SFWMD Laboratory Total Nitrogen Methods Fact Sheet

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Analytical Services Section
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Summary:

The SFWMD Laboratory is changing the way it determines total nitrogen (TN) in water samples. The approach for many years has been to determine two forms of nitrogen in the sample, Total Kjeldahl Nitrogen (TKN) and NOX (nitrite + nitrate as N) and add them together to calculate the total (TN = TKN + NOX). While this approach has provided acceptable results, the TKN procedure is potentially dangerous and labor/energy intensive (the sample along with digestion reagents must be evaporated at high temperature (380^{o}C) and ambient pressure and brought back to volume after digestion) and requires specialized equipment to perform the necessary digestion (including costly digestion tubes and a dedicated fume hood with specialized ventilation to remove acid fumes and heat generated during digestion). In the new procedure TN is determined directly by digesting a portion of the water sample in a closed vessel at elevated temperature and pressure in an autoclave. This procedure does not require bringing the sample back to original volume and acid fumes are not released during digestion. In addition, this new procedure provides the added benefit of lower detection limits with lower levels of associated analytical method uncertainty than the traditional method of calculating TN from TKN and NOX.

There is also a new counterpart, TDN (Total Dissolved Nitrogen), to the new TN parameter for the determination of total nitrogen in a filtered sample. This parameter will replace TDKN, the similar counterpart to TKN.

Full implementation of the new TN method is estimated to provide a long term annual cost savings of $5-$10 per test. Based on an annual TN workload of about 13,000 tests, full adoption of the new method will yield estimated savings (cost avoidance) in the range of $65,000 to $130,000 annually.

Implications of the Method Change:

The use of the new method will require some changes to existing monitoring permits and parameter lists to fully implement. Total Nitrogen is not a pollutant parameter listed in 40 CFR Part 136 and there are therefore no approved methods listed. As such, the choice of a “suitable” method can be made by the permit applicant without seeking approval from EPA (see Appendix A at the end of this document for details). The method the District is proposing to use is SM4500NC and is fully described in Standard Methods for the Examination of Water and Wastewater. The District laboratory received NELAP certification for this method in 2014 from FDOH.

In cases when only the measurement of TN is needed for permit compliance, the requested parameter list can be reduced from TKN and NOX to TN only. For permits that require that both TN and NOX be measured for compliance, the requested parameter list will need to be changed to include TN instead of TKN. If there are permits that specifically require a determination of TKN for compliance, the permit conditions will need to be revised with TKN being replaced by TN. The reference method for the new TN parameter is Standard Methods SM4500NC (Standard Methods for the Examination of Water and Wastewater, 21st Edition). The SFWMD SOP for this parameter is SFWMD-SOP-3090-003. The new TN method has a detection limit of 0.02 mg/L while 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. Samples for TN and TDN will be collected and preserved in the same bottles and with the same filters and preservatives used for TKN and TDKN and 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 non-refrigerated auto-sampler collected bottle used for TP. Pre-preserved composite samples are not suitable for the NOX procedure since the NOX samples must be filtered prior to adding the acid preservative. The means that calculated TN is not viable for these applications whereas samples for the direct TN procedure may be pre-preserved along with the usual TP samples from auto-samplers.

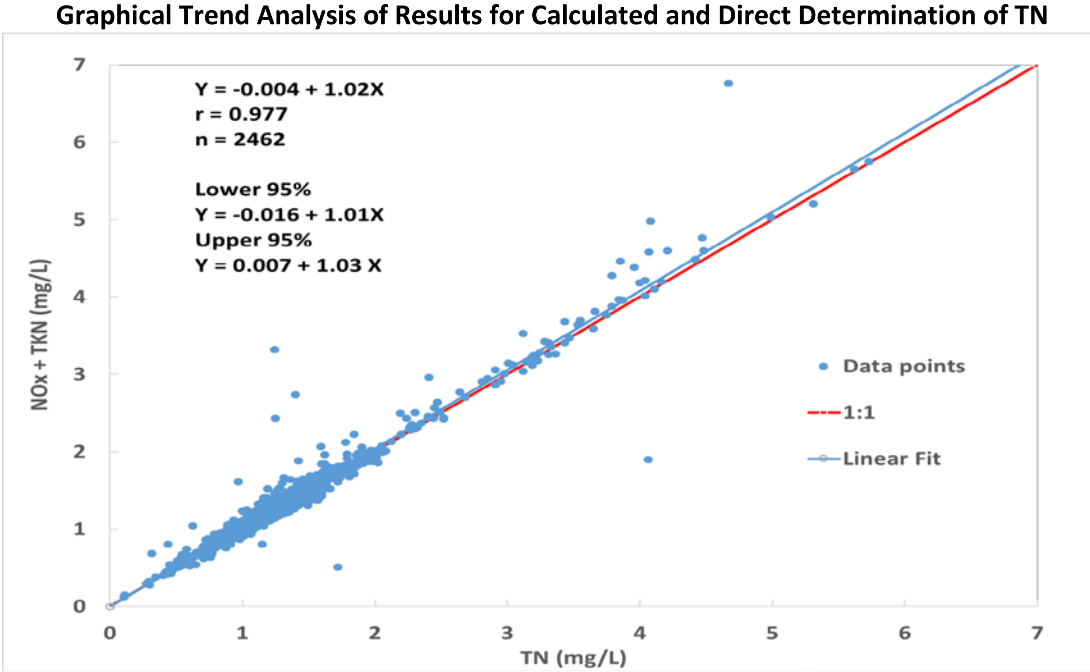
Refrigerated auto-samplers may be used, but this equipment is subject to mechanical problems and frequent failures during the extreme hot weather months. Once the direct measurement of TN is fully implemented the refrigerated auto-samplers may be switched back to regular auto-samplers.

The SFWMD laboratory will continue to conduct TKN analyses as needed until all permit modifications are accomplished (target FY16).

Method Comparison:

The two methods for determination of TN, calculation as NOX + TKN, and direct determination of TN using SM4500NC produce comparable results as shown in the graph below that charts the results of 2462 determinations of TN using both methods in the SFWMD laboratory for a variety of routine water samples. Performance testing on blind samples from the Environment Canada and Quality Assurance of Information for Marine Environmental Monitoring in Europe (QUASIMEME) programs using the new TN method also show good agreement with consensus means and do not indicate any significant bias in freshwaters, low salinity estuarine waters, or seawater. Details of recent results from both PT programs are included at the end of this document. The SFWMD laboratory will utilize the new TN method for all performance evaluation studies conducted in the future.

Graphical Trend Analysis of Results for Calculated and Direct Determination of TN



Comparative Analysis **Marsh Water Transport Stations per TOC Request**

Station	Average of TN (Calculated)	Standard Deviation of TN (Calculated)	Average of TN (Measured)	Standard Deviation of TN (Measured)	Number of paired measurements
C123SR84	1.31	0.15	1.29	0.18	15
L28I	1.10	0.12	1.09	0.12	8
L3BRS	1.35	0.14	1.33	0.14	24
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
S140	1.27	0.06	1.25	0.07	24
S142	1.57	0.17	1.58	0.20	12
S145	1.56	0.37	1.56	0.37	18
S150	1.17	0.23	1.19	0.22	9
S151	1.45	0.15	1.45	0.16	18
S177	0.76	0.28	0.75	0.29	34
S178	0.67	0.27	0.65	0.26	47
S18C	0.66	0.23	0.67	0.27	67
S190	1.17	0.20	1.15	0.19	15
S31	1.40	0.16	1.39	0.18	12
S331-173	1.35	0.13	1.35	0.15	156
S332DX	1.05	0.24	1.03	0.22	379
S333	1.21	0.14	1.19	0.12	317
S34	1.47	0.19	1.46	0.19	17
S356-334	1.39	0.09	1.38	0.17	347
S38	1.47	0.33	1.48	0.34	26
S5A	1.61	0.53	1.56	0.52	47
S5AE	1.41	0.18	1.32	0.17	11
S5AS	1.44	0.60	1.43	0.58	12
S6	2.01	0.99	1.94	0.96	85
S7	1.38	0.33	1.39	0.35	34
S8	1.39	0.21	1.38	0.20	34
S9	1.50	0.10	1.49	0.09	19
S9A	1.46	0.10	1.46	0.09	14

TAMBR105	**0.82**	**0.16**	**0.79**	**0.16**	**16**
US41-25	**0.97**	**0.22**	**0.95**	**0.23**	**10**
USSO	**1.16**	**0.09**	**1.15**	**0.09**	**22**
Grand Total	**1.25**	**0.51**	**1.23**	**0.49**	**2462**

Measurement Uncertainty

The SFWMD Laboratory provides estimated uncertainty values for all analytes with sufficient data to calculate uncertainty constants. The definition of uncertainty (of measurement) can be found in the *International Vocabulary of Basic and General Standard Terms in Metrology*: "A parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand" (JCGM 1993).

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.

The uncertainty has been estimated using the nested hierarchical methodology by Ingersoll (2001) in combination with a mathematical model found in the Eurachem/CITAC (2000) guide on uncertainty. This QC-based nested approach uses the statistical QC data attributed to laboratory measurement activities and does not include uncertainty attributed to field sampling activities. The estimated uncertainty (95% Confidence Interval) is calculated using the following equation:

$$\mathbf{u(x)} = \sqrt{s_o^2 + (s_1^2 x^2)}$$

where:

u(x) is the combined standard uncertainty in the result x (95% CI).

$\mathbf{s_0}$ – a constant contribution to the overall uncertainty derived from the procedure to determine the MDL.

$\mathbf{s_1}$ – proportionality constant derived from nested hierarchical methodology by Ingersoll.

The uncertainty constants for the new TN method have been calculated using the procedures described above. The value of S_0 and S_1 are 0.02 and 0.075 respectively. For the TKN method the constants S_0 and S_1 are 0.05 and 0.067 respectively and for the NOx method are 0.005 and 0.056.

Using this information it is possible to determine if the concentrations obtained from the two TN methods conducted on the same sample are consistent with one another by determining the absolute value of the difference between the two results and combining the uncertainties to see if the resulting interval contains 0. This was done for each pair of results for the comparative analyses described above and of 1745 results (excludes blanks and field replicates) a total of only 69 results or (3.95%) were found to be inconsistent. As the procedure for estimating uncertainty is at the 95% confidence interval, the percentage of inconsistent results does not exceed expectation.

Environment Canada Proficiency Testing (PT) Program

This PT Study provides results and evaluations for inorganic parameters in nutrients in natural waters – below are the results for TN determinations conducted on blind samples. The samples are prepared in natural background waters from lakes, rivers or rainwater, and are fortified. The PT study reports feature tabulation of all results and provide extensive evaluations. Proficiency is ranked in terms of the number of biased parameters (systemic bias) and flagged results (precision measurement). Each laboratory receives a formal appraisal and z-score summary indicating the proficiency for each parameter submitted.

LAB RESULTS – March 2014

SAMPLE#	1	2	3	4	5	6	7	8	9	10
SFWMD [TN] (mg/L)	0.577	3.12	2.21	0.498	0.481	0.542	0.602	1.14	0.164	0.28
ASSIGNED VALUE *	0.570	3.20	2.24	0.505	0.497	0.545	0.593	1.164	0.168	0.283
R-STD DEV *	0.0273	0.113	0.057	0.0267	0.0253	0.0207	0.0364	0.0457	0.0106	0.0188
Z-Score Summary	0.25	-0.70	-0.52	-0.26	-0.63	-0.14	0.24	-0.52	-0.37	-0.15

Laboratory appraisal – Ideal, no biases

LAB RESULTS – September 2014

SAMPLE#	1	2	3	4	5	6	7	8	9	10
SFWMD [TN] (mg/L)	1.56	0.400	0.530	0.440	0.550	0.710	0.360	1.43	1.29	4.06
ASSIGNED VALUE *	1.58	0.434	0.490	0.461	0.554	0.698	0.361	1.45	1.31	4.22
R-STD DEV *	0.077	0.0214	0.0340	0.0265	0.0305	0.0533	0.0312	0.099	0.077	0.202
Z-Score Summary	-0.25	-1.58	1.17	-0.79	-0.13	0.22	-0.03	-0.20	-0.25	-0.79

Laboratory appraisal – Ideal, no biases

LAB RESULTS – March 2015

SAMPLE#	1	2	3	4	5	6	7	8	9	10
SFWMD [TN] (mg/L)	0.500	3.34	1.00	0.810	0.200	0.550	0.340	0.410	0.490	1.51
ASSIGNED VALUE *	0.494	3.34	0.977	0.786	0.191	0.545	0.337	0.408	0.487	1.47
R-STD DEV *	0.0304	0.164	0.0585	0.0456	0.0134	0.0353	0.0253	0.0295	0.0270	0.112
Z-Score Summary	0.19	0.00	0.39	0.52	0.67	0.14	0.11	0.06	0.11	0.35

Laboratory appraisal – Ideal, no biases

LAB RESULTS – August 2015

SAMPLE#	1	2	3	4	5	6	7	8	9	10
SFWMD [TN] (mg/L)	0.49	0.49	0.68	1.13	1.69	0.38	0.53	0.27	0.58	0.70
ASSIGNED VALUE *	0.487	0.489	0.686	1.13	1.65	0.395	0.534	0.280	0.578	0.684

R-STD DEV *	0.0372	0.0298	0.0525	0.069	0.121	0.0237	0.0429	0.0288	0.0439	0.0566
Z-Score Summary	0.08	0.03	-0.11	0.00	0.33	-0.63	-0.09	-0.34	0.04	0.28

Laboratory appraisal – Ideal, no biases

QUASIMEME Laboratory Performance Studies

Seawater & Concentrates

The test materials were prepared using seawater collected from the Atlantic Ocean. The three test materials differed from each other in respect of their nutrient concentrations (salinity >30 psu).

Following usual practices e.g. ISO 43, the z-scores can be interpreted as follows for laboratories which take part in QUASIMEME to assure the quality of their data for use in international marine monitoring programs.

$\|Z\| < 2$	Satisfactory performance
$2 < \|Z\| < 3$	Questionable performance
$\|Z\| > 3$	Unsatisfactory performance

Exercise 1023 – R73 Nutrients in Seawater & Concentrates: Oct 2013 – Feb 2014

Matrix	***Determinand***	***SFWMD [TN]***	***Units***	***Assigned Value***	***Total Error***	***Z Score***	***z***	***Total Dupl.***
QNU256SW	TOTAL-N	7.920	µmol/l	8.315	1.289	-0.3	S	1
QNU257SW	TOTAL-N	19.00	µmol/l	19.17	1.400	-0.1	S	1
QNU258SW	TOTAL-N	12.90	µmol/l	14.12	1.097	-1.1	S	1

The letters in the *z* column indicate: S – Satisfactory, Q – Questionable, U – Unsatisfactory

Round 2014.1 – Nutrients in Seawater & Concentrates: April – June 2014

Matrix	***Determinand***	***SFWMD [TN]***	***Units***	***NDA Mean***	***Target Error***	***Z Score***	***z***	***Total Dupl.***
Sample 1	TOTAL-N	5.64	µmol/l	5.666	0.590	-0.04	S	1
Sample 2	TOTAL-N	16.1	µmol/l	16.37	1.23	-0.22	S	1
Sample 3	TOTAL-N	10.5	µmol/l	9.931	0.846	0.67	S	1

Round 2014.2 – Nutrients in Seawater & Concentrates : October – December 2014

Matrix	Determinand	SFWMD [TN]	Units	NDA Mean	Target Error	Z Score	z	Total Dupl.
Sample 1	TOTAL-N	2.86*	µmol/l	5.408*	0.574	-4.43	U	1
Sample 2	TOTAL-N	11.4	µmol/l	14.25	1.11	-2.58	Q	1
Sample 3	TOTAL-N	6.43*	µmol/l	8.764*	0.776	-3.01	U	1

* Concentrations at or below the PQL

Round 2015.1 – Nutrients in Seawater & Concentrates: April – June 2015

Matrix	Determinand	SFWMD [TN]	Units	NDA Mean	Z Score	z	Total Dupl.
Sample 1	TOTAL-N	24.8	µmol/l	24.17	0.37	S	1
Sample 2	TOTAL-N	88.95	µmol/l	16.37	0.04	S	1
Sample 3	TOTAL-N	30.2	µmol/l	30.12	0.02	S	1
Sample 4	TOTAL-N	20.7	µmol/l	19.93	0.53	S	1

Estuarine and Low Salinity Seawater

The test materials were prepared using seawater collected from the Atlantic Ocean (estuarine water), and from the Baltic Sea (low salinity open seawater). The four test materials differed from each other in respect of their nutrient concentrations and the salinity of the water. The salinity of the water was approximately 7-15 psu.

Exercise 1024 – R73 Nutrients in Estuarine and low salinity seawater: Oct 2013 – Feb 2014

Matrix	Determinand	SFWMD [TN]	Units	Assigned Value	Total Error	Z Score	z	Total Dupl.
QNU259EW	TOTAL-N	33.30	µmol/l	32.99	2.230	0.1	S	1
QNU260EW	TOTAL-N	79.20	µmol/l	80.85	5.101	-0.3	S	1
QNU261EW	TOTAL-N	23.30	µmol/l	23.65	1.669	-0.2	S	1
QNU262EW	TOTAL-N	17.60	µmol/l	18.54	2.568	-0.4	S	1

The letters in the *z* column indicate: S – Satisfactory, Q – Questionable, U – Unsatisfactory

Round 2014.1 - Nutrients in Estuarine and low salinity open seawater: April – June 2014

Matrix	Determinand	SFWMD [TN]	Units	NDA Mean	Target Error	Z Score	z	Total Dupl.
Sample 1	TOTAL-N	36.5	µmol/l	37.3	2.49	-0.32	S	1
Sample 2	TOTAL-N	69.3	µmol/l	70.27	4.47	-0.22	S	1
Sample 3	TOTAL-N	23.0	µmol/l	22.73	1.61	0.17	S	1
Sample 4	TOTAL-N	17.4	µmol/l	17.45	1.30	-0.04	S	1

Round 2014.2 - Nutrients in Estuarine and low salinity open seawater: October – December 2014

Matrix	***Determinand***	***SFWMD [TN]***	***Units***	***NDA Mean***	***Target Error***	***Z Score***	***z***	***Total Dupl.***
Sample 1	TOTAL-N	24.3	µmol/l	27.75	1.92	-1.80	S	1
Sample 2	TOTAL-N	70.7	µmol/l	76.35	4.83	-1.17	S	1
Sample 3	TOTAL-N	22.1	µmol/l	25.23	1.76	-1.77	S	1
Sample 4	TOTAL-N	14.3	µmol/l	17.48	1.30	-2.45	Q	1

Round 2015.1 - Nutrients in Estuarine and low salinity open seawater: April – June 2015

Matrix	***Determinand***	***SFWMD [TN]***	***Units***	***NDA Mean***	***Z Score***	***z***	***Total Dupl.***
Sample 1	TOTAL-N	10.6	µmol/l	5.17	9.7	U	1
Sample 2	TOTAL-N	17.5	µmol/l	11.32	6.65	U	1
Sample 3	TOTAL-N	15.2	µmol/l	8.80	8.51	S	1

References:

Wageningen Evaluating Programmes for Analytical Laboratories, QUASIMEME, Laboratory Performance Studies. 2013. AQ-1 Nutrients in Seawater, Round 73- Exercise 1023, Issue 11-02-2014

Wageningen Evaluating Programmes for Analytical Laboratories, QUASIMEME, Laboratory Performance Studies. 2013. AQ-2 Nutrients in Estuarine Water and Low Salinity Seawater, Round 73-Exercise 1024, Issue 11-02-2014

Environment Canada, Proficiency Testing Program, March 24, 2014, Final Report for PT Study 0103

If you have further questions please contact Richard Walker at 561-681-2500 (X4525) or email riwalker@sfwmd.gov.

Appendix A – Information Regarding Method Requirements for NPDES Permits

40 CFR 122.21 (g)(7)

(7) *Effluent characteristics.* (i) Information on the discharge of pollutants specified in this paragraph (g)(7) (except information on storm water discharges which is to be provided as specified in §122.26). When "quantitative data" for a pollutant are required, the applicant must collect a sample of effluent and analyze it for the pollutant in accordance with analytical methods approved under Part 136 of this chapter unless use of another method is required for the pollutant under 40 CFR subchapters N or O. When no analytical method is approved under Part 136 or required under subchapters N or O, the applicant may use any suitable method but must provide a description of the method. When an applicant has two or more outfalls with substantially identical effluents, the Director may allow the applicant to test only one outfall and report that quantitative data as applying to the substantially identical outfall. The requirements in paragraphs (g)(7)(vi) and (vii) of this section state that an applicant must provide quantitative data for certain pollutants known or believed to be present do not apply to pollutants present in a discharge solely as the result of their presence in intake water; however, an applicant must report such pollutants as present. When paragraph (g)(7) of this section requires analysis of pH, temperature, cyanide, total phenols, residual chlorine, oil and grease, fecal coliform (including *E. coli*), and Enterococci (previously known as fecal streptococcus at §122.26 (d)(2)(iii)(A)(3)), or volatile organics, grab samples must be collected for those pollutants. For all other pollutants, a 24-hour composite sample, using a minimum of four (4) grab samples, must be used unless specified otherwise at 40 CFR Part 136. However, a minimum of one grab sample may be taken for effluents from holding ponds or other impoundments with a retention period greater than 24 hours. In addition, for discharges other than storm water discharges, the Director may waive composite sampling for any outfall for which the applicant demonstrates that the use of an automatic sampler is infeasible and that the minimum of four (4) grab samples will be a representative sample of the effluent being discharged. Results of analyses of individual grab samples for any parameter may be averaged to obtain the daily average. Grab samples that are not required to be analyzed immediately (see Table II at 40 CFR 136.3 (e)) may be composited in the laboratory, provided that container, preservation, and holding time requirements are met (see Table II at 40 CFR 136.3 (e)) and that sample integrity is not compromised by compositing.

ENVIRONMENTAL PROTECTION AGENCY, 40 CFR Parts 122 and 136, [EPA–HQ–OW–2009–1019; FRL–9915–18–OW]. RIN 2040–AC84, National Pollutant Discharge Elimination System (NPDES): Use of Sufficiently Sensitive Test Methods for Permit Applications and Reporting.

Where no EPA approved analytical methods exist, an applicant will need to select a method from another source of available analytical methods (e.g., Standard Methods for the Examination of Water and Wastewater) to measure that pollutant or pollutant parameter. Today's final rule does not require the applicant to develop new methods. The situation in which there are no EPA approved methods is uncommon because there are EPA-approved methods for most pollutants or pollutant parameters screened and regulated under the NPDES program. Under the existing regulations at 40 CFR 22.21(g)(7), the NPDES applicant has the flexibility to use any suitable analytical method when no EPA approved analytical method exists for that pollutant or pollutant parameter.