# Chapter 2A: Status of Water Quality in the Everglades Protection Area

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# SUMMARY

This chapter provides a review of water quality within the Everglades Protection Area (EPA) during Water Year 2005 (WY2005) (May 1, 2004 through April 30, 2005). The focus of this chapter is to provide an update to the 2005 South Florida Environmental Report - Volume I. The status of EPA water quality was determined by an analysis of the water quality parameters that did not meet water quality criteria, as specified in Section 62-302.530, Florida Administrative Code (F.A.C.). These criteria establish enforceable management and societal goals for water quality conditions within the EPA. The primary objective of this chapter is to provide a synoptic view of water quality standards compliance on a regional scale including Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), Water Conservation Areas 2 and 3 (WCA-2 and WCA-3), and Everglades National Park (ENP or Park). Discussions of any temporal or spatial trends observed for the parameters identified as concerns or potential concerns are also provided. Annual excursion rates were summarized in a manner similar to methods employed in the 1999 Everglades Interim Report, previous Everglades Consolidated Reports, and the 2005 South Florida Environmental Report. In the 2006 South Florida Environmental Report, water quality parameters that did not meet existing standards were classified into three categories based on excursion frequencies that were statistically tested using the binomial hypothesis test. This chapter also provides a discussion of the factors contributing to excursions from applicable water quality criteria and an evaluation of the natural background conditions for which existing standards may not be appropriate. The results of the evaluation detailed in this chapter are summarized below.

- With few exceptions, water quality has been in compliance with existing state water quality criteria during WY2005.
- Water quality criteria excursion rates were similar to previous periods, despite a very active hurricane season.
- Dissolved oxygen (DO) was categorized as a concern for the Refuge interior, Refuge inflows, WCA-2 interior, and WCA-3 interior. Additionally, DO was categorized as a potential concern for WCA-3 inflows. When nutrient unenriched

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areas were evaluated separately, DO was classified as a minimal concern for unimpacted areas of the Park and WCA-2, a potential concern for WCA-3, and a concern for the Refuge.

- Alkalinity was designated as a concern for the interior of the Refuge for WY2005 due to an excursion rate of  $19.2 \pm 4.7$  percent.
- pH was identified as a potential concern for the Refuge interior due to an excursion rate of 7.3 ± 2.9 percent. All recent pH excursions (WY2001–WY2005) occurred at stations distant from canal discharges (LOX3, LOX5, LOX7, LOX8, LOX9, LOX11, LOX13, LOX14, and LOX16). Because pH excursions within the interior of the marsh are linked to natural background conditions, the Florida Department of Environmental Protection does not consider pH levels within the interior of the Refuge to be in violation of state water quality standards.
- Conductivity was categorized as a potential concern for WCA-2 interior and inflow stations and a potential concern for Refuge inflows. The WY2005 excursion frequency (9.1  $\pm$  3.7 percent) for WCA-2 inflows was significantly less than both WY2004 (28.7  $\pm$  5.7 percent) and the WY1978–WY2003 historical period (15.8  $\pm$  1.4 percent).
- Similar to WY2002 through WY2004, un-ionized ammonia (NH<sub>3</sub>) was categorized as a concern for WCA-2 inflows during WY2005 due to a large number of excursions (11) at sites E0 and F0 located within the spreader canal that receive inflows from the Hillsboro Canal. Elevated dissolved ammonia concentrations were the primary cause of the WY2002–WY2005 excursions at stations E0 and F0.
- Thirteen pesticides or degradation products were detected between October 2003 and December 2004. Only atrazine and chlorpyrifos ethyl were classified as a concern.

# PURPOSE

This chapter provides an assessment of water quality constituents exceeding water quality standards or causing or contributing to adverse impacts in the Everglades Protection Area (EPA). More specifically, the primary purpose of this chapter is to provide an overview of the status of water quality, relative to Class III criteria, in the EPA during Water Year 2005 (WY2005) (May 1, 2004 through April 30, 2005). The water quality evaluation presented in this chapter updates previous analyses presented in the 1999 Everglades Interim Report, the 2000–2004 Everglades Consolidated Reports (ECRs) and the 2005 South Florida Environmental Report (SFER). More specifically, this chapter and its associated appendices use water quality data collected during WY2005 to achieve the following objectives:

- 1. Summarize areas and times where water quality criteria are not being met and indicate trends in excursions over space and time
- 2. Discuss factors contributing to excursions from water quality criteria and provide an evaluation of natural background conditions where existing standards may not be appropriate
- 3. Summarize areas and times where water quality criteria are not being met and indicate trends in excursions over space and time

- 4. Summarize specific conductance levels within the naturally low ionic strength waters of the Refuge and indicate temporal trends
- 5. Summarize sulfate concentrations in the EPA and indicate spatial and temporal trends
- 6. Present an updated review of pesticide and priority pollutant data made available during WY2005

# METHODS

An approach similar to the regional synoptic approach used in previous ECRs and the 2005 SFER was applied to the WY2005 data to provide an overview of the status of compliance with water quality criteria in the EPA. The consolidation of regional water quality data provides for analysis over time but limits spatial analyses within each region. However, spatial analyses can be made between regions because the majority of inflow and pollutants enter the northern one-third of the EPA and the net water flow is from north to south.

# WATER QUALITY DATA SOURCES

The majority of the water quality data evaluated in this chapter was retrieved from the South Florida Water Management District's (SFWMD's or District's) DBHYDRO database. The DBHYRDO monitoring projects evaluated for WY2005 included C111D, CAMB, ENP, ENRR, EVER, EVPA, HOLY, L31N, NECP, STA1W, and STA2. Additionally, water quality data from the nutrient gradient sampling stations monitored by the Everglades Systems Research Division (ESRD) in the northern part of Water Conservation Area 2A (WCA-2A), the southwestern part of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (Refuge), the west-central portion of WCA-3A, and Taylor Slough in the Everglades National Park (ENP or Park) were obtained from the SFWMD's ESRD Database.

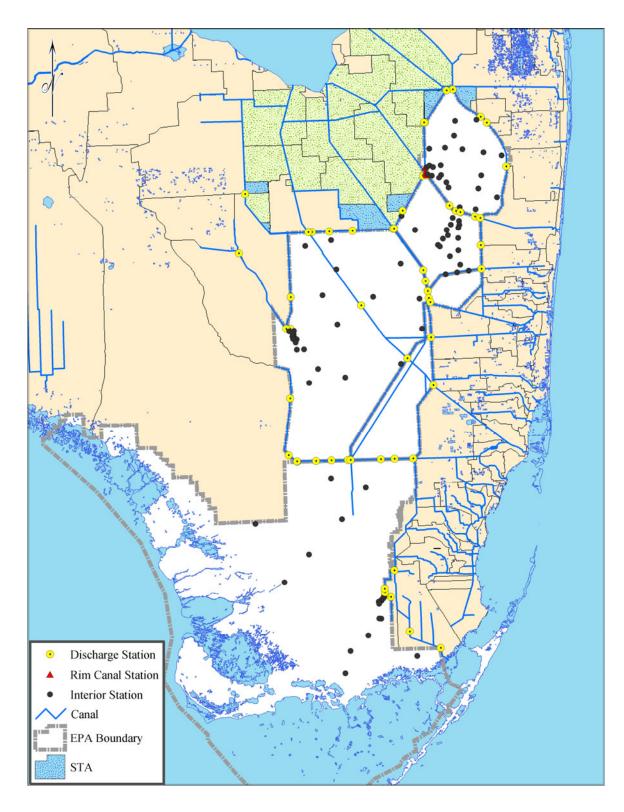
Before water quality data are entered into either database, the SFWMD follows strict quality assurance/quality control (QA/QC) procedures approved by the Florida Department of Health under the National Environmental Laboratory Accreditation Conference (NELAC) certification process. Both sampling and analytical methods are documented in the SFWMD's Quality Assurance Manual and in Standard Operating Procedures (SOPs) that are reviewed and updated annually. Contract laboratories used by the District also must be NELAC certified and must maintain the appropriate Quality Assurance Manual and SOPs.

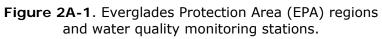
# EVERGLADES PROTECTION AREA WATER QUALITY SAMPLING STATIONS

The surface water in the portion of the Everglades represented by the sampling stations used in this report is classified as Class III freshwater of the state [Section 62-302.400, Florida Administrative Code (F.A.C.)]. Class III water quality criteria were established to protect recreation, propagation, and maintenance of a healthy, well-balanced population of fish and wildlife (Section 62-302.400, F.A.C.). Additionally, the Refuge and the Park are classified as Outstanding Florida Waters (Section 62-302.700, F.A.C.). Beyond the requirements of Class III water quality criteria, no degradation of water quality other than that allowed in Paragraphs 62-4.242(2) and (3), F.A.C. is to be permitted in Outstanding Florida Waters (Section 62-302.700, F.A.C.).

Water quality sampling stations located throughout the WCAs and the Park were categorized as inflow, interior, or outflow sites within each region based on their location and function (Figure 2A-1). This organization of monitoring sites allowed a more detailed analysis of the water quality status in each region of the EPA and assisted in the evaluation of potential causes for observed excursions from Class III water quality criteria. Several interior structures convey water between different regions in the EPA and therefore are designated as both inflow and outflow stations based on this categorization system. For example, the S-10 structures act as both outflow stations for the Refuge and inflow sites to WCA-2. Additionally, the S-11 structures are designated as outflows from WCA-2, as well as inflow points to WCA-3. The S-12 structures, S-355A, S-355B, and S-333 are outflows from WCA-3 and are also inflow sites to the Park. The interior sites of each region consist of marsh and canal stations as well as structures that convey water within the area. In addition to inflow, outflow, and interior sites, the Refuge has an additional site category (rim canal sites) to account for the fact that much of the water entering the interior of the Refuge is conveyed in rim canals that border the east and west levees of the Refuge. Waters discharged to the L-7 rim canal will either overflow into the Refuge interior when canal stages exceed the levee height or will bypass the marsh and be discharged to WCA-2A through the S-10 structures. The extent (distance) to which rim canal overflows permeate the marsh depends on the relative stages of the L-7 rim canal and the Refuge interior. The location and classification of monitoring stations used in this report are presented in Figures 2A-2 through 2A-5.

The current SFWMD monitoring programs were described by Germain (1998). Sampling frequency varies by site depending on site classification, parameter group, and hydrologic conditions (water depth and flow). Additionally, the District has created a web site describing its water quality monitoring projects, including project descriptions and objectives (<u>www.sfwmd.gov/org/ema/envmon/wqm</u>). The District's web site currently provides limited, site-specific information. Generally, interior monitoring stations were sampled monthly for most parameters reported in this chapter. Water control structures (inflows and outflows) were typically sampled biweekly when flowing, otherwise monthly.





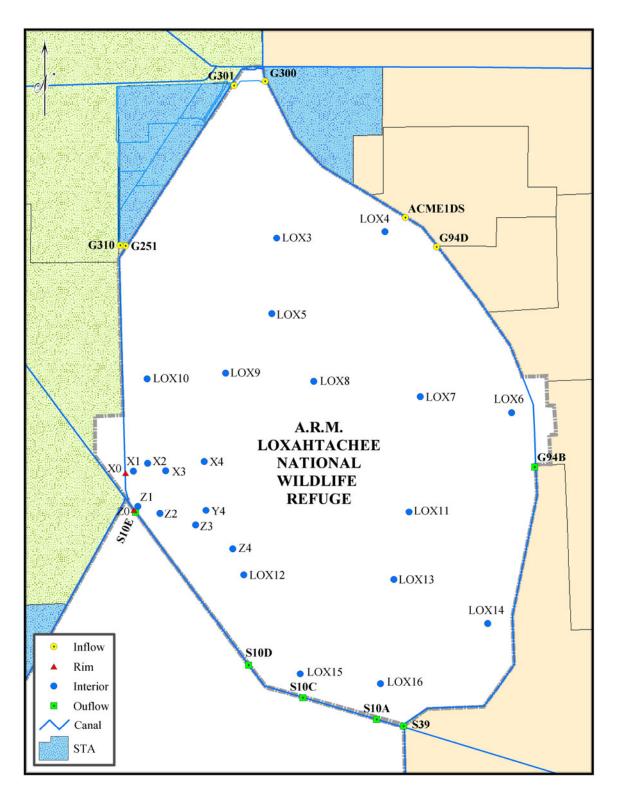
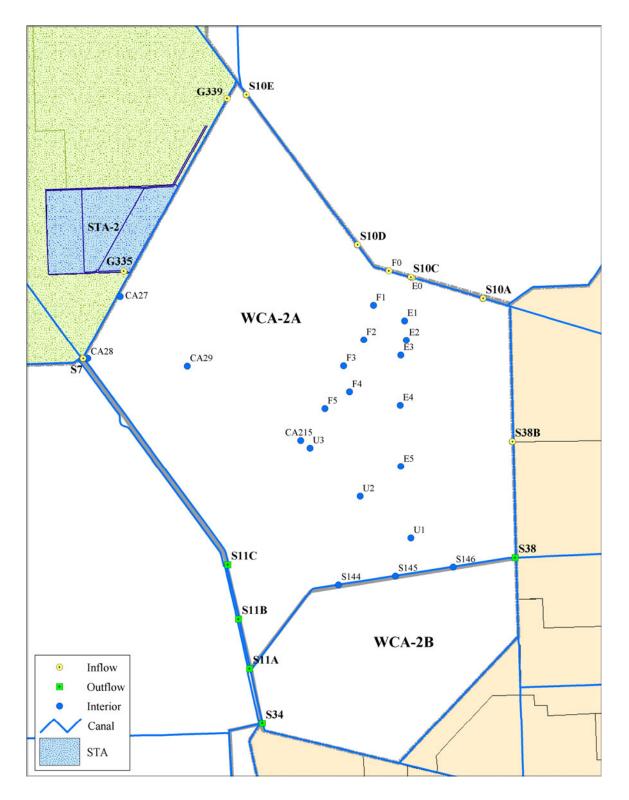
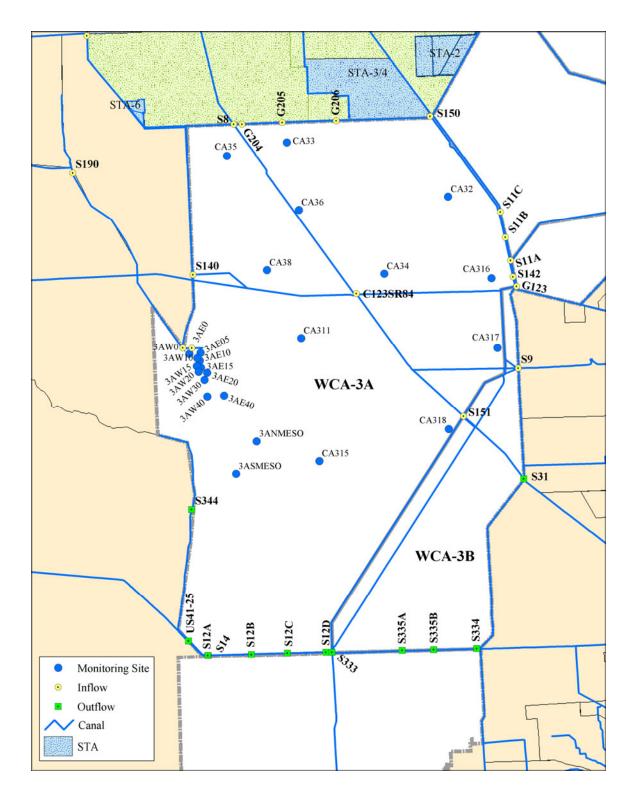
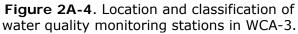


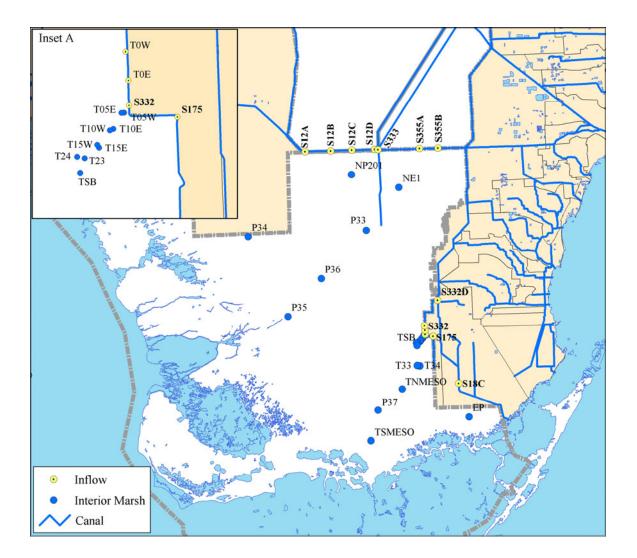
Figure 2A-2. Location and classification of water quality monitoring stations in WCA-1.



**Figure 2A-3**. Location and classification of water quality monitoring stations in WCA-2.







**Figure 2A-5**. Location and classification of water quality monitoring stations in the Everglades National Park (ENP or Park). Inset A provides the location of transect monitoring stations downstream of C-111 inflows in Taylor Slough.

### EVERGLADES PROTECTION AREA DATA ANALYSIS PERIOD

Water quality data collected from monitoring stations within the EPA regions during WY2005 are evaluated and discussed in this chapter. Additionally, pesticide data presented in this chapter was collected during quarterly sampling events conducted between October 2003 and December 2004. The period of record for pesticides was selected as an update to the data presented in the 2005 South Florida Environmental Report, rather than reflected by the water year.

# WATER QUALITY DATA EVALUATION

The District monitors approximately 109 water quality parameters within the EPA (Bechtel et al., 1999 and 2000). Given this chapter's focus on water quality criteria, the evaluation was primarily limited to parameters with Class III criteria pursuant to Chapter 62-302, F.A.C. The parameters evaluated included sulfate, 62 pesticides, and the following 18 water quality constituents:

- Alkalinity
- Dissolved oxygen (in situ)
- Specific conductance @ 25°C (in situ)
- pH (in situ)
- Total silver
- Total antimony
- Total arsenic
- Total beryllium
- Total cadmium

- Trivalent chromium
- Total copper
- Total iron
- Total lead
- Total selenium
- Total thallium
- Total zinc
- Turbidity
- Un-ionized ammonia

# DATA SCREENING AND HANDLING

Water quality data were screened based on laboratory qualifier codes, consistent with the state Quality Assurance Rule (Chapter 62-160, F.A.C.). Any datum with an associated fatal qualifier (,H, J, K, N, O, V, Q, Y, or ?) was removed from the analysis. Values that exceeded possible physical or chemical measurement constraints (e.g., pH greater than 14) had temperatures well outside seasonal norms (e.g., 6°C in July) or represented data transcription errors were excluded. Statistical outlier analysis was not performed for these data. Overall, 1.9 percent of the WY2005 data, including nutrients, were excluded due to quality assurance/quality control (QA/QC) issues (Appendix 2A-1). Qualification with a V, J, or Y qualifiers accounted for a majority (95.1 percent) of the data exclusions. All data passing the qualifier screening was used in the analysis. Samples collected at the same location on the same day were considered as one sample, with the arithmetic mean used to represent the sampling period.

Additional considerations in the handling of water quality data are the accuracy and sensitivity of the laboratory method used. Each analytical method for a particular water quality constituent has a Method Detection Limit (MDL) that defines the minimum concentration or the level at which the constituent can be identified. The MDL is usually statistically above the background noise level associated with the analytical method. A constituent present at a

concentration that is at or below the MDL may not be quantified within established limits of accuracy or precision using that method. The Practical Quantitation Limit (PQL) represents a practical and routinely achievable quantification level with a relatively good certainty that a value determined using that method is reliable (APHA, 1995). For purposes of summary statistics presented in this chapter, data reported as less than the MDL were assigned a value of one-half the MDL unless otherwise noted. All data presented in this chapter, including historical results, are handled consistently with regard to screening and MDL replacement. The percentages of results below detection (< MDL) for each constituent are reported in Appendix 2A-1.

# EXCURSION ANALYSIS

The Florida Department of Environmental Protection (FDEP) and the District have developed and clearly documented an excursion analysis protocol for use in the annual South Florida Environmental Report. The primary objective of the protocol is to provide a synoptic view of water quality standards compliance on a regional scale (Refuge, WCA-2, WCA-3, and Park). This protocol was developed to balance consistency with previous versions of this report, other state of Florida ambient water quality evaluation methodologies (e.g., Impaired Waters 303(d) designations), and the U.S. Environmental Protection Agency (USEPA) exceedance frequency recommendations, as well as to provide a concise summary to decision makers and the public. This methodology is being used in order to ensure that the results will be compatible with information provided to water managers from other sources.

To evaluate compliance with water quality criteria in WY2005, constituent concentrations were compared to their respective Class III criteria specified in Chapter 62-302, F.A.C. In addition to Class III criteria, pesticides were evaluated against known chronic toxicity values. An excursion was recorded when a reported value above the given MDL exceeded the applicable numeric criteria (Chapter 62-302.530, F.A.C.) or exceeded the chronic toxicity value. The excursions for each region of the EPA were tabulated, providing both the total number of samples and the percent of samples exceeding the criteria.

A multitiered categorical system was used in this chapter to rank the severity of excursions from state water quality criteria (**Table 2A-1**). Categories were assigned based on sample excursions frequencies evaluated using a statistically valid assessment methodology (i.e., binomial hypothesis test) that accounted for uncertainty in monitoring data. The basis for selecting the binomial approach is presented in Weaver and Payne (2004; 2005). Parameters without excursions were categorized as no concern and are not discussed further in this chapter. For any parameter with excursions and at least 28 samples during the period of record, the binomial hypothesis test at the 90 percent confidence level was applied to evaluate whether the given parameter was a concern; that is, whether it exhibited an excursion rate greater than 10 percent. If the binomial hypothesis test failed to reject the null hypothesis ( $H_0$ :  $f \le 0.10$ ;  $H_A$ :  $f \ge 0.10$ ), then the binomial test at the 90 percent confidence level was used to determine whether the parameter was a potential concern (excursion rate from 5 to 10 percent, i.e.,  $H_A$ :  $f \ge 0.05$ ) or a minimal concern (an excursion rate of 5 percent or less, i.e.,  $H_0$ :  $f \le 0.05$ ). Table 2A-1. Definitions of excursion categories for water qualityconstituents in the EPA. For conventional water quality constituents with atleast 28 samples, frequencies were statistically tested using the binomialhypothesis test at the 90 percent confidence level.

Excursion Category	Conventional Water Quality Constituents	Pesticides
Concern	≥ 10% Excursion <sup>1</sup>	Class III criterion and/or toxicity levels exceeded
Potential Concern	$\ge 5\%$ and $\le 10\%$ Excursions <sup>2</sup>	≥ MDL <sup>3</sup>
Minimal Concern	≤ 5% Excursions	N/A
No Concern	No Excursions	< MDL

1. For sample sizes less than 28, an excursion frequency of greater than 20 percent was used to define the concern category.

2. For sample sizes less than 28, an excursion frequency of less than or equal to 20 percent was used to define the potential concern category.

3. MDL = Method Detection Limit

Because the binominal hypothesis test does not adequately balance statistical error rates at sample sizes of less than 28, parameters with reported excursions and fewer than 28 samples were initially categorized as a concern and potential concern based on excursion frequencies (raw scores) of greater than 20 percent and less than 20 percent, respectively<sup>2</sup>. It is assumed that an observed excursion frequency greater than 20 percent provides substantial reason to suspect that the true exceedance frequency may exceed 10 percent and warrants further investigation. Furthermore, given the high degree of uncertainty associated with small sample sizes (< 28), any excursions warrant further review. However, extreme caution must be exercised when interpreting results drawn from such small samplings. As a means to reduce uncertainty, any parameter initially identified as a concern or potential concern based on fewer than 28 samples was further evaluated based on longer term (five-year) excursion rates. Utilization of a longer period of record assumes that exceedance frequencies are constant among years, that is, there is no trend. Parameters with human health-based criteria were evaluated under the assumption that the Class III criteria values represent instantaneous maximum concentrations for which any exceedance constitutes a non-attainment of designated use.

 $<sup>^{2}</sup>$  At sample sizes less than 28, the binomial hypothesis test is associated with unacceptably high Type II error rates (greater than 20 to 93 percent). A 20 percent raw-score criterion was selected because it provides a better balance between error rates than either a binomial test or a 10 percent raw score, i.e., at sample sizes between 1 and 27, both Type I and II error rates are intermediate (between) those associated with a binomial test or 10 percent raw score. However, this error rate compromise does not fully address the uncertainty inherent in the analysis of such small samples. Analysis of longer periods of record or increased sampling frequencies is required to confidently categorize excursion frequencies and acceptably balance Type I and II error rates.

As a supplement to the binomial hypothesis test, 90 percent confidence intervals (90% C.I.) were calculated around the estimated exceedance frequencies for WY2005. Inclusion of confidence intervals provides a measure of uncertainty associated with frequency estimates and excursion analyses. For example, if the lower confidence bound (frequency minus the 90% C.I.) is greater then 10 percent, then it can be concluded with at least 90 percent certainty that the parameter is a concern. However, if the confidence bound includes 10 percent (or 5 percent), then it cannot be concluded that the parameter is a concern).

Use of the binomial hypothesis test assumes a constant exceedance probability across all monitoring stations within an area and class (i.e., regional assessment units such as WCA-2 interior, Park inflows)<sup>3</sup>. If this assumption is violated, then there is a chance that a regional concern level will be incorrectly elevated due to the influence of a high localized exceedance frequency. Conversely, there is a chance of masking localized high exceedances frequencies within the regionally aggregated frequency. For example, if a region represented by 10 stations had total of 120 samples with 10 exceedances at only one station, then the water quality parameter would be categorized as a potential concern for the entire region; however, in reality the parameter is likely not a concern at nine stations but may be a concern at one. The assumption of homogeneous exceedance probabilities may not hold for every water quality parameter within an area as large as the Everglades. Subdividing each region into smaller, more homogenous sub-water bodies is a potential approach to ensure adherence to this assumption. However, this method does not meet the chapter's objective of providing regional summaries at the water body level (i.e., Refuge, WCA-2, WCA-3, and Park). Therefore, methods to detect and delineate localized exceedance patterns within each water body were utilized to supplement and refine the regional analyses. The binomial hypothesis test and excursion criterion were applied to individual station data. Because there are insufficient data (< 28 samples) over a single annual period, to confidently estimate station level exceedance frequencies for most water quality parameters, a longer period of record was necessary. Individual station assessments were based on the previous five years (WY2001–WY2005), rather than on the single year used for regional analyses. Use of a five-year period provided sufficient data for most parameters. No determination was made for any parameter with less than 28 samples. If one or more monitoring stations were categorized at a higher level of concern than the region as a whole, then a localized exceedance was recorded. Localized exceedances are noted in the summary tables and discussed in greater detail.

Because the USEPA recommended that a 10 percent excursion frequency does not apply to pesticides, the pesticide evaluation method presented in this chapter is identical to the method used in previous ECRs and the 2005 South Florida Environmental Report (USEPA, 1997 and 2002). Pesticides were categorized based on the exceedance of Class III criteria or chronic toxicity values and detection (measurement  $\geq$  MDL) frequency (**Table 2A-1**).

<sup>&</sup>lt;sup>3</sup> Constant exceedance probability is also an assumption of the previously used raw-score approach.

# SUMMARY OF FINDINGS FROM PREVIOUS EVERGLADES REPORTS

#### 1999–2004 EVERGLADES CONSOLIDATED REPORTS

Previous Everglades Consolidated Reports have demonstrated that, with few exceptions, water quality has been in compliance with existing state water quality criteria, though some excursions have been noted (Bechtel et al., 1999 and 2000; Weaver et al., 2001–2003; Weaver and Payne, 2004). Reported excursions have generally been localized to specific areas of the EPA, with the exception of dissolved oxygen (DO), which exhibited excursions in all areas. Furthermore, alkalinity, conductivity, and pH were identified as a concern for at least one EPA region in all previous ECRs. Additionally, the 1999 Everglades Interim Report and 2000 Everglades Consolidated Report identified  $NH_3$  as a concern in localized areas of the EPA. The 2003 and 2004 ECRs identified a localized NH<sub>3</sub> concern at two WCA-2 inflow sites (E0 and F0) to WCA-2. Previous ECRs have also evaluated pesticide monitoring results and have identified atrazine, chloriphyros ethyl, endosulfan, ethion, parathion methyl, diazinon, dichlorodiphenyltrichloroethane (DDT), dichlorodiphenyldichloroethene (DDE), and dichlorodiphenyldichloroethane (DDD) as a concern in localized areas for various years during the period of record.

Each of the previous ECRs have listed DO as a concern for the entire Everglades, with nearly all monitoring stations exhibiting excursions during each year. However, a majority of the DO excursions were the result of natural conditions and processes within the marsh and therefore do not constitute violations of state water quality standards. To more accurately characterize the natural DO regime within the marsh, a site-specific alternative criterion (SSAC), which used a mathematical model to describe the relationship between DO, time of day, and temperature to define a measurement methodology, was developed by the FDEP and was presented in the 2001 Everglades Consolidated Report. Application of the present SSAC for DO resulted in a significant reduction in the number of interior marsh stations at which DO was designated as a concern. The Everglades DO SSAC was adopted by the FDEP on January 26, 2004, and was subsequently approved by the USEPA as a revision to the Florida Water Quality Standards.

# 2005 SOUTH FLORIDA ENVIRONMENTAL REPORT

Chapter 2A of the 2005 SFER (Weaver and Payne, 2005) provides an overview of the status of compliance with water quality criteria in the EPA for WY2005. Comparisons of WY2004 water quality data with applicable Class III water quality criteria resulted in excursions for six identified water quality parameters. These excursions were localized to specific areas of the EPA, with the exception of DO, which exhibited excursions in all regions. Alkalinity and conductivity were classified as a concern for the Refuge interior. Dissolved oxygen was categorized as a concern for the Refuge interior, WCA-2 inflows, WCA-2 interior, and WCA-3 interior. Additionally, DO was categorized as a potential concern for Refuge inflows, Park inflows, and WCA-3 outflows. Specific conductance was classified as a concern for WCA-2 inflows and rim canal sites. Although 12 pesticides or degradation products were detected during the available period of record (September 2002– September 2003), only atrazine was classified as a concern.

# WATER YEAR 2005 RESULTS

WY2005 data for water quality parameters with Class III numeric criteria are summarized by region and monitoring station in Appendices 2A-1 and 2A-2, respectively. Comparisons of WY2005 water quality data with applicable Class III water quality criteria resulted in excursions for six identified water quality parameters. Similar to previous periods these excursions were localized to specific areas of the EPA, with the exception of DO, which exhibited excursions in all regions. Alkalinity and conductivity were classified as a concern for the Refuge interior (Table 2A-2). Because Everglades DO is assessed as an annual station average rather than as point measures, there were insufficient data to confidently apply the binomial hypothesis test to the regional assessment units on an annual basis. Therefore, excursion categories for DO were assessed based on a five-year period of record (WY2001-WY2005) for all areas. DO was categorized as a concern for the Refuge interior, WCA-2 interior, and WCA-3 interior and a potential concern for WCA-3 inflows. Alkalinity and pH were categorized as a concern and potential concern, respectively, for the Refuge interior. Un-ionized ammonia was categorized as potential concern for WCA-2 inflows due high excursion frequencies at sites E0 and F0. Specific conductance was classified as a potential concern for WCA-2 inflows and interior. Additionally, turbidity, pH, and un-ionized ammonia were categorized as minimal concerns for several EPA regions due to infrequent and localized excursions. Water quality parameters that were classified as minimal concerns will not be discussed further in this chapter. Thirteen pesticides, or breakdown products, were detected between October 2003 and December 2004. Of these pesticides, only atrazine and chlorpyrifos ethyl were classified as a concern. No other parameters exceeded state water quality criteria during WY2005, and therefore are not discussed in this chapter.

Excursion frequencies and categories for parameters with any recorded excursions in the last five water years (WY2001–WY2005) are summarized for three time periods (WY1978–WY2003, WY2004, and WY2005) to evaluate the presence of any temporal trends (**Table 2A-3**). Excursion categories for all periods are based on the methodology previously described in this chapter (**Table 2A-1**). Additionally, excursion frequencies and categories for individual monitoring stations are summarized in Appendix 2A-2. Excursion frequencies for WY2005 were generally within the range of the historical periods for most water quality parameters, with the exception of decreased specific conductance excursion rates for WCA-2 and Refuge inflows and outflows. Water quality parameters categorized as concerns or potential concerns for WY2005 are reviewed in greater detail below. The review includes discussions concerning the environmental significance associated with the observed excursions, potential causes of the excursions, and any actions taken to resolve the associated concerns, including evaluation of the applicable criteria and natural background conditions within the EPA.

The Everglades marshes showed little change in water quality as the result of the WY2005 hurricanes. Water quality within the EPA during WY2005 was similar to previous years and, with few exceptions, was in compliance with existing state water quality criteria. The increased rainfall associated with the WY2005 hurricanes increased runoff volumes discharged to the EPA from areas to the north, which resulted in the increased input of some parameters such as phosphorus and nitrogen (discussed in Chapter 2B), while conversely diluting others (e.g., dissolved ions). In fact, the decreased specific conductance excursion rates noted for Refuge and WCA-2 inflows and outflows were likely related to the storm-induced dilution. Any direct effects from the storms, such as disturbance of the water column and underlying sediments, were short-lived and had little or no adverse effect on the measured water quality parameters reported in this chapter.

**Table 2A-2.** Summary of water quality data and excursions from applicable criteria in the EPA for WY2005. Only water quality parameters with excursions in the given region and class are listed. Excursion categories of concern, potential concern, and minimal concern are denoted by "C," "PC," and "MC," respectively. Excursion categories with parentheses indicate a localized exceedance rate greater then the regional (area and class) classification; that is, one or more stations exhibited higher exceedance rates between WY2001–WY2005 than the WY2005 regional aggregate.

Area	Class	Parameter	Units	Class III Criteria	N	Mean	Standard	Min	Max	Excu	rsion
							Deviation			%±90%C.I.	Category
		Dissolved Oxygen	mg/L	SSAC <sup>1</sup>	5	4.65	1.74	1.97	6.52	20.0±29.4	C <sup>3</sup> /NA
	Inflow	рН	Units	≥ 6.0,≤8.5	129	7.53	0.30	7.01	8.54	0.8±1.3	MC
		Alkalinity	mg/L	≥ 20	193	75	63	7	332	19.2±4.7	С
ge		Dissolved Oxygen	mg/L	SSAC <sup>1</sup>	22	3.39	1.06	1.28	5.81	30.4±15.8	C <sup>3</sup> /C
Refuge		pН	Units	≥ 6.0,≤8.5	219	6.69	0.49	5.02	8.02	7.3±2.9	PC (C)
ш	Interior	Un-ionized ammonia	mg/L	≤0.02	187	0.0004	0.0024	<0.0001	0.033	0.5±0.9	MC
	Outflow	Turbidity	NTU	≤29	57	6.58	9.82	0.80	55.8	3.5±4.0	MC
	Rim	Specific Conductance	µmhos/cm	≤ 1275 <sup>2</sup>	22	1182	1611	654	8360	4.5±7.3	PC <sup>3</sup> /MC
		Specific Conductance	µmhos/cm	≤ 1275 <sup>2</sup>	165	955	259	142	1411	9.1±3.7	PC (C)
	Inflow	Turbidity	NTU	≤29	80	4.62	8.59	0.60	55.8	2.5±2.9	MC
N		Un-ionized ammonia	mg/L	≤0.02	98	0.0063	0.012	<0.0001	0.059	11.2±5.2	PC (C)
WCA-2		Dissolved Oxygen	mg/L	SSAC <sup>1</sup>	18	3.59	1.46	1.34	6.22	38.9±18.9	C <sup>3</sup> /C
3		рН	Units	≥ 6.0,≤8.5	204	7.44	0.33	4.82	8.70	1.0±1.1	MC
		Specific Conductance	µmhos/cm	≤ 1275 <sup>2</sup>	217	933	271	279	2317	7.8±3.0	PC (C)
	Interior	Un-ionized ammonia	mg/L	≤0.02	154	0.0012	0.0037	<0.0001	0.041	0.6±1.1	MC
		Dissolved Oxygen	mg/L	SSAC <sup>1</sup>	17	4.99	1.17	2.56	7.41	5.9±9.4	PC <sup>3</sup> /PC
A-3	Inflow	Un-ionized ammonia	mg/L	≤0.02	204	0.0024	0.0029	0.0001	0.023	0.5±0.8	MC
WCA-3		Dissolved Oxygen	mg/L	SSAC <sup>1</sup>	22	3.19	1.43	0.74	5.19	31.8±16.3	C <sup>3</sup> /C
	Interior	рН	Units	≥ 6.0,≤8.5	198	7.34	0.31	4.48	8.26	0.5±0.8	MC
Park	Interior	Dissolved Oxygen	mg/L	SSAC <sup>1</sup>	9	5.56	2.33	2.72	9.12	11.1±17.2	PC³/MC

1. The Everglades DO SSAC is based on a mathematical equation that models the sinusoidal diel cycle and seaonal variability of DO in the Everglades and is assessed as an annual average by station. The SSAC is discussed in the DO section of this chapter.

2. Specific conductance shall not be increased 50 percent above background or 1,275 µmhos/cm, whichever is greater. Assessment present in this report is based only on the 1,275 µmhoscm component of the criterion.

3. Insufficient sample size to apply binomial hypothesis test to WY2003 data alone; analysis was based on a five-year period of record from WY2001–WY2005.

# **Table 2A-3**. Summary of excursions from Class III criteria in the EPA for WY2005, WY2004, and historical data (WY1978–WY2003). An entry of "--" indicates that no samples were collected for the parameter during the given period of record.

Area	Class	Parameter	1978–2003		20	04	2005		
			Number of Percent		Number of Percent		Number of	Percent	
			Excursions	Excursions	Excursions	Excursions	Excursions	Excursions	
		Dissolved Oxygen	22 (130)	16.9 (C)	1 (4)	25.0 (C)	1 (5)	20.0 (C*)	
		pН	13 (2590)	0.5 (MC)	0 (134)	0.0 (NC)	1 (129)	0.8 (MC)	
		Specific Conductance	624 (2603)	24.0 (C)	15 (134)	11.2 (PC)	0 (125)	0.0 (NC)	
	Inflow	Total Iron	20 (532)	3.8 (MC)	0 (8)	0.0 (NC)	0 (8)	0.0 (NC*)	
	milow	Total Silver	3 (35)	8.6 (MC)					
		Turbidity	62 (2063)	3.0 (MC)	0 (80)	0.0 (NC)	0 (73)	0.0 (NC)	
		Un-ionized ammonia	39 (2250)	1.7 (MC)	0 (78)	0.0 (NC)	0 (70)	0.0 (NC)	
nge	Rim	Specific Conductance	103 (728)	14.1 (C)	4 (24)	16.7 (PC)	1 (22)	4.5 (PC*)	
Refuge		Alkalinity	526 (2123)	24.8 (C)	44 (219)	20.1 (C)	37 (193)	19.2 (C)	
	Interior	Dissolved Oxygen	58 (199)	29.1 (C)	8 (23)	34.8 (C)	7 (23)	30.4 (C*)	
	Interior	pН	218 (2193)	9.9 (PC)	7 (253)	2.8 (MC)	16 (219)	7.3 (PC)	
		Un-ionized ammonia	3 (2056)	0.1 (MC)	0 (229)	0.0 (NC)	1 (187)	0.5 (MC)	
		рН	3 (1228)	0.2 (MC)	2 (65)	3.1 (MC)	0 (58)	0.0 (NC)	
		Specific Conductance	152 (1251)	12.2 (C)	3 (65)	4.6 (MC)	0 (56)	0.0 (NC)	
	Outflow	Turbidity	11 (1215)	0.9 (MC)	0 (65)	0.0 (NC)	2 (57)	3.5 (MC)	
		Un-ionized ammonia	12 (1338)	0.9 (MC)	0 (65)	0.0 (NC)	0 (55)	0.0 (NC)	
	Inflow	Dissolved Oxygen	41 (129)	31.8 (C)	3 (9)	33.3 (C)	0 (8)	0.0 (NC*)	
		рН	6 (1705)	0.4 (MC)	2 (169)	1.2 (MC)	0 (166)	0.0 (NC)	
		Specific Conductance	274 (1730)	15.8 (C)	47 (168)	28.0 (C)	15 (165)	9.1 (PC)	
		Turbidity	15 (1372)	1.1 (MC)	0 (81)	0.0 (NC)	2 (80)	2.5 (MC)	
		Un-ionized ammonia	81 (1758)	4.6 (MC)	7 (103)	6.8 (MC)	11 (98)	11.2 (PC)	
-2	Interior	Dissolved Oxygen	104 (239)	43.5 (C)	11 (18)	61.1 (C)	7 (18)	38.9 (C*)	
WCA-2		pН	21 (3822)	0.5 (MC)	0 (270)	0.0 (NC)	2 (204)	1.0 (MC)	
5		Specific Conductance	368 (3766)	9.8 (PC)	40 (269)	14.9 (C)	17 (217)	7.8 (PC)	
		Un-ionized ammonia	12 (3683)	0.3 (MC)	0 (228)	0.0 (NC)	1 (154)	0.6 (MC)	
		Dissolved Oxygen	26 (114)	22.8 (C)	0 (5)	0.0 (NC)	0 (5)	0.0 (NC*)	
	Outflow	рН	7 (1494)	0.5 (MC)	0 (82)	0.0 (NC)	0 (76)	0.0 (NC)	
	•••••	Specific Conductance	27 (1506)	1.8 (MC)	0 (82)	0.0 (NC)	0 (78)	0.0 (NC)	
		Un-ionized ammonia	6 (1605)	0.4 (MC)	0 (79)	0.0 (NC)	0 (68)	0.0 (NC)	
		Dissolved Oxygen	94 (317)	29.7 (C)	2 (14)	14.3 (PC)	1 (17)	5.9 (PC*)	
		рН	35 (4770)	0.7 (MC)	0 (414)	0.0 (NC)	0 (402)	0.0 (NC)	
	Inflow	Specific Conductance	66 (4820)	1.4 (MC)	3 (413)	0.7 (MC)	0 (401)	0.0 (NC)	
		Total Beryllium	4 (22)	18.2 (PC*)					
WCA-3		Turbidity	56 (4062)	1.4 (MC)	0 (185)	0.0 (NC)	0 (185)	0.0 (NC)	
MC		Un-ionized ammonia	12 (4529)	0.3 (MC)	1 (215)	0.5 (MC)	1 (204)	0.5 (MC)	
		Alkalinity	4 (2169)	0.2 (MC)	0 (321)	0.0 (NC)	0 (197)	0.0 (NC)	
	Interior	Dissolved Oxygen	39 (131)	29.8 (C)	12 (23)	52.2 (C)	7 (22)	31.8 (C*)	
		pН	0 (2182)	0.0 (NC)	0 (349)	0.0 (NC)	1 (198)	0.5 (MC)	
		Dissolved Oxygen	35 (186)	18.8 (C)	1 (9)	11.1 (PC)	0 (10)	0.0 (NC*)	

		1						
		рН	44 (4049)	1.1 (MC)	0 (216)	0.0 (NC)	0 (186)	0.0 (NC)
		Turbidity	3 (3161)	0.1 (MC)	0 (177)	0.0 (NC)	0 (148)	0.0 (NC)
		Un-ionized ammonia	6 (3412)	0.2 (MC)	0 (180)	0.0 (NC)	0 (146)	0.0 (NC)
		Dissolved Oxygen	24 (193)	12.4 (PC)	2 (11)	18.2 (PC)	0 (11)	0.0 (NC*)
	Inflow	рН	54 (4748)	1.1 (MC)	0 (319)	0.0 (NC)	0 (265)	0.0 (NC)
		Specific Conductance	0 (4819)	0.0 (NC)	1 (285)	0.4 (MC)	0 (253)	0.0 (NC)
		Turbidity	3 (3620)	0.1 (MC)	0 (201)	0.0 (NC)	0 (165)	0.0 (NC)
Park		Un-ionized ammonia	20 (3921)	0.5 (MC)	0 (205)	0.0 (NC)	0 (163)	0.0 (NC)
Ра		Dissolved Oxygen	2 (168)	1.2 (MC)	1 (9)	11.1 (PC)	1 (9)	11.1 (PC*)
	Interior	рН	22 (1440)	1.5 (MC)	0 (101)	0.0 (NC)	0 (75)	0.0 (NC)
		Specific Conductance	21 (1558)	1.3 (MC)	1 (101)	1.0 (MC)	0 (75)	0.0 (NC)
		Total Iron	113 (1300)	8.7 (PC)				
		Un-ionized ammonia	21 (1532)	1.4 (MC)	0 (100)	0.0 (NC)	0 (75)	0.0 (NC)

Note: For the "Number of Excursions" columns, the number in front of the parentheses specifies the number of excursions, while the number inside the parentheses specifies the number of samples collected. Excursion categories of concern, potential concern, and minimal concern are denoted by "C," "PC," and "MC," respectively, and are provided within parentheses in the "Percent Excursions" columns. An asterisk (\*) associated with an excursion category indicates an insufficient sample size ( $\leq$  28) to confidently characterize the excursion frequency; categorization is preliminary, and further evaluation is required.

#### DISSOLVED OXYGEN

Oxygen gas dissolved in water is vital to the existence of most aquatic organisms. Oxygen is a key component in cellular respiration for both aquatic and terrestrial life. The concentration of dissolved oxygen in an aquatic environment is an important indicator of that environment's quality. Due to oxygen's importance to life, it is essential to understand the processes that influence DO concentrations in the Everglades. Within any water body, the maximum quantity of oxygen that can be held in solution (i.e., saturation concentration) is controlled by the solubility of oxygen in water. The solubility of oxygen in water is inversely related to temperature and chlorinity or salinity of the water. That is, higher concentrations of DO can be maintained under conditions. In any biologically active aquatic system, the actual concentration of DO within the water column is regulated by a variety of sources and sinks which are balanced in healthy systems resulting in sufficient levels of DO to support a variety of aquatic life.

In the Everglades open-water slough communities, where light penetration is high, high photosynthetic rates by periphyton and submerged aquatic vegetation (P/SAV) result in increasing oxygen concentrations during daylight hours (Belanger and Platko, 1986; McCormick et al., 1997). At night, respiration and sediment oxygen demand (SOD) reduce oxygen concentrations. Under natural conditions, oxygen production exceeds respiration during the photoperiod, allowing the accumulation of an oxygen reserve, which prevents concentrations from decreasing to extremely low levels at night (< 1.0 to 2.0 milligrams per liter, or mg/L). Cultural eutrophication results in increased productivity in the system and an increased accumulation of organic matter in the sediments. The breakdown of this organic matter increases the SOD, which results in oxygen declines throughout the diel cycle. Additionally, nutrient enrichment in the Everglades dramatically reduces the native P/SAV community and increases emergent aquatic vegetation coverage (Rutchey and Vilchek, 1994; McCormick et al., 1998; Payne et al., 1999; 2000; 2001a). Emergent aquatic vegetation contributes little oxygen to the water column while also shading P/SAV and resulting in further reductions in DO production within the water column.

As previously noted, the DO SSAC in the Everglades Protection Area was adopted by the FDEP on January 26, 2004, and was subsequently approved by the USEPA as a revision to the Florida Water Quality Standards. Because a single value criterion does not adequately account for the wide-ranging natural daily (diel) fluctuations observed in the marsh, the SSAC provides a mechanism to account for the major factors (e.g., time of day and season) influencing natural background DO variation in the Everglades. The SSAC is based on an algorithm that uses sample collection time and water temperature to model the observed natural sinusoidal diel cycle and seasonal variability. This model provides a lower DO limit (DOL) for an individual monitoring station and is described by the equation:

$$DOL_{i} = \begin{bmatrix} -3.70 - [1.50 \cdot \text{sine} (2\pi/1440 \cdot t_{i}) - (0.30 \cdot \text{sine} (4\pi/1440 \cdot t_{i}))] + 1/(0.0683 + 0.00198 \cdot C_{i} + 5.24 \cdot 10^{-6} \cdot C_{i}^{2})] - 1.1 \end{bmatrix}$$

Where:

DOL<sub>*i*</sub> is the lower limit for the  $i^{th}$  annual DO measurement in mg/L t<sub>*i*</sub> is the sample collection time in minutes (EST) since midnight of the  $i^{th}$  annual DO C<sub>*i*</sub> is the water temperature associated with the  $i^{th}$  annual DO measurement in °C To fully account for seasonal and annual variability in marsh DO concentrations, ambient assessment with the SSAC is based on a comparison between the annual average of multiple (e.g., monthly) DO measurements made throughout the year and the average of the corresponding DO limits specified by the above equation for that year. In other words, annual average observed DO at a monitoring station is to be compared to the annual average of all DOL<sub>*i*</sub> determinations for that year. DO excursion results for individual stations are provided in Appendix 2A-3.

Because DO is assessed as an annual station average rather than as point measures, there were insufficient data to confidently apply the binomial hypothesis test to the regional assessment units. Therefore, excursion categories for DO were assigned based on a five year period of record (WY2001–WY2005) for all areas. DO was categorized as a concern for the Refuge interior, Refuge inflows, WCA-2 interior, and WCA-3 interior. Additionally, DO was categorized as a potential concern for WCA-3 inflows.

Stations that failed to meet the SSAC were generally influenced either by altered hydrogeomorphic conditions caused by the construction of the canals and operation of the water control structures or by nutrient enrichment. Similar to the results reported in previous reports (Weaver et al., 2001–2003; Weaver and Payne, 2004; 2005), several of the water control structures (inflow and outflow sites) failed the SSAC test during WY2005. This pattern of non-compliance is likely due to a combination of factors, including the disturbance of bottom sediments, intrusion of low DO groundwater into the surface water at these structures, and effects of nutrient enrichment. Sediments are commonly mixed with canal surface waters during pumping events. These sediments typically increase oxygen demand within the water column and subsequently result in reduced DO concentrations (Environmental Services and Permitting, Inc., 1992). Groundwater intrusion is common at the Everglades pumping stations and canals dug below the water table. The influence of groundwater on DO at these structures represents a potentially "human-induced condition, which cannot be controlled or abated" (Chapter 62-302.800, F.A.C.) and should be addressed separately. The second group of stations failing the SSAC consists of interior marsh stations known to be biologically impaired as a result of phosphorus enrichment (e.g., E1, F1, Z1, and 3AW05). Conditions at these stations are expected to remain impaired until phosphorus concentrations in surface water and sediment are reduced and the biological communities recover.

It should be noted that the excursion categories assigned to the WCA interior regions were influenced by the high spatial monitoring intensity within enriched marsh areas. When unenriched areas are evaluated separately, DO is classified as a minimal concern for unimpacted areas of the Park and WCA-2, a potential concern for WCA-3, and a concern for the Refuge. DO excursions within the unimpacted Refuge marsh were localized in two areas. Between WY2001–WY2005, a total of nine exceedances were recorded among sites X3, X4, and Y4 on the west central side of the Refuge. During the same period, four excursions also occurred in the southern portion of the Refuge at site LOX16. The cause of these exceedances is uncertain, although nutrient enrichment does not appear to be a major factor. Five-year average geometric mean total phosphorus (TP) concentrations were less than or equal to 10 micrograms per liter ( $\mu$ g/L) at all four sites (1-sided t-test: p = 0.11-1.0).

# ALKALINITY AND pH

Alkalinity is a measure of water's acid neutralization capacity and provides a measure of the water's buffering capacity. In most surface water bodies, the buffering capacity is primarily the result of the equilibrium between carbon dioxide and bicarbonate and carbonate ions  $(CO_2, HCO_3^-, and CO_3^{2-})$ . The dissociation of calcium carbonate, magnesium carbonate, or other

carbonate-containing compounds entering the surface water through weathering of carbonate-containing rocks and minerals (e.g., limestone and calcite) contributes to water's buffering capacity. Therefore, in certain areas (such as the Park, WCA-2, and WCA-3) that are influenced by canal inflows primarily composed of mineral-rich agricultural runoff and groundwater, alkalinity levels are relatively high. Conversely, other areas, such as the interior of the Refuge, which receive most of their hydrologic load through rainfall, have very low alkalinities. Alkalinity protects aquatic life against dramatic pH changes. Rapid pH changes are difficult for living organisms to adapt to, result in severe stress, and may be lethal to sensitive species. Therefore, it is important that surface waters exhibit some minimal level of alkalinity or buffering capacity to restrict dramatic pH swings. The current Class III criterion for alkalinity specifies that this parameter shall not be lowered below 20 milligrams of calcium carbonate per liter (mg CaCO<sub>3</sub>/L).

The pH value is defined as the negative  $\log_{(base 10)}$  of the hydrogen (H<sup>+</sup>) ion activity. In low ionic-strength freshwaters, the activity of the H<sup>+</sup> ion is approximately equal to the concentration of H<sup>+</sup> ions. Because pH is based on a log scale, each pH unit change represents a ten-fold change in the concentration of H<sup>+</sup> ions (acidity). For example, a solution at a pH of 3.0 is 10 times more acidic than one at a pH of 4.0. Most living organisms, especially aquatic life, function best in a pH range of 6.0 to 9.0, although individual species have specific ideal ranges. For instance, most fish fail to spawn if conditions are below a pH of 5.0, and many species die if conditions are below a pH of 4.0. Amphibians also are particularly sensitive to extreme pH levels as well as drastic pH changes. Some amphibian declines have been attributed to declining pH (Wyman, 1990). Additionally, the pH of water affects the toxicity and solubility of other substances (e.g., ammonia, aluminum, cadmium, and iron). The current Class III criterion for pH specifies that this parameter shall not be lowered below 6.0 units or raised above 8.5 units in predominately fresh waters.

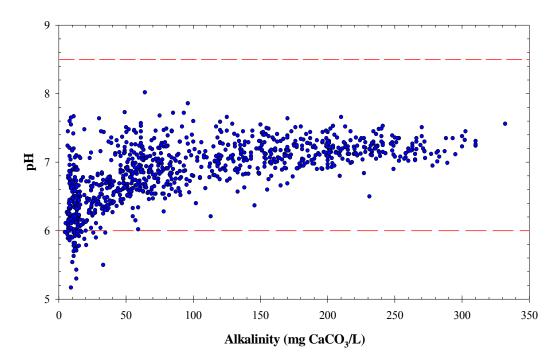
There are a number of interrelationships between pH, photosynthesis, and  $CO_2$  in water. When  $CO_2$  enters fresh water, small amounts of carbonic acid are formed, which then dissociate into H<sup>+</sup> and  $CO_3^{2^-}$  ions, thereby resulting in a lowering of pH. Because photosynthesis and respiration alter  $CO_2$  concentration in the water, these processes exert an influence on pH. During the day, while photosynthetic processes are consuming  $CO_2$ , the concentration of carbonic acid declines and pH rises. The addition of  $CO_2$  by respiration at night reverses the reactions and lowers pH. In poorly buffered systems (low alkalinity), the daily changes in pH can be dramatic.

Given the regulating effect of alkalinity on pH, these two parameters are evaluated together in this section. Excursions of state Class III water quality criteria for both parameters have historically occurred in the interior of the Refuge (Bechtel et al., 1999 and 2000; Weaver et al., 2001–2003; Weaver and Payne, 2004 and 2005). As in previous years, alkalinity was designated as a concern for the interior of the Refuge for WY2005 due to an excursion rate of  $19.2 \pm 4.7$  percent. As stated above, the low alkalinity values in the Refuge are primarily attributed to hydrology. Additionally, pH was identified as a potential concern for the Refuge interior due to excursion rate of  $7.3 \pm 2.9$  percent.

The low alkalinities and pH values in the Refuge are primarily caused by the hydrologic nature of the area. Most of the water entering the Refuge (approximately 54 percent) is low-alkalinity rainwater (SFWMD, 1992). Along the western periphery of the Refuge, harder (i.e., more mineral rich) canal waters permeate into the marsh along the L-7 rim canal; however, canal waters tend to penetrate only a few kilometers into the marsh and thus have little or no influence on the soft-water conditions within the interior. The dichotomy of the soft-water interior and the hard-water periphery creates steep pH, alkalinity, and other ionic gradients in the Refuge from the canals into the marsh (Swift and Nicholas, 1987; Richardson et al., 1990; Weaver et al.,

2001; Weaver and Payne, 2004). Alkalinity within the Refuge decreases with distance from the rim canal (Payne et al., 2000; Weaver et al., 2001, Weaver and Payne, 2004). In fact, stations in the central region of the Refuge have the lowest alkalinity levels, with median concentrations at or below the state criterion of 20 mg CaCO<sub>3</sub>/L. Therefore, alkalinity excursions within the Refuge are not a result of a controlled discharge or pollution source but are due to the natural softwater, rainfall-driven nature of the system. The low alkalinity values represent the normal background conditions typical of this ecosystem; therefore, the FDEP does not consider these low values in the interior of the Refuge to be in violation of state water quality standards.

Excursions for pH are linked to the naturally low alkalinities within the Refuge's interior marsh. Given that the buffering capacity within the interior is low, small changes in the production or consumption of  $CO_2$  by marsh biota or absorbance of  $CO_2$  from the atmosphere produce significant changes in pH. All recent excursions (WY2001–WY2005) from the pH criterion have occurred at alkalinities below 40 mg CaCO<sub>3</sub>/L and at stations distant from canal discharges (LOX3, LOX5, LOX7, LOX8, LOX9, LOX11, LOX13, LOX14, and LOX16), which is consistent with patterns noted for previous periods (Weaver et al., 2001, Weaver and Payne, 2004). Additionally, the greatest variability in pH has occurred at alkalinities of less than 100 mg CaCO<sub>3</sub>/L (**Figure 2A-6**). Such fluctuations in pH at low alkalinities in areas free of discharges are typically caused by changes in  $CO_2$  concentrations due to natural processes of photosynthesis and respiration within the environment. Because pH excursions within the interior of the marsh are linked to natural background alkalinity conditions, the FDEP does not consider pH levels within the interior of the Refuge to be in violation of state water quality standards.



**Figure 2A-6.** Relationship between pH variability and alkalinity within the interior marsh of the Refuge from WY2001–WY2005. PH variability is highest at low alkalinity levels (50 mg CaCO<sub>3</sub>/L). Dashed horizontal lines show the lower (6.0) and upper (8.5) Class III pH criteria.

### SPECIFIC CONDUCTANCE

Specific conductance (conductivity) is a measure of water's ability to conduct an electrical current and is an indirect measure of the total concentration of ionized substances (e.g.,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $Cl^-$ ,  $HCO_3^-$ , and  $SO_4^{2-}$ ) in the water. Conductivity will vary with the number and type of these ions in solution. In some cases, it can be used to differentiate among various water sources, such as groundwater, rainwater, agricultural runoff, and municipal wastewater. Changes in conductivity beyond natural background variability can result in potentially deleterious effects to aquatic life. For example, very high conductivities would be detected under conditions of saltwater intrusion. The current state water quality criteria for Class III freshwaters, which allows for a 50 percent increase in the specific conductance or 1,275 micromhos per centimeter ( $\mu$ mhos/cm), whichever is greater, is meant to preserve natural background conditions and protect aquatic organisms from stressful ion concentrations. Given that background conductivities are low within the EPA, excursions were calculated using the 1,275  $\mu$ mhos/cm criterion (Weaver et al., 2001 and 2002).

For WY2005, conductivity was categorized as a potential concern for WCA-2 interior and inflow stations and a potential concern for Refuge inflows. The WY2005 excursion frequency (9.1  $\pm$  3.7 percent) for WCA-2 inflows was significantly less than both WY2004 (28.7  $\pm$  5.7 percent) and the WY1978–WY2003 historical period (15.8  $\pm$  1.4 percent). Similar to previous periods, the WY2005 excursions in WCA-2 were localized to a few monitoring stations, which resulted in specific conductance being categorized as a concern for the interior stations F1, F2, F3, and CA28 and inflow station G-335. All of the excursions into WCA-2 occurred at the G-335 structure. Previous ECRs explained that the elevated conductivity levels at water control structures (e.g., G-335) and stations near canal inflows were probably linked to groundwater intrusion into canal surface waters (Weaver et al., 2001 and 2002). This groundwater intrusion can occur due to seepage into canals, via pumping station operation (which can pull additional groundwater into surface water), and as a result of agricultural dewatering practices.

All WY2005 exceedances at sites F1, F2, and F3 occurred during periods when there were no recorded flows through the upstream structures (S-10A, S-10C, and S-10D). Furthermore, over the previous five water years, the majority (76.5 percent) of exceedances at these stations occurred during periods of no flow. The excursions during these periods may be related to either the concentration of ions associated with the evaporation of marsh water or the seepage of groundwater into the WCA-2 marsh, practically near site F1. Recent studies south of the S-10 structures support the hypothesis that groundwater seepage occurs during dry periods (Krest and Harvey, 2003).

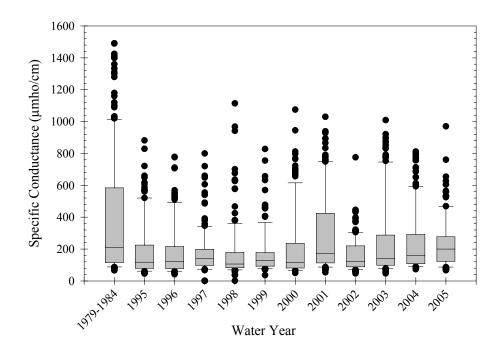
#### **REFUGE INTERIOR SPECIFIC CONDUCTANCE**

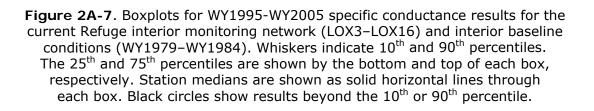
As stated above, the Refuge is naturally a rainfall-dominated system with surface water exhibiting a low mineral or ion content. In fact, the periphyton community within the Refuge shows a response to ion concentrations, such as alkalinity, chloride, and calcium. In interior regions of the Refuge with low mineral content (i.e., low conductivity), the periphyton assemblage is comprised primarily of numerous species of desmids and filamentous green algae, which form a thin, hairy green to brown coating (sweater) on plant stems. As mineral content increases in oligotrophic areas near the rim canal, the periphyton community becomes dominated by calcareous blue-green algae (particularly *Scytonema* and *Schizothrix*) with numerous diatoms that form a thick cream to yellowish-brown mat with calcite crystals; that is, the community shifts to one more like the hardwater potions of WCA-2 and WCA-3 (Payne et al., 2001b). Given this characteristic, the current specific conductance standard may not be fully protective of this area.

Although the current standard may not be fully protective, changes or trends in major ions can be tracked over time to ensure that the water body is not being degraded. Overall, specific conductance levels within the interior (LOX3, LOX4, LOX5, LOX6, LOX7, LOX8, LOX9, LOX10, LOX11, LOX12, LOX13, LOX14, LOX15, and LOX16) of the Refuge show neither a trend since inception (WY1995) of the current monitoring program nor an increase relative to a baseline period from WY1979–WY1984 (**Figure 2A-7**)<sup>4</sup>. However, the variability of specific conductance measurements has increased during several recent years (i.e., 2001, 2003, 2004, and 2005), but not when compared to baseline years.

The FDEP and the District will continue to evaluate specific conductance conditions in the Refuge. This evaluation will include further analysis of the observed trends to determine if the recent increases are due to increased inflow of high conductivity water, increased groundwater influence, or highly variable climatic conditions. It will also include an assessment of regulatory options designed to acknowledge the natural low ion content of the water, which may be achieved through an SSAC, revised standard, or definition of background conditions. It is anticipated that the results of these evaluations will be reported in future *South Florida Environmental Reports*.

<sup>&</sup>lt;sup>4</sup> The baseline period was selected to be consistent with the one used to establish existing ambient Outstanding Florida Waters baseline conditions for phosphorus in the federal Settlement Agreement. Analytical methods between the two periods may not be completely comparable. Specific conductance was analyzed in the laboratory during the baseline period, while contemporary (WY1995–WY2004) measurements were conducted in the field.





### UN-IONIZED AMMONIA

Un-ionized ammonia (NH<sub>3</sub>) is a colorless gas with a pungent odor that is very soluble in water at low pH. Ammonia can serve as an important source of nitrogen for plant life but is toxic to aquatic life when present in excess. In the aquatic environment, ammonia is very soluble and is readily hydrolyzed to form ammonium (NH<sub>4</sub><sup>+</sup>) ions as shown in the following reaction:

$$NH_3 + H_2O = NH_4^+ + OH^-$$

The  $NH_4^+$  ions produced as a result of the hydrolysis are not toxic to aquatic life. However, even though ammonia is highly soluble in water, the hydrolysis is not complete and some portion of the total ammonia remains in the toxic unionized ( $NH_3$ ) form. The equilibrium established between the unionized ( $NH_3$ ) and ionized ( $NH_4^+$ ) forms of ammonia is a function of temperature and pH. As shown in the above equation, increases in pH (increased levels of OH<sup>-</sup> ions) as well as temperature forces the reaction to the left resulting in increasing levels of  $NH_3$ . For example, in freshwater at 25°C, an increase in pH from 7.0 to 8.0 results in an increase in the percent of  $NH_3$  in the un-ionized form from 0.5 to 5.4 percent. At a pH of 9.0, more than one-third (36 percent) of the total dissolved ammonia (i.e., the concentration of ammonia measured in the water column,  $NH_3 + NH_4^+$ ) is in the un-ionized form. The resulting  $NH_3$  is able to diffuse across cell membranes more readily and is acutely toxic to aquatic life at relatively low concentrations.

Ammonia is unique among regulated water quality constituents because it is both a source of nitrogen (a nutrient required for life) and an endogenously produced toxicant for which organisms have developed a variety of strategies to excrete as a waste product. The concentration of  $NH_3$  necessary to become toxic is highly variable because the toxic effect of  $NH_3$  is affected by temperature, pH, DO concentrations,  $CO_2$  concentrations, previous acclimation to  $NH_3$ , and the presence of other toxic compounds. High external  $NH_3$  concentrations reduce or reverse diffusion gradients used by organisms to excrete excess  $NH_3$ . This excess  $NH_3$  can accumulate in the organism, thereby resulting in altered metabolism, loss of equilibrium, hyperexcitability, increased respiratory activity and oxygen uptake, and increased heart rate. Even slightly elevated concentrations of  $NH_3$  have been associated with a reduction in hatching success in some animals, a reduction in growth rate and morphological development in others, and injuries to gill tissue, liver, and kidneys. In fish, extremely high levels of  $NH_3$  can result in convulsions, coma, and even death.

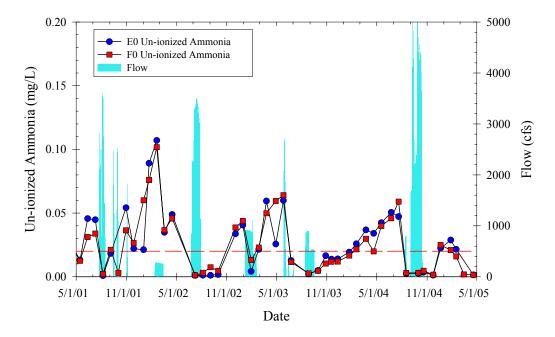
The current state Class III water quality criterion for  $NH_3$  is  $\leq 0.02$  mg/L.  $NH_3$  is calculated from pH, temperature, and total dissolved  $NH_3$  measurements from the same sample. During WY2005, 11 calculated  $NH_3$  values above 0.02 mg/L were recorded. Based on the aggregated regional analysis,  $NH_3$  was categorized as a potential concern for WCA-2 inflows; however, all WCA-2 WY2005 excursions were localized at two inflow stations (E0 and F0). Furthermore,  $NH_3$  was categorized as a localized concern for E0 and F0 based on an analysis of WY2001–WY2005 data.

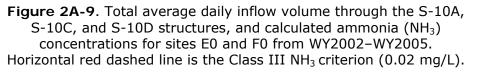
The localization of NH<sub>3</sub> excursions at E0 and F0 continues a pattern initially noted in the 2003 Everglades Consolidated Report. Stations E0 and F0 are located within the WCA-2A spreader canal, which receives Hillsboro Canal discharges from the S-10A, S-10C, and S-10D structures and, in turn, overflows into the marsh when canal stages exceed the height of a low berm. A review of hydrologic and water quality monitoring records suggests that the high NH<sub>3</sub> levels at sites E0 and F0 were likely related to the stagnant (i.e., low DO), low-water conditions in the spreader canal during WY2002–WY2005. The spreader canal can become stagnant and anaerobic during periods of no or low flow, such as when the S-10A, S-10C, and S-10D

structures are closed, resulting in substantial changes in biogeochemical conditions and constituent concentrations within the canal. Flow records indicate that discharges via the S-10A, S-10C, and S-10D structures were limited during recent years with the NH<sub>3</sub> excursion episodes occurring following periods of no flow (**Figure 2A-9**).

As discussed in the 2003 and 2004 Everglades Consolidated Reports, the elevated total dissolved ammonia concentrations measured in the canal most likely arose from internal nitrogen cycling. Nutrient-enriched surface water within the spreader canal can support substantial growth of algae that accumulate when the canal is stagnant and is not being flushed by incoming water from the Hillsboro Canal. When the accelerated growth of algae can no longer be supported, then the algae die, fall to the bottom, and decay, resulting in the release of ammonia under anaerobic conditions. Because the anaerobic conditions inhibit the oxidation of the released ammonia to nitrite and nitrate, the ammonia accumulates (concentration increases) within the canal.

The elevated total dissolved ammonia levels continue to be the proximal cause of the E0 and F0 NH<sub>3</sub> excursions (**Figure 2A-10**), which is expected if the cause were related to the release of NH<sub>3</sub> under low-flow or stagnant conditions, as described above. For WY2005, the median total dissolved NH<sub>3</sub> concentrations at sites E0 and F0 were 1.1 and 0.74 mg/L, respectively. Furthermore, during the entire monitoring record (WY1994–WY2005) at these two stations, elevated total dissolved NH<sub>3</sub> concentrations were the proximal cause of all 69 NH<sub>3</sub> excursions within the WCA-2 spreader canal. The phenomenon of periodically elevated total dissolved NH<sub>3</sub> concentrations is apparently isolated to the spreader canal and has not contributed to excursions in the marsh adjacent to the spreader canal. From WY1994–WY2005, the total dissolved NH<sub>3</sub> concentrations at the marsh transect stations E1 and F1 (1.8 to 2.2 km) downstream of the spreader canal have been significantly lower (Kruskal-Wallis; p < 0.001; median = 0.041–0.054 mg/L) than concentrations observed at stations E0 or F0 (median = 0.27–0.37 mg/L).





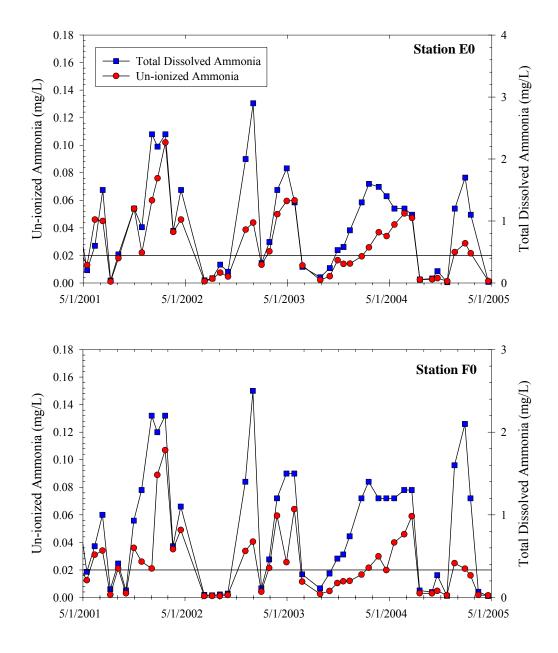


Figure 2A-10. Total dissolved ammonia concentrations and calculated  $NH_3$  values for sites E0 (top) and F0 (bottom) during WY2002–WY2005. Horizontal solid black line is the Class III  $NH_3$  criterion (0.02 mg/L).

### SULFATE

Currently, the state has no surface water criterion for sulfate  $(SO_4^{2-})$ ; however, recent research has provided evidence of a link between sulfur biogeochemistry in sediment and pore water and mercury methylation, as reported in Chapter 2B of the 2005 SFER – Volume I and previous ECRs (Atkeson and Parks, 2002; Atkeson and Axelrad, 2003; Axelrad et al., 2005). Sulfate in the surface waters of the Everglades is derived from a variety of natural and human sources. Bates et al. (2002) found that the major source of sulfate within the EPA was drainage from the Everglades Agricultural Area (EAA). Stormwater runoff from the EAA contains high concentrations of sulfate that arise from both the current and historical use of sulfur-containing fertilizers and soil amendments (Bates et al., 2002). Additionally, under some conditions in the Everglades, groundwater containing elevated sulfate levels can rise to the surface (Atkeson and Parks, 2002).

The sulfate monitoring results in the EPA are presented in this chapter to provide an overview of current concentrations and evaluate temporal and spatial patterns. Sulfate concentrations are summarized in **Table 2A-4** for WY2005, WY2004, and WY1978–WY2003 based on arithmetic mean and median values.

Given that one of the primary sources of sulfate entering the EPA is stormwater runoff from the EAA, sulfate concentrations in the inflow and interior marsh generally follow trends similar to those observed for total phosphorus (TP) and total nitrogen (TN); that is, sulfate concentrations exhibit a general north-to-south gradient extending from the sources in the north to relatively unenriched areas in the south similar to those identified for nutrient levels (Figure 2A-11). High inflow concentrations in EAA runoff enter the Refuge, WCA-2 and, to a lesser extent, WCA-3. The highest concentrations within the EPA have been observed at the Refuge and WCA-2 inflow stations. However, as previously discussed, a significant amount of the surface water entering the Refuge does not permeate deeply in the marsh but remains around the periphery of the area in the rim canal and is discharged to WCA-2 through the S-10 structures. Due to this hydrologic characteristic, the Refuge interior has remained relatively uninfluenced by the inflow of sulfate-rich water. Among the EPA marsh areas, the interior of WCA-2 exhibits the highest sulfate concentrations and is the area most affected by EAA runoff, with a WY2005 median concentration of 44 mg/L. Sulfate concentrations at stations in the interior of WCA-3 have also been elevated by inputs of sulfate-enriched runoff, although this is not readily apparent in WY2005 given the median sulfate concentration of 2.3 mg/L. As demonstrated in the 1995, 1996, and 1999 USEPA Regional Environmental Monitoring and Program (REMAP) studies, a pronounced north-to-south sulfate gradient is evident within WCA-3 (Atkeson and Parks, 2002). This gradient is apparent within the District's monitoring network (Figure 2A-11). The highest WY2005 sulfate concentrations within the WCA-3 interior were observed at station CA32 (median = 49.2 mg/L) in the northeastern portion of this area. Concentrations decreased through the marsh, following the southerly flow of water. The lowest median sulfate concentration observed during WY2005 at sites in the WCA-3 marsh (median < 0.10 mg/L) was observed at station CA315, the most southerly sampling location in WCA-3.

Region	Class	Period	Ν	Arithmetic Mean	Std. Deviation	Median	Min.	Max.
	Inflow	1978–2003	836	58	43	50	<0.1	461
		2004	60	73	24	73	8.3	123
		2005	58	54	19	52	14.1	94
		1978–2003	584	53	26	48	1.6	140
	Rim	2004	24	79	28	78	39	120
Refuge		2005	23	53	18	44	36	100
Refi		1978–2003	2136	15	67	3.6	<0.1	2900
	Interior	2004	229	15	24	3.6	<0.1	110
		2005	202	8.9	16	2.3	<0.1	84
		1978–2003	366	48	46	41	1.42	571
	Outflow	2004	24	47	27	39	8.2	98
		2005	26	46	20	46	4	77
		1978–2003	726	51	41	46	6.151	644
	Inflow	2004	71	64	22	60	14.9	106
		2005	72	49	20	44	4	99
7	Interior	1978–2003	3305	44	36	42	0.1	1400
WCA-2		2004	217	36	24	32	5.93	121
8		2005	158	43	18	44	5.2	100
	Outflow	1978–2003	379	36	26	31	2.34	224
		2004	20	36	17	35	10.43	73
		2005	24	41	13	41	14.8	69
		1978–2003	1080	26	25	18	0.5	286
	Inflow	2004	68	18	16	10	0.8	73
		2005	75	23	19	18	1.6	69
ę		1978–2003	2025	10	15	5.3	<0.1	262
WCA-3	Interior	2004	324	5.8	9.1	2.2	<0.1	45
8		2005	195	12	17	2.3	<0.1	57
		1978–2003	565	12	17	8.2	<0.1	113
	Outflow	2004	40	3.3	5.5	0.12	<0.1	17
		2005	49	7.8	11	0.60	<0.1	36
×		1978–2003	535	12	17	8.1	<0.1	113
les Parl	Inflow	2004	41	3.8	5.1	0.78	<0.1	16
Everglades lational Par		2005	49	6.9	9.6	1.9	<0.1	36
erg on;		1978–2003	1452	6.6	18	2.9	<0.1	403
Everglades National Park	Interior	2004	96	2.3	2.8	0.95	<0.1	11
Z		2005	75	7.3	28	1.3	<0.1	242

# Table 2A-4. Summary of sulfate concentrations (mg/L) in the EPAfor WY2005, WY2004, and WY1978–WY2003.

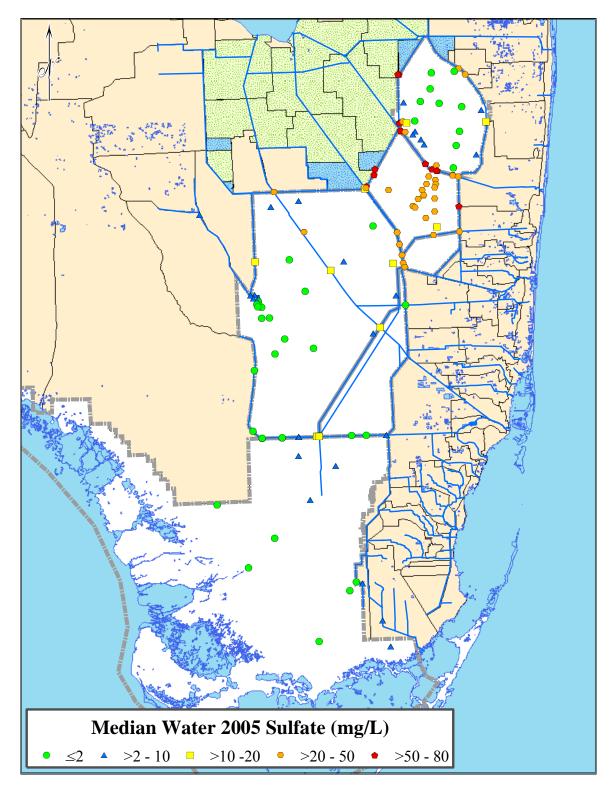


Figure 2A-11. Summary of median WY2005 sulfate concentrations (mg/L)at stations across the EPA. Median sulfate concentrations are classifiedutilizing five levels as follows:  $\leq 2 \text{ mg/L}$ , 2 to 10 mg/L, 10-20 mg/L,20 to 50 mg/L, and > 50-80 mg/L.

# PESTICIDES

The SFWMD has maintained a pesticide monitoring program in South Florida since 1984. The pesticide monitoring network includes sites designated in the Park Memorandum of Agreement (MOA), the Miccosukee Tribe MOA, the Lake Okeechobee Operating Permit, and the non-Everglades Construction Program (non-ECP) Structure Permit. The current monitoring program in the EPA consists of 29 sites (**Figure 2A-12**). These sites were grouped by basin for analysis.

Surface water concentrations of pesticides are regulated under criteria established in Chapter 62-302, F.A.C. Chemical-specific numeric criteria for a number of pesticides and herbicides (e.g., DDT, endosulfan, and malathion) are listed in Section 62-302.530, F.A.C. Compounds not specifically listed, including many contemporary pesticides (e.g., ametryn, atrazine, and diazinon), are evaluated based on acute and chronic toxicity. A set of toxicity-based guidelines for non-listed pesticides were presented in the 2001 Everglades Consolidated Report (Weaver et al., 2001). These guideline concentrations were developed based on the requirement in Section 62-302.530(62), F.A.C., that surface waters of the state shall be free from "substances in concentrations, which injure, are chronically toxic to, or produce adverse physiological or behavioral response in humans, plants, or animals."

The 2006 South Florida Environmental Report analyzes data collected during pesticide monitoring events conducted between October 2003 and December 2004. Monitoring results were evaluated relative to Class III water quality criteria, chronic toxicity guidelines, and detected concentrations. Pesticides exceeding either the Class III criteria or chronic toxicity guideline concentrations were classified as concerns for the basin in which the exceedance occurred. Parameters classified as "concerns" have a likelihood of resulting in an impairment of the designated use of the water body. Detected water quality constituents ( $\geq$  MDL) that did not exceed either a guideline or criterion were categorized as a "potential concern." This classification signifies that the water quality constituent is known to be present within the basin at concentrations reasonably known to be below levels that result in adverse biologic effects, but may result in a problem at some future date or in interaction with other compounds. The "no concern" category was used to designate pesticides that were not detected at sites within a given area.

Thirteen pesticides or degradation products were detected between October 2003 and December 2004 (**Table 2A-5**). Only atrazine and chlorpyrifos ethyl were classified as a concern. A total of three atrazine (guidance concentration =  $1.8 \ \mu g/L$ ) excursions were recorded at inflows to the Refuge and WCA-2. Atrazine excursions occurred at S-5A ( $2.2 \ \mu g/L$ ) on March 16, 2004 and S-38B ( $2.2 \ and 2.0 \ \mu g/L$ ) on April 15, 2004 and July 21, 2004, respectively. Excursions from the toxicity guideline for chlorpyrifos ethyl ( $0.002 \ \mu g/L$ ) were recorded at S-5A ( $0.021 \ \mu g/L$ ) and S-142 ( $0.029 \ \mu g/L$ ) on March 16, 2004 and July 20, 2004, respectively.

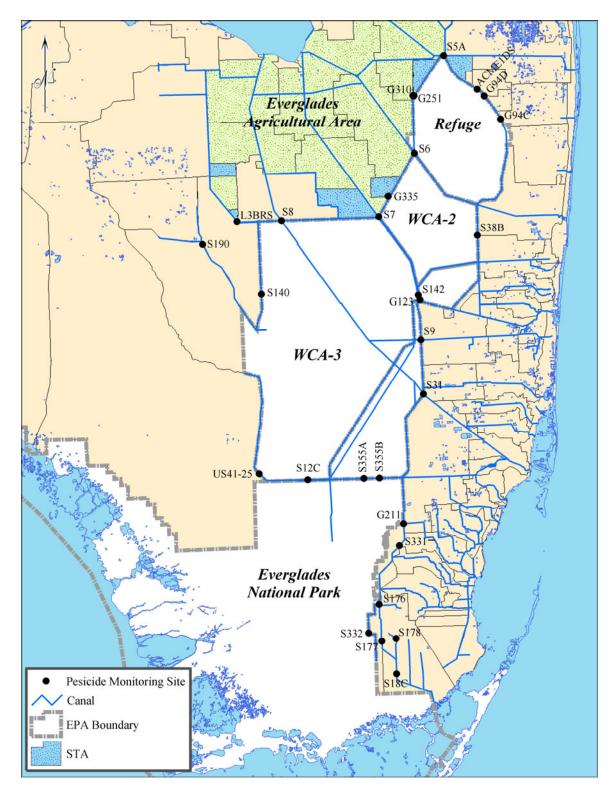


Figure 2A-12. SFWMD pesticide monitoring sites in the EPA.

**Table 2A-5**. Pesticide detections and exceedance categories in the EPA inflows, canals, and structures between October 2003 and December 2004. The categories of "concern" and "potential concern" are denoted by "C" and "PC," respectively; all others are considered "no concern." Number of detections and total number of samples are in parentheses.

Parameter	Refuge <sup>1</sup>	WCA-2 <sup>2</sup>	WCA-3 <sup>3</sup>	Park <sup>4</sup>	C-111⁵
Ametryn	PC (35:35)	PC (8:10)	PC (17:40)	(0:20)	(0:30)
Atrazine	C (35:35)	C (10:10)	PC (30:40)	PC (11:20)	PC (11:30)
Atrazine Desethyl	PC (21:35)	PC (7:10)	PC (10:39)	PC (1:20)	(0:30)
Atrazine Desisopropyl	PC (4:32)	PC (4:10)	PC (2:33)	(0:20)	(0:25)
Bromacil	(0:18)	(0:10)	PC (2:29)	(0:16)	(0:23)
Chlorpyrifos ethyl	C (1:20)	(0:10)	C (1:40)	(0:20)	(0:30)
Dichlorophenoxy Acetic Acid, 2,4- (2-4-D)	(0:20)	(0:9)	PC (1:32)	(0:12)	(0:22)
Endosulfan (alpha +beta)	(0:20)	(0:10)	(0:40)	PC (11:20)	PC (2:30)
Endosulfan sulfate	(0:20)	(0:10)	(0:40)	PC (2:15)	(0:28)
Hexazinone	PC (11:20)	(0:10)	PC (4:35)	PC (1:20)	(0:29)
Metolachlor	PC (1:20)	(0:10)	PC (1:35)	PC (1:20)	(0:29)
Norflurazon	(0:20)	(0:10)	PC (9:36)	(0:20)	(0:30)
Simazine	PC (9:20)	PC (1:10)	PC (5:40)	(0:20)	(0:30)

1. ACME1DS, G-251, G-94D, G-310, and S-5A (via STA-1W).

2. S-38B, S-6 (via STA-2), and S-7.

3. G-123, L3BRS, S-140, S-190, S-8, S-9, S-142, and S-31.

4. S-12C, S-18C, S-332, S-335A, S-355B, and US41-25.

5. G-211, S-176, S-177, S-178, and S-331.

6. Both alpha and beta endosulfan forms were detected, but are combined in the total and are considered as a single constituent.

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