

## A preliminary methods comparison for measurement of dissolved organic nitrogen in seawater

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**Abstract**

Routine determination of dissolved organic nitrogen (DON) is performed in numerous laboratories around the world using one of three families of methods: UV oxidation (UV), persulfate oxidation (PO), or high temperature combustion (HTC). Essentially all routine methods measure total dissolved nitrogen (TDN) and calculate DON by subtracting the dissolved inorganic nitrogen (DIN). While there is currently no strong suggestion that any of these methods is inadequate, there are continuing suspicions of slight inaccuracy by UV methods. This is a report of a broad community methods comparison where 29 sets (7 UV, 13 PO, and 9 HTC) of TDN analyses were performed on five samples with varying TDN and DIN concentrations. Analyses were done in a “blind” procedure with results sent to the first author. With editing out one set of extreme outliers (representing 5 out of 145 ampoules analyzed), the community comparability for analyzing the TDN samples was in the 8–28% range (coefficient of variation representing one standard deviation for the five individual samples by 28 analyses). When DIN concentrations were subtracted uniformly (single DIN value for each sample), the comparability was obviously worse (19–46% cv). This comparison represents a larger and more diverse set of analyses, but the overall comparability is only marginally better than that of the Seattle workshop of a decade ago. Grouping methods, little difference was seen other than inconclusive evidence that the UV methods gave TDN values for several of the samples higher than HTC methods. Since there was much scatter for each of the groups of methods and for all analyses when grouped, it is thought that more uniformity in procedures is probably needed. An important unplanned observation is that variability in DIN analyses (used in determining the final analyte in most UV and PO methods) is essentially as large as the variability in the TDN analyses. This exercise should not be viewed as a qualification exercise for the analysts, but should instead be considered a broad preliminary test of the comparison of the families of methods being used in various laboratories around the world. Based on many independent analyses here, none of the routinely used methods appears to be grossly inaccurate, thus, most routine TDN analyses being reported in the literature are apparently accurate. However, it is not reassuring that the ability of the international community to determine DON in deep oceanic waters continues to be poor. It is suggested that as an outgrowth of this paper, analysts using UV and PO methods experiment and look more carefully at the completeness of DIN conversion to the final analyte and also at the accuracy of their analysis of the final analyte. HTC methods appear to be relatively easy and convenient and have potential for routine adoption. Several of the authors of this paper are currently working together on an interlaboratory comparison on HTC methodology. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Dissolved organic nitrogen; UV oxidation; Persulfate oxidation; High temperature combustion

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**1. Introduction**

Although attempts to measure dissolved organic nitrogen (DON) in seawater extend over a century (at least as far back as Putter, 1909), it could probably be argued that modern methods began with publication of a method based on ultraviolet (UV) light oxidation (Armstrong et al., 1966). Because of apparent problems with incomplete oxidation of recalcitrant organic compounds by UV, use of the strong chemical oxidant, potassium persulfate, was introduced in the 1970s (see Koroleff, 1976) as an alternate method. There was indication that the persulfate oxidation

(PO) method gave better recovery of standard chemicals and slightly higher values for DON in natural marine samples than the UV method (D’Elia et al., 1977; Solorzano and Sharp, 1980). Similar higher values by PO than UV have been demonstrated for rainwater (Cornell et al., 1995; Scudlark et al., 1998). Nonetheless, many laboratories have used some variant of either UV or PO methods for the past 20–30 years. Sometimes, UV methods use higher energy UV sources and different geometry than the original Armstrong et al.’s instrument; however, some current routine methods use essentially the same system as the original.

A high temperature combustion (HTC) method was described in the 1980s that appeared to measure considerably higher concentrations of DON in seawater (Suzuki et al., 1985) than either wet chemical method. While this method created considerable interest, other analysts were not able to reproduce the high DON values using HTC methods (e.g., Koike and Tupas, 1993; Hansell, 1993; Lopez-Vernoni and Cifuentes, 1995) and the method as originally published was eventually withdrawn (Suzuki, 1993). Essentially, all other HTC methods used since the early 1990s report DON values within the same range as the wet chemical methods. However, most comparisons have been indirect.

A direct comparison performed several years ago in one laboratory showed comparable results with both the UV and HTC methods and apparently comparable results with PO for oceanic samples (Walsh, 1989). Also, good comparability between HTC and PO methods was demonstrated for river and domestic wastewater samples (Ammann et al., 2000).

The DON subgroup report from the Seattle DOC/DON workshop evaluated published reports of various DON methods and unpublished results from the participants; they concluded that there was no strong indication of wet chemical methods giving lower yields than HTC methods (Hopkinson et al., 1993). A direct comparison was also made at that workshop by 13 analysts using a variety of HTC instruments and two wet chemical methods (Hedges et al., 1993). While agreement among the analyses was not great, there was no indication of wet chemical methods measuring less DON than HTC (Hedges et al., 1993). With data from the 13 analyses, the reproducibilities of analyses gave coefficients of variation values (see Section 2.2 below) of 9–49% for the four samples.

A direct comparison between a commercial HTC analyzer and PO and UV methods was done in Bronk's laboratory recently (Bronk et al., 2000). In that comparison, differences between methods were found for standard chemicals and for natural samples with differing distinctions. For example, the PO method gave best recovery of most standard chemicals, but not all, and the HTC method gave higher values for oceanic samples than wet chemical methods but did not for nearshore samples. The UV method, in its standard format, appeared not to give

complete recovery for standard compounds and gave lower values for natural samples. When modified using persulfate as an added oxygen source instead of peroxide, the UV method gave better results. Most of the natural samples in this comparison had relatively high DON content. One oceanic sample appeared to give comparable results by HTC and PO but lower values by UV even with the modified chemistry. It was concluded that different methods have advantages for different types of samples (Bronk et al., 2000).

At this time, large differences in DON concentrations are not expected by different methods, and there is an inherent assumption that all methods are acceptable. However, recent publications give indirect comparison of large scatter for subsurface oceanic DON concentrations. Examining some of the recent literature, DON concentrations for oceanic samples below 200 m ranged from less than 2 to over 8  $\mu\text{M N}$  (Hansell and Waterhouse, 1997; Kahler et al., 1997; Wheeler et al., 1997; Ogawa et al., 1999). These reports represent use of UV, PO, and two hybrid HTC methods. Thus, it appears that a broad community evaluation of DON methodology is timely.

Several of us involved in this paper (Sharp, Hansell, Burdige, Cauwet, and Ogawa) started a small-scale methods comparison recently; results of which have been reported in national meetings. Samples from an oceanic depth profile and from an estuarine gradient were analyzed by UV, PO, and HTC methods. For the depth profile, there was relatively good agreement for total dissolved nitrogen (TDN) analysis but after subtracting the large dissolved inorganic nitrogen (DIN) concentration, the variability for the small remaining DON pool was large in relative terms. In the estuarine gradient with TDN concentrations in the range of 10–50 and DON in the range of 7–9, good agreement was found (unpublished data). A larger community effort was thought to be the best next step.

This study involves a comparison of a small number of samples by a large number of analysts, i.e., a broad community comparison with replicate samples sent to all interested participants. The comparison represented here is different from recent DOC comparisons (Sharp et al., 2002) in that it included only five samples, all seawater, and no blank or pure water references were included. Also, the majority of

analysts participating in the DOC comparison used HTC methods; the majority for this DON comparison used wet chemical methods.

## 2. Materials and methods

### 2.1. Samples, sample preparation, and analysts

Five samples were used, from estuarine, coastal, and open ocean surface and deep environments. Most samples were aged for several months to allow oxidation of more reduced inorganic ions ( $\text{NH}_4^+$  and  $\text{NO}_2^-$ ) to the highest oxidation state ( $\text{NO}_3^-$ ) and decomposition of labile dissolved organic matter. The purpose of the aging, in 5-gal glass carboys closed with silicone rubber stoppers, was to render the samples stable for the period of time necessary to include a large number of analysts (about 6 months). The deep Sargasso Sea sample was collected from the *RV Weatherbird* in April 1999 during a regular BATS cruise and shipped back from Bermuda. The other samples were collected from the *RV Cape Henlopen* in 1998 and 1999, and returned to the laboratory directly from the ship. The fresh estuarine water sample was collected from the harbor at the Graduate College of Marine Studies in Lewes, Delaware just prior to preparation of the ampoules. With the exception of the deep Sargasso Sea sample, all samples were filtered immediately on collection using GF/F filters. Samples were monitored during aging to verify that the reduced inorganic ion concentrations were decreasing and  $\text{NO}_3^-$  was increasing.

For the comparison, 50-ml aliquots were sealed in glass ampoules that had been rendered “organic-free” by baking overnight in a 450 °C oven. The ampoules were then filled from an aspirator bottle with silicone rubber tubing in a fashion similar to that used for DOC intercalibration samples (Sharp et al., 2002). Unlike the DOC samples, the water for this comparison was not acidified. One of the aged samples was augmented before preparing ampoules to give it relatively high  $\text{NO}_2^-$  and  $\text{NH}_4^+$  concentrations. All ampoules of that sample and of the comparatively fresh estuarine sample were autoclaved (about 1 h) after sealing to inhibit further microbial oxidation. Ampoules were filled and shipped to analysts in

January 2000, results were received from the analysts in the period of January–May. The five samples are shown in Table 1.

An attempt was made to include all active marine DON analysts who were interested. Laboratory groups that participated have listing as co-authors of this paper. Several other active DON analysts expressed interest but were not able to do the analysis in the short period requested for return in this exercise. From experience with DOC intercalibrations (Sharp, 1997; Sharp et al., 2002), it is recognized that it takes more than a few months to successfully include all interested participants. Therefore, this exercise should not be viewed as a qualification exercise for all potential analysts, but rather as a preliminary test of the comparison of the families of methods now being used in various laboratories around the world.

Analysts from 24 laboratories in 23 institutions performed 29 individual sets of analyses on the samples. Each participant was asked to report the TDN content for the five samples. Several also reported inorganic nitrogen ion and dissolved organic carbon concentrations. The DIN and DOC values in Table 1 are from the laboratory of the first author; comparison to other laboratories is discussed below in Section 3. When the samples were sent, analysts were told that expected TDN concentrations were in the 5–25  $\mu\text{M N}$  range with no identity of individual samples. Identity of the samples and DIN concentrations were sent to participants only after all results were received. Further information on the laboratories and individuals involved from each laboratory is given in Table 2.

### 2.2. Analytical and statistical methods

Analysts used a variety of HTC, PO, and UV methods to measure TDN. Most of the UV and PO

Table 1  
The five methods comparison samples with concentrations of inorganic N ions (in  $\mu\text{M N}$ ) and dissolved organic carbon ( $\mu\text{M C}$ ) from analysis in the laboratory of the first author

Sample	$\text{NO}_3^-$	$\text{NO}_2^-$	$\text{NH}_4^+$	DOC
CSW—central shelf water	1.84	0.01	0.05	88
SBW—shelf-break water	9.80	0.04	0.02	93
DSS—deep Sargasso Sea water	19.21	0.26	0.04	64
CPN—shelf water plus N	3.03	5.00	4.98	103
FHW—fresh lower estuary water	5.33	0.23	2.29	254

Table 2  
Information on participating laboratories for the DON methods comparison

Laboratory	Analyst(s)	Institution
Xosé A. Alvarez-Salgado	Marylo Doval	Instituto de Investigaciones Mariñas, Vigo, Spain
Jean Yves Benaim	Christophe Le Poupon	Université Toulon, France
Deborah Bronk	Marta Sanderson	University of Georgia—now College of William and Mary
David Burdige	Kip Gardner	Old Dominion University
Gustave Cauwet	Mireille Pujo-Pay, Louise Oriol	Laboratoire Arago, Banyuls sur Mer, France
Steven Emerson	Jeffrey Abell	University of Washington
Dennis Hansell	Wenhao Chen	BBSR, Bermuda—now at University of Miami
Charles Hopkinson	Amy Nowlin, Nat Weston	Marine Biological Laboratory, Woods Hole, MA
Gerhard Kattner	Carmen Hartmann	Alfred Wegener Institute, Bremerhaven, Germany
Nancy Kaumeyer		University of Maryland, CBL Analytical Laboratory
William McDowell	Jeff Merriman	University of New Hampshire
Karen McGlathery	Kristina Russell, Anna C. Tyler	University of Virginia
Axel E.J. Miller	Georgina Spyres	Plymouth Marine Laboratory, United Kingdom
Nick Morley		Southampton Ocean Center, United Kingdom
Klaus Nagel	A.-Maria Welz, Oliver Primm	Institut für Ostseeforschung Warnemünde, Rostock, Germany
Hiroshi Ogawa		Ocean Research Institute, University of Tokyo, Japan
Carol Pollard		Virginia Institute of Marine Sciences Analytical Laboratory
Patrick Raimbault		Centre d'Océanologie de Marseille, France
Raymond Sambrotto		Lamont Doherty Earth Observatory, Columbia University
Sybil Seitzinger	Renee Styles	Rutgers University
Jonathan Sharp	Katherine Rinker	University of Delaware
Frank Tirendi	Jane WuWon	Australian Institute of Marine Science, Townsville, Australia
William Ullman	Karen Savidge	University of Delaware
Ted Walsh		University of Hawaii—SOEST Analytical Services Laboratory
C.S. Wong	Keith Johnson	Institute of Ocean Sciences, British Columbia, Canada

methods depended upon oxidation of all reduced inorganic ions and DON to nitrate with a final colorimetric analysis for  $\text{NO}_3^-$  plus  $\text{NO}_2^-$  (N&N) after reduction to  $\text{NO}_2^-$ . All of the HTC methods involved conversion of all inorganic nitrogen ions and DON to nitrogen oxides ( $\text{NO}_x$ ) and measurement with a chemiluminescence detector (modification of the method of Garside, 1982). For comparison of data, the assumption was made that all of the organic and inorganic nitrogen was converted to the final analyte that represented TDN. To calculate DON, the sum of the DIN as determined in the laboratory of the first author was subtracted from the TDN. By using a single DIN value, similar to the practice in the Seattle workshop (Hedges et al., 1993), the variability of DON analysis was considerably minimized.

The methods used for analyses were HTC (Merriam et al., 1996; Alvarez-Salgado and Miller, 1998; Ogawa et al., 1999; Burdige and Zheng, 1998), PO (D'Elia et al., 1977; Solorzano and Sharp, 1980; Koroleff, 1983; Raimbault et al., 1999; Bronk et al., 2000), and UV (Armstrong and Tibbitts, 1968; Walsh, 1989). Most of

the PO and UV methods were wet chemical procedures that do not use commercial instruments; some used manual determination of N&N but most used auto-analyzers. Fine details of the procedures for PO and UV methods vary between laboratories, and while all details are not reported, Table 3 gives information on all the methods used. Among the UV methods, the duration of the UV exposure can vary from 6 to 18 h, the type and age of the UV lamp may be critical, and most analysts used  $\text{H}_2\text{O}_2$  to enhance oxidation, but not all. There are also variations in the chemistry of the PO methods employed, especially in the pH buffering needed for several of the steps. In the PO methods, the duration of the autoclaving step and temperature and pressure of the autoclave are also variables that are not necessarily standardized. We do not feel that it is informative to compare these fine details since the main intent of this paper is to compare families of methods. The HTC methods include both stand-alone TN analyzers and hybrid ones connecting a commercial TOC analyzer to a chemiluminescence detector (Table 3). In addition to the results reported here, results from use of

Table 3  
Methods used for the TDN comparison

Stand-alone HTC instruments			
#	Instrument	Combustion temperature (°C)	
14	Skalar Formacs HT	850	
24	Dohrmann DN-1900	850	
	Antek 7000N	1000	
Hybrid HTC instruments			
#	Combustion instrument	NO detector	Combustion temperature (°C)
4	Shimadzu TOC 5000	Antek 720	680
6	Shimadzu TOC 5000	Antek 7020	680
8	Shimadzu TOC 5000	Seivers	680
12	Shimadzu TOC 5000	Antek 705E	680
15	Shimadzu TOC 5000	Antek 705D	680
16	Shimadzu TOC 5000	Yanaco TN-7	680
26	Homemade combustion	Antek 7020	900
UV methods			
#	UV instrument or procedure	NO <sub>3</sub> measurement	Post UV check
2	Walsh (1989)	Technicon AA	Yes
10	Walsh (1989)	Lachat AA	Yes
13	Armstrong and Tibbitts (1968)	Manual color	No
17	Walsh (1989)	Technicon AA	Yes
23	Armstrong and Tibbitts (1968)	Manual color	Yes
25	Ace Glass UV Oxidizer	Bran and Luebbe AA	Yes
27	Automated UV-persulfate	Technicon AA	No
Persulfate methods			
#	Procedure	Oxidation method	NO <sub>3</sub> measurement
1	Solorzano and Sharp (1980)	Autoclave digestion	Manual color
3	Solorzano and Sharp (1980)	Autoclave digestion	Technicon AA
5	D'Elia et al. (1977)	Autoclave digestion	Technicon AA
7	Solorzano and Sharp (1980)	Autoclave digestion	Technicon AA
9	Raimbault et al. (1999)	Autoclave digestion	Technicon AA
11	Solorzano and Sharp (1980)	Autoclave digestion	Lachat AA
18	Koroleff (1983)	Autoclave digestion	Perstorp AA
19	Koroleff (1983)	Autoclave digestion	Skalar AA
20	Koroleff (1983)	Autoclave digestion	Skalar AA
21	Raimbault et al. (1999)	Autoclave digestion	Technicon AA
22	Koroleff (1983)	Autoclave digestion	Bran and Luebbe AA
28	Solorzano and Sharp (1980)	Autoclave digestion	Alpkem AA
29	Bronk et al. (2000)	Autoclave digestion	Alpkem AA

Under nitrate measurement, most analyses used auto analyzers (AA) or various manufacturers. Some analysts using the UV method measure nitrite and ammonium after UV for completion of oxidation (post UV check).

a third commercial instrument made by Antek were added in revision of the original manuscript and are discussed with results but are not in the data tables.

To compare results for both TDN and DON, means of all values, or subsets of values (for families of methods) of a sample were used to calculate means

and standard deviations; a coefficient of variation (%cv) was calculated from the standard deviation and mean ( $1 \text{ S.D.}/\text{mean} \times 100$ ). Performance was evaluated by summing %cv values to get a mean %cv. To compare means by different families of methods, a two-tailed *t*-test was used based on heteroscedastic sample sets, performed using an Excel spreadsheet.

### 2.3. Stability of samples in ampoules

Ampoules were opened and TDN and DIN were analyzed periodically in the laboratory of the first author by the PO method from January through October 2000 to check for stability. Samples CSW and SBW (see Table 1), without  $\text{NO}_2^-$  and  $\text{NH}_4^+$ , consistently showed zero values for these two inorganic ions and constant values for (N&N) and DON over this period. Sample DSS had a measurable low  $\text{NO}_2^-$  concentration ( $0.26 \mu\text{M}$ ) in January which disappeared by October while there was no apparent change in TDN in the same period;  $\text{NH}_4^+$  remained consistently at zero and there was too much scatter in the data to detect a change in N&N (at  $19.5 \mu\text{M}$ ) from

the slight  $\text{NO}_2^-$  decrease. The DSS sample must have become slightly contaminated in the collection and shipping since it did have a measurable  $\text{NO}_2^-$  concentration when ampouled (several months after collection) and also had elevated DOC. The DIN that we measured in this sample was about  $19.5 \mu\text{M}$  ( $19.5$  in Table 1;  $19.8 \pm 0.4$  by the “best” analyses in Table 4), which is higher than an average of  $18.1 \pm 0.6 \mu\text{M}$  measured by one of us on Hansell’s BATS deep water DOC reference sample (M.D. Doval, unpublished data). The measured DOC was  $64 \mu\text{M C}$  (Table 1), the expected value for the BATS deep water is about  $45 \mu\text{M}$  (calibration values are  $44.0 \pm 1.5 \mu\text{M}$  for Sharp DOC reference and  $44.7 \pm 3.2 \mu\text{M}$  for Hansell DOC reference). Samples CPN and FHW had appreciable  $\text{NO}_2^-$  and  $\text{NH}_4^+$  concentrations initially and when checked 10 months after ampoules were sealed, the concentrations of these two ions were essentially identical to the original values. N&N and TDN also appeared to be unchanged. Thus, it would appear that for the period of the test, autoclaving the ampoules preserved against measurable microbial oxidation of these reduced ions even when stored at room temperature. The conclusion is that with the exception of

Table 4  
Initial dissolved inorganic nitrogen data from participants in the TDN exercise

Number	$\text{NO}_3^-$ plus $\text{NO}_2^-$					$\text{NO}_2^-$					$\text{NH}_4^+$				
	CSW	SBW	DSS	CPN	FHW	CSW	SBW	DSS	CPN	FHW	CSW	SBW	DSS	CPN	FHW
1	1.85	9.84	19.47	8.03	5.56	0.01	0.04	0.26	5	0.23	0.05	0.02	0.04	4.98	2.29
2	1.62	9.85	19.46	7.65	5.25						0	0	0.01	4.65	2.28
8	1.93	11.97	23.3	9.52	6.43										
10	7.37	14.29	21.22	11.18	10.79										
11	2.42	10.1	20.68	8.43	5.57										
18	1.5	9.4	17.8	7.1	5						0.4	0.2	0.1	5	3.8
21	1.78	10.1	20.2	7.89	5.59	0.01	0.1	0.31	4.63	0.23					
22	1.7	9.58	19.28	8.42	5.15	0.01	0.01	0.01	4.75	0.23	0.15	0.15	0.12	5.52	2.86
23	1.49	6.9	12.52	6.74	4.97	0	0	0.16	4.87	0.1	2.57	3.3	2.34	4.72	2.22
24	2.06	10.3	20.21	7.82	5.51						0	0	0	4.15	2.12
25	1.55	9.18	18	11.9	6.21	0.06	0.02	0.29	4.79	0.21	0.05	0.05	0.07	2.82	1.48
29	1.57	9.78	19.87	7.98	5.2										
Mean	2.24	10.11	19.33	8.56	5.94	0.02	0.03	0.21	4.81	0.20	0.46	0.53	0.38	4.55	2.44
S.D.	1.64	1.74	2.58	1.56	1.59	0.02	0.04	0.12	0.14	0.06	0.94	1.22	0.86	0.87	0.72
%cv	73.3	17.2	13.4	18.3	26.8				2.9	28.3				19.1	29.7
* Mean	1.76	9.91	19.75	7.97	5.38	0.01	0.05	0.19	4.79	0.23	0.05	0.04	0.04	4.83	2.39
* S.D.	0.18	0.25	0.40	0.26	0.20	0.00	0.05	0.16	0.19	0.00	0.07	0.07	0.05	0.58	0.32
*%cv	10.1	2.6	2.0	3.3	3.7				3.9	0.0				11.9	13.6

The mean, one standard deviation (S.D.) and the coefficient of variation for 1 S.D. as percent of mean (%cv) are given for the full set of analyses. The second set of summary statistics\* are for data sets 1, 2, 21, 22, 24, and 29 only.

slight  $\text{NO}_2^-$  oxidation in sample DSS, the samples were stable over the period that the comparative analyses were performed; the slight change of inorganic ion speciation in sample DSS did not cause a significant change in TDN. This stability is important since the participants in this exercise analyzed their samples over a period of several months and since the samples were stored at room temperature.

### 3. Results

A number of laboratories also performed analysis of N&N prior to treatment for the TDN analysis and reported those data along with the TDN data. Some of them also analyzed for  $\text{NO}_2^-$  and  $\text{NH}_4^+$ . Results of all of these DIN data are listed in Table 4. For the 12 N&N analyses, the agreement is not very good (%cv values ranging from 13% to 73%). In addition, some samples by a few analysts had higher initial N&N than the final TDN for that same sample, potentially indicating error in initial DIN analyses. If only the six most consistent DIN data sets (arbitrarily selected on basis of DSS N&N values) are used, the %cv values reduce to the 2–10% range (bottom of Table 4); this also eliminates a few suspiciously high N&N values. This selection of the most consistent is arbitrary. However, since some of the participants in this exercise do not routinely perform oceanic analyses, it could be argued that a subset is more indicative of what could be expected of experienced oceanic nutrient analysts. Although there were fewer values for  $\text{NO}_2^-$  and  $\text{NH}_4^+$ , agreement from the select group for the two samples with measurable concentrations gave reproducibility in the 4–14% range (samples with close to zero concentrations were not included in these averages). Despite the large variability, these average values are similar to the DIN values from the single laboratory listed in Table 1 and used for the DON calculations.

Data for all 29 analyses are listed as TDN in Table 5. The reported values were derived from standardization and blank subtraction individual to each analyst. Unlike the DOC intercalibration (Sharp et al., 2002), no uniform blank nor standardization check was included in the sample set because blank problems were not expected to be as difficult as with DOC. However, this lack of controlled standardization could

Table 5

Concentrations of total dissolved nitrogen as  $\mu\text{M N}$  from all analyses submitted

Number	Method	CSW	SBW	DSS	CPN	FHW
1	PO	5.7	16.0	22.7	17.6	21.7
2	UV	8.2	16.5	24.3	19.8	22.4
3	PO	8.0	16.5	24.7	19.9	23.1
4	HTC	6.7	14.2	25.1	18.1	22.4
5	PO	8.2	17.7	25.8	19.2	24.2
6	HTC	6.5	14.9	20.7	17.0	22.4
7	PO	6.4	14.8	22.2	17.3	21.1
8	HTC	5.9	15.6	22.8	17.8	23.4
9	PO	7.8	18.8	28.2	21.9	27.4
10	UV	6.6	15.2	23.7	18.8	22.3
11	PO	<b>14.2</b>	<b>22.2</b>	<b>37.9</b>	<b>29.9</b>	<b>42.5</b>
12	HTC	6.8	15.8	23.9	18.1	22.7
13	UV	6.6	17.8	26.9	18.4	25.0
14	HTC	6.3	15.2	23.3	16.7	21.0
15	HTC	6.3	13.4	20.3	19.7	20.8
16	HTC	6.1	14.4	22.3	17.0	21.6
17	UV	6.7	16.4	24.2	18.9	24.0
18	PO	3.3	11.9	20.1	14.8	19.1
19	PO	6.5	15.9	25.0	19.2	24.1
20	PO	7.1	15.9	24.5	18.1	23.0
21	PO	6.3	15.4	23.4	17.2	21.9
22	PO	7.3	15.1	23.0	18.4	22.7
23	UV	15.2	14.7	26.4	16.1	16.4
24	HTC	6.9	14.7	23.3	18.6	29.1
25	UV	7.4	16.2	25.0	19.9	24.9
26	HTC	6.5	13.8	21.7	16.2	19.8
27	UV	5.2	21.0	27.8	18.6	14.9
28	PO	9.3	15.6	24.5	18.6	21.7
29	PO	5.1	14.9	23.0	18.0	21.5
Mean		7.21	15.88	24.37	18.61	23.00
S.D.		2.35	2.09	3.28	2.59	4.65
%cv		32.7	13.1	13.5	13.9	20.2
Mean *		6.96	15.65	23.89	18.21	22.31
S.D. *		1.97	1.73	2.05	1.43	2.80
%cv *		28.3	11.0	8.6	7.9	12.6

Numbers in bold are those later removed as outliers (see discussion in text). The second set of summary statistics\* are for the data without the five values in bold.

contribute to some of the TDN variability. With all the TDN data, the agreement among analyses is 13–33% (%cv). Looking at the full data set, the values from analysis 11 are consistently higher than the other analyses for all the samples; these were eliminated. There were only two other individual extremely high values in the entire data set, but they did not indicate a systematic error like that of analysis 11. Statistics are shown in the table for the full set of analyses and for

Table 6  
Dissolved organic nitrogen (DON) data from selected data (after removal of 10 outliers) as  $\mu\text{M N}$

Number	CSW	SBW	DSS	CPN	FHW
1	3.8	6.1	3.2	4.6	13.9
2	6.3	6.6	4.8	6.8	14.6
3	6.1	6.6	5.2	6.9	15.3
4	4.8	4.3	5.6	5.1	14.6
5	6.3	7.8	6.3	6.2	16.4
6	4.6	5.0	1.2	4.0	14.6
7	4.5	4.9	2.7	4.3	13.3
8	4.0	5.7	3.3	4.8	15.6
9	5.9	8.9	8.7	8.9	19.6
10	4.7	5.3	4.2	5.8	14.5
12	4.9	5.9	4.4	5.1	14.9
13	4.7	7.9	7.4	5.4	17.2
14	4.4	5.3	3.8	3.7	13.2
15	4.4	3.5	0.8	6.7	13.0
16	4.2	4.5	2.8	4.0	13.8
17	4.8	6.5	4.7	5.9	16.2
18	1.4	2.0	0.6	1.8	11.3
19	4.6	6.0	5.5	6.2	16.3
20	5.2	6.0	5.0	5.1	15.2
21	4.4	5.5	3.9	4.2	14.1
22	5.4	5.2	3.5	5.4	14.9
23	13.3	4.8	6.9	3.1	8.6
24	5.0	4.8	3.8	5.6	21.3
25	5.5	6.3	5.5	6.9	17.1
26	4.6	3.9	2.2	3.2	12.0
27	3.3	11.1	8.3	5.6	7.1
28	7.4	5.7	5.0	5.6	13.9
29	3.2	5.0	3.5	5.0	13.7
Mean	5.06	5.75	4.39	5.21	14.51
S.D.	1.97	1.73	2.05	1.43	2.80
%cv	38.9	30.0	46.2	27.4	19.3
Range	1.4–13.3	2.0–11.1	0.6–8.7	1.8–8.9	7.1–21.3

DON equals reported individual TDN values minus uniform DIN values from Table 1.

the reduced set removing those five values from analysis 11 (of total 145 reported values, 3.5% were removed). Unlike the DOC comparison, there does not appear to be a serious problem of sporadic gross contamination of ampoules, thus, any outliers may be due to individual analyses in that laboratory or on that analysis date rather than ampoules contaminated in preparation. With the removal of those few outliers, the agreement of the 29 TDN analyses for the five samples ranges from 8% to 28% (bottom of Table 5).

With this slight trimming of data that gave reproducibility for TDN averaging 14%, it is possible to subtract the DIN and calculate the DON in the

samples. Table 6 lists the DON for the 29 analyses (all samples from analysis number 11 removed) calculated by subtracting the DIN values in Table 1 from the TDN. Because the DON value is smaller than TDN, the relative reproducibility (19–46%) is, as expected, not as good as is the TDN reproducibility. Sample DSS had high  $\text{NO}_3^-$  little other DIN and low DON. Because of the large subtraction of the  $\text{NO}_3^-$  and low DON, the reproducibility for this sample was the worst. Sample CSW with low  $\text{NO}_3^-$ , essentially no other DIN and low DON should give better reproducibility (and would if not for one extreme values); sample FHW with moderate DIN and high DON had the best reproducibility. Sample CPN was set up to have close to the same concentrations of  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , and DON. It gave the best reproducibility for TDN, but not very good for DON.

To evaluate the effectiveness of different DON techniques, data were grouped by families of methods.

Table 7  
Analysis of the five samples grouped by the three types of method

Sample	CSW	SBW	DSS	CPN	FHW
HTC					
Mean	6.44	14.67	22.60	17.69	22.58
S.D.	0.33	0.80	1.53	1.08	2.68
%cv	5.1	5.4	6.8	6.1	11.0
Persulfate					
Mean	6.75	15.71	23.93	18.75	22.65
S.D.	1.59	1.67	2.03	2.21	2.05
%cv	23.6	10.6	8.5	11.8	9.0
UV					
Mean	7.99	16.83	25.47	18.64	21.41
S.D.	3.31	2.09	1.56	1.26	4.10
%cv	41.4	12.4	6.1	6.8	19.2
TDN mean	6.96	15.65	23.89	18.21	22.31
HTC					
Mean	4.54	<b>4.77</b>	<b>3.10</b>	4.69	14.78
S.D.	0.33	0.80	1.53	1.08	2.68
Persulfate					
Mean	4.85	5.81	4.43	5.75	14.85
S.D.	1.59	1.67	2.03	2.21	2.05
UV					
Mean	6.09	<b>6.93</b>	<b>5.97</b>	5.64	13.61
S.D.	3.31	2.09	1.56	1.26	4.10
DON mean	5.06	5.75	4.39	5.21	14.51

Values for TDN are listed at the top and for DON at the bottom of the table. Mean values in bold for DON analysis indicates that the UV method gave a statistically higher value than HTC for samples DSS and SBW. No other pairs of means were significantly different from each other at the 95% confidence level.

Table 7 contains TDN and DON means and standard deviations for the five samples grouped by method. Fig. 1 shows comparison for three of the samples for DON. Examining Fig. 1 and DON data in Table 7, it would appear that the HTC methods give lower values and the two wet chemical methods give higher values. Using a *t*-test, the UV methods give higher mean values than the HTC methods for samples DSS and SBW. No other means were significantly different from each other with the two-tailed *t*-test at 95% confidence interval. Since a relatively small number of analyses were done by each group and the variability for each family of methods was large, it is not surprising that more discrimination between methods cannot be seen. Samples DSS and SBW have high  $\text{NO}_3^-$  contents (19 and 10  $\mu\text{M}$ , respectively) and low DON while the other three samples have DON concentrations higher than  $\text{NO}_3^-$ . It is also worth noting that the average %cv for TDN analyses for the HTC methods was 7%, as contrasted to 13% for the persulfate and 17% for the UV methods (Table 7).

A relatively strict deadline, in May 2000, was used for receiving results so that analysis of data could proceed and results could be discussed in the comparative summary among the analysts and in public presentations of comparative data (made at international meetings). A 30th set of results arrived in August. These were performed by HTC analysis using a commercial Antek instrument. Although the data from that analysis were not included in the data analysis above, the laboratory involved in these is included in the authorship of this paper and in Table 2.

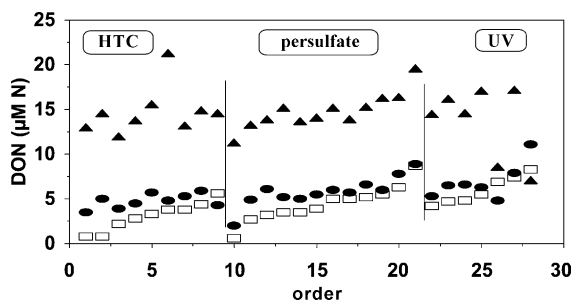


Fig. 1. Calculated dissolved organic nitrogen (DON) concentrations for three of the samples by all analysts with separation by method. Samples are ordered in increasing concentration by each method for sample DSS (open squares); the other samples are SBW (filled circles) and FHW (filled triangles). Note: The order for *x*-axis does not correspond to the same numbers as used in tables.

The TDN values for this set of analyses were similar to the other 29 analyses and the DON values (with same uniform DIN subtractions; CSW=7.1, SBW=5.7, DSS=3.9, CPN=7.4, and FHW=13.7) were within the range of the other 29 analyses. These results are mentioned here because of the importance of the analyzer used (see discussion below).

#### 4. Discussion

The three families of methods (HTC, PO, and UV) differ in chemistry of conversion of TDN and in complexity of analysis. The wet chemical methods entail oxidation of all nitrogen to the highest oxidation state in aqueous medium while the HTC methods use pyrolysis to yield an intermediate gaseous form that is not in the highest oxidation state. The HTC methods are more automatic with less handling while the other two methods involve more manual manipulation and, hence, have more potential for problems from mistakes and contamination. The PO method, with an autoclaving step in separate containers, has the most manipulation of the three. In addition, both the PO and UV methods usually rely on a final  $\text{NO}_2^-$  reduction step with N&N colorimetric analysis, giving them additional avenues for mistakes and variability. As is suggested by the results in Table 4, the variability in this final analysis step probably contributes to the scatter in wet chemical TDN results. A question of importance is whether or not any of the methods is inaccurate because of not recovering all of the TDN as the final analyte.

The suggestion that HTC methods measure higher concentrations of DON than wet chemical methods (Suzuki et al., 1985) is not verified by our extensive comparison of the multiple analyses by three families of methods (UV, PO, and HTC). This result appears to be consistent with Walsh's earlier conclusion (Walsh, 1989) and that of the Seattle workshop (Hedges et al., 1993) that UV, PO, and HTC methods give similar values. All three families of methods measure the same TDN quantity, and each is a method that can give similar results in multiple laboratories. However, it is not reassuring that the variability for TDN analysis is large and the variability for the derived smaller DON value is comparatively even larger. It can be seen in Table 6 that the range of reported

values for DON in the deep ocean sample (DSS) is from 0.6 to 8.7  $\mu\text{M N}$ . This unacceptably large range is similar to that found in the recent literature, observed in the Introduction.

Some experiments were done in the laboratory of the first authors testing DIN species before and after treatments in the PO and UV methods. There was reason to expect the UV methods might be inaccurate since the literature indicated that UV oxidation gave poor yields of specific organic nitrogen compounds (e.g., Solorzano and Sharp, 1980) and since the method in its standard chemical format gave values lower than PO or HTC (Bronk et al., 2000). Our results showed  $\text{NH}_4^+$  remaining after UV treatment but not after persulfate treatment (Table 8). This incomplete oxidation of  $\text{NH}_4^+$  had been noted earlier in our laboratory with inconsistent results from sample to sample (unpublished data). If  $\text{NH}_4^+$  is not fully oxidized and the initial DIN concentration is subtracted from the TDN, then the resultant DON would be low. It is also possible that any  $\text{NH}_4^+$  found in the sample after the UV treatment could be from partial breakdown of DON that was not oxidized completely to  $\text{NO}_3^-$ . In either case, any  $\text{NH}_4^+$  in the samples after UV treatment creates a problem unless measured and compensated for.

UV oxidation can result in incomplete oxidation of  $\text{NO}_2^-$  to  $\text{NO}_3^-$ , perhaps even photoreduction of some  $\text{NO}_3^-$  to  $\text{NO}_2^-$  with UV exposure (Walsh, 1989). In the original presentation of the UV method, Armstrong et al. (1966) indicated that there was photoreduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$ . In analyzing DIN compounds after UV treatment, we have seen  $\text{NO}_2^-$  equal to and higher than the initial sample (Table 8) that would appear to support the idea of photoreduc-

tion. As with  $\text{NH}_4^+$ , there appears to be no remaining  $\text{NO}_2^-$  with the PO method. The final analysis with most applications of the UV method is the measurement of N&N with colorimetry after quantitative reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  with a Cd–Cu amalgam column. Usually, the  $\text{NO}_3^-$  columns are not 100% efficient in the reduction, so a calibration factor is determined with  $\text{NO}_3^-$  standards to assess column efficiency; which often can vary from about 80–95% (usually consistent throughout an analytical run). If the final calculation of N&N is based on a calibrated efficiency factor, an overestimate is made since the  $\text{NO}_2^-$  that was present initially is not subject to the incomplete conversion of  $\text{NO}_3^-$  that is accommodated for with the calibration factor. Several participants in this comparison measured  $\text{NO}_2^-$  and  $\text{NH}_4^+$  after UV treatment to check for completeness of DIN conversion and/or to correct the column efficiency, but others did not (see Table 3). At least one analyst reported that significant blank problems were found when  $\text{H}_2\text{O}_2$  was added, elevating the  $\text{NO}_3^-$  prior to the UV exposure (this analyst did not add  $\text{H}_2\text{O}_2$ ). Because of these variable problems with UV methods, it is not surprising that the %cv for the UV method is greater than that for the groups of PO and HTC analyses (Table 7).

The HTC analyses grouped here as a family of methods are diverse (see Table 3). The column packing and temperature of the combustion tubes varied as well as the method of standardization. One participant indicated that standardization with  $\text{NO}_3^-$  gave higher response than standardization with organic N compounds in his instrument. Another participant indicated incomplete recovery of  $\text{NO}_2^-$ . Even though the overall variability among the HTC analysts was smaller than that from the PO and UV methods, there may be significant differences in the HTC methods that could contribute to variability and ultimately to the HTC method underestimating the TDN. This possibility is being further examined at present.

In comparing results in this exercise, the UV method did not appear to underestimate DON compared to the other two families of methods. This is not consistent with preconceived ideas and earlier literature. In fact, for two of the five samples, the UV method gave significantly higher DON values than did the HTC methods. These two samples (SBW and DSS) are the ones with highest original  $\text{NO}_3^-$  con-

Table 8  
Conversion of DIN species by persulfate oxidation (PO) and UV methods

Method	$\text{NO}_2^-$ before	$\text{NO}_2^-$ after	$\text{NH}_4^+$ before	$\text{NH}_4^+$ after	$\text{NO}_3^-$ before	$\text{NO}_3^-$ after
PO	9.37	0.03	0.23	<0.5	1.43	10.54
PO	3.11	0.03	5.26	<0.5	–	–
PO	0.24	0.02	2.70	<0.5	–	–
UV	0.60	2.99	18.73	0.22	1.81	20.6
UV	0.01	0.27	12.8	6.21	0.01	6.02

Determination of  $\text{NH}_4^+$  after persulfate oxidation has an elevated blank because of contamination in the calibrated acid that is added to neutralize.

centrations, so if there were an overestimate of the final TDN due to photoreduction, this would, at least partially, explain the higher values. Also, standardization problems and problems with  $\text{NO}_2^-$  in HTC analysis could cause the HTC analysis to be low in the high  $\text{NO}_3^-$  samples.

Early experimentation with HTC hybrid instruments found difficulties with complete conversion of some inorganic forms to the final analyte,  $\text{NO}_x$ , in some cases losing some of the N as  $\text{NO}_3^-$  (C. Hopkinson, unpublished data). With improved methods, there is still concern about incomplete recovery of  $\text{NO}_2^-$  (H. Ogawa, unpublished data) although other researchers have found complete recovery of  $\text{NO}_2^-$  (Alvarez-Salgado and Miller, 1998). While this should not be a significant problem with oceanic waters, one of the samples for this comparison (CPN with  $5 \mu\text{M NO}_2^-$ ) was designed to test if HTC methods gave poor recovery. Although the HTC methods gave a lower TDN mean for CPN than the other two families of methods, the difference was not statistically significant.

Looking further at the results of this exercise, it should be recognized that the families of methods were probably not singular methods run in a consistent fashion from lab to lab. There was no attempt at this time to thoroughly compare the different methods in each family. However, from discussions among analysts using HTC methods, it is clear that the oxidation tube chemistry, the temperature of combustion, the gas transfer into the chemiluminescence detector, and the actual detectors varied. The PO and UV methods had some variability in the actual processing of the sample for the oxidation as well as independent analyses of the final analyte, usually,  $\text{NO}_3^-$ . In one PO method, both  $\text{NO}_3^-$  (colorimetry) and  $\text{NO}_x$  (chemiluminescence) were measured with good comparability. In some of the UV methods, the DIN components were measured after UV exposure and an attempt was made to compensate for  $\text{NO}_2^-$  found after the UV treatment. Other UV methods did not routinely carry out the post UV exposure  $\text{NO}_2^-$  and  $\text{NH}_4^+$  analyses (Table 3). The variability in the analyses of N&N among the 12 analysts who reported these data also indicates that an appreciable portion of the TDN variability for PO and UV methods could be just in the measurement of the final analyte; these methods had

an average of 6% and 10% higher cv values than the average HTC methods.

It should also be noted that results received late using a commercial Antek instrument were comparable to the other HTC results. It is worth noting the good results from this one analyst using the Antek instrument (listed in Table 3) after difficulties with this instrument for several years (experience of several of us).

At this point, it is possible to make several important conclusions about DON determination. First, at an international level, fairly good agreement (8–28%) can be found among diverse analysts using the most popular methods to measure TDN. Second, none of the routinely used families of methods (UV, PO, and HTC) is currently obvious for being grossly inaccurate for the determination of DON. Third, contrary to some recent thoughts and literature, UV methods do not necessarily underestimate DON. Fourth, much of the variability in current wet chemical measurements may be due to inaccurate analysis of the final analyte, N&N.

In the Introduction, it was stated that the agreement among 13 analysts in the 1991 Seattle workshop for TDN was in the 9–49% range for the four samples analyzed. Here, we showed agreement with five samples and 29 analysts in the 8–28% range (reinserting the one outlying set of values, this was 13–33%). Although we may claim slight improvement in community analytical capability, it certainly is not much progress in the past decade. In addition, it is disconcerting to see that much of variability may be due to poor ability to measure nitrate.

Even worse than the moderate agreement among multiple analyses for TDN, the ability to determine low levels of DON in diverse DIN backgrounds is clearly not adequate, on the order of 19–46% variability, especially bad for deep ocean samples with high  $\text{NO}_3^-$  background and low DON. For the comparison in this paper, a single set of DIN values was used to calculate DON; if individual DIN values from each analyst's laboratory had been subtracted from the measured TDN values, the agreement for DON surely would have been even poorer. In the Introduction, it was stated that perusal of some recent literature showed variability for DON in deep water from 2 to  $8 \mu\text{M N}$ . Our comparison, with 29 analyses, showed a variability of 0.6–8.7  $\mu\text{M N}$ .

Although it is desirable to quickly solve the analytical problems of DON analyses, we are not there yet. An open evaluation of an exercise like this one will hopefully stimulate experimentation in individual laboratories that will move us as a community toward better analyses. Clearly, more thorough evaluation of the actual chemistry of individual applications of the UV and PO methods is needed. More accurate DIN analyses are needed both for determination of the final analyte and for subtraction of the initial DIN. Also, better direct comparison of HTC methods is needed. This latter need is being met by an effort currently underway by several of the authors of this paper.

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### References

- Alvarez-Salgado, X.A., Miller, A.E.J., 1998. Simultaneous determination of dissolved organic carbon and total dissolved nitrogen in seawater by high temperature catalytic oxidation: conditions for precise shipboard measurements. *Mar. Chem.* 62, 325–333.
- Ammann, A.A., Ruttimann, T.B., Burgi, F., 2000. Simultaneous determination of TOC and TN in surface and wastewater by optimised high temperature catalytic combustion. *Water Res.* 34, 3573–3579.
- Armstrong, F.A.J., Tibbitts, S., 1968. Photochemical combustion of organic matter in sea water for nitrogen, phosphorus, and carbon determination. *J. Mar. Biol. Assoc. U. K.* 48, 143–152.
- Armstrong, F.A.J., Williams, P.M., Strickland, J.D.H., 1966. Photo-oxidation of organic matter in sea water by ultraviolet radiation, analytical and other applications. *Nature* 211, 481–483.
- Bronk, D.A., Lomas, M.W., Glibert, P.M., Schukert, K.J., Sander-son, M.P., 2000. Total dissolved nitrogen analysis: comparisons between persulfate, UV, and high temperature oxidation meth-ods. *Mar. Chem.* 69, 163–178.
- Burdige, D.J., Zheng, S., 1998. The biogeochemical cycling of dissolved organic nitrogen in estuarine sediments. *Limnol. Oce-anogr.* 43, 1796–1813.
- Cornell, S., Rendell, A., Jickells, T., 1995. Atmospheric inputs of dissolved organic nitrogen to the oceans. *Nature* 376, 243–246.
- D’Elia, C.F., Steudler, P.A., Corwin, N., 1977. Determination of total nitrogen in aqueous samples using persulfate digestion. *Limnol. Oceanogr.* 22, 760–764.
- Garside, C., 1982. A chemiluminescent technique for the determi-nation of nanomolar concentrations of nitrate and nitrite in sea-water. *Mar. Chem.* 11, 159–167.
- Hansell, D.A., 1993. Results and observations from the measure-ment of DOC and DON in seawater using a high-temperature catalytic oxidation technique. *Mar. Chem.* 41, 195–202.
- Hansell, D.A., Waterhouse, T.Y., 1997. Controls on the distribution of organic carbon and nitrogen in the eastern Pacific Ocean. *Deep-Sea Res., Part I* 44, 843–857.
- Hedges, J.I., Bergamaschi, B.A., Benner, R., 1993. Comparative analyses of DOC and DON in natural waters. *Mar. Chem.* 41, 121–134.
- Hopkinson, C., Cifuentes, C., et al., 1993. DON subgroup report. *Mar. Chem.* 41, 23–36.
- Kahler, P., Bjornsen, P.K., Lochte, K., Antia, A., 1997. Dissolved organic matter and its utilization by bacteria during spring in the Southern Ocean. *Deep-Sea Res., Part II* 44, 341–353.
- Koike, I., Tupas, L., 1993. Total dissolved nitrogen in the Northern North Pacific assessed by a high-temperature combustion meth-od. *Mar. Chem.* 41, 209–214.
- Koroleff, F., 1976. Total and organic nitrogen. In: Grasshoff, K. (Ed.), *Methods of Seawater Analysis*. Verlag Chemie, Wein-heim, Germany, pp. 167–181.
- Koroleff, F., 1983. Total and organic nitrogen. In: Grasshoff, K., Ehrhardt, M., Kremling, K. (Eds.), *Methods for Seawater Anal-ysis*. Verlag Chemie, Weinheim, Germany, pp. 162–168.
- Lopez-Vernoni, D., Cifuentes, L.A., 1995. Transport of dissolved organic nitrogen in Mississippi River plume and Texas–Loui-siana continental shelf near-surface waters. *Estuaries* 17, 796–808.
- Merriam, J., McDowell, W.H., Currie, W.S., 1996. A high-temper-ature catalytic oxidation technique for determining total dis-solved nitrogen. *J. Soil Sci. Soc. Am.* 60, 1050–1055.
- Ogawa, H., Fukuda, R., Koike, I., 1999. Vertical distributions of dissolved organic carbon and nitrogen in the Southern Ocean. *Deep-Sea Res., Part I* 46, 1809–1826.
- Putter, A.F.R., 1909. *Die Ernährung der Wassertiere und der Stoff haushalt der Gewässer*, Jena, Fischer.
- Raimbault, P., Pouvesle, W., Diaz, F., Garcia, N., Sempere, R., 1999. Wet-oxidation and automated colorimetry for simultane-ous determination of organic carbon, nitrogen, and phosphorus dissolved in seawater. *Mar. Chem.* 66, 161–169.
- Scudlark, J.R., Russell, K.M., Galloway, J.N., Church, T.M., Keene, W.C., 1998. Organic nitrogen in precipitation at the mid-Atlan-tic U.S. coast—methods evaluation and preliminary measure-ments. *Atmos. Environ.* 32, 1719–1728.
- Sharp, J.H., 1997. Marine dissolved organic carbon: are the older values correct? *Mar. Chem.* 56, 265–277.
- Sharp, J.H., Carlson, C.A., Peltzer, E.T., Castle-Ward, D.M., Sav-idge, K.B., Rinker, K.R., 2002. Final dissolved organic carbon broad community intercalibration and preliminary use of DOC reference materials. *Mar. Chem.* 77, 239–253.

- Solorzano, L., Sharp, J.H., 1980. Determination of total dissolved nitrogen in natural waters. *Limnol. Oceanogr.* 25, 751–754.
- Suzuki, Y., 1993. On the measurement of DOC and DON in seawater. *Mar. Chem.* 42, 287–288.
- Suzuki, Y., Sugimura, Y., Itoh, T., 1985. A catalytic oxidation method for the determination of total nitrogen dissolved in seawater. *Mar. Chem.* 16, 83–97.
- Walsh, T.W., 1989. Total dissolved nitrogen in seawater: a new high temperature combustion method and comparison to photo-oxidation. *Mar. Chem.* 26, 295–311.
- Wheeler, P.A., Watkins, J.M., Hansing, R.L., 1997. Nutrients, organic carbon and organic nitrogen in upper water column of the Arctic Ocean: implications for the sources of dissolved organic carbon. *Deep-Sea Res., Part II* 44, 1571–1592.