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National Park Service
U.S. Department of the Interior

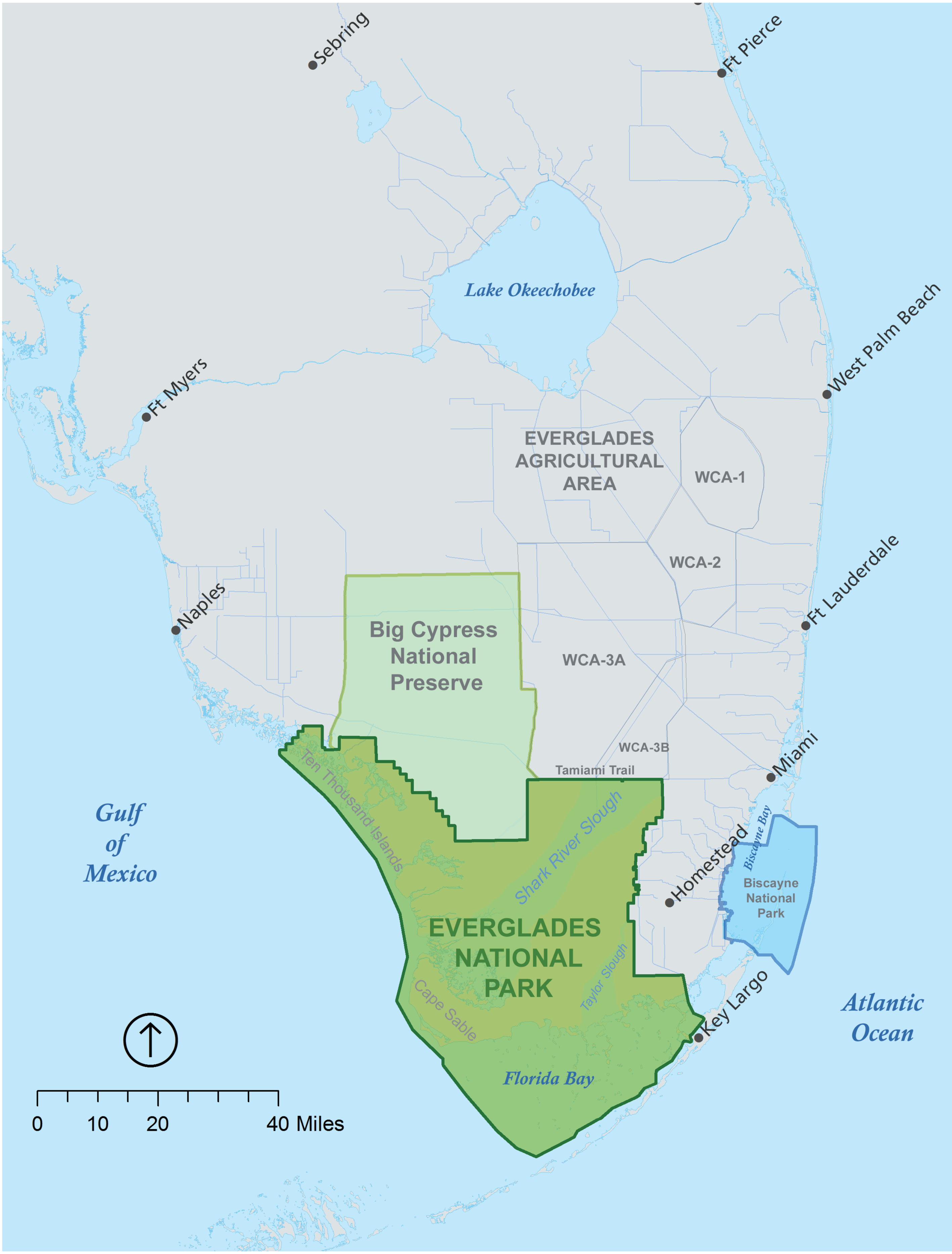
South Florida Natural Resources Center
Everglades National Park

Contaminant Assessment and Risk Evaluation Project

Everglades National Park, Biscayne National Park, & Big Cypress National Preserve

Summary Report

2016


Sebring
Ft Pierce
Lake Okeechobee
West Palm Beach
Ft Myers
EVERGLADES AGRICULTURAL AREA
WCA-1
WCA-2
Ft Lauderdale
Naples
Big Cypress National Preserve
WCA-3A
WCA-3B
Tamiami Trail
Miami
Ten Thousand Islands
Shark River Slough
Homestead
Biscayne Bay
Biscayne National Park
Gulf of Mexico
EVERGLADES NATIONAL PARK
Taylor Slough
Cape Sable
Key Largo
Atlantic Ocean
Florida Bay
0
10
20
40 Miles

Contaminant Assessment and Risk Evaluation Project

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Summary Report

Prepared by the

National Park Service
and
Florida International University
2016

South Florida Natural Resources Center
Everglades National Park
Homestead, Florida

National Park Service
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PREFACE

This report is a summary of the results and interpretations of data from the Contaminants Assessment and Risk Evaluation project (CARE), a study conducted by Florida International University and Everglades National Park. The CARE project was initiated in 2005 to provide information needed about contaminants in south Florida environments that may pose risks to the federally managed lands and waters of Everglades National Park (ENP), Biscayne National Park (BNP), and Big Cypress National Preserve (BCNP). The project was designed to identify specific contaminants that may pose a threat to natural resources, evaluate the scope of ecological risk, and develop a means of integrating complex data into ecological indices useful to resource managers. This report summarizes the results of the CARE project to assist the federal and state agencies with the planning of Everglades ecosystem restoration and the management of natural resources in south Florida. The definition of contaminants in this work includes chemicals and metals resulting from human activity, but excludes nutrients and mercury, for which there is a large body of scientific literature.

The working hypothesis for the project was that federally managed units such as ENP, BNP, and BCNP are sufficiently protected from significant exposures and risks associated with pesticide use in farming and urban practices by factors such as geographic distance, water management, and regulation of chemical use. To examine this hypothesis, a number of field and laboratory studies were undertaken to provide information on contaminants relevant to the three National Park units. In addition to providing baseline contaminants information in the study areas, the data were used in conducting ecological risk assessments relevant to park natural resources. The full project report (Gardinali et al. 2015) provides details on the project, including the project design, analytical and ecotoxicological methods, and the lines of evidence developed for the ecological risk assessments. The findings of the project have also been published in the scientific literature, where additional details on methods, results, and discussions can be found.

Joffre Castro
Piero Gardinali
Gary Rand

October 2016

INTRODUCTION

The Everglades is a region located at the southern end of the Florida peninsula and is characterized by a low, flat, wet plain covered by a wide, grassy river with alternating ridges and sloughs, covering an area of about 10,000 km^2. The freshwater portion of Everglades National Park (ENP) represents about one-third of the original Everglades, which historically extended for 160 km from Lake Okeechobee in the north to Florida Bay (FB) in the south, and 60 km from the Coastal Pineland Ridge in the east to the Big Cypress Flatwoods in the west. This extensive freshwater ecosystem comprised wet prairies, sawgrass marshes, cypress and mangrove forests, and coastal lagoons and bays, a portion of which was protected with the establishment of ENP. Today ENP, as well as Biscayne National Park (BNP) and Big Cypress National Preserve (BCNP), continue to provide a highly diverse area of wildlife habitats, surrounded by agriculture, urban development, and a regional water management system.

In the late 1940s, the federal government implemented a major water control project to provide water supply and flood protection for south Florida, which profoundly changed the hydrology and ecology of the Everglades. Today an extensive network of canals and structures allows the rapid redistribution of flows throughout the system but also facilitates the movement of pollutants, including agricultural pesticides, into surface waters (Harmon-Fetcho et al. 2002; Scott et al. 2005). Much of the water discharged into park coastal waters is a mixture of rainfall and runoff from the urban and agricultural areas of southeast Florida.

Sources of Pollution Adjacent to Protected Lands in South Florida

The activities of agricultural production, despite regulatory efforts, inevitably produce effluents composed of pesticides, herbicides, fungicides, and excess fertilizer. Urban landscaping activities, not as intensively regulated, produce similar pollutants. Other urban sources of pollutants include urban stormwater, the domestic waste stream, and mosquito control activities. Survey reports by the U.S. Department of Agriculture indicate that in the 16-county region served by the South Florida Water Management District, agricultural activities result in the application of nearly 45 million pounds of pesticide active ingredients per year, nearly double the national average. This includes 169 active ingredients, with 46 fungicides, 36 herbicides, 66 insecticides, and 21 other pesticides (FDACS 2010). In addition to chemicals currently used in south Florida, there is the presence of pesticides no longer in use. The organochlorine pesticide DDT (dichlorodiphenyltrichloroethane) was banned from use in 1972, but it and its breakdown products, DDE and DDD, persist in the south Florida environment.

Another class of contaminants, chemicals released by domestic consumers, has recently been identified as a potential pollution risk. Termed *chemicals of emerging concern* (ECs), common products like household chemicals, prescription and over-the-counter medication, antibacterial soaps, insect repellent, and compounds in vehicular emissions contribute to the diversity of man-made chemicals entering the region. Pharmaceuticals are specifically engineered to be biologically active and may persist in the environment. These compounds are largely unregulated, and their occurrence in the environment and their ecological effects are largely unknown.

Chemicals of Potential Ecological Concern (COPECS)

ORGANIC CONTAMINANTS

Since the mid-1980s, the South Florida Water Management District has been monitoring contaminants in south Florida surface water and sediments. Other agencies that have conducted relevant contaminant studies include the National Ocean and Atmospheric Administration, the U.S. Department of Agriculture, Miami-Dade County Department of Environmental Resources Management, the U.S. Geological Survey, and the U.S. Environmental Protection Agency (U.S. EPA).

In south Florida, recent monitoring data indicate that several pesticides—including DDT, its breakdown products DDE and 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 these 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 pose a high hazard to aquatic organisms (Harman-Fetcho et al. 2005).

METALS

While some metals are ubiquitous in the environment and some are essential micronutrients, all can be toxic to biota above some threshold concentration. Metals are introduced into the environment by weathering of rocks and as a result of human activity. In the Everglades ecosystem, mercury is the primary metal that has received consideration in aquatic systems (e.g., Rumbold 2005, 2006; Frederick et al. 2010). Because it is well documented, mercury was not included as part of the Contaminant Assessment and Risk Evaluation project (CARE). Metals typically are among the most common sediment contaminants (U.S. EPA, 2001) and metal concentrations correlate well with sediment toxicity (Field et al. 2002). Unlike pesticides, few studies have been conducted to examine the risk of metals in sediment from south Florida canals. Metals of ecological concern include those used in agriculture, such as copper and arsenic, and metals that originate from urban areas, such as lead, chromium, nickel, and zinc. Typically, these metals exhibit a toxic effect at relatively low levels and often may have a long-term, adverse environmental impact.

Assessing Environmental Effects

Chemical contamination is the presence of a substance where it either should not occur (e.g., the presence of a synthetic chemical) or occurs at concentrations above natural background concentrations. Pollution is contamination that results in, or can result in, adverse effects to human health or the health of wildlife species. All pollutants are contaminants, but not all contaminants are pollutants. The point at which a contaminant concentration has a biological effect is called the threshold, beyond which adverse impacts are expected. Many, but not all, contaminants have regulatory thresholds provided by the State of Florida or the U.S. Environmental Protection Agency.

Concentrations of a contaminant vary in time and location, particularly in water, making assessment of impacts a complex process. Chemical analyses provide essential information on concentrations as a first step. Another critical step is to ascertain whether they are pollutants—contaminant concentrations that cause adverse biological effects in the ecosystem. To evaluate the ecological significance of contaminants, where detected, requires a well-considered assessment of both chemical concentrations and measurements of biological effects to determine biological significance and risk of adverse impacts.

An initial step in assessing impacts is to screen the chemistry data to identify which sample sites and which contaminants merit consideration. Environmental data are often diverse and complex among sites and difficult to interpret in a meaningful way. To reduce complexity, the chemical data from the CARE project were integrated into indices that permit distinction between concentrations with little or no effect from concentrations that may adversely affect a single site or an area with multiple sites.

CONTAMINANT CONDITION INDICES

To determine if a metal concentration could have an adverse effect, it is compared to environmental quality standards, such as the Florida's Sediment Quality Assessment Guidelines, which provide effect thresholds for sediments (MacDonald 1994; MacDonald et al. 2003). To conduct a screening process, we used three ecological indices to identify *possible effects* (Po), *probable effects* (Pr), and a *contaminant condition index* (CI) that aggregates the Po scores for the metals in sediments for an overall measure of contaminant conditions at a site (Castro et al. 2013). For chemicals other than metals, which don't have quality standards, we developed an *overall status indicator* index (OSI) based on a critical concentration that aggregates site CIs within a geographic subregion. The critical concentration was estimated as the 85th percentile, following guidelines by the National Oceanic Atmospheric Administration. The OSI is a further refinement of the CI—aggregates CIs and scales them between 1 and 10—thus providing a simple but effective means of ranking degree of contamination. The CIs were aggregated because sometimes the number of samples with measurable levels of chemicals in this study was very small. For example, the fraction of detection in fish tissue samples was only 5 percent, in water 9 percent, and in sediments 31 percent. This often meant that there were not enough data points (detections) at individual stations to do a meaningful evaluation. Instead, groups of stations were aggregated (pooled) by region or by chemical type and then normalized to a 1-10 scale. An OSI of 10 indicates a much higher chemical concentration than an OSI of 1. For each of 14 subregions (Table 1), monitoring station data within a subregion were pooled for computation of an OSI for the subregion.

ECOLOGICAL RISK ASSESSMENT

Once chemicals of potential ecological concern (COPEC) that could be causing an adverse impact are identified, further assessment is made to relate the chemical data to specific effects on biological receptors (i.e., fish, wildlife). Methods have been developed to combine toxicity and its effect on a species to develop an estimate of risk of harm. The process, termed ecological risk assessment, is a complex set of scientific methods to define and estimate the probability and magnitude of an adverse effect. Ecological risk assessment techniques focused on the relationships between *exposure* (concentration of contaminant present) and *effects*, which is the toxicity response by the organism. Toxicity response varies widely among species and is influenced by environmental conditions. These data are developed from laboratory studies to provide the relationship between exposure and response across a range of contaminant concentrations and among multiple species.

For the CARE project, we used ecological risk assessment as a methodology to determine the nature and likelihood of adverse effects of pollution in the study areas. In general, we used the framework provided by the U.S. Environmental Protection Agency (U.S. EPA 1992; U.S. EPA 1998). To take into consideration some of the many factors that influence the probability and magnitude of the potential impact, we also employed a weight-of-evidence (WOE) methodology that uses multiple lines of scientific information to assess impacts (U.S.EPA 1998; Chapman et al. 2002). We used lines of evidence that included the screening indices, ecological sensitivity (toxicity response), uptake and storage rates of contaminants by organisms, degree of exposure, fates of the contaminant, and contaminant sources. Use of the WOE methodology for evaluation for contaminant data in the CARE project provided a more robust and more holistic approach to impact assessment, allowing predictions of risk that are of greater significance and relevance.

Field technician collecting a "grab" sample of canal water. FIU photo.

Project Design and Study Area

The CARE project was designed to:

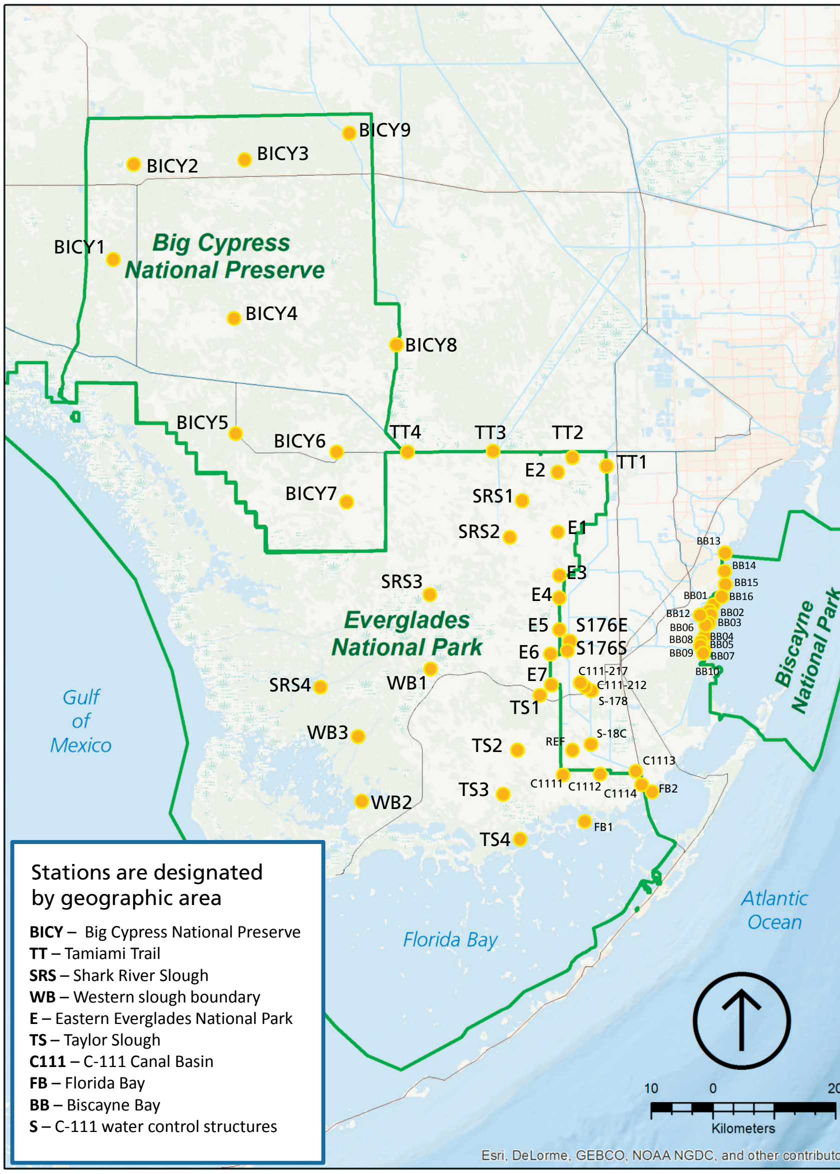
1. Improve environmental data in areas important to ENP, BNP, and BCNP with a monitoring program for pesticides, metals, and contaminants of emerging concern;
2. Identify chemicals and metals of potential ecological concern and assess the ecological risk associated with exposure to existing levels of pollution.

To accomplish these objectives, a monitoring study was initiated at sampling stations within ENP, BNP, and BCNP. Considered less affected by human activity, these areas are relatively pristine and represented a natural baseline. Areas on park boundaries and adjacent to ENP and BNP were similarly sampled to permit an evaluation of conditions on the borders of these parks, where natural resources are under the influence of agricultural land use, water management, and urban development. As contaminants were identified as potential risks, ecological risk assessments were conducted to better define the magnitude and probability of adverse impacts. Where appropriate, laboratory toxicity testing was conducted to fill information gaps to improve the quality of ecological risk assessment.

MONITORING STUDY

Monitoring stations were established within and adjacent to ENP, BNP, and BCNP (Fig. 1). Where feasible, these were sited at existing water quality monitoring stations to permit use of historical water quality data. Table 1 provides brief details of the monitoring network and how they are grouped into subregions. A complete description of monitoring sites may be found in the CARE project report.

Water, sediment, and fish/invertebrate tissue samples were collected between January 2006 and May 2009 from 30 stations within and around ENP, 9 stations within BCNP, 11 stations within BNP, 6 stations within the canal and control structures of the C-111 canal, and 3 stations in Loveland



Samples were analyzed for:

Organic compounds, such as:

- Organochlorine pesticides
- Organonitrogen herbicides
- Organophosphorus insecticides
- Phenoxy-acid herbicides
- Polyaromatic hydrocarbons
- Polychlorinated biphenyls

Metals:

- lead
- zinc
- arsenic
- copper
- nickel
- chromium

Chemicals of Emerging Concern:

- Caffeine – Domestic wastewater
- DEET – Insect repellant
- Triclosan – Bactericidal soaps
- Estrone – Human hormone
- Coprostanol –Domestic waste
- b-Estradiol – Human hormone

Figure 1. CARE project study area and monitoring stations.

Slough (C-111E). A station in lower southeast Taylor Slough was established as a reference station, isolated from the network of water management canals.

Samples were analyzed for organic contaminants (i.e., pesticides, PCBs, PAHs), and metals. The chemistry of environmental samples can be complex, and up to 10 methods could be applied for a particular sample.

Detection and measurement methods included techniques in mass spectroscopy coupled with gas chromatography, liquid chromatography, and inductively-coupled plasma generation. For details on sampling and procedures used in chemical analysis of the samples, please see the full project report.

Sediment toxicity and uptake data for endosulfan sulfate, a COPEC identified as a potential risk in previous studies, were not available for a relevant risk assessment. To fill this data gap and improve our risk analysis, we conducted over 200 toxicity tests as part of the CARE project, and used the information in conducting risk assessments for endosulfan. Detailed results and discussion of the toxicity and bioconcentration studies can be found in the CARE project report and in the published literature.

Results Overview

The monitoring study comprised a total of 3,243 samples and 73,852 determinations from a total of 50 sites in the three National Park units and adjacent areas.

Table 1. Monitoring station design for the CARE project, which provides the general geographic scope. Where detections of contaminants were few, site data were combined into subregional groups to be used for the interpretation of the environmental and statistical data.

Unit	Number of Stations	Description	Station IDs	Subregion Group ID
BCNP	7	North of US 41, except for BC05	BICY: 1-5, 8, 9	BCG1
BCNP	2	South of US 41	BICY: 6, 7	BCG2
BNP	11	Western boundary; mangrove fringe	BB: 1-4, 8, 9, 11, 12, 14-16	BBG1
BNP	4	Marinas	BB: 5, 7, 10, 13	BBG2
BNP	9	Open water[1]	BB: 17-25	BBG3
ENP	5	Northeastern boundary	E: 1, 3-6	EB
ENP	5	Eastern Florida Bay[1]	FB: 1-4; TS4	FB
ENP	9	Shark River Slough[1]	SR: 1-3, 5-8; EB2	SR
ENP	6	Taylor Slough[1]	TS: 1-3, 5, 6; EB7	TS
ENP	6	Tamiami Trail[1]	TT: 1-6	TT
ENP	4	Southwestern boundary	WB: 1-3; SR4	WB
Outside Park	9	Lower C-111 basin[1]	EP: 1-9	EP
Outside Park	7	Homestead Agricultural Area	HA: 1-7	HA
Outside Park	1	Reference station	OT	Ref

[1] Includes stations from other monitoring studies.

- A total of 196 chemicals, mostly in water but also in sediments and biological tissues, were targeted.
- The overwhelming majority of the analytes, with the exception of those with natural sources like metals, were *not detected* in a large portion (85%) of the samples tested.
- In water, analytes detected were dominated by atrazine, metolachlor, endosulfan sulfate, caffeine, DEET, and low molecular weight polyaromatic hydrocarbons (PAHs). Detections of sediment contamination were dominated by legacy DDT metabolites (DDE), endosulfan sulfate, hexachlorobenzene and both low and high molecular weight PAHs. Detections in fish tissue were dominated by endosulfan sulfate and legacy DDT metabolites (DDE).
- These detections reflect both the past and present use of agrochemicals and inputs from urban anthropogenic sources.
- Overall Status Indicators (OSIs) were used to rank the chemicals that posed a risk of adverse impacts and potentially impacted areas. Considering that OSIs are based on statistical thresholds (a substitute for the absence of quality standards) and thus not having a direct relevance to ecosystem health, OSIs could be used to identify chemicals whose presence needs to be evaluated more closely and regions subject to anthropogenic stress.
- Across all regions in the project, organic contaminants were detected 7% of the time in water, 15% of the time in sediment, and 3% of the time in tissue (Fig. 2).

An important finding from the CARE monitoring program is that among the large number of analyses conducted for contaminants (organic and inorganic), there were only a few compounds that represent risk, and they are limited to confined regions along the parks' boundaries. The CARE project also represents one of the first assessments for emergent contaminants in the region, and based on the low frequency of detections and small concentrations of individual chemicals, there is presently no widespread occurrence or evidence of transport of them into the watersheds monitored. There are areas on the boundaries of ENP and BNP, however, with an increased incidence of organic contaminants, described and discussed in the sections that follow.

The monitoring results also revealed that of the 10 metals evaluated, only copper, lead, and zinc had elevated concentrations in a few localized areas in ENP and BNP. Two other metals, chromium and arsenic, were also found to be evident but pose a lower risk of adverse impacts.

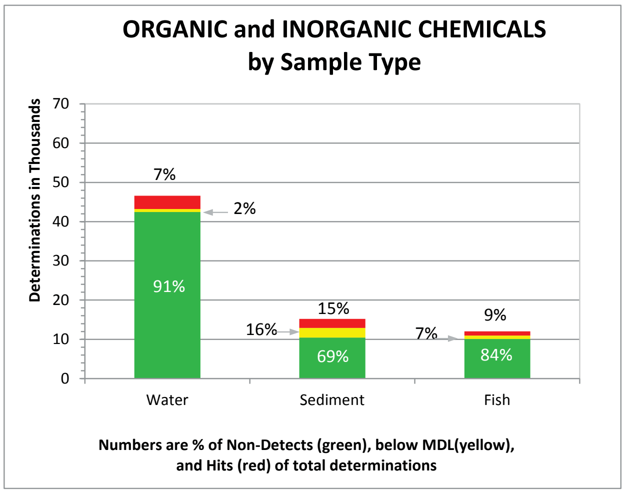


Figure 2. Summary of the frequency of detection of metals and organic chemicals in water, sediment, and fish during the CARE project.

CARE PROJECT RESULTS

Overview: Specific Contaminants of Concern

ORGANIC CONTAMINANTS

Of the suite of organic contaminants included in the CARE project for consideration, only two were found to constitute potential serious ecological risk. These were the metabolites of the legacy pesticide DDT (DDD and DDE) and those of the pesticide endosulfan (endosulfan isomers and endosulfan sulfate). Both are organochlorine pesticides, known for their persistence in the environment. The main environmental transformation product of DDT is 4,4 DDE, which had a high frequency of detection and relatively high concentration in sediment and water stations along the eastern boundary of ENP, and in the drainage basin of C-111 canal and S178 and in the Loveland Slough area. Fish body burdens (fish tissue concentrations) of DDE were also high at monitoring site S178.

Endosulfan sulfate, *a*-endosulfan, and *B*-endosulfan were often found in water samples. Occurrence and distribution of endosulfan isomers and endosulfan sulfate in water within ENP, BNP, and BCNP showed the highest frequency of detections and concentrations in stations along the eastern and western boundaries of ENP, and the drainage basin of C-111 canal. Endosulfan concentrations often exceeded the U.S. EPA water quality criteria for chronic impacts at several monitoring sites. Total endosulfan was also frequently detected in sediments and endosulfan sulfate was a major compound detected in fish tissue. Although the insecticide is being phased out by the U.S. EPA, it will still be used until 2016. Monitoring environmental residues should be continued at targeted areas in the C-111 canal system after its ban from use to fully understand the continuing impacts and ecological risk associated with this persistent contaminant.

METALS

Metals and metalloids are naturally occurring elements that become pollutants when human activity raises their concentrations in the environment above natural levels. Metal concentrations in water during the CARE study were within Florida water quality standards. However, based on United Nation water quality standards, sites in ENP (Shark River Slough) may be under stress from copper concentrations in water. From the 20 elements monitored in sediments, copper, zinc, and lead show significantly high concentrations in localized areas of ENP and BNP. Copper and zinc were elevated in marinas along BNP, while lead was detected in relatively high concentrations in the northern portion of ENP's eastern boundary. The eastern boundary of ENP is under stress due to its proximity to agricultural and urbanized areas which are a primary source of contaminants. The Everglades National Park Protection and Expansion Act of 1989 added 157,000 acres of former agricultural land, and their legacy agrichemical residues, along the eastern boundary of ENP. This area is under higher stress from contaminants and merits continued monitoring and periodic evaluation of potential pollution impacts.

METALS IN FISH

The two metals of concern in fish tissue were zinc and arsenic. Zinc concentrations exceeded the maximum value permissible reported by the Food and Agricultural Organization (FAO) of 50 µg g-1 (Qiu et al. 2011) in three fish species: sailfin fish (*Poecilia latipinna*) in Florida Bay, mosquitofish (*Gambusia* sp.) in the C-111 canal and NPS eastern boundary, and bluefin killifish (*Lucania goodei*) in Shark River Slough. Arsenic is toxic at low levels and tends to bioaccumulate, starting with plant uptake at the base of the food web. Zinc may become toxic at exposure levels sufficiently high enough to adversely affect metabolism.

The elevated levels of arsenic and zinc found in these fish species might be of ecotoxicological importance, stressing the need to continue monitoring and assessment projects. These species are part of the forage base for predators in the food web (i.e., birds, game fish, and reptiles) and the transfer of metals within the food web has ecological significance. Our results indicate some degree of stress is present in both freshwater and coastal food webs from zinc and arsenic. To better determine the risk of adverse impacts to wildlife, monitoring and assessment of these metals in consumer species is needed.

CONTAMINANTS OF EMERGING CONCERN

Emergent contaminants (EC) were related to specific localized inputs and are unlikely to be a problem in the near future. With respect to Everglades restoration, delivery of additional water should not impose a significant risk to the federally protected areas. There remains, however, a distinct concern should reclaimed domestic wastewaters be used to augment flows. In the CARE project, the three most frequently detected compounds in the EC group were DEET, caffeine and triclosan, if cholesterol is not included. The average concentrations of all ECs detected in the three National Park units were added up and results are shown in Figure 3. The concentrations of ECs measured in the CARE study were relatively low and do not present an immediate risk of harm to the biota. However, the presence of hormones, though infrequent, were high enough (up to 6.0 ng L^{-1} of estrone) to merit further investigation because of the potential ecotoxicological implications towards fish and reptile populations.

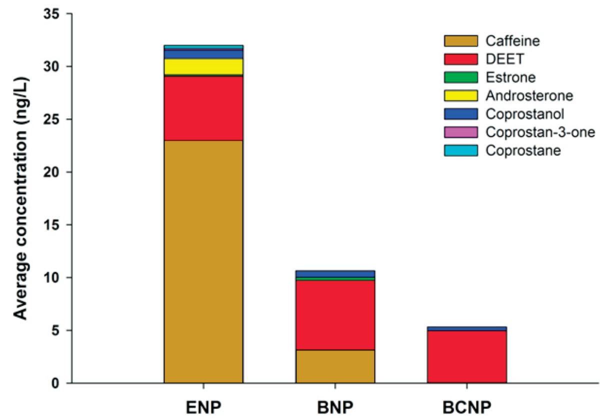


Figure 3. Average aggregate concentrations of all pharmaceuticals detected by park unit.

Environmental Indices

To assist in evaluating the chemical concentration information for soils/sediment from the monitoring study, we calculated environmental indices (EI) of possible effects (EI_Po) and probable effects (EI_Pr) (Castro et al. 2013). We also calculated a site condition index (CI) that combines the measures of EI_Po and EI_Pr data at a monitoring station (Castro et al. 2013) to provide a measure of site quality. A CI is computed only at sites with concentrations high enough to meet or exceed the threshold for adverse effects. To better understand the distribution and status of contaminants across the landscape, we employed an overall status index (OSI) that aggregates data from the group of sites within a subregion (Fig. 4, see also Table 1). We used these indices in screening-level evaluations to identify trace metals and organic chemicals whose concentrations approach or exceed toxic conditions and merit a more comprehensive analysis of ecological risk. The following tables of resulting indices identify important COPECs that should receive careful consideration when evaluating the potential impacts associated with hydrologic restoration within or adjacent to the CARE project area. While the indices represent environmental conditions at a site or within a subregional group, they are also a measure of pollution stress on species that depend on the area.

METALS

The sites most affected by metal contamination with probable adverse impacts (Table 2, EI_Pr) are at the public marina site BB10 adjacent to BNP and at ENP eastern boundary stations E1, E3, and E5—the EL_Pr index shows probable effects for a metal at a single site. These sites were also identified as having a high metal condition index (Table 3, CI)—this index is a measure of contamination from multiple metals at a site. Monitoring sites BB10, E3, and E5 are the top three sites affected by metal contamination. Monitoring sites in ENP with high CIs were mostly located along the eastern boundary of the park (E1 through E6, except E2) and in the lower reaches of Shark River Slough (SRS3). Stations along the eastern boundary of ENP appeared to be most heavily affected by lead (Pb), zinc (Zn), and chromium (Cr), likely from agricultural and urban runoff.

Some of these stations were located in or near former agricultural lands, which were part of the Homestead agricultural area and had been known to be a source of pesticides and nutrients to nearby marshes and coastal basins (Scott et al. 2002; Harman-Fetcho et al. 2005; Carriger et al. 2006).

For BCNP, sites with a CI greater than 0 were located within two major flow ways in the southern half of the preserve (BICY5 and BICY6), where chromium (Cr) appears to be of concern. Because Cr is strongly correlated to iron and aluminum in the samples, it is inferred that the high Cr observed at these stations may have come from soil erosion (Guertin et al. 2004), caused by past or on-going construction projects

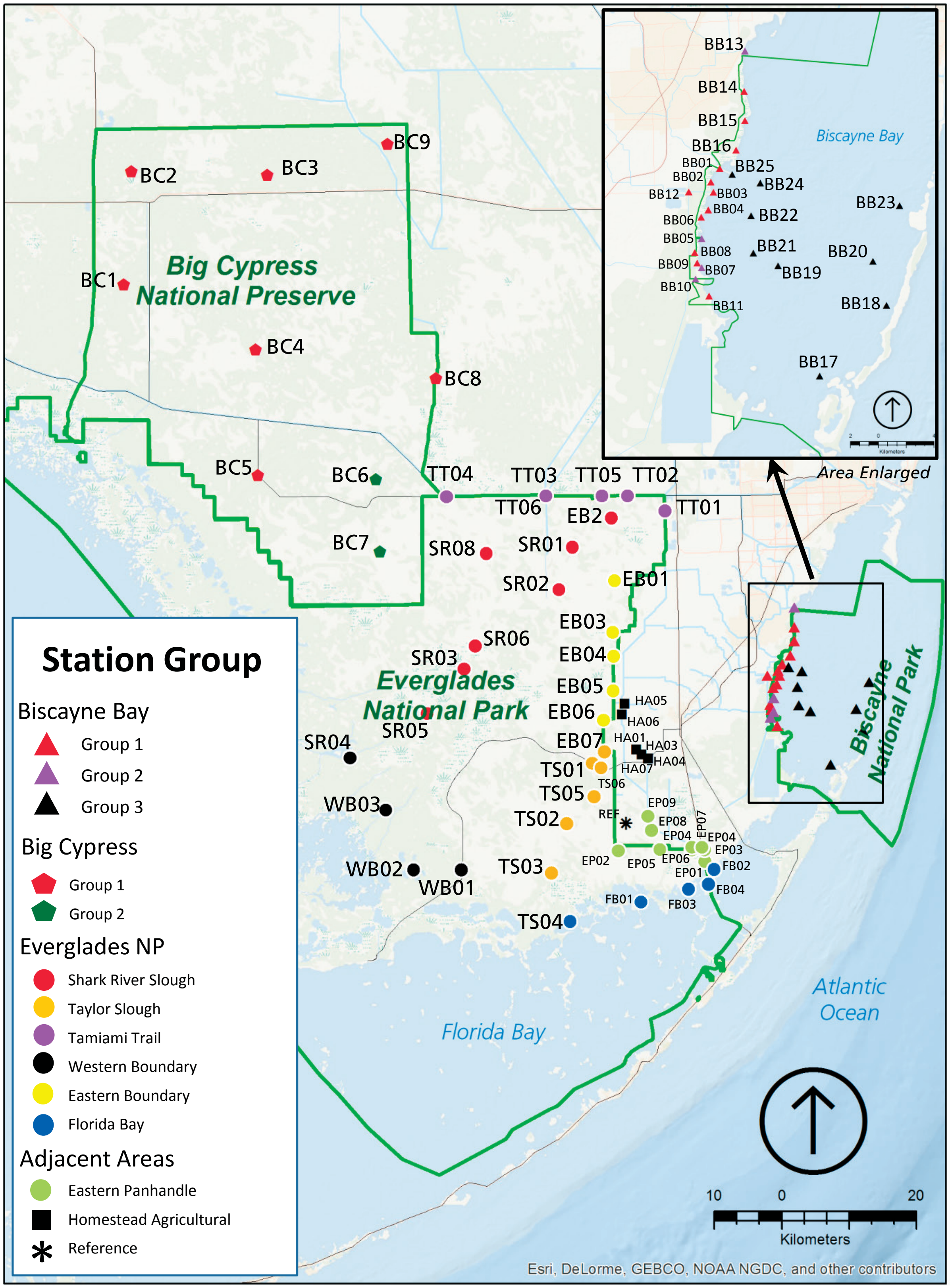


Figure 4. **Sampling station groups within Everglades National Park, Big Cypress National Preserve, Biscayne National Park, and adjacent areas. Inset shows the sample sites within and along Biscayne National Park.**

Table 2. Soil/sediment metal indices of effects. Of the ten trace metals measured, five had concentrations above effect-level standards: arsenic (As), chromium (Cr), copper (Cu), lead (Pb), and zinc (Zn). Higher index values indicate higher potential for adverse effects.

Park	Metal	Monitoring Site	Index of Possible Harm: EI_Po	Index of Probable Harm: EI_Pr
Big Cypress National Preserve	Cr	BICY5	0.34	
		BICY6	0.25	
Biscayne National Park	Cu	BB10	11.32	1.13
		BB1	0.48	
		BB3	0.39	
		BB5	0.09	
	Zn	BB10	0.47	
Everglades National Park	As	SRS3	0.10	
	Cr	E5	2.56	0.39
		E6	0.78	
		E3	0.49	
		E1	0.34	
		E4	0.03	
	Pb	E3	9.54	1.95
		E1	3.91	0.37
		E5	2.55	
	Zn	E3	0.69	
Adjacent to ENP	Pb	S178	0.34	

Table 3. Summary of contaminant condition indices (CIs) and overall status indices (OSIs) calculated for monitoring sites using effect-level standards and sediment metal concentrations. A lower CI means less contamination, but all sites with a CI have metal concentrations high enough to represent an impact risk. The OSI ranks the sites' index of effect from least (1) to most (10).

Location	Monitoring Site	Metals in Sediments	
		Contaminant Condition Index (CI)	Contaminant Overall Status Index (OSI)
Big Cypress National Preserve	BICY5	0.42	1
	BICY6	0.25	1
Biscayne National Park	BB10	11.78	10
	BB1	0.48	1
	BB3	0.39	1
	BB5	0.09	1
Everglades National Park	E3	10.72	9
	E5	5.12	5
	E1	4.25	4
	E6	0.78	2
	SRS3	0.10	1
	E4	0.03	1
Adjacent to ENP	S178	0.34	1

upstream of these stations. For BNP and vicinity, sites with a relevant metal CI are located within the Bay Front Marina (BB10), Black Creek Marina (BB1), the Princeton Canal (BB3), which drains several nurseries, agricultural fields, and urban areas and may collect leachate from a nearby landfill (Long et al. 1999; O'Donnell et al. 2005), and the Military Canal (BB5), which collects runoff from a partially closed military airbase (classed as a U.S. EPA Superfund Site). At sites adjacent to ENP, the site with a significant CI was S178, which drains agricultural fields from the Loveland Slough basin. Although lead (Pb) was the only metal of concern identified here, this site has received a great deal of attention for its high levels of pesticide contamination (Miles and Pfeuffer 1997; Fulton et al. 2004; Carriger et al. 2006; Carriger and Rand 2008a, b). Figure 5 shows the distribution of CIs across the CARE study area. The OSI conveys the same information as the CI, except that it is scaled between 1 (least effects) to 10 (most effects).

ORGANIC CONTAMINANTS

While a large number of organic chemical contaminants were measured (176 analytes), the assessment of the data identified only a few compounds as potential risks to parks and preserve resources within the CARE study area. Because of the low frequency of detections, data from a sample type (fish, sediment, and water) or within station groups were pooled to calculate an overall status index (OSI), discussed in the following sections.

Organochlorine Pesticides and PCB Compounds

Both organochlorine pesticides and polychlorinated biphenyl (PCB) compounds are considered persistent organic pollutants, characterized by a long resident time in sediment. The three highest scoring organic contaminants (Table 4) were 4,4' DDE for fish tissue and sediment—OSI was 10 (highest) for

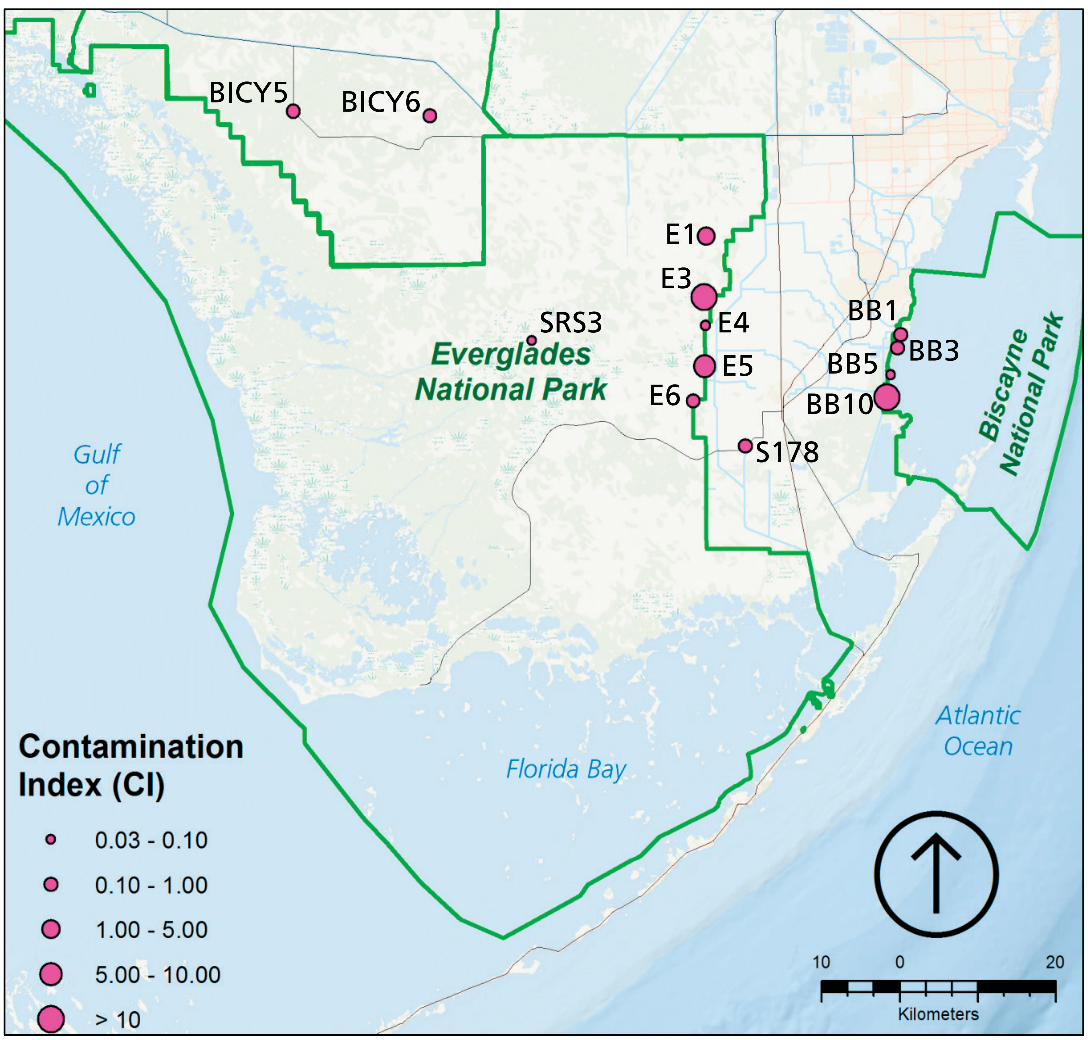


Figure 5. Geographic distribution of the Contaminant Condition Index (CI) for metals in sediment.

Table 4. Overall status indicators (OSI) for the three highest ranking organochlorine pesticides at all sites sampled.

PESTICIDE	OSI			OSI Summary: Fish-Sediment-Water
	FISH	SEDIMENT	WATER	
4,4' DDE	10	10	4	10.10.4
Endosulfan sulfate	7	2	10	7.2.10
Endosulfan α	2	7	3	2.7.3

fish and sediment and 4 (medium) for water, 10.10.4); endosulfan sulfate in fish tissue and water (OSI 7.2.10); and endosulfan in sediments (OSI 2.7.3).

The OSI for organochlorine pesticides in subregional groups of sites was computed for fish tissue, sediment, and water (Table 5). The Homestead Agricultural area (HA) has, by far, the highest scores of all regions (OSI Summary: 10.10.10) for fish tissue, sediment, and water. The HA is an area of intensive agricultural activity, with winter and summer crops, located just east of Everglades National Park and separated by the L31N Canal in the north and C-111 Canal in the south . The high OSI values for the Homestead Agricultural Area are likely due to continued detection of elevated concentrations of total endosulfan (sum of the three forms of endosulfan, α + β + endosulfan sulfate).

The second highest OSI score (OSI Summary: 1.7.1) was found in Big Cypress National Preserve, Group 1 (BCG1), in the northwest area downstream from agricultural areas around the town of Immolakee. The Northeastern boundary group (EB) in Everglades National Park has the second highest score for fish tissue (OSI Summary: 4.1.1).

Organonitrogen Herbicides

Commonly used organonitrogen herbicides in south Florida include atrazine, bromacil, metolachlor, norflurazon, and simazine. This class of compounds was detected only in water, thus the OSI consists only of the water score. The highest OSI was in the Tamiami Trail group (OSI= 10, not shown), which is the northern border of Everglades National Park, and the organonitrogen herbicide of greatest concern was atrazine (OSI= 10), a widely used herbicide in agricultural areas south of Lake Okeechobee. The presence of atrazine in this region of the ENP may be explained by the fact that a large fraction of the surface water inflows into the park are delivered by structures along the Tamiami Trail. The discharges may be characterized by a strong agricultural signature typical of surface runoff from the Everglades Agricultural Area, south of Lake Okeechobee. All other scores, by region or pesticide, were significantly lower than 10 (OSI< 3.5).

Polycyclic Aromatic Hydrocarbons (PAHS)

Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 different chemicals that are typically released from burning organic substances, such as oil, wood, coal, trash, plastics, or may be released from agricultural burning or transportation activities. The OSI for PAHs includes scores for fish tissue, sediment, and water. The eastern boundary (EB and EP regions) of Everglades National Park had the highest scores. In the EB area, the highest score was for fish tissue (10.3.1) and in the EP area the highest score was for sediments (0.10.1). The eastern boundary of Everglades National Park is one of the regions of this study most affected by agricultural and urban development. Common sources of PAHs in the south Florida environment are from human activity, including burning organic materials such as vegetation/wood, gasoline (driving and boating), oil, and plastics.

Ecological Risk Assessment Results: Metals

The following sections identify important metals that should receive careful consideration when assessing changes to the landscapes and hydrology within or adjacent to DOI-managed lands. While the indices represent environmental conditions at a site or within a subregional group, they are also a measure of habitat quality for species that depend on the area. Based on our results, metals that are priority contaminants of potential ecological concern (COPECs) to DOI-managed lands in south Florida are, in order of importance, copper, zinc, arsenic, chromium, and lead.

COPPER

Copper (Cu) should be considered the most important COPEC to natural resource managers in south Florida. This is based on existing literature and the CARE project findings:

Table 5. Overall status indicators (OSIs) for organochlorine pesticides based on concentration data within site groups.

Locale	Description	Subregion Group ID	OSI FISH	OSI SEDIMENT	OSI WATER	OSI Summary: Fish-Sediment-Water
Big Cypress National Preserve	North of US 41, except for BC05	BCG1	1	7	1	1.7.1
	South of US 41	BCG2	1	1	1	1.1.1
Biscayne Bay National Park	Western boundary; mangrove fringe	BBG1	1	1	1	1.1.1
	Marinas	BBG2	1	2	1	1.2.1
Everglades National Park	Northeastern boundary	EB	4	1	1	4.1.1
	C111 outside ENP	EP	2	3	1	2.3.1
	Eastern Florida Bay	FB	1	3	1	1.3.1
	Shark River Slough	SR	1	2	1	1.2.1
	Taylor Slough	TS	3	3	1	3.3.1
	Tamiami Trail	TT	1	1	1	1.1.1
	Southwestern boundary	WB	1	1	2	1.1.2
Homestead Agricultural Area	Agricultural area between ENP and BNP	HA	10	10	10	10.10.10

Existing Literature

- The widespread distribution and high volume use of copper in Florida:
  - In agriculture as a fungicide,
  - In marinas as an antifoulant toxicant (public use),
  - In surface water as an algaecide,
- Cu is prevalent in soil above background concentrations, especially in citrus agriculture areas,
- High copper concentrations have been documented in the edible tissue of the Florida apple snail, the main source of food for the endangered Everglade snail kite,
- Cu bioconcentrates in aquatic organisms and it is persistent in aquatic environments,
- Prior and present background information on soil and sediment levels and ecological risk assessments of Cu in south Florida indicate significant environmental exposures and potential risks to aquatic organisms.

CARE Project Findings

- Cu concentrations exceeded water quality criteria (subregions WB and SRS),
- Cu concentrations in sediment exceeded probable effect levels at sites BB1 and BB10 and was high at sites E3 and S178,
- Biscayne Bay sediment copper concentrations were consistently higher than at other areas measured,
- Cu had the highest probable effect index at site BB10,
- The sediment bioaccumulation factor for Cu by fish was greater than 1,
- Ecological risk assessment conducted for Cu indicated that it has impacts at the lowest concentrations of all metals detected and for the highest potentially affected fraction of species tested (PAF) for organisms at the base of the food chain (plants/algae),

- Cu has the highest PAF values from sediment exposures for arthropods,
- PAF values for fish and plants/algae at sites EP, BBG1 and BBG2 were also relatively high,
- Ecological risk assessment conducted for Cu indicated that Cu has the lowest estimated hazardous concentration at which 5% of the species from a distribution exhibit an effect.

ZINC

As with lead, zinc (Zn) was identified in earlier studies as a COPEC in sediment for Biscayne and Everglades National Parks (Rand and Gardinali 2005) and in sediments of south Florida canals (Rand and Schuler 2009). The CARE study results indicate:

- Concentrations of Zn in sediment exceed possible effect concentrations at sites E3 and BB10, but were also high at other sites,
- Zn concentrations were higher in fish tissue at SRS, Loveland Slough, and EB than at other sites,
- The highest bioaccumulation factors (BSAFs) were at FB and TS. The BSAF for Zn in fish was also greater than 1,
- High msPAF values (high PAFs based on multiple substance exposures) for plants/algae, at sites in regions BBG1 and BBG2,
- For Zn concentrations in water there were:
  - High potentially affected fraction of species (PAF) values for arthropods, at site EB,
  - High multiple species PAF values for plants/algae, at sites in regions BBG1 and BBG2,
  - High multiple species PAF values for arthropods, at sites in region BBG2.

ARSENIC

Arsenic (As) concentrations in sediment exceeded the possible effect levels at CARE site SRS3. The biota sediment accumulation factor for arsenic in fish was greater than 1, indicating arsenic uptake, which is associated with food web impacts. Like copper, arsenic causes impacts at low concentrations and affects many species (high PAF values) of organisms at the base of the food chain—plants/algae. Plants, including algae, are a food resource in the diet of many invertebrate and fish species, at various times in their life cycles. The latter is significant since fish tissue concentrations of arsenic from Florida Bay were much higher than those found at other areas.

CHROMIUM

Chromium (Cr) was also identified as a COPEC in sediment of south Florida canals based on metals monitored at 32 sampling sites, based on a weight-of-evidence assessment:

- Cr had a high exceedance probability at S178 (Rand and Schuler 2009),
- Cr had the highest probable effect index at site E5 in the CARE project,
- Concentration of Cr exceeded the possible effect level at site BICY5 and BICY6 in BCNP, and at sites E1 through E6, except E2, at ENP,
- The potentially affected fraction of all species exposed is high and indicates high potential risks from Cr to aquatic organisms for:
  - Arthropods, fish, plants/algae at sites in subregions: BCG1, BCG2, EB, BBG2, FB, and WB (West Boundary of ENP),
  - Fish and plants/algae at sites in subregions: SR, TS, TT and BBG1.

LEAD

In earlier studies, lead (Pb) was identified as a COPEC at sites in subregions EB and TT (Rand et al. 2005). Lead has also been identified as a COPEC in sediment of south Florida canals based on metals monitored at 32 sampling sites (Rand and Schuler, 2009). Lead had the two highest probable effect index at sites E3 and E1 in ENP. The concentration of lead exceeded the probable effect index at E5 in ENP and at site S178 in the Loveland Slough—adjacent to ENP.

Ecological Risk Assessment Results: Organic Contaminants

Out of over 40 organic COPECs evaluated, two were identified as meriting concern: the organochlorine pesticide endosulfan and the metabolites of the legacy pesticide DDT (DDE and DDD).

ENDOSULFAN

Endosulfan sulfate, the metabolite of the pesticide endosulfan, was identified early in the project as a contaminant of potential concern based on previous studies. During the CARE project, it was detected along the eastern boundary of ENP adjacent to the Homestead Agricultural Area (HAA). Exposed organisms tend to either accumulate the chemical preferentially or to metabolize the parent compound rapidly. The characterization of water, sediments, and biota from the Loveland Slough area clearly indicated the introduction of endosulfan into aquatic habitats through agricultural application, with a fast uptake and transformation by exposed aquatic organisms. CARE exposure studies indicated relative high toxicity in water and sediments and thus relatively high risk to nontarget organisms. Elevated concentrations of endosulfan sulfate were found in sediments, waters, and organisms in the Loveland Slough region, with the site at S178 being the most contaminated. In contrast, the lower portions of the C-111 basin leading to Florida Bay and Biscayne Bay were less affected by chlorinated pesticides, including endosulfan.

As a result of this information and that of other studies, the U.S. EPA has decided to ban the use of endosulfan in 2016. Although the insecticide is being phased out, it will still be used until 2016; therefore it should be monitored at targeted areas in the C-111 canal system during and after its ban to fully understand the effects of the change in use and the area that may still be potentially affected.

DDT (DICHLORODIPHENYLTRICHLOROETHANE)

Developed in the 1940s as one of the first synthetic pesticides, DDT was banned from use by the U.S. EPA in 1972. The main environmental transformation product of DDT is 4,4 DDE, which is frequently detected in water and sediment samples from ENP, BNP, and BCNP. It has a high frequency of detections and concentrations in sediment and water stations along the eastern and western boundary of ENP, and the drainage basin of C-111 canal/S178 and Loveland Slough areas. Tissue concentrations of DDE are high at site S178. Although DDT has been banned for over 30 years, the occurrence of this relevant COPEC is probably related to legacy farming activities, potential transport of contaminated sediments as a result of their disturbance during Everglades restoration projects or drainage modifications. The presence of DDE in sediments and wildlife body burdens represent an ecological stressor that merits ongoing consideration.

SUMMARY

The CARE project is the most comprehensive analytical chemistry monitoring and ecological risk assessment conducted in south Florida to-date. The analytical components of the project included 50 stations which were used to sample and analyze water, sediment, and biota tissue from ENP, BNP, and BCNP for chemicals of potential ecological concern and 20 common emerging contaminants (pharmaceutical and personal care products) including human hormones. Toxicity tests were also conducted according to standard methodologies in the laboratory with test species exposed to field-collected whole sediment samples from saltwater and freshwater stations using survival and growth as measures of effects. A number of ecological risk assessments were conducted using historical chemistry data for pesticides and metals. To evaluate the biological significance of the CARE chemistry data, we also conducted an integrated aquatic ecological risk assessment, using a weight-of-evidence approach with multiple lines of evidence to assess the risk of pollution impacts in the CARE study area (Table 6).

One of the most important results of the project is that among the large number of contaminants measured (organic and inorganic) there were only a few compounds that represented immediate potential risks, and these were mostly limited to border regions adjacent to contamination sources. From over 40 organic chemicals of potential ecological concern, two were identified from CARE-project data as meriting concern: the organochlorine pesticide endosulfan and the metabolites of the legacy pesticide DDT (DDE and DDD). Two metals, copper (Cu), and arsenic (As), were identified as having a high ecological risk potential, primarily at sites in eastern ENP and coastal BNP.

Table 6. Summarized rank of importance of chemicals that represent contaminant risk based on the assessment of multiple lines of evidence produced during the CARE project and supplemented by available literature/studies (see legend below).

Line of Evidence		Inorganic					Organic	
		Cu	As	Cr	Pb	Zn	DDD/DDE	EndoS
Source	Anthropogenic	Yes	No	?	No	No	No	Yes
	Bioavailable	Yes	Yes	?	No	No	No	Yes
Exposure	Concentrations	Yes	Yes	?	Yes	No	No	Yes
	Exceedances	?	Yes	Yes	Yes	Yes	No	Yes
Fate	Transport	No	?	No	No	Yes	No	Yes
	Bioaccumulates	Yes	Yes	No	No	No	Yes	Yes
Risk	Risk Assessment Results	No	No	Yes	No	No	No	Yes
	Keystone Species	?	Yes	?	No	No	No	Yes
Overall Risk								

LEGEND - Yes or No is assigned according to these conditions:			
Yes	There is a potential detrimental impact.		
No	There is no potential detrimental impact.		
?	Unknown		
Exposure	Concentrations	Were concentrations substantially higher than the 90th percentile (90%) for the exposure benchmark data?	
	Exceedances	Did concentrations exceeded state or federal standards?	
Risk	Risk Assessment	What is the probability that exposure concentrations will exceed concentrations protective of aquatic life?	
	Keystone Species	Could any protected, federally-listed, or primary producer species potentially become affected?	
Source	Anthropogenic	What was the source of the chemical and is it used regularly or in high quantity?	
	Bioavailable	Could the chemical become bioavailable?	
Fate	Transport	Could the chemical be mobilized and transported by water or air?	
	Bioaccumulates	Could the chemical accumulate through the food web?	
Overall	Low potential impact		One or more impact factors were present, but there were low concentrations, limited reach, and little or no bioavailability of the contaminant.
	Moderate potential impact		More than two indicators including elevated concentrations, some exceedances, bioavailability and risk.
	High potential impact		The majority of the lines of evidence factors became an impact consideration.

RECOMMENDATIONS AND FUTURE CONSIDERATIONS

Implementation of the Comprehensive Everglades Restoration Plan (CERP) under the Water Resources Development Act of 2000 requires acquisition of thousands of acres of land for maintaining hydrologic buffer areas and for the creation of storm-water treatment areas, water storage reservoirs, and wetlands. A large portion of these lands is currently or was formerly agricultural—managed for row crops and citrus fruit orchards and once treated with fertilizers, soil additives, and pesticides. Besides copper, present in herbicide and fungicide formulations, other metals (arsenic, chromium, lead, and zinc) may also be present as impurities in fertilizers and pesticide formulations.

Sediment in aquatic systems is therefore a natural reservoir for metals present in surface runoff. Under the CERP, metal-enriched soils of acquired lands may be periodically or permanently flooded, converting dry aerobic environments to inundated anaerobic sediments which will likely promote the mobilization of Cu and other metals from the soils. Comprehensive chemical and biological monitoring, in concurrence with extreme hydrological changes, should be a priority for future projects to understand the potential risks associated with re-wetting of areas affected by changes in land uses. While there are several metals of concern as contaminants in south Florida, it is strongly recommended, and critical, that copper be at the top of the list for further biological and chemical monitoring, especially in areas in or near citrus agriculture.

In freshwater and saltwater, chemical monitoring should consist of analyses of water, sediment, and tissue in biota (benthic and water column organisms including plants). In the watersheds, analyses of soil/sediment and surface runoff should also be considered. The monitoring could initially consist of sampling two times per year to evaluate active versus inactive periods of fertilizer and fungicide usage. Biological background data (from literature) of zooplankton and phytoplankton populations should first be collected in the areas where chemical analyses are being conducted to determine the dynamics of these populations overtime. The latter will provide results where biomonitoring of populations should continue and be more intensive. The objective would be to determine whether any potential relationships exist between metal measurements in water, soil, sediment and tissue and the population dynamics of phytoplankton and zooplankton. The emphasis should be on trophic transfers at the base of the food chain: the primary producers, phytoplankton and

Recommendations:

- Long-term monitoring will be needed to assess the success of the endosulfan ban in 2016 in reducing endosulfan pollution in the C111 drainage.
- The relationship between managed hydroperiods with respect to metal speciation and bioavailability should be fully explored for elements like copper.
- Data gaps still exist in the understanding of the trophic transfer of contaminants already present in the system.
- Application of CI and OSIs will greatly benefit the interpretation of continued assessments to prevent further degradation by early intervention.
- The focus of future efforts should consider changes in land use, water delivery, and the introduction of emergent pollutants to the ecosystem and how they may affect habitat quality in affected areas.

zooplankton. The other metals (As, Cr, Pb, Zn) are also of ecological concern and should be considered in the design of studies on the fate of metals in the Everglades ecosystem.

The presence of legacy pesticides (DDD/DDE and endosulfan sulfate) should be carefully monitored in soils, sediments, and benthic organisms on a yearly basis in those localized areas designated in this and other available reports to establish if reductions in concentrations are observed over time. Despite the long-term ban on DDT, residues of its metabolites are still present in aquatic fauna in south Florida environments. For endosulfan, impact assessments in low and high trophic level organisms should be continued to evaluate the results of its ban beyond 2016. It will be extremely useful to determine the trophic transfer of existing residues after use of this highly persistent pesticide is discontinued.

Creation of a regulatory framework often occurs after pollution impacts are initially detected; as a consequence, some of these chemicals have spread globally before their usage was limited. Our initial assessment of selected pharmaceuticals was an example of proactive, preregulatory consideration of the emerging contaminants group of chemicals. To avoid potential long-term problems, the effort should continue, particularly with respect to future changes of water delivery from the implementation of restoration projects. Wastewater reuse, an attempt to augment available water, presents a specific challenge in evaluating contaminant risk and avoiding damage to wildlife populations.

Despite the overall efforts of the CARE project, biological samples were collected only from fish and other selected organisms at the lower end of the food chain with the specific aim to observe localized micro-environments. Additional evaluation of the presence of contaminants in tissue is recommended, to include systematic or opportunistic sampling of wading birds, reptiles, and small mammals. In addition to providing the status of body burdens among different trophic levels, the fate and rates of transfer of contaminants will improve assessment of wildlife and habitat health in the areas under protection.

Land use patterns in the urbanized areas of Monroe, Collier, and Miami-Dade Counties have been fluid in the last decade due to the volatility of the housing market. Areas adjacent to ENP, BNP, and BCNP have been subjected to persistent shifts from agricultural and residential/commercial usage. As a result, anthropogenic emissions from both activities are likely a source of potential stresses on wildlife resources from multiple, but chemically variable, sources. We recommend that long-term contaminant monitoring in key sentinel locations be maintained. The CARE project provided a set of management tools, the Contaminant Condition Index (CI) and the Overall System Indicator (OSI), that use this information to help assess contaminant status in a simple yet systematic approach. The objective would be to establish a proactive means of supporting early intervention actions, rather than create the need for habitat remediation or trigger regulatory actions after degradation of protected areas.

The reality is that the bulk of the water available for Everglades restoration is coming from reservoirs already impacted by human activities. Getting water quantity and delivery timing right may actually be the easier step; getting the water quality right will need a concerted, comprehensive, and long-term effort of monitoring and ecological risk assessment to identify and resolve contaminant issues with a science-based decision-making process.

PUBLICATIONS BASED ON CARE PROJECT RESULTS

The following publications resulted as direct or indirect contributions of work by participants in the CARE project.

Analytical Chemistry

Arroyo, L., and P.R. Gardinali. 2006. Determination of phenoxy acids herbicides in organic rich sediments by (ASE-SPE) and electrospray ionization-mass spectrometry (ESI-LC/MS). Revista Costaricense de Ciencias Forenses 1: 45-53. "The article describes a robust HPLC/MS analytical method for the analysis of a group of commonly used herbicides in typical marsh sediments and soils with extremely high levels of organic carbon."

Arroyo, L., T. Trejos, P. Gardinali, and J. Almirall. 2009. Optimization and validation of a LA-ICP-MS method for the routine analysis of soils and sediments. Spectrochimica Acta Part B 64:16-25. "The article describes a simple, rapid and sensitive method for the routine analysis of trace elements on sediments and soils by UV-ns-LA-ICP-MS. The homogenization procedure that reduces the particle size of the samples to less than 1 m diameter was found to be a key factor to allow for a representative sampling of the bulk soil at the micro-scale and to improve reproducibility and cohesion of the sample without requiring the use of any binder."

Arroyo, L., T. Trejos, T. Hosick, S. Machemer, J. Almirall, and P. Gardinali. 2010. Analysis of soils and sediments by laser ablation ICP-MS: An innovative tool for environmental forensics. Environmental Forensics 11:315-327. "This article describes the applicability of a rapid laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) method for the analysis of soil and sediment samples with broad chemical and physical properties and the comparison of its analytical performance to digestion protocols commonly used in environmental sciences."

Bell, S., and P. Gardinali. 2010. Assessment of silicone polymer composites for environmental forensic applications: A proof of concept study. Journal of Forensic Sciences 55:1245–1250. "The study reports the use of polydimethylsiloxane polymer composites (PDMS, Fe–PDMS) as a passive sampling media to preconcentrate analytes found in environmental settings typical of south Florida canals and marshes. This proof of concept work created a surrogate system to limit the need for organism collections."

Quinete, N., J. Wang, A. Fernandez, J. Castro, and P.R. Gardinali. 2013. Outcompeting GC for the detection of legacy chlorinated pesticides: Online-SPE UPLC APCI/MSMS detection of endosulfans at part per trillion levels. Analytical and Bioanalytical Chemistry 405:5887-5899. "This work describes a selective, sensitive, and fast online solid-phase extraction (SPE) method coupled with liquid chromatography separation and tandem mass spectrometry (LC-MS/MS) for the determination of endosulfan isomers and endosulfan sulfate in water samples at low part per trillion levels with very little sample preparation."

Environmental Assessment

Carriger, J.F., and G.M. Rand. 2008a. Aquatic risk assessment of pesticides in surface waters in and adjacent to the Everglades and Biscayne National Parks: I. Hazard assessment and problem formulation. Ecotoxicology 17:660–679. "This article provides the results of the initial phase of a probabilistic ecological risk assessment for pesticides relevant to ENP and BNP."

Carriger, J.F., and G.M. Rand. 2008b. Aquatic risk assessment of pesticides in surface waters in and adjacent to the Everglades and Biscayne National Parks: II. Probabilistic analyses. Ecotoxicology 17:680–696. "Results of the analysis phase of a probabilistic ecological risk assessment for pesticides relevant to ENP and BNP."

Carriger, J.F., T.C. Hoang, and G.M. Rand. 2010. Survival time analysis of mosquitofish (*Gambusia affinis*) and least killifish (*Heterandria formosa*) exposed to endosulfan sulfate. Archives of Environmental Contamination and Toxicology 58:1015-1022. "Single-species flow-through toxicity tests were conducted to determine the times-to-death of two indigenous fish to south Florida—least killifish (*Heterandria formosa*) and mosquitofish (*Gambusia affinis*)—from acute exposure to endosulfan sulfate. The 96-h LC_{50}s for least killifish and mosquitofish estimated using the trimmed-Spearman–Karber method were 2.0 and 2.3µg/l, respectively."

Carriger, J.F., T.C. Hoang, G.M. Rand, P.R. Gardinali, and J. Castro. 2011. Acute toxicity and effects analysis of endosulfan sulfate to freshwater fish species. Archives of Environmental Contamination and Toxicology 60:281-289. "This study determines the acute toxicity (LC_{50}s and LC_{10}s) of endosulfan sulfate to three inland Florida native fish species (mosquitofish [*Gambusia affinis*]; least killifish [*Heterandria formosa*]; and sailfin mollies [*Poecilia latipinna*]) as well as fathead minnows (*Pimephales promelas*)."

Castro, J.E., A.M. Fernandez, V. Gonzalez-Caccia, and P.R. Gardinali. 2013. Concentration of trace metals in sediments and soils from protected lands in south Florida: background levels and risk evaluation. Environmental Monitoring and Assessment 185:6311-6332. "The article describes a comprehensive environmental evaluation on 20 metals: two reference metals (Fe, Al) and several minor trace metals (As, Ba, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn) for surface soils and sediments collected from 50 sites in Everglades National Park (ENP), the coastal fringes of Biscayne National Park (BNP), and Big Cypress National Preserve. The work also provides innovative management tools to interpret environmental trace-metal data using objective statistical methods."

Hoang, T.C., G.M. Rand., P.R. Gardinali, and J. Castro. 2011. Bioconcentration and depuration of endosulfan sulfate in mosquito fish (*Gambusia affinis*). Chemosphere 84:538-43. "The work describes a standardized bioconcentration study for the major endosulfan metabolite (endosulfan sulfate) in common fish prevalent along south Florida ecosystems at environmentally relevant concentrations. Mosquito fish do accumulate endosulfan sulfate directly from the water column."

Quinete, N., J. Castro., A. Fernandez, I.M. Zamora-Ley, G.M. Rand, P.R. Gardinali. 2013. Occurrence and distribution of endosulfan in water, sediment, and fish tissue: An ecological assessment of protected lands in south Florida. Journal of Agricultural and Food Chemistry 61:11881-11892. "This study reports the presence and potential consequences of the presence of endosulfans, including endosulfan sulfate in multimedia samples within the protected areas of Everglades National Park, Biscayne National Park, and Big Cypress National Preserve."

Rand, G.M., J.F. Carriger, P.R. Gardinali, and J. Castro. 2010. Endosulfan and its metabolite, endosulfan sulfate, in freshwater ecosystems of south Florida: A probabilistic aquatic ecological risk assessment. Ecotoxicology 19:879-900. "A comprehensive probabilistic aquatic ecological risk assessment was conducted to determine the potential risks of existing exposures to endosulfan and endosulfan sulfate in freshwaters of south Florida based on historical and recent data (1992–2007)."

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