

Chemical Results from the May 2004 NPEO Project

Water sampling procedure

The aircraft (Twin Otter) sampling approach used successfully in 2001–2003 was undertaken to effectively reoccupy NPEO 2001 and a subset of NPEO 2000 and 2003 hydrocast stations during 26–28 April 2004. For details regarding the sampling approach, please refer to the 2001 chemical data report. The NPEO 2001 reoccupations form a transect extending from near the North Pole toward Alaska and the NPEO 2000 and 2003 stations extend from the North Pole toward Ellesmere Island (Fig. 1).

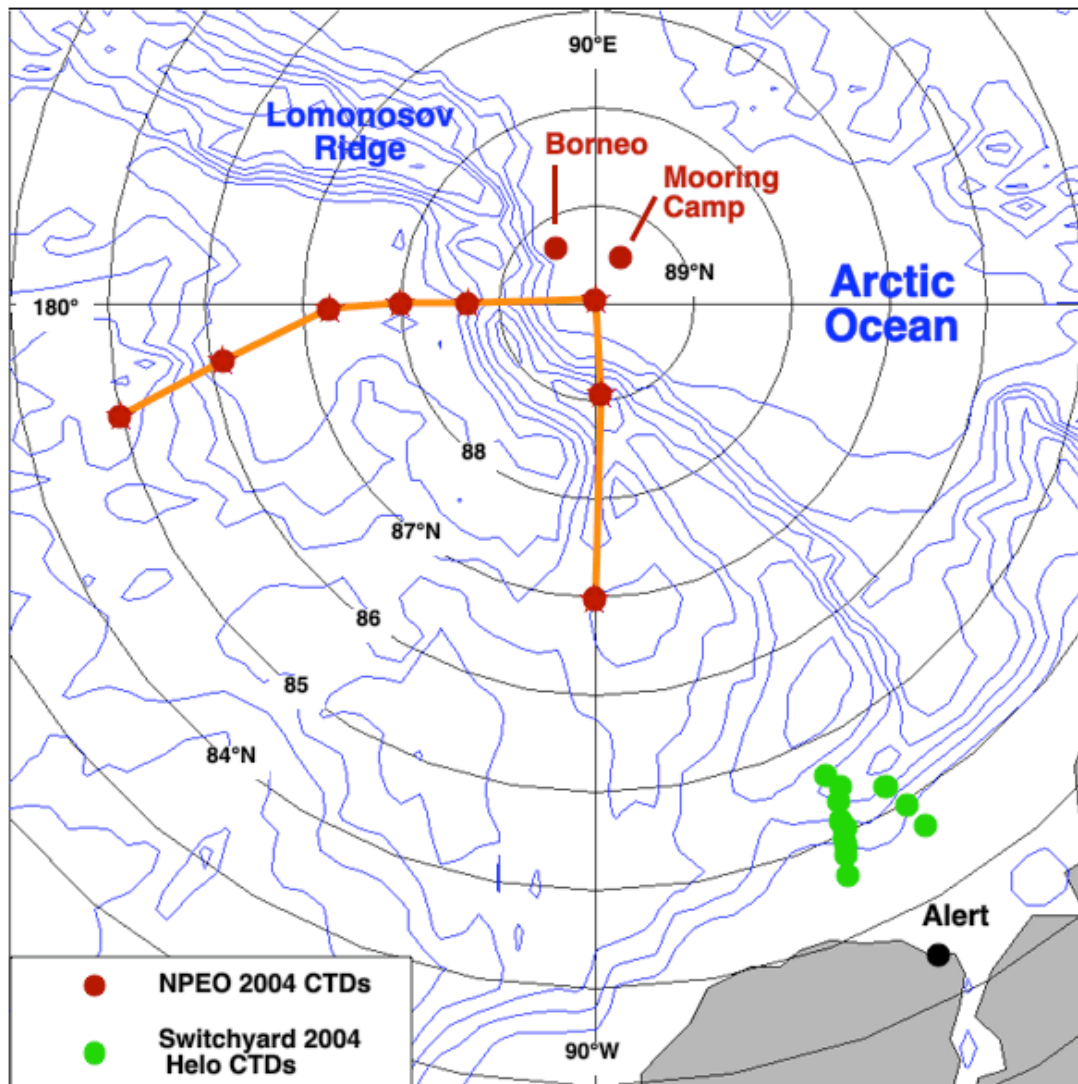


Fig. 1. Station locations: The numbers indicate 2004 CTD cast number. Bathymetry is from Jacobsson et al., 2000. The Sitchyard stations were part of a project lead by M. Steele carried out by helicopter over the same time as the NPEO work.

Kelly Falkner and Jamie Morison carried out the fieldwork with assistance from Unaalik Air pilot Paul Trask and co-pilot-engineer Brent Este. 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. Temperatures ranged from -20 to -10 deg C and wind was variable but generally less than 10 knots throughout the mission.

Seawater samples were obtained using the generator-powered portable winch to cast 4 1.5-L Niskins at a time. 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 and soaking for 3 minutes, a messenger was deployed. 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). Once sealed, distilled water was added above the ground glass joint and the joint was sealed with parafilm. 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. Random replicates were taken for each parameter at least once for each cast.

Analytical procedures

Dissolved O₂ was analyzed by Robert Willimas of Scripps Institution of Oceanography by means of automated Winkler titrations with UV detection back at Alert on 3 May 2004. Before analysis, the samples had warmed to room temperature and desolved a visible gas bubble. Two test samples demonstrated that numerous small gas bubbles in the warmed samples interfere with the UV light path and so adversely affect results. We tried cooling 2 of the samples to 5 deg C and found that this eliminated the small bubble problem. However upon cooling, the seawater sample contracts more than the glass container. Thus, fluid above the ground glass joint is drawn back into the flask. An upper limit for the error introduced in the process of recooling the samples was estimated as follows. A maximal volume of 0.4 ml of O₂-saturated distilled water at 5degC is assumed to be drawn into the flask. Based on O₂-saturation expressions of Weiss, (1970) this fluid will contain 8.9 ml-O₂/L or 0.004 ml of O₂. Since the samples from this part of the Arctic contain ≥ 6 ml O₂/L, then the fluid contributes $\leq 0.5\%$ to the measured signal. Under optimal circumstances, this amount would contribute a measureable error. Based on analysis of replicate samples, however, it appears that the flasks may have been insufficiently flushed during the sample draw. Sampling error based on replicates exceeded the recooling error by up to a factor of 2. All samples were rechilled to 5degC. Fluid above the ground glass joint was tipped out and the joint rinsed with distilled water which was also tipped before the flasks were opened

and acidified. Automated titrations were initially rapid to avoid loss of iodine and then slowed to a careful determination of the endpoint based on UV detection. Based on replicates, it appears that a precision on the order of 1% is attainable under these circumstances. Unfortunately absolute concentrations appeared to be too high by at about 10% in all of the samples based on previous ship data in the region and so the data are not reported in Table 1 (separate tab delimited ASCII file: Table1NPEO2004.txt). This was an extremely disappointing result and the working hypothesis is that bubbles entrained in the dry draw tubes contributed to the problem. It is surprising that precision was as good as it was under such circumstances. Next year the draw tubes will be transported in a seawater surfactant solution that will be somehow be prevented from freezing during the sample mission.

For the remainder of the bottle measurements, the data are reported in Table 1 (separate tab delimited ASCII file: Table1NPEO2004.txt) along with 1 standard deviation for replicate samples. The latter are in accord with uncertainty estimates based on assessing measurements on longer terms 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. By the fourth flush, the upward drift in the signal was apparent. Humidifying the displacement air-stream would have been useful for assuring top quality measurements. Precision for these determinations was somewhat less than optimal but better than 0.004 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 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 μ M; and ammonium, 0.03 μ M. 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).

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. Oxygen isotopes were analyzed by the CO₂-equilibration method on the COAS Finnegan Mat 251. Results are reported in del units relative to VSMOW with 1-sigma precisions of +/- 0.03

Results

The CTD-O₂ properties were assigned to individual Niskin bottles by matching the bottle salinity to a linearly interpolated downcast CTD-O₂ salinity near the target depth. The bottle salinity in the sample closest to the surface (15 m) exceeded CTD-O₂ salinities within the upper 20 m of the profile except within the hole where refreezing artifactually raises salinity. Although we waited for 3 minutes before dropping the messenger, it appeared that the water from the hole wasn't

fully flushed from the Niskin. The samples are contaminated by <10% of water from the hole that while evident in CTD-O₂ properties, shouldn't markedly affect the other chemical measurements with small sub surface gradients and larger relative errors. CTD-O₂-salinities bracketing or equal to measured bottle values were observed within ± 2 m of the 65-200 m target bottle depths. This lends confidence that the Niskins were tripped correctly, did not leak and did not experience freezing problems. The deepest niskins (300-500 m), however, were located in a section of the water column having a number of intrusions. This engendered ambiguity and thus somewhat larger errors in their CTDO property assignments. The magnitude of this uncertainty varies somewhat from profile to profile and is up to ± 30 m in some cases.

References

- Falkner, K.K., R.W. MacDonald, E.C. Carmack, and T. Weingartner, The potential of barium as a tracer of Arctic water masses, in *The Polar Oceans and Their Role in Shaping the Global Environment: The Nansen Centennial Volume, AGU Geophys. Monograph Series*, edited by O.M. Johannessen, R.D. Muench, and J.E. Overland, pp. 63-76, AGU Books, Washington DC, 1994.
- Gordon, L.I., J.J.C. Jr., A.A. Ross, and J.M. Krest, A suggested protocol for continuous flow automated analysis of seawater nutrients (phosphate, nitrate, nitrite and silicic acid) in the WOCE Hydrographic Program and the Joint Global Ocean Fluxes Study. WOCE Operations Manual, Vol. 3: The Observational Program, Section 3.1: WOCE Hydrographic Program, Part 3.1.3: WHP Operations and Methods., pp. 52 loose-leaf, Woods Hole, Mass., 1994.
- Horibe, Y., Kodama, Y., Shigehara, K., 1972. Errors in sampling procedure for the determination of dissolved oxygen by Winkler method. **28** 203-206.
- Jakobsson, M.N.Z., N.Z. Cherkis, J. Woodward, R. Macnab, and C. B., New grid of Arctic bathymetry aids scientists and mapmakers, *EOS, Transactions, American Geophysical Union*, 81 (9), 2000.
- Weiss, R.F., 1970. The solubility of nitrogen, oxygen and argon in water and seawater. *Deep-Sea Research* **17** 721-735.

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