

# A New SFWMD Method for Determination of Total Nitrogen (TN) in Water

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## *New SFWMD Method for the Determination of TN in Water*

- **Historical practice (Calculated TN = TKN + NO<sub>x</sub>)**
- **New procedure (Direct TN and TDN measurement)**
- **Development activities**
- **Implications**
- **Validation**
- **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

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- **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
- Potential long term cost savings (equipment, supplies and energy )
- 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

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- **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<sub>x</sub> to TN only
  - As appropriate, NO<sub>x</sub> 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 NO<sub>x</sub> (0.005) or 0.055 mg/L

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- **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 auto sampler collected bottle used for TP. This was not possible with calculated TN because the NOX sample required filtration prior to preservation.
  - However, a separate sample will still be required if separate determination of NOX is needed

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- **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***

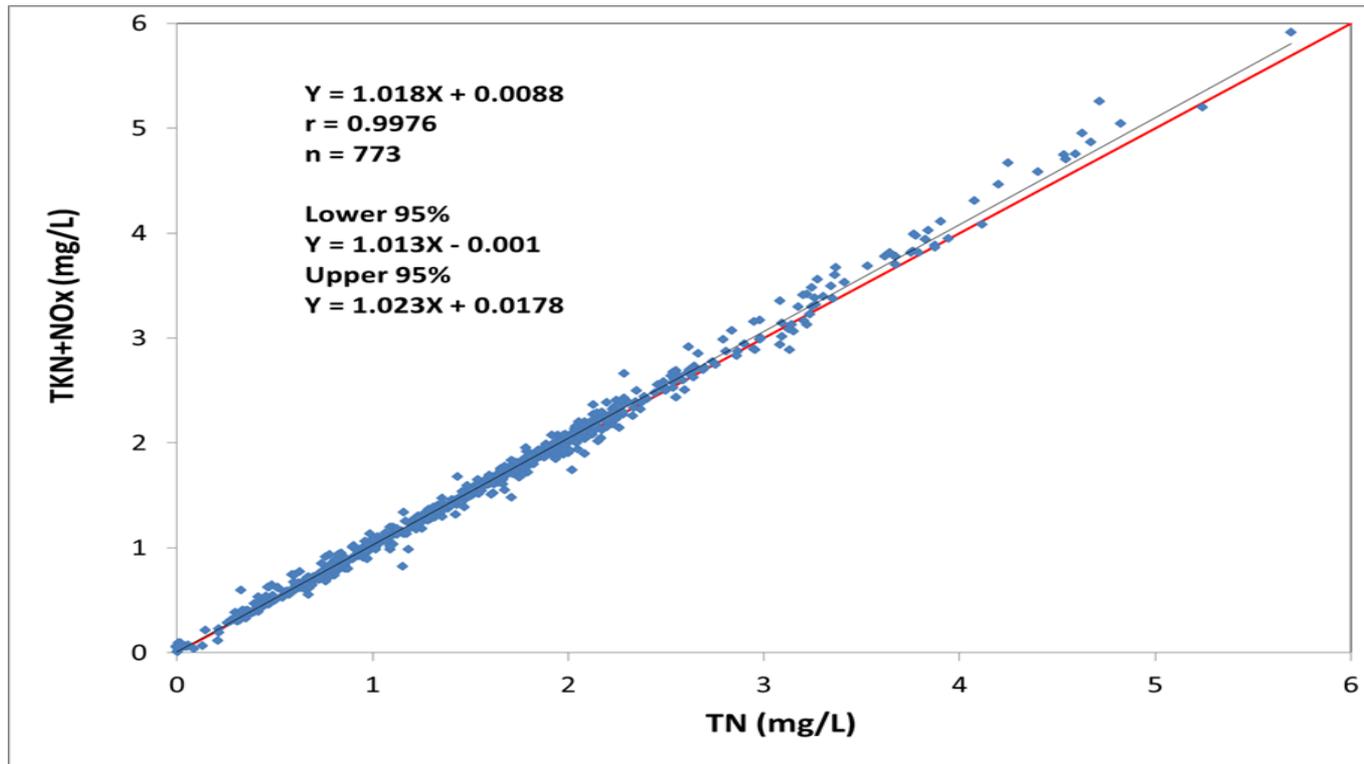
- **Validation**

- **Routine quality control samples for the new method are well within the typical recovery ranges for our laboratory**
- **The laboratory obtained satisfactory results during ongoing participation in two separate blind performance testing studies:**
  - Marine Environmental Monitoring in Europe (QUASIMEME); exercise 1023 for seawater samples and exercise 1024 for estuarine waters, October 2013 through February 2014
  - Environment Canada; ten blind surface water samples, March 2014

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- Validation (continued)

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*

- **Implementation**

- Seek approval of the TOC to transition the laboratory methodology for nitrogen species as other mandates and permit modifications are approved

Questions?

