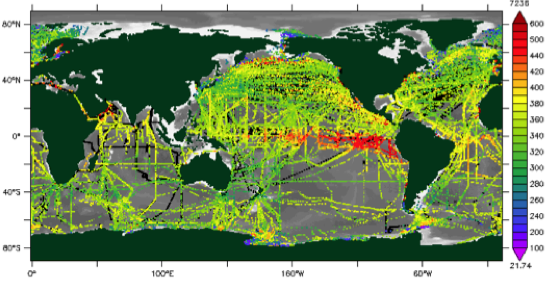
In line measurements :

An underutilized opportunity

* as time series measurements in its own right, and
* in support of (fixed) time series

measurements

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In line measurements pertain to automated measurements and sampling from seawater intakes on research ships and ships of opportunity. Points 1 and 2 listed below are related to the in-line system itself. Points 3-10 deal with discussed parameters. Point 11 provides some more general comments.

In line measurements are a powerful way of extending fixed-point time series, providing quality measurements, and instrument/technique development. Quality of ship’s infrastructure with regards to inline system (tubing, pumps) is critical.

A lot of consideration was given to various aspects of the inline system:

1. Depth of sampling needs to be recorded in the metadata
   1. It is highly variable between different ships
   2. The inlet to be in the bulk mixed layer (below warm layer ≈ 1-2 m) –depth needs to be well documented
   3. Intake should be right from the bow to avoid contamination from ship’s discharges and hull (not from the sea chest if possible)
2. In line system
   1. Flow rate should be well documented (often a critical QC information)
   2. Knowing and documenting the transit time of water in the pipe is important
   3. Temperature measurements and control
      1. Measuring the temperature at the inlet to determine SST (sea surface temperature)is ideal (sensor installed as close to the inlet as possible, before other instruments and technical equipment like pumps and flow meters)
         1. In case the temperature at the inlet can’t be measured directly, surface temperature from the CTD is acceptable, if sufficient CTD casts are taken for good interpolation
         2. In case temperature at the inlet can’t be measured directly, a hull mounted temperature sensor is acceptable
         3. Bucket sampling is not recommended unless no other method is available
         4. Back-calibration to determine SST upon installing of the inlet temperature sensor is recommended
      2. Temperature measured at instrument/in the lab is fundamental for the data quality and correction for analysis of temperature dependent parameters such as pCO2 and pH.
         1. Temperature sensors (platinum resistance thermistor) are very stable over years. However annual calibration is recommended (ideally to 0.01 ˚C; 0.02 ˚C is still acceptable)
         2. Manufacturer calibration is ideal but more expensive
         3. Lab calibrations are completely acceptable
      3. Short distance between seawater intake and instrument/lab as well as thermal insulation of seawater line is recommended to minimize temperature changes.
   4. Cleaning the seawater line is a very important issue (see Juranek et al. 2010, GRL)
      1. Strainers should be installed right at the intake and should be cleaned regularly as required
      2. Clean the seawater line with bleach every 6 months or more frequently in eutrophic waters. There are concerns related with potential oxidation of organic matter in the line.
      3. Backflush line with freshwater every time in port and leave filled with fresh water when seawater line is not used
   5. Pumps
      1. Centrifugal pumps are most widely used – there are some possible issues with fluorescence measurements (induced fluorescence by agitation)
      2. Large piston pumps are an alternative but expensive, not well tested and possible issues with pulsation
      3. Jet pumps have known issues with creating bubbles
   6. Material- Materials should be tested. A good way to test materials and biofouling issues is to stop the flow for a period of time and measure relevant concentrations right upon start-up
      1. Soft steel piping are problematic
      2. Other steel and alloy not optimal
      3. No strong recommendation of synthetics but generally the harder materials are better for gases (Teflon is good for trace metals but less so for gases)
      4. Long lengths for (garden) hose are not optimal for connecting system components. “Conditioning” of new material is recommended.
   7. De-bubblers- remove bubbles from breaking waves and pump cavitation from the seawater lines
      1. Salinometer and optical sensors/instruments that are impacted by bubbles should be placed after the de-bubbler
      2. Effect of the de-bubbler on gases is not established with insoluble gases such as oxygen being more vulnerable than *p*CO2.
3. TEMPERATURE
   1. BEST
      1. A sensor with quantifiable accuracy (e.g. SeaBird 38, SeaBird 21)
      2. Don’t just rely on manufacturers stated accuracy, lab calibrations and at sea comparisons (e.g. with CTD) are recommended
4. CONDUCTIVITY/Salinity
   1. BEST
      1. Take discrete samples for calibration in situ.
      2. Calibrate against the values from CTD
      3. Factory calibration is suggested by manufacturers at a frequency of once per year
      4. Required accuracy depends on the aim of the measurement
5. *p*CO2
   1. BEST- measurements are accurate to within 2 µatm
      1. In general follow the SOCAT cookbook recommendations (www.SOCAT.info)
      2. Head-space, equilibrator based, IR or GC based approach with use of, at minimum, 2 non-zero traceable standard gases
   2. EMERGING TECHNOLOGY
      1. Cavity Ring-Down Spectroscopy analyzer
         1. Much more expensive
         2. Potential for minimization of calibration/standardization issues
         3. Lower cost IR’s (e.g LICOR 840)
      2. IOCCP has a list of manufacturers on their website. Recommendations regarding the use of new platforms and sensors for *p*CO2 measurements will be available soon
6. pH
   1. BEST
      1. Spectrophotometric method
   2. EMERGING TECHNOLOGY
      1. Ion sensitive field effect transistor (Durafet) sensors
      2. This is a very active and rapidly developing field
   3. STANDARDS
      1. Standardization is a critical next step and we strongly support initiatives aiming at establishing relevant standards
      2. Use of purified dyes for pH is recommended (REF)
      3. Issues with commercially available dyes (impurities)
      4. Choice of a dye should be dictated by the expected range in the study area
7. 13C of DIC
   1. EMERGING TECHNOLOGY
      1. Based on Cavity Ring-Down Spectroscopy analyzer good to 0.3 per mil (Becker et al. 2012)
8. DIC (total dissolved inorganic carbon)
   1. AVAILABLE (EMERGING) TECHNOLOGY
      1. Based on modifications to the IR based discrete sampling instruments
      2. More automation is required, at the moment it is a labour intensive technique
9. FLUORESCENCE
   1. Based on fluorometer (e.g. WetLab ECO and Turner 10-AU-005)
      1. Systematic calibration procedure and protocols are critical
      2. Calibration frequency should account for a diurnal (daily or 24 hours?) variability
      3. Recommended frequency: at least twice a day, optimally 4 times a day (BEST)
      4. Comparison to the extracted cholorophyll obtained from CTD bottled data is acceptable as a validation procedure (GOOD)
      5. Uncalibrated measurements provide qualitative information on spatial and temporal variability which is useful if the fluorometers are frequently cleaned.
10. OXYGEN
    1. Sensor technology has matured. Use of available sensors (e.g. SeaBird IDO, Aanderaa Optode, JFE Advantech RINKO III) is generally acceptable following implementation of calibration procedures:
       1. Pre-cruise/lab calibration is required
       2. Frequent in-situ calibration required (against Winkler samples) as some sensors might deviate even when pre-calibrated (Bittig et al. 2012)
       3. Comparison to the CTD bottled data is acceptable
    2. UNITS
       1. Use of μmol/kg of seawater is recommended
       2. Use of μmol/l is acceptable
       3. Use of mg/l is not recommended
11. GENERAL COMMENTS
    1. Use of ship-based time series platforms is well suited for testing of new technology
    2. Taking multiple discrete samples allows for groundtruthing of the moored sensors and/or satellite data
    3. Taking multiple discrete samples offers the opportunity to calibrate sensors/instruments