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**THE OCCURRENCE OF METALS
IN BROWARD COUNTY WATERWAYS**

**ENVIRONMENTAL MONITORING DIVISION
DEPARTMENT OF NATURAL RESOURCE PROTECTION**

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A SURVEY OF THE OCCURRENCE OF SELECTED METALS IN BROWARD COUNTY WATERWAYS

EXECUTIVE SUMMARY

A study of the occurrence of metals in Broward County surface waters was conducted to update information regarding ambient metal concentrations and to assess the suitability of newly acquired laboratory instrumentation to conduct this type of work. An evaluation of rainfall impact was investigated and the possible sources and risks of metals in surface waters are discussed. Information regarding the frequency of exceedances of surface water standards is compiled. Trends in surface water metals concentrations over the last 26 years are examined.

In order to update information on the occurrence of metals in Broward County waterways, the Environmental Monitoring Division (EMD) of the Broward County Department of Natural Resource Protection (DNRP) performed a one-year study of metals in county waterways as measured at the 44 stations in the DNRP surface water quality monitoring network. The metals studied were cadmium, chromium, nickel, copper, iron, lead, tin, zinc and arsenic. This group of metals were selected for study due to their common use and their potential for adverse environmental impacts. These data will be useful for updating the database of ambient metals concentrations and for detecting trends in the occurrence of these metals in surface waters.

The work was facilitated by the acquisition by the EMD laboratory of an inductively-coupled plasma (ICP) spectrometer capable of performing the required analyses in a rapid and cost-effective manner.

Despite the fact that heavy rainfall occurred on only one of the 7 sampling days and only 13.6% of all samples were collected on that day, the metal concentrations on that day were much higher than during dry weather. The metal detections on that day accounted for 44% of all detections, excluding iron, an element that commonly occurs at relatively high levels (>1,000 ug/l) in ground and surface waters.

Water quality standards, which may be dependant upon classification (marine or fresh), were rarely exceeded (less than 10% of the samples) with the exception of copper. Of the 176 samples collected in this study, a total of 82 samples (46.6%) were collected from water classified as marine (conductivity greater than 5,000 umhos/cm) and 94 samples (53.4%) were collected from water classified as fresh. Copper was found in excess of the of 3 ug/l standard 17.0% of the time. The detection limit for copper in this study, however, was 10 ug/l, therefore, the extent of the exceedances for this metal was probably underestimated. Similar instrumental limitations were evident for cadmium, nickel and lead. Given the generally low levels of metals in surface waters seen in this study, future studies should employ a methodology with greater sensitivity such as heated graphite atomization atomic absorption spectrometry for those elements with standards below ICP detection limits.

Copper, tin, iron, and zinc were commonly detected in this study. Despite the fact that all of these metals are associated with marine industry activities, the metals were not found to be higher in marina areas than other areas of the county.

The failure to detect metals in the water column more often is not entirely unexpected because metals tend to associate with particulate matter and to settle into bottom sediments. Indeed, previous studies of sediments within marina areas showed elevated levels of some of these metals in marina sediments (BCDNRP, 1993).

The Snake Creek Canal, which receives most of its flow from iron-enriched groundwater, was found to have the greatest iron concentrations.

An review of data taken from the EPA's STORET database of environmental data indicates that there is a trend toward lower levels of certain metals in Broward County surface waters. The data indicate that levels of zinc, lead and copper have decreased over the last 26 years. This trend may be attributable to the consolidation of many domestic wastewater treatment plants that have historically discharged treated wastewater to County waterways into regional systems with ocean outfalls or deep wells as well as the efforts of DNRP to prevent pollution including the recommendation of Best Management Practices for various industries in the County.

I. INTRODUCTION

Study Objective

The objective of this study was to survey the waterways of Broward County to determine the occurrence and concentration levels of a small group of metallic elements. These data will be used to update information regarding ambient metals concentrations for the purpose of evaluating the effectiveness of regulations governing the release of pollutants into the environment and to detect trends in the occurrence of metals in surface waters. The metals studied were cadmium, chromium, iron, lead, arsenic, copper, nickel, tin and zinc. These metals were selected because of their common use and their potential for adverse environmental impacts.

What is the importance of monitoring metals in surface water?

Many metals are toxic to aquatic animals. Furthermore, some metals have the ability to bioaccumulate in the animals. The bioaccumulation of mercury in fish and other animals in many areas of Florida is one of the most recognized problems of metal contamination (Atkeson, 1994). Metals occurring in surface waters tend to become associated with particulate matter and settle into bottom sediments. Bottom-dwelling organisms are then exposed to the toxic and bioaccumulative effects of the metals. The measurement of metals in sediments and surface waters is a useful indicator of the health of the waterways and the effectiveness of regulatory and pollution prevention efforts of the Broward County Department of Natural Resource Protection.

Historical Data on the Occurrence of Metals in Broward County Surface Waters

Many agencies have sampled and analyzed surface waters in certain areas of Broward County over the years including DNRP's study of the New River drainage basin in 1993 (BCDNRP, 1993). A search of the EPA's STORET (*STORage and RETrieval*) national database of environmental data, revealed that 5 different agencies have collected samples in Broward County since 1970. There has not been an attempt, however, to examine surface water metals concentrations from a comprehensive, county-wide perspective.

The acquisition by DNRP's Environmental Monitoring Division (EMD) of new analytical instrumentation greatly facilitated this work. The instrumentation, an inductively-coupled plasma spectrometer, permits the rapid determination of metals in environmental samples by exciting metal atoms in an argon-plasma torch and subsequently measuring their characteristic emission spectra. Using this instrumentation, EMD was able to measure the concentrations of the nine metals in a water sample in less than one minute.

Metals in water bodies are usually associated with sediments

While it is known that metals tend to accumulate in bottom sediments, microbe-metal interactions in aquatic environments and their exact role in transport and transformations of toxic metals are poorly understood. For instance, on-going research in Lake Chapala, Mexico, the major water source of the City of Guadalajara, provided an opportunity to study the microbiological aspects of metal-cycling in the water column. Researchers found that constant re-suspension of sediments provided a microbiologically rich aggregate-based system. The data indicate that toxic metals are concentrated on aggregate material and bioaccumulate in the food chain (Ford & Ryan, 1995).

Metals Contamination May Result from Industrial Sources

While Broward County does not have the heavy industry common in the northeastern United States, and lacks any discharges of waste water to county waterways, Broward County's history of

discharging treated wastewater to surface waters is a scenario similar to the situation in the northeast. An Environmental Defense Fund (EDF) study found that toxic metal contamination threatened marine life in New York-New Jersey harbor and its tributaries and could also jeopardize other costly pollution control efforts (Clark, 1990). The Hudson-Raritan Estuary was once a world-renowned commercial fishery that supported beds of oysters, clams, crabs and many fish species. Highly toxic metals such as mercury, lead and copper were found in waters throughout the fragile estuary at levels exceeding state and Federal limits. They were accumulating in shellfish tissue and concentrating in sediments on the harbor floor where they can persist for decades.

Sewage treatment plants were the main source of these heavy metal discharges into the estuary because the majority of industrial plants in New York City and northern New Jersey discharged their waste into municipal sewers. EDF found that most plants had made slow progress in improving the quality of their effluent, in part because there was no incentive to do so until states imposed limits on the metals each plant could discharge. The study's author called for vastly improved industrial pretreatment programs and strict control of metals leaching from pipes. "The key to cleaning up heavy metals in the Harbor, is controlling toxic metals at their source--before they enter the sewers" (Clark, 1990).

The Toxicity and Uses of the Metals Tested in this Study

A group of 9 metals was examined in this study. Those metals were chromium, cadmium, nickel, lead, arsenic, tin, copper, zinc, and iron. The presence of metals in surface waters can have adverse consequences for the ecological health of surface waters. However, the toxicity of metals on aquatic species can vary greatly. Some of the factors affecting toxicity include the specific species itself, the hardness of the water, the form of the metal and the duration of exposure. With such variability, extensive toxicology data are not always available. Nonetheless, an attempt has been made to define some measure of aquatic fish toxicity for each metal. Caution, however, must be exercised when using this data.

In addition to ecological health impacts, contamination of surface waters with metals may have human health impacts. The fact that the county's drinking water supplies lie just below the surface in the Biscayne Aquifer means the potential exists for the groundwater supplies to be contaminated by surface water pollutants. Some facts concerning potential impacts of metals are discussed below:

Arsenic

Severe poisoning can arise from the ingestion of as little as 100 mg arsenic; chronic effects can appear from its accumulation in the human body at low intake levels. Carcinogenic properties have also been imputed to arsenic. The arsenic concentration of most potable waters seldom exceeds 10 ug/l, although values as high as 100 ug/l have been reported. Arsenic may occur in water as a result of mineral dissolution, industrial discharges or the application of insecticides (Rand, et al, 1975). The concentration of arsenic in the form of sodium arsenate lethal to 50% (LC₅₀) of juvenile green sunfish (*Lepomis cyanellus*) in a chronic (209 hr) exposure was found to be 30,000 ug/l (Ramamoorthy and Baddaloo, 1995).

Cadmium

Cadmium is highly toxic and has been implicated in some cases of poisoning through food. Minute quantities of cadmium are suspected of being responsible for adverse changes in arteries of human kidneys. A cadmium concentration of 200 ug/l is toxic to certain fish. On the other hand, there is an indication that cadmium might be a dietary essential. The cadmium concentration of U.S. drinking waters has been reported to vary between 0.4 and 60 ug/l, with

a mean of 8.2 ug/l. Cadmium may enter water as a result of industrial discharges or the deterioration of galvanized pipe (Rand, et al, 1975).

Chromium

The hexavalent chromium concentration of U.S. drinking waters has been reported to vary between 3 and 40 ug/l with a mean of 3.2 ug/l. Chromium salts are used extensively in industrial processes and may enter a water supply through the discharge of wastes. Chromate compounds are frequently added to cooling water for corrosion control. Chromium may exist in water supplies in both the hexavalent and the trivalent state although the trivalent form rarely occurs in potable water (Rand, et al, 1975). When atherinids (*Atherinamosa microstoma*) were exposed to chromium in the form of the sodium salt of chromic acid at a concentration of 19,300 ug/l, no observable adverse effect (NOAE) was noted (Ramamoorthy and Baddaloo, 1995).

Copper

Copper salts are used in water supply systems for controlling biological growths in reservoirs and distribution pipes and for catalyzing the oxidation of manganese. The corrosion of copper-containing alloys in pipe fittings may introduce measurable amounts of copper into the water in a localized pipe system. Copper is essential to humans and the adult daily requirement has been estimated at 2,000 ug (Rand, et al, 1975). The concentration of copper in the form of cupric sulfate lethal to 50% (LC₅₀) of mummichogs (*Fundulus heteroclitus*) in a 96 hour acute toxicity assay was 3,100 ug/l (Ramamoorthy and Baddaloo, 1995).

Iron

In filtered samples of oxygenated surface waters iron concentrations seldom reach 1,000 mg/l. Some ground waters and acid surface drainage may contain considerably more iron. Iron in water can cause staining of laundry and porcelain and also a bittersweet astringent taste detectable by some persons at levels above 1,000 or 2,000 ug/l.

Under reducing conditions, iron exists in the ferrous state. In the absence of complex-forming ions, ferric iron is not significantly soluble unless the pH of the water is very low. On exposure to air or addition of oxidants, ferrous iron is oxidized to the ferric state and may hydrolyze to form insoluble hydrated ferric oxide. This is the predominant form of iron found in most laboratory samples unless the samples are collected under anoxic conditions to avoid oxidation.

The form of iron present in water also may undergo alteration as a result of the growth of bacteria in the samples during storage or shipment. In acid waste at pH less than 3.5, ferric iron state also may be soluble. Iron may be in true solution, in a colloidal state that may be peptized by organic matter, in the inorganic or organic iron complex, or in relatively coarse suspended particles. It may be either ferrous or ferric, suspended or filterable. Silt and clay in suspension may contain acid-soluble iron. Iron oxide particles are sometimes collected with a water sample as a result of flaking of rust from pipes. Iron may come from a metal cap used to close the sample bottle (Rand, et al, 1975).

Lead

Lead is a serious cumulative body poison. Natural waters seldom contain more than 20 ug/l, although values as high as 400 ug/l have been reported. Lead in a water supply may come from industrial, mine, and smelter discharges, or from the dissolution of old lead plumbing. Tap waters that are soft, acid, and not suitably treated may contain lead resulting from an attack on the lead service pipes (Rand, et al, 1975). Lead, in the form of lead sulfate, was found to be lethal to 100% (LC₁₀₀) of the goldfish (*Carassius auratus*) in a 4 hour chronic toxicity test at a concentration of 25,000 ug/l (Ramamoorthy and Baddaloo, 1995).

Nickel

The single largest nickel source found in the atmosphere is from fuel oil combustion. Other sources include atmospheric emission from mining and refining operations, atmospheric emission from municipal waste incineration, and windblown dust.

Sources of nickel in water and soil include stormwater runoff, soil amended with municipal sewage sludge, wastewater from municipal sewage treatment plants, and groundwater near landfill sites. Very small amounts of nickel have been shown to be essential to some species of animals, so that small amounts may also be essential to humans. High levels of nickel and nickel compounds are clearly toxic. Nickel or its compounds can cause effects on the lungs and on the body's immune system regardless of how long you are exposed. Intake of nickel or its compounds by ingestion of drinking water is typically less than through diet; however, ingestion of nickel in drinking water can be increased significantly by consumption of drinking water from plumbing or faucets that contain nickel (ORNL, 1987). The LC₅₀ of divalent nickel in a 96 hour acute toxicity assay using mummichogs (*Fundulus heteroclitus*) was 350,000 ug/l (Ramamoorthy and Baddaloo, 1995).

Tin

Elemental tin is an almost silver-white, lustrous, soft, very malleable and ductile metal. It is used chiefly for tin plating, soldering alloys, and babbitt-type metals, the manufacture of tin salts and collapsible tubes. Organic tin compounds may enter the environment by leaching from biocides in anti-fouling bottom paint (Budavari, et al, 1975). The organic form of tin used in biocides is tributyltin (TBT) oxide. The LC₅₀ of TBT-oxide was found to be 16 ug/l in a 96 hour acute toxicity assay using armed bullhead (*Agonus cataptaractus*) as the test organism.

Zinc

Zinc is an essential and beneficial element in body growth. Concentrations above 5,000 ug/l however, can cause a bitter astringent taste and an opalescence in alkaline waters. The zinc concentration of U.S. drinking waters varies between 60 and 7,000 ug/l, with a mean of 1,330 ug/l. Zinc most commonly enters the domestic water supply from the deterioration of galvanized iron and the de-zincification of brass. In such cases the presence of lead and cadmium also may be suspected, because they are impurities of the zinc used in galvanizing. Zinc contamination in surface water also may result from industrial waste pollution (Rand, et al, 1975). The LC₅₀ of zinc, in the form of zinc chloride, was found to be 11,500 ug/l in a 96 hour acute toxicity assay using yellow-eye mullet (Ramamoorthy and Baddaloo, 1995).

II. METHODOLOGY

Sample Sites

Samples were collected from each of the 44 stations in the DNRP Surface Water Quality Monitoring Network. The stations in the network were selected to represent ambient water quality in each of the major drainage basins in Broward County. The network is represented in Figure 1. Site descriptions appear in Appendices.

Sampling Protocol

Grab samples were collected just below the water's surface at each of the stations in April, July, and October 1996 and in January 1997. The samples were preserved by adding 5 ml per liter of high purity concentrated nitric acid. This procedure stabilizes the samples for up to 6 months although in this study all analyses were completed within 30 days.

Sample Preparation and Analysis

Whole water samples were prepared for analysis using EPA Method 3015 (USEPA, 1986), a microwave-assisted acid digestion for total metals, using a CEM Corporation model MDS-2100 microwave oven. Metal analyses in environmental samples have traditionally been done by atomic absorption spectroscopy whereby the concentration of metals in a sample is determined by measuring the amount of light that is absorbed by a "cloud" of atomized sample containing metal atoms in a specific state of atomic excitation. In this study, metal analyses were performed using EPA Method 6010, inductively-coupled plasma (ICP) atomic emission spectroscopy using a Perkin-Elmer model Optima 3000XL with axial-view torch configuration. In ICP spectroscopy, atoms in a sample are excited in an argon plasma and the concentration of metals in the sample is proportional to the resultant emission. Conductivity measurements were performed in the field according to EPA Method 120.1 using a Hydrolab model Surveyor II multifunction meter. Conductivity readings were not available for samples collected on the August 8, 1996 sampling event. Instead of actual conductivity readings, the data table in Appendices shows the samples collected on this date labeled as "fresh" or "marine" based upon historical conductivity readings.

FIGURE 1
DNRP Surface Water Quality Monitoring Network

Rainfall Records

Information on rainfall during this study was obtained from 5 locations in the county. Those locations were:

- o Broward County 2A Water Treatment Plant, 1390 NE 51st St., Pompano Beach
- o Coral Springs Improvement District (CSID) Water Treatment Plant, 10300 NW 11th Manor, Coral Springs
- o Broward County 1A Water Treatment Plant, 3701 N. State Road 7, Fort Lauderdale
- o Fort Lauderdale Peele-Dixie Water Treatment Plant, 1500 S. State Road 7, Fort Lauderdale
- o Hollywood Water Treatment Plant, 3441 Hollywood Blvd., Hollywood

The geographic distribution of these monitoring stations provides a reasonable assessment of any rainfall events that could impact surface water metals concentrations resulting from stormwater runoff.

Comparison of Metals Concentrations to Historical Record

The concentrations of metals detected in this study were compared to levels detected during the DNRP survey of the New River Basin conducted in 1991-92. In addition, metals data was extracted from the EPA's STORET database from 1970 through 1996 for samples collected in Broward County by a variety of government agencies including the South Florida Water Management District, the Florida Department of Environmental Protection, the U.S. Geological Survey, U.S. Army Corps of Engineers and DNRP.

Statistical Treatment of Data

Means and standard deviations were not tabulated for all metals in this study because the large number of "not detected" results would cause the calculated means to appear lower than they actually are. Other measures of distribution assessment such as minimum, maximum and median were tabulated instead since these statistics may be a more meaningful way to summarize the findings. For the purpose of calculating statistics in this study, duplicate samples, when collected, were averaged and treated as a single sample.

III. RESULTS

Occurrence of Metals in Surface Waters

Table 1 summarizes the findings of this study.

TABLE 1
Summary of Results

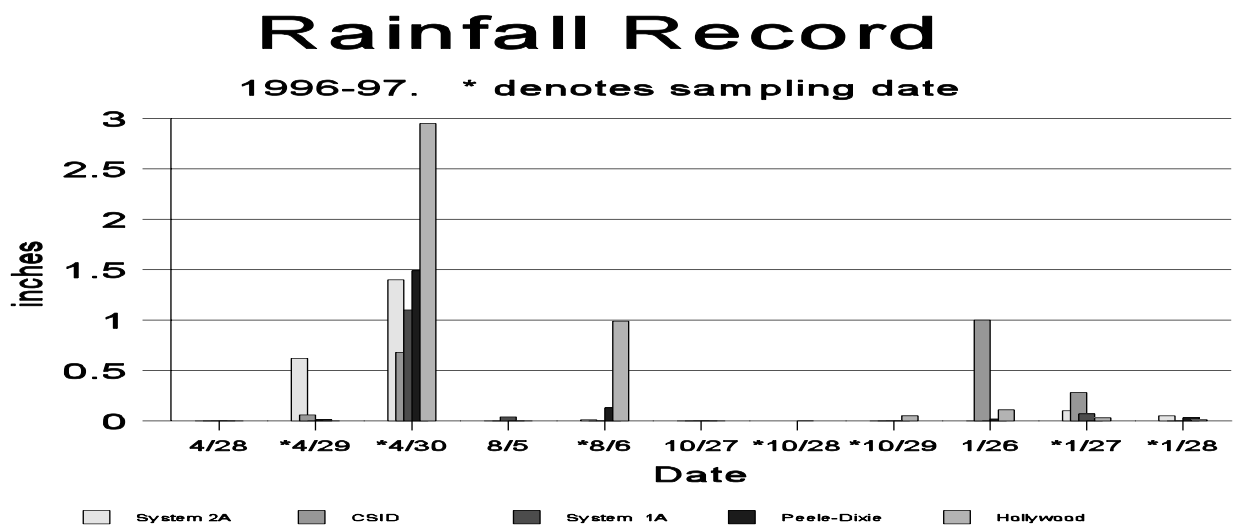
Metal	*Detect %	Min ug/l	Max ug/l	Detection Lim., ug/l	Median ug/l	Standard ug/l	*% Std Exceedances
As	5.1	ND	20.1	5-8	ND	50	0.0
Cd	0.6	ND	17.1	2.5	ND	5 marine/1 fresh	0.6/0.0
Cr	0.6	ND	27.2	5.3	ND	50 fresh	0.0
Cu	17.0	ND	25.2	10	ND	3	17.0
Fe	75.6	ND	2,470	7.5	23.8	300 mar./1000 frsh	0.6/1.7
Ni	0.6	ND	13.5	13.5	ND	8.3 mar./100 frsh.	0.6/0.0
Pb	5.1	ND	277	22	ND	5.6 mar./30 frsh.	1.1/4.0
Sn	15.3	ND	68.6	9.5	ND	None	NA
Zn	10.2	ND	304	16	ND	86	0.6

* (percentages based on a total of 176 samples)

Rainfall Record

Figure 2 shows rainfall amounts recorded during and 24 hours preceding all sampling days. While rainfall in excess of 0.5" occurred somewhere in the county on 4 days near sampling events, heavy rain fell county-wide only on April 30, 1996.

FIGURE 2



Effect of Rainfall on Surface Water Metals Concentrations

Table 2 is presented to illustrate the effect of rainfall on metal detections. It shows the number of samples in which metals were detected on specific sampling dates and the amount of rain that fell on that day. The table indicates that concentrations of arsenic, copper and tin in surface waters are higher following rain. The number of samples with detectable levels of these metals was highest on April 30, 1996 when an average of 1.52 inches of rain fell. The reverse is the case for lead and zinc which were not detected during the heavy rain. Iron detections were highest on August 6, 1996, a day of minor rainfall.

TABLE 2
Number of Metal Detections versus Rainfall

Date	# Samples Collected	Rain, Avg. in.	Number of Detections								
			As	Cd	Cr	Cu	Fe	Ni	Pb	Sn	Zn
04-29-96	20	0.14	2	0	0	9	13	1	0	7	2
04-30-96	24	1.52	5	1	0	13	16	0	0	19	0
08-06-96	44	0.23	0	0	0	2	43	0	1	1	13
10-28-96	21	0.00	0	0	1	0	19	0	0	0	2
10-29-96	23	0.01	1	0	0	0	20	0	0	0	1
01-27-97	20	0.10	0	0	0	2	9	0	4	0	0
01-28-97	24	0.02	1	0	0	4	13	0	4	0	0
Totals	176		9	1	1	30	133	1	9	27	18

Comparison of Metals Concentrations to Historical Record

Table 3 compares the concentrations of metals detected in this study with those that were reported in the survey of the New River Basin in 1991-92 and from data taken from the EPA's STORET database for the period of 1970 to 1996. In comparison with the New River Basin study, the copper concentrations found in the current study were very similar while all of the other metals detected were much higher in the current study. When compared with the STORET data, the results of this study were comparable with the exception of copper, zinc and arsenic which were somewhat higher in the STORET database. There was no data available in STORET regarding tin.

TABLE 3
Surface Water Metal Concentrations, Present Versus Historical

Metal		EPA STORET Data Base 1970-96	New River Basin Study 1991-92	This Study 1996-97
Copper, ug/l	Min	None detected (ND)	ND	ND
	Max	90	19.1	25.2
	Median	1	6.1	ND
Cadmium, ug/l	Min	ND	ND	ND
	Max	20	2.59	17.1
	Median	ND	ND	ND
Lead, ug/l	Min	ND	ND	ND
	Max	400	21.2	277
	Median	3	1.8	ND
Tin, ug/l	Min	No data available	ND	ND
	Max		10.2	68.6
	Median		ND	ND
Zinc, ug/l	Min	ND	ND	ND
	Max	510	88	304
	Median	20	20	ND
Chromium, ug/l	Min	ND	Not Analyzed	ND
	Max	40		27.2
	Median	ND		ND
Iron, ug/l	Min	ND	Not Analyzed	ND
	Max	2,400		2,470
	Median	50		23.8
Nickel, ug/l	Min	ND	Not Analyzed	ND
	Max	26		13.5
	Median	3		ND
Arsenic, ug/l	Min	ND	Not Analyzed	ND
	Max	200		20.1
	Median	2		ND

IV. DISCUSSION

This study found few exceedances of surface water standards for metals, however, the detection limit for certain metals may be too high to detect some violations. The highest levels of metals in surface waters coincided with rainfall. There was no apparent relationship between elevated concentrations of metals commonly found in marine maintenance applications and marina areas. An examination of historical data on metals concentrations in surface waters showed a general downward trend.

Exceedances of Surface Water Standards

With the exception of copper, metal concentrations in surface water rarely exceeded Broward County standards, however, the limited ability of the instrumentation used to detect the metals at concentrations near the standard means that the extent of the exceedances may be underestimated. For instance, the standard for copper is 3 ug/l. This standard was exceeded in 17% of the samples. This percentage probably underestimates the actual frequency of exceedances because the detection limit for copper, which for this study was 10 ug/l, allows exceedances to go undetected. Similarly, the standards for cadmium in freshwater (1 ug/l), nickel in marine water (8.3 ug/l), and lead in marine water (5.6 ug/l) are also lower than the instrumental detection limits of 2.5 ug/l, 13.5 ug/l and 22 ug/l respectively. Therefore, the level of exceedances for these metals may also be underestimated.

Effect of Rainfall on Surface Water Metals Concentrations

Rainfall had a large impact on surface water metal concentrations. Heavy rain fell on only one sampling day during this study. Excluding iron, a naturally-occurring element in ground and surface waters, approximately 44% of all metal detections, however, occurred on that day. Two sampling days had minimal rain (less than 0.01"). Only 5.6% of all detections occurred on these days. These observations clearly indicate that county surface waters receive a significant dose of metals following rainfall.

The fact that the concentration of metals in surface waters increases as a result of rainfall is not unexpected. The results of stormwater runoff tests done for DNRP's National Pollutant Discharge Elimination System (NPDES) Stormwater Permit Program indicates that stormwater runoff can be elevated in metals. For instance, the concentration of copper and zinc in runoff was shown to be as high as 142 and 384 ug/l respectively (personal communication, Carol Millman, DNRP Water Resources Division).

The fate of these metals could include flushing, ultimately to the ocean or association of the metals with particulate matter that ultimately settles to the bottom to become canal sediment. DNRP has proposed a study to examine sediments in lakes of varying ages in an effort to determine accumulation rates.

Table 4 shows that, in this study, copper and tin levels are dramatically elevated with rainfall while iron and zinc concentrations decrease.

TABLE 4
Mean Surface Water Metal Concentrations under Wet and Dry Conditions
(mean \pm 1 standard deviation)

	Copper, ug/l	Iron, ug/l	Tin, ug/l	Zinc, ug/l
Dry Weather	2.0 \pm 5.8	83.4 \pm 269.6	1.34 \pm 5.94	5.03 \pm 26.5
Wet Weather	9.5 \pm 9.1	50.7 \pm 79.8	19.7 \pm 16.2	Not Detected

Occurrence of Metals in Surface Waters

Cadmium, chromium and nickel (one detection each) were rarely detected in Broward County surface waters at the detection limits of this study. Arsenic and lead were detected only infrequently (9 detections each).

Copper, tin, iron and zinc were commonly detected. These metals are frequently used in marina industry applications. In order to determine whether there was any association between elevated concentrations of these metals and marine maintenance areas, 3 sampling stations located near areas where marine maintenance work is performed were examined. The three sites were #20 near Bradford Marine on “Marina Mile”, #38 at the 17th Street Causeway in Port Everglades, and #24 on the Dania Cutoff Canal at U.S 1, just west of a concentration of marinas. Table 5 shows that, with the exception of copper at station #24, the maximum concentrations at these stations are far below the maximum levels seen county-wide. The copper value at station #24 was recorded on April 30, 1996 and may be attributed to the heavy rainfall that occurred on that day. In general, therefore these areas in Broward County known for active marine industry operations (e.g., Port Everglades, Marina Mile, etc.) were not among those areas with the highest metals concentrations.

TABLE 5
Maximum Metal Concentrations Near Marine Maintenance Areas Versus County-wide

	Copper, ug/l	Tin, ug/l	Iron, ug/l	Zinc, ug/l
# 20 Marina Mile	ND	ND	107	ND
#38 Port Everglades	ND	ND	19.7	21.0
#24 Dania Cutoff	20.9	ND	28.2	ND
County-wide	25.2	31.6	2,470	304

Iron was detected in 76% of the samples. Iron is a common component of groundwater. One possible source of the iron in surface waters is the seepage of groundwater into the surface waters. Bolstering this possibility is the fact that 2 of the 3 stations having the highest iron concentrations are located on the Snake Creek Canal. This canal is known to receive a large portion of its flow from groundwater recharge (SFWMD, 1987).

Comparison of Metals Concentrations to Historical Record

The concentrations of metals detected in this study were generally higher than those of the New River Basin Study in 1991-92. This observation may be attributable to the fact that the current study encompassed the entire county while the former report dealt only with a single drainage basin. Indeed, with the exception of site #49 (max. zinc, 304 ug/l), the stations where the maximum metal concentrations were detected in this study were not sampled in the New River Basin study.

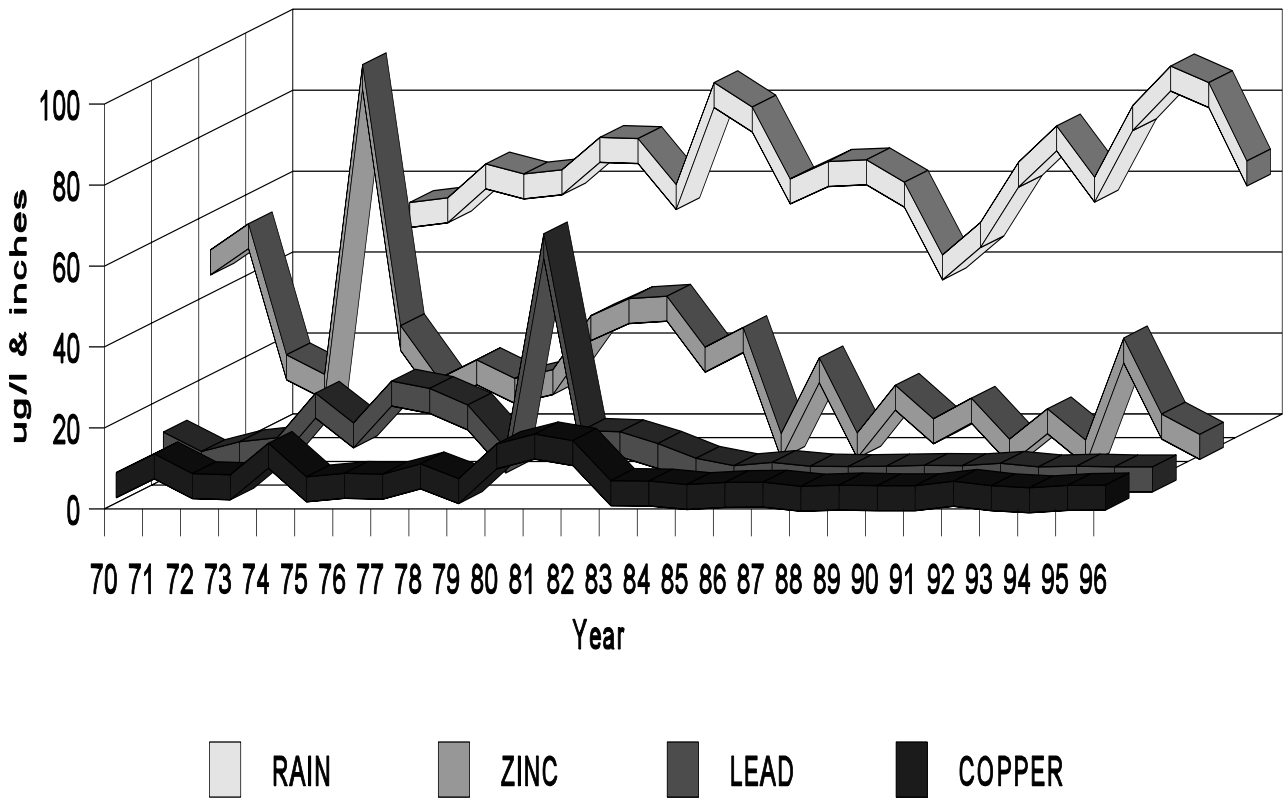
The observation of higher concentrations of copper, zinc and arsenic in the STORET database as compared to the results of this study may reflect the effectiveness of efforts to eliminate the sources of metals in the environment such as the NPDES Stormwater Permit program and DNRP's Best Management Practices for marine maintenance industry as well as 1984 prohibition of industrial discharges to surface waters. It may also reflect the consolidation of many small domestic wastewater treatment plants over the years into large regional plants with ocean outfalls and deep-well injection disposal. Indeed, as can be seen in Figure 3, the general trend is toward lower levels of copper, lead

and zinc in surface waters. Although the temporary elevations apparent in the chart during the 1979-83 period could not be associated with any specific event or activity, the rainfall during that time period was slightly higher than normal and may have been a contributing factor.

FIGURE 3

METAL CONCENTRATION TRENDS IN SURFACE WATER

Annual Means, from EPA STORET Database



V. CONCLUSIONS

This survey indicates that surface water metals concentrations were generally quite low during dry weather conditions although the analytical methodology used, inductively-coupled plasma spectroscopy, provided insufficient sensitivity to adequately assess surface water metals concentrations under dry weather conditions. Rainfall causes metal concentrations in surface waters to increase dramatically. The disappearance of metals from surface waters during dry weather suggests that metals are flushed to the ocean or rapidly assimilated in bottom sediments. An investigation of the rate of sediment accumulation in bottom sediments may provide some interesting insights regarding the fate of metals in surface waters.

Of the metals surveyed, cadmium, chromium and nickel were rarely detected. Exceedances of standards were rarely seen except for copper which exceeded standards 17% of the time. Given that the detection limit for copper as well as cadmium, nickel and lead were greater than the standard, the extent of the exceedances was probably underestimated. The instrumentation used for this study, inductively-coupled plasma spectroscopy, generally lacks adequate sensitivity to detect metals at ambient concentrations. Future studies should employ an analytical method suitable for detecting metals at lower concentrations such as heated-graphite tube atomic absorption spectrophotometry or ICP-mass spectrometry. The most commonly detected metals were copper, tin, iron, and zinc. While all of these metals are associated with marine applications, there was no apparent relationship between the occurrence of these metals and areas where marine industry activities are common.

Iron levels were shown to be highest in the Snake Creek Canal which receives most of its flow from iron-enriched groundwater.

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APPENDICES

90	961029	958	59951	2800	<5.27	<2.47	<5.27	<10.4	55.90	<13.5	<22.0	<9.51	<16.0
1	970127	1020	60401	17100	<8.01	<2.47	<5.27	<10.4	31.00	<13.5	<22.0	<9.51	<16.0
2	970127	1120	60402	773	<8.01	<2.47	<5.27	18.10	<7.47	<13.5	43.10	<9.51	<16.0
3	970127	1220	60403	804	<8.01	<2.47	<5.27	<10.4	15.70	<13.5	<22.0	<9.51	<16.0
4	970127	1320	60404	956	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
5	970127	1115	60405	3210	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
6	970127	1305	60406	703	<8.01	<2.47	<5.27	<10.4	13.00	<13.5	<22.0	<9.51	<16.0
7	970127	1340	60407	593	<8.01	<2.47	<5.27	<10.4	50.10	<13.5	<22.0	<9.51	<16.0
8	970127	1445	60408	619	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
9	970127	1400	60409	741	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
10	970127	1035	60442	2840	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
10	970127	1005	60410	2840	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
11	970127	916	60411	986	<8.01	<2.47	<5.27	<10.4	52.80	<13.5	<22.0	<9.51	<16.0
12	970127	942	60412	727	<8.01	<2.47	<5.27	<10.4	16.00	<13.5	<22.0	<9.51	<16.0
13	970127	1012	60413	705	<8.01	<2.47	<5.27	<10.4	44.30	<13.5	<22.0	<9.51	<16.0
13	970127	1015	60443	705	<8.01	<2.47	<5.27	<10.4	38.30	<13.5	32.60	<9.51	<16.0
14	970127	1045	60414	840	<8.01	<2.47	<5.27	<10.4	76.40	<13.5	207.00	<9.51	<16.0
33	970127	1000	60433	13500	<8.01	<2.47	<5.27	<10.4	56.60	<13.5	<22.0	<9.51	<16.0
34	970127	1130	60434	54800	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
35	970127	1140	60435	53100	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
36	970127	1235	60436	34800	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
37	970127	1213	60437	37800	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
89	970127	1120	60489	652	<8.01	<2.47	<5.27	16.30	<7.47	<13.5	45.30	<9.51	<16.0
15	970128	1105	60415	39600	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
16	970128	1145	60416	7900	<8.01	<2.47	<5.27	21.30	30.50	<13.5	173.00	<9.51	<16.0
17	970128	1220	60417	493	<8.01	<2.47	<5.27	17.90	7.93	<13.5	49.30	<9.51	<16.0
18	970128	1344	60444	493	<8.01	<2.47	<5.27	15.20	<7.47	<13.5	34.80	<9.51	<16.0
18	970128	1335	60418	492	<8.01	<2.47	<5.27	17.10	<7.47	<13.5	43.80	<9.51	<16.0
19	970128	1020	60419	11000	<8.01	<2.47	<5.27	<10.4	15.80	<13.5	<22.0	<9.51	<16.0
20	970128	1135	60420	10900	<8.01	<2.47	<5.27	<10.4	11.20	<13.5	<22.0	<9.51	<16.0
21	970128	1215	60421	722	<8.01	<2.47	<5.27	<10.4	23.80	<13.5	<22.0	<9.51	<16.0
22	970128	1245	60422	752	<8.01	<2.47	<5.27	<10.4	85.70	<13.5	<22.0	<9.51	<16.0
23	970128	1320	60423	908	<8.01	<2.47	<5.27	<10.4	155.00	<13.5	<22.0	<9.51	<16.0
24	970128	1300	60424	43900	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
25	970128	1237	60425	23100	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
26	970128	1210	60426	32400	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
27	970128	1145	60427	646	<8.01	<2.47	<5.27	<10.4	82.70	<13.5	<22.0	<9.51	<16.0
28	970128	1055	60428	703	<8.01	<2.47	<5.27	<10.4	45.10	<13.5	<22.0	<9.51	<16.0
29	970128	1400	60429	818	9.63	<2.47	<5.27	<10.4	119.00	<13.5	<22.0	<9.51	<16.0
31	970128	1020	60431	702	<8.01	<2.47	<5.27	<10.4	178.00	<13.5	<22.0	<9.51	<16.0
32	970128	935	60432	742	<8.01	<2.47	<5.27	<10.4	31.20	<13.5	<22.0	<9.51	<16.0
38	970128	1045	60438	50500	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
39	970128	1115	60439	49500	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
40	970128	1335	60440	50500	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
41	970128	1345	60445	46700	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
41	970128	1330	60441	46700	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
47	970128	1145	60447	50800	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
49	970128	1040	60449	30000	<8.01	<2.47	<5.27	<10.4	<7.47	<13.5	<22.0	<9.51	<16.0
90	970128	1105	60490	12600	<8.01	<2.47	<5.27	21.80	11.10	<13.5	277.00	<9.51	<16.0

SAMPLING SITE DESCRIPTIONS

<u>Site #</u>	<u>Latitude</u>	<u>Longitude</u>	<u>Description</u>
1	26 19 30.0	080 05 27.6	HILLSBORO CANAL; FEDERAL HIGHWAY (US 1) - HILLSBORO CANAL
2	26 19 40.8	080 07 51.6	HILLSBORO CANAL; W SIDE OF SALINITY CONTROL STRUCTURE - HILLSBORO CANAL
3	26 19 37.2	080 12 10.8	HILLSBORO CANAL; STATE RD. 7 (US 441) - HILLSBORO CANAL
4	26 21 10.8	080 17 24.0	HILLSBORO CANAL; BRIDGE TO SOUTHEAST GROWERS' ASSOCIATION -HILLSBORO CANAL
5	26 13 19.2	080 06 14.4	POMPANO CANAL; FEDERAL HIGHWAY (US 1) - POMPANO CANAL
6	26 12 21.6	080 07 58.8	CYPRESS CREEK CANAL; DIXIE HIGHWAY BRIDGE - CYPRESS CREEK CANAL
7	26 13 08.4	080 10 15.6	CYPRESS CREEK CANAL; SOUTH PALMAIRE DRIVE - CYPRESS CREEK CANAL
8	26 13 48.0	080 12 18.0	POMPANO CANAL; STATE RD 7 - POMPANO CANAL
9	26 13 48.0	080 15 10.8	POMPANO CANAL; UNIVERSITY DRIVE - POMPANO CANAL
10	26 08 16.8	080 07 04.8	MIDDLE RIVER; E SUNRISE BLVD - MIDDLE RIVER
11	26 10 22.8	080 10 15.6	MIDDLE RIVER; NW 21ST AVE BRIDGE - MIDDLE RIVER
12	26 10 22.8	080 11 13.2	MIDDLE RIVER; NW 31ST AVE - MIDDLE RIVER
13	26 10 22.8	080 13 15.6	MIDDLE RIVER; ROCK ISLAND RD - MIDDLE RIVER
14	26 09 00.4	080 15 25.2	MIDDLE RIVER; UNIVERSITY DRIVE - MIDDLE RIVER
15	26 07 04.8	080 08 38.4	NEW RIVER; ANDREWS AVE BRIDGE - NEW RIVER
16	26 07 15.6	080 09 46.8	NORTH FORK NEW RIVER; BROWARD BLVD - NORTH FORK NEW RIVER
17	26 08 06.0	080 11 42.0	PLANTATION CANAL; W SIDE OF SALINITY CONTROL STRUCTURE - PLANTATION CANAL
18	26 08 06.0	080 12 46.8	PLANTATION CANAL; NW 9TH DRIVE - PLANTATION CANAL
19	26 06 32.4	080 09 32.4	S FORK NEW RIVER; RIVER REACH CONDO - SEAWALL E SIDE OF S FORK OF NEW RIVER
20	26 05 13.2	080 11 02.4	NORTH FORK NEW RIVER; BRADFORD MARINA DOCK - NORTH FORK NEW RIVER
21	26 05 49.2	080 14 16.8	NORTH NEW RIVER CANAL; W SIDE OF FLOOD CONTROL STRUCTURE ON THE NORTH NEW RIVER CANAL 1/4 MI W OF TURNPIKE
22	26 06 57.6	080 19 01.2	NORTH NEW RIVER CANAL; SW 125TH AVE BRIDGE OVER NORTH NEW RIVER CANAL (C15)
23	26 07 19.2	080 20 34.8	NORTH NEW RIVER CANAL; US 27 AT NORTH NEW RIVER CANAL
24	26 03 32.4	080 08 38.4	DANIA CUTOFF CANAL; US 1 BRIDGE OVER DANIA CUTOFF CANAL
25	26 02 52.8	080 09 18.0	HOLLYWOOD CANAL; STIRLING ROAD BRIDGE OVER THE HOLLYWOOD CANAL (E OF BRYAN BLVD)
26	26 04 04.8	080 10 08.4	DANIA CUTOFF CANAL; RAVENSWOOD ROAD BRIDGE OVER THE DANIA CUTOFF CANAL

SAMPLING SITE DESCRIPTIONS

<u>Site #</u>	<u>Latitude</u>	<u>Longitude</u>	<u>Description</u>
27	26 03 57.6	080 12 32.4	SOUTH NEW RIVER CANAL; WEST SIDE OF FLOOD CONTROL STRUCTURE ON SOUTH NEW RIVER CANAL
28	26 03 46.8	080 18 50.4	SOUTH NEW RIVER CANAL; FLAMINGO ROAD BRIDGE OVER THE SOUTH NEW RIVER CANAL
29	26 03 39.6	080 26 02.4	SOUTH NEW RIVER CANAL; US 27 BRIDGE OVER THE SOUTH NEW RIVER CANAL
31	25 57 50.4	080 18 43.2	SNAKE CREEK CANAL; FLAMINGO ROAD BRIDGE OVER THE SNAKE CREEK CANAL
32	25 57 25.2	080 25 55.2	SNAKE CREEK CANAL; US 27 BRIDGE OVER THE SNAKE CREEK CANAL
33	26 18 50.4	080 04 55.2	ICW; HILLSBORO BLVD BRIDGE OVER THE INTRACOASTAL WATERWAY
34	26 15 39.6	080 05 02.4	ICW; HILLSBORO INLET; 100' N OF MARKER 71; 50' W OF E BANK
35	26 15 00.0	080 05 27.6	ICW; 100' N OF NE 14TH STREET BRIDGE; E FENDER; 100' W OF EAST BANK
36	26 11 20.4	080 06 14.4	ICW; 100' N OF COMMERCIAL BLVD BRIDGE E FENDER; 100' W OF EAST BANK
37	26 08 16.8	080 06 32.4	ICW; 100' N OF SUNRISE BLVD BRIDGE E FENDER; 100' W OF E BANK
38	26 06 00.0	080 07 12.0	ICW; 100' N OF 17TH STREET CAUSEWAY BRIDGE E FENDER 100' W OF E BANK
39	26 03 57.6	080 06 54.0	ICW; 300' N OF MARKER #35; 50' W OF E BANK
40	26 02 02.4	080 07 04.8	ICW; 100' N OF SHERIDAN STREET BRIDGE E FENDER; 50' W OF E BANK
41	25 59 09.6	080 07 15.6	ICW; 100' N OF HALLANDALE BEACH BLVD BRIDGE E FENDER; 50' W OF E BANK
47	26 03 46.8	080 07 04.8	DANIA CUTOFF CANAL; DANIA CUTOFF CANAL; 200' W OF ICW
49	26 07 12.0	080 07 19.2	SOSPIRO CANAL; LAS OLAS ISLE BRIDGE OVER SOSPIRO CANAL
89	26 05 06.0	080 10 55.2	POMPANO CANAL; CENTER OF CANAL W SIDE OF NOB HILL ROAD BRIDGE OVER POMPANO CANAL N OF SOUTHGATE ROAD
90	26 13 44.4	080 16 55.2	S FORK NEW RIVER; E BANK OF S FORK NEW RIVER ABOUT 15 METERS N OF SERVICE ROAD PARALLEL TO SR 84

1. TITLE AND SUBTITLE <i>THE OCCURRENCE OF METALS IN BROWARD COUNTY WATERWAYS</i>		2. REPORT DATE <i>March 1998</i>	
3. CONTRIBUTORS <i>WILLIAM A. BARTO, CRAIG S. WILBUR, RUSS RAND, ANIEL PIERRE-LOUIS, ROBERT JENSEN AND GEORGE F. RILEY</i>		4. PERFORMING ORGANIZATION REPORT NO. <i>TECHNICAL REPORT SERIES TR:98-</i>	
5. RESPONSIBLE DEPARTMENT AND DIVISION <i>BROWARD COUNTY DEPARTMENT OF NATURAL RESOURCE PROTECTION 218 SW 1ST AVENUE FORT LAUDERDALE, FL 33301</i>		6. STRATEGIC ASSESSMENT PROGRAM ELEMENT NO.	
		7. CONTRACT/GRANT NO.	
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10. SUPPLEMENTARY NOTES			
11. ABSTRACT <i>A study of the occurrence of metals in Broward County surface waters was conducted. An evaluation of rainfall impact was investigated and the possible sources and risks of metals in surface waters are discussed. Information regarding the frequency of exceedances of surface water standards is compiled. Trends in surface water metals concentrations over the last 26 years are examined.</i> <i>Rainfall occurred on only one of the 7 sampling days yet 44% of all detections, excluding iron, occurred on that day.</i> <i>Water quality standards were rarely exceeded (less than 10% of the samples) with the exception of copper. Copper was found in excess of the of 3 ug/l standard 17.0% of the time.</i> <i>Metals associated with marine maintenance activities, copper, tin, iron, and zinc, were commonly detected in this study, however, these metals were not found to be higher in marina areas as compared to other areas of the county.</i> <i>The Snake Creek Canal, which receives most of its flow from iron-enriched groundwater, was found to have the greatest iron concentrations.</i> <i>An review of data taken from the EPA's STORET database indicated that there is a trend toward lower levels of certain metals in Broward County surface waters. The data indicate that levels of zinc, lead and copper have decreased over the last 26 years.</i>			
12. KEY WORDS <i>metals surface water rainfall</i>			
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