

AX2 surface sampling information and file format

Sampling information:

During most cruises, seawater was pumped from a depth of ~3-5 m depending on the ship (in 06/1993 and 01/1994, water was collected with a bucket and its temperature measured with a calibrated thermometer). Sea Surface Salinity (SSS) was from discrete salinity samples. Sea Surface Temperature (SST) was either from continuously recording ThermoSalinoGraph (TSG seabird Electronics, Inc. USA, model 21) corrected for an average bias to sea surface temperature, or from nearly simultaneous XBT temperature profiles (at 3 m). SST and SSS accuracies were estimated to be 0.2°C and 0.01 respectively (SSS is a practical salinity, in psu). As samples are collected sequentially within usually a maximum of 5 minutes, the measured salinity might differ from the actual salinity of the other samples, when there is spatial/time variability as when crossing fronts.

Macro-nutrient concentrations (nitrate, phosphate, silicic acid), DIC/TA, water isotopic composition and $\delta^{13}\text{C}_{\text{DIC}}$ were also obtained from discrete samples collected every 3-5 hours and analyzed later in laboratories (on land).

Macro-nutrient concentrations:

Samples for macro-nutrient concentrations were collected starting in 2001 in pre-cleaned bottles that were frozen on board (for two crossings, the samples were probably not correctly frozen, and are not reported here). Macro-nutrient concentrations were measured usually within 3 months of collection with standard colorimetric methods at the Marine Research Institute (Reykjavik, Iceland). The analytical procedure and the quality control for the nutrient analyses have been described in detail in Olafsson et al. (2010) where the long term accuracy has been estimated as $\pm 0.2 \mu\text{mol l}^{-1}$ for nitrate (includes also nitrite) and silicate, and $\pm 0.03 \mu\text{mol l}^{-1}$ for phosphate. Additional uncertainties could result from contamination during collection, or from poor conservation of the nutrients in the frozen samples. Earlier samples for phosphate in 1993-1994 were analyzed at LDEO.

DIC/TA:

At LOCEAN (since June 2001), DIC (actually, no filtering done, so it should probably be total inorganic carbon) is determined at the same time as total alkalinity (TA) by potentiometric titration derived from the method developed by Edmond (1970) using a closed cell and a CRM calibration and calibrated Certified Reference Material (CRM) provided by Prof. A. Dickson (Scripps Institution of Oceanography, San Diego, USA). Analytical accuracy of the DIC concentrations is $\pm 3 \mu\text{mol kg}^{-1}$ (further details in Corbière et al. (2007)). Most of the bottles used at LOCEAN since 2003 were with screw caps (before that and for a few isolated samples since 2003, bottles had a ground glass stopper and use of Apiezon grease). For some of these bottles, we found that samples presented systematic biases in 2013-2015, either in DIC or TA. That led to their replacement and since 2016, most bottles are from a new set. In recent years (since 2005), poison (saturated (or half saturated) mercuric chloride solution) volumes were kept to 0.3 ml, and no correction was applied for dilution. In earlier years, poison solution volume has evolved, and data reported are usually corrected for the dilution effect. For the period 06/1993-02/1997, the samples were stored in bottles with ground glass stopper and Apiezon grease was used, and DIC was determined by a coulometric method at LDEO (Chipman et al., 1993). For some samples in 2005-2006 associated with a $\delta^{13}\text{C}_{\text{DIC}}$ value, DIC was also estimated manometrically during acid CO_2 extraction procedure with

somewhat lesser accuracy ($\pm 5 \mu\text{mol kg}^{-1}$). This value is reported instead of the LOCEAN one if there was no DIC/AT value estimated at LOCEAN. There are also been comparisons with DIC/AT also collected for other institutions that will be reported later on.

$\delta^{13}\text{C}_{\text{DIC}}$:

Over the period 2005-06, DIC concentrations were estimated manometrically during acid CO_2 extraction procedure for $\delta^{13}\text{C}_{\text{DIC}}$ measurements from helium stripping technique. This analytical method has been described previously by Quay et al. (1992, 2003). These measurements have an accuracy of $\pm 0.02\text{‰}$ for $\delta^{13}\text{C}_{\text{DIC}}$ based on a helium stripping technique adapted from the one used by Kroopnick (1974) and $\pm 5 \mu\text{mol kg}^{-1}$ for DIC based on a comparison to coulometric DIC values and to Certified Reference Material (CRM) provided by Prof. A. Dickson (Scripps Institution of Oceanography, San Diego, USA).

Over the period 2010-16 during some of the SURATLANT cruises, $\delta^{13}\text{C}_{\text{DIC}}$ were measured by mass spectrometry via an acid CO_2 extraction method in a vacuum system developed by Kroopnick (1974) whereas further details on the sampling methods and analytical techniques are provided in Racapé et al. (2014) for $\delta^{13}\text{C}_{\text{DIC}}$. Water was collected in small glass bottles poisoned by at least 1 ml of saturated solution of mercuric chloride, and stored in the dark when possible at 4°C (at least, after return to the lab, when it was stored for up to a year before analysis). $\delta^{13}\text{C}_{\text{DIC}}$ values should have a precision of $\pm 0.01\text{‰}$ (Vangriesheim et al., 2009) and a reproducibility of $\pm 0.02\text{‰}$. Issues on the accuracy of some of these samples have been raised, and will be examined in intercomparison exercises.

Water isotopologs:

Since 12/2011, the oxygen isotopic composition of discrete sea water samples has been analyzed usually with a PICARRO CRDS (cavity ring-down spectrometer; model L2130-I Isotopic H_2O) at LOCEAN-IPSL (Paris, France). Based on repeated analyses of an internal laboratory standard over several months, the accuracy of the $\delta^{18}\text{O}$ measurements is usually better than $\pm 0.05 \text{‰}$. δD is also measured, and d-excess has been computed ($\delta\text{D}-8 \delta^{18}\text{O}$). All sea water samples before 04/2016 have been distilled to avoid salt accumulation in the vaporizer and its potential effect on the measurements (e.g., Skrzypek and Ford, 2014). Further information is provided in Benetti et al. (2016). Between 04/2016 and 07/2016, the analysis has been often done without distillation and with a salt trap mesh. The 09-10/2016 samples were instead analyzed on a GV Instruments Isoprime dual inlet IRMS coupled with Aquaprep sample preparation system (at IES, Reykjavik, Iceland). A recent study (Benetti et al., 2017, in review) suggests that different corrections have to be applied on the data depending on the method used to report the data in ‘absolute concentration scale’. We use their recommendation and report both data adjusted to ‘absolute concentration scale’ and original data. For the 12/2011 section, some samples were analyzed by the PICARRO CRDS, but some with a GV Instruments Isoprime dual inlet IRMS coupled with Aquaprep sample preparation system (with $\delta^{18}\text{O}$ adjusted to the PICARRO measurements). Accuracy of these samples is probably not as high (and are corrected as if using distillation on CRDS).

The $\delta^{18}\text{O}$ values of samples in 1993-1995 were analyzed at the Lamont Doherty Earth Observatory on a GV Instruments Isoprime dual inlet IRMS coupled with Aquaprep sample preparation system. As information on the exact processing of these samples has been lost (they were calibrated with an internal standard, probably corresponding to deep Atlantic Ocean water), and based on the data values available, we apply no correction to these data and assume that they are reported in calibration scale. Absolute accuracy for the samples from 07/1993 might be a little less accurate than later cruises.

File:

<https://suratlant.locean-ipsl.upmc.fr/surfacedata.19932016c>

File format:

One line per sample collection

Index, date, latitude, longitude, SST, SSS, DIC, AT, PO₄, NO₃+NO₂, silicate, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$, δD , d excess, index(method), original $\delta^{18}\text{O}$, δD , d excess

Date (year, month, day, hour, minute), and position most commonly correspond to beginning of sampling collection. The data might be collected over up to 10-15 minutes, which can result in scatter in the water collected for the different analyses.

The water isotopologs ($\delta^{18}\text{O}$, δD , and computed d excess) are first reported in absolute concentration scale (relative to VSMOW). Then an index(method) is provided as well as the original data ($\delta^{18}\text{O}$, δD). The index(method) is equal to 0 if on IRMS, 1 if the distilled sample is measured with PICARRO CRDS, and 2, if the sample is directly measured (with a salt trap) on PICARRO CRDS.

Some dubious data of nutrients or DIC/TA are reported with a negative value.

Otherwise, missing data or bad data are replaced by a missing value: 9.999 ($\delta^{13}\text{C}_{\text{DIC}}$) 99.99 (nutrients, SST), 99.999 ($\delta^{18}\text{O}$, δD , SSS), 9999.99 (TA and DIC).

References

- Chipman, D. W., Marra, J. and T. Takahashi, 1993. Primary production at 47N and 20W in the North Atlantic Ocean: a comparison between the ¹⁴C incubation method and the mixed layer carbon budget. *Deep-Sea. Res.* **40**(1/2), 151–169.
- Edmond, J. M., 1970. High precision determination of titration alkalinity and total carbon dioxide content of sea water by potentiometric titration. *Deep-Sea Res.* **17**, 737–750.
- Kroopnick, P., 1974. Correlations between ¹³C and ΣCO_2 in surface waters and atmospheric CO₂. *Earth and Planet. Sc. Lett.* **22**, 397-403.
- Olafsson, J., Olafsdottir, S. R., Benoit-Cattin, A., and T. Takahashi, 2010. The Irminger Sea and the Iceland sea time series measurements of sea water carbon and nutrient chemistry 1983-2008. *Earth Syst. Sci. Data* **2**, 99-104.
- Quay, P., Tilbrook, B. and C. Wong, 1992. Oceanic uptake of fossil fuel CO₂: Carbon-13 evidence. *Science* **256**, 74–79.
- Quay, P., and J. Stutsman, 2003. Surface layer carbon budget for the subtropical N. Pacific: $\delta^{13}\text{C}$ constraints at station ALOHA. *Deep-Sea Res.*, **I**, **50**, 1045-1061.
- Skrzypek, G., and D. Ford, 2014. Stable Isotope analysis of saline water samples on a cavity 546 ring-down spectroscopy instrument. *Environmental Science & Technology*, **48**(5), 2827–2834.
- Vangriesheim A., Pierre, C., Aminot A., Metzl, N., Baurand, F. and J.-C. Caprais, 2009. The influence of Congo river discharges in the surface and deep layers of the Gulf of Guinea. *Deep-Sea Res. II* **56**, 2183-2196, doi: 10.1016/j.dsr2.2009.04.002.

References on SURATLANT data

- Corbière, A., N. Metzl, G. Reverdin, C. Brunet, T. Takahashi, 2007. Interannual and decadal variability of the oceanic carbon sink in the North Atlantic subpolar gyre. *Tellus B*, **59**, 2, 168-178, doi :10.1111/j.1600-0889.2006.00232.x.
- Benetti, M., G. Reverdin, C. Pierre, S. Khatiwala, B. Tournadre, S. Olafsdottir, A. Naamar. Variability of sea ice melt and meteoric water input in the surface Labrador Current off Newfoundland. <https://suratlant.locean-ipsl.upmc.fr/benettietal2016.pdf>
- Metzl, N., A. Corbière, G. Reverdin, C. Brunet, D. Thuillier, R. Wanninkhof, D., Pierrot, A. Olsen, T. Takahashi and J. Olafsson, 2010. Recent acceleration of the winter fCO₂ growth

rate in the North Atlantic subpolar gyre surface waters, 1993-2008. *Global Biogeochem. Cycles*, 24, GB4004, doi:10.1029/2009GB003658.

Racapé, V., N. Metzl, C. Pierre, G. Reverdin, P.D. Quay and S.R. Olafsdottir, 2014. The seasonal cycle of $\delta^{13}\text{C}_{\text{DIC}}$ in the North Atlantic subpolar gyre. *Bio-geosciences*, 11, 1683-1692, doi:10.5194/bg-11-1683-2014.

G. Reverdin, 2010. North Atlantic subpolar gyre surface variability (1895-2009). *J. Climate*, 17, 4571-4584. Doi:10.1175/2010JCLI3493.1

Figures with data distribution for four parameter (DIC, phosphate, $\delta^{13}\text{C}_{\text{DIC}}$, $\delta^{18}\text{O}$)



