September 2005

Environmental Technology Verification Report

SHIMADZU SCIENTIFIC INSTRUMENTS, INC. TNPC-4110(C) ON-LINE WATER QUALITY ANALYZER FOR NUTRIENT MONITORING

Prepared by
Battelle

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EPA **U.S. Environmental Protection Agency**

ETV ETV ETV

September 2005

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ETV Advanced Monitoring Systems Center

SHIMADZU SCIENTIFIC INSTRUMENTS, INC. TNPC-4110(C) ON-LINE WATER QUALITY ANALYZER

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development, has financially supported and collaborated in the extramural program described here. This document has been peer reviewed by the Agency. Mention of trade names or commercial products does not constitute endorsement or recommendation by the EPA for use.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's air, water, and land resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, the EPA's Office of Research and Development provides data and science support that can be used to solve environmental problems and to build the scientific knowledge base needed to manage our ecological resources wisely, to understand how pollutants affect our health, and to prevent or reduce environmental risks.

The Environmental Technology Verification (ETV) Program has been established by the EPA to verify the performance characteristics of innovative environmental technology across all media and to report this objective information to permitters, buyers, and users of the technology, thus accelerating the entrance of new environmental technologies into the marketplace. Verification organizations oversee and report verification activities based on testing and quality assurance protocols developed with input from major stakeholders and customer groups associated with the technology area. ETV consists of six verification centers. Information about each of these centers can be found on the Internet at http://www.epa.gov/etv/.

Effective verifications of monitoring technologies are needed to assess environmental quality and to supply cost and performance data to select the most appropriate technology for that assessment. Under a cooperative agreement, Battelle has received EPA funding to plan, coordinate, and conduct such verification tests for "Advanced Monitoring Systems for Air, Water, and Soil" and report the results to the community at large. Information concerning this specific environmental technology area can be found on the Internet at http://www.epa.gov/etv/centers/center1.html.

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List of Abbreviations

AMS	Advanced Monitoring Systems
PPA	aminomethyl phosphonic acid
BQL	below quantitation limit
C	carbon
°C	degree Celcius
CI	confidence interval
m^3/min	cubic meters per minute
DI	deionized
DMA	dimethyl amine
DC	direct current
EPA	U.S. Environmental Protection Agency
ETV	Environmental Technology Verification
F&R	Froehling & Robertson, Inc.
LCS	laboratory control standard
L	liter
LOD	limit of detection
µg	microgram
mA	milliamp
mg	milligram
mL	milliliter
mm	millimeter
MS	matrix spike
MSD	matrix spike duplicates
NIST	National Institute of Standards and Technology
N	nitrogen
NA	not applicable
OMI	Operations Management International, Inc.
PE	performance evaluation
%D	percent difference
%R	percent recovery
%RSD	percent relative standard deviation
P	phosphorus
QA	quality assurance
QC	quality control

QMP	quality management plan
QL	quantitation limit
RPD	relative percent difference
SD	standard deviation
TSA	technical systems audit
TKN	total Kjeldahl nitrogen
TN	total nitrogen
TOC	total organic carbon
TP	total phosphorus

Chapter 1
Background

The U.S. Environmental Protection Agency (EPA) supports the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through performance verification and dissemination of information. The goal of the ETV Program is to further environmental protection by accelerating the acceptance and use of improved and cost-effective technologies. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized testing organizations; with stakeholder groups consisting of buyers, vendor organizations, and permitters; and with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

The EPA's National Exposure Research Laboratory and its verification organization partner, Battelle, operate the Advanced Monitoring Systems (AMS) Center under ETV. The AMS Center, in collaboration with the DuPont Company, recently evaluated the performance of the Shimadzu Scientific Instruments, Inc., TNPC-4110(C) on-line water quality analyzer in quantifying total nitrogen (TN) and total phosphorus (TP) concentrations in wastewater at an industrial wastewater treatment plant.

Chapter 2
Technology Description

The objective of the ETV AMS Center is to verify the performance characteristics of environmental monitoring technologies for air, water, and soil. This verification report provides results for the verification testing of the TNPC-4110(C) for TN and TP. Following is a description of the TNPC-4110(C), based on information provided by the vendor. The information provided below was not verified in this test.

The TNPC-4110(C) is capable of analyzing or monitoring TN, TP, and total organic carbon (TOC). (TOC monitoring was not verified in this test, although measurements were conducted during on-line monitoring of effluent wastewater.) It can be used for nutrient monitoring and process control, and automatically performs sampling, pretreatment (physical and chemical), digestion, and analysis for each measurement. Calibration is required before starting measurements, and both off-line and automatic calibrations can be conducted. For automatic calibrations, an initial calibration is performed followed by additional calibrations during on-line measurement at specified intervals. For this verification test, automatic calibrations were performed every seven days.

Figure 2-1. Shimadzu Scientific Instruments, Inc., TNPC-4110(C) On-line Water Quality Analyzer

TP is measured using ozone as the oxidizer, with advanced photochemical oxidation, heat, sulfuric acid, and ultraviolet irradiation, leading to complete oxidation of the phosphorus in the sample. To ensure complete oxidation of the dissolved and particulate phosphates, the oxidation is performed at near boiling-water temperature. Sulfuric acid ammonium molybdate reacts with the phosphate ions, converting them to phosphomolybdate complex. The phosphomolybdate is then reduced, using ascorbic acid, to molybdenum blue. The intensity of the blue color is proportional to the phosphate concentration present in the sample. The minimum measurement cycle for TP is 43 minutes.

TN is measured using a catalytic combustion method, which involves the decomposition of nitrite, nitrate, ammonia, and organic nitrogen compounds into nitrogen monoxide at 720°C. The carrier gas containing the nitrogen

monoxide is cooled and dehumidified using an electronic dehumidifier and passed to a chemiluminescence detector. Within the chemiluminscence detector, ozone is generated, which interacts with the nitrogen monoxide, producing excited nitrogen dioxide. A silicon diode is used to detect the light emitted from the excited molecules, which results in a signal that is proportional to the concentration of TN. The TN minimum measurement cycle is 4 minutes.

Measurements can be conducted continuously (i.e., approximately every 4 minutes for TN only, every 43 minutes for TP only, or every 43 minutes for TN, TP, and TOC conducted in parallel) or every 1, 2, 3, 4, 6, 12, or 24 hours. The TNPC-4110(C) can be configured to begin on-line measurements immediately or at a specified time. During this verification test, on-line measurements were conducted for TN, TP, and TOC at 1-hour intervals. In the off-line measurement mode, samples are introduced through the off-line sample tube. Each sample can be measured up to six times, with the number of replicates determined by user input, or additional replicates can be conducted until the target standard deviation (SD) or maximum number of replicates is achieved, whichever occurs first. Replicate measurements are conducted continuously (i.e., immediately upon completion of previous measurement).

Nutrient measurement concentrations [in units of milligrams (mg) per liter (L)] and operational parameters of the TNPC-4110(C) can be output using several methods. The TNPC-4110(C) is equipped with a thermal printer, which can be configured to print reports of calibration measurements, off-line measurements, on-line measurements, hourly and/or daily measurement summaries, errors and alarms, and other information. Results obtained during this verification test were obtained using the hard-copy print-outs from the TNPC-4110(C). Other external communication devices are available on the TNPC-4110(C), but were not utilized during this verification test. The TNPC-4110(C) has contact inputs and outputs that can be used to control the analyzer and external processes, respectively. Analog inputs can be configured to input process flow rates for use in performing nutrient load calculations. Analog outputs can be used to record TN, TP, and/or TOC concentrations, and other information. Analog outputs can be configured in the following ranges: 4 to 20 milliamps (mA) direct current (DC), 0 to 16 mA DC, or 0 to 1 volt DC. Optional external communication devices include RS-422 and RS-232 serial signals.

The TNPC-4110(C) consists of an automated pretreatment filtration system (optional), a multifunction injection system, an oxidation reactor vessel, and an absorbance detector, all in one unit for indoor installation. The dimensions of the TNPC-4110(C) are 980 millimeters (mm, 38.6 inches) in width, 1,560 mm (61.4 inches) in height, and 490 mm in depth (19.3 inches), excluding the pretreatment filtration system. It weighs approximately 100 kilograms (220 pounds) and costs $34,000. For this verification test, the TNPC-4110(C) was equipped with a backwash strainer sample pretreatment unit, intended to prevent adhesion of contaminants, slime, and/or algae; backwashing the strainer prevents it from clogging.

Chapter 3
Test Design and Procedures

3.1 Introduction

High nutrient concentrations reduce the quality of water in lakes, rivers, and estuaries. Excess nitrogen (N) and phosphorus (P) reduce water quality by causing harmful algal blooms and hypoxia, create declines in wildlife habitat, and may increase human pathogen levels. EPA is developing region-specific nutrient criteria to reduce the nutrient loading of the nation's aquatic environment. On-line monitoring of nutrients in wastewater is a critical component in reducing nutrient loading because the composition of wastewater varies considerably depending upon the sampling location, source, and/or treatment methods. Using wastewater from the DuPont Company's industrial wastewater treatment facility at the Spruance Plant in Richmond, Virginia, as a sample matrix in this test provides a single example (not a comprehensive overview) of possible matrix effects associated with wastewater monitoring.

This verification test was conducted according to procedures specified in the *Test/QA Plan for Verification of Nutrient Analyzers at a Wastewater Treatment Plant*.[1] Testing was conducted for six weeks between May 5 and June 16, 2005, during which time the TNPC-4110(C) measured nutrient concentrations in wastewater and prepared nutrient standards of known concentration. The performance of the TNPC-4110(C) was evaluated in terms of

- Accuracy
- Bias
- Linearity
- Limit of detection (LOD)
- Reproducibility
- Span and zero drift
- Matrix effects
- Data completeness
- Operational factors.

3.2 Site Description

The host facility for the nutrient analyzer verification test was the DuPont Spruance Plant in Richmond, Virginia. At this plant, DuPont manufactures engineering polymers/plastics and fibers (e.g., NOMEX® flame retardant and KEVLAR®). Operations Management International (OMI), Inc., operates the wastewater treatment plant at the Spruance Plant under contract with

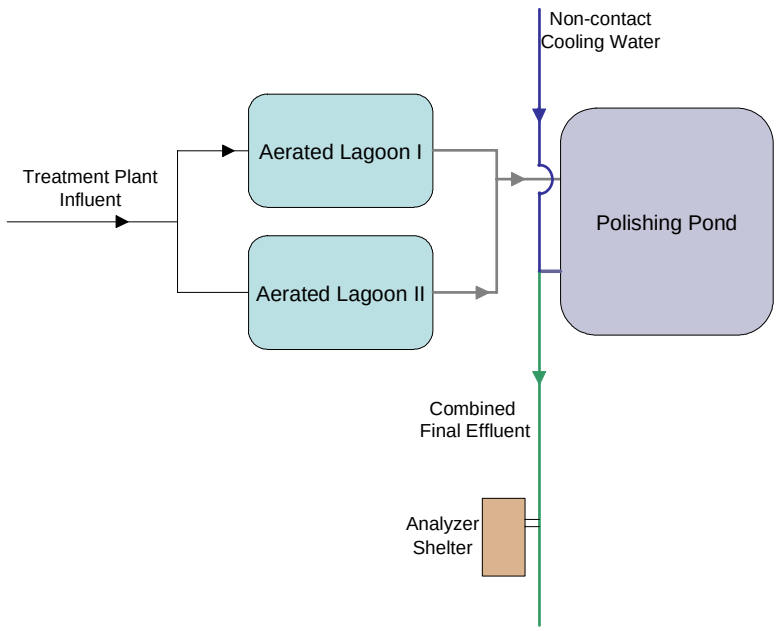


Figure 3-1. Test Site (not drawn to scale)

DuPont and provided the day-to-day logistical support for this verification test. The generalized layout of the test site with respect to the treatment facility is shown in Figure 3-1 (not drawn to scale). The waste treatment processes used at the plant include aerated lagoons and a polishing pond. Flow leaving the polishing pond joins a flow of non-contact cooling water from the plant in an open drainage ditch, shown in Figure 3-2, that empties into the James River. Table 3-1 summarizes the characteristics of this final effluent stream at the Spruance Plant, based on data provided by DuPont and OMI for the previous year. The test site was located along the combined final effluent stream. Figure 3-3 shows the temperature-regulated shelter where the TNPC-4110(C) was installed. The final effluent was pumped out of the open drainage ditch into the shelter through 1-inch Tygon® tubing. A multi-spigot tap was installed in the shelter to supply the final effluent flow to the TNPC-4110(C) at a flow rate sufficient to operate the backwash strainer unit. (Valves on each spigot allowed for manual adjustment of the flow rate by apportioning the final effluent flow to the TNPC-4110(C) and the overflow drain.) An in-line filter screen was installed upstream of the multi-spigot tap to catch larger debris before reaching the TNPC-4110(C). The in-line filter screen is shown in Figure 3-4, pictured at the beginning and end of the verification test prior to back-flushing. To reduce build-up of debris in the in-line filter screen, it was back-flushed twice daily and hand-cleaned if necessary (Monday through Friday).

Figure 3-2. DuPont Spruance Final Outfall

Table 3-1. Effluent Characteristics at the Test Site

Parameter	Range	Average	Standard Deviation
Temperature (ºC)	18 - 39	27	7
Total organic carbon [mg carbon (C)/L]	6.6 - 20	8.8	2.5
pH	6.8 - 7.8	7.4	0.3
Total nitrogen (mg N/L)	0.6 - 6.4	3.0	1.6
Nitrate-N (mg N/L)	<0.1 - 2.7	1.3	0.8
Nitrite-N (mg N/L)	0.05 - 1.06	0.11	0.08
Ammonia-N (mg N/L)	0.2 - 1.6	0.6	0.5
Total phosphorus (mg P/L)	0.09 - 0.26	0.14	0.03

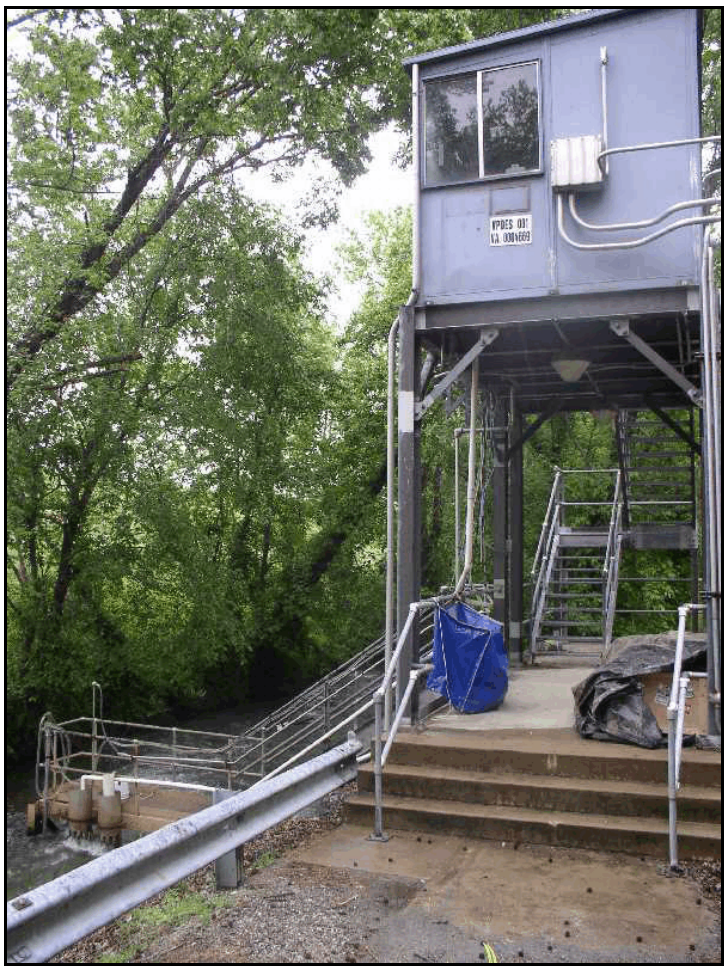


Figure 3-3. Test Site Showing Analyzer Shelter

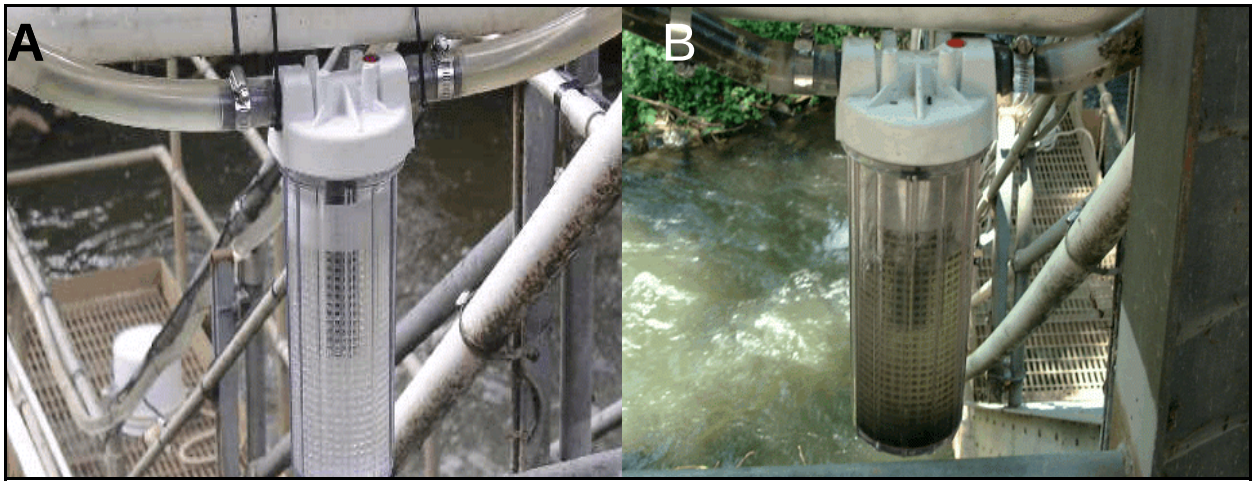


Figure 3-4. In-line Filter Screen and Inlet Tubing Before (A) and After (B) the Verification Test

3.3 Test Design

Table 3-2 shows the activities involved in preparing for and conducting the verification test. All testing activities, which are described in the following sections, were conducted by Battelle and/or OMI staff.

Prior to the start of the verification test, Shimadzu furnished a list of site preparation requirements, shown in Appendix A, for the TNPC-4110(C). Since the test site chosen for the verification test did not have tap water or compressed air supplies, the vendor furnished two air compressors (Craftsman Model 15214) and a combustion gas generator (Parker TOC 1250) for use during the verification test and chose a pretreatment filtration system (backwash strainer sample pretreatment unit) that did not require the use of tap water. The TNPC-4110(C) was installed at the test site by vendor representatives. Battelle and OMI staff worked with the vendor representatives to establish procedures for operating the TNPC-4110(C) during this verification test. Instructions for operating the TNPC-4110(C) in off-line and on-line measurement modes were provided by the vendor representatives and are included in this report as Appendix B. The vendor representatives trained Battelle and OMI staff to check several instrument parameters to verify the operation of the TNPC-4110(C) and identify signs of malfunction. A checklist, provided by the vendor representatives, and included as Appendix C, was completed daily (Monday through Friday) by Battelle or OMI staff. In general, Battelle or OMI staff verified that the power and ready lights were illuminated, checked the air supply and carrier gas pressures, and checked reagent supply and other fluid levels. In the event of a malfunction, Battelle and/or OMI staff could contact the vendor representative and conduct minor troubleshooting procedures as necessary, but were not expected to make any major repairs. TNPC-4110(C) measurement data, collected at one-hour intervals for on-line measurement and as prompted for off-line measurements, reported on the hard copy print-outs were entered into Microsoft Excel, where the results were analyzed using the procedures outlined in Chapter 5 of this report. The hard copy print-outs were taped into a laboratory research book. Since print on thermal paper can fade with time, all of the TNPC-4110(C) data were photocopied and stored in the test records.

Table 3-2. Test Activities

Week of	Activities
May 2, 2005 Analyzer Installation Off-line Phase I (Week 1)	• Test preparations by OMI and Battelle staff • TNPC-4110(C) installation • Training of OMI and Battelle staff by vendor representatives • Conduct trial operations • Nutrient standard challenges for accuracy, reproducibility, and span/zero drift baseline response • Deionized (DI) water challenges for LOD determination
May 9, 2005 Off-line Phase I (Week 2)	• Multi-level nutrient standard challenges for accuracy, bias, and linearity • pH-adjusted nutrient standard challenges for matrix effects • Chlorophyll *a*-containing nutrient standard challenges for matrix effects • DI water challenges for LOD determination
May 16, 2005 On-line Effluent Monitoring (Week 1)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
May 23, 2005 On-line Effluent Monitoring (Week 2)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
May 30, 2005 On-line Effluent Monitoring (Week 3)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
June 6, 2005 On-line Effluent Monitoring (Week 4)	• Nutrient standard and DI water challenges for span/zero drift and LOD • On-line monitoring of wastewater effluent • Three reference samples collected and submitted for analysis • Routine operation
June 13, 2005 Off-line Phase II	• Nutrient standard and DI water challenges for span/zero drift and LOD • Plant effluent challenges for matrix effects • Plant process challenges for matrix effects • Plant influent challenges for matrix effects • Nutrient standard challenges for accuracy • Remove TNPC-4110(C) from test site

The TNPC-4110(C) was evaluated for the performance parameters summarized in Table 3-3 and discussed in detail in the following sections. The test had two components: off-line testing (two phases) and on-line effluent monitoring. During off-line Phase I testing, the TNPC-4110(C) was challenged with nutrient standards and other samples in a DI water matrix. During off-line Phase II, the TNPC-4110(C) was challenged with wastewater and nutrient standards. Grab samples of the final effluent (reference samples) were collected three times per week during the on-line effluent monitoring portion of the verification test. All nutrient standards used to challenge the MP-1 and reference samples were analyzed by a reference laboratory, Froehling and Robertson (F&R), Inc., of Richmond, Virginia, using standard methods

Table 3-3. Verification Test Performance Parameters

Performance Parameter	Method of Evaluation
Accuracy	Closeness of analyzer response to nutrient standards compared to reference method value
Bias	Systematic error in analyzer response to nutrient standards compared to reference method value
Linearity	Analyzer response to multi-level nutrient standards compared to reference value
LOD	Calculated from analyzer response to repeated measurements of DI water
Reproducibility	Percent relative standard deviation (%RSD) of repeated analysis of the same nutrient standard
Span and zero drift	Stability of analyzer response to DI water and nutrient standards over time
Matrix effects	Analyzer response to nutrients in several sample matrices (chlorophyll *a*, varied pH, wastewater) compared to response to nutrients (nitrate and ortho-phosphate) in DI water
Data completeness	Percentage of maximum data return over field period
Operational factors	Operator observations, records of needed and performed maintenance, vendor activities, use of expendable supplies

Nutrient standards used to perform the testing activities were prepared from high-purity solids (e.g., potassium nitrate, potassium dihydrogenphosphate) dissolved in DI water (Millipore Milli-Q Academic Ultrapure Water Purification system, 18.2 megaohm · centimeter resistivity) or wastewater (influent, process, and effluent) samples. The total volume prepared for each nutrient solution varied from 5 L to more than 25 L. The nutrient solutions were not prepared quantitatively since each performance evaluation (PE) used the reference laboratory analysis result for each prepared solution, rather than the nominal concentration calculated from the sample preparation. However, the solutions were prepared as close to the target concentrations outlined in the test/QA plan[1] as possible.

3.3.1 Accuracy, Bias, Linearity, and Limit of Detection

During off-line Phase I testing, the TNPC-4110(C) was challenged with nutrient standards and DI water. Samples were supplied to the TNPC-4110(C) by immersing the off-line sample tube in the nutrient standard solution in off-line sampling mode.

Multi-level nutrient standard challenges were conducted for TN and TP. For each nutrient, three non-consecutive measurements were recorded at each of five nominal concentrations (including zero); the three measurements at each concentration were conducted within the same day for TN analysis and within a span of two days for TP analysis. Table 3-4 shows the approximate concentration values for the multi-level nutrient standards supplied to the TNPC-4110(C) and the order in which the standards were supplied. The TNPC-4110(C) was challenged with the nutrient standards shown in Table 3-5 for the determination of accuracy for several forms of N and P. Additional nutrient standards (not included in the test/QA plan[1]) were sampled by the TNPC-4110(C), as requested by the vendor representative. The samples were prepared from certified standards for simple and complex nutrients (NSI Solutions, Inc., Raleigh, North Carolina). The certified standards were diluted quantitatively in DI water to the concentrations listed in Table 3-5. The TNPC-4110(C) sampled DI water to obtain an additional blank measurement at least once each day during off-line Phase I testing to evaluate the instrumental LOD. Since the method detection limit will vary depending on the sample matrix, the LOD provides a more general measure of performance.

Table 3-4. Nutrient Concentrations and Sequence of Multi-level Challenges

Measurement Number	Target Nutrient Concentration	
	Total Nitrogen (mg N/L)[a]	Total Phosphorus (mg P/L)[b]
0	0	0
1	0.5	0.5
2	5	1
3	10	3
4	20	5
5	0	0
6	10	3
7	5	1
8	20	5
9	0.5	0.5
10	0	0
11	20	5
12	10	3
13	5	1
14	0.5	0.5
15	0	0

[a] N in the form of nitrate (from potassium nitrate).
[b] P in the form of phosphate (from potassium dihydrogenphosphate).

Table 3-5. Additional Standards for Accuracy Analysis

Nutrient	Nutrient Source	Total Nutrient Concentration	
		Target Nitrogen (mg N/L)	Target Phosphorus (mg P/L)
Total Nitrogen	"Ammonia" Ammonium chloride (NH_4Cl)	5	NA
	"Nitrite" Sodium nitrite ($NaNO_2$)	5	NA
	"Nitrate" Potassium nitrate (KNO_3)	5	NA
	"Organic Nitrogen" Dimethyl amine (DMA) ($(CH_3)_2NH$)	5	NA
	"Mixed Nitrogen" (Approximately equally apportioned NH_4Cl, $NaNO_2$, KNO_3, DMA)	10	NA
Total Phosphorus	"Inorganic Phosphorus" Potassium dihydrogenphosphate (KH_2PO_4)	NA	3
	"Organic phosphorus" Aminomethyl phosphonic acid (PPA) ($H_2NCH_2P(O)(OH)_2$)	1.4[(a)]	3
	"Mixed Phosphorus" Approximately equally apportioned (ortho-phosphate and PPA)	1.1[(a)]	5
Certified Simple Nutrient Standard[(b)]	Ammonia	6.96	NA
	Nitrate	8.44	NA
	Ortho-phosphate	NA	0.336
Certified Complex Nutrient Standard[(b)]	Total Kjeldahl Nitrogen (TKN)	7.76	NA
	Total Phosphorus	NA	2.80

NA = not applicable

[(a)] This form of organic P also contains N. The N concentration in the standard at the target PPA concentration is listed here for reference purposes.

[(b)] Samples diluted quantitatively from simple and complex nutrient standard certified for the nutrients listed. TNPC-4110(C) response compared to the calculated concentration in addition to the reference laboratory result.

3.3.2 Reproducibility

The reproducibility of the TNPC-4110(C) results was evaluated during off-line Phase I testing (on the first day of testing). The TNPC-4110(C) was challenged with a mixed standard containing potassium nitrate and potassium dihydrogenphosphate at approximately 5 mg N/L and 3 mg P/L, respectively. The mixed nutrient standard was delivered six times sequentially.

3.3.3 Span and Zero Drift

The "baseline" response of the TNPC-4110(C) to a mixed nutrient standard and DI water was determined during the reproducibility check on the first day of testing. The average and SDs of the TNPC-4110(C) response to the mixed nutrient standard supplied for the reproducibility checks were calculated from six replicates for TN and TP. Similarly, the average and SDs of the TNPC-4110(C) response to DI water were calculated from the first six DI water measurements obtained during the verification test.

Once each week during on-line effluent monitoring and off-line Phase II of the verification test, DI water and the mixed nutrient standard were supplied to the TNPC-4110(C) for a total of five zero/span checks. Each response was compared to the baseline response to determine whether drift had occurred in the analyzer response to DI water or the nutrient standard.

3.3.4 Matrix Effects

During off-line Phase I and Phase II testing, the TNPC-4110(C) was challenged with a series of samples containing altered matrices. In off-line Phase I, synthetic samples containing nutrients at three pH levels and in the presence and absence of chlorophyll *a* (present in algal blooms) were prepared in DI water and delivered to the TNPC-4110(C). In off-line Phase II, wastewater samples were collected from three points in the treatment process—effluent, process, and influent—and delivered to the TNPC-4110(C) both unspiked and after spiking with nitrate and ortho-phosphate. Off-line Phase II measurements of the wastewater samples were conducted at the end of the verification test to minimize the potential impact of analyzer fouling from potentially high total suspended solids levels in the influent samples. Additional effluent samples were delivered to the TNPC-4110(C) before and after spiking quantitatively with the certified simple and complex nutrient standards described in Section 3.3.1. Table 3-6 summarizes the samples that were delivered to the TNPC-4110(C). Except for samples spiked with the certified nutrient standards, TNPC-4110(C) responses were compared to reference laboratory analysis results for the same samples to determine the percent recovery (%R) for each sample. For the samples spiked with the certified nutrient standards, the %R was also calculated relative to the nominal concentration.

During on-line effluent monitoring, TNPC-4110(C) matrix effects were evaluated for the final effluent. The TNPC-4110(C) sampled the final plant effluent for a period of approximately four weeks. Three times per week, reference samples of the plant effluent were collected for analysis in coordination with TNPC-4110(C) on-line measurement times. The reference samples were collected from the overflow outlet of the TNPC-4110(C) backwash strainer sample preparation unit so that the reference sample was as representative as possible of the aliquots sampled by the TNPC-4110(C). The TNPC-4110(C) response to the final effluent at the time of the reference sample collection was compared with the reference laboratory result to determine the %R for each sample. A total of 12 reference samples was collected and used to determine matrix effects.

Table 3-6. Sample Specifications for Evaluation of Matrix Effects

Matrix (Variable)	Sample Description	Number of Measurements	Target Nutrient and Spike Concentration (mg/L)	
			Nitrogen[(a)]	Phosphorus[(b)]
pH	pH = 5	1	5	3
	pH = 7	1	5	3
	pH = 9	1	5	3
Chlorophyll *a* (pH 7)	120 microgram (µg)/L Chlorophyll *a*	1	0	0
	0 µg/L Chlorophyll *a*	1	5	3
	120 µg/L Chlorophyll *a*	1	5	3
Influent sample	Influent	3	0	0
	Influent spike	3	5	3
Process sample	Process	3	0	0
	Process spike	3	5	3
Effluent sample	Effluent	3	0	0
	Effluent spike	3	5	3
Effluent sample[(c)]	Effluent	1	0	0
	Simple Nutrient Effluent Spike	1	7.7	0.168
	Complex Nutrient Effluent Spike	1	3.88	1.463

[(a)] KNO_3
[(b)] KH_2PO_4
[(c)] Samples diluted quantitatively in effluent wastewater from simple and complex nutrient standard certified for the nutrients listed. TNPC-4110(C) response compared to the calculated concentration in addition to the reference laboratory result.

3.3.5 Data Completeness

Data completeness was assessed based on the overall data return achieved by the TNPC-4110(C).

3.3.6 Operational Factors

Operational factors such as maintenance needs, calibration frequency, data output, consumables used, ease of use, and repair requirements were evaluated based on the observations of Battelle and OMI staff.

3.4 Reference Method

One aliquot of each nutrient standard and wastewater sample described in Sections 3.3.1 through 3.3.4 was submitted to a local commercial laboratory (F&R) for analysis. F&R is state-certified in Virginia, North Carolina, and South Carolina and is inspected yearly by the Virginia Department of Environmental Quality. Samples [either 250 milliliters (mL) or 500 mL] were collected in high-density polyethylene bottles and stored at 4°C until transfer to the commercial laboratory, for analysis. Preservative (2 mL concentrated sulfuric acid per L) was added to sample bottles for all analyses except for nitrate or nitrite only (samples for nitrate + nitrite analysis were acid-preserved). Samples were transported to the laboratory on ice in coolers and were stored at 4°C at the laboratory until analysis. Table 3-7 provides the methods that were used for each analysis, method quantitation limits (QL), preservation methods, and maximum holding times. The preservation methods listed in the table are standard procedures,[2] but are different from those listed in the test/QA plan.[1] A deviation report was filed to address the use of different preservation methods; the quality of the reference method data was not impacted by the deviation.

Table 3-7. Reference Methods

Parameter	Method	Method QL mg/L	Preservation and Storage Conditions	Maximum Holding Time
Ammonia	4500-NH3 H (Parts B and C)[2] (Distillation and Nesslerization Method)	0.05	2 mL H_2SO_4/L; 4°C	28 days
Nitrate	4500-(NO3F and NO2B) minus NO2B[2]	0.02	4°C for nitrate or nitrite individually	48 hours
Nitrite	4500-NO2B[2]		2 mL H_2SO_4/L; 4°C for nitrate + nitrite	28 days
Total Nitrogen	sum of total Kjeldahl nitrogen (TKN) (EPA 351.1),[3] nitrate, and nitrite	0.52	2 mL H_2SO_4/L; 4°C	48 hours
Organic Nitrogen	TKN minus ammonia	0.5	2 mL H_2SO_4/L; 4°C	28 days
Total Phosphorus	4500-P (Parts B and F)[2]	0.05	2 mL H_2SO_4/L; 4°C	28 days
Dissolved Inorganic Phosphorus	4500-P (Parts B and E)[2] TP minus organic P	0.05	2 mL H_2SO_4/L; 4°C	28 days
Organic Phosphorus	4500-P (Parts B and E)[2] TP minus reactive and acid hydrolyzable P)	0.05	2 mL H_2SO_4/L; 4°C	28 days

Chapter 4
Quality Assurance/Quality Control

QA/QC procedures were performed in accordance with the quality management plan (QMP) for the AMS Center[4] and the test/QA plan for this verification test,[1] with the exception of two deviations, which have been addressed in this report. Briefly, the preservation methods used by the reference laboratory were different from those listed in the test/QA plan[1] and the statistical approach for determination of matrix effects was modified. These deviations are changes to the procedures outlined in the test/QA plan[1] that did not negatively impact the quality of this verification test.

4.1 Reference Method Quality Control Results

F&R followed their standard QA/QC protocols, which included analysis of blanks, laboratory control samples (LCS), matrix spikes (MS), and matrix spike duplicates (MSD). The tolerances for each analysis and QA/QC sample are listed in Table 4-1. LCS and MS results were evaluated in terms of the %R; MSDs were evaluated in terms of relative percent difference (RPD). All of the blanks and LCS results were within the tolerances listed in Table 4-1. Nine of the MS samples [four for nitrate+nitrite (%R values of 116%, 119%, 84%, and 119%), two for ammonia (80% and 128%), two for TKN (498% and 80.4%), and one for TP analysis (70%)] did not meet the acceptance criterion. Of those samples, five were performed on samples from other batches (i.e., not from this verification test). Since the LCSs from the same batches were within tolerances, these failed MS samples did not indicate a problem with the reference analyses. The MSD results for the two failed TKN MS samples were 46.8% (%D) and 50.1%; all other MSD results were within the 20% tolerance. For the one failed MS sample that was from the set for this verification test, the unspiked measurement is suspected to be incorrect based on knowledge of the sample and the MS results; the MS sample analysis was conducted on a blank sample (i.e., DI water), and the unspiked analysis result was 0.37 mg P/L. The sample was spiked with 1.00 mg P/L and the two matrix spike results were 1.09 and 1.07, which is consistent with an initial sample concentration near zero. Thus, none of the discrepancies in the QC results indicated that the reference analyses for this verification test were affected.

Table 4-1. Reference Method QA/QC Protocols and Tolerances

Analysis	Blank	LCS (%R)	Matrix Spike (%R)	Matrix Spike Duplicate (RPD)
Nitrate	BQL[a]	86.5 – 110	85 – 115	<20
Nitrite	BQL	85 – 115	85 – 115	<20
Ammonia	BQL	80.9 – 114.8	85 – 115	<20
TKN	BQL	78.6 – 121.4	85 – 115	<20
Total P	BQL	84.5 – 115.5	85 – 115	<20
Inorganic P	BQL	84.5 – 115.5	85 – 115	<20

[a] BQL = Below quantitation limit.

4.2 Audits

4.2.1 Performance Evaluation Audits

PE audit samples were submitted to F&R for analysis to assess the quality of nutrient reference method measurements. The PE audit of the nutrient reference methods was performed by supplying for each reference method a blind, National Institute of Standards and Technology (NIST)-traceable nutrient standard independent of those used for testing the TNPC-4110(C). The PE samples were analyzed in the same manner as all other samples, and the analytical results for the PE samples were compared to the nominal concentration. The target criterion for the PE audit samples was agreement of the analytical result within 25% of the nominal nutrient concentration by percent difference (%D). If the PE audit results did not meet the tolerances required, they were repeated. PE audits were required to be performed once prior to the verification test and once during the verification test; these audits were performed once prior to and twice during the test. The PE audit samples submitted to F&R for analysis are summarized in Table 4-2.

As shown in Table 4-2, several of the PE audit samples submitted on April 14, April 20, and May 6, all of which were prepared with the same NIST-traceable nutrient standards, did not meet the acceptance criterion. However, the laboratory QA/QC samples analyzed during the same sample batches were within acceptable tolerances. New standards intended specifically for nutrient analysis were purchased (the standards used for the April and May PE audit samples were intended for ion chromatography) and the PE audits repeated. The simple and complex nutrient standards were diluted in DI water and effluent wastewater, and submitted to F&R on June 17 for analysis. All analyses of the PE audit samples that were prepared from the simple and complex nutrient standards were within 25% of the nominal concentration. The April and May PE audit failures were attributed to unreliable/inaccurate standards and did not impact the results of this verification test.

Table 4-2. PE Audit Sample Results

Sample Submission Date	Spiked Nutrient	Analysis	Sample Matrix	Expected Result (mg/L)	F&R Result (mg/L)	%D	Pass/ Fail
4/14/2005	Phosphate	TP	DI water	0.75	0.86	14	Pass
4/14/2005	Nitrate Nitrite Ammonia	Nitrate + Nitrite	DI water	8.00	8.08	1	Pass
		TN	DI water	10.0	16.20	62	Fail
4/20/2005	Nitrate	Nitrate	DI water	2.00	2.00	0	Pass
5/6/2005	Nitrate	Nitrate	Wastewater	4.72	6.20	31	Fail
5/6/2005	Phosphate	TP	Wastewater	8.01	7.70	4	Pass
5/6/2005	Nitrate Nitrite Ammonia	Nitrate + Nitrite	Wastewater	8.77	8.02	9	Pass
		TN	Wastewater	19.75	29.30	48	Fail
5/17/2005	Simple Nutrients	Ammonia	DI Water	6.96	6.38	8	Pass
		Nitrate	DI Water	8.44	8.28	2	Pass
		TP	DI Water	0.336	0.29	14	Pass
5/17/2005	Complex Nutrients	TKN	DI Water	7.76	7.9	2	Pass
		TP	DI Water	2.87	2.82	2	Pass
5/17/2005	Simple Nutrients	Ammonia	Wastewater	3.92	3.46	12	Pass
		Nitrate	Wastewater	4.52	4.46	1	Pass
		TP	Wastewater	0.25	0.24	3	Pass
5/17/2005	Complex Nutrients	TKN	Wastewater	5.28	5.80	10	Pass
		TP	Wastewater	1.52	1.45	4	Pass

4.2.2 Technical Systems Audits

The Battelle Quality Manager performed a technical systems audit (TSA) on May 10, 2005, to ensure that the verification test was being performed in accordance with the AMS Center QMP,[4] the test/QA plan,[1] published reference methods, and any standard operating procedures used by DuPont or OMI. In the TSA, the Battelle Quality Manager toured the test site, observed the nutrient reference method sampling and sample recovery, inspected documentation of nutrient sample chain of custody, and reviewed analyzer-specific record books. The Battelle Quality Manager also visited F&R's laboratories, viewed the reference methods used by F&R, compared actual test procedures to those specified by the test/QA plan,[1] and reviewed data acquisition and handling procedures.

Observations and findings from this audit were documented and submitted to the Battelle Verification Test Coordinator for response. No findings were documented that required any corrective action. The records concerning the TSA are stored for at least seven years with the Battelle Quality Manager.

4.2.3 Audit of Data Quality

At least 10% of the data acquired during the verification test were audited. To ensure the integrity of the reported results, Battelle's Quality Manager or his designee traced the data from the initial acquisition, through reduction and statistical analysis, to final reporting. All calculations performed on the data undergoing the audit were checked.

4.3 Quality Assurance/Quality Control Reporting

Each assessment and audit was documented in accordance with Sections 3.3.4 and 3.3.5 of the QMP for the ETV AMS Center.[4] Once the assessment report was prepared, the Battelle Verification Test Coordinator ensured that a response was provided for each adverse finding or potential problem and implemented any necessary follow-up corrective action. The Battelle Quality Manager ensured that follow-up corrective action was taken. The results of the TSA were sent to the EPA.

4.4 Data Review

Records generated in the verification test were reviewed before these records were used to calculate, evaluate, or report verification results. Table 4-3 summarizes the types of data recorded. The review was performed by a technical staff member involved in the verification test, but not the staff member who originally generated the record. The person performing the review added his/her initials and the date to a hard copy of the record being reviewed.

Table 4-3. Summary of Data Recording Process

Data to Be Recorded	Where Recorded	How Often Recorded	By Whom	Disposition of Data
Dates, times, and details of test events, analyzer maintenance, down time, etc.	ETV laboratory record books or data recording forms	Start/end of test procedure, and at each change of a test parameter or change of analyzer status	Battelle if on-site; DuPont or OMI at other times	Used to organize and check test results; manually incorporated in data spreadsheets as necessary
Analyzer calibration information	ETV laboratory record books or electronically	At analyzer calibration or recalibration	Electronic data by vendor; Battelle if on-site; DuPont or OMI at other times	Incorporated in verification report as necessary
Analyzer nutrient readings	Hard copy data printed by the TNPC-4110(C) and taped into the ETV laboratory record books.	Printed after each measurement for hard copy print-outs.	Analyzer vendor, for transfer to Battelle	Entered into spreadsheet for statistical analysis and comparison
Sample collection and reference method analysis procedures, calibrations, QA, etc.	Laboratory record books or data recording forms	Throughout sampling and analysis processes	Battelle if on-site, DuPont or OMI at other times, and reference laboratory	Retained as documentation of reference method performance
Reference method nutrient analysis results	Electronically from analytical method	Every sample analysis	Reference laboratory	Transferred to spreadsheets for statistical analysis and comparison to TNPC-4110(C) results

Chapter 5
Statistical Methods and Reported Parameters

The statistical methods presented in this chapter were used to evaluate the performance parameters listed in Section 3.1.

5.1 Accuracy

Accuracy of the TNPC-4110(C) with respect to the individual nutrient standards was assessed as the %R, using Equation 1:

$$\%\mathrm{R} = \left[1 + \left(\frac{\mathrm{Y} - \mathrm{X}}{\mathrm{X}}\right)\right] \times 100 \tag{1}$$

where Y is the measured TNPC-4110(C) value and X is the reference laboratory nutrient concentration. The average, minimum, and maximum %R values were reported for each series of multi-level nutrient challenges. A %R value of 100% indicates perfect agreement between the TNPC-4110(C) result and the reference laboratory nutrient concentration.

5.2 Bias

Bias of the TNPC-4110(C) was defined as a systematic error in measurement that resulted in measured error that was consistently positive or negative compared to the reference value. The bias was calculated as the average %D of the TNPC-4110(C) compared to the reference laboratory nutrient concentration and was calculated for the entire series of multi-level nutrient standard challenges for each nutrient, using Equation 2:

$$\%\,\overline{\mathrm{D}} = \frac{1}{k}\sum_{j=1}^{k}\left(\frac{\mathrm{Y} - \mathrm{X}}{\mathrm{X}}\right)_j \times 100 \tag{2}$$

where k is the number of valid comparisons, and Y and X are the same as in Equation 1. A %D value of 0% indicates that no bias was present in the TNPC-4110(C) measurements.

5.3 Linearity

Linearity was assessed by a linear regression analysis using the nutrient concentration determined by the reference laboratory as the independent variable and results from the TNPC-4110(C) as the dependent variable. Linearity was expressed in terms of slope, intercept, and coefficient of determination (r^2). The 95% confidence interval (CI) was also calculated for the slope and intercept using Microsoft Excel's Analysis Toolpack.

5.4 Limit of Detection

The LOD is the minimum nutrient concentration that is significantly different from the blank or background signal and is defined for this verification test as the average blank signal ($\overline{Y}_b$) plus three times the SD_b, where SD_b is the standard deviation of the blank measurements. Based on this definition, there is a 99.7% probability that samples at or above the LOD represent concentrations truly above the background noise. The LOD was calculated separately for TN and TP from at least 15 blank (DI water) measurements using Equations 3 and 4:

$$SD_b = \sqrt{\frac{\sum\left(Y_b - \overline{Y}_b\right)^2}{n - I}} \tag{3}$$

$$LOD = \overline{Y}_b + 3SD_b \tag{4}$$

where Y_b is an individual blank measurement and n is the number of blank measurements used to determine the LOD.

5.5 Reproducibility

The reproducibility of the TNPC-4110(C) was evaluated from six repeated measurements of a mixed nutrient standard. Reproducibility was defined as the %RSD of the six measurements, using Equation 5:

$$\%RSD = \frac{SD}{\overline{Y}} \times 100 \tag{5}$$

where $\overline{Y}$ is the average TNPC-4110(C) concentration for the mixed nutrient standard, and SD is the SD of the analyzer measurements. Reproducibility was calculated separately for TN and TP.

5.6 Span and Zero Drift

The baseline response of the TNPC-4110(C) to DI water and the mixed nutrient standard was established early in the verification test. The mean ($\overline{Y}$) and SD of the TNPC-4110(C) response to DI water and the mixed nutrient standard were calculated from the six replicate measurements conducted for the reproducibility checks. From these values, a control chart was constructed, and the $\overline{Y} \pm 2SD$ "warning limit" and the $\overline{Y} \pm 3SD$ "action limit" were calculated. Span drift was defined as having occurred if three consecutive span checks fell either above or below the warning limit. Zero drift was defined as having occurred if three consecutive zero checks fell either above or below the warning limit. However, if the SD from the baseline DI water challenge was equal to zero, the absolute difference to the zero air baseline mean was reported for each zero check. Since the actual baseline response and span drift check standard concentrations varied over the five drift checks (ranged from 4.56 to 5.41 mg N/L for TN and from 2.52 to 3.04 mg P/L for TP), the TNPC-4110(C) span measurements for the baseline response and drift checks were normalized to the target concentration, as shown in Equation 6:

$$Y_{norm} = Y_{span} \times \frac{X_{target}}{X_{span}} \tag{6}$$

where Y_{norm} is the normalized TNPC-4110(C) measurement, Y_{span} is the TNPC-4110(C) measurement value for the drift check, X_{target} is the target nutrient concentration standard concentration, and X_{span} is the actual reference method measurement.

5.7 Matrix Effects

Matrix effects on the TNPC-4110(C) with respect to each matrix sample were assessed based on the %R value for each sample. The basis for this comparison was changed from that in the test/QA plan,[1] which described determination of matrix effects relative to the average ± 2SD range calculated for the on-line effluent measurements conducted during on-line effluent monitoring. The %D was also calculated for pH and chlorophyll *a* matrix effects test samples relative to nutrient samples at pH = 7 in the absence of chlorophyll *a* since the matrix variable could be isolated. For on-line effluent monitoring results, a two-tailed paired *t*-test was applied to determine whether the reference method and TNPC-4110(C) gave significantly different values for the mean TN and TP concentrations. The experimental *t* value (t_{exp}) was calculated using Equation 7:

$$t_{exp} = \frac{\sum_i (Y - X)_i}{n} \times \frac{\sqrt{n}}{SD} \tag{7}$$

where Y is the measured TNPC-4110(C) value, X is the corresponding reference method measurement, *n* is the number of measurement pairs, and SD is the standard deviation of the absolute differences. The critical values of *t* (t_{crit}) for (*n*-1) degrees of freedom at the 95% confidence level were calculated separately in Microsoft Excel software for the number (*n*) of

TN and TP measurement pairs used to calculate t_{exp}. A value for t_{exp} that was less than t_{crit} indicates that the two methods did not give significantly different values for the mean TN or TP concentration. A deviation report was filed to address this change from the test/QA plan.[1]

5.8 Data Completeness

Data completeness was calculated as the percentage of the total possible data return achieved over the entire field period. This calculation used the total number of analyses conducted by the TNPC-4110(C), divided by the total number of analyses expected during off-line Phases I and II, and during on-line effluent monitoring. No distinction was made in this calculation between data recorded during a specific test activity (e.g., data recorded for off-line testing) and that recorded during the on-line effluent monitoring phase.

Chapter 6
Test Results

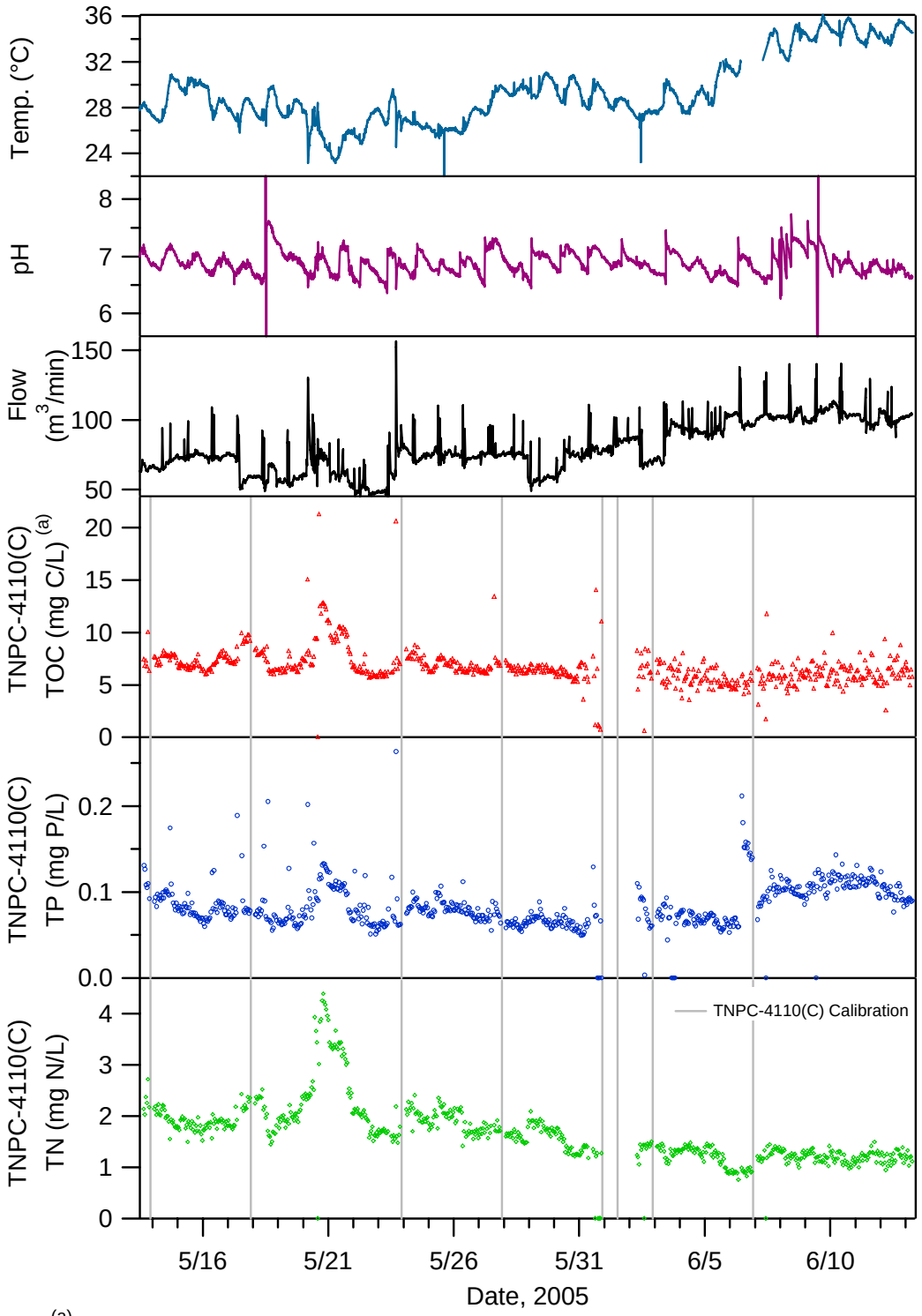
The results of the verification test of the TNPC-4110(C) are presented in this section. The TNPC-4110(C) was calibrated by the vendor representative prior to the start of the verification test for operation in the following ranges: 0 to 20 mg/L TN and 0 to 5 mg/L TP. Automated calibrations were performed at least every seven days at 2200 hours, using the standard prepared by the vendor representative.

The temperature and pH of the final effluent were monitored by DuPont at the same site where this verification test was conducted; and the effluent flow rate, reported in units of cubic meters per minute (m^3/min), was monitored approximately 200 meters upstream of the test site. The TNPC-4110(C) TN and TP measurement data from on-line effluent monitoring are shown in Figure 6-1 with TOC, the effluent temperature, pH, and flow rate. Automated and manual calibrations are shown in the figure (gray traces). The average TN concentration measured by the TNPC-4110(C) over the four-week on-line monitoring phase was 1.67 mg N/L, with a range of 0 to 4.39 mg N/L. The TP concentrations ranged from 0 to 0.26 mg P/L with an average of 0.08 mg P/L.

6.1 Accuracy

The TNPC-4110(C) was challenged with nutrient standards at several concentrations (0.5 to 20 mg/L for TN and 0.5 to 5 mg/L for TP), as listed in Table 3-4. Table 6-1 presents the TN and TP concentrations measured by the TNPC-4110(C) and the corresponding %R values relative to the reference method results. The TNPC-4110(C) responses to DI water are also presented for reference purposes. As shown in Table 6-1, TN (in the form of nitrate) %R values ranged from 109% to 140%, with an average of 131%. The TNPC-4110(C) %R values for TP (in the form of ortho-phosphate) ranged from 111% to 133%, with an average of 118%.

Accuracy results for the TNPC-4110(C) measurements of the nutrient standards in Table 3-5 are summarized in Table 6-2. Accuracy was calculated relative to the reference method results and the nominal concentration for dilutions of the certified simple and complex nutrient standards. Accuracy for non-nitrate forms of nitrogen ranged from 31% to 129%. Organic and inorganic phosphorus resulted in %R values of 103% and 113%, respectively; the mixed phosphorus standard %R value was 110%. The TNPC-4110(C) %R TN and TP values for the simple and complex nutrient standards ranged from 95% to 153% relative to the nominal concentration and from 110% to 178% relative to the reference method results.



(a) Not verified in this test

Figure 6-1. Water Quality Parameters and TNPC-4110(C) TN, TP, and TOC Measurements

Table 6-1. Accuracy Results for Multi-level Nutrient Challenges

Measurement Number	TN Concentration (mg N/L)[a]				TP Concentration (mg P/L)[b]			
	Target	Reference Method	TNPC-4110(C)	TN %R	Target	Reference Method	TNPC-4110(C)	TP %R
0	0	0.00	0.0000	NA	0	0.00	0.0648	NA
1	0.5	0.57	0.6214	109	0.5	0.44	0.5200	118
2	5	5.34	7.2370	136	1	0.90	1.0670	119
3	10	9.32	12.5300	134	3	2.90	3.3120	114
4	20	19.60	25.9700	133	5	4.90	5.4200	111
5	0	0.00	0.0000	NA	0	0.00	0.0833	NA
6	10	9.32	12.6000	135	3	2.55	2.8960	114
7	5	5.34	7.4550	140	1	1.14	1.3810	121
8	20	19.60	26.1700	134	5	4.77	5.3380	112
9	0.5	0.57	0.7301	128	0.5	0.42	0.5601	133
10	0	0.00	0.0000	NA	0	0.00	0.0350	NA
11	20	19.60	26.2800	134	5	4.77	5.2720	111
12	10	9.32	12.3500	133	3	2.55	2.9390	115
13	5	5.34	7.4260	139	1	1.14	1.3830	121
14	0.5	0.57	0.6676	117	0.5	0.42	0.5116	122
15	0	0.00	0.0000	NA	0	0.00	0.0174	NA
Average				131				118
SD				9				7
Minimum				109				111
Maximum				140				133
Bias (%$\overline{D}$)				+31				+18

[a] Nitrogen in the form of nitrate (from potassium nitrate).
[b] Phosphorus in the form of phosphate (from potassium dihydrogenphosphate).
NA = Not Applicable

Table 6-2. Accuracy Results for Additional Nutrient Forms

Nutrient Source	TN				TP			
	Target (mg N/L)	Reference Method (mg N/L)	TNPC-4110(C) (mg N/L)	%R	Target (mg N/L)	Reference Method (mg N/L)	TNPC-4110(C) (mg N/L)	%R
Ammonia	5	4.13	1.958	47	0	–[a]	0.016	NA
Nitrite	5	4.64	5.966	129	0	–	0.045	NA
Nitrate	5	5.68	6.536	115	0	–	0.001	NA
Organic Nitrogen	5	4.40	1.343	31	0	–	0.000	NA
Mixed Nitrogen	10	12.00	7.850	65	0	–	0.000	NA
Inorganic Phosphorus	0	–	0.000	NA	3	3.04	3.420	113
Organic Phosphorus	(1.4)[b]	1.45	1.519	105	3	3.04	3.121	103
Mixed Phosphorus	(1.1)[b]	–	1.344	NA	5	5.08	5.585	110
Certified Simple Nutrient Standard[c]	15.4	12.6	14.57	116 (95)[d]	0.336	0.29	0.515	178 (153)[d]
Certified Complex Nutrient Standard[c]	7.76	7.9	9.313	118 (120)[d]	2.80	2.82	3.112	110 (111)[d]

[a] This reference analysis was not requested.
[b] This form of organic phosphorus also contains nitrogen. The nitrogen concentration in the standard at the target concentration is listed here for reference purposes.
[c] Samples diluted quantitatively from simple and complex nutrient standard certified for the nutrients listed as “target” concentration .
[d] TNPC-4110(C) response compared to the calculated concentration rather than from the reference laboratory result.

6.2 Bias

Bias in the TNPC-4110(C) response to TN and TP nutrient standards was assessed for the multi-level nitrate and phosphate challenges presented in Table 6-1 and calculated separately for TN and TP. Bias of +31% was observed for the TNPC-4110(C) TN measurements for standards containing N in the form of nitrate. For TP, the TNPC-4110(C) showed a bias of +18% for standards containing P in the form of dissolved, inorganic ortho-phosphate.

6.3 Linearity

Figures 6-2 and 6-3 show the linearity results for the TN and TP multi-level accuracy checks, respectively. For each check, a linear regression was calculated from the results presented in Table 6-1 (TNPC-4110(C) versus reference method) over the range of 0 to 20 mg N/L for TN and 0 to 5 mg P/L for TP. The 95% CIs for the slope and intercept of each regression were also calculated (and are shown in the following text in parenthesis). For TN, the slope of the regression line was 1.34 (± 0.02), with an intercept of 0.03 (± 0.22) and an r^2 value of 0.9998. For TP, the linear regression showed a slope of 1.10 (± 0.02), an intercept of 0.08 (± 0.06), and an r^2 of 0.9996. Over the range of concentrations tested, the TNPC-4110(C) demonstrated a high degree of linearity.

6.4 Limit of Detection

The TNPC-4110(C) measured DI water blanks 15 times during the verification test. The average ($\overline{Y}_b$) and SD_b were calculated separately for TN and TP blanks and used to determine the LOD for TN and TP, respectively. All of the TNPC-4110(C) TN measurements for DI water were 0.000 mg N/L. Thus, the average and SD were also equal to zero, giving a detection limit of 0 mg N/L. Based on the consistent reporting of non-detects in the response to DI water blanks, it is suggested that a method detection limit be determined by the user for each sample matrix. The average TNPC-4110(C) TP measurement for DI water blanks was 0.044 mg P/L, with an SD of 0.032 mg P/L, resulting in a TP LOD of 0.141 mg P/L for the range setting of 0 to 5 mg P/L, which uses a five-fold sample dilution. It should be noted that many of the on-line TP measurements conducted by the TNPC-4110(C) during the on-line monitoring phase were less than 0.1 mg P/L and therefore below the TNPC-4110(C) detection limit as configured for this verification test, with a range of 0 to 5 mg P/L. This range was most appropriate for the nutrient standard challenges planned for this verification test. The lowest measurement range for TP measurements on the TNPC-4110(C) is 0 to 0.5 mg P/L; and, under normal monitoring conditions, the range could be changed to better reflect the measured concentrations. The vendor-reported LOD for TNPC-4110(C) measurements using the lowest measurement range (0 to 0.5 mg P/L) is 0.01 mg P/L. Reference measurement results for the DI water used to challenge the TNPC-4110(C) were below the reference method quantitation limit, which was 0.05 mg P/L. One DI water result reported by the reference laboratory was 0.37 mg P/L and this measurement was discussed in Section 4.1. The TNPC-4110(C) measurement for this sample was 0.000 mg P/L.

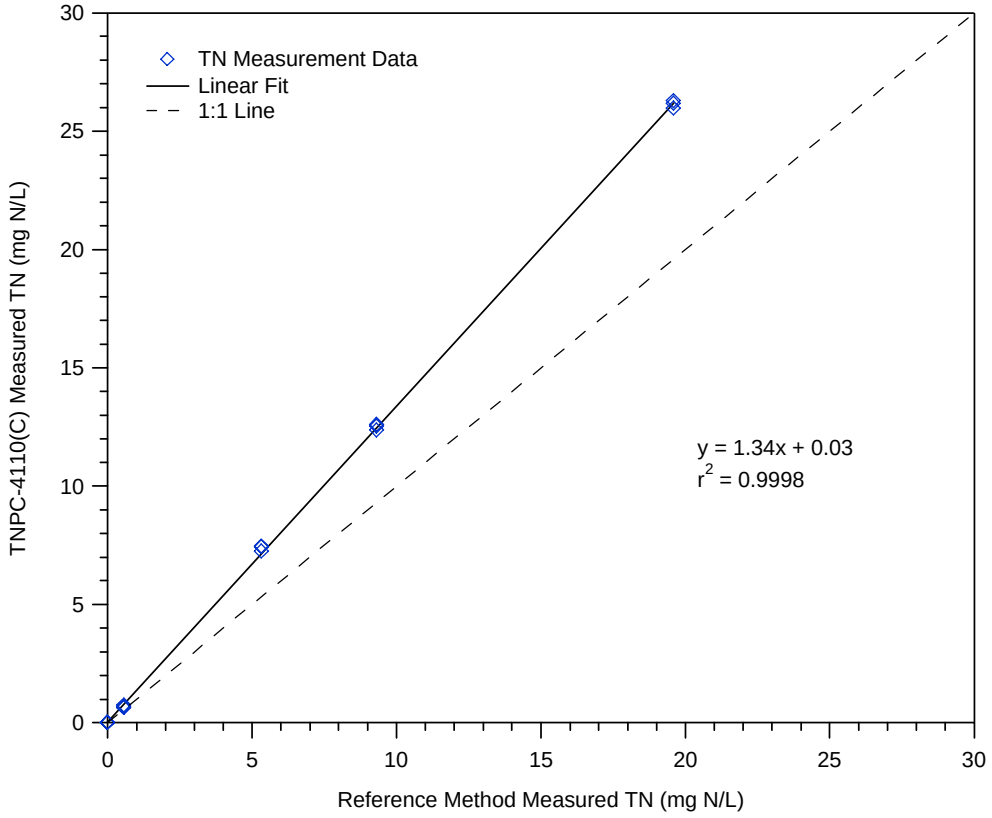


Figure 6-2. TNPC-4110(C) Linearity Results for TN

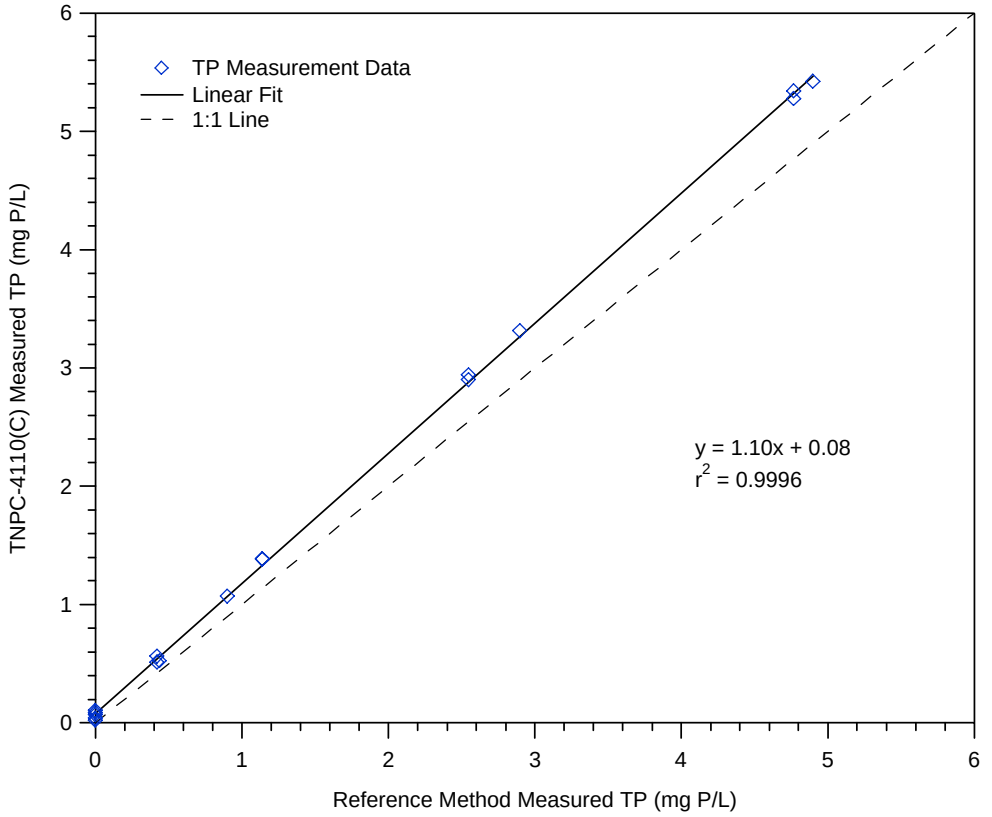


Figure 6-3. TNPC-4110(C) Linearity Results for TP

6.5 Reproducibility

The reproducibility results from replicate challenges of a mixed nutrient standard (~5 mg N/L nitrate and ~3 mg P/L ortho-phosphate) for the TNPC-4110(C) are shown in Table 6-3. The mixed nutrient standard was delivered six times sequentially. The reproducibility, determined as the %RSD, for TNPC-4110(C) TN and TP measurements was 2% and 1%, respectively.

Table 6-3. Reproducibility Results

TN Concentration (mg N/L)			TP Concentration (mg P/L)		
Target	**Reference Method**	**TNPC-4110(C)**	**Target**	**Reference Method**	**TNPC-4110(C)**
5	5.41	6.382	3	2.98	3.163
		6.435			3.231
		6.545			3.183
		6.319			3.145
		6.595			3.207
		6.370			3.192
Average		6.441			3.187
SD		0.108			0.031
%RSD		2			1

6.6 Span and Zero Drift

The baseline response of the TNPC-4110(C) to the mixed nutrient standard used in the reproducibility checks (Section 6.5) and DI water blanks was determined during the first week of testing. The measurements for TN and TP for each replicate are shown in Table 6-4. The $\overline{Y} \pm$ 2SD warning and $\overline{Y} \pm$ 3SD action limits were calculated for the mixed nutrient span standard and DI water blanks and are also shown in the table.

Span and zero drift checks were performed once per week beginning with the on-line effluent monitoring portion of the verification test, for a total of five drift checks. The results of the span drift checks for TN and TP are shown in Table 6-5. Results of the TP zero drift checks are shown in Table 6-6; all TN zero drift check measurements were 0.000 mg N/L and are not shown. Control charts were prepared from the data shown in Tables 6-4, 6-5, and 6-6 to demonstrate graphically whether drift occurred over the duration of the verification test. The control charts are shown in Figures 6-4, 6-5, and 6-6 for TN span, TP span, and TP zero drift, respectively. The absolute responses measured during automated calibrations are also shown in Figures 6-4, 6-5, and 6-6 to demonstrate any changes in the absolute sensitivity of the TNPC-4110(C). The control chart for TN zero drift is not shown since all measurement values were equal to zero and therefore no drift occurred. Drift in the TN span response was not observed for the

Table 6-4. Span and Zero Baseline Response

Span Response					Zero Response				
	TN (mg N/L)		TP (mg P/L)			TN (mg N/L)		TP (mg P/L)	
Week and Day	**Reference Method**	**TNPC-4110(C)[a]**	**Reference Method**	**TNPC-4110(C) [a]**	**Week Day**	**Reference Method**	**TNPC-4110(C)**	**Reference Method**	**TNPC-4110(C)**
Week 1 Thursday	5.41	5.898	2.98	3.184	Week 1 Thursday	<0.58	0.000	<0.05	0.000
Week 1 Thursday	5.41	5.947	2.98	3.253	Week 1 Friday	<0.54	0.000	<0.05	0.083
Week 1 Thursday	5.41	6.049	2.98	3.204	Week 2 Monday	<0.54	0.000	<0.05	0.065
Week 1 Thursday	5.41	5.840	2.98	3.166	Week 2 Tuesday	<0.58	0.000	<0.05	0.083
Week 1 Thursday	5.41	6.095	2.98	3.229	Week 2 Wednesday	<0.54	0.000	<0.05	0.075
Week 1 Thursday	5.41	5.887	2.98	3.213	Week 2 Thursday	<0.54	0.000	<0.05	0.061
Baseline Response		5.953		3.208			0.000		0.061
SD		0.100		0.031			0		0.031
Warning Limit		5.754 to 6.152		3.146 to 3.270			0	-0.002 to 0.124	
Action Limit		5.654 to 6.251		3.115 to 3.301			0	-0.033 to 0.155	

[a] Concentration normalized to target concentrations of 5 mg N/L for TN and 3 mg P/L for TP.

TNPC-4110(C), although four of five span drift check results were outside the warning limit, and the last span drift check result was 1.143 mg N/L greater than the average baseline response. As shown in Table 6-5 and Figure 6-5, the last three TP drift checks fell above the warning limit, indicating that drift occurred in the TNPC-4110(C) span response. The final TP drift check value was 0.073 mg P/L greater than the average baseline response. All of the TP zero drift checks fell within the warning limits, indicating that drift did not occur in the TNPC-4110(C) response to DI water blanks.

Table 6-5. Span Drift Check Results

Check Date	TN				TP			
	Reference Method (mg N/L)	TNPC-4110(C)[a] (mg N/L)	Within Warning Limit? (5.754 to 6.152)	Within Action Limit? 5.654 to 6.251	Reference Method (mg P/L)	TNPC-4110(C)[a] (mg P/L)	Within Warning Limit? (3.146 to 3.270)	Within Action Limit? (3.115 to 3.301)
5/17/05 Monday	4.76	6.169	No	Yes	2.90	3.259	Yes	Yes
5/23/05 Monday	4.67	6.955	No	No	2.52	3.168	Yes	Yes
5/31/05 Tuesday	4.80	5.978	Yes	Yes	2.53	3.434	No	No
6/6/05 Monday	4.87	5.176	No	No	3.04	3.546	No	No
6/13/05 Monday	4.56	7.096	No	No	2.95	3.281	No	Yes

[a] Concentration normalized to target concentrations of 5 mg N/L for TN and 3 mg P/L for TP.

Table 6-6. TP Zero Drift Check Results

Check Date	Reference Method (mg P/L)	TNPC-4110(C) (mg P/L)	Within Warning Limit? (-0.002 to 0.124)	Within Action Limit? (-0.033 to 0.155)
5/17/05 Monday	<0.05	0.000	Yes	Yes
5/23/05 Monday	<0.05	0.005	Yes	Yes
5/31/05 Tuesday	0.37[a]	0.000	Yes	Yes
6/6/05 Monday	<0.05	0.075	Yes	Yes
6/13/05 Monday	<0.05	0.029	Yes	Yes

[a] Results from F&R matrix spikes suggest that actual concentration is <0.05.

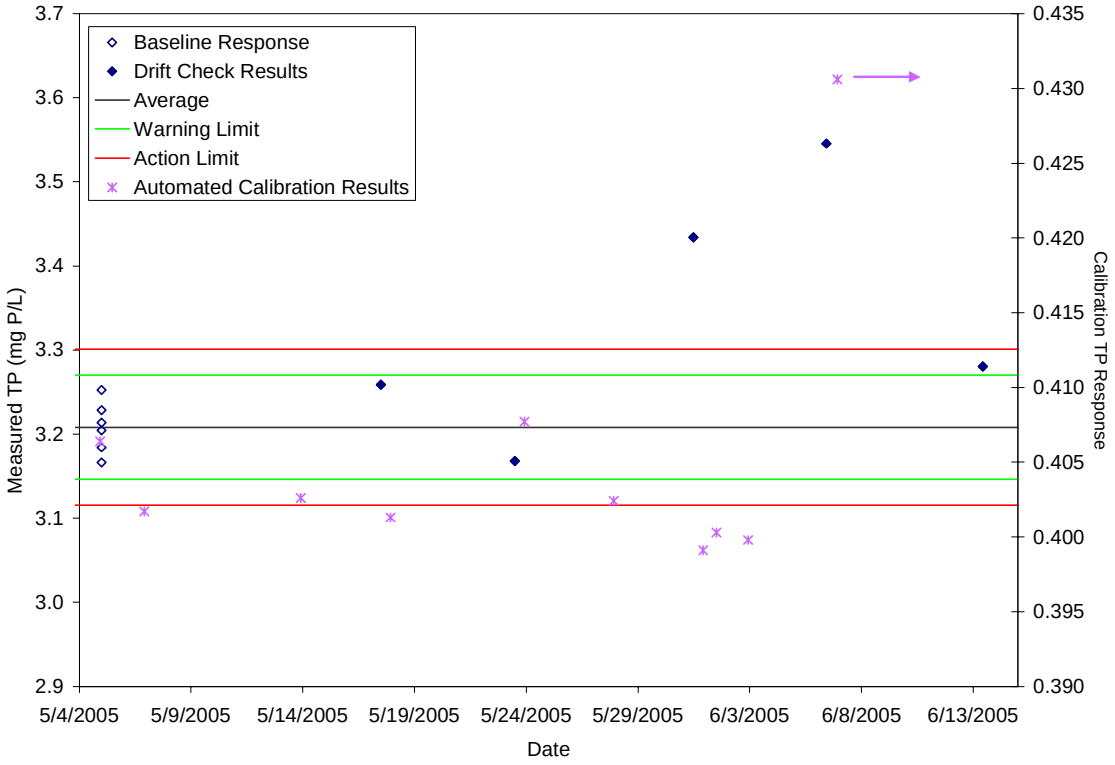


Figure 6-4. TN Span Drift Control Chart

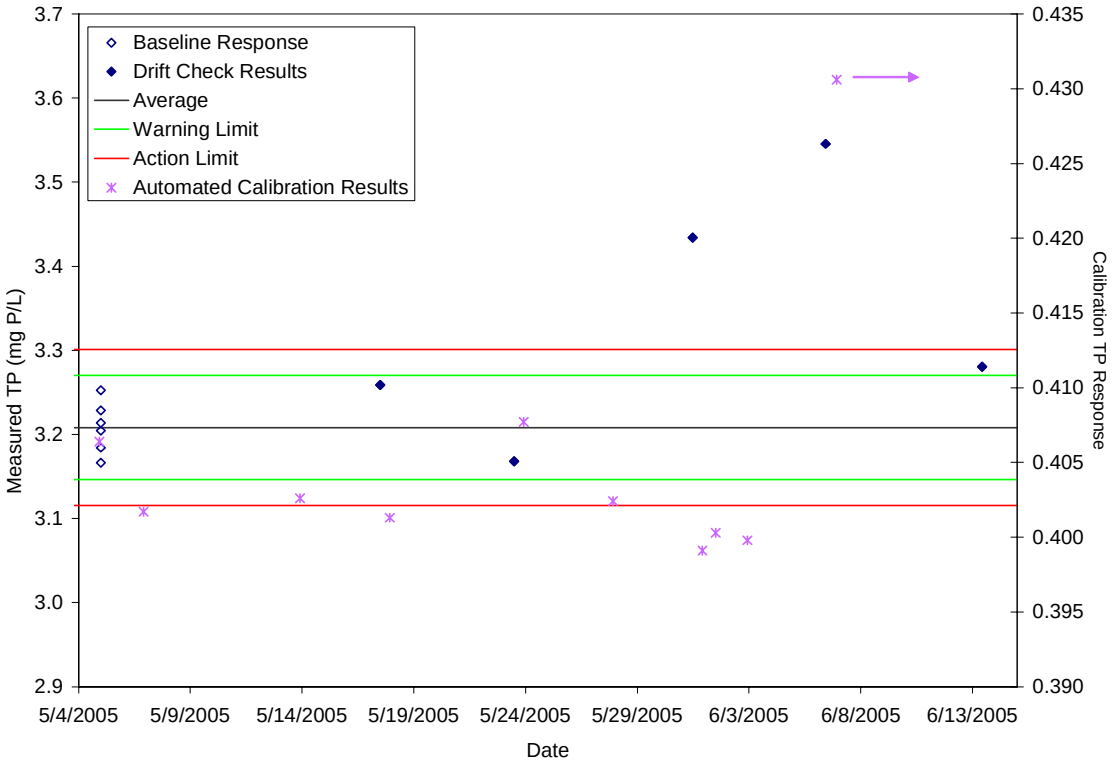


Figure 6-5. TP Span Drift Control Chart

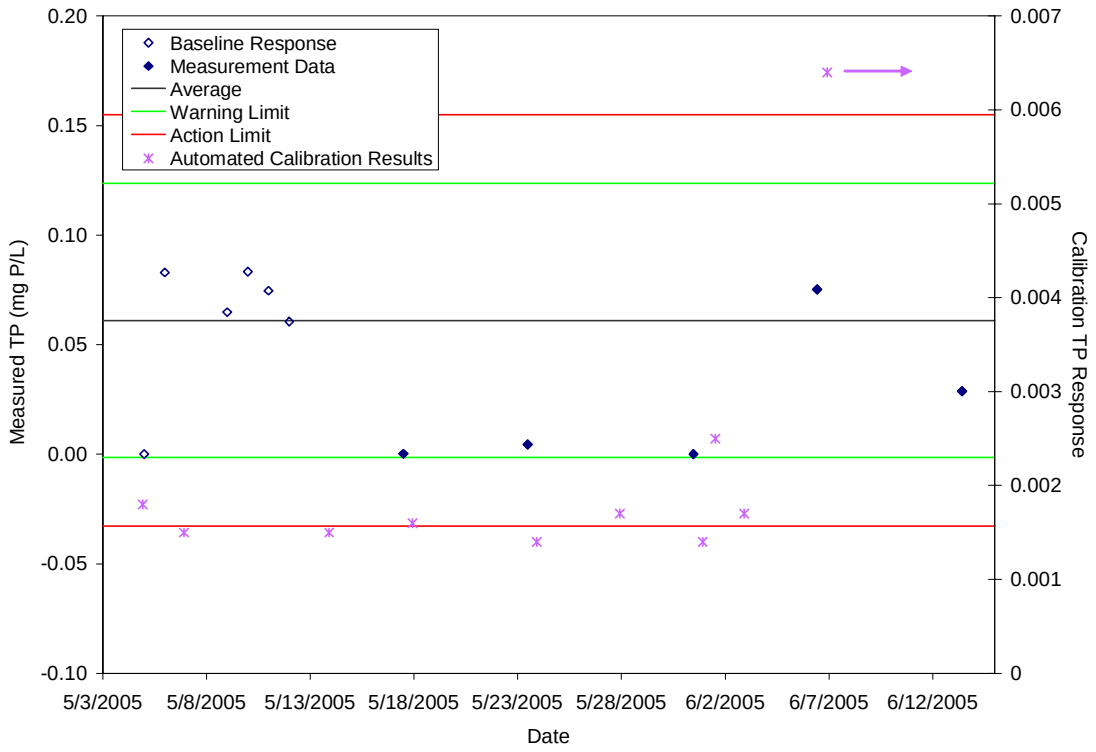


Figure 6-6. TP Zero Drift Control Chart

6.7 Matrix Effects

Matrix effects were evaluated during off-line Phases I and II and during on-line monitoring by calculating the %R value for each sample. The off-line matrix effects results are shown in Table 6-7. Some test samples were analyzed by the TNPC-4110(C) more than once. In these cases, the average response was used to calculate the %R. The number of replicates (*n*) for each test sample are shown in Table 6-7. It should be noted that the effluent and influent wastewater samples contained suspended solids and were not stirred before being sampled by the TNPC-4110(C); suspended solids may have settled on the bottom of the sample container, potentially causing low measurement values. The process wastewater sample did not appear to contain suspended solids. The matrix variable could be isolated for test samples with varied pH and in the presence of chlorophyll *a*. For these test samples, the %D was calculated to aid in assessing matrix effects. The %D values for pH 5 and 9 TN and TP measurements were calculated relative to the pH 7 sample and were within 3% of the measurements at pH 7. The TN measurement in the presence of chlorophyll *a* was 27% lower than the measurement at the same nitrate concentration in the absence of chlorophyll *a*. The TP measurements of phosphate in the presence and absence chlorophyll *a* were within 1% of each other.

The TNPC-4110(C) on-line effluent wastewater TN and TP measurements are shown in Figure 6-7 with the reference method data. The TNPC-4110(C) reported TN and TP values equal to or near zero on several occasions, as shown in Figure 6-7. Based on information provided by Shimadzu, these near-zero values were most likely caused by clogs in the sampling tube.

Table 6-7. Matrix Effects Results for Off-Line Testing

Matrix (Variable)	Sample Description	TN Reference Method (mg/L)	TN Average TNPC-4110(C) (mg/L)	TN *n*	TN %R	TP Reference Method (mg/L)	TP Average TNPC-4110(C) (mg/L)	TP *n*	TP %R
pH	pH = 5	5.16	6.938	1	134	2.71	3.081	1	114
	pH = 7	5.17	7.042	1	136	2.73	3.052	1	112
	pH = 9	5.20	6.866	1	132	2.74	3.069	1	112
Chlorophyll *a* (pH 7)	120 microgram (µg)/L Chlorophyll *a*	<0.52	0.000		NA	<0.52	0.004		NA
	120 µg/L Chlorophyll *a* nutrient spike	4.66	4.599	1	99	2.93	3.370	1	115
Effluent sample	Effluent	1.49	1.159	3	78	0.09	0.139	3	155
	Effluent spike	5.77	8.276	3	143	2.99	3.682	3	123
Process sample	Process	68.0	21.008[a]	3	31	<0.52	0.105	3	NA
	Process spike	68.9	22.376[a]	3	32	2.90	2.989	3	103
Influent sample	Influent	12.9	8.102	3	63	0.35	0.562	3	161
	Influent spike	17.9	11.77	3	66	3.31	3.520	3	106
Effluent sample[b]	Effluent	1.76	1.403	1	80	0.08	0.192	1	240
	Simple Nutrient Effluent Spike	9.72 (9.46)[b]	8.174	1	84 (75)[b]	0.24 (0.25)[b]	0.313	1	72 (71)[b]
	Complex Nutrient Effluent Spike	6.19 (5.64)[b]	6.114	2	99 (87)[b]	1.45 (1.52)[b]	1.679	2	95 (98)[b]

NA = Not applicable.

[a] Sample out of TNPC-4110(C) range (0 to 20 mg N/L).

[b] Samples diluted quantitatively in effluent wastewater from simple and complex nutrient standard certified for the nutrients listed. TNPC-4110(C) response compared to the calculated concentration in addition to the reference laboratory result.

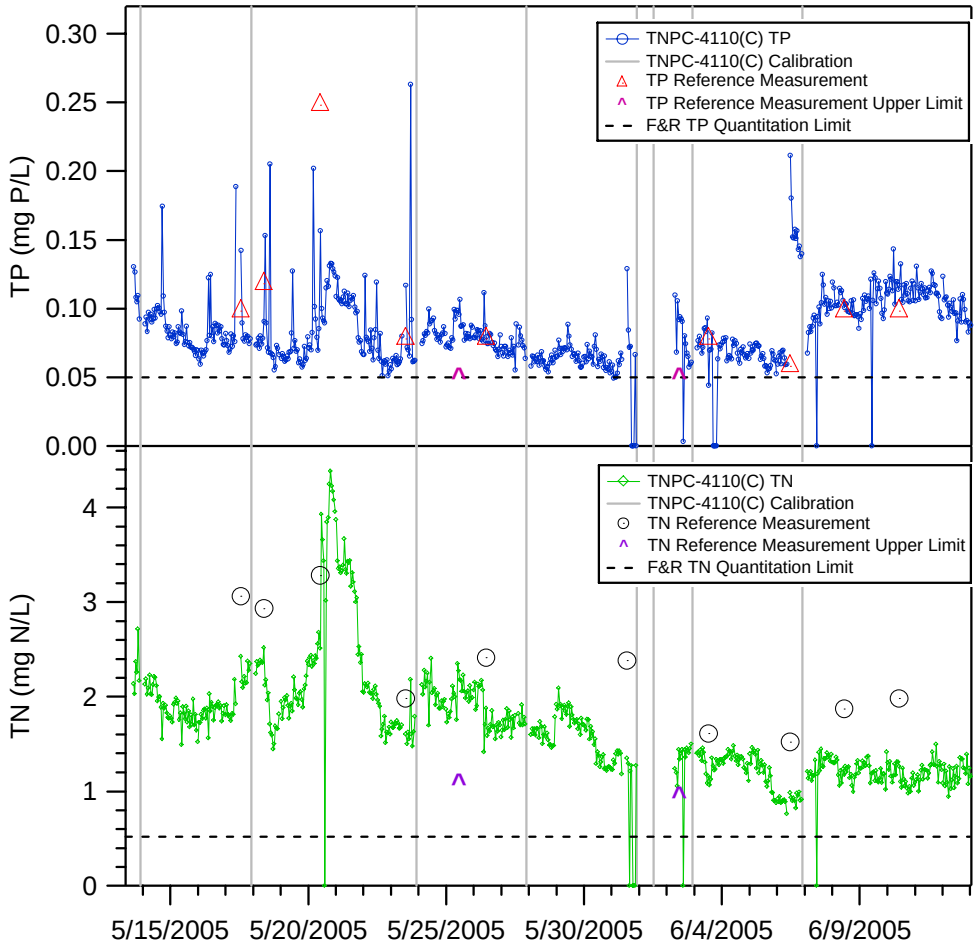


Figure 6-7. On-line TNPC-4110(C) and Reference Method Results for TN and TP

The TNPC-4110(C) and reference method data are also presented in Table 6-8 with the corresponding %R values. The %R values for the on-line TN measurements ranged from 57% to 86%, with an average of 72%. The average TP %R was 128% and the individual %R values ranged from 55% to 353%. A paired *t*-test was applied to the on-line effluent monitoring results to determine if the two analytical methods [reference method versus the TNPC-4110(C)] for each nutrient gave significantly different values for the mean nutrient concentrations. For the 10 TN measurement pairs, the SD of the absolute differences was 0.20 mg N/L, giving a value for t_{exp} of 9.852. The value for t_{crit} for the 95% confidence level and 9 degrees of freedom is 2.262. Since t_{crit} was less than t_{exp} for TN measurements, the differences between the mean TN concentration measured by the two methods can be considered to be significant. Even so, linear regression analysis of the TNPC-4110(C) TN measurements versus the reference method shows that the results are highly correlated, as indicated by an r^2 value of 0.90 (slope = 0.93, intercept = −0.45). It should be noted that the differences observed between the TN measurements made by the TNPC-4110(C) and the reference laboratory can not be attributed specifically to matrix effects and could have been caused by a number of factors (e.g., differences in calibration standards). For TP measurements, nine measurement pairs were compared and the SD of the absolute differences was 0.07 mg P/L. The TP t_{exp} value was 0.438, which is less than the t_{crit} value of 2.306, indicating

Table 6-8. Matrix Effects Results for On-Line Testing

	TN				TP			
Sample Date and Time	Reference Method (mg/L) (X)	TNPC-4110(C) (mg/L) (Y)	Y−X	%R	Reference Method (mg/L) (X)	TNPC-4110(C) (mg/L) (Y)	Y−X	%R
5/17/05 13:30	3.06	2.422	−0.64	79	0.10	0.142	0.04	142
5/18/05 9:30	2.93	2.517	−0.41	86	0.12	0.091	−0.03	75
5/20/05 10:30	3.28	2.508	−0.77	76	0.25	0.157	−0.09	63
5/23/05 13:00	1.98	1.603	−0.38	81	0.08	0.117	0.04	146
5/25/05 11:00	<1.09	2.273	NA	NA	<0.05	0.096	NA	NA
5/26/05 11:00	2.41	1.878	−0.53	78	0.08	0.079	−0.00	99
5/31/05 13:30	2.38	1.348	−1.03	57	NA[a]	0.129	NA	NA
6/2/05 10:30	<0.96	1.440	NA	NA	<0.05	0.092	NA	NA
6/3/05 12:30	1.61	1.157	−0.45	72	0.08	0.044	−0.04	55
6/6/05 11:30	1.52	0.982	−0.54	65	0.06	0.212	0.15	353
6/8/05 10:30	1.87	1.173	−0.70	63	0.10	0.101	0.00	101
6/10/05 10:30	1.98	1.261	−0.72	64	0.10	0.117	0.02	117
Average	2.30	1.69	−0.62	72	0.11	0.12	0.01	128
SD	0.62	0.60	0.20	10	0.06	0.05	0.07	90
Minimum	<0.96	0.982		57	<0.05	0.08		55
Maximum	3.28	2.517		86	0.25	0.16		353

NA = Not applicable.
[a] The reference laboratory did not report a value for TP.

that the two methods did not give significantly different values for the mean TP concentration at the 95% confidence level. It should be noted that, because of the small sample size and high variance in the TN and TP measurements, the probability of detecting a true difference in the mean concentrations measured by the TNPC-4110(C) and reference method is relatively low (less than 17%). Other statistical tests, including the non-parametric Wilcoxon signed rank test, were applied to the TN and TP measurements. Since the results were the same as the *t*-test, only the *t*-test was presented.

6.8 Data Completeness

The TNPC-4110(C) experienced 34 hours of down time following a failed automatic calibration during on-line effluent monitoring; 94% and 93% of the possible number of measurements were conducted for TN and TP, respectively. Calibrations during the verification test consumed the time equivalent to 37 measurements. Data for a few measurements were lost when tape was inadvertently applied over the text on the thermal print-outs. Upon contact with the tape, the text disappeared completely and could not be recovered. Over the duration of the verification test, the TNPC-4110(C) conducted 766 TN and 755 TP measurements (including both on-line and off-line measurements).

6.9 Operational Factors

The TNPC-4110(C) was installed at the test site by three representatives from Shimadzu: two representatives from the United States and one representative from Japan, who provided technical guidance, particularly for the effluent inlet configuration and in installing the in-line filter screen described in Section 3-2. The TNPC-4110(C) installation was essentially performed by one of the vendor representatives with assistance from OMI staff in carrying the TNPC-4110(C) up the stairs to the shelter. The installation was completed in approximately one day, which also included the initial calibration. The TNPC-4110(C) was set up to perform automated calibrations at 2200 hours every seven days during the verification test. Data were collected as hard-copy print-outs from the TNPC-4110(C) thermal printer. The TNPC-4110(C) could be operated by a user with minimal experience and access to the analyzer manual, which was quite complete. A checklist was provided by the vendor representatives to establish whether the analyzer was in proper working order during the verification test. The checklist, shown in Appendix C, was completed by Battelle or OMI staff during daily checks of the TNPC-4110(C) operating status. The checks were simple and quick, requiring approximately five minutes each day to complete. The vendor representatives provided a supply of reagents that would last up to one month. Fresh reagents were prepared by OMI staff twice during the verification test using chemicals provided by Shimadzu in addition to hydrochloric acid, sulfuric acid, and sodium hydroxide, which were provided by OMI. It took approximately one hour to prepare the reagents, most of which was spent waiting for the molybdic acid to dissolve. The TNPC-4110(C) generated approximately 30 L of waste (>90% water) over the six-week duration of the verification test (approximately 2 mL liquid waste per on-line measurement; off-line measurements produce more waste due to flushing of the sample inlet). Once during the verification test, the backwash strainer sample pretreatment unit was back-flushed, which improved sample throughput. Figure 6-8 shows the pretreatment unit at the completion of the verification test. Build-up, similar to that observed on the effluent tubing in Figure 3-4B, on the inside of the unit is clearly visible. (The canister and tubing were clear when the verification test began).

Figure 6-8. TNPC-4110(C) Backwash Strainer Sample Pretreatment Unit

Over the first weekend of the verification test, power to the test site was lost for more than 12 hours. Care was taken to unplug the TNPC-4110(C) before re-powering. However, one of the air compressors failed over that weekend, most likely as a result of losing or regaining power at the site. A new compressor was obtained on Monday, and the analyzer was operational once the air-compressed ballast pressure was high enough to feed the Parker gas generator and the TNPC-4110(C) combustion reactor reached operating temperature.

During the calibration performed on May 31, the sample inlet tube was curled up inside the calibration standard reservoir; the end rose above the liquid level of the calibration solution. The calibration failure was discovered during the daily checks the following day. The alarm light was illuminated, and the Alarm Screen showed a “Cal error.” The tubing was adjusted, and the calibration solution level was increased. The alarm was cleared, and on-line measurement was restarted. The vendor representative was informed of the calibration error and advised OMI staff to perform a manual calibration. The calibration was started at approximately 1230 hours and was still running at 1530 hours when OMI staff left for the day; on-line measurements were resumed the following day.

Chapter 7
Performance Summary

The performance of the TNPC-4110(C) was evaluated for its accuracy, bias, linearity, LOD, reproducibility, span and zero drift, matrix effects, data completeness, and operational factors while sampling prepared nutrient standards and wastewater. The TNPC-4110(C) measurement data were compared to reference measurements for the same samples to evaluate each performance parameter. The results of this evaluation are described below.

The accuracy of the TNPC-4110(C) was assessed over the range of 0.5 to 20 mg/L for TN and 0.5 to 5 mg/L for TP in terms of %R relative to reference method measurements. TN (in the form of nitrate) %R values ranged from 109% to 140%, with an average of 131%. The TNPC-4110(C) %R values for TP (in the form of ortho-phosphate) ranged from 111% to 133%, with an average of 118%. TN accuracy for non-nitrate forms of nitrogen ranged from 31% to 129%. Organic and inorganic phosphorus resulted in %R values of 103% and 113%, respectively; the mixed phosphorus standard %R value was 110%. The TNPC-4110(C) %R values (TN and TP) for a certified simple nutrient standard ranged from 95% to 153% relative to the nominal concentration and from 110% to 178% relative to the reference method results.

Bias of +31% was observed for the TNPC-4110(C) TN measurements for standards containing N in the form of nitrate. For TP, the TNPC-4110(C) showed a bias of +18% for standards containing P in the form of dissolved, inorganic ortho-phosphate.

Linearity was evaluated in terms of slope, intercept, and r^2 over the range from 0 to 20 mg N/L for TN and 0 to 5 mg P/L for TP. The 95% CIs for the slope and intercept of each regression were also calculated (and are shown in the following text in parenthesis). For TN, the slope of the regression line was 1.34 (± 0.02), with an intercept of 0.03 (± 0.22) and an r^2 value of 0.9998. For TP, the linear regression showed a slope of 1.10 (± 0.02), an intercept of 0.08 (± 0.06), and an r^2 of 0.9996. Over the range of concentrations tested, the TNPC-4110(C) demonstrated a high degree of linearity.

The TNPC-4110(C) LOD for TN and TP were determined from 15 blank measurements conducted over the duration of the verification test. All of the TNPC-4110(C) TN measurements for DI water were 0.000 mg N/L. Thus, the average and SD were also equal to zero, giving a detection limit of 0 mg N/L. Based on the consistent reporting of non-detects in the response to DI water blanks, it is suggested that a method detection limit be determined by the user for each sample matrix. The average TNPC-4110(C) TP measurement for DI water blanks was 0.044 mg P/L, with an SD of 0.032 mg P/L, resulting in a TP LOD of 0.141 mg P/L for the range setting of 0 to 5 mg P/L, which uses a five-fold sample dilution. The vendor-reported LOD for TNPC-4110(C) measurements using the lowest measurement range (0 to 0.5 mg P/L) is 0.01 mg

P/L. Reference measurement results of the DI water used to challenge the TNPC-4110(C) were below the 0.05 mg P/L quantitation limit, with one exception.

The reproducibility of the TNPC-4110(C) was evaluated as the %RSD from six replicate challenges of a mixed nutrient standard (~5 mg N/L nitrate and ~3 mg P/L ortho-phosphate). The reproducibility for TNPC-4110(C) TN and TP measurements was 2% and 1%, respectively.

Drift, defined as three consecutive drift check results that fell either above or below the warning limit (±2 SD), was calculated for the TNPC-4110(C) span (~5 mg N/L for TN and ~3 mg P/L for TP) response and zero response (to DI water). Drift did not occur in the TN and TP TNPC-4110(C) zero response to DI water blanks. Drift in the TN span response was not observed for the TNPC-4110(C); although four of five span drift check results were outside the warning limit, and the last span drift check result was 1.143 mg N/L greater than the average baseline response. The last three TP drift checks fell above the warning limit, indicating that drift occurred in the TNPC-4110(C) span response. The final TP drift check value was 0.073 mg P/L greater than the average baseline response.

Matrix effects were evaluated by calculating the %R value for several matrices. The percent difference (%D) was calculated for test samples with varied pH and in the presence of chlorophyll *a*. TN %R values ranged from 132% to 136% over pH 5 to 9 and TP %R values ranged from 112% to 114%. The TNPC-4110(C) TN and TP measurements at pH 5 and 9 were within 3% (by %D) of measurements at pH 7. The TN measurement in the presence of chlorophyll *a* (99%R) was 27% lower than the measurement at the same nitrate concentration in the absence of chlorophyll *a* (130%R). The TP measurements of phosphate in the presence and absence of chlorophyll *a* were within 1% of each other (%R of 115% and 119%). Percent recovery values for off-line measurements of effluent, process, and influent wastewater samples ranged from 31% to 143% for TN and 72% to 240% for TP. The %R values for the on-line TN measurements of effluent wastewater ranged from 57% to 86%, with an average of 72%. The average TP %R was 128%, and ranged from 55% to 353%. A paired *t*-test applied to the on-line effluent monitoring results indicated that differences in the mean TN concentration measured by the TNPC-4110(C) and the reference method can be considered to be significant at the 95% confidence level. However, the two methods did not give significantly different values for the mean TP concentration. It should be noted that differences between TNPC-4110(C) and reference method measurements cannot be attributed specifically to matrix effects and could have been caused by a number of factors (e.g., differences in calibration standards).

The TNPC-4110(C) experienced 34 hours of down time following a failed automatic calibration during on-line effluent monitoring; 94% and 93% of the possible number of measurements were conducted for TN and TP, respectively. Calibrations during the verification test consumed the time equivalent to 37 measurements, and data for a few measurements were lost when tape was inadvertently applied over the text on the thermal print-outs. Upon contact with the tape, the text disappeared completely and could not be recovered. Over the duration of the verification test, the TNPC-4110(C) conducted 766 TN and 755 TP measurements (including both on-line and off-line measurements).

A user with minimal experience with access to the TNPC-4110(C) instruction manual could install and operate the TNPC-4110(C). Maintenance required during the verification test included replenishing reagents and DI water, adjusting the calibration span solution after one of the

automated calibrations failed, and back-flushing the backwash strainer sample pretreatment unit once during the verification test. One of the air compressors used by the TNPC-4110(C) was damaged during a power loss at the wastewater treatment plant and needed to be replaced. Daily checks of the TNPC-4110(C) were simple and quick, requiring less than five minutes per day.

Chapter 8
References

1. *Test/QA Plan for Verification of Nutrient Analyzers at a Wastewater Treatment Plant*, Battelle, Columbus, Ohio, April 2005.

2. *Standard Methods for the Examination of Water and Wastewater,* 18th Edition, American Public Health Association, Washington, DC, 1992.

3. *EPA Method 351.1 for Total Kjeldahl Nitrogen by Automated Colorimetry*, Issued 1971; Editorial Revision 1974 and 1978.

4. *Quality Management Plan (QMP) for the ETV Advanced Monitoring Systems Center,* Version 5.0, U.S. EPA Environmental Technology Verification Program, Battelle, Columbus, Ohio, March 2004.

APPENDIX A
TNPC-4110(C) Site Preparation Requirements

Shimadzu Scientific Instruments, Inc.
7102 Riverwood Drive, Columbia, MD 21046

Shimadzu TNPC-4110C Site Prep

Please read the entire document and verify that the installation facility is prepared. The document MUST be signed and E-mailed or FAXed (410-381-1222) to Shimadzu. Without this signed two (2) page document, Shimadzu Scientific Instruments cannot install the TNPC-4110C Series Instrument.

I, _____ (user name) of _____ (company name) have read this document and completed all the installation procedures with respect to the TNPC-4110C Series on _____(Month, Day, and Year). I understand that my company will be charged Shimadzu Service Rates (and airfare rates if required) if a return visit is required because the facility is not prepared properly.

TNPC-4110C General Installation Requirements:

- One 120V Power Source
- Compressed Air with ¼" male NPT Fitting (must be regulated at 80 psi)
- Tap Water with ¼" male NPT Fitting
  Note 1: For optional Flow Line Switcher
  Note 2: Rinse water can only be used if TOC is much lower than sample TOC
  Requires 150kPa (22 psi)
- Gravity Drain for Waste, need tubing with ID 0.377 inch (x2)
- Exhaust Pipe, need tubing with ID 0.967 inch
- Ambient Temperature: 34-110 ºF; 1-40 ºC
- Sample Types: System uses either A) or B) below.

A. Particulated Sample Stream

I. Backwash Strainer Sample Pretreatment:

- Requires a backwash strainer sample pretreatment unit (P/N 638-41507-03)

II. Single Stream Suspended Solids Pretreatment:

- Requires a single stream SS pretreatment unit (P/N 638-93163-00).

Sample Requirements: Sample flow rate must be approximately 1 L/min for the stream. **The customer MUST supply each sample stream with female ¾" NPT fitting.**

III. Multi-Stream Suspended Solids Pretreatment:

The "Suspended Particle Flow Line Switcher" is for samples containing particulates. When using the Suspended Flow Line Switcher or "Sample Thief" the following sample plumbing connections are required:

- Suspended Flow Line Switcher (P/N 220-95311-0**X**), where "**X**" equals 1 to 6 for stream.
- The above Flow Line Switcher packages include for each stream: 1 pipe (P/N 631-40312-00), 1 union (P/N 220-95255-00), 1 back ferrule (P/N 220-95256-00), and 1 front ferrule (P/N 220-95257-00).

Sample Requirements:
Sample flow rate must be approximately 10 L/min for each stream. **The customer MUST supply each sample stream with female ¾" NPT fitting.**
The flow rate can be reduced to 3 L/min with optional parts: Flared sample tube (P/N 633-15237-00) and Sample thief flow reducer (P/N 633-15505-00).

Drain:
The drain is a gravity type drain for the TNPC-4110C Series analyzer. When the Suspended Flow Line Switcher (638-93129-0x) is used, an additional gravity drain is required for each stream. The system can use 1" Tygon® tubing for the 28-mm (1.1") O.D. male sleeve.

Sample Pipe Configuration for up to 3 streams:

- Clean Stream Sample Pretreatment (220-95310-0**X**) "**X**" is equal to the number of streams, max 3 steams.

Sample Requirements:
Each sample pipe has an inlet and outlet sample flow. **The customer MUST provide a ½" male PVC or NPT pipe connector for the inlet and outlet, for each stream.**

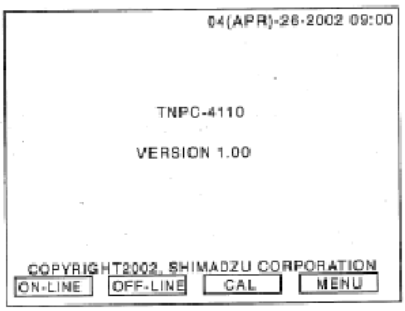
The sample must be constantly supplied at a flow rate that is approximately 1-3 L/min for each stream.

Closed Sample System Requirements:
If the customer wants a system closed to the atmosphere, then 1" PVC caps can be purchased in the plumbing section of large hardware stores. The caps can be glued onto the top of the overflow pipes. Note: the top of the overflow pipe is the only area where the sample stream is open to the atmosphere. The opening is to vent any purgeables that may get trapped in the sample stream. If there are no purgeables then the 1" PVC caps may be installed.

Drain:
The drain is a gravity type drain for the TNPC-4110C Series analyzer. When the Flow Line Switcher (638-93153-0X) is used, an additional gravity drain is required. The system can use 1" Tygon® tubing or glue a union with 1" I.D. female sleeve on one side and a ¾" male NPT pipe on the other side.

APPENDIX B
TNPC-4110(C) Measurement Instructions

OFF-LINE MEASUREMENT



1. Set the sample by placing Line 2 into sample.

2. Select **OFF-LINE** by pressing **[F2]**

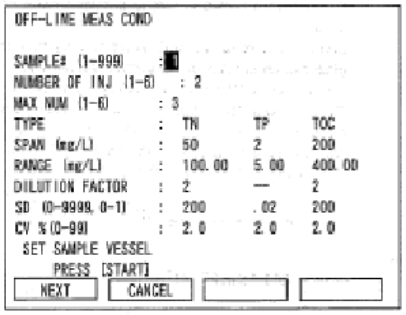
3. Select **OFF-LINE** by pressing **[F1]** (Next).

4. Under sample # enter an ID (1-999), **[ENTER].**

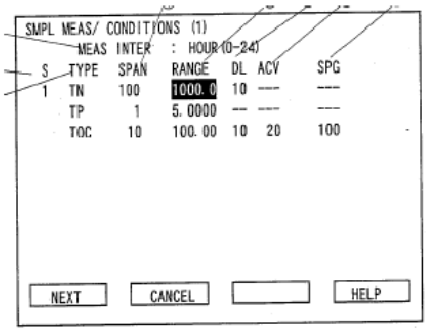
5. Select the minimum and maximum number of measurements. Press **[ENTER].**

6. Select the type of measurements to be performed by scrolling using **[⮜] [⮞]** keys. Press **[ENTER]** to select/deselect measurement types. Deselected appears as (**).

7. Select **NEXT** by pressing **[F1]**, then **[START]**.



ON-LINE MEASUREMENT



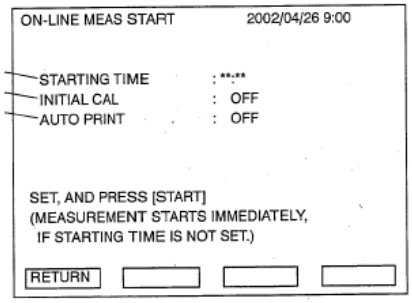
1. Press **[F4]** Menu and using **[⮝] [⮟]** select SAMPLE MEASUREMENT/CONDITIONS Press **[ENTER].**

2. Set Measure INTER: (**0, 1, 2, 3, 4, 6, 12, 24**) hours. Press **[ENTER]**. Zero is the best for this test.

3. Select the Type(s) of Measurement(s) to be performed using the **[SEL]** key. Set the measurement(s) by pressing **[ENTER]**. Deselected measurements appear as (**).

4. Return to the Main screen by pressing **[F1]** (Next) then **[F2]** (cancel), then **[F1]** (Return).

5. Select ON-LINE measurement by pressing **[F1].** Leave the start time blank (***), leave Inti. Cal. **OFF**, and Auto Print **ON.** Press **[Start]** key to begin measurement.



APPENDIX C
TNPC-4110(C) Daily Checklist

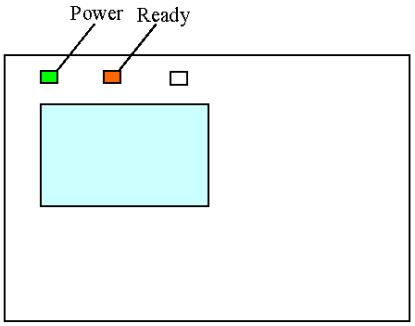
SHIMADZU

Daily Checklist and Operation: TNPC-4110C

Vendor Contact Information:

Instrument Operating conditions:

1. Please verify that both the instrument **Power** and **Ready** lights are illuminated. Refer to adjacent diagram for identification and location.



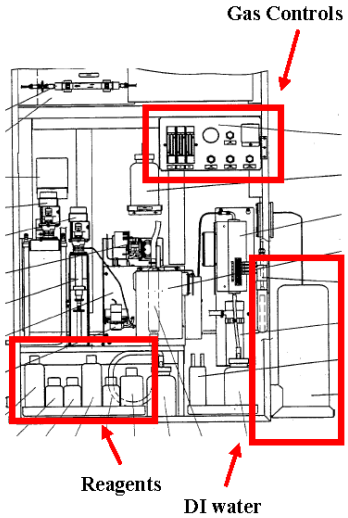
Power: ☐ On ☐ Off
Ready: ☐ On ☐ Off

2. Air Source:

Air Compressor (Craftsman) — Tank Pressure __>110__ psi ☐ OK ☐ NG
Supply Pressure __>110__ psi ☐ OK ☐ NG

Instrument (TNPC-4110C)

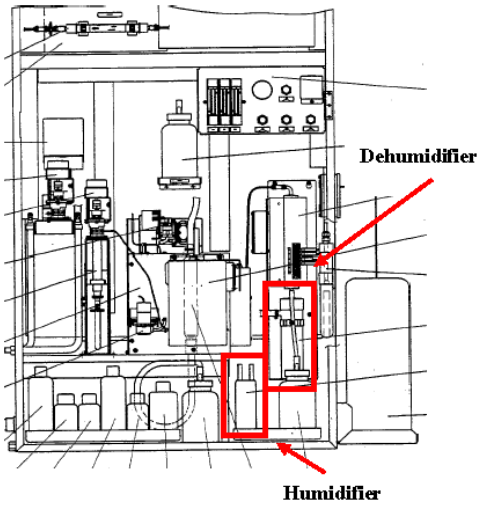
Pressure ___200___ kPa ☐ OK ☐ NG
Carrier Gas ___150___ mL/min ☐ OK ☐ NG
Sparg Gas ___100___ mL/min ☐ OK ☐ NG
Ozone Gen.___0.50___ L/min ☐ OK ☐ NG



2. Reagent Supply Acceptable Range

Dilution water_____> 1 L ☐ OK ☐ NG
Sulfuric Acid_____> 20 mL ☐ OK ☐ NG
Sodium Hydroxide___> 20 mL ☐ OK ☐ NG
Ascorbic Acid_____> 20 mL ☐ OK ☐ NG
Molybdic Acid _____> 20 mL ☐ OK ☐ NG

3. Fluid Levels



Dehumidifier:

Filled to "overflow" tubing with DI water

☐ OK ☐ NG

Humidifier:

Filled to be between high and low marks with DI water

☐ OK ☐ NG

Waste Container:

Drain lines (two on bottom left side) should not have fluid backing up the line. In addition the level of fluid in waste container should be below the drainage lines.

☐ OK ☐ NG

Operator Signature_____ Date_____

Comments

_____
_____
_____
_____
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