EuroGO-SHIP
Enhancing ocean observations

D3.3. Report on updated salinity best practice

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1. Introduction

The EuroGO-SHIP project aims to develop a concept for a European Research Infrastructure (RI) for hydrography, that is, the measurement of ocean physical and biogeochemical properties from the platform of a marine vessel. Measurements of parameters like ocean salinity and velocity, dissolved oxygen and inorganic carbon, inorganic nutrients and transient tracers throughout the water column are essential for understanding the ocean’s role in local and global climate and ecosystems, and thus society’s need for hydrographic data is growing. Currently many observations are made on a nation-by-nation or even institution-by-institution basis, producing data of variable quality in a fragmented way. The EuroGO-SHIP RI would address gaps in facilities and best practices, enabling the European hydrographic community to increase the quality, traceability, and availability of hydrographic data.

The aim of EuroGO-SHIP Work Package (WP) 3 is to demonstrate the principles and operations of a European RI for hydrography through pilot activities, including demonstrations of sharing knowledge and equipment, organising and comparing data, and contributing to updated best practices among the project partners. Salinity was one of the parameters used to demonstrate several of these aspects because it is both one of the key variables for characterising both physical and chemical properties of seawater, and a variable where equipment, training, and methodology used in its measurement vary widely. There is a need to update best practices for salinity sampling and analysis including uncertainty, and to apply them to ensure the quality and comparability of salinity data across different regions and time periods.

1.1. Background and context of the deliverable

Accurate and consistent measurements of salinity are essential for understanding the ocean's role in climate, ecosystems, and human activities. The standard for measuring salinity is by CTD (conductivity-temperature-depth) sensors, which are subject to (temperature- and pressure-dependent) drifts away from factory calibration settings and require laboratory analysis of water samples collected by Niskin bottles attached to the same frame as the CTD for calibration to the highest accuracy; however, these measurements themselves are subject to various sources of uncertainty. Once salinity samples are collected, the laboratory analysis of the sample salinity uses salinometers, instruments that measure the electrical conductivity of water. The resulting discrete sample salinities contain error introduced in the samples (contamination at sampling or by degradation in storage) or their analysis (salinometer calibration, standardisation and linearity of response; uncertainties in the temperature- and composition-dependent conversion from conductivity to salinity), as well as the real variability between the sample volume and the coincident-in-time CTD measurement.

The current standard for salinity best practice, by Kawano (2010) in the GO-SHIP manual, has some clear opportunities for updating, optimisation, and expansion to use cases beyond GO-SHIP. For instance, it describes the use of a particular model of salinometer, when other models are now available and commonly used; it was developed for open ocean waters with salinity not far from the IAPSO standard and where a number of deep, stable samples are available, whereas European hydrography also encompasses fresher marginal seas and shallow shelf seas; it requires, or assumes, good control of environmental and salinometer/sample temperature, which is not possible on every expedition or vessel; it does not incorporate data or recommendations on sample storage beyond an expedition, thus requiring the availability of an expensive salinometer on each cruise; and it requires the use of a large number of bottles of IAPSO-standard seawater, which are too expensive for some groups.

While D3.2 reports on the pilot activities as a whole, this report, D3.3, focuses on the optimisation of salinity best practices via both analysis of existing practices used by EuroGO-SHIP salinity-measuring groups, and intercomparison of salinity data collected during the project using several different methodologies. It will inform ongoing WP3.1 work on best practices. By providing information on differences that may arise between data from different cruises using different salinometers, sample bottles, and analysis methods, it will also it will also inform the WP2.3 development of an uncertainty-incorporating secondary QC system for hydrographic measurements from multiple cruises.

1.2. Objectives and scope of the deliverable

The main objective of this deliverable is to report on the results and outcomes of the pilot activities relevant to best practices for salinity sampling and analysis. Its specific objectives are:

- To test the impact of sampling, storage, and analysis protocols, of salinometer model and of laboratory conditions, using data from a range of regional seas and open ocean conditions
- To quantify the impact of these factors on salinity sample uncertainties and on their use for CTD calibration
- To present recommendations for revisions to best practice as well as for "real-world" best practices suitable to different constraints and levels of uncertainty
- To present a recommendation for future studies to address unanswered questions

1.3. Structure of the deliverable

The deliverable is structured as follows:
Section 1. Introduction: background and objectives
Section 2. Current salinity practices: comparison of salinity sampling and analysis practices in use by EuroGO-SHIP groups, including deviations from the existing GO-SHIP best practice
Section 3. Optimisation of practices: comparison of differences produced by selected variations in sampling and analysis methods, revealed by replicate analyses
Section 4. Conclusions, lessons learned, and recommendations regarding updates to best practices and future work toward optimisation

2. Current salinity sampling and analysis practices

2.1. Methodology

Comparing the range of current practices, as expressed in a combination of written documentation (in various forms and languages) as well as unwritten knowledge, was necessarily an iterative process. While the planned focus of the replicate intercomparison (described in Section 3) was on differences in salinometer model, use of standards, and control of sample temperature during analysis of conductivity, it is apparent that other aspects might be at least as important as sources of methodological difference resulting in different levels of error, and therefore should be considered in any attempt to codify a set of best practices. The scope was informed by previous experiences (e.g. difficulties with laboratory temperature control and stability of conductivity measurements) and unpublished internal experiments (e.g. GEOMAR's "introduce artificially a sampling error" experiment, MI's experiments with stored sample stability), and evolved based on discussions related to the D3.2 pilot activities as well as to other EuroGO-SHIP workpackages (notably on uncertainty and metadata).

Sources of information on current, formalised (written) best, standard or recommended practices were:

- The GO-SHIP salinity best practice (Kawano, 2010)
- Documents submitted by salinity expert groups within EuroGO-SHIP. These groups and the types of documents submitted were:
    - NOC (standard operating procedure),
    - GEOMAR (standard operating procedure and manuals),
    - CNR (standard operating procedure),
    - IEO (set of cruise reports).

In addition, notes on procedures deriving from other pilot activities including training provided by NOC and IEO to GeoEcoMar (D3.2 report) and development by CNR and NOC of a protocol for collecting and analysing intercomparison samples on the CNR cruise, as well as discussions between EuroGO-SHIP salinity expert groups, provided additional details.

The information was synthesised by first recasting the GO-SHIP manual (Kawano, 2010) into a step-by-step protocol, then reorganising the steps into a set of questions and selectable options (e.g. "when doing activity A, which of the following steps do you use?"). The documents submitted by each group, and the information revealed in the course of other parts of the activity (D3.2 report), were then analysed in detail to construct a set of example replies to the questions, including explanations of steps different from or not included in Kawano (2010). Some of these variations (e.g. steps derived from the Optimare procedure) were then added as options in the survey, and the replies updated accordingly. The information was organised as follows:

- Sampling procedure (including preparation and storage)

- Salinometer maintenance, configuration, and standardisation, along with the laboratory environment
- Conductivity measurement procedures
- Quality control (QC) and reporting of (meta)data
- Common issues and special cases (e.g. high-sediment samples)

Finally feedback from each group was used to refine the sample replies.

2.2. Summary of current practices

The survey is presented in the boxes starting on the following pages, with replies from five groups -- CNR, GEOMAR, IEO, MI, and NOC -- as well as “TK10” to indicate procedures specified in Kawano (2010). Although the goal was to capture all significant aspects of salinity sampling and analysis practices, the results still have gaps, so that it is not possible in each case to reconstruct a full salinity sampling and analysis procedure for a given group from the survey below. This reflects the significant role of informal and unwritten knowledge, which tends to be passed on in “live” training of early career researchers (ECRs), technicians, and others participating in salinity measurements.

Procedure for taking salinity samples

Where do you take salinity samples?

- ❑ We take samples from the full range of depths/pressures (including the surface mixed layer and below 1000 dbar), temperatures, and salinities. NOC CNR GEOMAR
- ❑ We take samples from regions with small gradients in temperature and salinity. NOC GEOMAR
- ❑ We take samples from every Niskin where any discrete sample (e.g. DIC) is being drawn. NOC CNR
- ❑ We take replicates from a single Niskin. IEO GEOMAR
- ❑ Other (include details or information not covered above):

NOC: exception to sampling from every Niskin used: replicate Niskins at the same depth are not always sampled.

IEO: Samples only taken below 1000 dbar. Replicates (4 samples) taken from a single Niskin at 1500 dbar.

GEOMAR: low S-gradient regions, replicates (duplicates and triplicates) only done if there are not many deep CTDs.

CNR: exception to sampling from every Niskin used: not always for Niskins used for large-volume sample.

What type of bottle do you use for salinity samples and how is it closed?

- ❑ OSIL bottles with ribbed plastic inserts and outer screw caps. NOC IEO CNR MI
- ❑ We use glass bottles with rubber stopper and crimp seals.
- ❑ We use glass bottles with outer screw caps only. CNR
- ❑ We use standard glass swing-top bottles (e.g. commercially available beer bottles) with rubber seal. GEOMAR CNR
- ❑ Other (include details or information not covered above):

NOC: A sampling tube and gloves are not required but may be used if kept clean (rinsed with Niskin water).

CNR: Glass bottles, 120-250 mL. Insert is recommended but not always used.

When collecting salinity samples, which steps do you use:

- ❑ We check inserts for deformation before use. NOC CNR
- ❑ We rinse inserts in DIW (deionized water) and air-dry before use. NOC IEO
- ❑ We rinse each bottle two to three times with water from the Niskin. NOC IEO CNR GEOMAR
- ❑ We rinse by completely filling or overfilling (TK10). IEO GEOMAR
- ❑ We leave headspace; only fill to the base of the neck or approximately 2 cm below the top (TK10). NOC IEO CNR GEOMAR
- ❑ We dry the bottle top with paper towel, including just inside the mouth, and the threads (if applicable). NOC CNR
- ❑ We rinse caps in Niskin water and dry with paper towel before placing on bottles (TK10). IEO CNR
- ❑ Other (include details or information not covered above):

NOC: Sample bottles are part-filled and shaken to rinse. Caps are rinsed with DIW and air-dried before use. Care taken to not introduce grease or salt crystals to the bottle top or insert/cap.

IEO: Recent change in procedure from rinsing caps in Niskin water to using clean (DIW-washed) caps.

CNR: Take care that rainwater or surface seawater does not drip into the sample bottle. Tighten the cap and insert tightly.

GEOMAR: We take care to not touch the valve of the bottle neck or the cap with the finger.

When preparing samples for storage, which steps do you use:

- ❑ We rinse sealed bottles with fresh water before storage (TK10).
- ❑ We store bottles upright. NOC CNR
- ❑ We store bottles upside down (TK10). IEO
- ❑ Other (include details or information not covered above):

IEO: bottle tops are covered with film after bringing back to the laboratory, samples are stored in A/C multipurpose lab on ship.

What special procedures (not covered above) do you follow, and what issues do you commonly encounter with sampling?

- ❑ Special procedures for sediment-rich waters (details below)
- ❑ Special procedures to store samples for longer (details below)

- ❑ Issues with collecting samples (details below) IEO

IEO: Issues with Niskin bottle condition.

Procedures for analysis

Where do run your salinity sample analysis?

- ❑ At sea in dedicated lab. NOC GEOMAR CNR MI
- ❑ At sea in multipurpose lab. GEOMAR CNR
- ❑ Temperature-controlled laboratory on shore. IEO GEOMAR
- ❑ Other lab on shore. MI
- ❑ Other (include details or information not covered above):

GEOMAR: Salinity sample analysis is run at sea in dedicated lab when available, otherwise we use a multipurpose lab. We also run samples that come in from volunteering ships without a salinometer on board in our temperature-controlled lab on shore.

CNR: Salinity sample analysis is run at sea in dedicated lab when available, otherwise we use a multipurpose lab.

MI: Sample analysis usually at sea in temperature-controlled lab; in some cases samples must be stored and run ashore.

What type of salinometer do you use?

- ❑ Autosal. NOC IEO CNR GEOMAR
- ❑ Portasal. CNR MI
- ❑ Optimare. GEOMAR
- ❑ Other (include details or information not covered above):

When preparing samples for analysis, which procedure do you use:

- ❑ Samples are equilibrated in the laboratory where salinity is to be measured to come to the same temperature as the laboratory (please specify minimum storage times below; TK10). NOC CNR MI
- ❑ Samples are equilibrated in a water bath. GEOMAR
- ❑ Samples are over-warmed, degassed by shaking and venting, then cooled back to specified temperature below salinometer bath temperature. GEOMAR
- ❑ Standard seawater is treated the same way as samples. NOC CNR
- ❑ Other (include details or information not covered above):

NOC: Samples should equilibrate for 4-24 hours in the lab.

CNR: Samples should equilibrate for at least 4-5 hours.

MI: Samples stored at room temperature with salinometer at least 2 hours before analysis.

For installing and maintaining the salinometer, which procedures do you follow:

- ❑ The salinometer is checked and maintained periodically by manufacturer-certified technicians (TK10). NOC
- ❑ A regulated power supply is used for the salinometer, and voltage and frequency match settings on the salinometer (TK10). NOC
- ❑ The salinometer is electrically grounded (TK10). NOC
- ❑ The salinometer bath is filled and left to temperature stabilise for 24 hours before use. NOC GEOMAR
- ❑ The conductivity cell is cleaned regularly (e.g. daily; TK10).
- ❑ Conductivity cell cleaning uses a cleaning solution followed by rinsing with DIW until conductivity is near zero (TK10). NOC GEOMAR
- ❑ The conductivity cell and/or pump are serviced by removal and disassembly during the cruise if problems occur. NOC GEOMAR CNR
- ❑ When not in use the conductivity cell is filled with DIW. NOC GEOMAR CNR MI
- ❑ Other (include details or information not covered above):

NOC: The conductivity cell is cleaned with solution only if bubbles are persisting.

IEO: Autosal is calibrated every few years. Conductivity cell only cleaned with DIW.

CNR: The salinometer is turned on at least 2 hours before analysis.

GEOMAR: If bubbles persist, the conductivity cell is cleaned with diluted Mucasol, sit for 1 hour, rinse 8 times with DIW. Measurement cells should be kept wet even during transport.

MI: Salinometer bath is filled and left to stabilize at set temperature for at least 12 hours.

How are the salinometer settings and environment configured and monitored:

- ❑ The salinometer internal pump is used with a vacuum sealing bung. GEOMAR
- ❑ A peristaltic pump is used (TK10). NOC IEO CNR

- ❑ The salinometer laboratory has air conditioning set to –2 to +1C of salinometer bath temperature (TK10). NOC IEO GEOMAR CNR MI
- ❑ The lab temperature is monitored continuously/digitally. CNR
- ❑ The temperature in the lab is monitored manually on a regular basis. NOC MI
- ❑ The humidity in the lab is monitored. CNR
- ❑ The bath temperature is recorded digitally/continuously. GEOMAR
- ❑ Real-time measured bath temperature (rather than bath thermostat setting) is used in converting conductivity ratio to salinity. GEOMAR
- ❑ The suppression (sensitivity) dial/setting is adjusted at the start of the cruise and not afterwards (TK10). NOC CNR
- ❑ The zero and standby settings are monitored. NOC GEOMAR CNR
- ❑ The salinometer standardisation dial/setting is adjusted, using multiple bottles of standard seawater, only at the start of the cruise and after major maintenance (TK10). NOC
- ❑ The salinometer standardisation setting is adjusted, using multiple bottles of standard seawater, more regularly (e.g. daily). CNR GEOMAR MI
- ❑ Other (include details or information not covered above):

IEO: Standardisation applied using OSIL/Guildline software calibration option.

CNR: Each standardisation uses multiple SSW bottles until 2-3 of them coincide with the nominal value.

GEOMAR: The salinometer standardisation setting is adjusted at the start of the day if the SSW value drifts by more than 0.002 psu from the initial (start of the cruise) value. When using Optimare, bath temperature recorded digitally/continuously and real-time bath temperature is used in converting conductivity ratio to salinity.

When analysing a set of salinity samples, which steps do you follow:

- ❑ One or more new bottles of SSW are run at the start and end of each day of running samples.
- ❑ One or more new bottles of SSW are run at the start and end of each batch of up to 24 samples. NOC
- ❑ When a new bottle of SSW is run its conductivity ratio is tracked for later adjustments to data. NOC
- ❑ A dummy sample is run before starting a batch of samples. GEOMAR
- ❑ Old or opened bottles of SSW are used to flush the cell before a new bottle of SSW. NOC CNR MI
- ❑ A sub-standard is run regularly to alert to drift (TK10). GEOMAR
- ❑ Previously-opened bottles of SSW are used to monitor and alert to drift. IEO
- ❑ A single batch of IAPSO standard seawater is used (TK10). NOC CNR
- ❑ Sub-standards are made up by filtering a large volume of deep seawater (TK10). GEOMAR
- ❑ Unopened bottles are stirred by inverting or gentle shaking before being run (TK10). CNR GEOMAR MI
- ❑ The cap or insert is checked for salt crystals before and after opening and the top of the bottle is patted dry. NOC CNR
- ❑ Before placing a new bottle, the intake tube (and bung, if used) is wiped dry. NOC GEOMAR MI
- ❑ Other (include details or information not covered above):

NOC: A new bottle of SSW should also be run if there is a break of more than half an hour while running a batch of samples. Unopened bottles are mixed by vigorous shaking followed by allowing air bubbles to rise for a couple of minutes.

IEO: A new bottle of SSW is run at the start of each batch of samples. Opened standards bottles run at the end of a batch of samples to check for drift (but not used to adjust data). Substandard seawater used to check salinometer stability before running a new OSIL standard (following two flushes of the cell).

CNR: A new standard is run at least daily.

GEOMAR: At least one new bottle of SSW is run at the start of each day.

MI: Standards are measured at the start of a run. Sample bottle is inverted at least 3 times.

When taking measurements of conductivity from each sample or standard, which procedures do you follow:

- ❑ The cell is flushed and filled 6 times before taking the first measurement. CNR
- ❑ Before switching to read, the salinometer bath light must indicate stable temperature. NOC IEO CNR

- ❑ The salinometer pump is switched off when switching to read. NOC GEOMAR
- ❑ Suppression switch is adjusted to match conductivity range and show positive values. NOC GEOMAR
- ❑ Measurements are not started until 25-30 s after switching to read. GEOMAR
- ❑ Conductivity ratio is recorded by software as the average of a number of measurements over several seconds. NOC IEO GEOMAR MI
- ❑ Where standard deviation of double conductivity ratio over the measurement interval exceeds 0.00001, the data from that fill are discarded.
- ❑ Acceptable range of double conductivity ratio from multiple fills is 0.00002 (Autosal; TK10) / 0.00003 (Portasal). CNR MI
- ❑ Conductivity (ratio) is initially measured from two successive fills (TK10). CNR
- ❑ If the range between the first set of fills meets the acceptable range, the values are averaged; otherwise an additional filling of the cell is measured.
- ❑ If the conductivity ratio range between the last two is over the acceptable range, two additional fillings are measured and the median of five fillings is used (TK10).
- ❑ Other (include details or information not covered above):

NOC: The cell is flushed and filled 4 times before taking the first measurement. Before switching to read, wait 10 s then check that bath lights indicate stable temperature. The salinometer internal pump is left on but the peristaltic pump is switched off when switching to read. On switching to read the software measurement is started promptly. Allowable standard deviation over the measurement interval is 0.00002, and allowable range over multiple fills is 0.00002 for standards or 0.00005 for samples. Initially 3 successive fills are measured. If the range is not within acceptable limits, one additional filling is measured and 2-3 fills that do fall within the range are averaged.

IEO: The cell is flushed and filled 3 times before taking the first measurement. Only a single fill is measured and five successive readings (average of 31 measurements each as above) are taken from it. These are averaged, except if standard deviation is high only the last is used. Sometimes some replicated samples are analysed by a different method, measuring over a longer cycle.

CNR: Fills and readings are repeated until two consecutive fills' readings match within 0.00002, when the last value is recorded.

GEOMAR: The cell is flushed and filled at least 4 times before taking a sample measurement, or at least 7 times before taking a standard measurement (though salinometer standardisation may be adjusted on 6th fill if standard has drifted, see above section). Measurements are taken from 3 or more fills.

MI: Cell is flushed and filled three times before taking a reading, or 5 times for standards.

What other steps do you follow, or issues do you commonly encounter, not covered above?

- ❑ Special procedures for certain regions (e.g. shelf seas waters, fresher waters)
- ❑ Issues with keeping salinometer clean or running well NOC CNR GEOMAR
- ❑ Issues with temperature control NOC MI
- ❑ Other issues (details below) IEO CNR MI

NOC: Persistent bubbles in the cell: either the sample is too cold, or sediment/biology has built up in the cell. If salinometer bath lamps or readings are not stabilising, try slowing the peristaltic pump, and check sample temperature.

IEO: Equipment available but no space to analyse at sea (or store more replicate samples?); need to use freshly opened OSIL standards to check/correct for salinometer drift. Samples in old bottles show more noise.

CNR: Changes in pH of the stored sample can cause changes in salinity value. Deposits or persistent bubbles in the salinometer cell should be rinsed out repeatedly with deionised water (avoiding soap or acidic solutions which can throw off the factory calibration of the instrument), removing and disassembling to clean if necessary.

GEOMAR: Persistent bubbles in Autosal cell: needs cleaning (see above). Slow filling of the cell: slippage of the drive belt, or dried out pump pistons. Measuring cell should be kept wet even during transport.

MI: Reliability of salinometer. Difficulties with temperature control in shore-side lab.

Procedure for QC and distribution of salinity sample data and metadata

What quality control measures do you follow on the set of data:

- ❑ Plotting the conductivity (ratio) of SSW vs time, and using offsets to adjust the measured conductivity (ratio) of samples. NOC

- ❑ The SSW adjustment is a trend or slow variation over the cruise (or between major maintenance of the salinometer; TK10). NOC
- ❑ Lower or higher salinity standards are used to check the linearity of the salinometer.
- ❑ Precision is estimated by comparing the double conductivity ratios for replicate samples (pairs of samples drawn from same Niskin bottle). IEO
- ❑ Multiple conductivity ratio measurements from each sample are examined to exclude outliers before averaging, with flags updated accordingly. NOC
- ❑ Plotting of differences between CTD salinity and Autosal salinity to find outliers (TK10). NOC IEO
- ❑ Bottles with large residual from the CTD are reported but flagged questionable and not used in calibration. NOC CNR
- ❑ Bottles with large residual are uniformly excluded or flagged as bad. IEO CNR
- ❑ WOCE flags for bottle data are used. NOC CNR
- ❑ Uncertainty estimates on individual or sets of samples are quantified.
- ❑ Other (include details or information not covered above):

NOC: SSW adjustments may be applied as trends over a day or a set of 24 samples.
IEO: Outliers flagged based on CTD-bottle residuals (threshold of 0.012 psu).
CNR: Outliers flagged based on CTD-bottle residuals (threshold of 0.012 psu).

How are data and metadata reported?

- ❑ Metadata are included with the sample data.
- ❑ Metadata are in the cruise report. NOC
- ❑ Metadata include the batch number of SSW. NOC
- ❑ Metadata include information on salinometer. NOC
- ❑ Salinity sample data are submitted to national data center. NOC IEO CNR GEOMAR
- ❑ Salinity sample data are submitted to global repository (e.g. CCHDO). NOC
- ❑ Salinity sample data are rarely updated after initial submission. NOC
- ❑ Other (include details or information not covered above):

What other QC steps (not covered above) do you perform?

What (if any) other parameters from your cruise (e.g. nutrient data) do you use in your salinity QC?

- ❑ Use other Niskin sample parameters to help QC salinity data NOC
- ❑ Use “outside” data (from other cruises, or climatologies) to QC salinity data (details below)
- ❑ Use other special procedures, commonly or in selected cases (details below) IEO

NOC: Other bottle measurements (oxygen, oxygen temperature, carbon, nutrients) are used in combination with salinity to look for bad Niskins.
IEO: Salinity is used to QC other bottle parameters.

2.3. Differences in current practices

Areas where most (but not all) groups follow similar practices include:

- Sampling through the full depth range
- Leaving a headspace in the sample bottle
- Cleaning and maintaining the salinometer during the cruise with cleaning solution, only when necessary
- Sealing sample bottles with either a plastic insert or rubber-gasketed swing top
- Taking multiple conductivity readings from multiple fills of the cell from each (sample or standard) bottle

Areas where there is no consensus on the details of best practices include:

- Use of replicate samples
- Use of substandards
- How often to run a new standard and whether to adjust the salinometer or record the offset

- Preparing samples: time to temperature equilibrate, degassing or not, shaking or inverting
- Running samples: how many flushes and fills before taking the first reading, how many readings to average, by what method, and with what requirements for consistency

Areas where the results of the analysis are not clear include:
- Data QC thresholds and procedures
- Data and metadata dissemination

Areas where deviations or problems, even if uncommon, are likely to have a significant impact include:
- Poor sealing (not using inserts, or using inserts or a swing-top seal that are not in good condition)
- Introduction of salt crystals by lack of thorough drying, or by other contamination to the sample bottle
- Storage for more than a few months (for typical bottles)
- Not flushing cell sufficiently
- Not measuring more than one fill from a given bottle

Some of the deviations may have significant impact on results. The improvement in data quality following a change in IEO sampling procedure described in the D3.2 report is one example. The next section attempts to quantify the effects of some of the other methodological differences, notably in bottle type and salinometer model.

3. Replicate analyses

3.1. Data sources

Replicate samples were collected on several field experiments and analysed in a number of laboratory setups, summarised in Table 1. Details of the cruises, laboratories, and equipment are given below.

1) Field experiments: Collecting replicate water samples for salinity analysis during four cruises in different regions of the European seas using different sampling bottles (OSIL glass bottles with inserts, or generic swing-top bottles) and storage times ranging from hours to several months. The cruises were:
- MI cruise on R/V Celtic Explorer in the NE Atlantic in January 2023, CE202301
- CNR cruise on R/V Dallaporta in the Mediterranean in April 2023, here referred to as Med2304
- GeoEcoMar cruise on R/V Mare Nigrum in the Black Sea in July 2023, MN244
- NOC/Miami cruise on R/V Endeavor in the NW Atlantic in July 2023, EN705
- NOC cruise on RRS Discovery in the NE Atlantic in March 2024, DY174

2) Laboratory analyses: Analyzing the water samples in different labs, using different salinometers (Portasal, Autosal, Optimare), lab conditions (temperature, humidity) and protocols for standards/substandards. The labs and some differences were:
- MI on R/V Celtic Explorer, using Portasal

- MI shore lab in Ireland, using Portasal – note temperature control not as good as in ship lab
- NOC Calibration lab in UK, using Autosal and Portasal – good temperature and humidity control and monitoring
- NOC-operated lab on R/V Endeavor, using Autosal and Portasal – variable temperature control
- NOC lab on RRS Discovery, using Autosal
- GeoEcoMar container lab on the R/V Mare Nigrum, using Autosal
- CNR lab on the Italian Vessel "G. Dallaporta", using Portasal

Table 1: Numbers of samples collected from each cruise in each type of bottle (columns) and analysed in each laboratory setting on each type of salinometer (rows). Numbers in parenthesis are approximate delays, in months, between collection and analysis for samples analysed off-ship. Note: some CNR samples analysed at NOC are not included due to unclear recording of the bottle number.

	CE23001 (MI), OSIL bottles	Med2304 (CNR), OSIL bottles	Med2304 (CNR), swing-top bottles	MN244 (GeoEco-Mar), OSIL bottles	EN705 (NOC), OSIL bottles	DY174 (NOC), OSIL bottles	DY174 (NOC), swing-top bottles
MI Lab, Portasal	33 (<1)						
Celtic Explorer (MI), Portasal	33 (6)	21 (3)	20 (3)				
Mare Nigrum container lab (GeoEcoMar), Autosal				50			
Dallaporta container lab (CNR), Portasal		44	6				
Endeavor (NOC), Portasal					12		
Endeavor (NOC), Autosal					12		
Discovery (NOC), Autosal						22	12

NOC Calibration Lab, Portasal	34 (3)	17 (2)	19 (2)	50 (2)			
NOC Calibration Lab, Autosal	34 (3)					22 (1.5)	24 (1.5)

3.1.1 Data shortcomings

All the comparisons presented here have fewer degrees of freedom than would be ideal to account for multiple variables. It is thus not generally possible to distinguish differences due to sample temperature equilibration/control in different laboratory conditions or with different models of salinometer from differences in stability and temperature control of salinometers of the same model. Different sample storage and shipping conditions are another complicating factor for the comparisons across laboratories, and were one reason for attempting to analyse replicate samples on the cruises themselves.

Attempts were made to collect data sufficient to disentangle the effects of different sample bottle types from salinometer or replicate order. Notably, samples from the CNR cruise in the Mediterranean were collected in triplicate in two different types of sampling bottles. To account for the possible effects of sampling order (biases or increased noise in samples drawn later from the same Niskin), a protocol was drawn up that would randomise the allocation of bottle types and analysis laboratory relative to sampling order over the course of 10 planned casts at 5 sites. However, only two sites (4 casts) were able to be completed. Bottles were redistributed to keep a single laboratory from only analysing samples in a single type, but some crossovers, for instance between CNR-analysed samples in swing-top bottles and MI-analysed samples in the same bottles, had relatively few replicates; in addition, some comparisons were available only at a small subset of the depth range (visible in the next section).

3.2. Results

3.2.1 Multivariate comparisons

Analysed salinities from samples collected on CE23001 (Figure 1) did not show large differences whether analysed shortly after the cruise at MI, or three months later by the NOC Calibration Laboratory using either an Autosal or a Portasal; the mean offset was 0.002 psu for the Autosal and a larger 0.006 psu for the Portasal, while the standard deviation of the difference was 0.005/0.006 psu. Salinities analysed 6 months later, however, showed three bottles with anomalously fresh salinities (differences of >-0.04 psu) compared to their matching samples. This is consistent with previous sample storage experiments by MI showing that the cutoff for sample consistency is at about 4 months. Thus, while it is possible that the positive offsets of most of the samples analysed in April reflect evaporation during storage, given the small number of data points it could also reflect a difference in standardisation or a difference between nominal and actual temperature for the MI Portasal. No significant difference in consistency is observed between the Autosal and Portasal in the NOC Calibration Lab.

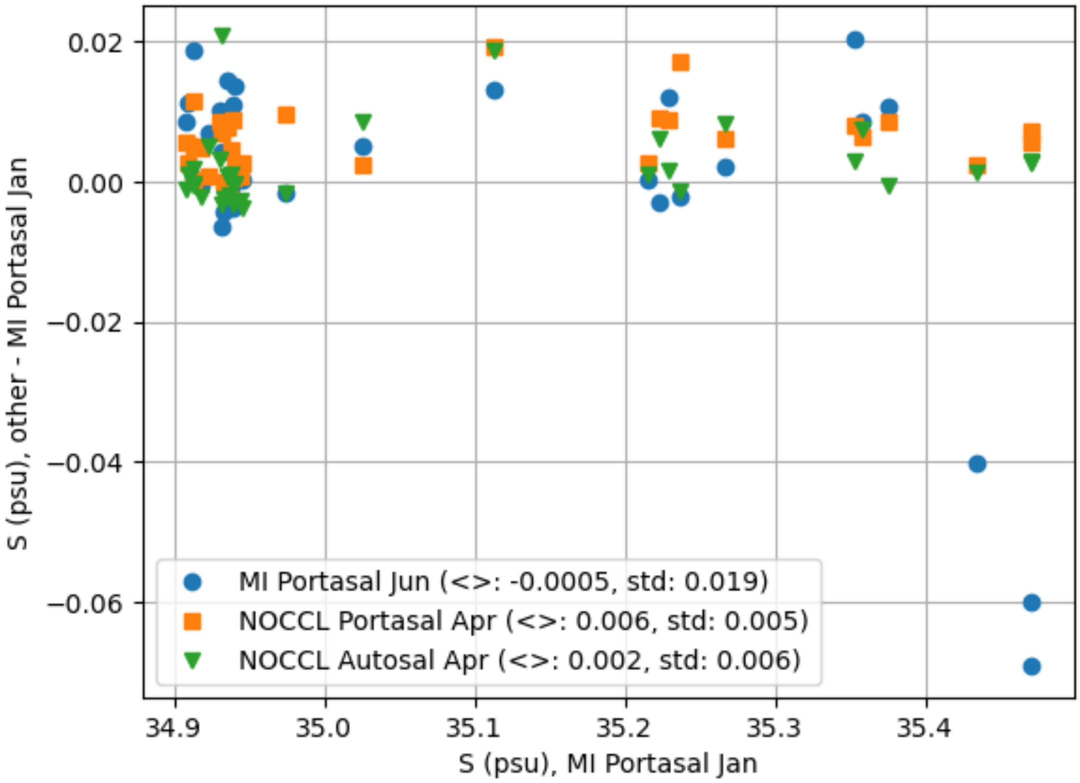

Figure 1: Differences between samples analysed shortly after CE23001 at MI, and later-analysed replicates.

The Mediterranean cruise samples were all analysed on Portasals. Samples analysed at MI three months later were 0.002 psu saltier (median) than those analysed on the ship, with a standard deviation of the difference of 0.004 psu, while those analysed at NOC two months after the cruise were 0.005 psu saltier with a standard deviation of the difference of 0.005 psu. The MI-analysed values were relatively saltier at higher salinities, while the CNR-NOC Cal Lab residual does not depend on salinity. Separating comparisons into those between samples collected in the same type of bottle (OSIL-type bottle to OSIL-type bottle comparisons) and those collected in different types of bottle (Figure 2) shows that the offset of MI samples also depends on whether they were collected in the same bottles as the CNR or NOC analysed samples, and that this could account for the apparent salinity dependence of the difference. It does not appear to be possible, from these data, to confidently distinguish the effects of different laboratory conditions from those of storage time.

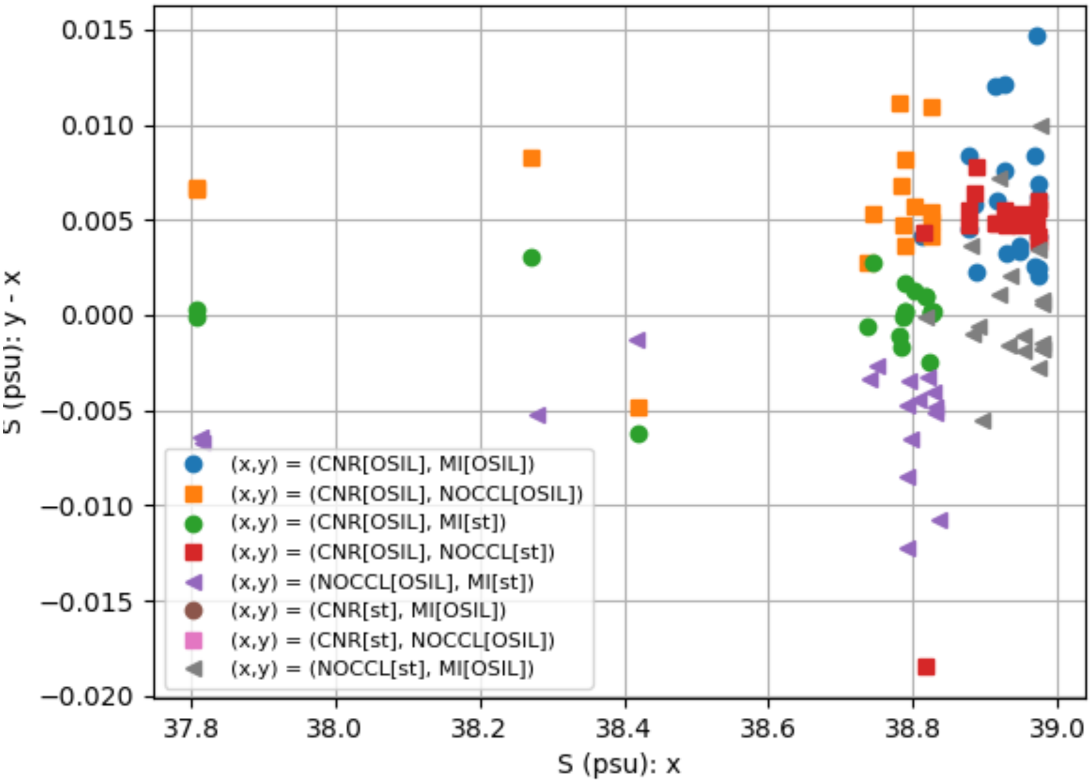

Figure 2: Differences between replicates analysed ashore and samples analysed on Mediterranean cruise in April 2023.

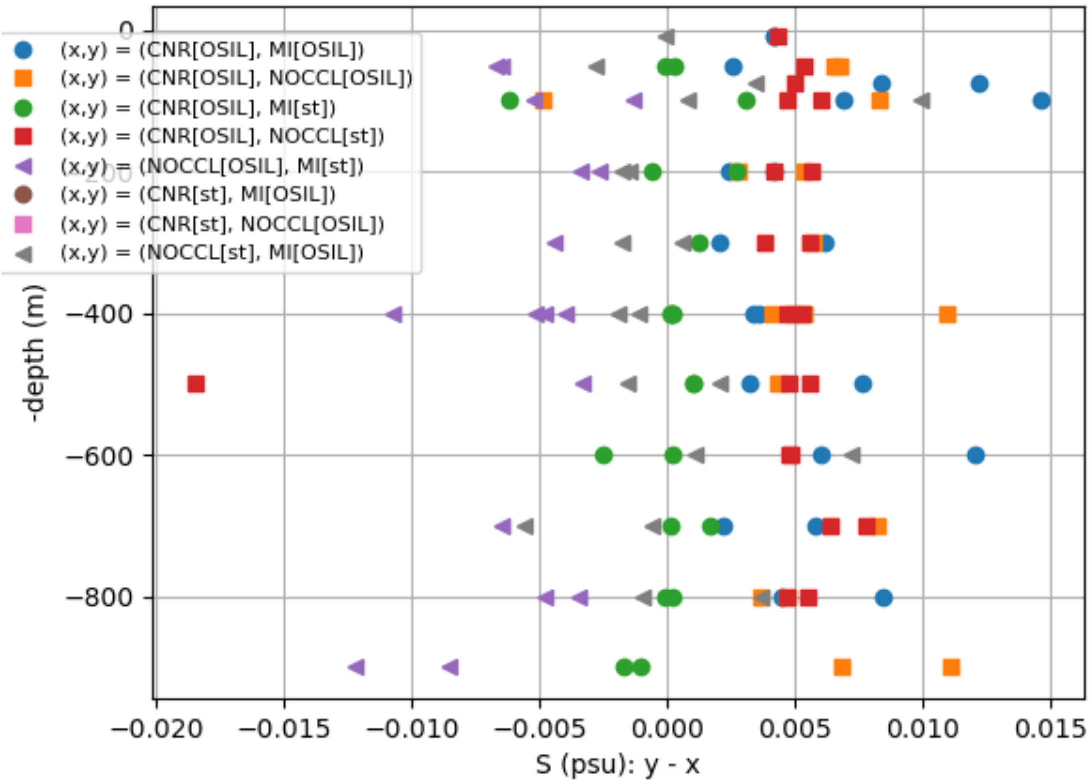

Figure 3: As in Figure 2, but plotted against nominal Niskin bottle closure depth.

As the calibration of CTD salinity depends on depth, the depth-dependence of the salinity analysis is a potentially important aspect. Residuals between Mediterranean cruise replicate samples do not show significant depth-dependence (Figure 3) except for comparisons with NOC-analysed samples in OSIL bottles. The depth range under consideration, however, is limited to the top 900 m.

Comparisons of replicates analysed on MN244 and in the NOC Calibration Laboratory are shown in the report for D3.2 (Schroeder et al., 2024).

3.2.2 Single-variable comparisons

Replicates collected from 24 Niskins over 5 casts on EN705 were run on an Autosal and Portasal both installed in the shipboard laboratory. The residuals tend to increase as salinity increases above 35 -- the nominal salinity of standard seawater (Figure 4). As the saltier waters on this subtropical cruise are found near the surface, this would result in the Autosal samples suggesting a stronger depth dependence of the CTD calibration than the Portasal samples (not shown). Additional data would be required to determine if this effect is an artifact of the two individual salinometers or a feature of Autosal and Portasal linearity.

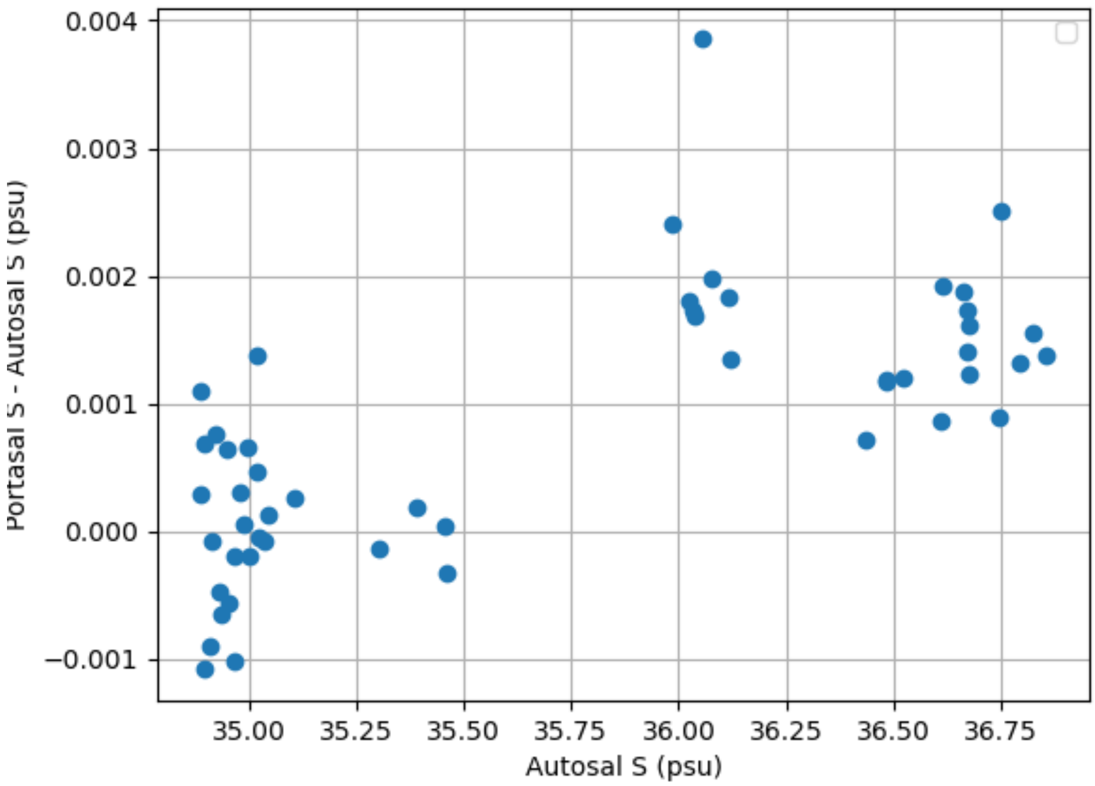

Figure 4: EN705 bottle – CTD salinity residuals as functions of depth and salinity.

On DY174, replicate samples were collected in both OSIL and swing-top bottles from three casts (12 Niskins each), with samples from one cast analysed onboard ship on an Autosal, and from the other two in the NOC Calibration Laboratory within a month of the cruise (having been stored in the shipboard salinometry laboratory in the interim), again on an Autosal. Samples analysed onboard the ship differed by 0.0008 psu (standard deviation), on the larger side compared to other replicate differences. More data are required to determine whether sample bottle type affects results, and whether this depends on the length of storage.

3.2.3 Use of standards and substandards

Analyses by CNR aboard the Mediterranean cruise included enhanced use of standards and substandards, with a new bottle of OSIL-supplied IAPSO standard seawater run at the start,

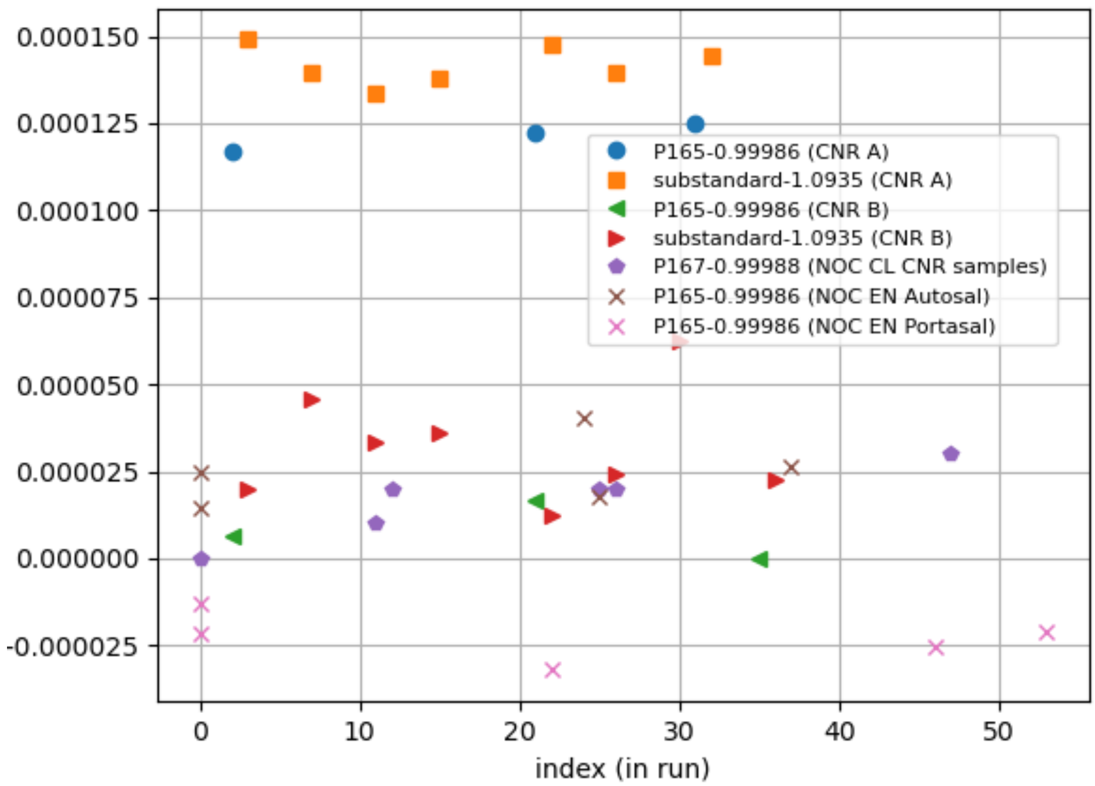

Figure 5: Difference of standard seawater conductivity ratio readings from nominal value, and of substandards from initial value, for shipboard-analysed values from CNR Mediterranean cruise and from EN705.

middle, and end of each set of 18-21 samples, and substandards run every 3 samples. The substandards (Figure 5) were broadly successful at tracking the drift confirmed by the standards (an increase in salinometer conductivity ratio reading over the course of the first set of samples and the first half of the second, followed by a decrease). They show some variability even between standards (that is, within a set of 12 samples), suggesting that trends in standards values reflect short timescale drifts in standardisation (or, with equivalent effect, unaccounted-for drifts in cell temperature). This reinforces the result from EN705 suggesting caution in fitting a depth-dependence to CTD calibrations, especially where, as on EN705, standards readings change from the start to the end of a run. It also suggests that increased use of standards relative to the Kawano (2010) recommendation may be necessary to have confidence in standardisation.

3.2.4 Averaging of replicate measurements from each sample

The survey of current practices described in Section 2 revealed a range of different protocols for the way to make replicate measurements from a given salinity sample. As such replicates not only reduce noise but potentially bias (for instance allowing for detection and exclusion of insufficiently-flushed cell fills), these procedural differences may be significant. Data from the Mediterranean cruise (Figure 6) show that using measurements from a single fill can produce mean salinity differences of 10^{-5} to 10^{-4} psu, with standard deviation of $3x10^{-4}$ psu, relative to averaging over three fills – potentially undoing the benefit of applying standard seawater offsets.

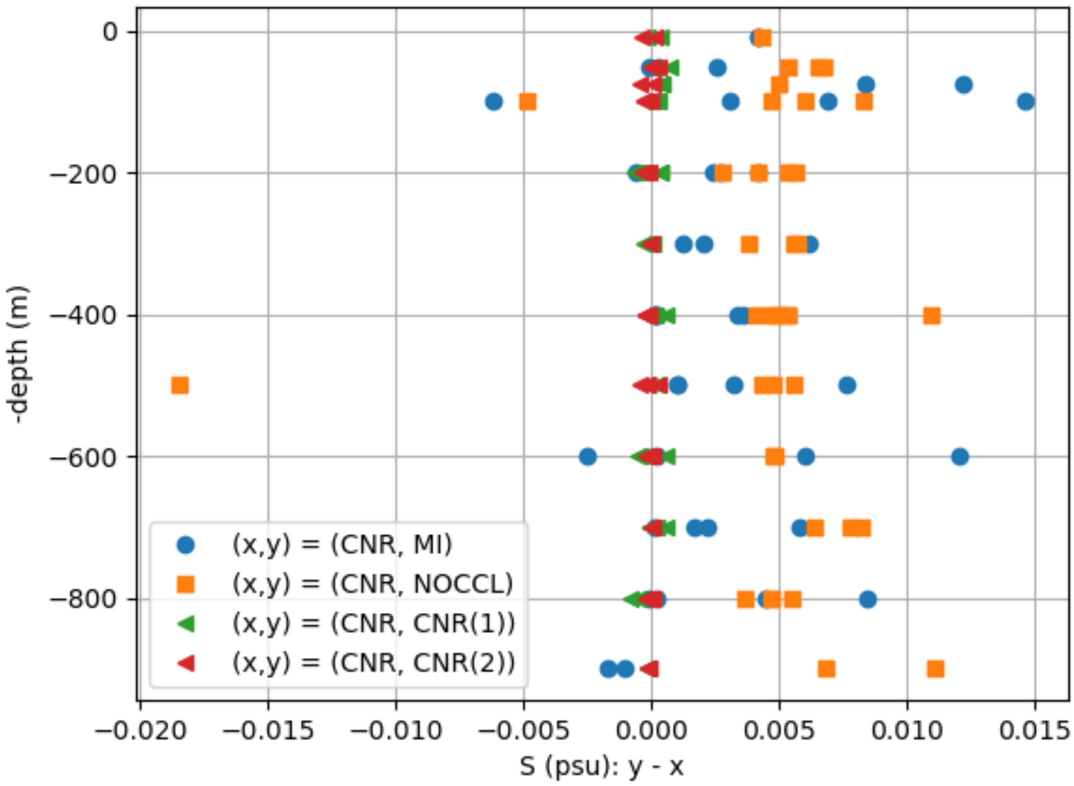

Figure 6: Salinity differences between replicates (as in Figure 3) and between onboard analyses averaging over measurements from one [CNR(1)], two [CNR(2)] or three [CNR] successive fills of the salinometer cell from each sample bottle.

4. Recommendations for current and future updates to best practices

4.1. Recommended changes

4.1.1 Best practices

Best practices should be updated to include newer models of salinometers, as well as the possibility of more direct (density-based) measurements of salinity (Le Menn and Nair, 2022).

They should also include a consideration of real-world best practices, and a quantification of the effect on uncertainty of practical deviations from the ideal in terms of replicates, (sub)standards, sample storage, and salinometer maintenance, to aid in the design of a more metrologically traceable salinity data set (Seitz et al., 2011).

4.1.2 Current or real-world best practices

The recommendations that can be made now are based on steps that have been demonstrated to be important, either here or previously, and may be part of existing best practices, but which (as revealed by the comparison of existing practices in Section 2) are not uniformly followed. These include:

1) Sample distribution: samples should be collected from the full depth range in order to check the pressure-dependence of the CTD calibration.
2) Sampling: where sample bottle caps are separate from the bottle (e.g. OSIL type screw caps) they should be kept clean, not rinsed in Niskin water (even if dried, this introduces a source of error in the form of salt crystals).
3) Replicate conductivity ratio measurements from each sample (or standard) bottle: these should come from at least two different fills of the salinometer cell (from a given bottle).
4) Substandards: substandards made up as a large batch (either of deep Niskin water, or of mixed-together opened/old standards bottles) should be used to track salinometer standardisation and performance during a run; running a substandard at the start, middle, and end of a set of up to 24 samples will allow the analyst to be alerted to problems, while running one every three samples would increase confidence in applying a standard offset trend across the run.
5) Standards: multiple bottles of standard seawater should be analysed per run to reduce noise; to detect drift values should be recorded throughout the run (rather than only at the start).

4.2 Additional investigation

4.2.1 Questions to address in real-world best practices

To account for changes in equipment as well as to expand the applicability of best practices beyond GO-SHIP or GO-SHIP type open-ocean cruises, these questions related to the analysis of salinity by the conductivity ratio should be addressed:

- Additional salinometer models: how does the Optimare salinometer compare to the Guildline Autosal and Portasal?
- What is the effect of over-warming and degassing samples – should this be implemented for Autosal and Portasal samples as well, and does it produce an increase in salinity through evaporation?
- Does bath temperature monitoring produce an improvement in results?

- What steps are recommended for treatment of high sediment load samples, low (or high) salinity samples, and samples that require longer storage? How can sample degradation be slowed?
In addition, the growing possibility of measuring salinity by other methods such as via density (Le Menn and Nair, 2022) should be included.

4.2.2 Data collection and design of comparisons

In order to address the questions above, both salinometer consistency/noise in sample values, and salinometer stability/depth-dependence of CTD calibration should be considered. Quantification of uncertainty in order to recommend different real-world best practices for different applications will require either more specially-collected data, such as side-by-side replicate analyses involving several of each type of salinometer, or a big data approach analysing large quantities of existing data, using bottle-CTD residuals as a measure of noise, and intercomparisons between different cruises sampling stable waters in the same areas to back out offsets.

5. Conclusions

5.1. Summary and main findings of the deliverable

The main finding related to the range of current practices is that practices for salinity sampling and analysis differ significantly even across EuroGO-SHIP salinity expert groups, none of which follow the GO-SHIP best practices (Kawano, 2010) exactly.
The main findings from the intercomparison experiments were:

1) No significant difference in noisiness of data was detected between the Guildline Autosal and Portasal based on replicate analyses. There may be a difference in linearity.
2) Differences between samples collected in OSIL-type bottles (using a screw cap with insert) and swing-top bottles (e.g. generic beer bottles) were significant, but not consistent when accounting for other variables.
3) Differences between samples analysed in ship-board laboratories or other spaces with limited temperature control, and those analysed in the temperature- and humidity-controlled calibration laboratory, were not significant when considering the other variables.

The findings are limited by the limited number of samples relative to the variables being compared, so the overarching main finding is that a better-designed intercomparison, whether using new data or existing data, is indicated.

5.2. Contributions to the project and the European hydrography community

The results on current practices from Section 2 will feed into a more broadly-distributed survey on salinity practices and capabilities being designed as part of WP2.1 (shared facilities). The results on procedure from Section 3 (sample bottle, storage, or salinometer-based) differences will be used in constructing the synthetic data being used in WP2.3 to design an improved secondary QC system. Both will inform a report on best practices systems.

The preliminary recommendations summarised in Section 4 may help the European hydrography community to collect higher-quality salinity data, and/or to contextualise differences between datasets collected with different methods. The report on D3.2 already describes one example, where the sampling recommendation was implemented and increased the percentage of salinity samples useable for calibration. Four of the five recommendations in Section 4.1 are relatively low cost (in terms of time and expense), and further work to quantify their benefits could help expand the fraction of the European hydrographic community collecting well-calibrated CTD salinity profiles.

5.3. Limitations and outlook

The data analysis was limited first by the difficulty in organising a side-by-side comparison of replicate samples, which would minimise confounding variables such as sample storage and shipping as well as different laboratory conditions, and further by equipment problems which reduced the samples collected on the first two opportunistic cruises. The experiments also did not directly address methods for sample preservation for longer storage, nor variations in seawater chemistry (Pawlowicz et al., 2011). The recommendations on updated practices offered are thus limited to some extent to better compliance with the existing GO-SHIP manual (Kawano, 2010). There is good scope for expanding on these recommendations, however. Dedicated experiments planned with enough lead time to evaluate one factor at a time (e.g. side-by-side replicate analyses with different salinometers) would be one way to do so. Some sources of uncertainty could also be quantified through analysis of a larger body of existing data collected using different salinometer models, use of standards, and sampling protocols.

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