Chapter 4
Maintaining Inter-Comparability of Nutrient Measurements

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Abstract Measurements of marine nutrient concentrations are necessary to investigate global biogeochemical cycles, including in the context of climate change, as nutrients are closely coupled to the carbon cycle. To study these phenomena on a global scale, measurements must be internationally comparable between laboratories and calibrated to a metrologically traceable reference standard. In this chapter, we describe how well-trained chemical analysts following Good Laboratory Practice can meet these requirements. Inter-laboratory comparability is not possible without first achieving consistent and reproducible measurements within a single laboratory. First, the measurement reproducibility must be monitored and kept constant within each session of analysis. Second, this criterion should be maintained from one analysis session to the next, for example by using an internal laboratory reference standard and/or conducting duplicate measurements across different sessions. Third, an internationally accepted Certified Reference Material (CRM) should be used to assess the comparability of the data with other laboratories worldwide. Regular participation in laboratory inter-comparison exercises can also reveal systematic bias, thus helping to improve general data quality. Improving analytical quality involves many aspects, such as calibrating volumetric flasks and pipettes gravimetrically to reduce systematic errors, but also a number of seemingly small procedural improvements that can noticeably improve measurement precision and consistency. Each step in the

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overall procedure from sampling, calibration and analysis through to data reporting contributes to the precision and accuracy of the results.

Keywords CFA · Precision · Reproducibility · Consistency · Bias · International comparability · CRM · Normalisation

4.1 Introduction

Dissolved inorganic nutrients are central to the functioning of the global marine ecosystem and the carbon cycle. The main marine "macronutrients" (those with interior ocean concentrations typically in the μM range include nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), phosphate (PO_4^-) and silicate (Si)). Near the ocean surface, these nutrients are often the limiting factor controlling the growth of phytoplankton at the base of the marine food web (Moore et al., 2013) although micronutrients (trace metals) play an important role too (Anderson, 2020). Deeper down in the water column, the chemical signature of nutrient concentrations can be used to infer biogeochemical processes such as organic matter remineralisation (e.g. Humphreys et al., 2022) and to distinguish water masses in combination with physical parameters (Tomczak, 1981). Accurate measurements of nutrient concentrations are therefore essential to understand global biogeochemical cycles and to observe changes in the marine ecosystem, for example in response to climate change.

However, it is challenging to obtain nutrient measurements sufficiently accurate to investigate these processes as highlighted in the 2007 Intergovernmental Panel on Climate Change report: "Uncertainties in deep ocean nutrient observations may be responsible for the lack of coherence in the nutrient changes. Sources of inaccuracy include the limited number of observations and the lack of compatibility between measurements from different laboratories at different times" (Bindoff et al., 2007). It is estimated that differences in nutrient measurements between laboratories and expeditions lead to discrepancies of 1–3%, (Aoyama et al., 2018) and the goal set by the Global Ocean Ship-based Hydrographic Investigations Program (GO-SHIP) for the near future is to be comparable within 1% through improvements of analytical and calibration procedures, including the growing use of international certified reference material (CRM) (Hydes et al., 2010; Becker et al., 2020).

Consistency of existing nutrient measurements in the deep open ocean can also be assessed and improved by using cross-over analysis. For example, data compilation projects such as CARINA (Carbon Dioxed in the Atlantic Ocean; Tanhua et al., 2010) and its successor GLODAP (Global Ocean Data Analysis Project; Lauvset et al., 2022) compare deep ocean nutrient measurements from different oceanographic expeditions at close-by sampling stations and apply adjustments to ensure consistency when significant offsets are found. However, while this approach can help to maximise the scientific value of existing datasets, it should not be considered as the primary route to consistency as the adjustment process is somewhat subjective and could lead to real trends in deep ocean nutrient concentrations being hidden. It

should also be noted that these data compilations are primarily focussed on marine carbonate system measurements, with the nutrients included as useful auxiliary variables. Instead, our focus moving forwards should be on producing accurate nutrient measurements that do not require adjustments.

During the seventies and until the early nineties, the only way of knowing the quality of a laboratory's data was by joining a comparison exercise of the International Council for the Exploration of the Sea (ICES) and measuring unknown samples that would be compared against results from many participants. The World Ocean Circulation Experiment (WOCE) program from 1990 set a data quality goal of an overall reproducibility of 1–3% with a precision of better than 0.4% for nutrients depending on the species analysed. At the time, accuracy was not mentioned as CRMs were not available (Joyce et al., 1994). Unfortunately, the WOCE goal was not always achieved, but nevertheless, it was a good starting point. Nowadays, most oceanographic laboratories are capable of analysing nutrients with data quality close to, or within those goals set by WOCE in 1991.

In this chapter, we discuss the steps required for producing precise, accurate and internationally comparable nutrient measurements. We begin with precision, illustrating various points of methodology that lead to precise, repeatable measurements within individual sessions of analysis. We then consider how consistent measurements can be produced across separate analysis runs within the same laboratory, illustrating the approach with a case study of nutrient measurements from several research expeditions to the Weddell Sea. Finally, we discuss how inter-laboratory comparison exercises (e.g. Aoyama et al., 2010, 2013, 2016, 2018) and the recent advent of widely available and reliable nutrient CRMs can deliver the internationally consistent measurements demanded by marine biogeochemical research at the present time of profound environmental change.

4.2 Internal Precision Using a Tracking Standard

Before 2000, overall precision reported for nutrients was typically referred to as "% of *full-scale* values," where full scale denotes the highest point of the used calibration, e.g. 0.4% of the full scale within a run and 0.6% in-between analytical runs. However, this precision is not representative for mid-to-lower concentrations in the calibration range. Nowadays, precision is usually calculated for at least three concentrations from at least five replicate samples as the Relative Standard Deviation (RSD) in percentage or Coefficient of Variation at that concentration (Taylor, 1987).

Prior to the introduction of Certified Reference Materials (CRMs) in 2012, some analysts used an internal Quality Check by monitoring a deep-water sample (e.g. 20 L of seawater from deeper than 1500 m), collected at the start of an expedition as a reference sample for tracing any drift during an expedition. However, the deep-water samples monitored during different expeditions often had stability issues with values drifting over time. Possible causes are biological activity that changes the nutrient concentration or evaporation of the deep-water sample during the expedition (Hydes

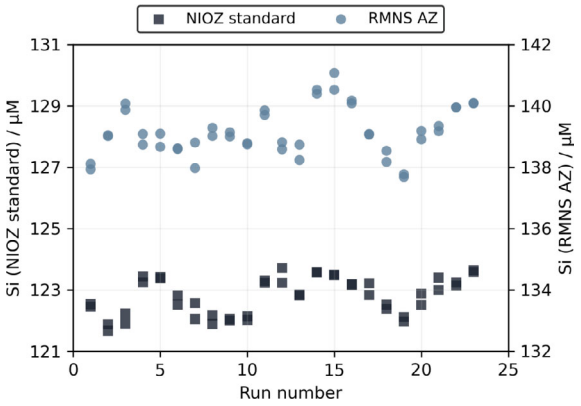

Fig. 4.1 NIOZ Silicate tracking standard (NIOZ standard) and a reference material for nutrients in seawater (RMNS batch AZ) as tracking standards to monitor analytical performance in a series of analytical runs

et al., 2010). However, it is possible to produce stable internal tracking standards as described below and this can help improve quality controls.

The idea is that by monitoring the concentration of an internal tracking standard, the daily measured values can be plotted in a so-called Shewhart chart (Fig. 4.1) or similar. Outliers in this dataset can be detected using upper and lower limits of confidence and possible problems solved before an expedition has been completed. Moreover, by analysing such a stable tracking standard containing the major nutrients of interest in every analytical run, it is possible to normalise data based on the average value of this standard to produce a dataset that is more internally consistent.

As an example of this procedure, the nutrient laboratory from the Royal Netherlands Institute for Sea Research (NIOZ) started using an independent internal lab reference as a tracking standard in 1996 to normalise data and improve internal consistency. The idea originated in 1992 on a Weddell Sea expedition with a week-long algae growth experiment. Specifically, an in-situ bio-assay experiment under iron limitation was conducted and samples needed to be analysed for NO_3^- every day to monitor nutrient drawdown. Analysis of such samples that are expected to have similar concentrations are ideally measured in a single run to avoid differences in accuracy or precision between runs. However, this was not possible as a microbial growth would go on during storage in a fridge as the temperature would be similar or even warmer than the environmental conditions. Therefore, the samples were measured every day in combination with a lab tracking standard which was independent from the calibration, to see if it was conceivable to back-correct or normalise to this tracking standard and in this way eliminate the influence of any day-to-day variability as much as possible. The use of this tracking standard at a concentration close to the concentration of the experimental samples seemed to be successful (Table 4.1) as the corrected concentration either remained similar between days or decreased, whereas the raw data also showed an increase between days (Fig. 4.2), which is not likely unless there was contamination. Overall, one cannot conclude the absolute values were better, but consistency in-between days seemingly improved by using this normalisation.

Table 4.1 Nitrate concentrations during a shipboard incubation experiment in year 1992 as published some years later (Van Leeuwe et al., 1997). The measured concentrations for the day-to-day sample analysis are given, followed by the concentration of the tracking standard in the next column, measured in the same analytical run. Based on the average value of the tracking standard, a correction factor was calculated and in bold the corrected data as used in Fig. 4.2 in light blue is reported

Day no.	Measured data (NO_3 µM/L)	Tracking standard (NO_3 µM/L)	Correction factor	Corrected data (NO_3 µM/L)
0	28.8	27.4	0.992	28.6
1	28.5	27.2	0.999	28.5
2	28.5	27.2	0.999	28.5
3	28.4	27.1	1.003	28.5
5	27.9	26.8	1.014	28.3
6	28.0	27.2	0.999	28.0
7	27.7	27.4	0.992	27.5
Average		27.19		
St. Dev		0.20		
C.V. %		0.75		

Note St. Dev. Indicates standard deviation; C.V. indicates coefficient of variation

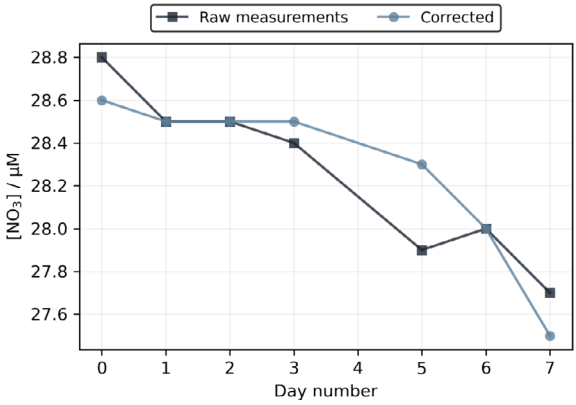

Fig. 4.2 The nitrate concentrations during the shipboard incubation experiment in year 1992 experiment with uncorrected raw measurements in dark blue and the corrected values in light blue. This was part of the experiment II in a suite of six experiments II through VI (Van Leeuwe et al., 1997)

The same approach of normalisation described above was later used along an oceanographic transect on the R.V. Polarstern (Expedition ANT-XIII/4) in the Weddell Sea in 1996.

4.3 Case Study of Nutrient Measurements in the Weddell Sea

Silicate concentrations in the Atlantic Ocean typically range from zero near the surface to around 40 μM or higher in Antarctic Bottom Water. In a system with such a large gradient, a reproducibility between stations of 1% is sufficient to discern the overall spatial distribution and differentiate between different water masses, mixing and biogeochemical processes. However, in the Weddell Sea, macro-nutrient concentrations vary by less than 0.8% over a depth range of 3000 m. Silicate concentrations vary by only ±1 μM at a concentration of 127 μM (i.e. <0.8%), over a depth range from 1000 to 4000 m (Fig. 4.3). As such, the Weddell Sea is a challenge for analysts, with the small variation in nutrients below the surface layer requiring the highest possible reproducibility and accuracy to distinguish trends over time (Hoppema et al., 2015). From our experience, to produce a reliable transect plot over this depth range, the precision needs to be better than 0.4% in each single run, allowing a reproducibility better than the aim of 0.6% between multiple analytical runs. However, such between-run reproducibility is only achievable by normalising to an independent standard containing the major nutrients PO_4, NO_3 and Si.

An independent lab tracking standard was produced for the 1996 Weddell Sea expedition ANT-XIII/4 aboard R.V. Polarstern. This standard contained a known mixture of PO_4, Si and NO_3 at high concentrations and was sterilised using mercuric (II) chloride ($HgCl_2$). For every analytical run, this high-concentration stock mixture was diluted in Low Nutrient Seawater (LNSW) to the same concentration (near the local deep ocean concentrations) and measured in triplicate. After completion of the section through the Weddell Sea, the average value of the tracking standard was calculated (after removing outliers that deviated more than 2 standard deviations from the average) and the deviation from this average was calculated as a factor for each run, which was used to normalise the data from the different analytical runs. To verify that this indeed reduced run-to-run variation, in every run a near bottom duplicate sample from a previous station was re-analysed in consecutive runs resulting in a series of duplicate samples from every station (except the last station of the expedition) that were analysed in separate runs. Reproducibility between these duplicates was compared before and after the correction factor was applied. As an example, for the Si data from this expedition the root-mean-square deviation of all duplicates decreased from 0.60 to 0.35%. This indicates that the correction based on the tracking standard improved the consistency of the data by decreasing the effect of run-to-run variability. This was also visible in the contour plots of the section data by showing smoother distributions and fewer concentration anomalies for the 1996 expedition (Fig. 4.3). To maintain longer term consistency within a lab, the same tracking standard should ideally be used indefinitely (Hoppema et al., 2015): however, this is not necessarily feasible, as in practice, such a standard would run out eventually. Instead, any new tracking standard should be carefully calibrated against a previous one by measuring them together over multiple analytical runs.

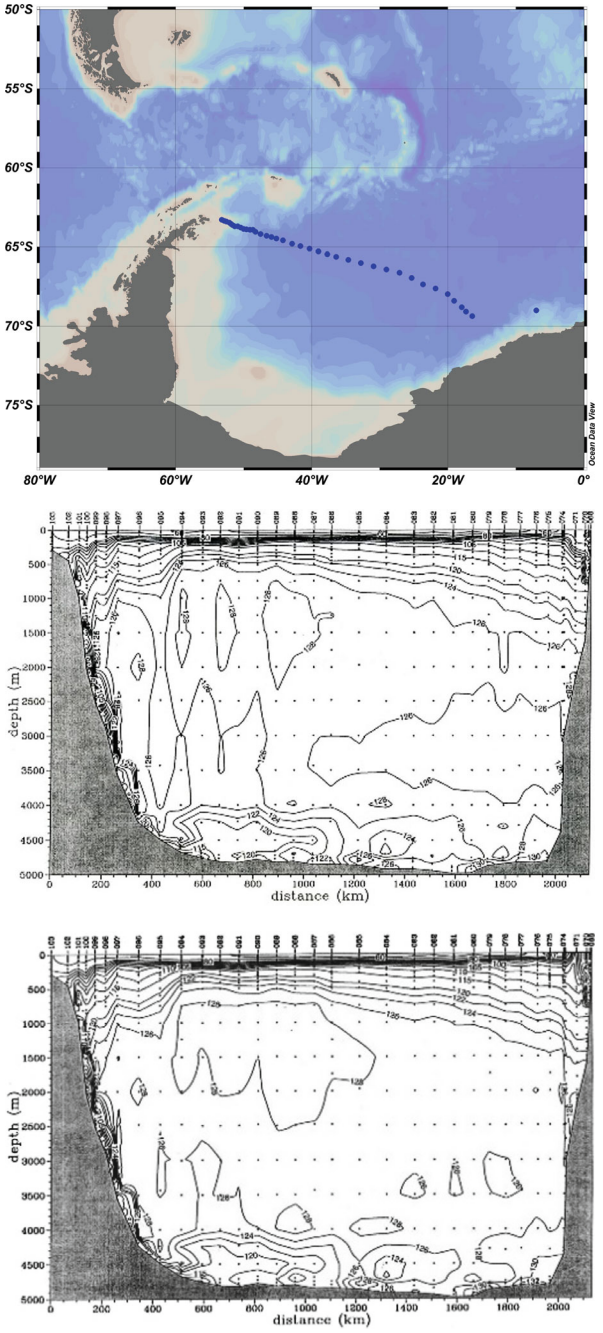

Fig. 4.3 Silicate concentrations (μM/L) of a Weddell Sea hydrographic section from 1996, expedition ANT-XIII/4 with R.V. Polarstern. Upper image shows the uncorrected silicate data and the lower image shows the corrected silicate data using the external tracking standard. Plots made by A. Wisotzki in 1996 on request during the expedition

Given the successful application in 1996, this procedure became common practice in the NIOZ laboratory and was for example also used in 2008 for a repeat occupation of the same transect, but with Reference Material for Nutrients in Seawater (RMNS) batch AZ rather than the previously used NIOZ tracking standard (Fig. 4.4). Additionally, within-analytical run consistency of uncorrected data has improved in our lab over the years as well (compare upper images from Fig. 4.3 uncorrected silicate with Fig. 4.4), mainly by better temperature control during sample analysis and covering open sample tubes with parafilm to avoid evaporation. For the Weddell Sea section of 2008, the differences in concentrations of the duplicate samples are also sorted from low to high (Fig. 4.5) showing that when correctly used, an RMNS or CRM can indeed improve the internal consistency of the data. To also improve the comparability between expeditions, any used RMNS should be the same, or at least be calibrated against a previously used RMNS. Besides the use of an RMNS, inter-comparisons have also been tremendously valuable to achieve (international) comparability.

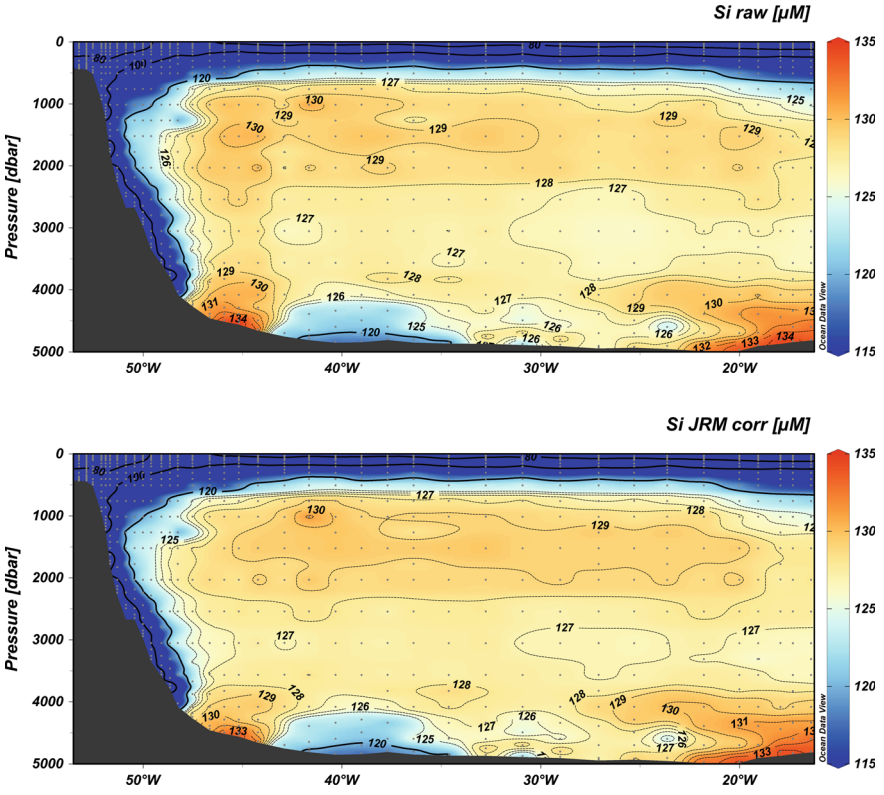

Fig. 4.4 Silicate concentrations (µM/L) of a Weddell Sea Hydrographic Section from 2008, expedition ANT-XXIV/3 with R.V. Polarstern. Upper image shows the uncorrected silicate data and the lower image shows the corrected silicate data using the external RMNS (Batch AZ)

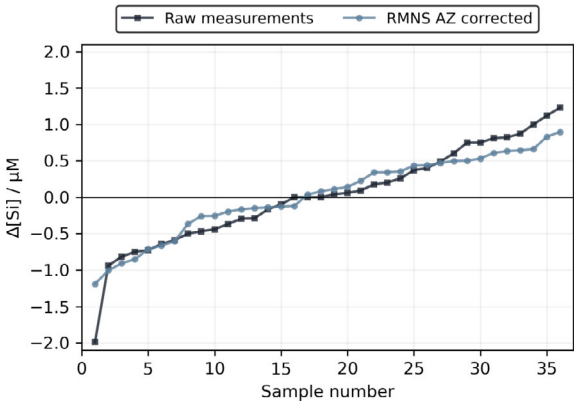

Fig. 4.5 Concentration differences between analysis of duplicate samples in successive runs, sorted from low too high for both uncorrected raw data (dark blue) and data corrected using the external tracking standard RMNS, batch AZ (light blue)

4.4 Inter-Comparison Exercises and Certified Reference Material

The Meteorological Research Institute of Japan (MRI) organised inter-comparisons (ICs) in time periods of 3 years (Aoyama et al., 2010, 2013). During these ICs, the participants' data on unknown, homogenous and sterile seawater samples were published together with the names and addresses of the participating labs. The participation of marine laboratories in ICs, like Quality Assurance of Information for Marine Environmental Monitoring in Europe and the IOCCP-JAMSTEC organised in Japan that have been going on for years, have undoubtedly improved the comparability of data. Notably, ICs provide participants the opportunity to compare their data with laboratories and detect possible bias from the mean value. Moreover, the exchange of information on methods and calibration procedures can lead to a generally accepted methodology that can also improve the comparability of marine nutrient concentration data. For example, NIOZ in combination with Plymouth Marine Laboratory (PML) organised a workshop in 2012 focussing on problems encountered with PO_4 analysis where a selection of 10 laboratories worked together to establish best possible practices for analysing PO_4 (Aoyama et al., 2015). Subsequently, the following IOCCP-JAMSTEC inter-comparisons (Aoyama et al., 2016, 2018) showed better consistency of the PO_4 data produced than obtained in previous ICs (see Table 4.2), underlining both the success and importance of such workshops.

Overall, due to the open mindset from the nutrient community participants in the ICs, a lot of progress has been made. Participants have been willing to improve their techniques and thereby over the years resulting in less bias for PO_4. Silicate RSD has remained the same which has been somewhat surprising as Si is usually analysed without many issues or difficulties. There are several potential reasons for the lower accuracy for silicate. Silicate standards are mostly made by weighing in sodium hexafluorosilicate (Na_2SiF_6) with a purity better than 97% and these salts are hard to completely dissolve, potentially leading to uncertainty. Additionally, different choices of source material between labs, such as quartz material or alkaline NIST

Table 4.2 Comparing 2008 and 2018 results for the IC study with consensus S.D. expressed as RSD showing a clear improvement in PO_4 analysis after the joint workshop

IC 2008 (n = 31)				IC 2018 (n = 54)		
	Mean (μM/kg)	S.D (μM/kg)	RSD (%)	Mean (μM/kg)	S.D (μM/kg)	RSD (%)
NO_3	21	0.33	1.6	23.7	0.38	1.6
PO_4	1.6	0.04	2.5	1.7	0.03	1.8
Si	59	0.84	1.4	56	0.78	1.4

Note S.D. indicates standard deviation; RSD indicates relative S.D

standards that first need to be neutralised before being used in LNSW, could introduce further biases. Recently, ongoing efforts have been made by the international community to prepare an internationally accepted concentrated silicate stock solution which would be available for the nutrient community to overcome this lower accuracy issue. Although the RSD for NO_3 also remained the same, more investigation within the nutrient community is needed to attempt to improve this value.

The unknown, homogeneous and sterile seawater samples used over the years in the MRI and IOCCP-JAMSTEC ICs were in fact different CRMs produced. The production and use of internationally accepted CRMs for marine nutrients and the reporting of the analysed CRMs with its assigned value as metadata together with the nutrient dataset makes it now possible to compare nutrient data worldwide. CRMs are scarce and expensive and hence at NIOZ we still use an internal standard daily, in addition to fewer measurements of the CRM. It should be noted that even though CRMs are indeed the key to compare data, the internal precision of nutrient data produced by a laboratory should be optimal before CRMs are used for comparing. Using an internationally accepted CRM is the best tool to achieve international comparability where it should be noted that this is most useful after underlying causes for bias between groups have been identified and addressed as described in the next section.

4.5 Achieving High Precision and Some Practical Considerations

The overall procedure from the preparation of standards to sampling, analysis and data quality control, determines the precision of the final measurements. Generally, the aim is to produce comparable, precise and accurate data without bias. We strongly recommend using the methods published in the GO-SHIP Repeat Hydrography Nutrient Manual (Becker et al., 2020) as the basic approach, with some important notes being mentioned here of processes that in our experience positively contributed to improved precision and accuracy in the NIOZ nutrient lab, while acknowledging that this list is not exhaustive and that laboratories can achieve good precision in different ways.

When preparing for an analytical run, one should consider the calibration range which should be based on the expected values of nutrients in the research area (e.g. previously measured concentrations can be found in Geochemical Ocean Sections or eWOCE databases). Theoretically, the best approach is to analyse samples in-between 20–70% of the used calibration range, but this is of course not always possible when encountering nutrient-depleted waters. Diluting stock standards with pipettes and volumetric flasks may introduce systematic errors. Therefore, we recommend that when preparing the calibration standards, to use the same set of pipettes and individual numbered plastic pre-calibrated volumetric flasks. Systematic errors for calibrated flasks are small, around ±0.05% (accuracy from calibration on a balance), and precision of a micropipette is about 0.2% but sometimes with only 0.8% accuracy. Therefore, consistently using the same combination of volumetric flasks and pipettes during an expedition results in an uncertainty of approximately 0.2% for the calibration points whereas any bias stays the same for all, where such bias could be corrected by the use of a CRM straight away for use without dilution.

Sampling seawater in the open ocean is usually done using a Conductivity-Temperature-Depth (CTD) profiler mounted to a rosette frame equipped with 24 or 36 so-called Niskin samplers, but of course many other sampling techniques and sampler types exist (e.g. Middag et al., 2023). Niskin bottles or similar samplers are lowered down into the sea and during the upcast the samplers are closed at a chosen depth. At this chosen depth, it is recommended that the winch is stopped to make sure that the actual water from that specific depth is collected (Swift, 2010). Given that Niskins have a relatively small opening diameter relative to the total diameter of the bottle, we found that a waiting time of 2 min is required after stopping the winch before closing the Niskin to obtain consistent nutrient concentrations from sequentially closed bottles at the same depth, notably when there are steep gradients observed in the water column (Paver et al., 2020). To improve the flushing of the samplers, NIOZ developed its own samplers (Rijkenberg et al., 2015), but nevertheless still observes the 2-min waiting period. Additionally, differences in the size and construction of the frame holding the samplers may also cause water to be dragged up from deeper depths affecting the collection of water. This wake effect combined with the hampered flushing of regular Niskin samplers can be clearly identified in analysed samples such as salinity or oxygen for which the values can be compared to the sensor data. This is especially seen when the CTD passes through strongly stratified water. Paver et al. (2020) showed that data from water collected from a sampler closed without waiting were consistent with sensor data from 8 ± 2 m deeper.

Preferably at the start of an expedition and if time permits, it is recommended to close all CTD-Rosette bottles at one depth and take samples from all bottles to measure the nutrient concentrations as a check for malfunctioning or contamination of samplers. Such a run can also give a good impression of the precision for all the nutrients being analysed. As described in section (*Case study of nutrient measurements in the Weddell Sea*) to observe in-between run reproducibility, re-analysing a duplicate sample from a previous station (e.g. the deepest sampled depth) in the subsequent analytical run is good practice, especially when done in combination with an independent lab reference or better a CRM.

After collection, samples should be left to condition in the dark for approximately 2 hours to reach the lab temperature prior to analysis. It is crucial to analyse samples at the same temperature as the calibration standards to ensure the same reaction conditions and to avoid thermal expansion or contraction at different temperatures in the sampler. This temperature should also be noted together with the salinity of the sample to be able to convert concentrations that are measured in μM/l to units of μM/kg.

Finally, during lab tests, we observed that evaporation due to extremely dry environments can notably change the concentration of a sample or calibrant while it awaits analysis when left open and uncovered (AWI, 1981–2000, pages 38–39). In principle this effect can be corrected for using a sensitivity drift standard during the analysis run, however, it doesn't necessarily correct for samples that may be open for longer periods in such environments and it is better to avoid the need for such a correction. It is advisable to carry out such tests and if necessary to cover the Continuous Flow Analysis (CFA)-cups using highly stretched parafilm to avoid evaporation as much as possible and where a sharpened sampler needle can still penetrate through the stretched covering.

Overall, as said at the start of this section, there are many steps and considerations involved in obtaining high-quality data for which we refer the reader to more detailed descriptions (Becker et al., 2020), with some additional suggestions provided here.

4.6 Summary

Producing high-quality marine nutrient concentration data that provides insights into (changing) biogeochemical cycles and that is inter-comparable between labs and oceanographic research expeditions starts with high-precision measurements in individual labs. Subsequently, the consistency needs to be optimised to minimise variability between analytical runs and any drift over time. Only when internal precision is sufficient and between-run variability has been minimised, inter-laboratory comparisons become useful. Recent inter-comparisons organised in Japan in 2018 with participants from mainly oceanographic institutes showed a good agreement within 2% for most nutrient species of the average mean. However, deviations of as much as 10% still exist between some labs, especially for phosphate and silicate (Aoyama et al., 2018). By organising workshops on specific methods and reporting the outcome to the community, improvements can be obtained, underlining the importance of such exercises. Besides inter-comparisons, the use of CRMs has resulted in an important step in the journey to inter-laboratory comparability. Nevertheless, despite all the progress that has been made, there is still room for further improvements, notably for silicate.

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analytical steps, including how final data output in general is obtained. Together with our NIOZ colleagues Jan van Ooijen and Malcolm Woodward from PML, two international workshops were organised that led to a published report from which the nutrient community could benefit and we thank all participants for their contributions. We also thank Andreas Wisotzki for producing Fig. 4.3 back in 1996 to be able to visualise the effects of normalisation of data while onboard. Finally, many thanks to Stephen Coverly who was always willing to answer questions and issues related to segmented flow chemistry.

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