

Chemical Results from the May 2003 NPEO Project

Water sampling procedure

The aircraft (Twin Otter) sampling approach used successfully in 2001 and 2002 was undertaken to reoccupy the five NPEO 2000 hydrocast stations. For details regarding the sampling approach, please refer to the 2001 chemical data report. The five stations form a transect extending from near the shelf break off Alert (Ellesmere Island, Canada) to the North Pole (Fig. 1).

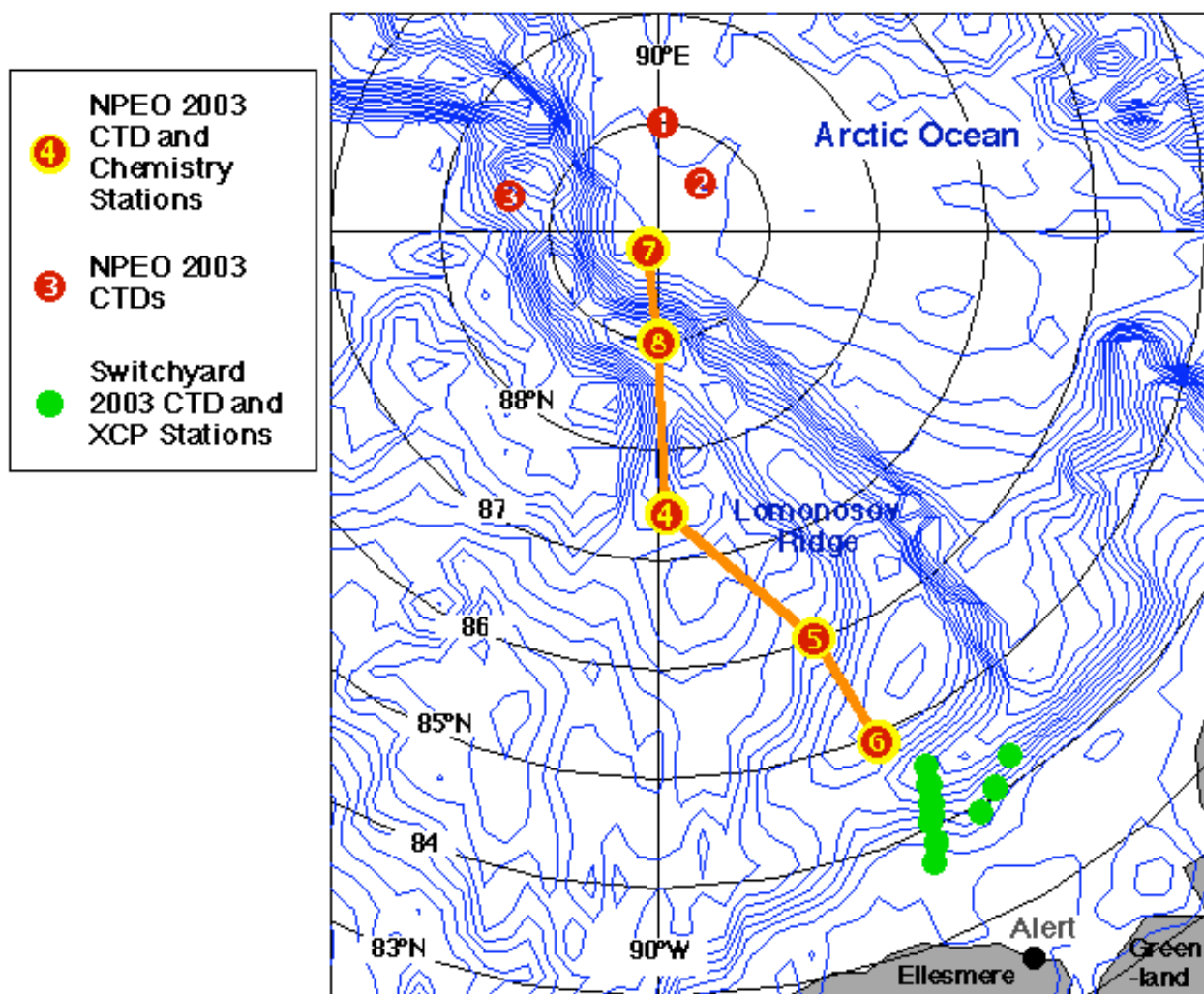


Fig. 1. Station locations: The numbers indicate 2003 CTD cast number. Casts 4-8 correspond to 2000 stations 4-6, 1 and 2 respectively. Bathymetry is from Jacobsson et al., 2000. The Sitchyard stations were part of a project lead by M. Steele carried out by helicopter over the same time as the NPEO work.

Kelly Falkner and Jamie Morison carried out the fieldwork with assistance from Borek Air pilot Jim Haffey and co-pilot Dave Hanberg. Alert served as the base camp and support for the project was provided by logistics coordinator Andy Hieberg and Borek Air engineer Paul Pitzner. It is noted that three hydrocasts without water sampling were made from the Borneo base camp by Jamie Morison just prior to the Alert based work. Those data are not presented here.

Generally, the casts were made through fairly smooth, snow covered ice that was 1-2 m thick with the exception of station 4 where it was 3.3 m thick. Ice conditions are of course selected for suitability of landing the aircraft and expediency of science operations. Station 4 was the first station at which we worked with this team of pilots. While quite safe for landing, the thick ice was near the limit of our auger lengths and so drilling was cumbersome. Conducting casts though a longer hole poses greater risks and difficulties with lowered equipment. Subsequent sites with thinner ice posed much more straightforward conditions for operations. Temperatures ranged from -15 to -10 deg C and wind was variable but generally less than 15 knots throughout the mission.

Seawater samples were obtained using the generator-powered portable winch to cast 4 1.5-L Niskins at a time. At station 5 we experienced trouble with our winch which failed to pay out line smoothly mid-way in the cast and we ended up casting only three bottles. The custom constructed Niskins (General Oceanics model 1010 with 8" extension and modified plunger) were mounted on a small diameter Kevlar line, with the deepest one mounted about 1 meter above an internally recording Seabird SBE19 CTD-O₂ system. Upon lowering the shallowest bottle to 5 m, a messenger was dropped immediately. Upon retrieval, each Niskin was transferred to a rack in the heated aircraft and samples were drawn immediately. First, dissolved O₂ samples were drawn directly into calibrated flasks and were preserved with the usual reagents (MnCl₂ and NaOH/NaI) immediately upon collection following standard procedures (Dickson, 1994). Unfortunately, several flasks were lost to thermal shock during sample collection. Until the problem was recognized, the flasks sat in the pathway of the heat ducting from the cockpit. They were filled with seawater at the freezing point and reagents added. When the flasks were shaken to mix the reagents a clean shock fracture would develop around the base of the flask and the contents would be lost. Fortunately I worked over a plastic Tuffbin box that contained the mess and so spared the aircraft cabin. Redirecting the heatstream from the cockpit solved the problem. Salinity samples were collected into 125-ml glass bottles the caps of which were fitted with conical polyethylene inserts. Oxygen isotope samples were collected into similar containers of smaller volume (20-ml). Barium samples were collected into 20-ml polyethylene scintillation vials. Nutrient samples were collected into 60-ml polyethylene bottles and stored frozen until analysis.

At station 5, the nutrient samples were inadvertently left on the ice. We conducted station 6 the next morning and then returned to Alert while the pilots set out again to set up a fuel cache. They also took it upon themselves to try and recover the lost samples and were successful against the "needle in a haystack" odds. The pilots relocated the piece of ice by applying observed drift rate and direction they determined at station 6 to the coordinates of station 5. In approaching the targeted location, the pilot recognized the pattern of ridging from the previous's day's search for a

suitable landing site. We had apparently run over the frozen samples when taxiing for take-off. The Zip-lock bag that the samples were in was destroyed and the bottles were slightly crushed but intact. The incident in no way compromised the samples but does demonstrate the incredible level of commitment of the people that we work with in the north!

Analytical procedures

Dissolved O₂ was analyzed by Winkler titration back at Alert within 24 hours of sample collection. The samples were allowed to come to room temperature, initially titrated rapidly to avoid loss of iodine and then carefully titrated in a light box to a starch indicator (visual) endpoint. Given the difficulties of securing the groundglass stopcocks in the field, inevitably some of the reagents escaped above the seal and precipitated. It is important for good precision to rinse this material out of the top of the flasks before they are opened for titration. Failure to do this contributed to poor precision of early replicates and inaccuracies. Based on replicates, it appears that a precision on the order of 1% is attainable under these circumstances. Given the learning curve, only two samples can be taken as trustworthy representatives of the environment. The results of replicate sample analyses are reported as 1 standard deviation in data Table 1. Accuracy was checked by running the reagents before and after the mission under more controlled circumstances in the laboratory at OSU using whole-flask titrations and amperometric end-point detection using a PC-controlled titrator (Culberson and Huang, 1987). The actual apparatus was adapted to PC's following Knapp et al. (1989).

Bottle salinities were analyzed using a Guildline Autosal standardized with IAPSO standard seawater. Precision for these determinations was 0.002 practical salinity units. Analyses of the frozen phosphate, silicic acid, nitrate, nitrite and ammonia samples were performed at OSU using a hybrid Alpkem RFA 300 and Technicon AA-II (AutoAnalyzer II) — based system and the JGOFS/WOCE suggested nutrient protocols (Gordon et al., 1994). The silicic acid, nitrate plus nitrite and nitrite channels were RFA-based, the phosphate and ammonium channels, AA-II. The samples were thawed and immediately analyzed for all nutrients. After standing overnight in the dark, the samples were reanalyzed for silicic acid to avoid polymerization effects (Gordon et al., 1994). The short-term precision of the nutrient analyses is typically: Silicic acid, 0.2%; phosphate, 0.4%; nitrate 0.3%; nitrite, 0.02 μM; and ammonium, 0.03 μM. However, the inter-cruise reproducibility achieved during the WOCE Hydrographic Program, Pacific One-Time Survey was for silicic acid, phosphate and nitrate, respectively, ca. 1%, 2% and 1% (unpublished data, Ross et al., 2000). The results of replicate sample analyses are reported as 1 standard deviation in data Table 1.

Barium was determined by isotope-dilution using an VG Thermo Excel inductively coupled quadrupole mass spectrometer as previously described with minor modifications (Falkner et al., 1994). Precision is estimated to be 3% for this suite of Ba measurements. Oxygen isotopes were analyzed by the CO₂ equilibration method on the COAS Finnegan Mat 251. Results are reported in ‰ units relative to VSMOW and 1-sigma precision is estimated to be +/- 0.03. Again for both Ba and oxygen isotopes, results of replicate sample analyses are reported as 1 standard deviation in data Table 1.

Table 1: NPEO 2003 Hydrochemical Data (1st of 2 pages)

STN	CTD cast	Location		Time begin		CTD Downcast					CTD Upcast		
						Target depth	Depth	Temp (ITS90)	Sal (PSS78)	O2	Depth	Temp (ITS90)	Sal (PSS78)
No.	No.	latitude	longitude	(UTC)	date	m	m	degC		ml/L	m	degC	
1	7	89°49.0'N	113°0.00'W	18:38	9May03	5	1.6	-1.703	31.263	8.65	0.9	-1.724	31.263
1	7	89°49.0'N	113°0.00'W	18:38	9May03	60	61.5	-1.747	33.399	7.74	59.8	-1.744	33.399
1	7	89°49.0'N	113°0.00'W	18:38	9May03	125	126.1	-1.188	34.256	7.37	124.8	-1.268	34.256
1	7	89°49.0'N	113°0.00'W	18:38	9May03	300*	300.7	1.420	34.871	6.94	293.1	1.367	34.871
2	8	88°59.0'N	88°59.0'W	22:27	9May03	5	1.8	-1.725	31.385	8.65	1.5	-1.732	31.385
2	8	88°59.0'N	88°59.0'W	22:27	9May03	60	59.7	-1.682	32.805	7.40	58.2	-1.684	32.805
2	8	88°59.0'N	88°59.0'W	22:27	9May03	125	125.8	-1.110	34.234	7.19	119.6	-1.177	34.234
2	8	88°59.0'N	88°59.0'W	22:27	9May03	300	305.0	0.884	34.842	6.89	298.3	0.910	34.842
4	4	87°24.3'N	87°52.3'W	22:38	6May03	5	2.7	-1.762	31.744	8.51	3.6	-1.748	31.744
4	4	87°24.3'N	87°52.3'W	22:38	6May03	50	66.9	-1.739	31.735	8.52	57.3	-1.744	31.735
4	4	87°24.3'N	87°52.3'W	22:38	6May03	105	98.5	-1.722	33.389	7.25	99.7	-1.724	33.389
4	4	87°24.3'N	87°52.3'W	22:38	6May03	230	211.6	-0.039	34.564	6.64	211.5	-0.054	34.564
5	5	85°59.8'N	68°48.0'W	17:42	7May03	5	1.7	-1.721	31.541	8.64	1.5	-1.741	31.541
5	5	85°59.8'N	68°48.0'W	17:42	7May03	60	67.3	-1.733	31.606	8.50	62.6	-1.739	31.606
5	5	85°59.8'N	68°48.0'W	17:42	7May03	125	126.5	-1.625	33.801	6.93	126.6	-1.632	33.801
6	6	84°53.5'N	66°29.7'W	15:25	8May03	5	1.3	-1.710	31.444	8.69	0.9	-1.735	31.444
6	6	84°53.5'N	66°29.7'W	15:25	8May03	60	62.2	-1.714	31.436	8.59	57.4	-1.722	31.436
6	6	84°53.5'N	66°29.7'W	15:25	8May03	125	125.8	-1.507	33.791	6.45	122.8	-1.520	33.791
6	6	84°53.5'N	66°29.7'W	15:25	8May03	300	304.7	0.423	34.813	6.16	296.2	0.405	34.813

Table 1: NPEO 2003 Hydrochemical Data (2nd of 2 pages)

bottle samples

STN	target depth	Sal (PSS78)	O2	Ba	del18O	PO4	NO3+N O2	NO2	NH4	Si								
No.	m		ml/L	nM	SMOW	μM	μM	μM	μM	μM								
1	5	31.263		60.2	-3.76	0.728	1.71	0.027	0.043	8.57								
1	60	33.399		48.1	-1.50	0.487	4.27	0.021	0.043	6.04								
1	125	34.256		42.8	-0.30	0.670	8.12	0.010	0.053	5.18								
1	300*	34.871	7.09	0.13	42.2	0.27	0.846	11.71	0.004	0.043	6.20							
2	5	31.385		61.3	0.7	-3.57	0.795	1.70	0.007	0.063	8.49							
2	60	32.805		56.4	0.4	-1.80	1.109	8.17	0.011	0.063	16.51							
2	125	34.234		44.5	0.8	-0.29	0.759	8.74	0.019	0.092	5.99							
2	300	34.842	7.12	0.07	44.0	0.19	0.878	11.78	0.003	0.072	6.31							
4	5	31.744		9.72*	62.8	1.0	-3.01	1.018	1.65	0.017	0.249	9.40						
4	50	31.730	0.008	9.30*	63.4		-2.87	1.018	1.75	0.020	0.239	9.43						
4	105	33.389		7.76*	59.7		-1.44	0.03	0.877	7.67	0.00	0.249	12.22					
4	230	34.564		7.55*	42.7		-0.05		0.883	11.38	0.003	0.239	8.89					
5	5	31.541		9.36*	59.8	2.5	-2.75		0.936	1.08		0.015	0.169	6.79				
5	60	31.606		9.46*	62.1		-3.08	0.03	0.907	1.49		0.019	0.120	7.91				
5	125	33.801		7.44*	50.7		-1.10		0.858	0.003	8.51	0.08	0.014	0.011	0.150	0.028	11.75	0.06
6	5	31.444		9.53*	0.03	58.0		-2.43	0.912	0.67		0.021	0.141	4.78				
6	60	31.436	0.000	9.64*	56.0	0.3	-2.45		0.918	0.77		0.025	0.180	4.80				
6	125	33.791	0.001	7.27*	51.7		-1.03		1.071	10.25		0.009	0.190	17.08				
6	300	34.813			41.4		0.12	0.02	0.937	12.57		0.003	0.180	8.81				

*Not trustworthy; see text

Results

The CTD depths were assigned to individual Niskin bottles by matching the bottle salinity to a linearly interpolated CTD salinity near the target depth. Generally, salinities bracketing or equal to measured bottle values were observed in both the up and down CTD-casts near the target bottle depths. This lends confidence that the Niskins were tripped correctly and did not leak and there appeared to be no problems with samples freezing in the Niskins. Near the surface, the bottles apparently captured waters shallower than the intended 5 meters by several meters. Bottle dissolved O₂'s were about 1 ml/L above saturation values. This may have been a function of insufficient Niskin flushing since the surface Niskin was hung last, lowered at a slow rate and tripped first. Moreover the long Niskins integrate approximately a meter and so exact matching to sensor properties at a single depth, particularly where salinity and dissolved oxygen gradients are large, is imprecise.

Temperatures and oxygens were also linearly interpolated from the CTD casts according to measured bottle salinity. Differences in the temperature and salinity combinations between the up and down casts can be ascribed to a range of phenomena such as disturbance of the water column by the wake of the package on the upcast, passage of internal waves or fronts and mixing induced by instabilities in the water column. For example, small inversions in density signaled active mixing in the vicinity of the deepest water sample at station 1 and probably is the source of the temperature differences in the up and down cast assignments.

References

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