Water Environment Laboratory

Solutions

Covering Analytical Methods and Practices

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Proposed Rule Would Codify Requirements for 'Sufficiently Sensitive' Methods

A June 23 proposed rule from the U.S. Environmental Protection Agency (EPA) would stipulate that only "sufficiently sensitive" analytical test methods may be used as part of efforts to apply for a permit and when fulfilling a permit's monitoring requirements. Although the purpose of the proposal is widely supported, some have raised concerns that the rule, in certain cases, could increase costs associated with sampling and analysis.

Addressing Differing Methods

In cases in which multiple analytical methods exist for a pollutant regulated under the Clean Water Act, EPA typically has approved more than one method under 40 *CFR* 136 or 40 *CFR* Chapter I, Subchapter N or O. In certain cases, however, some of the approved analytical methods for the same pollutant differ in terms of their sensitivity, lower minimum level, or method detection limit. (In the proposed rule, EPA defines "minimum level" as "either the lowest calibration point in a method or a multiple of the method detection limit, whichever is higher.")

In cases in which multiple analytical methods have been approved for an individual pollutant, EPA "has historically expected that applicants and permittees would select from the array of available methods a specific analytical method that is sufficiently sensitive to quantify the presence of a pollutant in a given discharge," according to the proposed rule. Although no estimates exist for the number of applicants and permittees that are not using sufficiently sensitive methods, "states and regions have provided anecdotal evidence that some applicants may be interpreting the current regulatory language to allow the use of insufficiently sensitive analytical methods," according to a statement provided by EPA.

Defining 'Sufficiently Sensitive'

EPA defines what is meant by a "sufficiently sensitive" method both in terms of National Pollutant Discharge Elimination System (NPDES) permit applications and efforts to document compliance with established permit limits. To this end, a method would be considered sufficiently sensitive under the following conditions:

- Its minimum level is at or below the level of the applicable water quality criterion or permit limitation for the measured pollutant or pollutant parameter.
- Its minimum level is above the

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In This Issue

Out of State, Out of Luck?

Some state accreditation bodies consider shutting their doors to nonlocal labs

Faced with large budget shortfalls and hiring freezes, states are looking to reduce everything, including accreditation of labs beyond their borders.

Some states that have accrediting authority under the NELAC Institute (TNI; Weatherford, Texas) are looking to limit their accreditation of environmental labs to those located within the state or region. With their associated travel expenses, out-of-state assessments are an easy target.

"All states are having financial problems and some of the accreditation bodies are being required to scale back," said Lara Autry, senior adviser for measurement, monitoring, and laboratory science at the U.S. Environmental Protection Agency (EPA) Office of the Science Adviser.

Under the TNI National Environmental Laboratory

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spend too much of their time thinking of ways to shortcut or circumvent the system instead of making it better. It is commonly held in fraud investigations that the cheater would have spent much less time and effort simply following procedures instead of designing clever ways to work around them.

If we all work smart, we can feel better about ourselves, protect public health, and improve the environment. Not a bad thing!

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For Further Reading

U.S. Environmental Protection Agency Office of Inspector General (2006). *Promising Techniques Identified To Improve Drinking Water Laboratory Integrity and Reduce Public Health Risks* (Report No. 2006-P-00036), Sept. 21. Washington, D.C.: U.S. Environmental Protection Agency.

Faster and Smarter

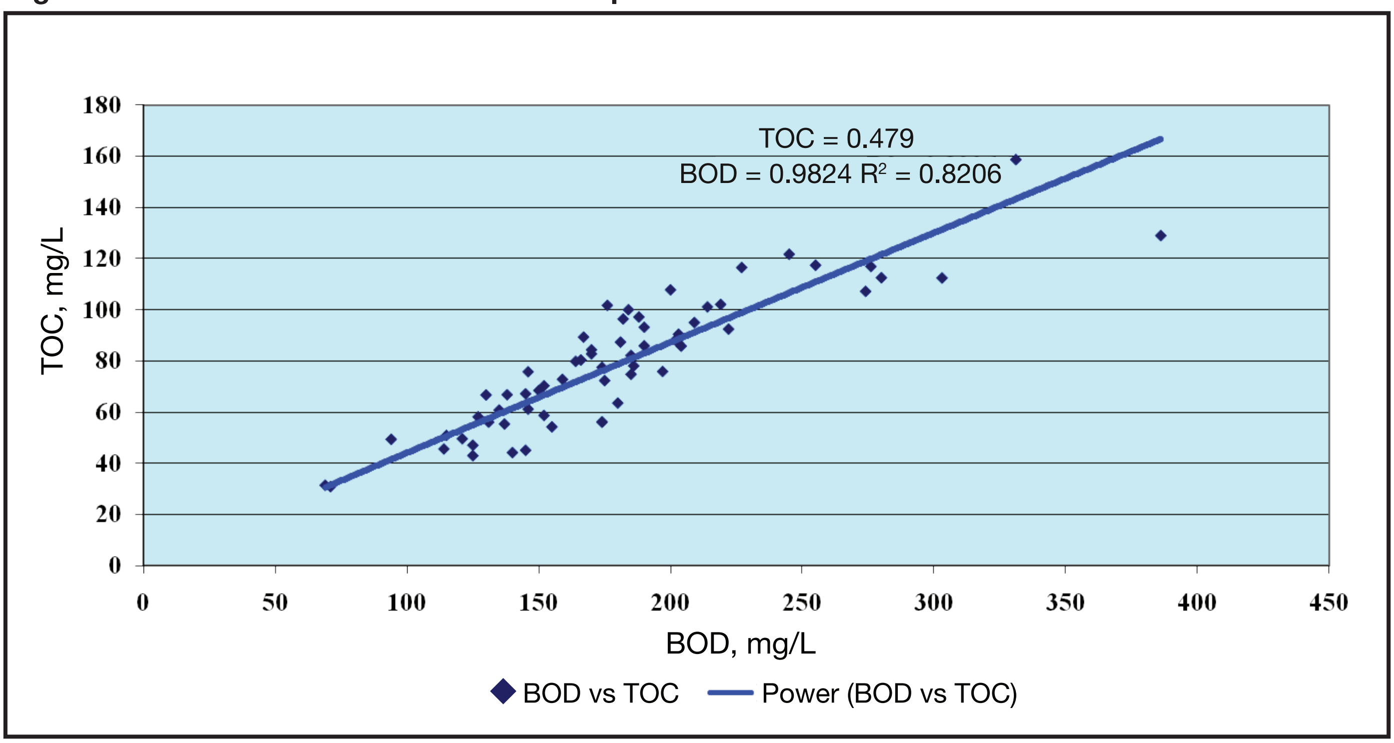
A BOD-to-TOC conversion enables quick response to process control needs

Akin Babatola and Tianfei Xu

The need for reliable and rapid process control options for wastewater treatment facilities (WWTFs) is perhaps equal only in importance to maintaining compliance with effluent discharge limits. The national effluent standard of 30 mg/L for biochemical oxygen demand (BOD) is technology-based and derived from the limitations of the BOD analytical process. The BOD analytical process and data impose specific challenges that have to be accommodated when comparing data derived from different types of BOD, such as between carbonaceous BOD (cBOD), ultimate BOD, and nitrogenous BOD. These challenges are also encountered when comparing BOD data to chemical oxygen demand and total organic carbon (TOC). These challenges, in addition to the long lag time for analytical data from BOD, minimize its utility for process control and other effective environmental management practices.

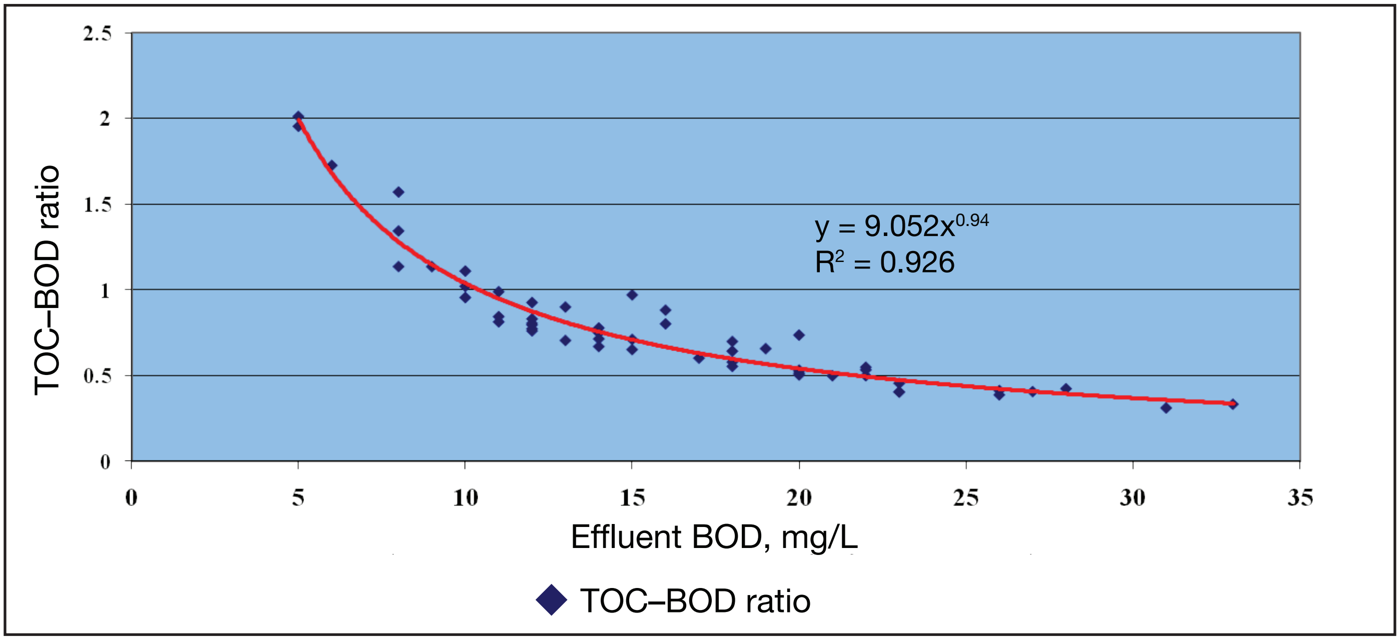
Thus, the laboratory at the City of Santa Cruz (Calif.) WWTF, in cooperation with the California Regional Water Quality Control Board, developed process control equations that express the long-term relationship between TOC and BOD measurements in influent and effluent. The 2-year study, which culminated in several changes to the facility's National Pollutant Discharge Elimination System limits, covered the typical wasteload characteristics

Figure 1. Influent TOC and BOD Relationship



BOD = biochemical oxygen demand.
TOC = total organic carbon.

Figure 2. Effluent TOC and BOD Relationship



BOD = biochemical oxygen demand.
TOC = total organic carbon.

Table 1. Influent BOD, TOC (mg/L) and TOC–BOD Ratio

Sample Date	Influent BOD, mg/L	Influent TOC, mg/L	Influent TOC–BOD ratio
11/04/05	185	74.87	0.40
11/10/05	203	87.06	0.43
11/16/05	167	89.41	0.54
11/22/05	174	56.19	0.32
11/28/05	209	95.11	0.46
12/04/05	180	63.64	0.35
12/10/05	182	96.48	0.53
12/16/05	219	102.2	0.47
12/22/05	125	43.08	0.34
12/28/05	114	45.66	0.40
01/03/06	71	30.96	0.44
01/09/06	131	56.17	0.43
01/15/06	140	44.25	0.32
01/21/06	145	45.16	0.31
01/27/06	166	80.45	0.48
02/02/06	130	66.80	0.51
02/08/06	181	87.43	0.48
02/14/06	202	88.46	0.44
02/20/06	150	68.54	0.46
02/26/06	186	78.16	0.42
03/04/06	138	66.87	0.48
03/10/06	125	47.15	0.38
03/16/06	127	58.25	0.46
03/22/06	159	72.89	0.46
03/28/06	94	49.44	0.53
04/03/06	69	31.5	0.46
04/09/06	121	49.67	0.41
04/15/06	152	58.79	0.39
04/21/06	185	82.25	0.44
04/27/06	115	50.99	0.44
05/03/06	190	86.02	0.45
05/09/06	135	60.87	0.45
05/15/06	146	75.85	0.52
05/21/06	190	93.29	0.49
05/27/06	137	55.41	0.40
06/02/06	145	67.24	0.46
06/08/06	152	70.38	0.46
06/14/06	200	107.9	0.54
06/20/06	146	61.25	0.42
06/26/06	203	90.55	0.45
07/02/06	170	82.84	0.49
07/08/06	214	101.2	0.47
07/14/06	227	116.6	0.51
07/20/06	176	101.8	0.58
07/26/06	188	97.27	0.52
08/01/06	386	129.1	0.33
08/07/06	164	79.9	0.49
08/13/06	222	92.53	0.42
08/19/06	174	56.29	0.32
08/25/06	197	75.97	0.39
08/31/06	174	77.62	0.45
09/06/06	170	84.45	0.50
09/12/06	155	54.34	0.35
09/18/06	175	72.4	0.41
09/24/06	184	100.1	0.54
09/30/06	303	112.5	0.37
10/06/06	204	85.9	0.42
10/12/06	280	112.6	0.40
10/18/06	331	158.8	0.48
10/24/06	276	117	0.42
10/30/06	255	117.5	0.46
11/05/06	274	107.3	0.39
11/11/06	245	121.8	0.50
Maximum	386.0	158.8	0.58
Minimum	69.0	31.0	0.31
Average	179.9	79.2	0.44

and operational practices at the Santa Cruz WWTF from May 2005 through November 2006.

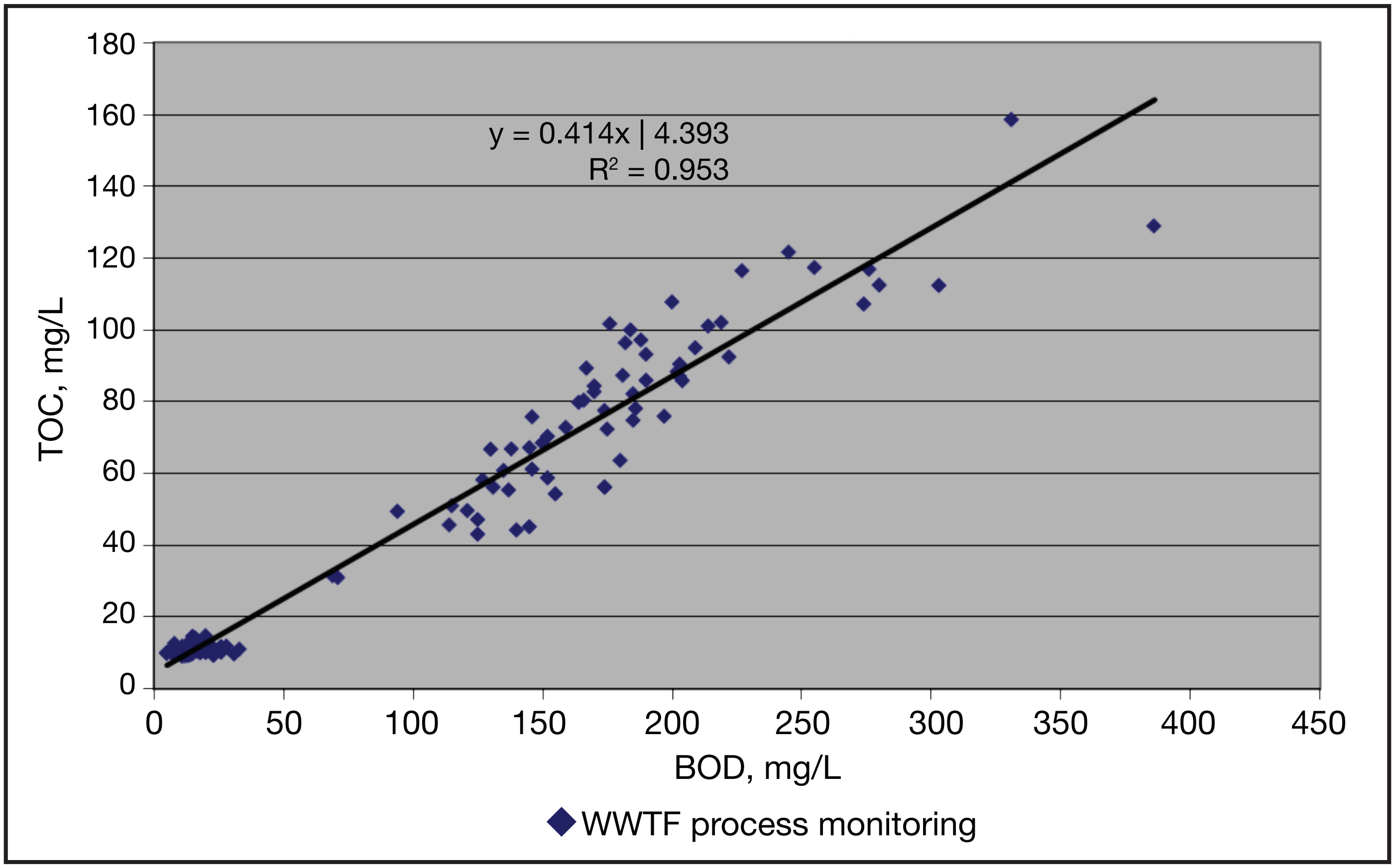
Sample Collection

The samples used in this study were from 24-hour composites collected for process and compliance monitoring at the Santa Cruz facility. Samples were routinely delivered to the laboratory on scheduled test dates by the facility's operators. BOD and cBOD samples were analyzed using Method 5210B, and TOC analyses were performed using Method 5310B from *Standard Methods for the Examination of Water & Wastewater* (19th edition).

Instrumentation and Analyses

All analyses were performed in batches within the 48-hour hold time allowed for BOD analyses

Figure 3. TOC and BOD Interconversion for Process Control



BOD = biochemical oxygen demand.
TOC = total organic carbon.
WWTF = wastewater treatment facility.

and within 5 days for TOC analyses. For cBOD and BOD samples, dissolved oxygen was measured (using the dissolved oxygen Meter 5100 manufactured by YSI [Yellow Springs, Ohio]) at the onset and conclusion of the analyses. All test samples were incubated in the dark at 20±1°C for 5 days within a low-temperature incubator from Fisher Scientific (Waltham, Mass.) at the laboratory. cBOD measurements were distinguished (from BOD measurements) by the inclusion of the nitrification inhibitor 2-chloro-6-(trichloromethyl) pyridine in the control and test samples.

A TOC-VCSH analyzer (Shimadzu Scientific Instruments [Kyoto, Japan]), optimized for nonpurgeable organic carbon analyses and fitted with the Shimadzu autosampler ASI-V and TOC Gas generator (Parker Hannifin [Cleveland]), was used for TOC analyses. Samples were injected through the sipper and needle with internal diameter of 0.5 mm. Analysis was catalyzed using the standard platinum catalyst on 1.98-mm (0.078-in.) alumina balls. Other notable TOC test specifications included

- combustion temperature = 680°C;
- sample volume = 50 mL; and
- method detection limit = 100 µg/L.

Results

The results of the project are presented in a sequence of tables and graphs. Table 1 (p. 8) lists influent TOC and BOD levels and TOC–BOD ratios. Figure 1 (p. 7) presents TOC and BOD data in plant influent from November 2005 through September 2006. Table 2 (p. 10) shows TOC–BOD ratios. This table includes descriptive statistics of the derived values for discussion of process effects on derivation of long-term relationships.

Figure 2 (p. 8) is a visual (log-normal trend) presentation of TOC and BOD in effluent before discharge and after treatment from November 2005 through September 2006. This graph demonstrates the remarkable stability of the treatment processes as depicted by a long-term relationship of effluent TOC to TOC–BOD ratios. Figure 3 (above) presents plant BOD and TOC values using all data generated from the influent and effluent through the study.

Discussion

Table 1 data were compiled over several months to provide sufficient analyses and adequately characterize the relationship between BOD measurements and TOC values at the WWTF. The data indicate a range of TOC–BOD ratios from 0.31 to 0.58, with an average of 0.44. This conservative range allows for the development of an equation to define the interconversion of BOD and TOC in influent.

Table 2. Effluent TOC, BOD, and TOC–BOD ratios

Sample Date	Effluent BOD, mg/L	Effluent TOC, mg/L	Effluent TOC–BOD ratio
11/04/2005	20	10.54	0.53
11/10/2005	20	10.28	0.51
11/16/2005	26	10.74	0.41
11/22/2005	33	10.99	0.33
11/28/2005	15	10.67	0.71
12/04/2005	22	10.98	0.50
12/10/2005	22	11.74	0.53
12/16/2005	27	10.99	0.41
12/22/2005	20	14.74	0.74
12/28/2005	12	9.97	0.83
01/03/2006	11	9.29	0.84
01/09/2006	14	9.38	0.67
01/15/2006	12	9.67	0.81
01/21/2006	12	9.28	0.77
01/27/2006	23	10.47	0.46
02/02/2006	11	8.95	0.81
02/08/2006	12	9.56	0.80
02/14/2006	11	10.89	0.99
02/20/2006	20	10.07	0.50
02/26/2006	15	9.78	0.65
03/04/2006	5	9.78	1.96
03/10/2006	8	9.10	1.14
03/16/2006	13	9.17	0.71
03/22/2006	10	9.56	0.96
03/28/2006	12	9.14	0.76
04/03/2006	18	9.98	0.55
04/09/2006	9	10.23	1.14
04/15/2006	5	10.07	2.01
04/21/2006	17	10.24	0.60
04/27/2006	14	10.01	0.72
05/03/2006	21	10.48	0.50
05/9/2006	23	9.28	0.40
05/15/2006	31	9.64	0.31
05/21/2006	26	10.08	0.39
05/27/2006	23	9.336	0.41
06/02/2006	10	10.22	1.02
06/08/2006	6	10.37	1.73
06/14/2006	14	10.49	0.75
06/20/2006	18	10.43	0.58
06/26/2006	20	10.65	0.53
07/02/2006	14	10.9	0.78
07/08/2006	19	12.49	0.66
07/14/2006	18	12.59	0.70
07/20/2006	15	14.57	0.97
07/26/2006	12	11.13	0.93
08/07/2006	10	11.11	1.11
08/13/2006	22	12.09	0.55
08/19/2006	28	11.86	0.42
08/25/2006	16	12.84	0.80
08/31/2006	8	12.58	1.57
09/06/2006	16	14.12	0.88
09/12/2006	18	11.58	0.64
09/18/2006	13	11.71	0.90
Minimum	5	8.95	0.31
Maximum	33	14.74	2.01
Mean	16.4	10.7	0.8
Standard deviation	6.5	1.4	0.4
25th percentile	12	9.7	0.53
67th percentile	19.84	10.90	0.81
75th percentile	20	11.08	0.87
90th percentile	25.40	12.56	1.13
Median	15.00	10.43	0.71
Mode	12	10.99	

Figure 1 shows that the influent TOC and BOD values at the WWTF have a steady and definable relationship. The graphical relationship can be expressed as follows:

$$TOC = 0.479\,(BOD)^{0.98} \qquad (1)$$

with a high correlation coefficient (R^2) value of 0.82. This correlation confirmed the feasibility of deriving site-specific equations for BOD to TOC.

The data in Table 2 show that treatment processes at the WWTF have a very high efficiency of BOD removal; therefore, many effluent BOD measurements are well within the Type 1 (underestimation/false negative) error range of BOD measurements in effluent. (The analytical detection limit for BOD at the WWTF laboratory is 2.0 mg/L, and BOD measurements at these lower levels are often confounded by nitrogenous compounds endemic to natural and wastewater sources.) However, there is strong statistical evidence of the relationship of effluent TOC to BOD at the WWTF.

This relationship becomes clearer with the graphical presentation of the same data (see Figure 2).

The TOC–BOD ratios in Table 2 have a range of 0.31 to 2.1, with

- a 25th-percentile value of 0.53,
- a mean value of 0.80, and

- a 75th-percentile value of 0.87,

thus demonstrating a conservative range of values in the ratios. Figure 2 visually confirms the nature of the relationship between BOD and TOC in effluent through the duration of the study and allows for the derivation of an equation that meets those characteristics:

$$TOC{:}BOD = 9.052\ (BOD)^{-0.9409} \quad (2)$$

with a high correlation coefficient (R^2) value of 0.927. This further confirms the feasibility of deriving site-specific conversion equations for BOD to TOC at the WWTF.

Figure 3, which displays the interconversion of TOC from BOD, shows a linear relationship between BOD and TOC and can be expressed in the following equation:

$$TOC = 0.4141\ BOD + 4.3937 \quad (3)$$

Permit Changes

Based upon the quality of the study, its duration, and its results, the executive officer of the California Regional Water Quality Control Board modified specific areas of the Santa Cruz WWTF permit as follows:

- The 30-day limit of 30 mg/L BOD in effluent was replaced with its site-specific equivalent using Equation 2 (with the standard deviation of 1.4 for error margin and variability). Thus, a monthly average limit of 30 mg/L of BOD would calculate to 15.5 mg/L of TOC.
- The 7-day average limit of 45 mg/L of BOD in effluent was replaced with its site-specific equivalent of 25 mg/L of TOC.
- The 30-day minimum BOD removal of 85% was replaced with its site-specific equivalent of 70% TOC removal.

This study demonstrated the feasibility of developing site-specific TOC values for effluents by publicly owned treatment works. The development also enhanced efficiency in operations by enabling the substitution of TOC analyses for BOD in plant process control because of the shorter turnaround times of less than 2 hours for TOC, compared to 5 days for BOD.

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The New TNI Standards

Anas Rabah

Since 2003, environmental labs seeking to attain or maintain accreditation under the National Environmental Laboratory Accreditation Program (NELAP) have been doing so by following the requirements found in the 2003 National Environmental Laboratory Accreditation Conference (NELAC) standard. This standard has served labs and environmental data users well over the years. It was a significant milestone in furthering the cause for a national accreditation program for environmental labs. Unfortunately, the time of the 2003 NELAC Standard is nearing an end (please hold back any tears or applause), and the time for the first true consensus standard, the TNI Standard, is upon us!

To summarize what's going on, the 2003 NELAC Standard is the current standard being used in NELAP. In September 2009, the NELAP board voted to adopt a new set of standards that would eventually replace the 2003 NELAC Standard. These new standards are collectively referred to as "the TNI Standard." ("TNI" stands for The NELAC Institute [Weatherford, Texas].) On Sept. 1, 2010, the new TNI Standard became effective. Labs can now begin taking the proper steps to come into compliance with the new standards before the July 1, 2011, implementation date.

What's New?

Don't be alarmed; the TNI Standard is not a new way of doing things. Rather, it is an improved, updated, and fine-tuned set of standards that responds to some of the criticisms of the 2003 standards. To find out what is new about the TNI Standard, visit TNI's Web site (www.nelac-institute.org) to gather information and view both new and old standards.

Here are some notable changes and highlights that apply to labs (note that this is not a comprehensive evaluation of the new standards).

Major Reorganization

The 2003 NELAC Standard is

Table. TNI Standards: Volumes and Modules

Volume 1: Management and Technical Requirements for Laboratories Performing Environmental Analysis	**Volume 2:** General Requirements for Accreditation Bodies
Module 1. Proficiency Testing (PT) Module 2. Quality Systems: General Requirements Module 3. Asbestos Testing Module 4. Chemical Testing Module 5. Microbiological Testing Module 6. Radiochemical Testing Module 7. Toxicity Testing	Module 1. General Requirements Module 2. Proficiency Testing Module 3. Onsite Assessment **Volume 3:** General Requirements for PT Providers **Volume 4:** General Requirements for an Accreditor of PT Providers