in the control over the distribution of metals in the Everglades as well. The highest concentrations of Cu, As, Pb and Zn were found in the peat soil where OM content is high.

Cations (Ni, Mn, Li and Be) had elevated concentrations in the south of the Everglades where pH is the highest.

Risk assessment using SQGs concluded that all toxic metals (Cd, Cr, Pb, Ni, Cu, Zn and As) exhibited average concentrations that were well below FL guidelines as well as other domestic and international guidelines. Although none of concentrations of toxic metals exceeded SQGs levels defined by "probable effects", several metals (As, Cr, Pb, Ni and Cu) had elevated concentrations at several sampling sites in northern ENP, WCA-2 and LNWR. Overall, based on the current study, the Everglades can be considered a pristine environment. This study can serve as a baseline for future analysis of metals in the Everglades area.

6. Future work

Some areas, such as northwestern and northeastern zone of ENP, contained elevated concentrations of toxic metals (Cr, As and Ni) which warrant further investigation into their sources and impacts. High concentrations of toxic metals (Cd, Cr and Pb) in the surrounding areas of EAA encourage the additional study of the influence on the toxic metals from the agricultural and developmental activities. A screening level Ecological Risk Assessment (ERA) with metals is recommended to quantify the likelihood that detrimental effects will incur in the sediment from metal exposures. The study of toxic metal pollutions in the Everglades fish and plants should be conducted as to assess the potential risk associated with metals. Future sediment-toxicity studies should also be carried out to distinguish between natural and anthropogenic effects on distributions of metals.

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