Chemical Results from the May 2005 NPEO Project

Water sampling procedure

The aircraft (Twin Otter) sampling approach used successfully in 2001–2004 was undertaken to occupy a transect along 90˚ longitude during 25-28 April 2005 (Fig. 1). The stations along the east longitude sampled remote areas of the Amundsen Basin for the first time during the NPEO program. Stations in the vicinity of the Pole and at west longitudes are effectively reoccupations of previous NPEO stations from 200, 2001 and 2004. For details regarding the sampling approach, please refer to the 2001 chemical data report.

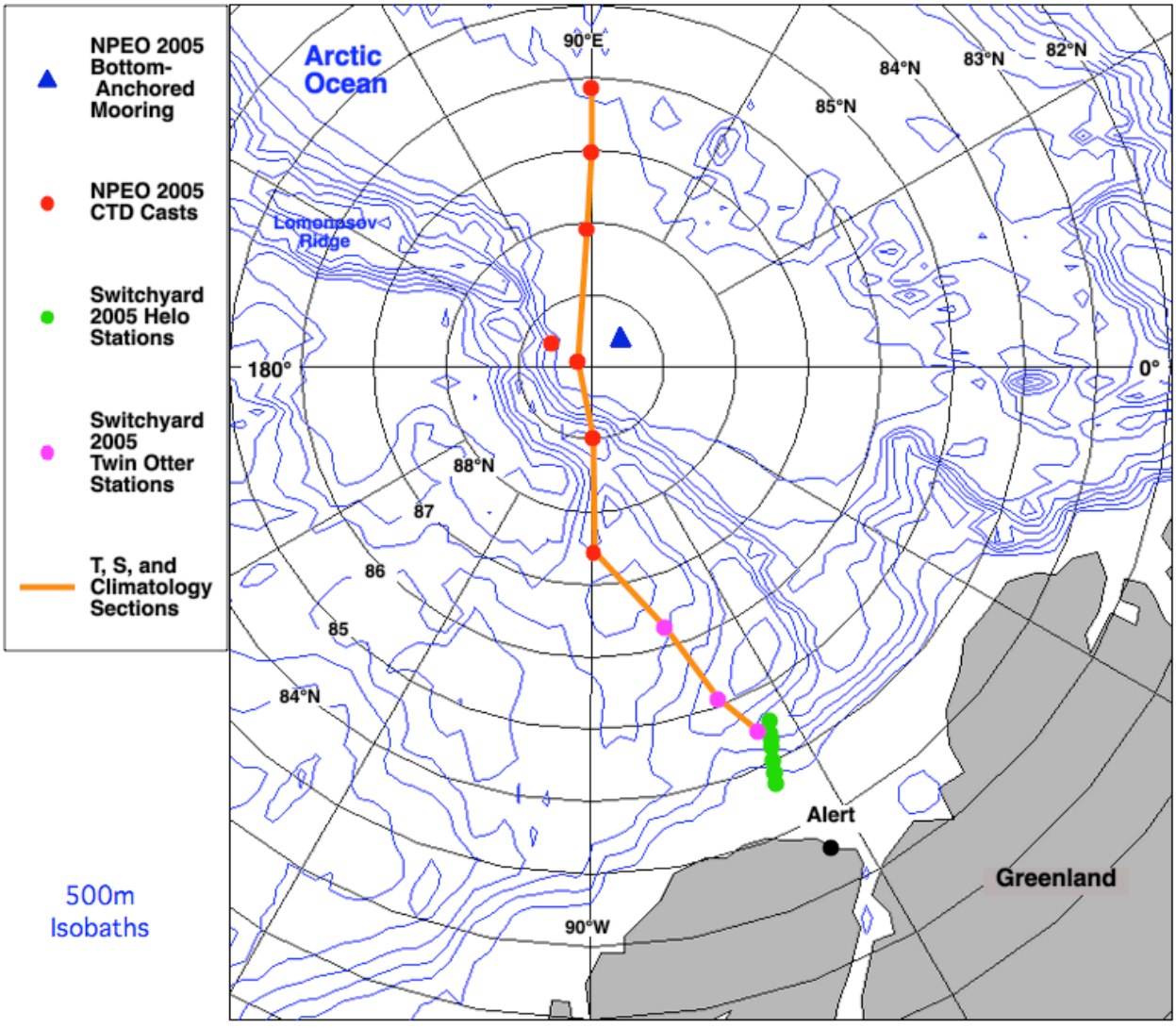

Fig. 1. Station locations: Bathymetry is from Jacobsson et al., 2000. The Switchyard stations were part of a project lead by R. Andersen and W. Smethie and carried out by helicopterand Twin Otter immediately following the NPEO work.

Kelly Falkner and Jamie Morison carried out the fieldwork with assistance from First Air pilot Don Boe, co-pilot Andrew Ysselmuiden and engineer Kevin Riehl. The Russian ice camp Borneo served as the base camp and Andy Hieberg coordinated logistics.

Generally, the casts were made through fairly smooth, snow covered ice that was 1-2 m thick. Ice conditions are of course selected for suitability of landing the aircraft and expediency of science operations so they are not necessarily representative. Temperatures ranged from -20 to -10 deg C and surface wind was variable but generally less than 10 knots throughout the mission. Despite several inches of drifted snow on the surface, the ice at 87°N 90°E was only about 15" thick. At that station the weight of the aircraft bowed the ice, such that seawater rose to the surface of the hole where normally there are at least several inches of freeboard. Since this thickness of ice was within specs for the aircraft at the ambient temperature, we proceeded sampling through the hole albeit supremely efficiently!

Seawater samples were obtained using the generator-powered portable winch to cast 4 1.5-L Niskins at a time. Unlike previous missions, we removed the generator from the aircraft and ran it on the ice at each station. This allayed the pilot's concern about a fire hazard in the aft storage compartment. Four custom constructed Niskins (General Oceanics model 1010 with 8" extension, modified plunger and short-handles end-caps) were mounted on a small diameter Kevlar line, with the deepest one mounted about 1 meter above an internally recording Seabird SBE19 (114) CTD system. (Unfortunately the SBE19 (2373) CTD-O_2 system experienced freezing upon deployment at the mooring camp that caused the conductivity cell to crack and compromised the O_2-sensor.) At the Borneo station two additional Nikins (General Oceanics model 1010 1.2-L with modified plungers) were deployed. It appeared that the long handles on the end caps could become problematic on upcasts. Moreover, the SBE19-114 memory allowed only enough time to cast to 4 bottles before it would start to overwrite itself and so these extra Niskins were not deployed for subsequent stations. Upon lowering the shallowest bottle to 20 m and soaking for 5 minutes, a stainless steel messenger was deployed. Upon retrieval, each Niskin was transferred to a rack in the heated aircraft and samples were drawn immediately. No dissolved O_2 samples were taken since there were no O_2-sensor profiles to calibrate. First, 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 precleaned 20-ml polyethylene bottles. Nutrient samples were collected into precleaned 60-ml polyethylene bottles and stored frozen. The samples experienced approximately 2 hours of partial melting upon transport to the laboratory from the field site. Random replicates were taken for each parameter at least once for each cast.

Analytical procedures

The data are reported in Table 1 along with $\pm$ 1/2 the range for replicate samples. The latter are denoted by the "unc" abbreviation for uncertainty in the table and are in reasonable accord with uncertainty estimates based on longer term measurement assessments as discussed below. Bottle salinities were analyzed at Alert using a model 8400A Guildline Autosal standardized with IAPSO standard seawater. The very dry atmosphere at Alert resulted in measurable evaporation into the sample head space as the water was displaced into the conductivity cell, hence timely

readings after the second flush were required. Nonetheless precision for these determinations was generally excellent at about $\pm$ 0.001 on the practical salinity scale. 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 analyzed within 2 hours for all nutrients. After standing 48 hr 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, 0.02μM; and ammonium, 0.03μM. 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). Negative ammonium concentrations occassionally occur when the levels encountered are below detection limits.

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% at the measured Ba concentration. Archived spiked GEOSECS samples were run to assure consistency with historical results. Oxygen isotopes were analyzed by the CO_2-equilibration method on the COAS Finnegan Mat 251. Results are reported in del units relative to VSMOW with 1-sigma precisions of about $\pm$ 0.03 ‰.

Table 1: NPEO 2005 Data

Sample ID					CTD Data						
Station	Cast	Latitude	Longitude	Date	Target depth	depth	press	In-situ T90	Pot T90	cond	salinity
	No.				m	m	dbar	degC	degC	S/m	psu
Borneo	1	89°21.5'N	147°26.9'E	25-Apr-05	10	9.9	10.0	-1.7281	-1.7282	2.4970	31.3909
Borneo	1	89°21.5'N	147°26.9'E	25-Apr-05	15	16.4	16.5	-1.7289	-1.7291	2.4977	31.3964
Borneo	1	89°21.5'N	147°26.9'E	25-Apr-05	40	43.0	43.3	-1.7848	-1.7855	2.5634	32.3504
Borneo	1	89°21.5'N	147°26.9'E	25-Apr-05	60	58.8	59.3	-1.7925	-1.7935	2.5807	32.5878
Borneo	1	89°21.5'N	147°26.9'E	25-Apr-05	150	147.7	148.9	-0.9882	-0.9923	2.7810	34.3866
Borneo	1	89°21.5'N	147°26.9'E	25-Apr-05	300	250.2	252.3	0.8136	0.8023	2.9734	34.8419
St86-90E	2	86°06.9'N	090°03.1'E	27-Apr-05	20	20.168	20.322	-1.8527	-1.853	2.64546	33.5817
St86-90E	2	86°06.9'N	090°03.1'E	27-Apr-05	60	61.3	61.7	-1.7409	-1.7421	2.6741	33.8278
St86-90E	2	86°06.9'N	090°03.1'E	27-Apr-05	100	101.38	102.175	-1.1614	-1.164	2.75515	34.2600
St86-90E	2	86°06.9'N	090°03.1'E	27-Apr-05	200	187.7	189.2	1.0163	1.0077	2.9831	34.7770
St87-90E	3	87°00.0'N	089°51.8'E	27-Apr-05	20	19.97	20.123	-1.8646	-1.8649	2.6525	33.6937
St87-90E	3	87°00.0'N	089°51.8'E	27-Apr-05	60	60.105	60.57	-1.8625	-1.8636	2.65447	33.6930
St87-90E	3	87°00.0'N	089°51.8'E	27-Apr-05	100	99.7	100.5	-1.5783	-1.5804	2.7118	34.1402
St87-90E	3	87°00.0'N	089°51.8'E	27-Apr-05	200	197.9	199.5	0.7667	0.7580	2.9583	34.7291
St88-90E	4	88°04.3'N	091°46.1'E	27-Apr-05	20	20.363	20.519	-1.8215	-1.8218	2.6088	33.0352
St88-90E	4	88°04.3'N	091°46.1'E	27-Apr-05	60	63.0	63.4	-1.8231	-1.8242	2.6171	33.1257
St88-90E	4	88°04.3'N	091°46.1'E	27-Apr-05	100	104.8	105.7	-1.4994	-1.5017	2.7174	34.1250
St88-90E	4	88°04.3'N	091°46.1'E	27-Apr-05	200	204.1	205.8	0.5401	0.5315	2.9384	34.7212
St89-90W	5	89°01.9'N	88°33.8'W	27-Apr-05	20	20.3	20.4	-1.7356	-1.7359	2.5047	31.4982
St89-90W	5	89°01.9'N	88°33.8'W	27-Apr-05	60	62.7	63.2	-1.7254	-1.7263	2.5198	31.6702
St89-90W	5	89°01.9'N	88°33.8'W	27-Apr-05	100	101.2	102.0	-1.5842	-1.5863	2.6991	33.9710
St89-90W	5	89°01.9'N	88°33.8'W	27-Apr-05	200	209.4	211.1	0.4265	0.4179	2.9246	34.6638
St90N	6	89°47.2'N	151°31.0'E	28-Apr-05	20	20.3	20.4	-1.7406	-1.7409	2.5109	31.5897
St90N	6	89°47.2'N	151°31.0'E	28-Apr-05	60	62.6	63.1	-1.7428	-1.7439	2.5932	32.7051
St90N	6	89°47.2'N	151°31.0'E	28-Apr-05	100	100.1	100.9	-1.5904	-1.5925	2.6988	33.9738
St90N	6	89°47.2'N	151°31.0'E	28-Apr-05	200	196.0	197.6	0.0211	0.0138	2.8877	34.6428
St87.5-90W	7	87°27.0'N	089°08.9'W	28-Apr-05	20	20.011	20.164	-1.7338	-1.7341	2.50127	31.4491
St87.5-90W	7	87°27.0'N	089°08.9'W	28-Apr-05	60	60.342	60.809	-1.7329	-1.7338	2.50284	31.4455
St87.5-90W	7	87°27.0'N	089°08.9'W	28-Apr-05	100	102.4	103.2	-1.6325	-1.6346	2.6665	33.5721
St87.5-90W	7	87°27.0'N	089°08.9'W	28-Apr-05	200	202.7	204.3	0.0445	0.0369	2.8824	34.5420

Table 1: NPEO 2005 Data

Sample ID		CTD Data.	Bottle Data							
Station	Target depth	density	Sal (PSS78)	unc Sal (PSS78)	Ba	unc Ba	del18O	del18O	PO4	PO4
	m	sigma-theta	psu	psu	nM	nM	SMOW	unc SMOW	µM	unc µM
Borneo	10	25.2455	31.4801	0.0002	128	29	-2.94	0.02	1.060	
Borneo	15	25.2500	31.3964	0.0000	110	11	-2.87	0.01	1.063	0.002
Borneo	40	26.0263	32.3504	0.0007	54.3	1.3	-2.81		0.688	
Borneo	60	26.2195	32.5878	0.0004	57.8	1.2	-2.76		0.617	
Borneo	150	27.6559	34.3866	0.0001	41.5	0.6	-0.13	0.01	0.720	
Borneo	300	27.9313	34.8419	0.0001	40.7	1.1	0.16		0.828	
St86-90E	20	27.0290	33.5715	0.0008	49.5		-1.72		0.428	0.003
St86-90E	60	27.2264	33.8278	0.0008	47.0	1.4	-0.90		0.578	
St86-90E	100	27.5597	34.2600	0.0007	40.4		-0.37		0.622	
St86-90E	200	27.8657	34.7770	0.0003	41.7		0.18	0.03	0.838	
St87-90E	20	27.1204	33.6716		47.6		-1.68		0.416	
St87-90E	60	27.1198	33.6721		50.9		-1.68		0.417	
St87-90E	100	27.4759	34.1402		44.6		-0.47		0.655	
St87-90E	200	27.8434	34.7291		40.3		0.15		0.834	
St88-90E	20	26.5839	33.0312		52.0	1.5	-2.39		0.452	
St88-90E	60	26.6575	33.1257		52.1		-2.14	0.03	0.485	
St88-90E	100	27.4611	34.1250	0.0001	47.0		-0.43		0.670	
St88-90E	200	27.8511	34.7212		43.8		0.19		0.714	0.090
St89-90W	20	25.3329	31.4982		61.0	0.5	-3.30		0.880	0.016
St89-90W	60	25.4724	31.6702	0.0091	59.6		-3.25	0.01	0.816	
St89-90W	100	27.3385	33.9710		43.9	0.9	-0.65		0.728	
St89-90W	200	27.8115	34.6638		40.5		0.17	0.03	0.871	
St90N	20	25.4073	31.5897		58.3		-2.94		0.867	
St90N	60	26.3138	32.7051		52.9		-2.27		0.560	
St90N	100	27.3411	33.9738	0.0018	45.2		-0.50		0.610	
St90N	200	27.8172	34.6428		40.0	0.0	0.11		0.679	0.082
St87.5-90W	20	25.2929	31.4407	0.0000	64.1	3.9	-2.90		0.912	
St87.5-90W	60	25.2900	31.4399	0.0003	59.3		-2.95		0.900	
St87.5-90W	100	27.0157	33.5721		52.2		-1.06		1.146	0.001
St87.5-90W	200	27.7346	34.5420		42.7		0.08		0.821	0.003

Table 1: NPEO 2005 Data

Sample ID		Bottle Data cont.							
Station	Target depth	NO3+NO2	NO3+NO2	NO2	NO2	NH4	NH4	Si	Si
	m	µM	unc µM	µM	unc µM	µM	unc µM	µM	unc µM
Borneo	10	1.86		0.069		0.005		8.30	
Borneo	15	1.68	0.16	0.067	0.014	-0.012	0.003	8.22	0.01
Borneo	40	2.41		0.067		0.015		4.56	
Borneo	60	2.99		0.092		0.067		4.54	
Borneo	150	9.26		0.081		0.120		5.17	
Borneo	300	11.78		0.131		0.006		5.20	
St86-90E	20	3.56	0.04	0.050	0.003	0.042	0.006	3.21	0.01
St86-90E	60	6.50		0.060		0.013		4.20	
St86-90E	100	7.70		0.067		-0.011		3.80	
St86-90E	200	12.17		0.046		-0.013		5.54	
St87-90E	20	3.34		0.126		0.031		3.02	
St87-90E	60	3.23		0.112		0.002		2.98	
St87-90E	100	7.83		0.133		0.041		4.57	
St87-90E	200	11.46		0.119		0.022		5.46	
St88-90E	20	2.51		0.101		-0.015		3.98	
St88-90E	60	3.12		0.085		0.019		4.47	
St88-90E	100	7.67		0.087		0.010		5.23	
St88-90E	200	9.5	1.5	0.107	0.010	0.12	0.10	4.64	0.68
St89-90W	20	1.88	0.02	0.107	0.010	0.076	0.038	10.0	2.8
St89-90W	60	2.54		0.092		0.150		7.67	
St89-90W	100	8.25		0.076		0.075		6.86	
St89-90W	200	11.91		0.059		0.219		7.91	
St90N	20	1.47		0.131		0.003		6.11	
St90N	60	4.03		0.129		0.001		5.62	
St90N	100	6.90		0.080		0.011		5.04	
St90N	200	8.6	1.4	0.062	0.006	0.057	0.016	4.21	0.71
St87.5-90W	20	1.53		0.092		0.112		8.05	
St87.5-90W	60	1.52		0.076		0.081		6.12	
St87.5-90W	100	10.56	0.00	0.060	0.001	0.098	0.006	20.1	0.3
St87.5-90W	200	11.15	0.16	0.053	0.001	0.072	0.001	7.61	0.61

Results

The CTD properties were assigned to individual Niskin bottles in one of two ways. For samples ≤ 20 m, if no CTD salinities matching the bottle measurements could be found within 5 m of the target depth, the CTD properties at the depth closest to the target depth were taken. Otherwise, as close to the target depth as possible, the CTD salinities that bracketed the measured bottle salinity were used to linearly interpolate CTD properties. In 2004 it was noted that the bottle salinity in the sample closest to the surface (15 m) exceeded CTD-O_2 salinities within the upper 20 m of the profile except within the hole where refreezing artifactually raises salinity. Despite a 3-minute delay before dropping the messenger, it appeared that the water from the hole wasn't fully flushed from the Niskin. Chemical analyses suggested that up to 10% of water from the ice hole remained in the samples. Accordingly, in 2005 we delayed the messenger drop to 5 minutes after lowering the last Niskin to the target depth. Only the bottle salinity taken at 10 m at the Borneo station showed evidence (0.09 practical salinity units higher than the CTD) of incomplete flushing and this was with a minor amount (≤0.3%) of ice hole water retained. Samples between 15 and 20 m either had bottle salinities matching the CTD at ± 1 m of the target depth (n=3) or the CTD salinity was slightly greater (by 0.004-0.022) than the bottle salinity. Such deviations are negligible with respect to errors in other chemical measurements. Thus 5 minutes is preferable to 3 minutes for the wait between attaining the desired depth for the last Niskin deployed and dropping the messenger. The bottle salinities in samples in the 40-100 m range and at 200 m matched CTD salinities within ± 3 m and ± 15 m of their target depths respectively. This lends confidence that the Niskins were tripped correctly, did not leak and did not experience freezing problems. The deepest Niskin (target 300 m), deviated by a substantial 50 m which may be a function of multiple intrusions in this depth zone, wire angle or meter wheel error.

It is noted that the shallow samples (10 & 15 m) at the Borneo site were of low salinity (about 31) and the highest in Ba (100-150 nM) ever observed in the central Arctic Ocean. The replicate samples for each these Niskins differed by more than 10 times analytical uncertainties. Hence, we acidified the samples and ran them a second time. The results corroborated the original findings. It is unclear how such results can come about. While we were clearly sampling over strong vertical gradients just below the ice, it seems surprising to us that such gradients would be preserved within a Niskin bottle. It is conceivable that the Niskins may have become contaminated, although none of the other Niskins seem to have been problematic and they were precleaned, packed and shipped in the same container and otherwise treated similarly. We note that relatively high Ba contents were also observed at 40 and 60 m at the Borneo station. At the same time the ^{18}O displayed negative values of about –2.9 ‰ over the upper 60 m. A salinity of about 31, ^{18}O of –2.9 to –3.3 ‰ and Ba of about 60 nM were also observed at 20 m at 89N 90W and the North Pole station. Provided there is no ice melt present and assuming a river endmember of –21‰ and seawater endmember of -.0.05‰, the ^{18}O results suggest river water contents of about 12-15% for all of these samples. Assuming salinity endmembers of 0.015 and 34.8 respectively, the salinity similarly suggests riverwater contents of 9-10%. Assuming an upper limit of 150 nM Ba for Russian rivers and background seawater of 45 nM Ba, corresponds to river contents of 12-15% for 40 and 60 m at Borneo and 20 m at 89N 90W and the North Pole station, closely matching the ^{18}O results. However, the Ba contents of the 10 and 15 m Borneo samples are too high to be explained by Russian river water concentrations alone. Mackenzie

River levels would have to be invoked to bring the river contribution into line with that indicated by ^{18}O. The P and Si levels in these samples are also quite high for surface waters. Analysis of N:P relationships in these samples (cf. Jones et al., 2003) shows that that the seawater component is within several percent error of being completely Pacific derived. Samples from 40 and 60 m at Borneo and 20 m at 89N 90W and the North Pole station have about a 90:10 Pacific:Atlantic seawater component mix.

Pronounced subsurface nutrient enrichment occurred the 87.5N 90W station at about 100 m and salinity of 33.6. In particular, Si concentrations reached about 20 μM. This is indicative of a contribution by Bering winter water which is typically centered at about 33.1-33.3 in salinity. The N:P relationship in this sample suggests about a 50:50 Pacific:Atlantic seawater component mix. Higher salinities and much lower nutrients with Atlantic character were encountered at comparable depths at the other stations (except at Borneo where 150 rather than 100 m was sampled) suggesting that a much diminished if non-existent Bering Winter Water influence elsewhere sampled in spring 2005.

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