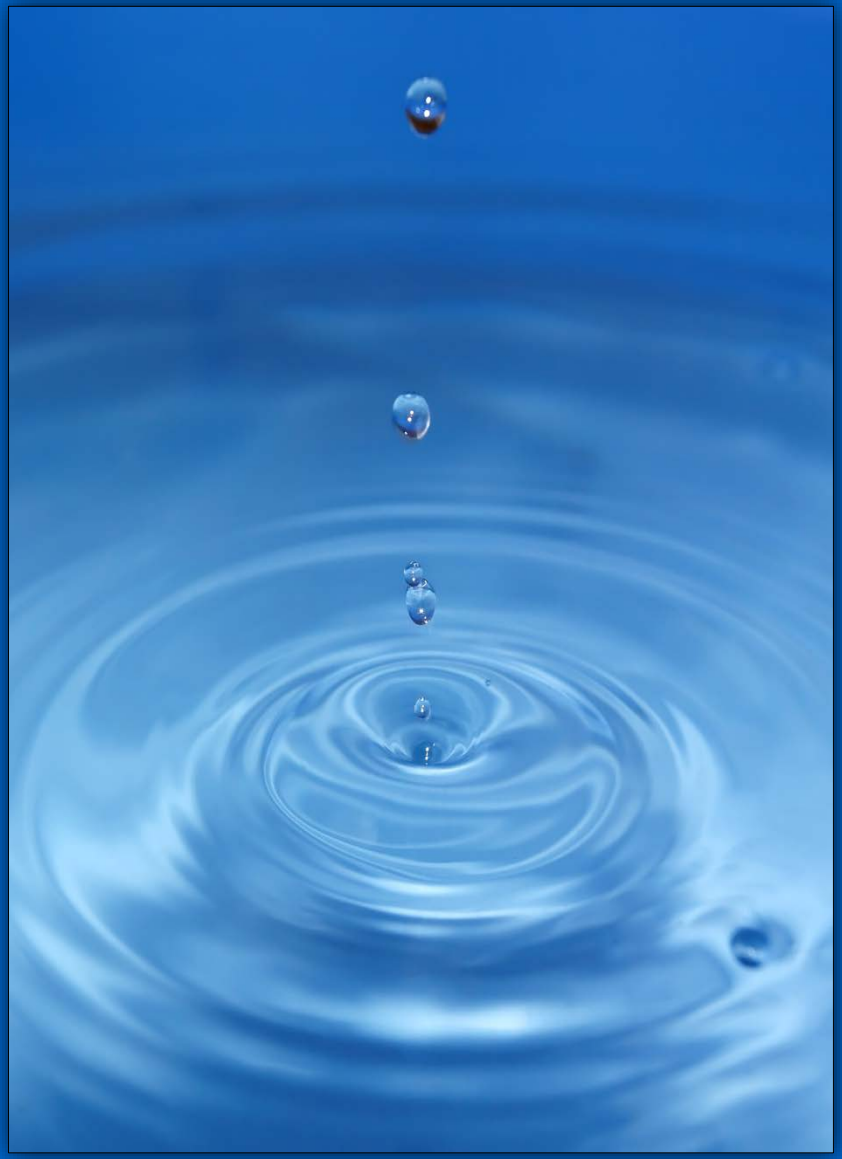


A New SFWMD Method for Determination of Total Nitrogen (TN) in Water - 2015 Update

Richard C. Walker
Laboratory Manager
Analytical Services Section
Water Quality Bureau

Technical Oversight Committee
October 27, 2014

sfwmd.gov

2015 Update Highlights

- **Accepted and Approved by FDEP for Several Permit Modifications**
- **Additional Comparative Analysis as Requested**
- **Certified for TN since April 2014**
- **13,744 Reportable TN/TDN Results in 18 months**

New SFWMD Method for the Determination of TN in Water

- **Partial List of FDEP Permit Modifications with TN:**
  - 8.5 Square Mile Area, S-357 Pump Station (File No. 0317442-003)
  - Biscayne Bay Coastal Wetland (File No. 0271729-008)
  - C-111 Spreader Canal Phase 1 (Western) (File No. 0293559-010)
  - G-161 Water Control Structure (File No. 0244327-006)
  - Lakeside Ranch Stormwater Treatment Area (File No. 0287326-008)
  - Rolling Meadows Restoration (File No. 0327454-002)
  - S-197 Control Structure (File No. 0306639-002)
  - Taylor Creek Stormwater Treatment Area (File No. 0194485-012)
  - Nubbin Slough STA WQ Revisions (File No: 0194483-016)

New SFWMD Method for the Determination of TN in Water

- Historical practice (Calculated TN = TKN + NO_X)
- New procedure (Direct TN and TDN measurement)
- Development Activities
- Implications
- Validation
- Comparative Analysis (as requested by the TOC)
- Implementation

New SFWMD Method for the Determination of TN in Water

- **Historical practice (TN = TKN + NO_X)**
  - **Two separate samples must be collected**
    - NO_X cannot be analyzed from the same sample due to filtration and preservation requirements (does not allow for TN measurement from composite samples).
  - **Two separate laboratory procedures**
    - The TKN procedure is labor intensive, requires specialized safety equipment to perform the necessary digestion and generates a more significant waste stream.
  - **Two separate results in the database**
    - Both results must be validated and posted to DBHYDRO.
    - The two results must be summed to obtain TN for reporting purposes .

New SFWMD Method for the Determination of TN in Water

- **New procedure (direct measurement)**
  - With the new procedure, TN is determined directly from a single sample using closed vessel digestion followed by automated flow injection analysis (similar to current Total Phosphorus (TP) procedure).
  - A single result for TN is reviewed, validated and posted to the database. No further calculations are required.
  - This new procedure provides improved detection limits with lower levels of associated uncertainty than the traditional method of calculating TN from TKN and NOX.

New SFWMD Method for the Determination of TN in Water

- **Method Development and Certification**
  - Long-term extensive method development program.
  - Provides improvements to sample collection procedures and laboratory workflows.
  - Increased safety for chemists:
    - Does not require open, high temperature digestion.
    - Uses fewer chemicals and glassware.
    - Does not require acid scrubber fume hood.
  - In 2013, the SFWMD Laboratory submitted an application for certification to the Florida Department of Health (FDOH), Bureau of Laboratories.
  - In April 2014, the FDOH conducted an on-site inspection and approved certification of the method.
  - Potential long-term cost savings (equipment, supplies and energy).

New SFWMD Method for the Determination of TN in Water

- **Implications**
  - **Some changes to existing monitoring permits and parameter lists may be required for full implementation.**
    - In general, the parameter lists on projects and permits may be changed from TKN and NO_X to TN only.
    - As appropriate, NO_X may remain as a monitored analyte.
  - **The reference method for the new TN parameter is Standard Methods SM4500NC.**
  - **The new TN method has a detection limit of 0.02 mg/L.**
    - The effective detection limit for calculated TN is the detection limit of TKN (0.05 mg/L) plus the detection limit of NOX (0.005) or 0.055 mg/L.

New SFWMD Method for the Determination of TN in Water

- **Implications (continued)**
  - Samples for TN and TDN may be collected and preserved in the same bottles and with the same filters and preservatives used for TKN and TDKN; there is no change in the sample volume required for analysis.
  - With the new direct TN method, it will now be possible to run TN analysis from the same autosampler collected bottle used for TP. This was not possible with calculated TN because the NO_X sample required filtration prior to preservation.
  - Refrigerated autosamplers may be used to properly collect the NO_X sample, but this equipment is subject to frequent failure during the summer months. Once the TN method is fully implemented, the refrigerated units may be switched back to regular autosamplers.
    - However, a separate, properly preserved sample will still be required if separate determination of NO_X is needed.

New SFWMD Method for the Determination of TN in Water

- **Implications (continued)**
  - The SFWMD laboratory will continue to conduct TKN analyses as needed until all project/permit modifications are accomplished.
  - Calculated results involving nitrogen fractions may be handled more directly and will involve less uncertainty.

New SFWMD Method for the Determination of TN in Water

- **Validation**
  - Routine quality control samples for the new method are well within the established accuracy and precision control recovery ranges for our laboratory.
  - The laboratory verifies performance of the method through participation in two separate international (ISO 43) blind performance testing studies:
    - Marine Environmental Monitoring in Europe (QUASIMEME) for seawater and estuarine samples. Results from all four studies since 2014 were satisfactory except for one seawater study in which contamination was identified and corrected.
    - Environment Canada provides fortified samples from natural surface water systems; satisfactory performance in four studies since 2014.

New SFWMD Method for the Determination of TN in Water

- **Validation (continued)**

Measurement Uncertainty

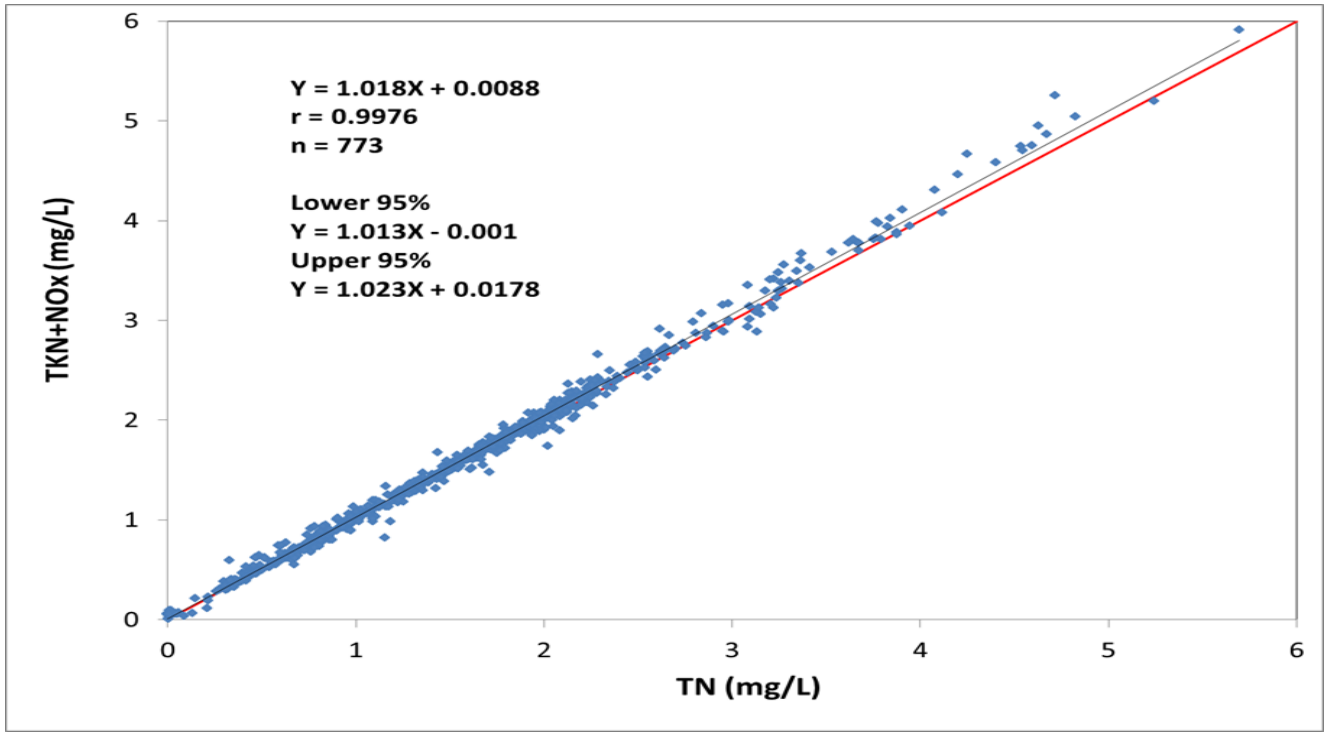
The SFWMD Laboratory provides estimated uncertainty values for all analytes with sufficient data to calculate uncertainty constants. The uncertainty has a probabilistic basis and reflects incomplete knowledge of the quantity. All measurements are subject to uncertainty and a measured value is only complete if it is accompanied by a statement of the associated uncertainty. The uncertainty is required in order to decide if the result is adequate for its intended purpose and to ascertain if it is consistent with other similar results.

- Paired, overlapping uncertainty analysis of 1,745 measurements demonstrates consistency with the 95% confidence interval.
- Only 69 of the 1,745 (<4%) paired results were found to be inconsistent.

New SFWMD Method for the Determination of TN in Water

- ## Comparative Analysis

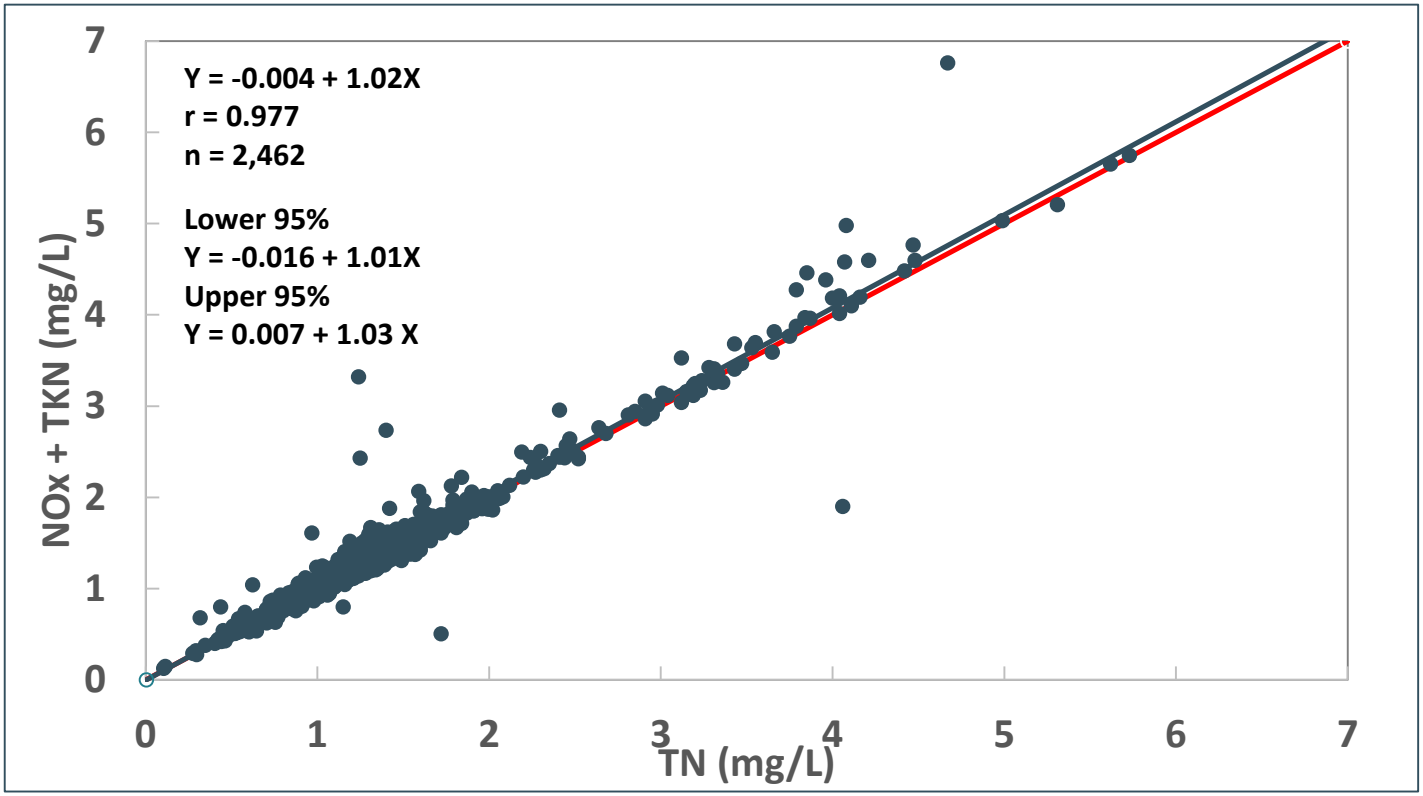
During the final stages of method development, the laboratory conducted comparative analysis of nearly 800 typical SFWMD surface water samples. The results were highly correlated, free of significant bias and showed agreement consistent with the estimated levels of uncertainty for each method.



New SFWMD Method for the Determination of TN in Water

- ## Comparative Analysis (continued)

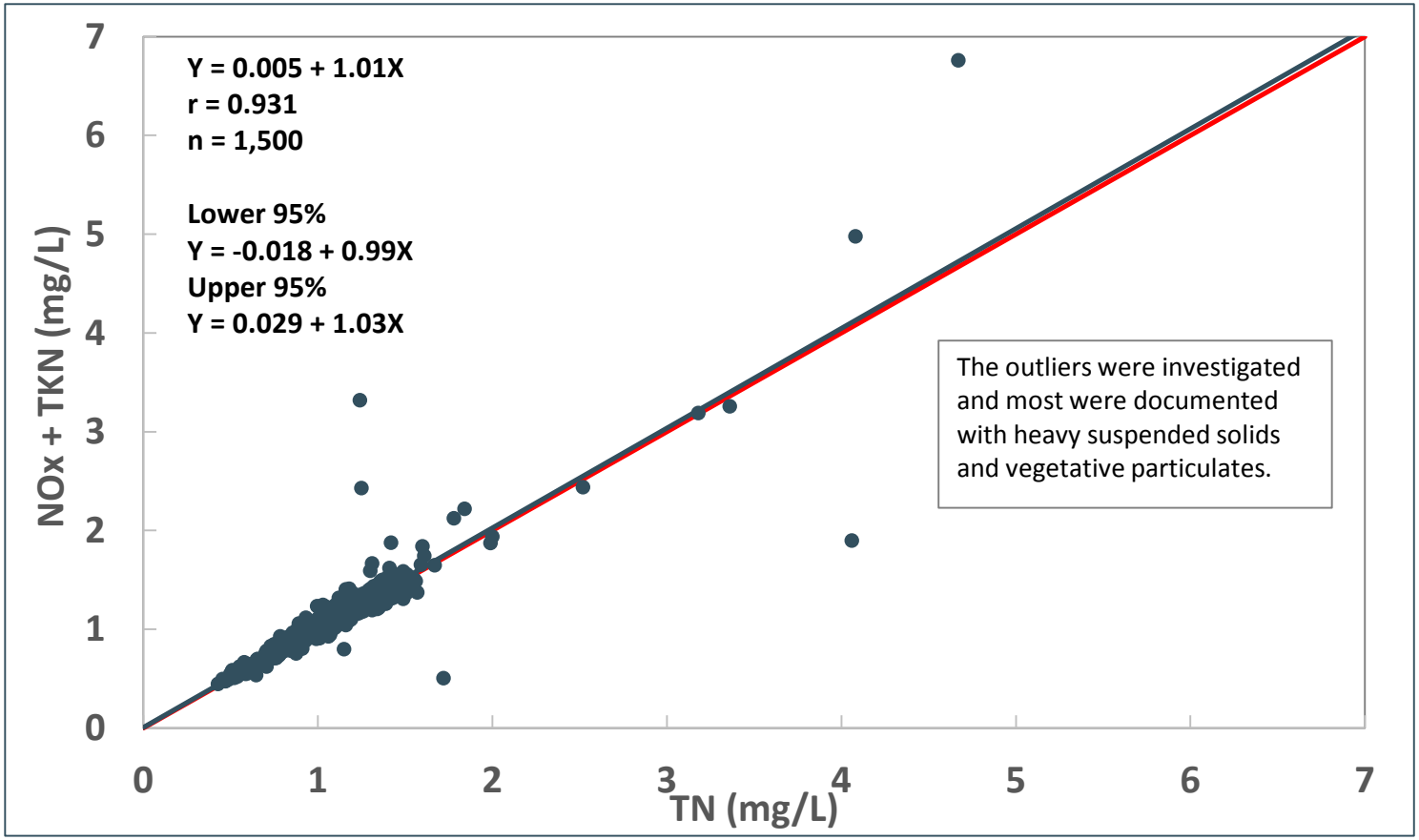
Following the initial TOC presentation in July 2014, the laboratory conducted an additional 2,462 comparative tests.



New SFWMD Method for the Determination of TN in Water

- ## Comparative Analysis (continued)

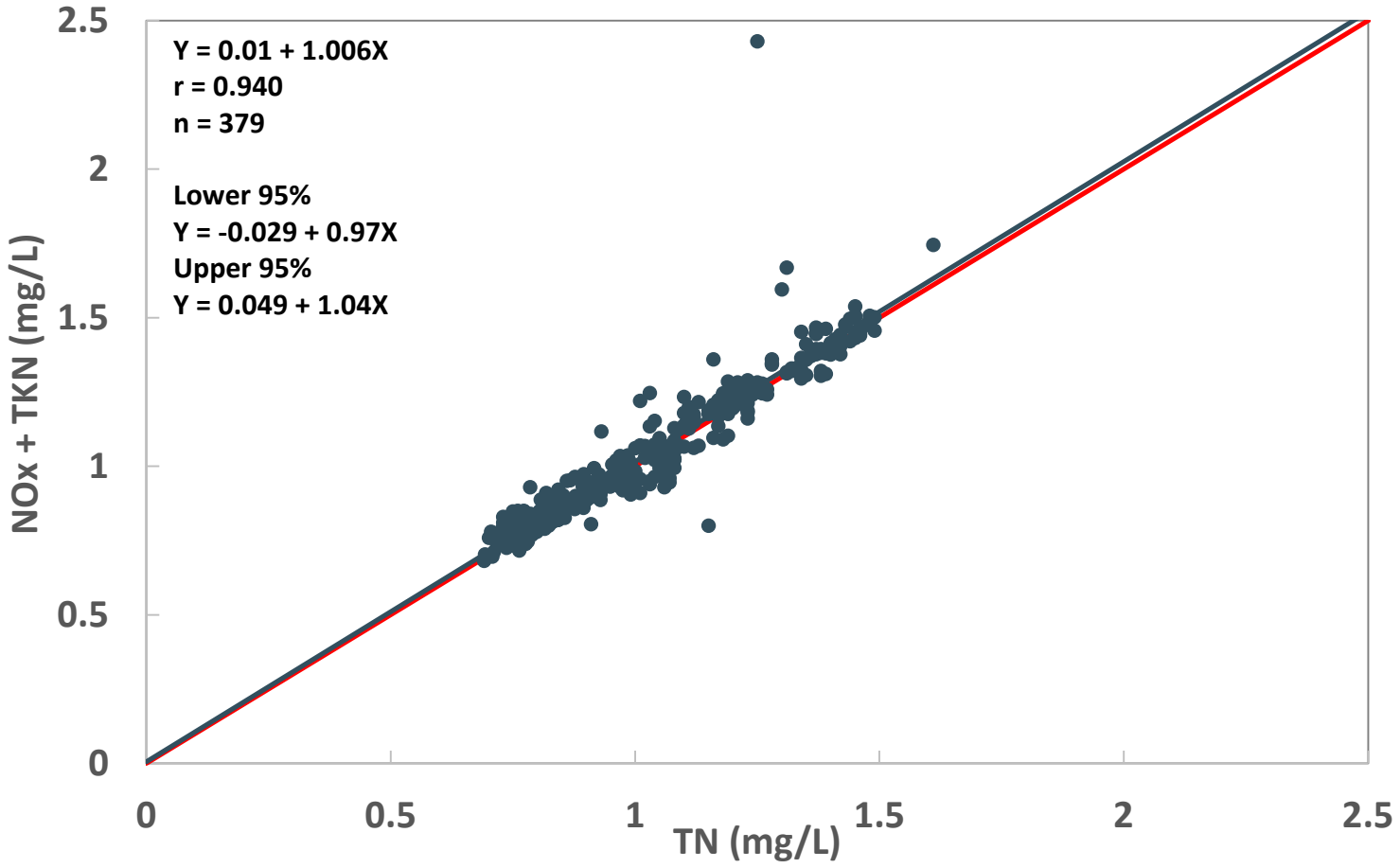
A total of 1,500 comparative tests were analyzed from sites of interest to the TOC.



New SFWMD Method for the Determination of TN in Water

- **Comparative Analysis (continued)**

As an example, the results from site S332DX were plotted and show a similar pattern over a narrow range of values.



New SFWMD Method for the Determination of TN in Water

- **Comparative Analysis (continued)**

Most sites of interest return TN values in a narrow range and are very comparable. (Partial table where N>30, complete data set in TN Fact Sheet.)

Station	Average of Total Nitrogen (Calculated)	Standard Deviation of TN (Calculated)	Average of TN (Measured)	Standard Deviation of TN (Measured)	Number of Paired Measurements
Grand Total	1.25	0.51	1.23	0.49	2462
S332DX	1.05	0.24	1.03	0.22	379
S12A	1.02	0.42	0.99	0.32	357
S356-334	1.39	0.09	1.38	0.17	347
S333	1.21	0.14	1.19	0.12	317
S331-173	1.35	0.13	1.35	0.15	156
S6	2.01	0.99	1.94	0.96	85
S18C	0.66	0.23	0.67	0.27	67
S178	0.67	0.27	0.65	0.26	47
S5A	1.61	0.53	1.56	0.52	47
S177	0.76	0.28	0.75	0.29	34
S7	1.38	0.33	1.39	0.35	34
S8	1.39	0.21	1.38	0.20	34

New SFWMD Method for the Determination of TN in Water

- **Comparative Analysis (continued)**

The marsh transport sites display similar characteristics. Also note minimal variability and stability over time.

Station	Average of Total Nitrogen (Calculated)	Standard Deviation of TN (Calculated)	Average of TN (Measured)	Standard Deviation of TN (Measured)	Number of Paired Measurements
S10A	1.22	0.13	1.23	0.13	15
S10C	1.42	0.12	1.42	0.09	12
S10D	1.48	0.13	1.49	0.11	11
S39	1.28	0.35	1.22	0.17	25
S11A	1.51	0.24	1.51	0.23	22
S11B	1.53	0.25	1.54	0.24	19
S11C	1.54	0.33	1.51	0.32	7
S12A	1.02	0.42	0.99	0.32	357
S12B	0.92	0.06	0.90	0.05	11
S12C	1.03	0.16	1.02	0.13	12
S145	1.56	0.37	1.56	0.37	18
S151	1.45	0.15	1.45	0.16	18
S333	1.21	0.14	1.19	0.12	317
S38	1.47	0.33	1.48	0.34	26
TAMBR105	0.82	0.16	0.79	0.16	16
US41-25	0.97	0.22	0.95	0.23	10

New SFWMD Method for the Determination of TN in Water

- **Implementation**
  - Additional information was provided to FDEP regarding implementation of the method in June 2015
  - FDEP accepted the new method and has incorporated the TN method into several District permit modifications
  - Currently continuing the transition of all monitoring projects to the new method
  - Provide requested information to the TOC to complete the transition

New SFWMD Method for the Determination of TN in Water

- **Requested Action**
  - In accordance with the intent of the Settlement Agreement, we are asking the TOC to approve implementation of the direct TN measurement procedure as described for monitoring TN at the Settlement Agreement stations.


Questions?