5.17 Nutrients of sampled water

(1) Personnel (*: Leg-1, **: Leg-2, ***: Leg-1+2)

Kunio Yoneyama*	(JAMSTEC)	- Principal Investigator (Leg-1)
Masaki Katsumata***	(JAMSTEC)	- Principal Investigator (Leg-2)
Masanori Enoki*	(MWJ)	- Operator (Leg-1)
Yasuhiro Arii**	(MWJ)	- Operator (Leg-2)

(2) Objectives

The vertical and horizontal distributions of the nutrients are one of the most important factors on the primary production. During this cruise nutrient measurements will give us the important information on the mechanism of the primary production or seawater circulation.

(3) Methods

Nutrient analysis was performed on the BL-Tech QUAATRO system. The laboratory temperature was maintained between 23-25 deg C.

The analytical methods of the nutrients, nitrate, nitrite, silicate and phosphate, during this cruise were same as the methods used in Kawano et al. (2009).

a. Measured Parameters

Nitrate + nitrite and nitrite were analyzed according to the modification method of Grasshoff (1970). The sample nitrate was reduced to nitrite in a cadmium tube inside of which was coated with metallic copper. The sample streamed with its equivalent nitrite was treated with an acidic, sulfanilamide reagent and the nitrite forms nitrous acid which reacted with the sulfanilamide to produce a diazonium ion. N-1-Naphthylethylene-diamine added to the sample stream then coupled with the diazonium ion to produce a red, azo dye. With reduction of the nitrate to nitrite, both nitrate and nitrite reacted and were measured; without reduction, only nitrite reacted. Thus, for the nitrite analysis, no reduction was performed and the alkaline buffer was not necessary. Nitrate was computed by difference.

Absorbance of 550 nm by azo dye in analysis is measured using a 1 cm length cell for nitrate and 3 cm length cell for nitrite.

The silicate method was analogous to that described for phosphate. The method used was essentially that of Grasshoff et al. (1983), wherein silicomolybdic acid was first formed from the silicate in the sample and added molybdic acid; then the silicomolybdic acid was reduced to silicomolybdous acid, or "molybdenum blue" using ascorbic acid as the reductant.

Absorbance of 630 nm by silicomolybdous acid in analysis is measured using a 1 cm length cell.

The phosphate analysis was a modification of the procedure of Murphy and Riley (1962). Molybdic acid was added to the seawater sample to form phosphomolybdic acid which was in turn reduced to phosphomolybdous acid using L-ascorbic acid as the reductant.

Absorbance of 880 nm by phosphomolybdous acid in analysis is measured using a 1 cm length cell.

b. Nutrients Standard

Specifications

For nitrate standard, “potassium nitrate 99.995 Suprapur®” provided by Merck, CAS No.: 7757-91-1, was used.

For nitrite standard, “sodium nitrate” provided by Wako, CAS No.: 7632-00-0, was used. The assay of nitrite salts was determined according JIS K8019 were 98.31%. We used that value to adjust the weights taken.

For phosphate standard, “potassium dihydrogen phosphate anhydrous 99.995 Suprapur®” provided by Merck, CAS No.: 7778-77-0, was used.

For the silicate standard, we use “Silicon standard solution SiO_2 in NaOH 0.5 mol/l CertiPUR®” provided by Merck, CAS No.: 1310-73-2, of which lot number HC097572 was used. The silicate concentration was certified by NIST-SRM3150 with the uncertainty of 0.5 %. Factor of HC097572 was signed 1.000, however we reassigned the factor as 0.976 from the result of comparison among HC074650 and RMNS in MR11-E02 cruise.

Ultra pure water (Milli-Q) freshly drawn was used for preparation of reagent, standard solutions and for measurement of reagent and system blanks.

Concentrations of nutrients for A, B and C standards

Concentrations of nutrients for A, B and C standards (working standards) were set as shown in Table 5.17.1 Then the actual concentration of nutrients in each fresh standard was calculated based on the ambient temperature, solution temperature and determined factors of volumetric laboratory wares.

The calibration curves for each run were obtained using 4 levels working standards, C-1, C-2, C-3, and C-4.

Table 5.17.1 Nominal concentrations of nutrients for A, B and C standards.

	A	B	C-1	C-2	C-3	C-4
Nitrate (μmol/l)	22000	900	0.05	9.4	28.1	46.9
Nitrite (μmol/l)	4000	40	0.01	0.4	1.2(0.8)	1.9(1.6)
Silicate (μmol/l)	36000	1385	1.39	15.2	42.8	70.6
Phosphate (μmol/l)	3000	60	0.05	0.7	1.8	3.1

Value in parentheses was used to calibration curve for Cast 001-017.

c. Sampling Procedures

Sampling of nutrients followed that oxygen and pH. Samples were drawn into two of virgin 10 ml polyacrylates vials without sample drawing tubes. These were rinsed three times before filling and vials were capped immediately after the drawing. The vials were put into water bath adjusted to ambient temperature, 24 ± 1 deg. C, in about 30 minutes before use to stabilize the temperature of samples. The samples of bottle 15, 21 and 20 (or 19) were measured in replicate and the rest were measured in single on each sample run.

No transfer was made and the vials were set an auto sampler tray directly. Samples were analyzed after collection basically within 24 hours.

Sets of 4 different concentrations for nitrate, nitrite, silicate, phosphate of the shipboard standards were analyzed at beginning and end of each group of analysis. The standard solutions of highest concentration were measured every 10 - 12 samples and were used to evaluate precision of nutrients analysis during the cruise. We also used reference material for nutrients in seawater, RMNS (KANSO Co., Ltd., Lot BT), for every 3 runs to secure comparability on nutrient analysis throughout the cruise. We used same serial RMNS for 6 days.

d. Low Nutrients Sea Water (LNSW)

Surface water having low nutrient concentration was taken and filtered using 0.45 μm pore size membrane filter. This water was stored in 20 liter cubitainer with paper box. The concentrations of nutrient of this water were measured carefully in January 2011.

(4) Results

Analytical precisions in this cruise Leg1 were 0.14% for nitrate, 0.22% for nitrite, 0.15% for silicate, 0.25% for phosphate in terms of median of precision, respectively. Analytical precisions in Leg2 were 0.09% for nitrate, 0.11% for nitrite, 0.11% for silicate, 0.17% for phosphate in terms of median of precision, respectively. Results of analytical precisions for nitrate, nitrite, silicate and phosphate are shown in Table 5.17.4.1 and Table 5.17.4.2 for the cast's comparability.

Results of RMNS analysis are shown in Table 5.17.4.3 and Table 5.17.4.4 for the cast's comparability.

Table 5.17.4.1 Summary of precision based on the analyses at Leg1.

	Nitrate CV %	Nitrite CV %	Silicate CV %	Phosphate CV %
Median	0.14	0.22	0.15	0.25
Mean	0.14	0.22	0.14	0.26
Maximum	0.27	0.45	0.23	0.53
Minimum	0.06	0.07	0.04	0.06
N	26	26	26	26

Table 5.17.4.2 Summary of precision based on the analyses at Leg2.

	Nitrate CV %	Nitrite CV %	Silicate CV %	Phosphate CV %
Median	0.09	0.11	0.11	0.17
Mean	0.10	0.11	0.10	0.16
Maximum	0.20	0.22	0.18	0.26
Minimum	0.03	0.04	0.02	0.07
N	29	29	29	29

Table 5.17.4.3 Results of RMNS Lot BT analysis in this cruise Leg1.

Date(UTC)	Serial	Cast	Nitrate (μmol/kg)	Nitrite (μmol/kg)	Silicate (μmol/kg)	Phosphate (μmol/kg)
30 Sep	1977	001	18.18	0.46	40.60	1.318
1 Oct	1364	003,005	18.11	0.45	40.82	1.320
1 Oct	1364	007,009	18.17	0.46	40.95	1.291
2 Oct	1364	011,013,015,017	18.21	0.46	40.93	1.309
3 Oct	1364	019,021,023,025	18.21	0.45	40.92	1.307
4 Oct	510	027,029,031,033	18.26	0.46	41.07	1.321
5 Oct	510	035,037,039,041	18.13	0.46	40.66	1.302
6 Oct	510	043,045,047,049	18.22	0.47	40.91	1.320
7 Oct	789	051,053,055,057	18.21	0.46	40.98	1.318
8 Oct	789	059,061,063,065	18.22	0.46	40.72	1.320
9 Oct	789	067,069,071,073	18.18	0.46	40.74	1.302
10 Oct	1314	075,077,079,081	18.19	0.46	40.94	1.316
11 Oct	1314	083,085,087,089	18.22	0.46	40.88	1.313
12 Oct	1314	091,093,095,097	18.19	0.46	40.89	1.316
13 Oct	1035	099,101,103,105	18.15	0.48	40.91	1.318
14 Oct	1035	107,109.111.113	18.16	0.47	40.78	1.339
15 Oct	1035	115,117,119,121	18.33	0.45	41.00	1.319
16 Oct	252	123,125,127,129	18.23	0.45	40.78	1.329
17 Oct	252	131,133,135,137	18.17	0.47	40.67	1.344
18 Oct	252	139,141,143,145	18.15	0.47	40.72	1.343
19 Oct	716	147,149,151,153	18.16	0.46	40.78	1.349
20 Oct	716	155,157,159,161	18.19	0.48	40.62	1.327
21 Oct	716	163,165,167,169	18.14	0.47	40.47	1.299
22 Oct	1879	171,173,175,177	18.15	0.47	40.67	1.311
23 Oct	1879	179,181,183,185	18.18	0.46	40.80	1.308
24 Oct	1879	187,189,191,193	18.40	0.46	40.57	1.311
		Median	18.18	0.46	40.79	1.318
		S.D.	±0.06	±0.01	±0.15	±0.014

Table 5.17.4.4 Results of RMNS Lot BT analysis in this cruise Leg2.

Date(UTC)	Serial	Cast	Nitrate (μmol/kg)	Nitrite (μmol/kg)	Silicate (μmol/kg)	Phosphate (μmol/kg)
31 Oct	739	194,196	18.09	0.46	40.53	1.313
1 Nov	739	198,200,202,204	18.17	0.46	40.80	1.332
2 Nov	739	206,208,210,212	18.16	0.46	40.76	1.313
3 Nov	1080	214,216,218,220	18.17	0.45	40.73	1.314
4 Nov	1080	222,224,226,228	18.20	0.46	40.77	1.318
5 Nov	1080	230,232,234,236	18.23	0.46	40.81	1.318
6 Nov	1532	238,240,242,244	18.21	0.46	40.95	1.316
7 Nov	1532	246,248,250,252	18.22	0.45	40.76	1.324
8 Nov	1532	254,256,258,260	18.21	0.45	40.79	1.318
9 Nov	1429	262,264,266,268	18.24	0.45	40.73	1.332
10 Nov	1429	270,272,274,276	18.24	0.46	40.81	1.330
11 Nov	1429	278,280,282,284	18.23	0.47	41.01	1.321
12 Nov	1629	286,288,290,292	18.22	0.46	40.78	1.312
13 Nov	1629	294,296,298,300	18.14	0.46	40.80	1.309
14 Nov	1629	302,304,306,308	18.14	0.46	40.68	1.295
15 Nov	1018	310,312,314,316	18.25	0.46	40.97	1.315
16 Nov	1018	318,320,322,324	18.23	0.46	40.79	1.326
17 Nov	1018	326,328,330,332	18.16	0.46	40.62	1.327
18 Nov	0877	334,336,338,340	18.07	0.46	40.56	1.319
19 Nov	0877	342,344,346,348	18.30	0.46	40.87	1.327
20 Nov	0877	350,352,354,356	18.25	0.47	40.86	1.323
21 Nov	0430	358,360,362,364	18.28	0.46	40.89	1.328
22 Nov	0430	366,368,370,372	18.19	0.47	40.70	1.322
23 Nov	0430	374,376,378,380	18.28	0.46	40.84	1.325
24 Nov	0440	382,384,386,388	18.26	0.47	40.86	1.336
25 Nov	0440	390,392,394,396	18.27	0.47	40.87	1.330
26 Nov	0440	398,400,402,404	18.31	0.47	40.90	1.314
27 Nov	0491	406,408,410,412	18.26	0.46	40.87	1.330
28 Nov	0491	414,416,418,420	18.18	0.45	40.91	1.326
		Median	18.22	0.46	40.80	1.322
		S.D.	±0.06	±0.01	±0.11	±0.009

(5) Data Archive

All data will be submitted to JAMSTEC Data Management Office (DMO) and is currently under its control.

(6) Reference

Grasshoff, K. (1970), Technicon paper, 691-57.

Grasshoff, K., Ehrhardt, M., Kremling K. et al. (1983), Methods of seawater analysis. 2nd rev. Weinheim: Verlag Chemie, Germany, West.

Kawano, T., Uchida, H. and Doi, T. WHP P01, P14 REVISIT DATA BOOK, (Ryoin Co., Ltd., Yokohama, 2009).

Murphy, J., and Riley, J.P. (1962), Analytica chim. Acta 27, 31-36.