

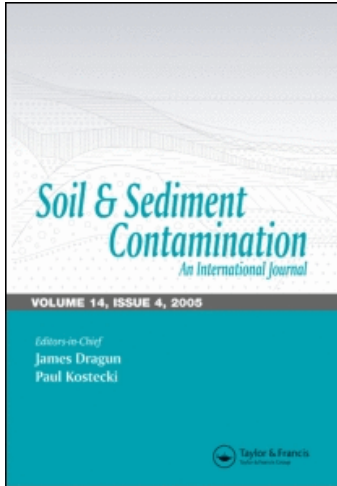
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## Aquatic Risk Assessment of Metals in Sediment from South Florida Canals

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*A major watershed restoration effort is underway in south Florida, yet there are significant gaps in scientific information on exposure and risks of contaminants to its natural resources. We conducted a two-tier aquatic screening-level ecological risk assessment for metals that were monitored in sediment at 32 sampling sites in south Florida freshwater canals from 1990–2002. For tier 1, the chemicals (or metals) of potential ecological concern (COPECs) were identified as arsenic, cadmium, chromium, copper, lead, nickel and zinc based on their exceedences of Florida sediment quality guidelines at 10 sites. For tier 2, we used a probabilistic risk assessment method 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. The overlap of pore water concentrations (90th centile for exposure) for metal COPECs and the effects distributions for arthropods (10th centile of LC50s) and all species (10th centile of chronic NOECs) were used as a measure of potential acute and chronic risks, respectively. Arsenic (25%) in the Holey Land tracts, in Broward County north of Everglades National Park (ENP), and chromium (25%) in the C-111 freshwater system, at the east boundary of ENP, were the most frequently detected COPECs in sediment. Antimony (6%), zinc (6%) and lead (5%) were the least frequently detected COPECs in sediment. The 90th centile concentrations for bulk sediment were highest for zinc (at S-178) and lead (at S-176) in the C-111 system. The 90th centile concentration for pore water exposure was highest for arsenic in the Holey Land tracts and lowest for cadmium and chromium. The estimated acute 10th centile concentration for effects was lowest for copper and arthropods. The probabilities of pore water exposures of copper exceeding the estimated acute 10th centile concentration from the species sensitivity distributions (SSD) of acute toxicity data (for arthropods) were 57 and 100% for copper at S-177 and S-178 in the C-111 system, respectively. The probability of pore water exposures of copper exceeding the estimated NOEC 10th centile concentration from the SSD of chronic toxicity data (for all species) was 93 and 100% for copper at S-177 and S-178, respectively. Uncertainties in exposure and effects analysis and risk characterization are identified and discussed. The study presents a straightforward approach to estimate exposure and potential risks of metals detected in sediment from south Florida canals.*

**Keywords** Ecological risk assessment, metals, sediment, south Florida canals

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## Introduction

In the past century, the south Florida ecosystem has been altered by human activities to the extent that the hydrology, water quality, and ecology of much of the region have been dramatically changed (Science Subgroup, 1996). In 2000, Congress passed the Comprehensive Everglades Restoration Plan (CERP) as a part of the Water Resources Development Act (1996) with the goal to restore and preserve the hydrology of the pre-drainage Everglades ecosystem, to protect the quality of the remaining habitat, to promote the return of populations of plants and animals and to foster human development compatible with sustaining a healthy ecosystem.

Well documented ecological changes in south Florida, including the Everglades, have been linked to elevated levels of phosphorus and mercury and to changes in the complex hydrological patterns of the natural system resulting from water management projects to control floods and water distribution (Science Subgroup, 1996). In fact, alterations in the hydrologic system are thought to be the main cause of dramatic declines of fish and wildlife populations because of habitat changes. Therefore, the basic premise behind all restoration activities identified by the Restoration Task Force for south Florida is that hydrologic restoration is a prerequisite to achieve ecosystem restoration and a sustainable south Florida ecosystem.

Little consideration has been given in the restoration effort to the role contaminants play in the structure and function of ecosystems, although this is clearly a recommendation of the Science Subgroup (1996) in all physiographic regions that comprise south Florida, which includes a broad range of natural habitats. This was further supported at the workshop "Linking Ecotoxicity and Risk Management to Sustainable Restoration of South Florida Ecosystems" which recommended screening-level ecological risk assessments with retrospective and prospective diagnostic studies (LaPoint et al., 1998). The results of limited studies on the south Florida ecosystem restoration indicate the need for studies on "more system-wide work on screening for contaminants" and the "risks faced by organisms living in areas with contaminants" (GAO, 2003).

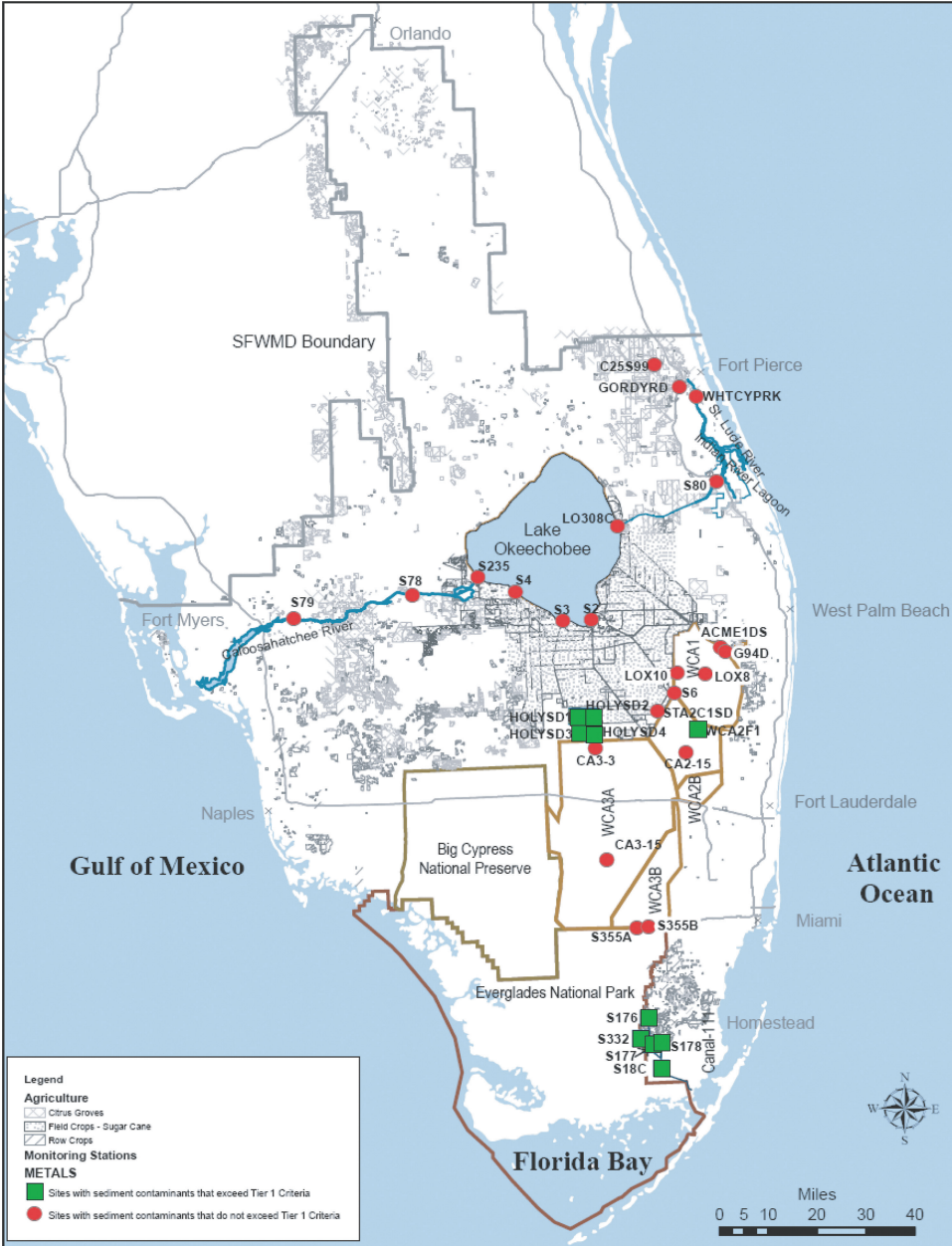
Since the mid-1980s, the South Florida Water Management District has been monitoring contaminants in south Florida surface water and sediments. For pesticides, recent monitoring data have indicated that several compounds, including DDT, DDE, DDD, ametryn, atrazine, dicofol, diquat and endosulfan sulfate, were frequently detected in sediment and surface water samples (Miles and Pfeuffer, 1997). Carriger et al. (2006) further examined this data using a two-tier ecological risk assessment (ERA) approach and determined that concentrations of organochlorine compounds (i.e., endosulfan, DDD) in sediment at several sites within south Florida freshwater canals were sufficient to pose a potential risk to aquatic organisms. In a monitoring study in south Florida canals and Biscayne Bay, insecticides (i.e., endosulfan, chlorpyrifos) in water were determined to have high hazard potential to aquatic organisms (Harman-Fetcho et al., 2005). More recently, a probabilistic risk assessment showed that mixtures of herbicides in freshwater canals of south Florida present potential acute risks to algae and plants (Schuler and Rand, 2008). Unlike that for pesticides, few studies have been conducted to examine the risk of metals in sediment from south Florida freshwater canals, although metals typically are among the most ubiquitous sediment contaminants (U.S.EPA, 2001) and metal concentrations correlate well with sediment toxicity (Field et al., 2002). Because of its presence in the Everglades ecosystem, mercury is the primary metal that has received consideration in aquatic systems (Rumbold, 2005, 2006) and in risk assessments with birds (Rumbold, 2008) and panthers (Barron et al., 2004).

Therefore, the objective of this study was to conduct a screening level ERA with metals to quantify the likelihood that adverse effects will occur from metal exposures in sediments of south Florida freshwater canals based on South Florida Water Management District (SFWMD) historical metal monitoring data from 1990–2002, using a two-tier approach to characterize risk. The study uses a probabilistic risk approach (PRA), which compares probability distributions of metal concentrations in pore water and species effects data from laboratory toxicity studies to determine the magnitude of overlap, which is a measure of risk. The results of this study fill a significant gap in the scientific information on the potential risks of metals in sediment to organisms in south Florida freshwater canals.

## Methods

The sediment ecological risk assessment (ERA) consisted of the first three phases of the United States Environmental Protection Agency (U.S.EPA) ERA framework (U.S.EPA, 1998): problem formulation, risk analysis, and risk characterization. For additional guidance on the risk of metals to aquatic organisms we also used the draft document “Framework for Inorganic Metals Risk Assessment” (U.S.EPA, 2004). In problem formulation, we summarized the metal-COPEC (chemicals of potential ecological concern) characteristics (i.e., physical-chemical, fate) and assessment (i.e., what is at risk and in need of protection) and measurement endpoints (i.e., what will reveal effects on assessment endpoint(s)). For risk analysis, we characterized two major risk components: exposure and effects. Risk characterization, the final phase, provided estimates of risk probability to the ecological entity listed as the assessment endpoint by comparing distributions of predicted pore water metal exposures with distributions of effects data from laboratory toxicity tests with metals. Risk characterization assumes organisms are directly exposed to metals in pore water, sediment-pore water exposure is a major source of toxicity to organisms and the effects concentration in pore water is similar to that found in water-only exposures (Burton, 1992; DiToro et al., 1991). The toxicity test data base with organisms exposed to single metals in spiked sediment was inadequate to develop probability distributions of effects for the individual metals to compare to our whole (bulk) sediment metal exposure concentrations. Therefore, whole sediment metal exposure concentrations were converted to pore water concentrations.

A two-tiered ERA approach was suggested by the Aquatic Risk Assessment and Mitigation Dialogue Group (ARAMDG) (SETAC, 1994) and endorsed by the U.S. EPA (ECOFRAM, 1999) that first uses a hazard quotient (HQ) to screen for COPECs followed by probabilistic risk assessment (PRA). This two-tier ERA approach was used to prioritize hazardous metal COPECs in sediment from data obtained in the South Florida Water Management District (SFWMD) DBHYDRO environmental database. SFWMD has monitored concentrations of 11 metals in sediment from 1990 to the present (R. Pfeuffer, SFWMD; personal communication) at 32 sampling sites in freshwater canals of eight counties in south Florida (Figure 1). All metal analyses were conducted by the Florida Department of Environmental Protection (FDEP) Central Laboratory (Tallahassee, FL) using U.S. EPA methods and quality assurance procedures. Metals examined in this assessment included arsenic, antimony, aluminum, beryllium, cadmium, chromium, copper, lead, nickel, selenium, and zinc. Mercury was therefore not considered here as it has already been the focus of several recent investigations (Rumbold, 2005, 2006, 2008). Natural background concentrations of certain metals do exist in sediment, but the significance of these concentrations is not well understood. An “added risk approach” was therefore not attempted because it



**Figure 1.** South Florida Water Management District sediment metal monitoring stations (from Diane Malone, South Florida Water Management District, West Palm Beach, FL).

is presently considered unreliable (U.S.EPA, 2004). Therefore, the potential risk of “total metal concentrations” in sediment to aquatic organisms was considered.

In Problem Formulation for Tier 1, whole sediment concentrations of the metals at each of the 32 sites in south Florida from 1990–2002 were compared to the FDEP Sediment Quality Assessment Guidelines (SQAG) (Table 1). When no FDEP SQAG was available

**Table 1**

Florida sediment quality assessment guideline (SQAG) or other sediment criteria for 11 metals (mg/kg, dw) monitored in sediment by South Florida Water Management District

Compound	Fresh Water	Criteria Source
Aluminum	58,000	ARCS ERM <sup>1</sup>
Antimony	3	NOAA UET <sup>2</sup>
Arsenic	9.8	FL TEC <sup>3</sup>
Beryllium	—	NG <sup>4</sup>
Cadmium	1	FL TEC
Chromium	43	FL TEC
Copper	32	FL TEC
Lead	36	FL TEC
Nickel	23	FL TEC
Selenium	—	NG <sup>4</sup>
Zinc	120	FL TEC

<sup>1</sup>Assessment and Remediation of Contaminated Sediments Program (ARCS): effects range median (ERM) (U.S.EPA, 1994); no Florida criteria available.

<sup>2</sup>NOAA; upper effects threshold (UET) (Buchman, 1999); no Florida criteria available.

<sup>3</sup>Florida threshold effect concentration (TEC) (Florida DEP, 2003).

<sup>4</sup>NG: No guidance for metal.

for a metal, we compared metal concentrations to the lowest sediment quality benchmark available (e.g., NOAA SQuiRTs). In this analysis, a metal was considered a COPEC when the HQ value exceeded the sediment screening benchmark by 0.5 HQ units (ECOFRAM, 1999) three or more times at a site.

***Risk Analysis Exposure***

Following the identification of potential metal COPECs in Tier 1, the actual measured whole sediment concentrations for each metal at each site were converted to predicted pore water (i.e., interstitial water) concentrations (PPW<sub>c</sub>) based on equilibrium partitioning (EqP) theory methodology (DiToro et al., 1991; Carriger et al., 2006). Theoretically derived sediment quality criteria for cationic metals are based on EqP (Ankley et al., 1996). The EqP approach is based on the strong correlation between the toxic effects of contaminants and their concentrations in sediment pore water and the control of concentrations in pore waters by the partitioning between dissolved and one or more components of the solid phase. The EqP assumes that the activity or fugacity of the chemical is the same at equilibrium. Therefore, the organism receives an equivalent exposure from water-only exposure as it does from a sediment pore-water equilibrium system since the chemical activity is the same in each system at equilibrium.

To convert from measured whole-sediment metal concentrations (mg/kg) for each COPEC to predicted pore water concentrations (PPW<sub>c</sub>), metal K<sub>p</sub> values (L/kg) (partition coefficient between pore water and sediment solids) were used in the following equation (Carriger et al., 2001):

$$PPW_c (\mu g/L) = \frac{MC_{sed}}{K_p}$$

**Table 2**  
Metal partition coefficients ( $K_p$ ) for sediment/porewater<sup>1</sup>

Metal	Log $K_p$
Antimony	3.7
Arsenic	2.4
Beryllium	2.8
Cadmium	3.3
Chromium	4.9
Copper	3.5
Lead	4.6
Nickel	3.9
Selenium (iv)	3.6
Selenium (vi)	0.6
Zinc	4.1

<sup>1</sup>From U.S. EPA (2005).

where  $MC_{sed}$  is the measured concentration of metal COPEC. Metal partition coefficients (Table 2) were obtained from U.S. EPA (2005).

The predicted pore water concentrations were then fit to lognormal exposure distributions when there were four or more values above the detection limit (Solomon et al., 2000). A log normal distribution of the exposure data was assumed (Solomon et al., 1996; Hall, Jr. et al., 1999) and metal concentrations were ranked at each site using the equation:

$$\text{Rank} = \frac{j}{n + 1} \times 100$$

where  $j$  is the rank assigned to a particular concentration and  $n$  is the total number of sample observations (including non-detects) at each site. Samples below the detection limit were given dummy values of 0, and although not included in the regression analysis, they were assigned a rank and assumed to be distributed at the lower end of the distribution (Hall, Jr. et al., 1999; Solomon et al., 1996). Centile rankings were converted to probits and plotted against the corresponding  $\log_{10}$  values of the PPWc using algorithms found in PRAT-1 software (Solomon et al., 2000). This approach also was followed for whole sediment concentrations of metals.

The 90th centile pore water exposure concentrations and 90th centile whole sediment concentrations were calculated from the lognormal concentration distribution for each COPEC at all sites. The 90th centile is an "exposure benchmark" used in PRAs (Solomon et al., 1996) because it is an empirical measure of high exposure and assumes that any sample taken has a 10% chance of exceeding the estimated 90th centile concentration if the values in the exposure distribution are unbiased and accurately represent the concentrations found over that time period and location (Giddings et al., 2000).

### Effects

All available toxicity data for the most sensitive freshwater trophic group (e.g., fish, arthropods, etc.) were used in the preparation of acute metal SSDs. We determined that predicting the likelihood of potential risks associated with chronic exposures would

also be an applicable scenario. Therefore, no observable effect concentrations (NOECs) from chronic tests were used to prepare chronic SSDs. Acute (e.g., LC50, EC50) and chronic toxicity data for freshwater organisms were obtained from the AQUIRE database (<http://www.epa.gov/ecotox/>) and regulatory reviews (i.e., water quality criteria documents).

The SSD distribution of acute and chronic (NOEC) toxicity data for each COPEC was evaluated using the approach described in SETAC (1994). However, for freshwater toxicity studies with metals, hardness is one water quality parameter that significantly influences toxicity (Hamelink et al., 1994). As water hardness increases the toxicity of trace metals to aquatic biota generally decreases due to its effects on the ability of an organism to osmoregulate or to its influence on altering metal bioavailability. The U.S. EPA addresses the influence of hardness on toxicity of metals in development of freshwater quality criteria (U.S. EPA, 2002). For metal toxicity data (i.e., cadmium, copper, chromium III, lead, nickel, zinc) used in this risk assessment, hardness was considered in the ranking of sensitivities of freshwater species. For these metals, the acute freshwater toxicity data were adjusted to a consistent hardness of 200 mg/L CaCO<sub>3</sub>. This value was selected because it approximates the mean hardness for south Florida freshwater ecosystems. If hardness data were not available with a freshwater toxicity test value for a species, then the toxicity data were not used in the analysis. The following equation was used to adjust the freshwater acute toxicity data (Warren-Hicks et al., 2002):

$$\text{Adjusted LC50} = \left( \frac{200}{\text{hardness}} \right)^{\text{slope}} * \text{LC50}$$

where hardness is that associated with the original toxicity test, 200 (mg/L CaCO<sub>3</sub>) is the adjusted hardness, and slope is the pooled slope taken from the water quality criteria document (U.S. EPA, 2002). Note that the adjusted toxicity values are based on total metals as we compared these toxicity distributions to distributions of predicted pore water concentrations, which are also based on total measured metal in sediment. Chronic toxicity data were not normalized to consistent hardness. Crommentuijn et al. (1997) point out that the relationship between hardness and chronic toxicity of metals appears to be much less consistent than between hardness and acute toxicity and the influence can be relatively small, especially in the range of hardness between 50 and 200 mg/L (as CaCO<sub>3</sub>).

Toxicity values (i.e., LC50s, NOECs) were ranked by concentration, and for each species toxicity value the centile rankings were calculated as described above in the exposure analysis. These centiles were plotted against log-transformed concentrations and linear regression was conducted to define each distribution. The 10th centile of the SSD (protection of 90% of the species 90% of the time) for each COPEC from acute (i.e., LC50, EC50) and chronic NOEC (no observed effect concentration) data were selected as the “toxicity benchmarks” used to characterize risk (SETAC, 1994; Solomon et al., 1996). Acute toxicity values were only used if they came from tests with measured concentrations. NOEC values were only used from toxicity tests greater than 96 hours in duration with endpoints that included survival, growth, development, and reproduction. If multiple acute toxicity endpoints were available for a single species, the geometric mean of the endpoints was used to represent the toxicity for that species (ECOFRAM, 1999).



### ***Risk Characterization-Tier 2***

Potential risk to freshwater organisms from exposures to metal COPECs in pore water was determined by comparing the predicted pore water exposure distributions by sampling site with the 10th centile values from the acute LC50 and chronic NOEC SSDs for each metal COPEC. The percent exceedence of the acute and chronic 10th centiles by the exposure distribution for each metal COPEC was used as risk estimates (Solomon et al., 1996). Since the lowest 10th centile of acute values (LC50s) were for arthropods, acute risk estimates were only calculated for this group. The database for chronic toxicity studies was small, therefore the chronic (NOEC) 10th centiles were based on a distribution of chronic toxicity studies from all freshwater species ("community based") for a metal COPEC.

The probability of exceedence of the FDEP SQAG TEC (threshold effect concentration) and PEC (probable effect concentration) standards were also determined for sites with metal COPECs (Hall, Jr. and Anderson, 2003).

## **Results and Discussion**

### ***Problem Formulation***

*Tier 1.* Arsenic, cadmium, chromium, copper, lead, nickel and zinc were determined to be metal COPECs since Florida SQAGs were exceeded at 10 sampling sites throughout the canals within the South Florida Water Management District (Table 3). Although there was no Florida sediment criteria for antimony it was a COPEC based on exceedence of the NOAA upper effects threshold. Figure 1 shows the sampling locations of the sediment quality violations for the metal COPECs. Metals in sediment had multiple sediment quality violations at sites from 1990 to 2002. From the analysis, it was determined that arsenic (25% detections) in the Holey Land tracts (in north Broward County) and chromium (25% detections) in the C-111 system (at the east boundary of Everglades National Park(ENP)) were the most frequently detected metal COPECs. The least frequently detected metal COPECs were cadmium (12% detections), nickel (11% detections), copper (10% detections), antimony (6% detections), zinc (6% detections), and lead (5% detections). Antimony, chromium, copper, lead, nickel, and zinc had sediment quality violations on parts of the C-111 system (S-176, S-177, S-178, S-18C), which may be important as a source of water for ENP. Cadmium was found to be a COPEC but only in the Holey Land tracts (SD 2, 3, 4). The 10 sites with COPECs represent approximately 31% of the total sediment sampling sites monitored by the SFWMD for metals.

Although antimony was a COPEC, there was insufficient toxicity data to prepare a species sensitivity distribution and therefore a PRA could not be conducted with this metal.

*COPEC Characteristics in the Environment.* The metal COPECs may be found in water and/or sediment in different valence states and forms (e.g., dissolved, bound). Their bioavailability in aquatic systems is modified by biological and abiotic (e.g., hardness, alkalinity, pH, pE, organic matter, iron and manganese oxides, sulfides, ionic strength, temperature) factors. In freshwater, an increase in hardness has been shown to generally reduce metal bioavailability and toxicity to aquatic organisms. Toxicity of the metals in sediment is correlated with dissolved metal concentrations in pore water (U.S.EPA, 2004). For more extensive information on the environmental chemistry and fate of these metals there are excellent reviews available (Eisler, 1985, 1986, 1988a, b, 1993, 1998a, b; Neff, 1997).

**Table 3**

Results of Tier 1 assessment: Use of screening benchmarks to determine metal COPECs in sediment

Chemical	COPEC	Comments
Arsenic	Yes	Detected in sediment 129 times. Exceeded SQC <sup>1</sup> 59 times. COPEC at sites: HOLYSD1, HOLYSD2, HOLYSD3, S18C and WCA2F1.
Antimony	Yes <sup>2</sup>	Detected in sediment 19 times. Exceeded SQC (NOAA UET) 14 times. COPEC at sites: S176, S177, S18C and S332.
Aluminum	No	Detected in sediment 161 times. Exceeded SQC once at CA3-3 and HOLYSD2.
Beryllium	No	Detected 71 times at multiple sites. No SQC available for compound
Cadmium	Yes	Detected in sediment 94 times. Exceeded SQC 16 times COPEC at sites: HOLYSD2, HOLYSD3 and HOLYSD4.
Chromium	Yes	Detected in sediment 142 times. Exceeded SQC 32 times. COPEC at sites: S176, S177, S178 and S18C.
Copper	Yes	Detected in sediment 144 times. Exceeded SQC 19 times. COPEC at sites: S177, & S178.
Lead	Yes	Detected in sediments 159 times. Exceeded SQC 35 times. COPEC at site S176.
Nickel	Yes	Detected in sediments 100 times. Exceeded SQC 14 times. COPEC at sites: S178 and S18C.
Selenium	No	Detected in sediments 59 times. No SQC for compound. Most frequently detected in Holey Land.
Zinc	Yes	Detected in sediments 133 times. Exceeded SQC 17 times. COPEC at site S178.

<sup>1</sup> SQC; Sediment Quality Criteria (HQ ≥ 0.5).

<sup>2</sup> Cannot conduct PRA for this compound because of insufficient toxicity data for SSD.

*Assessment and Measurement Endpoints.* The long-term viability of aquatic communities in south Florida canals was the assessment endpoint worthy of protection. The specific assessment endpoint was the protection of at least 90% of the species 90% of the time (10th centile from species sensitivity distributions) from metal COPEC exposures. Aside from acute sediment exposures, chronic sediment exposures and risk resulting from such exposures to organisms was a primary consideration because of the persistence of the metal COPECs in sediment. Measurement endpoints include all metal toxicity data (i.e., survival, growth, and reproduction) generated from laboratory toxicity studies. The latter were used to define acute and chronic impacts on aquatic communities.

The assessment endpoint is in keeping with the management goals set forth by the Science Subgroup (1996) of the south Florida ecosystem restoration. Not presently included within the assessment endpoint are any specific endangered or threatened species or species of concern.

**Table 4**

Lognormal distributions of bulk sediment and predicted pore water concentration data for COPECs including 90th centile concentrations

Site	COPEC	No. of times analyzed	No. of detections	90th centile sediment (mg/kg)	90th centile pore water ( $\mu\text{g/L}$ )
HOLYSD1	Arsenic	19	17	21.46	85.45
HOLYSD2	Arsenic	18	14	18.31	72.89
	Cadmium	18	10	1.28	0.64
HOLYSD3	Arsenic	17	8	6.98	27.77
	Cadmium	17	7	0.66	0.33
HOLYSD4	Cadmium	18	11	1.46	0.73
S176	Antimony	16	4	11.32	2.84
	Chromium	15	15	25.74	0.32
	Lead	11	11	105.17	2.64
S177	Antimony	15	4	13.96	3.51
	Chromium	15	13	26.92	0.34
	Copper	12	11	26.50	8.38
S178	Chromium	15	15	58.13	0.73
	Copper	12	12	82.42	26.06
	Nickel	15	11	22.73	2.86
	Zinc	14	14	227.62	18.08
S18C	Antimony	18	4	7.72	1.94
	Arsenic	16	14	13.71	54.57
	Chromium	16	15	27.36	0.34
	Nickel	17	14	15.17	1.91
S332	Antimony	15	3	9.47	2.38
WCA2F1	Arsenic	5	4	16.18	64.40

### **Risk Analysis**

*Exposure.* PRAs were conducted at the 10 sites that contained COPECs. The 90th centile values from the lognormal distributions of metal bulk sediment concentrations for the COPECs at the 10 sampling sites are summarized in Table 4. The highest 90th centile for bulk sediment was for zinc at S-178 followed by lead at S-176, both on the C-111 system. The highest 90th centiles for copper, chromium, and nickel were also at S-178. The lowest 90th centile values were for cadmium in the Holey Land tracts. Arsenic was detected in the Holey Land tracts SD1, 2, and 3. From the lognormal distributions of the predicted pore water concentrations, the highest 90th centile values were for arsenic in the Holey Land tracts. The lowest 90th centile values were for chromium in the C-111 system (S-176, S-177, S-178 S-18C) and cadmium in the Holey Land tracts (SD 2, 3, and 4). Antimony was detected infrequently.

*Effects.* Species acute effects data for COPECs are summarized in Table 5. Native and nonnative species of freshwater organisms were used in construction of the SSDs for each COPEC. Acute toxicity 10th centile values were lowest for copper and chromium VI in arthropods. It should be noted that based on the presence of measurable acid-volatile sulfide (AVS) (AVS 10th centile concentration:  $1.71 \mu\text{mol/g}$ ; median AVS concentration:

**Table 5**  
 Statistics for acute SSDs of metal COPECs including 10th centile concentrations ( $\mu\text{g/L}$ )  
 for arthropods

COPEC	No. of Species	Slope	Intercept	R <sup>2</sup>	Acute 10th Centile ( $\mu\text{g/L}$ )
Arsenic All	20	1.33	-0.30	0.89	1069.1
Arsenic Fish	10	1.49	-1.16	0.87	1903.6
Arsenic Arthropods	6	0.83	2.03	0.78	107.9
Arsenic Non-vertebrates	9	1.07	0.97	0.9	377.5
Cadmium All	60	0.76	2.75	0.96	18.5
Cadmium Fish	21	0.60	3.13	0.83	9.7
Cadmium Arthropods	19	0.67	2.97	0.96	13.3
Chromium VI All	41	0.62	2.63	0.87	58.7
Chromium VI Fish	20	0.99	0.55	0.66	1654.8
Chromium VI Arthropods	17	0.47	3.53	0.86	2.5
Chromium III All	23	0.80	1.66	0.74	359.7
Chromium III Fish	11	4.69	16.53	0.93	20735.5
Chromium III Arthropods	8	0.57	2.88	0.86	30.0
Copper All	38	1.03	2.46	0.76	16.5
Copper Fish	22	0.97	2.52	0.63	17.1
Copper Arthropods	8	0.63	3.50	0.71	2.2
Lead All	11	0.61	2.45	0.93	115.5
Lead Fish	5	0.76	1.94	0.85	223.2
Lead Arthropods	5	0.38	3.36	0.86	8.7
Nickel All	14	1.17	0.50	0.94	574.7
Nickel Fish	7	1.33	0.80	0.86	2543.2
Nickel Invertebrates	5	1.79	0.87	0.92	363.9
Zinc All	24	1.00	1.57	0.93	136.7
Zinc Fish	12	1.03	1.39	0.90	184.2
Zinc Arthropods	5	0.77	3.00	0.83	8.5

7.15  $\mu\text{mol/g}$ ) at sediment sites, it is assumed that Cr (VI), the toxic form of chromium, will not be present because it is unstable in reducing environments. Most of the Cr will therefore be in the trivalent form, which is relatively insoluble and nontoxic so that any toxicity at sites will not be related to Cr exposure (Berry et al., 2004).

AVS has also been shown to be a predictor of toxic effects in aquatic systems for cationic metals (i.e., Ag, Cd, Cu, Ni, Pb, Zn) in laboratory spiked and field sediment tests (DiToro et al., 1990, 1992; Berry et al., 1996, 1999; Boothman et al., 2001; Hansen et al., 1996). In these tests, when concentrations of AVS in sediments exceeded the sum of the simultaneously extracted metals (SEM), excess sulfide existed in sediment and there was a lack of toxicity. These metals react with iron sulfide and form insoluble non-toxic metal sulfides which limit pore water metal concentrations (i.e., toxicity is assumed to be caused by dissolved metals only, with no contribution from ingestion of particulate metals). Note that the  $\sum\text{SEM}/\text{AVS}$  method does not consider other sediment phases such as sediment particulate organic carbon, which may play a role in controlling pore water metal concentrations (DiToro et al., 2005). SFWMD did not measure SEM and therefore we could not use the SEM/AVS method for evaluating metal toxicity.

**Table 6**  
 Statistics for metal chronic SSDs of COPECs including NOEC 10th centile concentrations ( $\mu\text{g/L}$ )

COPEC	N	Slope	Intercept	R <sup>2</sup>	Chronic (NOEC) 10th Centile <sup>b</sup> ( $\mu\text{g/L}$ )
Arsenic	NA <sup>a</sup>	NA	NA	NA	NA
Cadmium	8	1.52	3.77	0.88	0.92
Chromium III or IV	NA	NA	NA	NA	NA
Lead	4	0.68	3.57	0.93	1.63
Nickel	4	0.74	3.26	0.76	4.19
Copper	15	0.99	3.89	0.88	0.68
Zinc	7	1.19	2.21	0.96	18.40

<sup>a</sup>NA: Not available.

<sup>b</sup>Chronic (NOEC)10th centile for all species tests.

Typically, arthropods had the lowest acute 10th centiles for all metals except cadmium where fish had the lowest acute 10th centile value (Table 5).

The SSDs of chronic NOEC data for each COPEC are presented in Table 6. The NOECs included all the available chronic toxicity data for the metal. The lowest NOEC 10th centile was for copper at 0.68  $\mu\text{g/L}$ . There was insufficient chronic toxicity test data for arsenic and chromium to determine NOEC 10th centile concentrations.

### **Risk Characterization**

The probability of pore water exposures for all COPECs exceeding the acute and chronic 10th centiles sediment benchmarks are presented in Table 7. Risk estimates were determined for arthropods for all metals except cadmium where fish represented the most sensitive trophic group to metals. Copper at S-178 and S-177 had the highest acute risk estimates followed by zinc at S-178. A recent paper places copper in the top tier of water impairments due to metals in the U.S. (Reiley, 2007). Arsenic and cadmium acute risk estimates were generally low ( $\leq 5.8\%$  for arsenic;  $\leq 0.6\%$  for cadmium).

Cadmium chronic risk estimates in the Holey Land tracts were also low (3.8 to 8.1%). The sites with the highest potential chronic risk from a single COPEC were in the C-111 system, based on the probability of predicted pore water exposures for copper exceeding the NOEC 10th centile value at 100% at S-178 and at 93% at S-177. The metal with the next highest probability of pore water exposures exceeding the NOEC 10th centile was for lead at 18.5% at S-176. Zinc and nickel were also present at S-178 but with low chronic risk. There was insufficient toxicity data to assess chronic risk for arsenic.

Acute and chronic risks of metals (i.e., mainly Cu) were localized to sites in the C-111 basin (S-176, S-177, S-178), which may eventually affect the water quality into Everglades National Park. When concentrations of pesticides were considered in sediments of south Florida canals (1990–2002), the organochlorine insecticide, endosulfan, also had the highest potential chronic risk to arthropods at S-178 in the C-111 basin (Carriger et al., 2006).

The probability of COPEC metal bulk sediment concentrations exceeding the FDEP freshwater SQAG TEC and PEC by site is also presented in Table 7. The probability

**Table 7**

Probability of exceeding the acute (arthropods) and chronic (all species) freshwater 10th centiles and toxicity benchmarks for predicted pore water concentrations at the South Florida Water Management District sediment monitoring sites

Site	COPEC	Exceedence Probability Acute 10th Centile <sup>a</sup> (%)	Exceedence Probability Chronic (NOEC) 10th Centile <sup>b</sup> (%)	Exceedence Probability of FDEP TEC (%)	Exceedence Probability of FDEP PEC (%)
HOLYSD1	Arsenic	5.8	NA <sup>d</sup>	38.5	3.4
HOLYSD2	Arsenic	4.6	NA	26.1	3.0
	Cadmium	0.6 <sup>c</sup>	7.5	12.16	2.89
HOLYSD3	Arsenic	0.0	NA	3.7	0.0
	Cadmium	0.17 <sup>c</sup>	3.8	6.96	1.16
HOLYSD4	Cadmium	0.43 <sup>c</sup>	8.1	13.97	2.75
S-176	Chromium	0.0	NA	0.08	<.01
	Lead	1.3	18.5	33.64	7.33
S-177	Chromium	0.0	NA	1.81	<.01
	Copper	57.7	93.3	6.81	0.07
S-178	Chromium	0.0	NA	39.11	0.03
	Copper	100.0	100.0	99.96	<.01
	Nickel	0.0	4.4	9.77	1.66
	Zinc	51.5	9.5	43.83	0.59
S-18c	Arsenic	1.8	NA	18.90	1.00
	Chromium	0.0	NA	1.08	<.01
	Nickel	0.0	1.9	4.42	0.67
WCA2F1	Arsenic	1.3	NA	35.78	0.49

<sup>a</sup>Exceedence of acute 10th centile for arthropods except for cadmium where fish are more sensitive; <sup>b</sup>Exceedence of chronic (NOEC) 10th centile is for all chronic toxicity studies; <sup>c</sup> Exceedences were based on cadmium acute toxicity to fish in Holey Land sites; <sup>d</sup> NA: not available.

of copper exceeding the sediment TEC was 99.96% at S-178 to 6.81% at S-177. The probability of zinc exceeding the TEC was 43.83% at S-178. The probability of chromium exceeding the sediment TEC was 39.11% at S-178 to 0.08% at S-176. The probability of cadmium exceeding the PEC in Holey Land tracts 2, 3 and 4 was between 6.96 and 13.97%. The probability of all of the metal COPECs exceeding the SQAG PEC was generally low (≤7.33%).

**Uncertainties**

*Exposure.* Exposure data for this assessment were obtained from the South Florida Water Management District monitoring program for 1990–2002 from 32 sampling sites in freshwater canals. This is the most comprehensive sediment contaminant database in south Florida. Although chemical analyses of all contaminants was from one laboratory, the total number of sampling sites in the monitoring program is limited considering the 1400-mile system of canals in south Florida. The sampling frequency is also limited since sites were sampled only 1–2 times per year and not consistently. Therefore, the database is inadequate to determine real differences in contaminant exposure between the wet and dry seasons.

Chromium is a COPEC based on measuring total Cr. Chromium speciation was not measured. We assumed that because AVS is formed in anoxic sediments, those sediments with measurable AVS concentrations will not contain concentrations of the toxic hexavalent Cr (VI) (Berry et al., 2004). Therefore, most of the chromium will be present as relatively non-toxic trivalent Cr (III).

Pore water concentrations for exposure distributions were estimated from the whole-sediment concentrations of COPECs based on the use of metal partition coefficients obtained from the literature by U.S.EPA (U.S.EPA, 2005). Partition coefficients are subject to several sources of uncertainty. For example, partition coefficients vary with pH with weight percent organic matter content and weight percent hydrous ferric oxides and corresponding oxides of aluminum and manganese (Janssen et al., 1997; Hassan and Garrison, 1996). Dissolved ligands in porewater (e.g., dissolved organic matter, anthropogenic organic acids) also may complex with metals, and reduce their affinity for sorption in proportion to the concentrations of ligands (Christensen et al., 1996). Jin et al. (1996) also reported that in systems with multiple metals there is competition among metals for sorption sites and a reduction in the partition coefficients compared with single-metal systems. Natural variability of sediment composition and associated pore waters may also result in variation of  $K_p$  for an individual metal. Furthermore, variability in laboratory techniques (e.g. metal detection limits and methods for analyses, presence of equilibrium conditions, etc.) by investigators to estimate partition coefficients may have added to uncertainties. Nonetheless, the U.S. EPA (2005) quantitatively ranked the confidence level for each metal partition coefficient based on the literature database. The U.S. EPA maintained a high level of confidence for the partition coefficients of arsenic, cadmium, copper, lead, and zinc but not for those for chromium and nickel.

It has also been demonstrated that many sediment-dwelling organisms form oxygenated burrows and may obtain metal tissue burdens from the overlying water and not from the sediment (Hare et al., 2001). Water (i.e., surface- and pore-water) may therefore be a more significant exposure route than sediment including ingestion of metal-contaminated particulates (Meyer et al., 2005).

*Effects.* Given the limited acute and chronic laboratory sediment toxicity studies available for the identified COPECs, we assumed that toxicity in pore water would be similar to water-only exposures and therefore used acute toxicity data from water only tests to prepare SSDs. There is uncertainty in this assumption since benthic organisms (infaunal and epibenthic) may show different sensitivities to metals than water column species.

There were insufficient acute and chronic water toxicity data for antimony to characterize SSDs. Chronic water toxicity data were not available for arsenic and chromium (III, VI). Therefore, chronic NOECs were not available for chronic risk characterizations of these metals. There were chronic water toxicity tests for lead, nickel and zinc but they were limited in number. Therefore, all NOECs from chronic tests were combined into one SSD for each metal.

As a result of the limited number of species used in acute and chronic toxicity tests for the COPECs there is uncertainty of extrapolating these data to responses of native species from South Florida ecosystems. However, many of the freshwater species used in toxicity tests with COPECs are native to south Florida ecosystems.

Using the 10th centile from the SSD of any metal may not be a sound and protective "toxicity benchmark" when keystone, endangered, threatened, commercially or recreationally important species represent part of the 10 percent of unprotected species. This is especially relevant within south Florida ecosystems since there are a large number of

threatened and endangered plant and animal species and species of concern as a result of loss of habitat and alteration of hydrological processes (Science Subgroup, 1996).

*Risk Characterization.* One source of uncertainty that was not considered is the potential effects of COPECs through joint or interactive effects with other contaminants. Runoff from agricultural and urban regions in South Florida is a concern for exposure to multiple metal and organic contaminants in South Florida canals (McPherson and Halley, 1996). Our characterization of ecological risk is limited to the locale of sites from which sediments were analyzed. However, there are regional implications, because of the likelihood of sediment transport to other parts of the water management system, including water conservation storage areas (WCA's), productive coastal estuaries, and Everglades and Biscayne National Parks.

There were insufficient chronic toxicity data for arsenic and chromium (III and VI) and chronic NOECs were not estimated. Therefore, there is uncertainty as to the extent of potential chronic risk for arsenic at five sites (Holey Land tracts SD 1, 2, and 3 and S-18C, WCA2F1) and chromium at four sites (S-176, S-177, S-178, S-18C). The C-111 sites are all potential sources of contaminants for ENP. Antimony was a COPEC but both the acute and chronic toxicity databases were limited so that risk characterizations could not be conducted.

## **Conclusions and Recommendations**

Based on a tier 1 hazard assessment of 11 metals in sediment at 32 sampling sites from south Florida freshwater canals, only arsenic, cadmium, chromium, copper, lead, nickel, and zinc exceeded FDEP SQAGs and were therefore classified as COPECs. In tier 2, the screening level PRA of the seven metal COPECs compared distributions of predicted pore water concentrations to distributions of toxicity effects and indicated that the risk associated with acute exposures of freshwater arthropods to copper (at S-177 and at S-178), and zinc (at S-178) was estimated to be high in the C-111 system, a source of water for Everglades National Park. In addition, the potential risk associated with chronic exposures to copper (at S-177 and at S-178) followed by lead (at S-176), was estimated to be high based on use of chronic NOEC 10th centiles. Small fish (e.g., mosquitofish) at S-178 have also shown high tissue residues of endosulfan sulfate, the metabolite of endosulfan (personal communication, P.R. Gardinali).

Copper followed by zinc and lead are COPECs that should be a priority for future sediment monitoring programs and risk assessments in south Florida canals (i.e., C-111 system) since these metals are located in areas that are potential sources of water that may adversely impact Everglades National Park. Furthermore, more toxicity data are needed for single metals in sediment in order to compare single metal toxicity distributions for organisms to distributions of total metal concentrations in whole sediment to assess the magnitude of overlap and potential risk.

Although there are uncertainties, this assessment provides regulators with a straightforward approach for determining metals of ecological interest in sediment and an estimate of their potential ecological risk. Chemical monitoring programs in south Florida generate valuable analytical data for the exposure analysis phase of ecological risk assessments. Better use of this exposure data becomes very relevant in south Florida freshwater systems as a result of the comprehensive restoration activities that are presently in progress and



the large number of plant and animal species that are threatened, endangered or of special concern in the state.

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