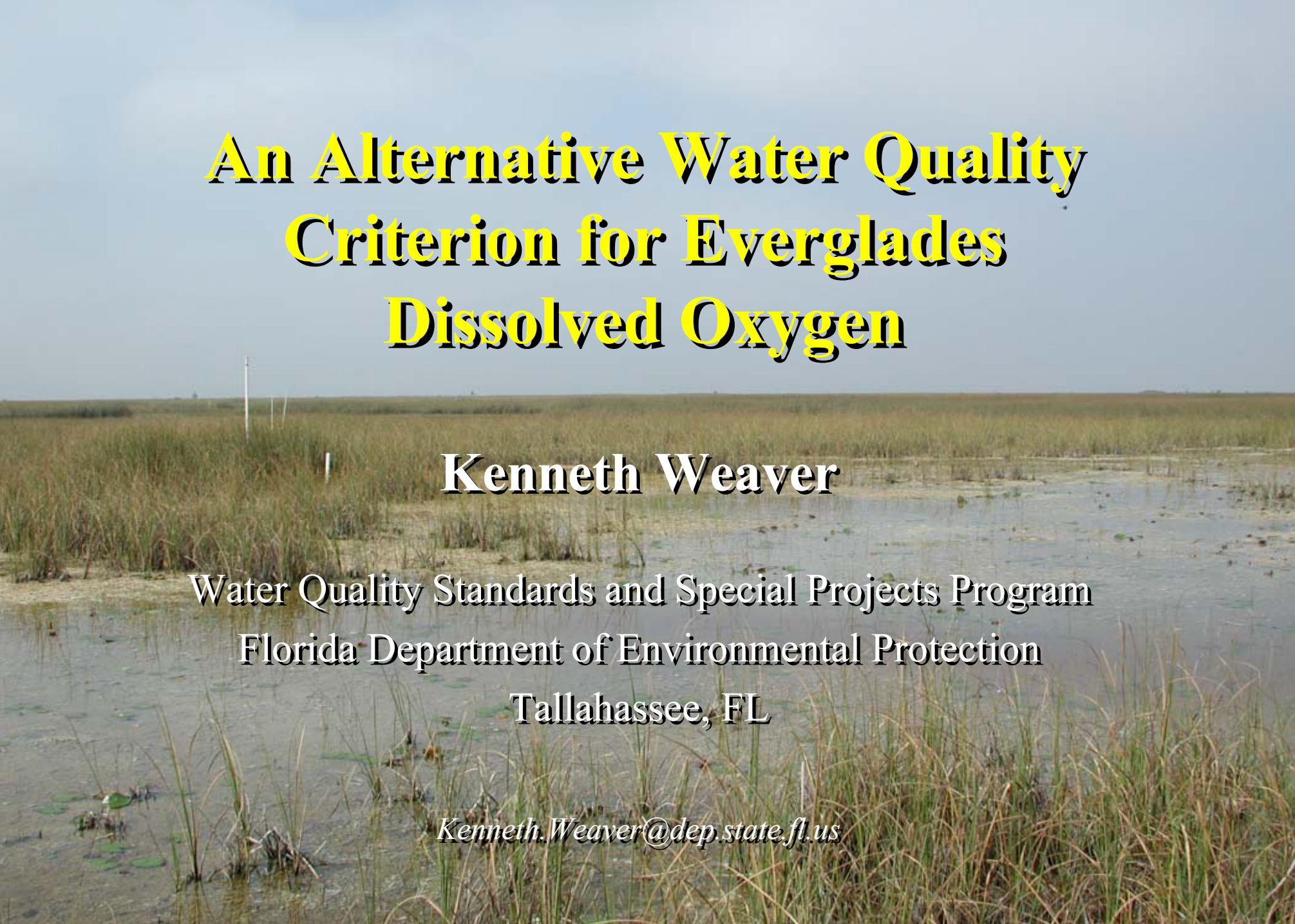


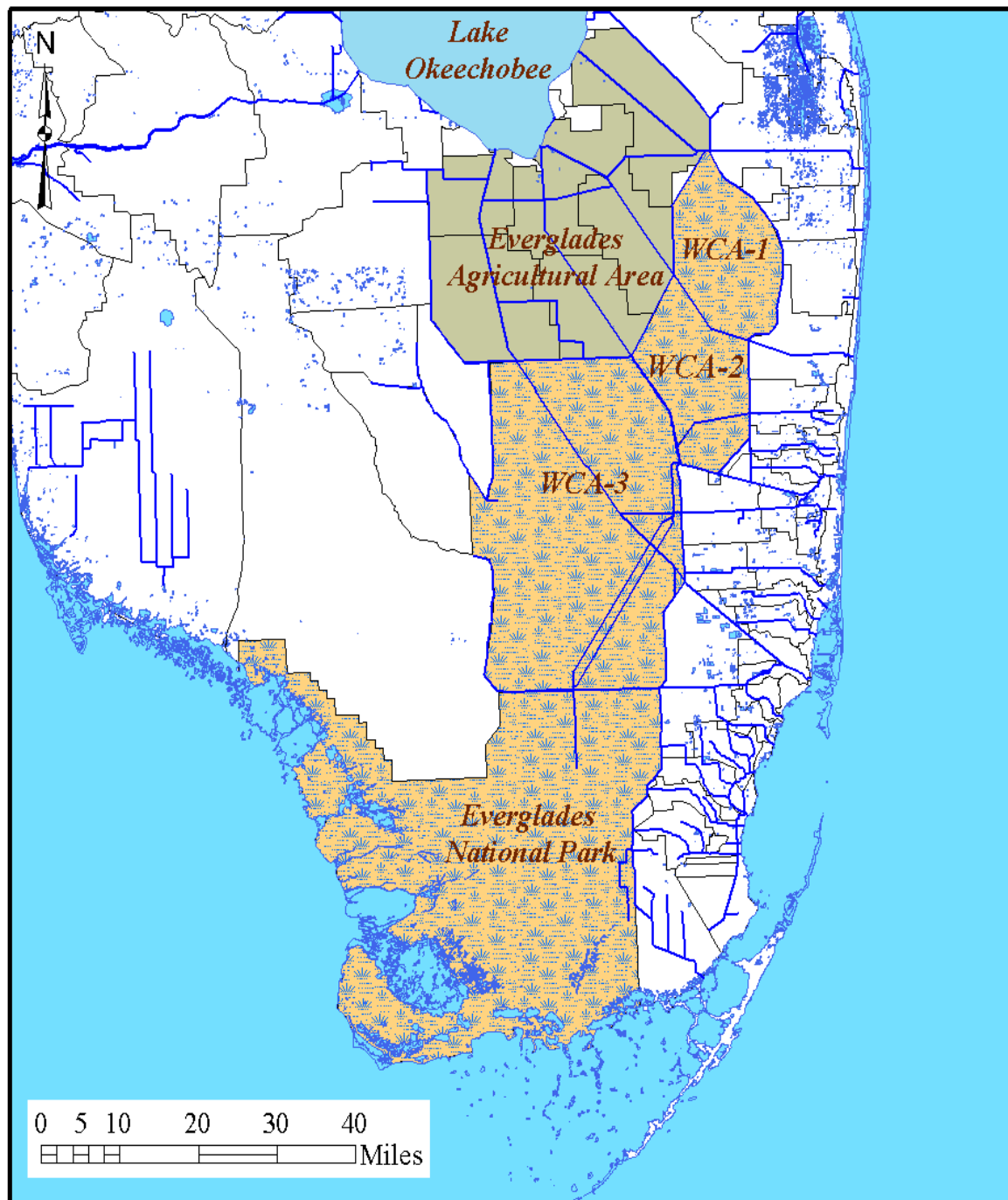


An Alternative Water Quality Criterion for Everglades Dissolved Oxygen

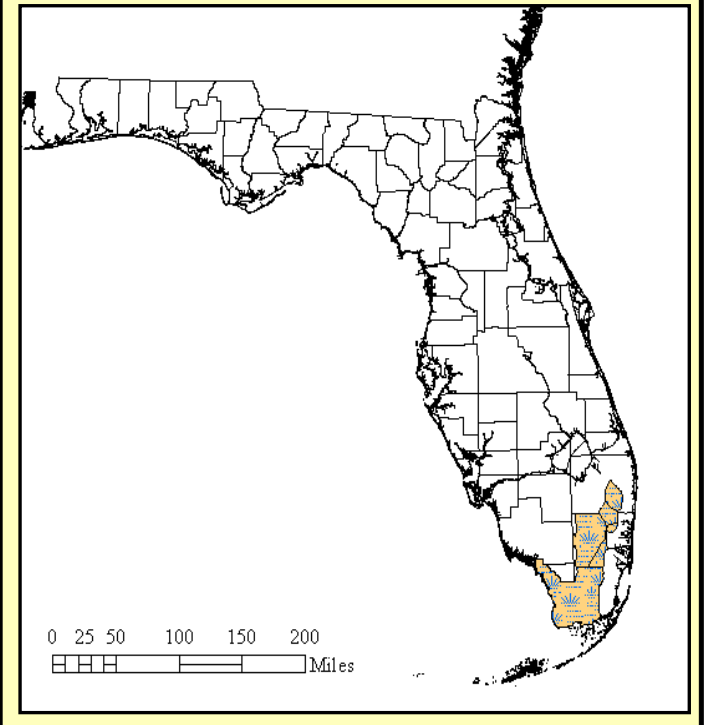
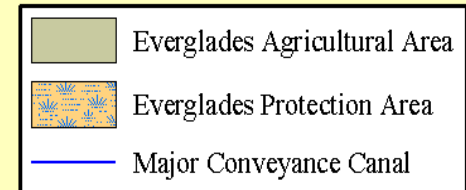
Kenneth Weaver

Water Quality Standards and Special Projects Program
Florida Department of Environmental Protection
Tallahassee, FL

Kenneth.Weaver@dep.state.fl.us



Location of Study Area



Regulatory Background

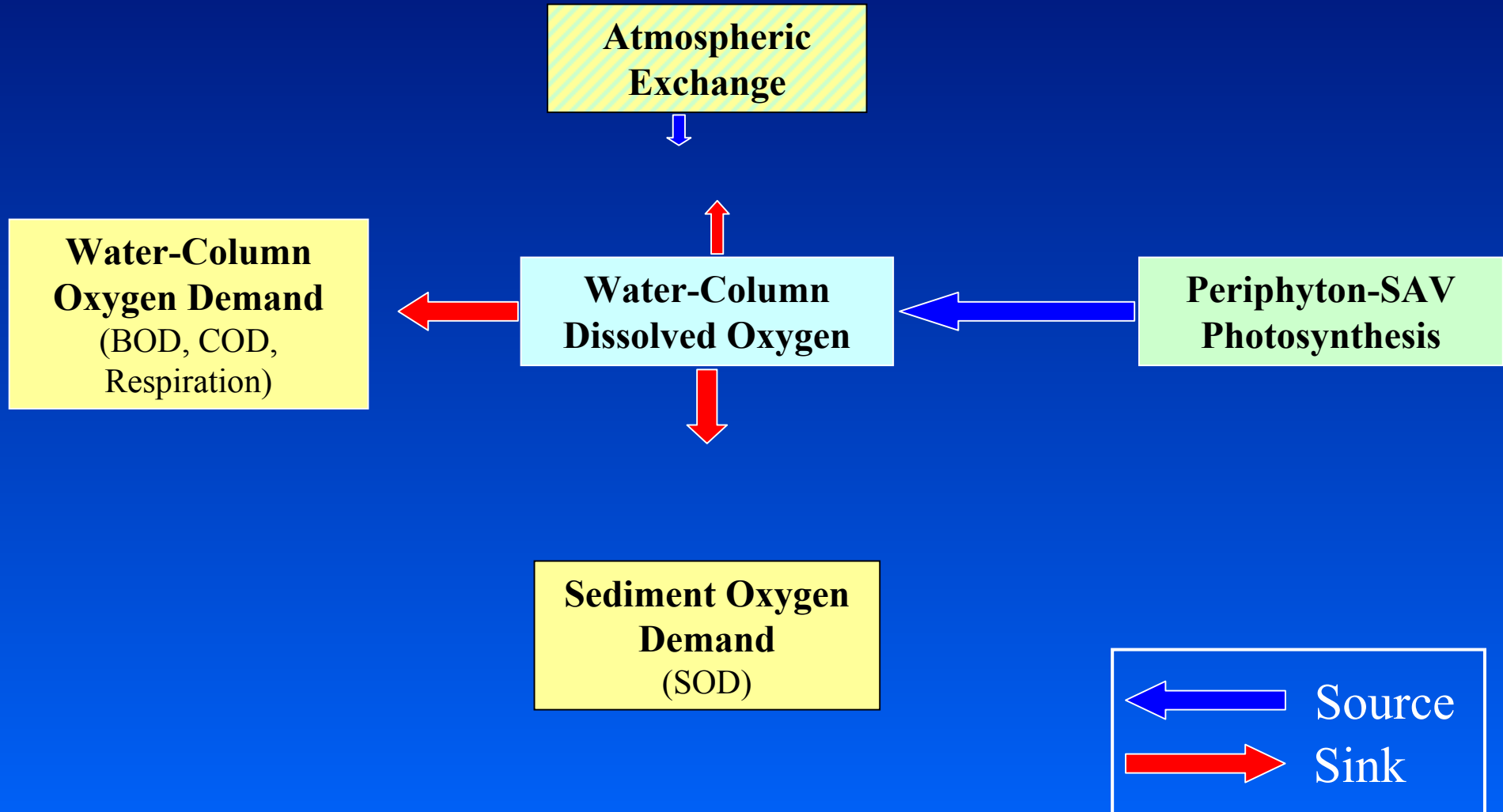
Subsection 62-302.530 (31), Florida Administrative Code

In Class III fresh waters, dissolved oxygen concentrations “shall not be less than 5.0 mg/L. Normal daily and seasonal fluctuations above these levels shall be maintained.”

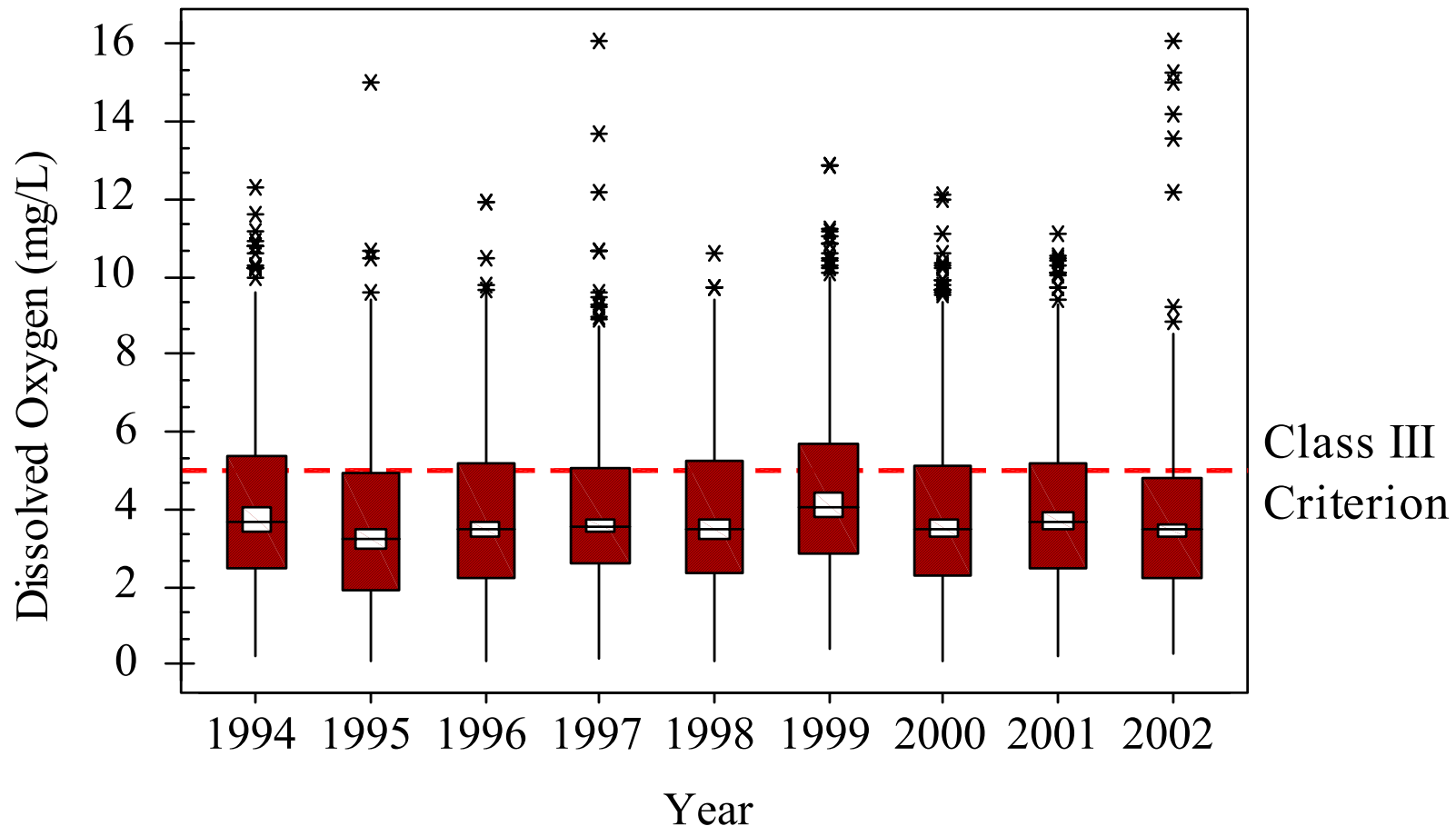
Periphyton/macrophyte dominated wetland environments, such as the Everglades, exhibit wide daily DO fluctuations due to natural processes of photosynthesis and respiration within the marsh (McCormick *et al.*, 1997; Everglades Consolidated and Interim Reports, 1999-2003).



Dissolved Oxygen Concentration is a Function of Ecosystem Processes



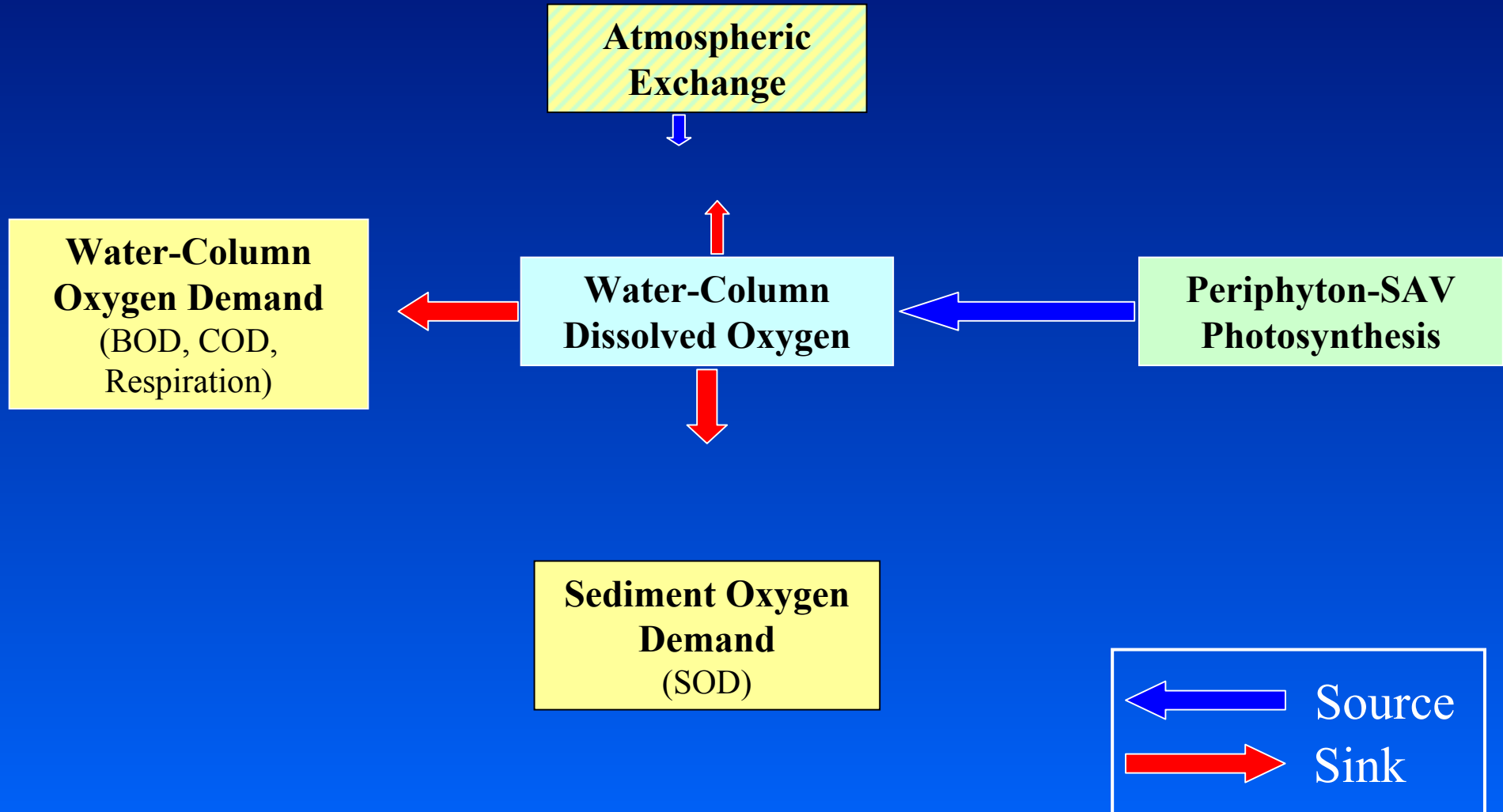
**Dissolved Oxygen Concentrations within Everglades Marshes
Routinely Fall Below the State Dissolved Oxygen Water Quality
Standard of 5.0 mg/L Even within Background Areas
(Data from 50 Sites across all areas of the EPA)**



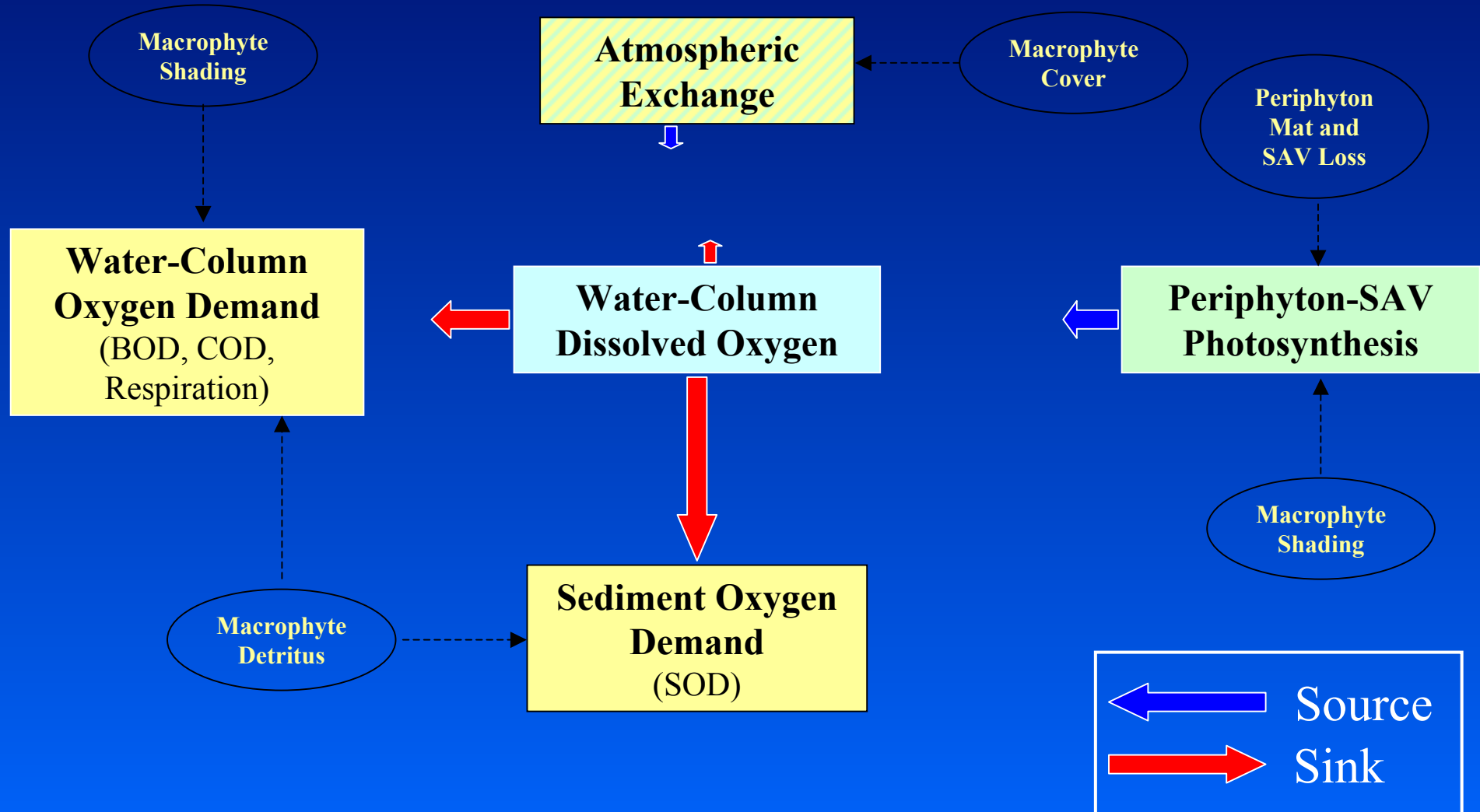
Attainment of Class III Criterion

Stations	Site-Years	Assessment Methodology	Number Exceedance	Percent Exceedance
Background	351	At Least One Measurement < 5 mg/L	335	95.4
		Greater than 10% of the Measurements < 5 mg/L	332	94.6
All	549	At Least One Measurement < 5 mg/L	531	96.7
		Greater than 10% of the Measurements < 5 mg/L	528	96.2

Dissolved Oxygen Concentration is a Function of Ecosystem Processes



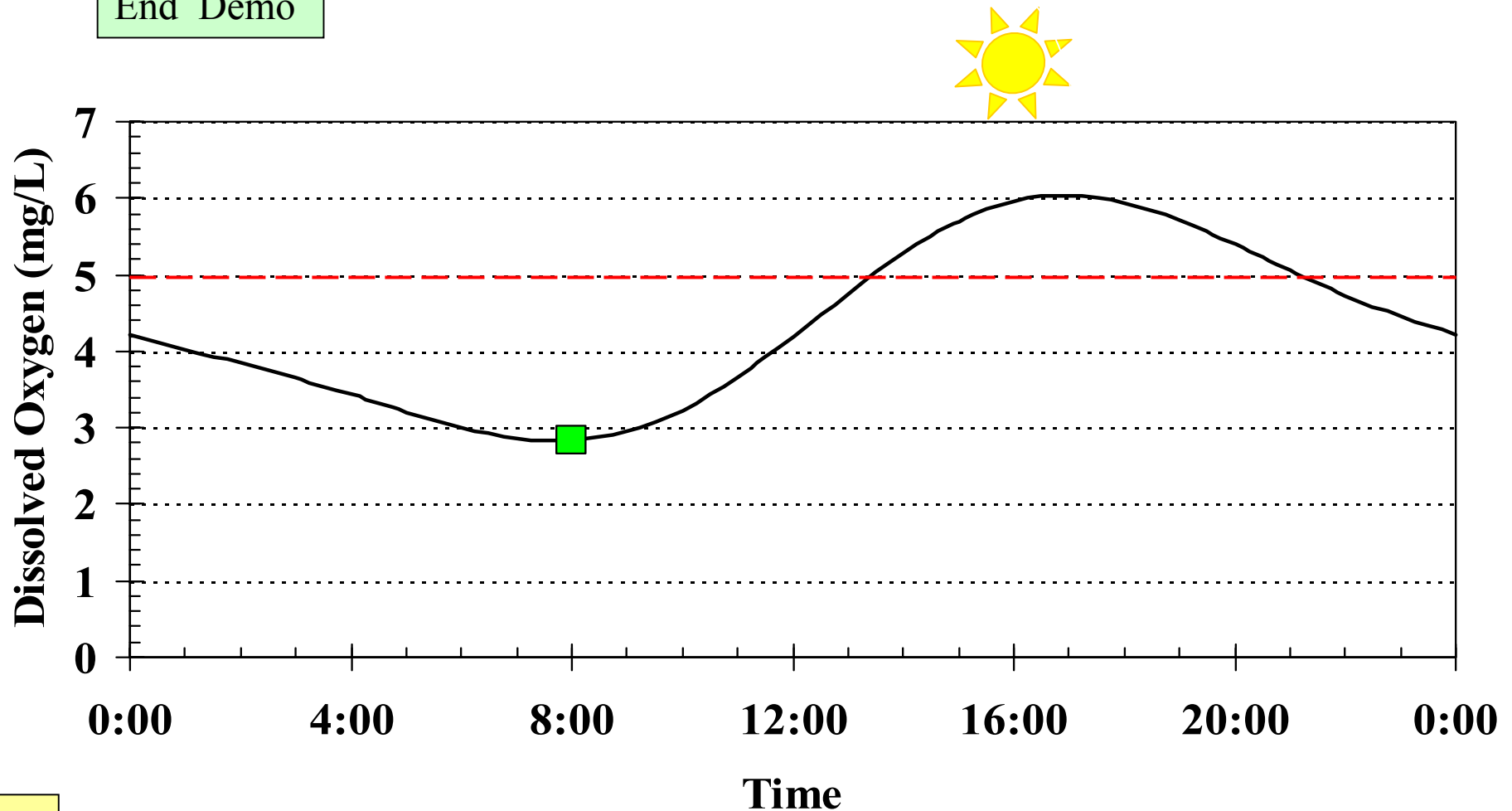
DO in Biologically Imbalanced Areas is Depressed Below Background Areas



Marsh Dissolved Oxygen Naturally Fluctuates on a Diel Basis

Run Demo

End Demo



Reset

Regulatory Solution

Paragraph 62-302.500(2)(f), F.A.C.

Dissolved oxygen levels that are attributable to natural background conditions or man-induced conditions which cannot be controlled or abated may be established as alternative dissolved oxygen criteria.

Proposed Site Specific Alternative Criterion (SSAC) developed to formally recognize the natural background conditions in the EPA marshes.

SSAC Development Approach

- ✓ **Model natural background dissolved oxygen conditions**

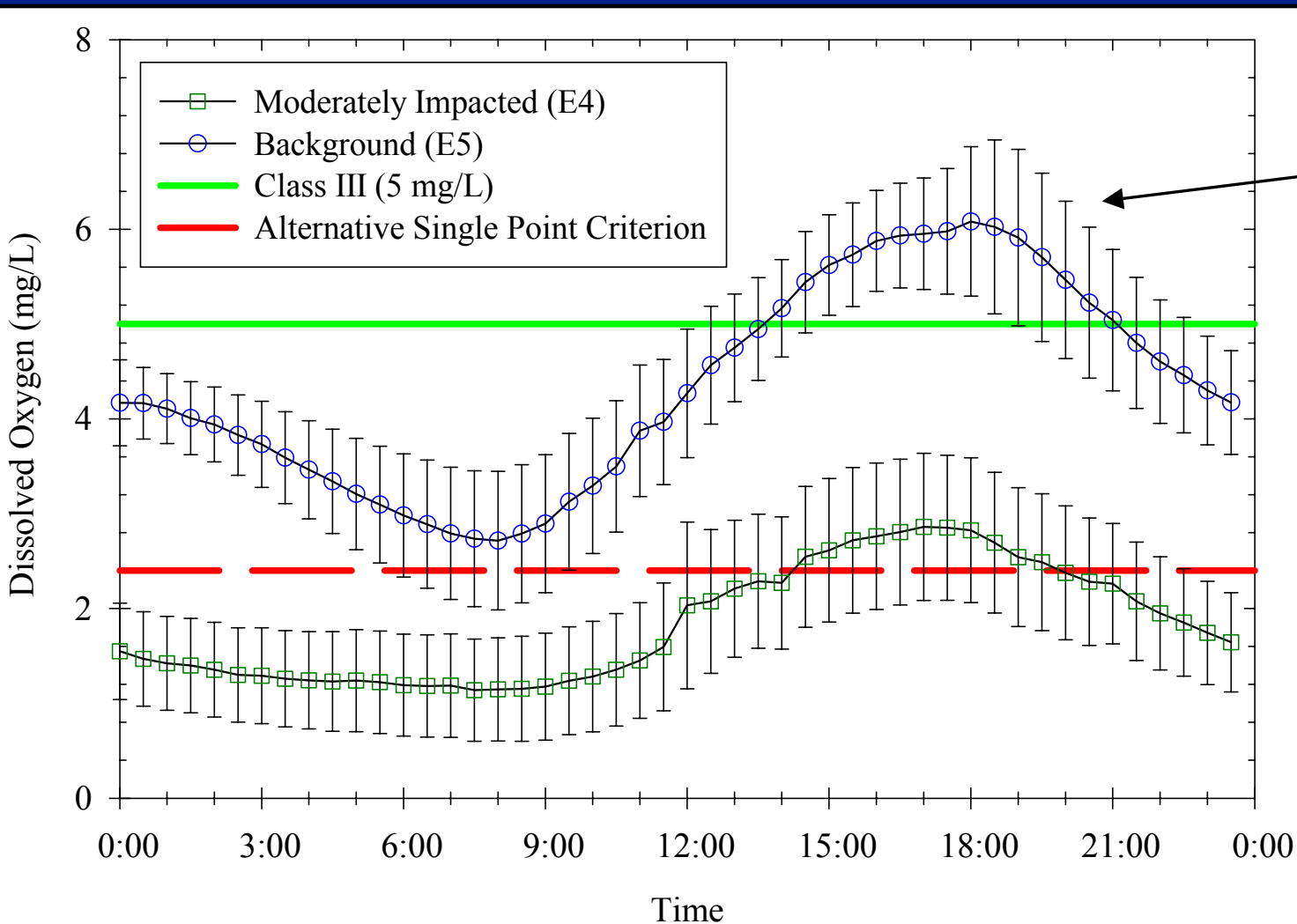
Validate model with a larger dataset from the entire EPA

Define compliance limit and methodology



Defining Natural Background Conditions

A New Single Point Criterion Would Not Adequately Describe Natural Diel Fluctuations



Solution: Model Background Diel Cycle

Ecological and Practical Considerations

- Under natural conditions, marsh DO concentrations exhibit periodic diel fluctuations where a minimum is reached within a few hours of sunrise and increase towards a maximum near sunset.
- Ecologically, the important components of the dissolved oxygen fluctuation are the daily minimum, the length of time at the minimum, and the magnitude of the daily range. However, it is impractical to measure all of these components on a regular basis over a large geographic area.
- Most of the fauna of the Everglades are adapted to periodic low DO and anaerobiosis. Impairment occurs when low DO conditions are protracted (e.g., nutrient impacted sites).
- A realistic compliance test must allow for some frequency of values below the SSAC threshold; given the tolerance of indigenous fauna to periodic low DO conditions.

Background Site Selection

- Utilized reference site approach to be consistent with background requirement of state statute
- Reference sites selected based upon
 - Availability of diel data sets
 - Phosphorus levels
 - Water column TP (geometric mean $\leq 10 \mu\text{g P/L}$)
 - Sediment P ($< 600 \text{ mg/kg}$)
 - Location relative to canals
 - Biological community (ecological data and site visits)

Diel Modeling Data

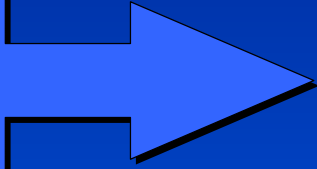
Extensive Diel DO data collected in WCA-2 associated with nutrient threshold research

- Collected over numerous weekly periods between 1994 and 1998 at 30 minute intervals
- Extensive ecological data sets were available to confirm background designation
- Approximately 4000 observations used to model background diel fluctuation



Background Model Selection

- Fit
 - Modeled from diel samples
 - Least squares regression
- Complexity
- Bias
- Cross-validation with grab samples
- Statistical Error (Type I and II)



**Saturation
Deficit**

Modeling Saturation Deficit

- The saturation deficit [SD] is the difference between the measured dissolved oxygen concentration and the concentration at saturation
- Expressed by the formula;

$$[SD] = DO - DO_{sat}$$

- Saturation concentration is a function of temperature given by the formula;

$$\ln [DO_{sat}] = -139.34411 + (1.575701 * 10^5 / K) - (6.642308 * 10^7 / K^2) + (1.2438 * 10^{10} / K^3) - (8.621949 * 10^{11} / K^4),$$

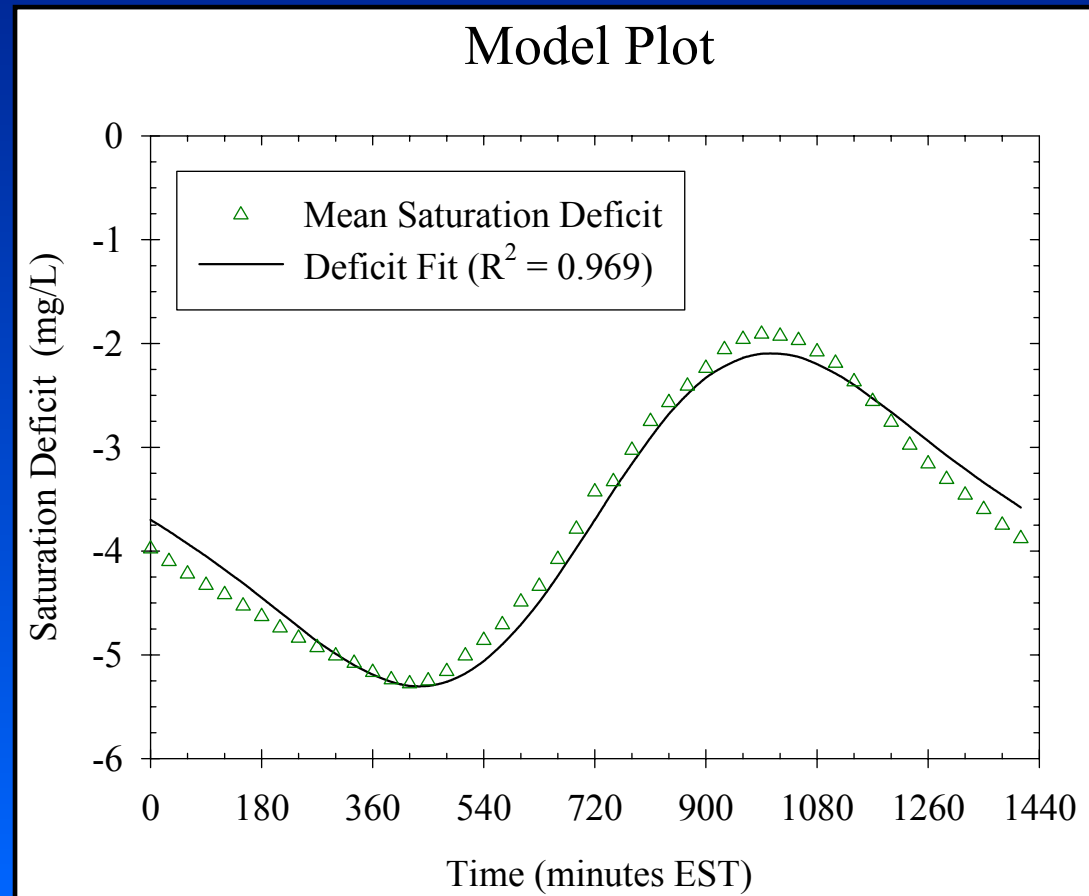
where DO_{sat} is the equilibrium oxygen concentration where K is the water temperature on the Kelvin scale ($K = ^\circ C + 273.15$) (APHA, 1992)

Curve Fitting

- Least squares fit to the sinusoidal equation:

$$[SD_t] = \beta_0 - (\beta_1 * \sin(2\pi/1440 * t) + \beta_2 * \sin(4\pi/1440 * t)),$$

where SD_t is the saturation deficit at time t in minutes (1440 minutes/day).



Model Simplification

- To simplify its application, the saturation deficit model was algebraically reordered to directly calculate a predicted dissolved oxygen concentration
- Recall: $SD = DO - DO_{sat}$
- Therefore: $DO = SD + DO_{sat}$, and

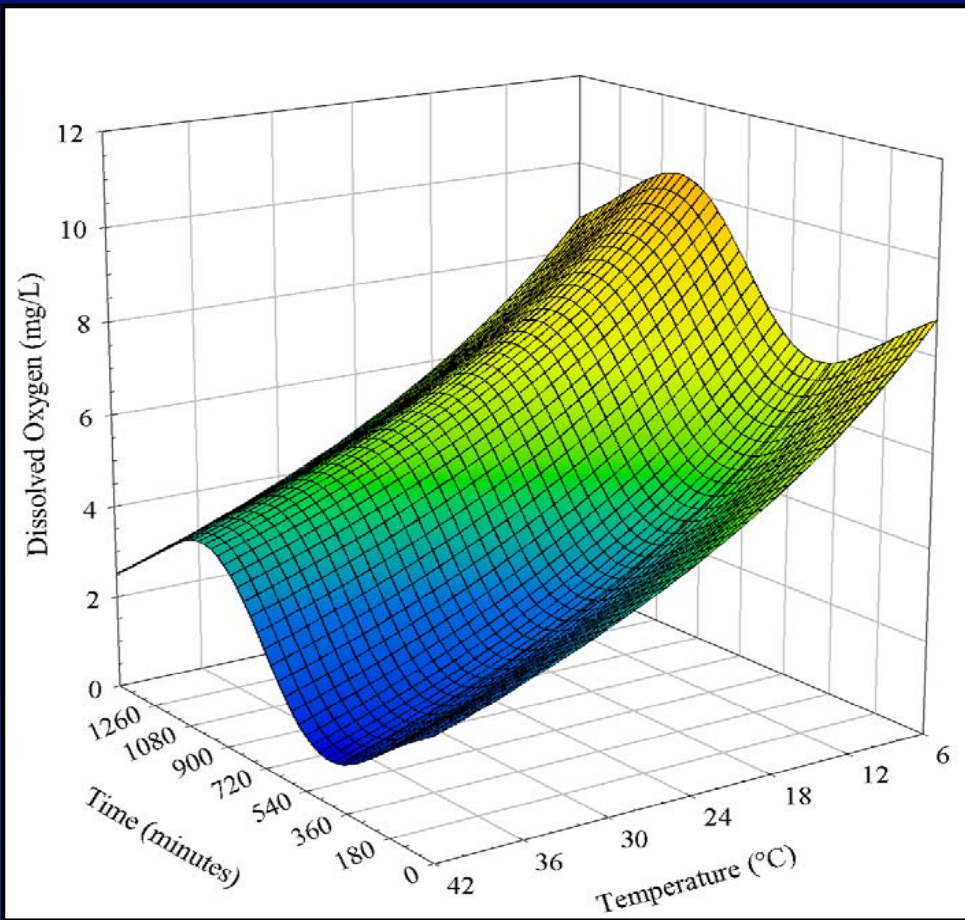
$$DO_t = \beta_0 - (\beta_1 * \sin(2\pi/1440 * t) + \beta_2 * \sin(4\pi/1440 * t)) + DO_{sat,t},$$

where DO_t and $DO_{sat,t}$ are the observed dissolved oxygen concentration and the dissolved oxygen concentration at saturation at time t , respectively.

- For temperatures between 6° and 42° C the saturation concentration can be expressed as;

$$DO_{sat} = 1/(0.0683 + 0.00198 * ^\circ C + 5.24 * 10^{-6} \cdot ^\circ C^2)$$

Selected Model of Diel Dissolved Oxygen



- Model Predicts Central Tendency (Arithmetic Mean) of the Diel Curve
- Utilizes Sample Collection Time and Temperature

$$DO_i = -3.70 - (1.50 \cdot \sin(2\pi/1440 \cdot t_i)) - 0.30 \cdot \sin(4\pi/1440 \cdot t_i) + 1 / (0.068 + 0.00198 \cdot C_i + 5.24 \cdot 10^{-6} \cdot C_i^2)$$

t_i = sample collection time (minutes) of the i^{th} sample

C_i = water temperature (°C) of the i^{th} sample

SSAC Development Approach

Model background diel dissolved oxygen fluctuation

- ✓ **Cross-validate model with a larger dataset from the entire EPA**

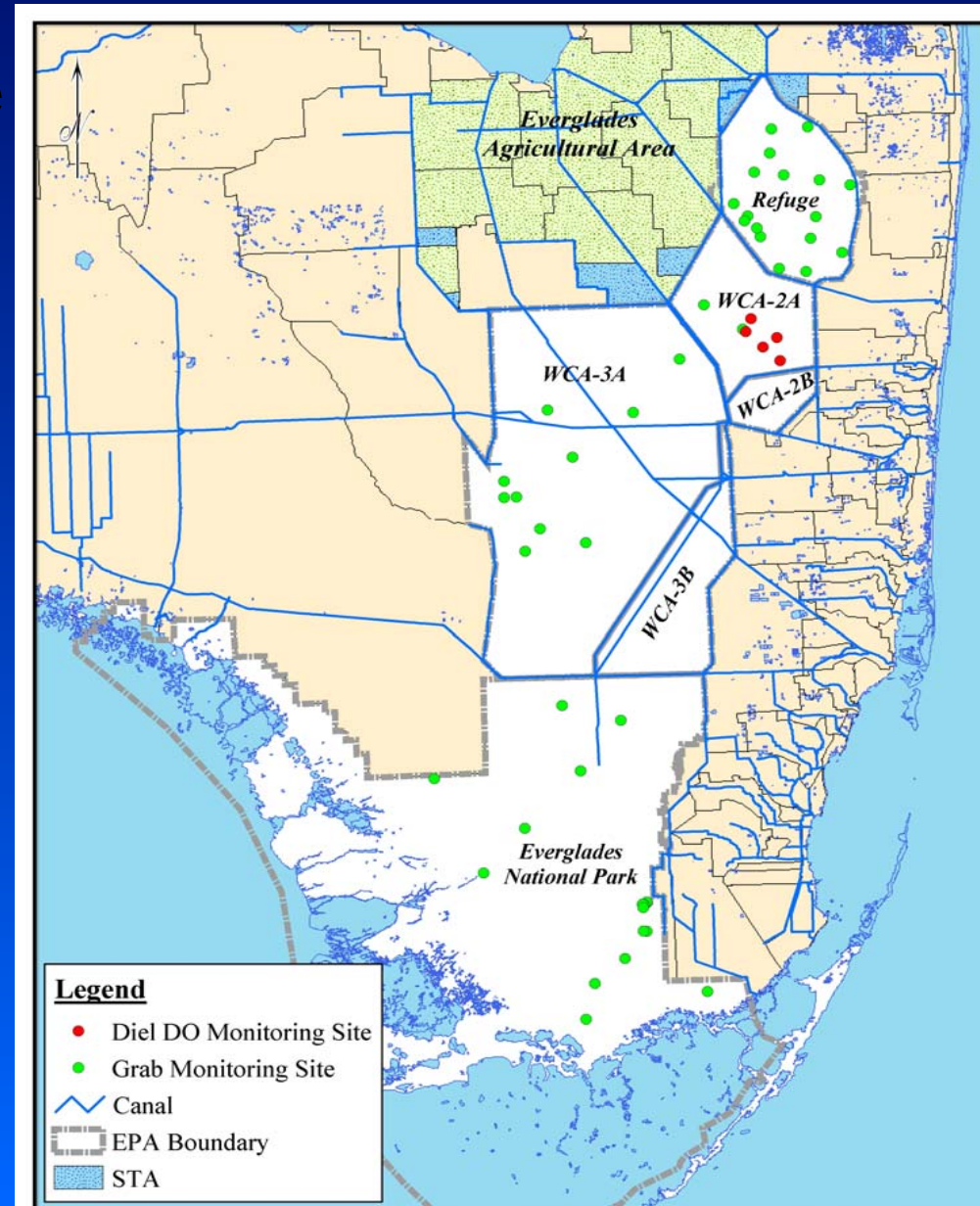
Define compliance limit and methodology



Cross-Validation Dataset

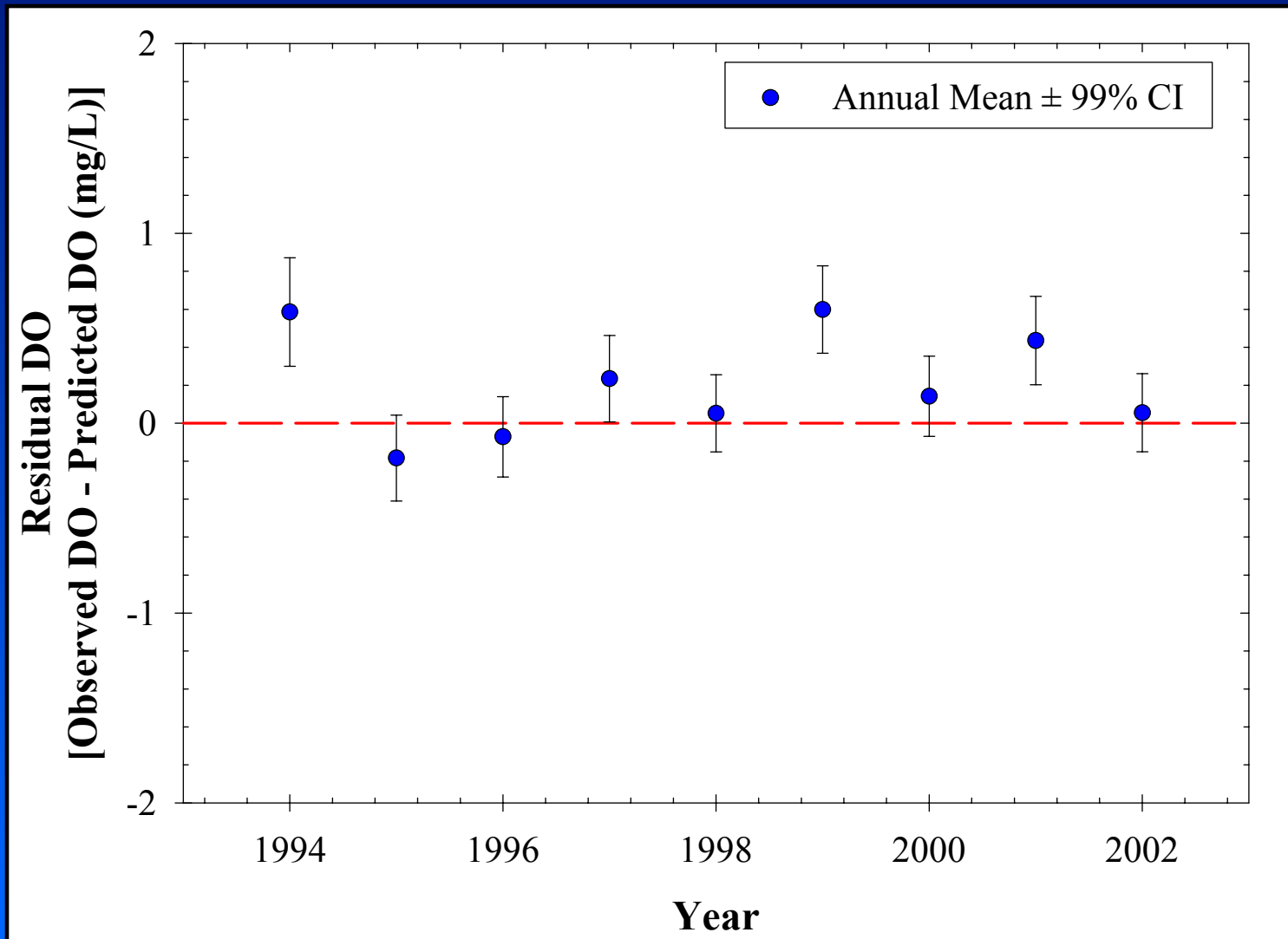
Grab samples collected at background sites throughout the Everglades

- Grab sampling is the most feasible method of compliance monitoring
- Selection of background sites based on same criteria as utilized for diel modeling sites
- In-situ measurement collected biweekly-monthly during the period from 1994 to 2002
- Approximately 4200 observations (351 Site-Years) used to cross-validate model and set compliance limit



Model Provides a Good Prediction of Average Grab Sample DO

Annual Sample Size Ranged from 348 to 598

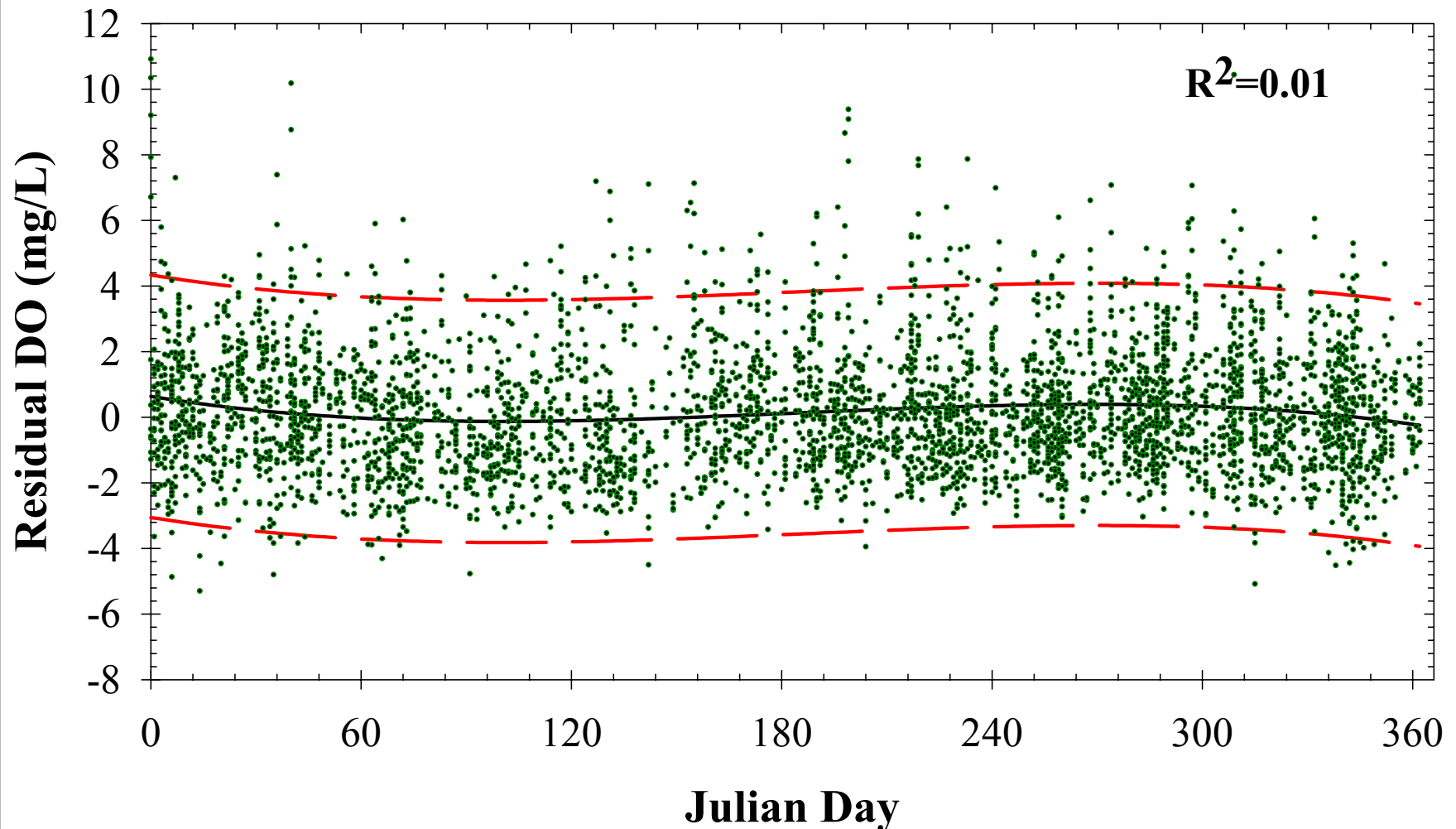


Cross-Validation Residuals versus Julian Day

Show No Significant Seasonal Bias

Solid line indicates third order curve of best-fit

Red-dashed line indicates the 95% prediction interval



SSAC Development Approach

Model background diel dissolved oxygen fluctuation

Cross-validate model with a larger dataset from the entire EPA

✓ **Define compliance limit and methodology**



Defining a Compliance Limit

- The diel model provides a prediction of the average annual dissolved oxygen condition within background areas of the EPA
- DO concentrations both above and below the model predicted values are expected to occur naturally due to random factors such as changes in cloud cover, rainfall, water depth, etc
 - Background site DO will be less than model prediction (exceedance) approximately 50% of the time due to random error
- The issue of compliance becomes a statistically testable hypothesis of whether observed deviations occur due to natural background variability

Defining a Compliance Limit

- To judge compliance with a SSAC, it is necessary to calculate or define the allowable frequency and magnitude of observations below the curve
- Current USEPA guidance recommends a maximum exceedance frequency of 10 percent from applicable water quality standards for conventional pollutants or constituents (USEPA, 1997; USEPA, 2002)
- Impaired Waters Rule specifies a $> 10\%$ exceedance rate to list waters on the State's 303(d) list
- Therefore, the compliance limit was derived using a 10% error rate

Annual Limit Calculation

- Derived by comparing measured grab sample DO levels with levels predicted by the model (residuals)
- Residuals provide the distribution of data around the model curve and show how often observations are below (or above) the curve
- Residuals were calculated as the mean annual observed concentration minus the mean annual model predicted concentration

Annual Limit Calculation

The statistical problem of calculating a 10% lower rejection limit is equivalent to the problem of calculating a prediction interval below which there is less than a 10% chance that new observations come from the same distribution as previously collected data. The lower prediction interval (PI_l) can be calculated by the equation:

$$PI_l = \bar{X} - t_{(\alpha, n-1)} \cdot \sqrt{S^2 + (S^2 / n)},$$

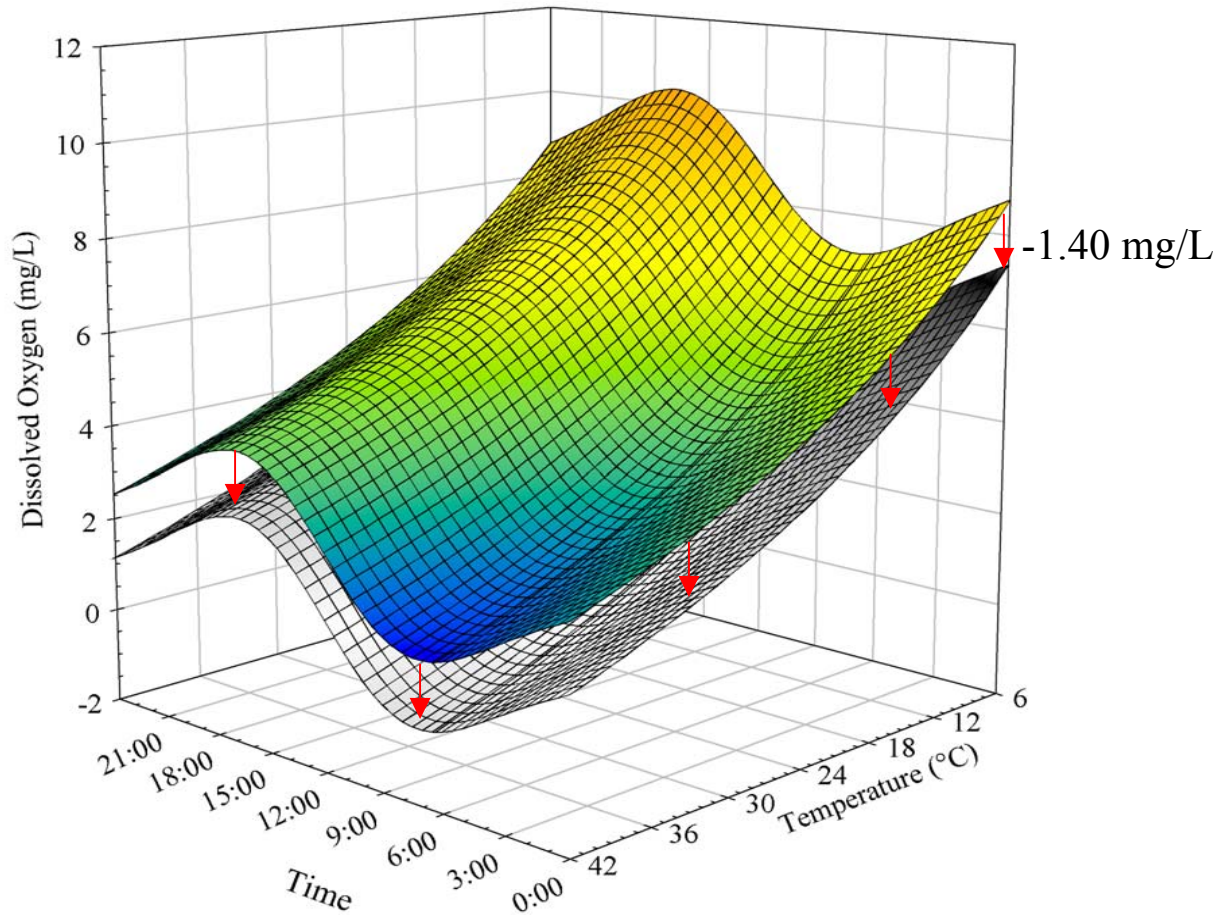
where S and n are the standard deviation and number of the individual observations, respectively, and $t_{(\alpha, n-1)}$ is the one-tailed t-test statistic for a probability of α with $n-1$ degrees of freedom

Lower Prediction Interval Calculation

Parameter	Value
Mean Residual ($\bar{X}$)	0.32
Standard Deviation of Residuals	1.34
n-1	350
$t_{(0.1,350)}$	1.28
Interval	-1.40

$$PI_l = \bar{X} - 1.28 \bullet \sqrt{1.34^2 + (1.34^2 / 350)} = 0.32 - 1.73 = -1.40$$

Calculation of Compliance Limit

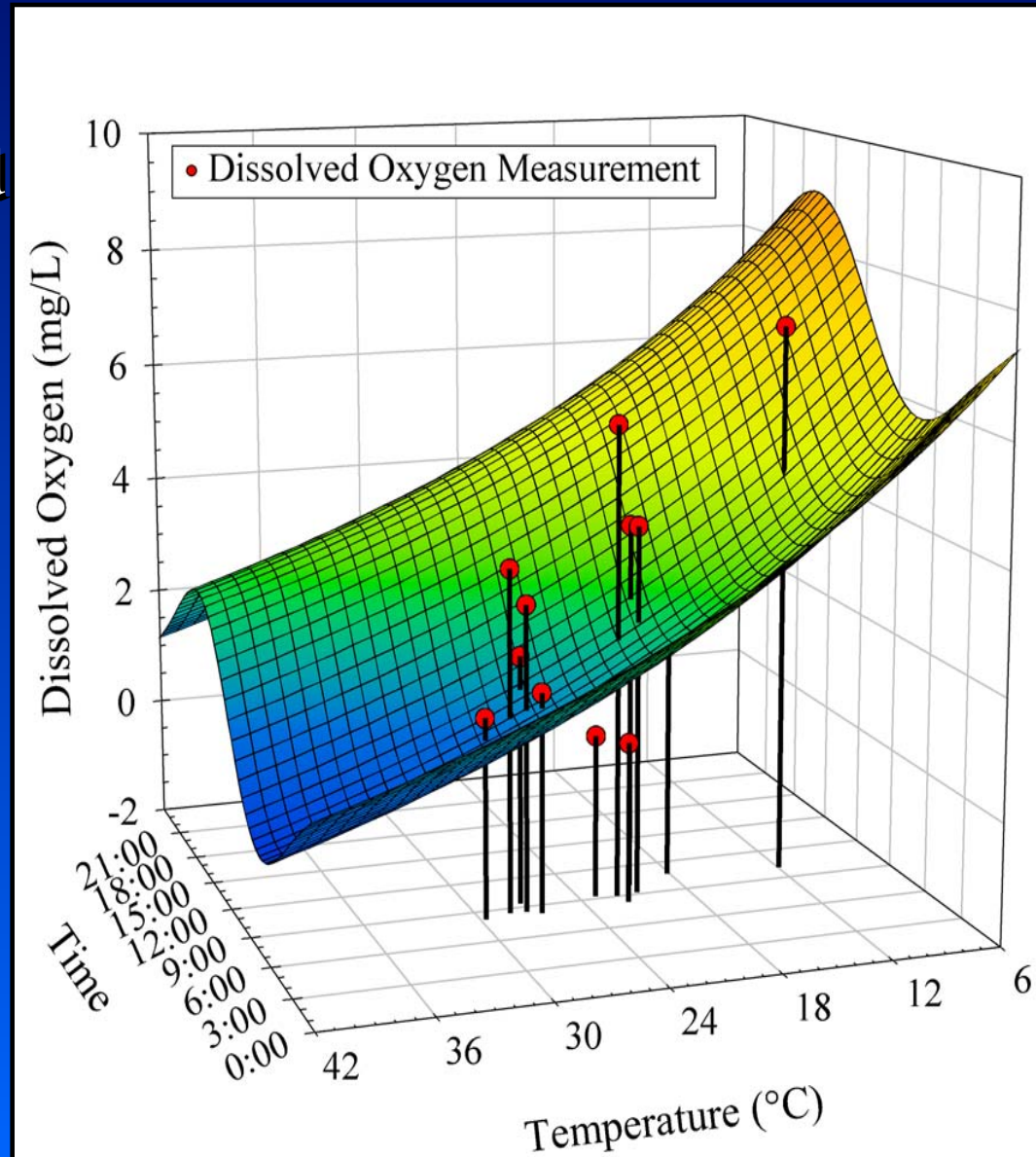


$$DO_{LL} = -3.70 - (1.50 \cdot \sin(2\pi/1440 \cdot t) - 0.30 \cdot \sin(4\pi/1440 \cdot t)) + 1/(0.0683 + 0.00198 \cdot C + 5.24 \cdot 10^{-6} \cdot C^2) - \underline{PI}_1 =$$

$$-3.70 - (1.50 \cdot \sin(2\pi/1440 \cdot t) - 0.30 \cdot \sin(4\pi/1440 \cdot t)) + 1/(0.0683 + 0.00198 \cdot C + 5.24 \cdot 10^{-6} \cdot C^2) - \underline{1.40}$$

Compliance Determination

- Calculate predicted DO for individual observations based on collection time and water temperature
- Compliance based on annual average DO levels
 - Observed annual average concentration compared to annual average predicted value
 - Provides an allowance for natural variability
 - Seasonal
 - Light intensity
 - Biological activity
 - Water level



Annual Assessment for An Individual Site

$$DO_{AL} = \frac{1}{n} \cdot \sum_{i=1}^n -3.70 - (1.50 \cdot \sin(\frac{2\pi}{1440} \cdot t_i) - 0.30 \cdot \sin(\frac{4\pi}{1440} \cdot t_i)) + \frac{1}{(0.068 + 0.00198 \cdot C_i + 5.24 \cdot 10^{-6} \cdot C_i^2)} - 1.40$$

Compare to:

$$\overline{DO} = \frac{1}{n} \cdot \sum_{i=1}^n x_i$$

Where

- DO_{AL} = Annual Compliance Limit (mean predicted value)
- $\overline{DO}$ = Annual mean measured dissolved oxygen
- n = Total Number of samples collected during year
- t_i = Sample collection time of the i^{th} sample
- C_i = Water temperature (°C) of the i^{th} sample
- x_i = Measured dissolved oxygen concentration of the i^{th} sample.

Example Application

Date	Collection Time (EST)	Time (Minutes)	Temp. (°C)	Observed DO (mg/L)	
1/14/98	14:22	862	19.95	6.0	
2/10/98	11:13	673	14.02	5.4	
3/17/98	12:13	733	18.86	4.2	
4/7/98	10:03	603	22.83	2.2	
5/5/98	10:00	600	24.06	1.8	
7/28/98	10:05	605	30.49	2.8	
8/25/98	8:05	485	27.32	1.4	
9/22/98	11:33	693	29.03	3.9	
10/20/98	9:52	592	25.10	3.3	
11/17/98	11:55	715	26.27	5.1	
12/15/98	11:17	677	19.66	2.9	

Example Application

Date	Collection Time (EST)	Time (Minutes)	Temp. (°C)	Observed DO (mg/L)	Predicted DO _{LL} (mg/L)
1/14/98	14:22	862	19.95	6.0	5.2
2/10/98	11:13	673	14.02	5.4	
3/17/98	12:13	733	18.86	4.2	
4/7/98	10:03	603	22.83	2.2	
5/5/98	10:00	600	24.06	1.8	
7/28/98	10:05	605	30.49	2.8	
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9/22/98	11:33	693	29.03	3.9	
10/20/98	9:52	592	25.10	3.3	
11/17/98	11:55	715	26.27	5.1	
12/15/98	11:17	677	19.66	2.9	

$$DO_{LL} = -3.70 - (1.50 \cdot \sin(2\pi/1440 \cdot 862) - 0.30 \cdot \sin(4\pi/1440 \cdot 862)) + 1/(0.0683 + 0.00198 \cdot 19.95 + 5.24 \cdot 10^{-6} \cdot 19.95^2) - 1.40 = 5.2$$

Example Application

Date	Collection Time (EST)	Time (Minutes)	Temp. (°C)	Observed DO (mg/L)	Predicted DO _{LL} (mg/L)
1/14/98	14:22	862	19.95	6.0	5.2
2/10/98	11:13	673	14.02	5.4	4.8
3/17/98	12:13	733	18.86	4.2	4.3
4/7/98	10:03	603	22.83	2.2	2.5
5/5/98	10:00	600	24.06	1.8	2.3
7/28/98	10:05	605	30.49	2.8	1.4
8/25/98	8:05	485	27.32	1.4	1.3
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10/20/98	9:52	592	25.10	3.3	2.1
11/17/98	11:55	715	26.27	5.1	2.9
12/15/98	11:17	677	19.66	2.9	3.7

$$DO_{LL} = -3.70 - (1.50 \cdot \sin(2\pi/1440 \cdot 677) - 0.30 \cdot \sin(4\pi/1440 \cdot 677)) + 1/(0.0683 + 0.00198 \cdot 19.66 + 5.24 \cdot 10^{-6} \cdot 19.66^2) - 1.40 = 3.7$$

Example Application

Date	Collection Time (EST)	Time (Minutes)	Temp. (°C)	Observed DO (mg/L)	Predicted DO _{LL} (mg/L)
1/14/98	14:22	862	19.95	6.0	5.2
2/10/98	11:13	673	14.02	5.4	4.8
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10/20/98	9:52	592	25.10	3.3	2.1
11/17/98	11:55	715	26.27	5.1	2.9
12/15/98	11:17	677	19.66	2.9	3.7
Annual Average (Compliance Limit)				3.5	3.0

Test Performance

Stations	Site-Years	Assessment Methodology	Number Exceedance	Percent Exceedance
Background	351	At Least One Measurement < 5 mg/L	335	95.4
		Greater than 10% of the Measurements < 5 mg/L	332	94.6
		SSAC	23	6.6
All	549	At Least One Measurement < 5 mg/L	531	96.7
		Greater than 10% of the Measurements < 5 mg/L	528	96.2
		SSAC	155	28.2*

*Non-random SSAC Exceedances Associated with Known Impacts from

- Nutrient Enrichment
- Canal and/or ground water influences

2001-2004 Everglades Consolidated Reports

“Cruising Testing the SSAC”

- Following development, the SSAC has undergone extensive evaluation over a wide range of climatic conditions
- Results of these evaluations reported in the peer-reviewed 2001-2004 Everglades Consolidated Reports
- Because DO concentrations at most stations were within the range of natural background conditions applying the SSAC to actual monitoring data from the EPA resulted in a substantially lower excursion rate than did the analysis based on the current 5.0 mg/L criterion
- SSAC successfully differentiates between impaired and background conditions

DO SSAC Received Favorable Comments from the Everglades Consolidated Report Peer Review Panel

- “The dissolved oxygen alternative criterion assessment is well developed and documented.”
- “The inclusion of a clear and well-documented definition of compliance in the study is viewed as being on the cutting edge of criteria development.”
- “The authors are to be complemented for adding this critical component to their criterion development. By adding a clear definition of compliance, future analysis of monitoring data for standard compliance is also defined.”

Summary

- SSAC formally recognize the natural background conditions in the EPA marshes
- SSAC Provides:
 - An accurate differentiation between impacted and background conditions relative to DO
 - More realistic information on ecosystem status than the existing Class III criterion
 - Variable environmental standard
 - Considers natural processes
 - Ecological factors
- Compliance limit
 - Utilizes feasible sampling methodology
 - Uncertainty
 - Natural variability
 - Provides defined and consistent statistical methodology

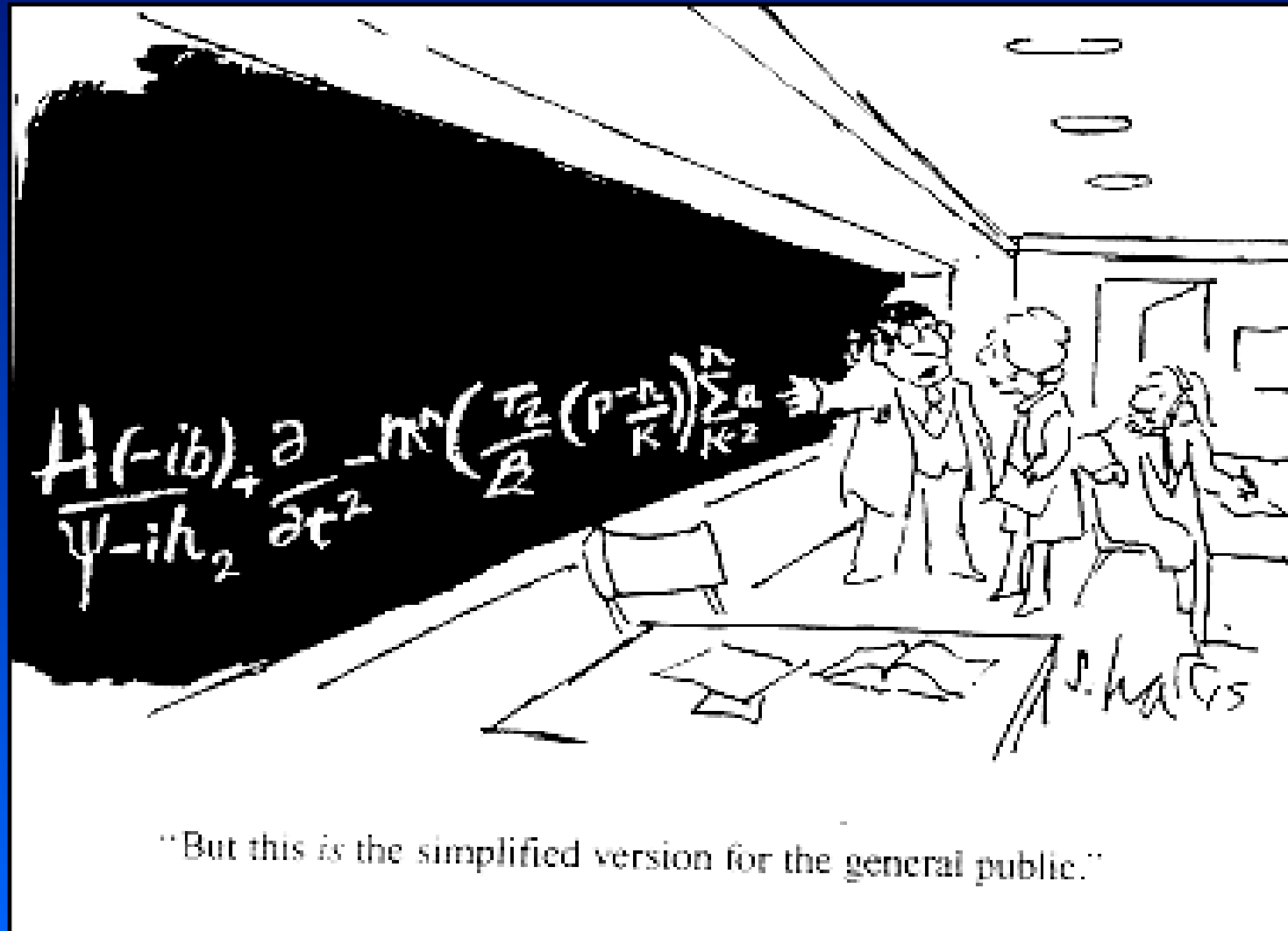
Acknowledgments

- Garry Payne and Temperince Morgan (FDEP) for review, comment and editorial assistance.
- Xu-Feng Niu, Pi-Erh Lin, Duane Meeter (FSU) and Lori Wolfe (FDEP) for statistical input and comment.
- Paul McCormick and the South Florida Water Management District for collecting and providing the necessary data.
- Dr. Robert Ward (Colorado State University) for his review, comment, and encouragement.

A detailed technical support document was provided in Appendix 4-II of the 2001 Everglades Consolidated Report. This report can be found on-line at:

http://www.sfwmd.gov/org/ema/everglades/consolidated_01/

Questions or Comments?



Annual Assessment for An Individual Site

$$DO_{AL} = \frac{1}{n} \cdot \sum_{i=1}^n - 3.70 - (1.50 \cdot \sin(\frac{2\pi}{1440} \cdot t_i) - 0.30 \cdot \sin(\frac{4\pi}{1440} \cdot t_i)) + \frac{1}{(0.068 + 0.00198 \cdot C_i + 5.24 \cdot 10^{-6} \cdot C_i^2)} - 1.40$$

Compare to:

$$\overline{DO} = \frac{1}{n} \cdot \sum_{i=1}^n x_i$$

Where

- DO_{AL} = Annual Compliance Limit (mean predicted value)
- $\overline{DO}$ = Annual mean measured dissolved oxygen
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- t_i = Sample collection time of the i^{th} sample
- C_i = Water temperature (°C) of the i^{th} sample
- x_i = Measured dissolved oxygen concentration of the i^{th} sample.

Range of SSAC Lower Limit DO Concentrations

