Monitoring ocean acidification and carbon cycling on FerryBox Ships of Opportunity with underway carbonate system sensors

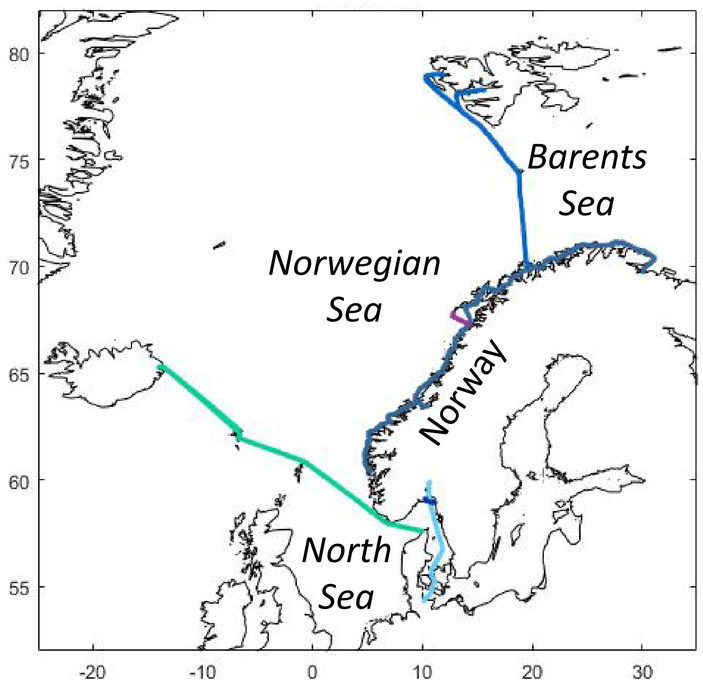
Andrew L. King, Sabine Marty, Marit Norli, Pierre Jaccard, Richard Bellerby, and Kai Sørensen

Marine Biogeochemistry and Oceanography
Norwegian Institute for Water Research
Gaustadalléen 21, Oslo NO-0349, Norway

Abstract

Observing variability in carbonate system chemistry is important for understanding carbon cycling in present day oceans, for monitoring ongoing ocean acidification, and for developing scenarios of how rising CO_2 may influence ecosystem structure and function. We have been developing continuous, underway spectrophotometric pH, spectrophotometric CO_3, and membrane equilibrator/infrared pCO_2 detection systems on FerryBox Ships of Opportunity to examine spatial and temporal variability in carbonate system chemistry and its relation to other biological and physical processes. The Norwegian Ships of Opportunity Program for marine and atmospheric research (NorSOOP) is a network of FerryBox systems that have been in operation for 15 years covering most of the Norwegian coastline in addition open/coastal waters in Northern Europe, the North Atlantic, and to the Arctic. FerryBox systems are excellent platforms for developing new advanced sensor technology to study carbonate system variables. Here we will present these sensors and how they are integrated into Ships of Opportunity observing platforms, as well as some examples of carbonate system observations.

NIVA FerryBox Ships of Opportunity



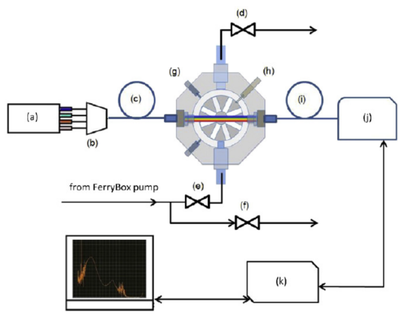
FerryBoxes are Ships of Opportunity that are outfitted with a variety of physical, chemical, and biological sensors that can make seawater measurements (intake at ~5-7 m depth) as well as deckboard measurements that include hyperspectral radiance/irradiance, atmospheric gases, and meteorological variables.

These ships are part of NorSOOP: Norwegian Ships of Opportunity Program for marine and atmospheric research: **come visit Booth 214B!** And visit us at: www.niva.no/norsoop

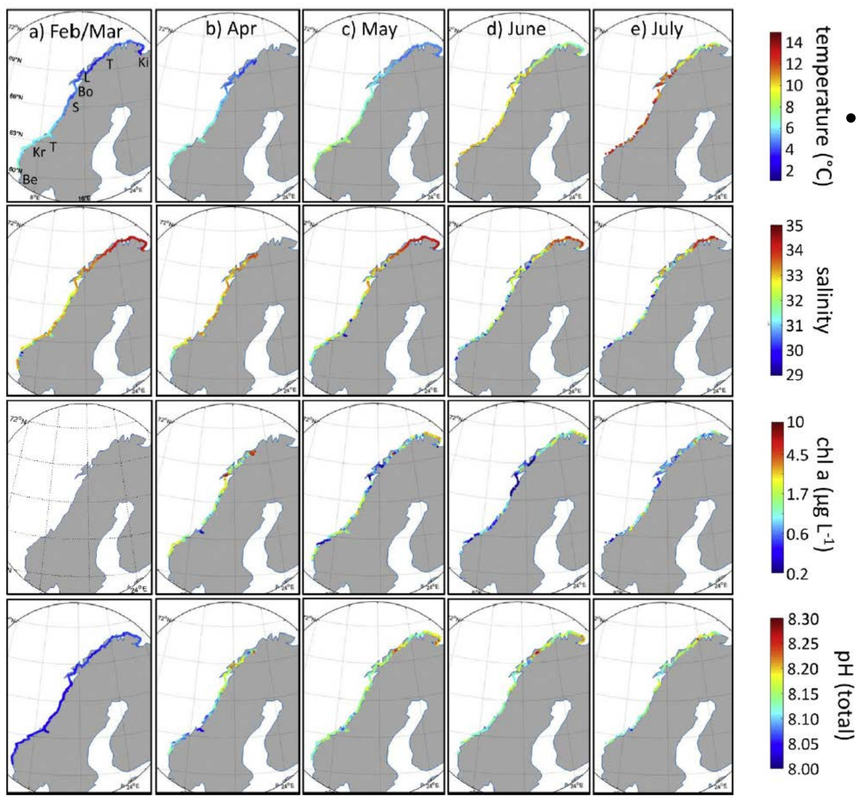
- Five FerryBoxes presently in operation:
  - M/S Color Fantasy: Oslo, NO-Kiel, DE
  - M/S Trollfjord: Bergen-Kirkenes, NO
  - M/S Norbjørn: Tromsø, NO- Svalbard
  - M/S Norröna: Hirtshals, DK-Seyðisfjørður, IS
  - M/S Roald Amundsen, Arctic/Antarctic explorer ship
- All have sensors for S, T, chl a fluorescence, turbidity
- Some have sensors for cDOM fluorescence, microplastics samplers, refrigerated autosamplers

Acknowledgments: The JERICO-NEXT project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 654410. The INTAROS project (www.intaros.eu) has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 727890. The NorSOOP project has received funding from the Research Council of Norway Research Infrastructure project No 269922. This work has been supported by additional funding from the Norwegian Environment Agency, Fram Centre OA Flagship, and NIVA's Ocean Acidification SIS funding.

NIVA underway spectrophotometric pH sensor

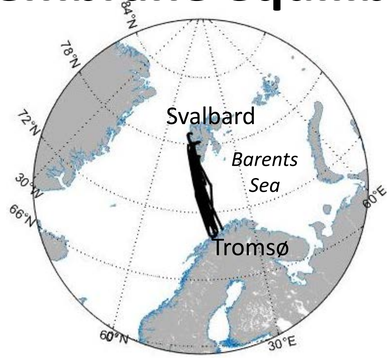


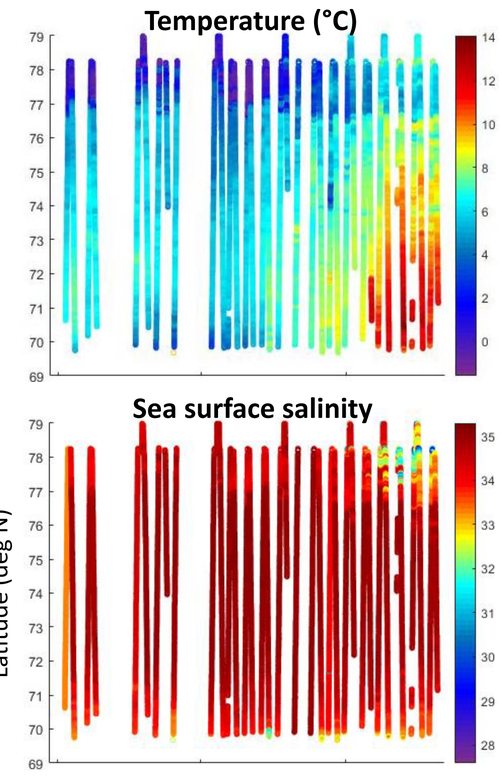
- Automated spectrophotometric pH measurements at near-*in situ* temperature
- Can be configured with LEDs for thymol blue or metacresol purple indicator dyes
- Uncertainty of <0.003; >15,000 measurements on 2 L dye = 4 months of measurements every 10 min
- Four point dye perturbation correction can be performed on each sample



Left: Example of seasonal and regional variability in sea surface temperature, salinity, chl a, and pH (total scale) from FerryBox sensors on M/S Trollfjord along coastal Norway between Feb-July 2015. Note regions and timing of pH >8.2 that coincide with high chl during the spring phytoplankton bloom (Reggiani et al., 2016)

Franatech/NIVA membrane equilibrator pCO_2 sensor





- Membrane equilibrator with IR detector; detector uncertainty ~5 ppm
- Flow, pressure, and temperature sensors in seawater and air circuits
- Calibrated with NOAA ESRL pCO_2 calibration gases

Right: Example of T, S, and fCO_2 in the Barents Sea Opening (BSO) FerryBox M/S Norbjørn from Jan-Sept 2018. Temperature and salinity indicate the Atlantic and Arctic water masses in the BSO. Substantial decrease in fCO_2 as year progresses into the warmer and more variable salinity spring/summer growing season

NIVA underway spectrophotometric $[CO_3^{2-}]$ sensor (coming soon!)

- Underway $[CO_3^{2-}]$ sensor under development based on similar architecture as pH sensor described above with modifications:
  - UV source instead of LEDs
  - UV spectrometer instead of VIS spectrometer
  - Pb chelating column to collect waste
- UV spectrophotometric detection using $PbCl_2$ or $Pb(ClO_4)_2$ based on (Byrne and Yao, 2008; Patasavas et al., 2015)

References cited: **Byrne**, R.H., Yao, W., 2008. Procedures for measurement of carbonate ion concentrations in seawater by direct spectrophotometric observations of Pb(II) complexation. Mar. Chem. 112 (1–2), 128–135. **Patsavas**, M. C.; Byrne, R. H.; Yang, B.; Easley, R. A.; Wanninkhof, R.; Liu, X. Procedures for direct spectrophotometric determination of carbonate ion concentrations: Measurements in US Gulf of Mexico and East Coast waters. Mar. Chem. 2015, 168, 80–85.**Reggiani**, E., A.L. King, M. Norli, P. Jaccard, K. Sorensen, and R.G.J. Bellerby. 2016. FerryBox-assisted monitoring of mixed layer pH in the Norwegian Coastal Current. Journal of Marine Systems, doi: 10.1016/j.jmarsys.2016.03.017.