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Title

A novel inter-comparison of nutrient analysis at sea: recommendations to enhance comparability of open ocean nutrient data

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Abstract

An inter-comparison study has been carried out on the analysis of inorganic nutrients at sea following the operation of two nutrient analysers simultaneously on the GO-SHIP A02 trans-Atlantic survey in May 2017. Both instruments were Skalar San^{++} Continuous Flow Analysers, one from the Marine Institute, Ireland and the other from Dalhousie University, Canada, each operated by their own laboratory analysts following GO-SHIP guidelines, while adopting their existing laboratory methods. High quality control of the nutrient analysis was achieved on both instruments and there was high comparability between the two datasets. Vertical profiles of nutrients also compared well with those collected in 1997 along the same A02 transect by the World Ocean Circulation Experiment. The comparison of the two 2017 datasets and individual laboratory methods, did however raise some interesting questions on the comparison of nutrients analysed from different systems, in particular the calibration range of daily standards and its influence on low nutrient samples, and the importance of using certified reference materials of high and low concentrations to identify bias in the data. Based on the results from this inter-comparison, a number of recommendations have been suggested that we feel will enhance the existing GO-SHIP guidelines to improve the comparability of global nutrient datasets.

The A02 nutrient dataset is currently available at the National Oceanographic Data Centre of Ireland; http://dx.doi.org/10.20393/CE49BC4C-91CC-41B9-A07F-D4E36B18B26F

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1. Introduction

Dissolved nutrients such as nitrate, nitrite, silicate and phosphate can be a critical limiting factor constraining growth of phytoplankton, which in turn form the base of the marine food web. They also provide useful chemical signatures (e.g. ratios of preformed nutrients) that can distinguish water masses and their origins (Broecker and Peng, 1982) as well as act as tracers for biogeochemical processes such as nitrogen fixation and denitrification (Deutsch and Weber, 2012). There is growing evidence for significant variability including long-term trends in nutrient levels in both coastal (Kim et al., 2011) and open ocean surface (Yasunaka et al., 2014), and deep waters (Kim et al., 2014). These changes reflect both direct human intervention in the global environment, especially the effects of the massive ongoing perturbation of the nitrogen cycle (Yang and Gruber, 2016) as well as changes in ocean circulation and biogeochemical cycling that may or may not be anthropogenically influenced (e.g. Di Lorenzo et al., 2008).

Identification and attribution of variability of nutrient concentrations has been complicated by the existence of systematic analytical errors in datasets collected by different groups at different times. This can lead to controversy over the significance of observed long-term changes (e.g. Zhang et al., 2001) and generally requires empirical correction of historical data, using a variety of ad hoc approaches and principles (Keller et al., 2002; Moon et al., 2016; Pahlow and Riebesell, 2000; Tanhua et al., 2009b). Recognition of such systematic errors within and between datasets led to a series of international comparison studies and the introduction of Certified Reference Materials for dissolved nutrients (Aoyama et al., 2016; Aoyama et al., 2007), as well as recommendations concerning standard protocols for sampling, sample preservation and analysis (Hydes et al., 2010). These steps have undoubtedly contributed to a general improvement in inter-laboratory comparability of field-collected data. However, it is notable that most inter-comparison studies rely on either: a) shore-based laboratory-based analysis of replicate samples in the context of specially organised inter-comparison studies; or b) crossover analysis of measurements made at nearby locations in the ocean where temporal and spatial variability is expected to be small.

The former approach is valuable, but most analysts are aware that conditions during an actual research cruise do not always match the stable, controlled conditions of a shore-based laboratory where a group can prepare carefully for their measurement of inter-comparison samples. On the other hand, the latter approach works well in oceanic regions where stable, unchanging nutrient concentrations can be expected. However, in regions such as the open ocean of the North Atlantic, or the Northwest Pacific and in coastal regions everywhere, significant “real” temporal and/or spatial variations can be expected which complicates the interpretation of crossover comparisons.

In this paper we report the results, findings and lessons learned from a rare opportunity in which two independent nutrient analysis teams participated jointly in a deep ocean hydrographic section as part of the international GO-SHIP program (Talley et al., 2016). Both teams followed standard protocols (Hydes et al., 2010) and both groups used Certified Reference Materials during the cruise. As such, the cruise provided an opportunity to assess the likely comparability of nutrient data collected following such protocols as well as helping to identify a number of issues encountered that could be of general relevance to groups conducting such measurements elsewhere. We are not aware of any other report of such an extensive, at-sea inter-comparison of nutrient measurement systems.

The GO-SHIP A02 survey was completed in April/May 2017 on the RV Celtic Explorer, travelling from St. John’s, Newfoundland, Canada, across the North Atlantic to Galway, Ireland with on-board teams from Ireland, Canada, Germany, the UK, and the USA. The survey provided an

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unusual opportunity for cross-comparison of methods, data quality procedures and exchange of technical expertise between the international scientific groups. The Marine Institute (MI) and Dalhousie University (Dal) teams brought separate nutrient Skalar San++ auto analysers on the survey to provide contingency against technical failures and allow for on-board inter-comparison of data as well as exploration of the impact on data quality of subtle differences in laboratory methods, procedures and instrument configurations that ostensibly conform to the same (GO-SHIP) guidelines and quality assurance criteria.

A total of 67 stations were occupied along the A02 transect (Fig. 1), with 1231 nutrient samples analysed for total oxidised nitrogen (TOxN), nitrite, phosphate and silicate on the MI nutrient system. Of these, 12 stations were sampled and analysed on the Dal nutrient system, allowing the comparison of 291 samples between the two systems. The 12 stations were also compared with historical data from the A02 transect completed on a World Ocean Circulation Experiment survey in 1997.

2. Methods

Sampling, sample preservation and analytical procedures on both systems followed methods outlined in the GO-SHIP guidelines for nutrient analysis at sea (Hydes et al., 2010), while both groups also incorporated their existing laboratory quality control (QC), which was specifically adapted to their individual instruments.

2.1 Sampling Procedures

Both groups collected nutrient samples directly from the Niskin bottles into falcon tubes (details in Table 1) and as per GO-SHIP guidelines, the samples were not filtered. Samples were analysed on board typically within 12 hours of sampling.

2.2 Analytical Methods

Analysis was carried out on two separate Skalar San Continuous Flow Analysers, setup in two separate on-board containerised laboratories brought by each team. Both nutrient systems run four channels of nutrients simultaneously; total-oxidised nitrogen, nitrite, silicate and phosphate. The Dal system also runs ammonia, however there were contamination issues in this channel during the survey and therefore, there is no further discussion of this method. Both instruments consist of an auto-sampler, where a needle draws the sample into the analyser which is then spilt into the four channels. Each channel has its own set of reagents, where the stream of reagents and samples is pumped through the manifold to undergo treatment such as mixing and heating before entering a flow cell to be detected. The air-segmented flow promotes mixing of the sample and prevents contamination between samples. The reagents act to develop a colour which is measured as an absorbance through a flow cell at a given wavelength. The Skalar Interface transmits all the data to the Skalar Flow Access software.

The reagents for both systems were made using high-purity chemicals, pre-weighed using a high-precision calibrated balance prior to the survey. They were stored in acid-washed polyethylene (PE) containers and mixed to final volume using Milli-Q water, see reagent compositions in Table 1.

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The analytical procedures for all nutrients are similar between the Dal and MI systems, with some differences in the chemical composition of reagents and volumes of reagents/sample going through the instruments (Table 1). For the determination of nitrite, the diazonium compounds formed by diazotizing of sulfanilamide by nitrite in water under acidic conditions (due to phosphoric acid in the reagent) is coupled with N-(1-naphthyl) ethylenediamine dihydrochloride to produce a reddish-purple colour which is measured at 540 nm.

For silicate determination the sample is acidified with sulphuric acid and mixed with an ammonium heptamolybdate solution forming molybdosilicic acid. This acid is reduced with L(+)ascorbic acid to a blue dye, which is measured at 810 nm. Oxalic acid is added to avoid phosphate interference.

For the determination of phosphate, ammonium heptamolybdate and potassium antimony(III) oxide tartrate react in an acidic medium (with sulphuric acid) with diluted solutions of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex by L(+)ascorbic acid and is measured at 880 nm.

For the determination of total oxidised nitrogen (TOxN) both methods buffer the sample to a pH of 8.2, which is then passed through a column containing granulated copper-cadmium to reduce nitrate to nitrite. The nitrite, originally present plus reduced nitrate, is determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to form a strong reddish-purple dye which is measured at 540nm. The difference between the two systems is that the MI use a buffer solution made of ammonium chloride and ammonia hydroxide solution, while the Dal buffer solution is made of imidazole and hydrochloric acid (Table 1). The MI uses a different Skalar cadmium column where no air bubbles are allowed through the column, while the Dal system allows air bubbles though their column but monitor the efficiency of the reduction process and re-activate the cadmium column with 1M hydrochloric acid solution and a copper sulfate solution if the efficiency falls below 95%.

Both instruments were calibrated daily using a suite of calibration standards (see calibration range in Table 2). The primary standard for each nutrient was made up in the MI and Dal laboratories just before the survey using a calibrated balance where the dry weight of each high purity chemical was diluted to 1L with Milli-Q water, as per Skalar methods. The primary stocks were stored in the fridge for the duration of the survey. Two batches of primary stocks were used on the MI system to ensure no bias from an individual batch, while one batch of primary stock was used on the Dal system. Weekly secondary stocks were made from the primary stocks into 100ml PP flasks which were stored in the fridge when not in use and could be used for one week. Daily standards were made from secondary stock into 100ml PP volumetric flasks.

The MI secondary and daily calibration standards were made using calibrated fixed volume pipettes while Dal standards were made using calibrated adjustable volume pipettes (0.1 – 1 ml, 0.5 – 5 ml) and one calibrated fixed volume pipette (10 ml). The adjustable pipettes were tested prior to the start of the survey to ensure that the volumes delivered were accurate. The MI secondary stocks were made using Milli-Q water, while the daily standards were made using artificial seawater (ASW) with salinity of 35. Both secondary and daily standards on the Dal system were made using ASW (salinity 33-35). Concentrations of daily standards for each system are in Table 2, where first order calibration was used and $R^2 > 0.99$ was deemed acceptable, as per Skalar methods.

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The MI use ASW as the baseline wash for all channels, at a similar salinity to the expected samples (salinity 35). Batches of sodium chloride used were tested prior to the survey to ensure no contamination with any of the nutrients. The Dal system uses Milli-Q water as the baseline wash and therefore a separate blank is run for each standard curve and set to 0 (e.g. Standard 1 in Table 2).

2.3 Quality Control

The Certified Reference Materials (CRMs) used on the survey by both groups were supplied from KANSO (Aoyama et al., 2016; Aoyama et al., 2007) and were analysed at the beginning and end of every run and monitored daily on quality control charts. Two batches were used (Batch CD and Batch BW) on the MI system to cover the full range of nutrients expected on the survey, Table 3. While Dal primarily analysed Batch CD, they analysed a small number of BW CRM as a comparison.

The nutrient laboratory at the MI is part of a Quality System and participates in the QUASIMEME laboratory quality control programme where test materials are analysed bi-annually over a large range of nutrient concentrations and submitted to assess laboratory performance. Since GO-SHIP guidelines do not give pass/fail criteria for CRMs used during nutrient analysis, CRMs from both groups were assessed using a z-score criteria as per Quasimeme Proficiency Testing Exercises, where a z-score < 2 is considered acceptable and z is the difference between the laboratory result and the certified value, divided by the total error (Cofino and Wells, 1994);

Equation 1; $$z - score = \frac{Measured\ value - Certified\ value}{Total\ error}$$

, where the total error is calculated as;

Equation 2; $$Total\ error = \frac{Assigned\ value\ x\ Proportional\ Error\ (6\%)}{100} + 0.5\ x\ Constant\ error$$

, and the constant error is 0.05, 0.01, 0.1 and 0.05 µmol/l for TOxN, nitrite, silicate and phosphate, respectively, which are defined by the Scientific Advisory Board of Quasimeme. Between 2008 and 2017, the average absolute z-scores |Z| from 84 proficiency test samples analysed during QUASIMEME exercises at the MI laboratory was 0.5 for TOxN, 0.4 for nitrite, 0.5 for silicate and 0.4 for phosphate. Over that period |Z|-scores were satisfactory for all results for which Z-scores were returned (>LOQ) with the exception of a single silicate result (Z = 2.04).

On the MI system every sample was analysed twice and relative percentage differences (RPDs) were calculated for replicates, Equation 3. If any RPDs were >10%, that sample was either re-analysed or flagged as questionable in the final dataset.

Equation 3; $$Replicate\ RPD = \frac{Replicate\ A - Replicate\ B\ concentration}{Average\ nutrient\ concentration} \times 100\%$$

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On the Dal system triplicate samples were measured for each sample. The coefficient of variation was calculated (CV %) for each triplicate (Eq. 4). If the CV (%) was greater than 5 and there was an obvious outlier, then it was rejected (max. 1 replicate of the 3 was rejected). As long as the CV (%) for the two replicates was now < 5, the sample was accepted and not re-analyzed. For samples with low concentrations (<0.5 µmol/l), the CV(%) was ignored unless there was an obvious outlier, as a difference of 0.01 µmol/l between replicates would cause the CV(%) to be too high for the lower concentrations. For samples with concentrations >10 µmol/l, outliers were removed if the CV (%) was greater than 3. Any samples that did not pass this CV (%) test after rejecting an outlier were rejected and re-analysed during the following run using a duplicate sample.

Equation 4; $$CV\% = \frac{\text{Standard deviation of replicates}}{\text{Average of replicates}} \text{ x } 100\%$$

The limit of detection (LOD) and limit of quantification (LOQ) for both instruments were calculated as 3*standard deviation (LOD) and 10*standard deviation (LOQ) from 10 replicates of low nutrient seawater solution, and are given in Table 4 below. Concentrations that fall between the LOD and LOQ value are reported as <LOQ, while concentrations lower than the detection limit are reported as <LOD.

Both systems analysed a drift sample after every 4 samples during the run to correct for instrumental drift. The drift was made from secondary stock and artificial seawater (see concentrations in Table 2).

System Suitability Standards (SSS) were made alongside the daily standards by the MI group using secondary stock standards and artificial seawater. They were analysed as an internal standard every 4 samples to ensure drift correction is accurate and to identify any problems during the course of a run. All SSS were checked in post processing: any that fell > ±10% of the SSS value were marked as failed QC. Samples on either side of a failed SSS had to be re-analysed or were flagged as questionable in the final dataset. The Dal group ran their drift sample as an unknown to act as a system suitability standard; this was also done every four samples, but between drift samples. Although the drift check was monitored throughout the run, there was no post-processing rejection based on a SSS on the Dal system, instead samples were individually rejected based on poor replicates or an entire run was rejected if the CRMs did not pass.

2.4 Comparison of data

To compare the final nutrient concentrations between the two instruments the sample relative percentage difference (RPD) was also calculated between the MI and Dal nutrient concentrations;

Equation 5. $$Sample\ RPD = \frac{Average\ MI\ concentration - Average\ Dal\ concentration}{Average\ nutrient\ (MI+Dal)\ concentration} \times 100\%$$

While nitrite was analysed on both instruments, there were issues with nitrite contamination in both systems, potentially due to the Milli-Q water. While all frozen samples were re-analysed at the MI after the survey with high quality data, a comparison of the nitrite methods and profiles will not be carried out in this study.

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3. Results

3.1 Comparison of instrument calibrations

Optimal calibration ranges for nutrient analysis depends on the concentrations being measured, but will also be specific to individual instruments and laboratory methods. The Dal system typically operates with a higher calibration range for all nutrients relative to the MI system, attributed to their higher volume of reagents relative to sample going through the analyser (Table 2). The MI instrument was initially established as a laboratory instrument, with high sample volumes relative to reagents to allow for precise measurements of low nutrient concentrations. The normal calibration ranges for TOxN and silicate was 0-15 µmol/l and 0-1.5 µmol/l for nitrite and phosphate. In normal laboratory use, any sample concentration outside this range is diluted into the calibration range using artificial seawater, with both sample and diluent volumes weighed accurately, and re-analysed. Because an analytical balance could not be used at sea, tests were carried out to determine the maximum range of the calibration standards, without compromising the low concentration nutrients. Phosphate and nitrite maintained linear calibrations to over 2.2 µmol/l without any changes to the methods, and therefore covered the full range of expected concentrations for the North Atlantic. With a small increase in reagent concentrations relative to sample volume, the calibration range increased to 0-30 µmol/l for TOxN and 0-60 µmol/l for silicate. Despite these changes the MI system typically had a greater sample volume relative to reagents for TOxN and silicate compared with the Dal system.

Early in the survey a negative bias was observed in the MI QC charts for the higher TOxN CRM (Batch BW, 24.6 µmol/l), while a comparison of the MI and Dal datasets also identified a negative bias in the MI TOxN data relative to the Dal data for samples from deeper in the water column (at concentrations > 15µmol/l). The reason for the bias was unclear. The TOxN calibration range on the MI system was increased from 0 – 30 µmol/l to 0 – 50 µmol/l to match the Dal system to determine if that had any effect on the TOxN QC comparison. This in fact reduced the negative bias in the BW CRM, without affecting the CD CRM (Fig. 2). Calibration standards up to 60µmol/l were analysed with all previous runs on the MI system to allow for the higher silicate range, which allowed the earlier runs to be recalculated to include standards up to 50 µmol/l.

Despite the 0-30 µmol/l range yielding the most accurate CRM values on the MI system before and after the survey (which would be expected since the MI instrument is configured for running lower nutrient concentrations), the 0-50 µmol/l range improved the higher concentration CRMs throughout the A02 survey. It is unclear why the method performed differently on the survey; a possibility is that it was due to a slight change in the light path of the photometer from ship vibrations which were more evident at the location of this containerised laboratory. However, the extra QC performed throughout the survey (two CRM batches of high and low concentration, extra calibration standards, internal SSS, a comparison with Dal and WOCE data) ensured the final results are of high quality.

A calibration test was carried out in the MI laboratory following the survey, where two rounds of 14 Quasimeme Proficiency test materials with a wide range in nutrient concentrations, were analysed with three batches of KANSO CRMs. The full suite of calibration standards (Table 2) were analysed during the run, while in the post-processing, results were exported selecting different standards and calibration coefficients (either first or second order calibration). This test was repeated a number of times and results illustrate that the range of calibration standards used can indeed have a significant effect on the final value, particularly in the low nutrient concentrations (Table 5). While nitrite and phosphate were also analysed in this experiment, the range used on

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the survey were not extended beyond 2.2 µmol/l and adjusting the lower calibration standards had minimal effect on the final concentrations. Therefore, only TOxN and silicate are discussed in this section.

For silicate, the use of different calibration standards had marginal effect in the mid and high sample concentrations, where almost all $|Z|$ scores were < 1 (all <4% bias). The only samples that illustrated a significant difference were those with concentrations < 2 µmol/l, where $|Z|$ scores increased to 2 if the higher calibration standards were included. For example, in the QNU 300 sample (Table 5), when using standards only up to 10 µmol/l, the measured value had a difference of 7% relative to the assigned value, which was increased to 21% if standards up to 60 µmol/l were included. There was more variation in the TOxN results depending on which standards were selected, but again it is clear that including the highest standards to 50 µmol/l results in a larger bias in the accuracy of low concentration TOxN samples. In the QNU 307 sample, the measured value was exactly the same as the assigned value (0% difference) if only standards up to 10 µmol/l were included, while the difference increased to ±19% if standards up to 50 µmol/l were included. This is likely specific to the MI Skalar system as it will depend on how the instrument can measure both high and low concentrations of nutrients and the true linearity of the calibration standards.

Following this calibration experiment and the finding that the lowest TOxN and Silicate concentrations showed less bias when using a smaller calibration range, the MI GOSHIP A02 data was recalculated, where TOxN and silicate concentrations below 5µmol/l were recalculated to only include standards up to 10 µmol/l (Table 2).

Another important finding from this experiment concerns the differences that can arise by selection of first or second order calibration curves. GO-SHIP guidelines currently state that either first or second order calibrations can be used but that forcing a linear fit to non-linear calibration data can lead to offsets of 3%. It is clear that TOxN can change very significantly in the higher concentration range, where the difference between the 1st and 2nd order calibration is close to 10% of the certified value of the CJ CRM and 8% of the BW CRM. This firmly supports the recommendations of Hydes et al. (2010) concerning the importance of understanding and evaluating the best fit for an individual CFA system.

3.2 Comparison of QC between systems

Both systems used the same Quasimeme z-score criteria for assessing the CRMs during the survey, and all CRMs had $|Z|$-scores within 2, see QC charts in Fig. 3. The Dal system primarily used the KANSO CD CRM, but ran a small number of BW CRMs for comparison towards the end of the survey. Despite passing the assigned CRM assessment criteria, there was a negative bias in the MI TOxN CD CRM (average difference -4%) while Dal measurements were closer to the certified value. Silicate CD measurements were similar between the two systems, and while phosphate CD measurements were closer to the certified value on the MI system, the Dal phosphate QC improved later in the survey following the inclusion of more standards in the lower range. The CV% for the CRMs (calculated as per Eq. 3) were typically below 5% for all nutrients, Table 6.

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383 **3.3 Vertical profiles**

384 Overall there was good agreement between vertical profiles of nutrients between the two
385 systems, see Fig. 4 and Supplementary Material, giving confidence in both the overall dataset and
386 individual methods from each group.

387

388 Looking at individual profiles of silicate, 90% of all samples compared have relative percentage
389 differences (RPDs) < 10%, with 70% of samples with RPD < 5%. The largest differences between
390 the two systems are in the top 400m (Fig. 5), which typically had < 6µmol/l TOxN, 3µmol/l silicate
391 and 0.4 µmol/l phosphate, where 8% of all the samples have RPD's between 11 – 117%, with the
392 highest RPD's in the stations with lowest silicate values.

393 TOxN vertical profiles also compare well with 97% of all TOxN compared with a RPD < 10%, with
394 77% of all RPDs < 5%. Virtually all TOxN samples with RPD > 10% are within the top 200m where
395 TOxN values are low (Fig. 5).

396 Despite slightly less comparability in phosphate between the two systems; 79% of all samples
397 had RPDs < 10%, with 38% of samples with RPD < 5%. Almost half of the samples with RPDs >
398 10% were in the top 400m (Fig. 5). The remaining samples with higher differences deeper in the
399 water column were analysed in the first three stations of the Dal system when they were
400 encountering problems with their phosphate channel. QC of Dal phosphate improved after the
401 they increased the number of phosphate standards in the lower concentration range, where the
402 CV% of the CD CRM decreased from 15% in the first three runs to 7.5% in subsequent runs. This
403 subsequently improved the comparison between the two systems.

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405

406 **3.4 Comparison with WOCE data and methods**

407 Nutrient analysis on the WOCE A02 survey in 1997 was also carried out on a Skalar Continuous
408 Flow Auto-Analyser (SA 4000) for photometric determination of nitrate, nitrite, phosphate and
409 silicate. Analytical methods were similar to the MI and Dal systems, with nutrients measured at
410 the same wavelengths, while calibrated flasks and pipettes were also used for the daily calibration
411 standards. There were no CRMs available for the 1997 cruise, instead the internal consistency of
412 the nutrient measurements between cruises were assessed by comparison of quality controlled
413 dissolved inorganic carbon (DIC) data, where any inaccuracies in the nutrient measurements
414 would show up as offsets or slope changes in the DIC-nutrient plots derived from various cruises.
415 The estimated accuracy on the WOCE survey was 0.02 µmol/l for nitrite, 0.1 µmol/l for nitrate,
416 0.05 µmol/l for phosphate and 0.5 µmol/l for silicate. There was no information provided in the
417 cruise report, and no articles published (that we know of) which states the calibration range used
418 on this survey. The vertical profiles of nutrient data compared quite well with the 2017 data (Fig.
419 4). Not every station on the 2017 survey could be compared with the 1997 survey due to
420 differences in some station positions, which coincided in bottom depth differences of over 500m
421 between the two surveys.

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4. Discussion

The comparison of the MI and Dal datasets from the A02 survey highlights the importance and effectiveness of following standard protocols for the sampling and analysis of nutrients at sea. Both groups followed the GO-SHIP manual for the sampling and determination of nutrients in seawater, while also incorporating their existing laboratory QC methods that were specifically adapted to their instruments.

One of the key findings in this study is the need for using two (or more) reference materials for nutrient analysis that covers the range of the expected nutrients for the survey. Hydes et al. (2010) also recommend the use of CRMs to improve the comparability of the global ocean nutrient data set, and that a minimum of three reference material solutions (low, mid and top range) should be used at regular intervals during a cruise to detect non-linearity. If only the CD CRM was used by both groups on the A02 survey, the negative bias in the MI TOxN at high concentrations would not have been identified. Without confirmation from the higher concentration CRM (Batch BW), it would not have been clear whether there was a negative bias in the MI data or a positive bias in the Dal data since both were producing similar values for the lower (CD) CRM. Although following all GO-SHIP guidelines and carrying out sufficient testing prior to the survey, there was an unexplainable change in QC in the at-sea analysis on the MI system. This highlights the necessity of including additional QC measures (e.g. high number of standards and CRMs) to allow for adjustments to the method while carrying out analysis at sea.

Results from 59 laboratories during the 2015 IOCCP-JAMSTEC inter-comparison exercise (2015 I/C exercise) indicate that non-linearity of the calibration curves for nutrient analysis is one of the significant sources of reduced comparability of nutrients data, and they also suggest that a set of reference materials should be used during analysis to cover the full range of nutrients expected (Aoyama et al., 2016). This is supported in our A02 inter-comparison, where the use of a high and low concentration CRM was able to identify analytical biases that were subsequently corrected through adjustments in the internal calibrations.

Hydes et al. (2010) suggest that the use of CRMs along with best practice in using analysis equipment and internal standardisation, should make it "commonly possible to achieve comparability of nutrient analysis to a level better than 1%". However, the ability to compare datasets to 1% will depend on the level of accuracy each laboratory can achieve. When comparing the MI and Dal nutrient data, the sample RPDs of < 1% accounted for less than 24% of samples. Below 400m, the comparison of sample concentrations results in average absolute RPD of 3.2% TOxN, 2.7% silicate and 3.7% phosphate (if the first 3 stations on the Dal system were removed).

In the 2015 I/C exercise, Aoyama et al. (2016) reported CV % of 1% TOxN, 2% silicate and 6% phosphate for the reference material batch BU (similar to Batch CD used on the A02 survey), and 2% for all nutrients for batch CA (similar to Batch BW). These CV% are lower than those produced by the MI and Dal groups on the A02 survey which were 4% for TOxN and phosphate and 5% for silicate by the MI group and 3% for TOxN, 4% silicate and 9% for phosphate by the Dal group. The CV% for the participating laboratories of the 2015 I/C exercise were calculated from measurements carried out in shore-based laboratories, a much more stable environment than at carrying out analysis at sea. Higher error in measurements of reference materials analysed at sea could be due to the use of pipettes (as opposed to balances) for daily calibration standards, different Milli-Q water supply, pre-weighed chemicals for reagents, different analysts and a moving platform with vibrations that could influence the light path of the instrument. The CV% of the KANSO CRMs (Batch CD) analysed in the MI laboratory (on shore) since the A02 survey was reduced to 3% for all nutrients (n=24).

In another inter-comparison study carried out in 2005 and 2006 (Sahlsten and Håkansson, 2006), five different laboratories from the monitoring institutes of Denmark, Norway and Sweden, compared nutrient concentrations from identical sets of natural seawater sub-samples (as opposed to prepared reference materials) that were analysed ashore in individual laboratories; results for the deep water samples indicated precision generally less than 5% CV between laboratories. This study indicated that the variation between laboratories could be explained by improper storage of the nutrient samples between sampling and analysis. Our results, however suggests that this level of comparability could instead be due to systematic differences between instruments and individual internal calibrations. Tanhua et al. (2009b) and Tanhua et al. (2009a) carried out cross over analysis as a secondary QC on the nutrient data in the Atlantic (CARINA), where an offset and standard deviation were calculated for nutrients at depths >1500m. They found nitrate data showed the largest consistency with RMSE of 2.9%, with a RMSE of 4.2% for phosphate and 7% for silicate, and suggested the larger differences in the data were likely due to analytical difficulties.

With availability of a range of CRMs for nutrients in seawater, there remains a need for acceptability criteria for oceanic nutrient measurements to meet GO-SHIP objectives. Such criteria exist for other biogeochemical parameters, for example, for dissolved inorganic carbon (DIC) and total alkalinity (TA) in the open ocean, a level of accuracy of ±2 μmol/kg for reference materials, (~ 0.1%), is recommended in order to assess annual or even decadal changes in the marine carbonate system (Dickson, 2010; ICES, 2014). In coastal waters, the level of accuracy required would be less since the range of carbonate parameters observed would be much wider than those in the open ocean. If criteria for nutrient measurements were set, laboratories could flag reported data where these were not achieved. The metadata supplied with published datasets should include all of the related QC information, including calibration ranges, batches of CRMs used, CRM assessment criteria, accuracy of CRMs achieved, sample storage prior to analysis, etc.

The largest differences between the MI and Dal nutrient concentrations were in the surface waters, where low levels of nutrients were observed due to primary production. Reduced comparability between the participating laboratories of the 2015 I/C exercise (Aoyama et al., 2016) was also observed in the low nutrient reference materials, which yielded CV% of up to 60%. Larger differences in low nutrient waters would be expected since any error in calibration standards, instrument baselines and detection limits would strongly impact concentrations close to the limit of detection. The MI instrument runs ASW as a baseline wash, while the Dal instrument runs Milli-Q water; while this could result in differences in low nutrient samples, it is unlikely to be the issue here since both groups were using the same Milli-Q water supply to make reagents and wash and the sodium chloride used for the ASW on the MI system was tested ahead of the survey to ensure no contamination in the batches used. The large differences in the low nutrient concentrations is instead likely due to the sample:reagent ratio of each system, where the instruments have different capability of measuring low nutrient concentrations.

It would appear from the vertical profiles that the low nutrient surface waters (<400m) would have little relevance when looking at the overall vertical distribution of nutrients across the North Atlantic. And while its significance would be minimal in comparing nutrient concentrations in intermediate and deep water masses, inaccurate nutrient concentrations in the euphotic zone would lead to large discrepancies in primary production estimates and near-surface N:P ratios. In the entire GO-SHIP A02 survey, 32% of all samples are within the top 400m of the water column, and therefore represent a large proportion of the entire dataset. Clearly, achieving high accuracy measurements across the large concentration ranges that are encountered from surface to deep waters remains an analytical challenge. It is difficult to compare upper water column

nutrients in cross-over analysis based on different cruises in the same area due to more variability on different time-scales (Tanhua et al., 2009a; Tanhua et al., 2009b). This inter-comparison study therefore addresses a key issue in comparability of nutrient data in low nutrient surface waters. There are currently no KANSO CRMs that have concentrations close to detection limits to quantify bias in low nutrient surface waters, which perhaps should be considered for the future.

The results of this inter-comparison strongly support the suggestions in Hydes et al. (2010) that individual laboratories or groups must carry out extensive internal testing on their own instruments to understand the full capability of their instruments and ensure their laboratory methods achieve the highest level of accuracy for the samples being measured. Results also highlighted the value of carrying out a between-laboratory testing exercise, which in this case, helped both groups to identify quality assurance issues in their internal procedures which would otherwise not have been evident. All laboratory groups should ensure they incorporate additional QC into their methods, including extra calibration standards, extra reference materials and internal standards, to allow for post-correction of data if some unforeseen changes to their instrument occurs while at sea.

5. Data Availability

The GO-SHIP A02 nutrient dataset (analysed on the Marine Institute Skalar nutrient analyser) is currently available at the National Oceanographic Data Centre of Ireland;
http://data.marine.ie/publication/dataset/ce49bc4c-91cc-41b9-a07f-d4e36b18b26f.html.

http://dx.doi.org/10.20393/CE49BC4C-91CC-41B9-A07F-D4E36B18B26F

6. Conclusions and Recommendations

For data to be of use to the scientific community, oceanographic data collected by different groups must be comparable in order to assess true changes in the marine environment. The presence of biases or imprecision in the measurement of nutrients in seawater reduce our ability to understand spatial and temporal trends in nutrient concentrations in the ocean. The comparison of two nutrient datasets from the 2017 A02 survey illustrated high quality control in the analytical methods and high comparability between datasets, highlighting the effectiveness of following standard protocols and using CRMs while at sea. The cross-comparison of laboratory methods, quality control and instrument configurations also allowed the MI and Dal groups to scrutinize their laboratory procedures in order to identify reasons for analytical bias while carrying out nutrient analysis at sea. Following this study, a number of recommendations are suggested which enhance those in the GO-SHIP manual (Hydes et al., 2010) for improved quality of global nutrient datasets;

- Multiple (At least two) CRMs should be used that cover the range of the expected concentrations on the survey to assess linearity and identify any analytical bias at different concentrations.
- Agreed CRM acceptance criteria for ocean observation nutrient measurement would aid in improving data quality and support flagging of reported data that doesn't meet these criteria
- Extensive testing must be carried out ahead of a survey to understand individual instrument capabilities and extra QC should be included to allow for changes to the methods due to unforeseen changes while carrying out analysis at sea.
- Metadata should include all information related to QC so to increase comparability and traceability between different nutrient datasets.

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Competing interests

The authors declare that they have no conflict of interest.

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662 Table 1. A comparison of sampling, instrument configurations (including sample and reagent tubing sizes)
663 and reagent compositions for each nutrient from the Marine Institute, Ireland (MI) and Dalhousie
664 University, Canada (Dal) systems.

	MI	Dal
Sampling		
Sample tubes	50ml falcon tubes	15 ml falcon tubes
Primary sample analysis	Within 12 hours of sampling	Within 12 hours of sampling
Replicate samples	Frozen immediately to -20°C	Stored at 4°C and analysed within 36 hours if necessary
Analysis		
Auto-sampler size	300 cups	50 cups (can be re-filled during a run)
Auto-sampler cup size	10ml	4ml
Baseline wash	Artificial Seawater	Milli-Q water
Reagents (Chemicals g/L or ml/L)		
Artificial Seawater	35g Sodium Chloride	35g Sodium Chloride
	0.5g Sodium hydrogen carbonate	
TOxN		
Sample tubing size	1.02 ml/min	0.16 ml/min
Colour Reagent	150ml Phosphoric Acid	150 ml Phosphoric acid
	10g Sulfanimide	10 g Sulfanilamide
	0.5g N-(1-Naphthyl)ethylene diamine dihydrochloride (NEDD)	0.5 g NEDD
		6 ml Brij solution
Reagent tubing size	0.42 ml/min	0.42 ml/min
Buffer Solution (pH 8.2)	80g Ammonium Chloride	17.5 g Imidazole
	~3ml Ammonia Solution	~25 ml 1M Hydrochloric Acid
	3ml Brij solution (surfactant)	1 ml Brij solution
Reagent tubing size	0.8 ml/min	1.6 ml/min
Cadmium column	Skalar 5358 activated Cd column	Skalar 5347 nitrate reduction coil
Copper Sulfate Solution		12 g copper sulfate
Nitrite		
Sample tubing size	0.42 ml/min	1.20 ml/min
Colour Reagent	150ml Phosphoric Acid	150 ml Phosphoric acid
	10g Sulfanilamide	10 g Sulfanilamide
	0.5g NEDD	0.5 g NEDD
		6 ml Brij solution
Reagent tubing size	0.23 ml/min	0.23 ml/min
Wash Solution	3ml Brij solution	NA
Reagent tubing size	1.00 ml/min	
Silicate		
Sample tubing size	1.40 ml/min	0.42 ml/min
Sulfuric Acid Solution	20ml Sulfuric Acid	5 ml Sulfuric acid
		1 g Lauryl sulfate
Reagent tubing size	0.23 ml/min	0.42 ml/min
Ammonium heptamolybdate	20g Ammonium heptamolybdate	10 g Ammonium heptamolybdate
Reagent tubing size	0.42 ml/min	0.42 ml/min
Oxalic Acid	44g Oxalic Acid	44 g Oxalic acid

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Reagent tubing size	0.42 ml/min	0.42 ml/min
L(+) Ascorbic Acid	40g Ascorbic Acid	40 g Ascorbic acid
Reagent tubing size	0.32 ml/min	0.32 ml/min
Phosphate		
Sample tubing	1.40 ml/min	1.60 ml/min
Ammonium heptamolybdate	0.23g Potassium antimony (III)	0.23 g Potassium antimony (III) oxide
	70ml Sulfuric Acid	70 ml Sulfuric acid
	6g Ammonium heptamolybdate	6 g Ammonium heptamolybdate
	2ml FFD6 (Surfactant)	5 ml FFD6
Reagent tubing size	0.42 ml/min	0.32 ml/min
L(+) Ascorbic Acid	11g Ascorbic Acid	11 g Ascorbic acid
	60ml Acetone	60 ml Acetone
	2ml FFD6	5 ml FFD6
Reagent tubing size	0.42 ml/min	0.32 ml/min

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687 Table 2. Concentrations of daily calibration standards in µmol/l on the MI and Dal systems. Standard 1 is
688 the blank made of artificial seawater (sal 35). Standards 2-4 with the * on the Dal system were added to
689 their standards only on the last 4 days of analysis following discussions with the MI group. SSS are the
690 system suitability standards that were analysed during a run as internal quality standards.

	MI				Dal			
STD #	**TOxN µmol/l**	**Silicate µmol/l**	**PO4 µmol/l**	**NO2 µmol/l**	**TOxN µmol/l**	**Silicate µmol/l**	**PO4 µmol/l**	**NO2 µmol/l**
1	0	0	0	0	0	0	0	0
2	0.26	0.26	0.05	0.05	1.25 *	1.25 *	0.1 *	0.15 *
3	0.5	0.5	0.15	0.15	2.5 *	2.5 *	0.2 *	0.3 *
4	2.5	2.5	0.25	0.25	5 *	5 *	0.4 *	0.6
5	5	5	0.5	0.5	10	10	0.8	1.2
6	10	10	1	1	20	20	1.6	1.8
7	15	15	1.5	1.5	30	30	2.4	2.4
8	22.5	22.5	2.25	2.25	40	40	3.2	3.0
9	30	30			50	50	4.0	
10	40	40						
11	50	50						
12		60						
SSS	10	10	1	1	40	40	3.2	2.4
Drift	10	10	1	1	40	40	3.2	2.4

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710 Table 3. Certified values for the two batches of KANSO CRMs used on the survey.

Certified values µmol/l	CD	BW
Nitrate	5.498	24.59
Nitrite	0.018	0.067
Silicate	13.93	60.01
Phosphate	0.446	1.541

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738 Table 4. The limit of detection (LOD) and limit of quantification (LOQ) in µmol/l, for both instruments.

	MI				Dal			
	TOxN	Nitrite	Silicate	Phosphate	TOxN	Nitrite	Silicate	Phosphate
LOD	0.02	0.01	0.03	0.01	0.14	0.02	0.13	0.04
LOQ	0.26	0.04	0.38	0.16	0.48	0.07	0.43	0.13

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Table 5. Results from a laboratory experiment testing the effect of using different calibration ranges, where STD in the first column of the table indicates the top standard included in the calibration. The second column (Order) indicates whether the first or second order calibration coefficient was used in the calibration. The samples are either Quasimeme test materials (QNU) or KANSO CRMs; MV is the measured value; AV is the assigned (or certified value); TE is the total error used for calculating the z-score; Z is the calculated z-score as per Eq. 1 and RPD is the relative % difference (MV-AV/AV*100%).

			TOxN					Silicate				
STD	**Order**	**Sample**	**MV**	**AV**	**TE**	**Z**	**RPD**	**MV**	**AV**	**TE**	**Z**	**RPD**
10	1st	QNU 304 EW	-0.04	0.07	0.03	**<LOD**		1.97	2.17	0.18	**-1.1**	-9
22	1st	QNU 304 EW	-0.09	0.07	0.03	**<LOD**		1.97	2.17	0.18	**-1.1**	-9
30	1st	QNU 304 EW	-0.16	0.07	0.03	**<LOD**		1.94	2.17	0.18	**-1.3**	-11
50	1st	QNU 304 EW	-0.77	0.07	0.03	**<LOD**		1.96	2.17	0.18	**-1.2**	-10
50	2nd	QNU 304 EW	0.10	0.07	0.03	**<LOQ**		1.81	2.17	0.18	**-2.0**	-17
60	1st	QNU 304 EW	Failed Calibration					1.95	2.17	0.18	**-1.2**	-10
60	2nd	QNU 304 EW	0.43	0.07	0.03	**11.6**	552	1.97	2.17	0.18	**-1.1**	-9
10	1st	QNU 307 SW	2.16	2.16	0.16	**0.0**	0	1.91	2.00	0.17	**-0.5**	-4
22	1st	QNU 307 SW	2.15	2.16	0.16	**-0.1**	-1	1.91	2.00	0.17	**-0.5**	-5
30	1st	QNU 307 SW	2.15	2.16	0.16	**-0.1**	-1	1.90	2.00	0.17	**-0.6**	-5
30	2nd	QNU 307 SW	2.15	2.16	0.16	**-0.1**	-1	1.90	2.00	0.17	**-0.6**	-5
50	1st	QNU 307 SW	1.75	2.16	0.16	**-2.6**	-19	1.82	2.00	0.17	**-1.0**	-9
50	2nd	QNU 307 SW	2.18	2.16	0.16	**0.1**	1	1.91	2.00	0.17	**-0.5**	-4
60	1st	QNU 307 SW	Failed Calibration					1.72	2.00	0.17	**-1.6**	-14
60	2nd	QNU 307 SW	2.22	2.16	0.16	**0.4**	3	1.92	2.00	0.17	**-0.4**	-4
10	1st	QNU 300 SW	2.92	2.75	0.19	**0.9**	6	1.46	1.57	0.15	**-0.8**	-7
22	1st	QNU 300 SW	2.91	2.75	0.19	**0.8**	6	1.45	1.57	0.15	**-0.8**	-8
30	1st	QNU 300 SW	2.91	2.75	0.19	**0.8**	6	1.43	1.57	0.15	**-0.9**	-9
50	1st	QNU 300 SW	2.57	2.75	0.19	**-0.9**	-7	1.35	1.57	0.15	**-1.5**	-14
50	2nd	QNU 300 SW	2.87	2.75	0.19	**0.6**	4	1.46	1.57	0.15	**-0.8**	-7
60	1st	QNU 300 SW	Failed Calibration					1.25	1.57	0.15	**-2.2**	-21
60	2nd	QNU 300 SW	2.89	2.75	0.19	**0.7**	5	1.47	1.57	0.15	**-0.7**	-6
10	1st	QNU 299 SW	6.69	6.75	0.43	**-0.2**	-1	5.36	5.36	0.37	**0.0**	0
22	1st	QNU 299 SW	6.66	6.75	0.43	**-0.2**	-1	5.37	5.36	0.37	**0.0**	0
30	1st	QNU 299 SW	6.50	6.75	0.43	**-0.6**	-4	5.34	5.36	0.37	**-0.1**	0
50	1st	QNU 299 SW	6.70	6.75	0.43	**-0.1**	-1	5.31	5.36	0.37	**-0.2**	-1
50	2nd	QNU 299 SW	6.30	6.75	0.43	**-1.1**	-7	5.35	5.36	0.37	**0.0**	0
60	1st	QNU 299 SW	Failed Calibration					5.31	5.36	0.37	**-0.1**	-1
60	2nd	QNU 299 SW	6.08	6.75	0.43	**-1.5**	-10	5.28	5.36	0.37	**-0.2**	-2
10	1st	KANSO CD	5.55	5.50	0.35	**0.2**	1		13.93	0.89		
22	1st	KANSO CD	5.53	5.50	0.35	**0.1**	0	14.30	13.93	0.89	**0.4**	3
30	1st	KANSO CD	5.53	5.50	0.35	**0.1**	1	14.34	13.93	0.89	**0.5**	3
50	1st	KANSO CD	5.39	5.50	0.35	**-0.3**	-2	14.45	13.93	0.89	**0.6**	4
50	2nd	KANSO CD	5.30	5.50	0.35	**-0.6**	-4	14.24	13.93	0.89	**0.3**	2
60	1st	KANSO CD	Failed Calibration					14.51	13.93	0.89	**0.7**	4
60	2nd	KANSO CD	5.24	5.50	0.35	**-0.7**	-5	14.18	13.93	0.89	**0.3**	2
22	1st	KANSO CJ	16.08	16.2	1.00	**-0.1**	-1		38.5	2.360		
30	1st	KANSO CJ	16.22	16.2	1.00	**0.0**	0		38.5	2.360		
50	1st	KANSO CJ	17.16	16.2	1.00	**1.0**	6	39.36	38.5	2.360	**0.4**	2

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50	2nd	KANSO CJ	15.59	16.2	1.00	**-0.6**	-4	39.32	38.5	2.360	**0.3**	2
60	1st	KANSO CJ	Failed Calibration					39.62	38.5	2.360	**0.5**	3
60	2nd	KANSO CJ	15.29	16.2	1.00	**-0.9**	-6	39.33	38.5	2.360	**0.4**	2
22	1st	KANSO BW		24.59	1.50				60.01	3.65		
30	1st	KANSO BW	24.56	24.59	1.50	**0.0**	0		60.01	3.65		
50	1st	KANSO BW	26.41	24.59	1.50	**1.2**	7		60.01	3.65		
50	2nd	KANSO BW	24.45	24.59	1.50	**-0.1**	-1	60.30	60.01	3.65	**0.1**	0
60	1st	KANSO BW	Failed Calibration					60.05	60.01	3.65	**0.0**	0
60	2nd	KANSO BW	24.06	24.59	1.50	**-0.4**	-2	60.88	60.01	3.65	**0.2**	1

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799 Table 6. Calculated coefficient of variation (CV%) for the KANSO CRMs analysed by the Marine Institute
800 (MI) and Dalhousie University (Dal), calculated as the (standard deviation/mean*100%). The KANSO
801 batches CD and BW were used by both groups, where n is the number of measurements.

Nutrient	MI		Dal	
	CV%	n	CV%	n
TOxN (CD)	4	*27*	3	*27*
Silicate (CD)	5	*27*	4	*27*
Phosphate (CD)	4	*27*	9	*27*
TOxN (BW)	3	*16*	1	*4*
Silicate (BW)	5	*16*	3	*4*
Phosphate (BW)	3	*16*	4	*4*

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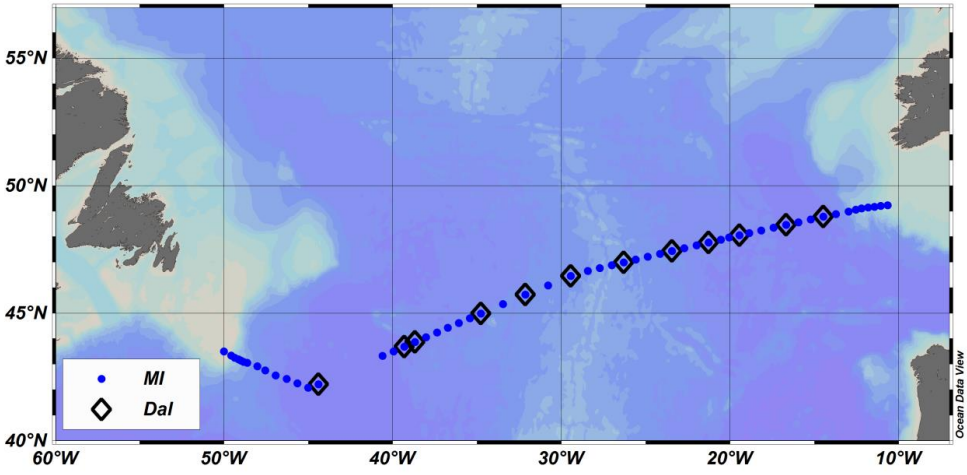

Figure 1. Station positions sampled along the GO-SHIP A02 trans-Atlantic survey completed in May 2017. The Marine Institute (MI) group sampled and analysed nutrient samples at every station along the transect, while the Dalhousie group (Dal) analysed nutrient samples from a selected number of sites marked with a diamond. Both groups analysed samples over the full water column.

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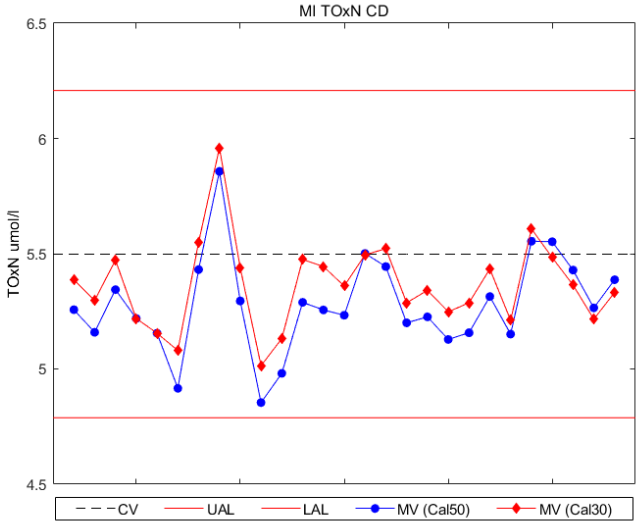
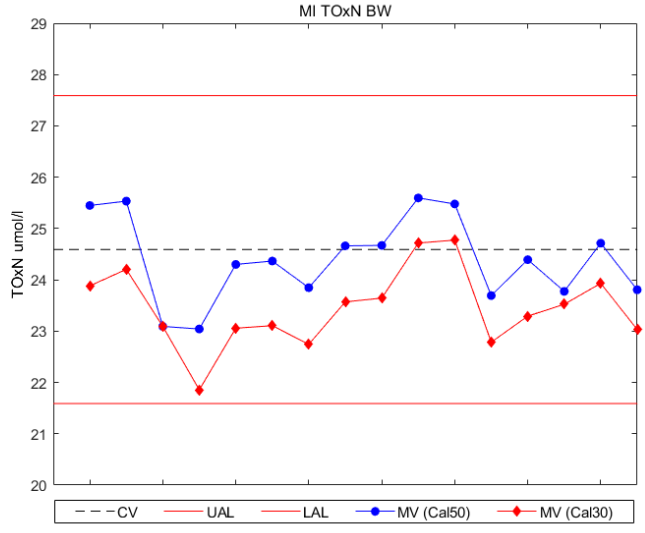


838 Figure 2a



839 Figure 2b

840 Figure 2 (a) and (b) Measured values for TOxN CD and BW CRMs on the MI system during the A02 survey
841 to illustrate the effects of using either a calibration ranges 0-50 µmol/l(Cal50) and 0-30 µmol/l (Cal30),
842 where CV is the certified value of each CRM and UAL and LAL, are the upper and lower action limits using
843 a z-score of 2 criteria. Each point represents CRM results from an individual run. Due to improved QC
844 using the TOxN range 0-50 µmol/l, the runs were re-calculated to include the higher standards.

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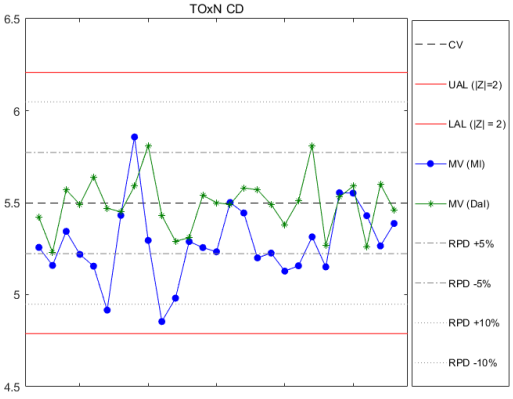
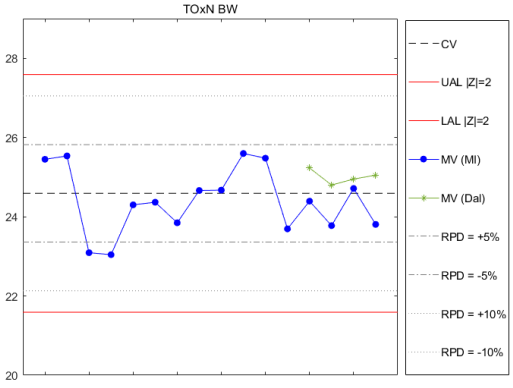
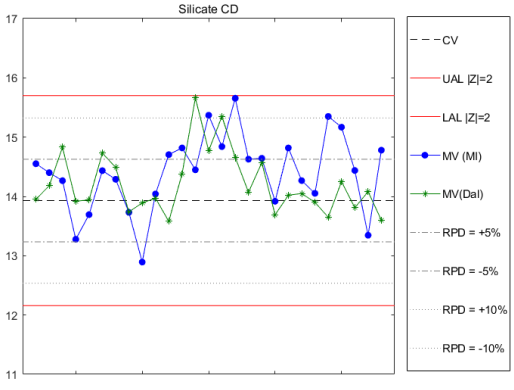


849 Figure 3a



850 Figure 3b



851 Figure 3c

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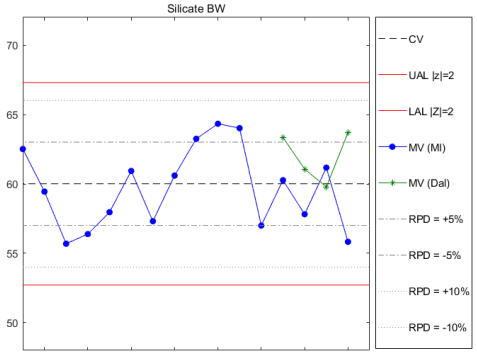

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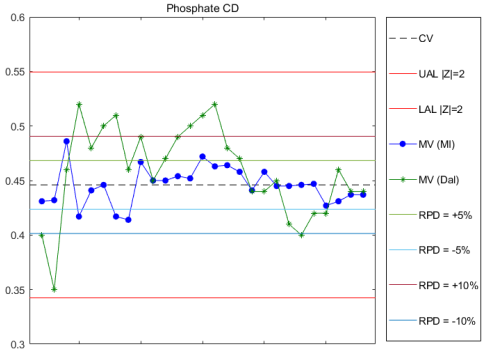
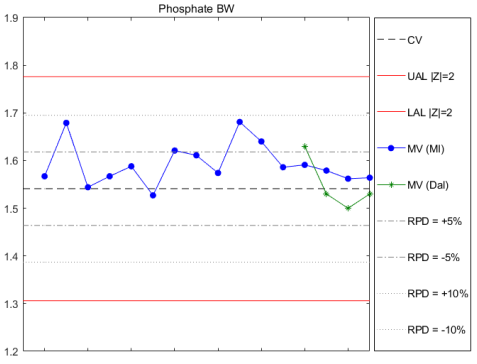


853 Figure 3e



854 Figure 3f

855 Figures 3a-3f Control charts of CRM concentrations from the MI and Dal systems. The dashed line
856 represents the certified value for each CRM (CV), while the red upper (UAL, upper action limit) and lower
857 (LAL, lower action limit) lines represent the z-score of 2 allowable limits criteria. MV (MI) and MV (Dal) are
858 the measured values from the MI and Dal systems, respectively. The dash-dot and dotted lines represent
859 the 5% and 10% relative percentage difference from the certified value. One CD CRM was run at the
860 beginning and end of every run on both systems, and one BW CRM was analysed at the beginning of every
861 run on the MI system. BW CRMs were run on only a selected number of runs of the Dal system for
862 comparison.

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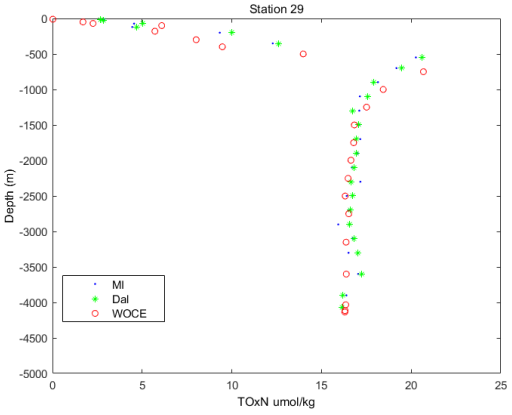
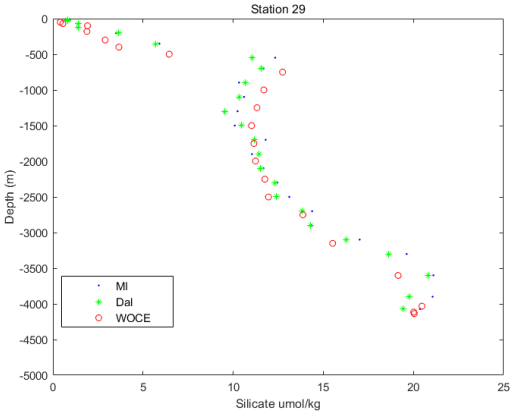
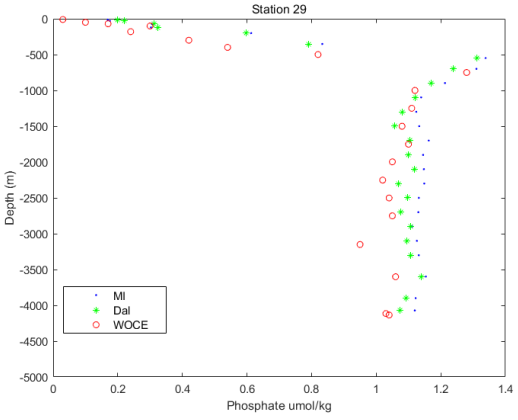


863 Figure 4a



864 Figure 4b



865 Figure 4c

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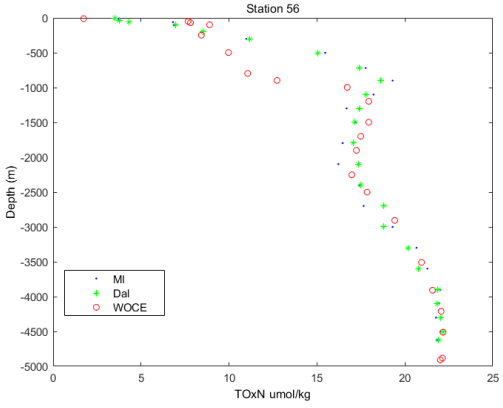
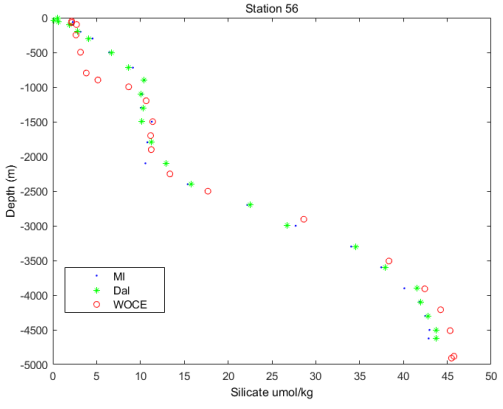


867 Figure 4d



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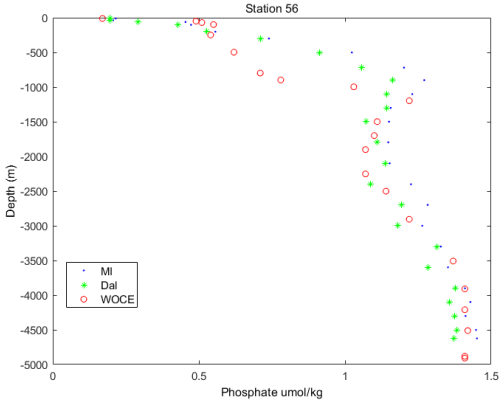

869 Figure 4f

870 Figure 4. Vertical profiles of TOxN, Silicate and Phosphate (in µmol/kg from the MI (Marine Institute), Dal
871 (Dalhousie University) and WOCE (World Ocean Circulation Experiment) datasets. Only station 29 and 56
872 are included here, all other stations compared are in the Supplementary Material.

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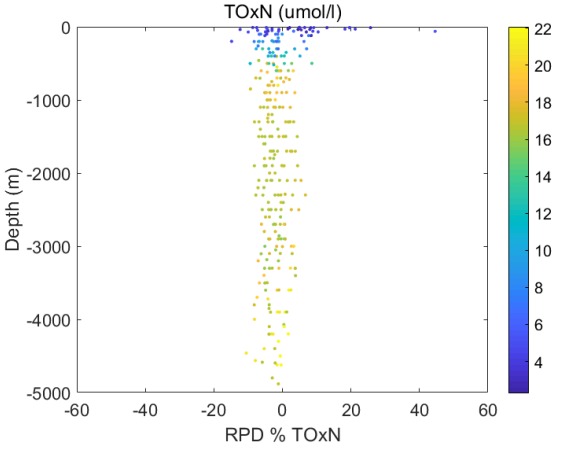
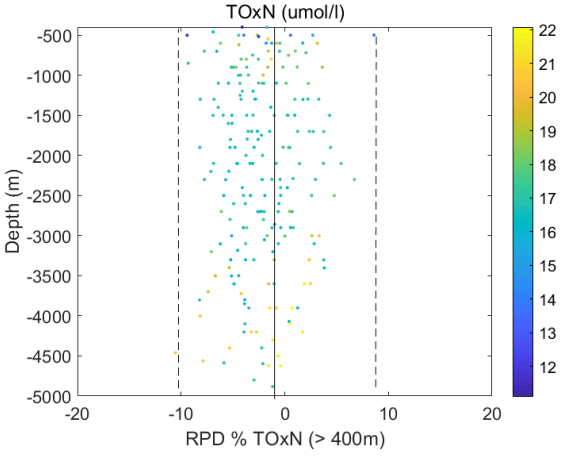
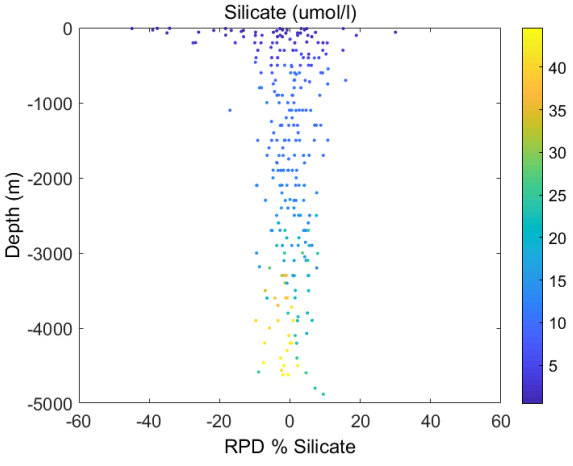


874 Figure 5a



875 Figure 5b



876 Figure 5c

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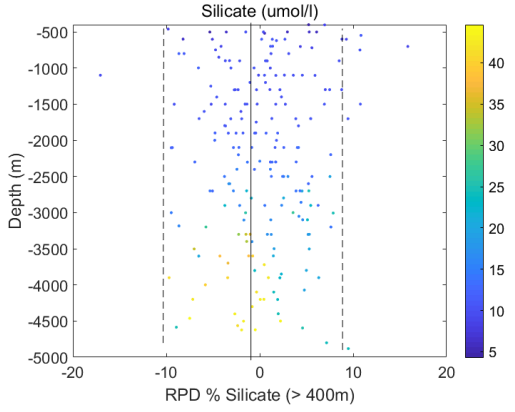

Figure 5d

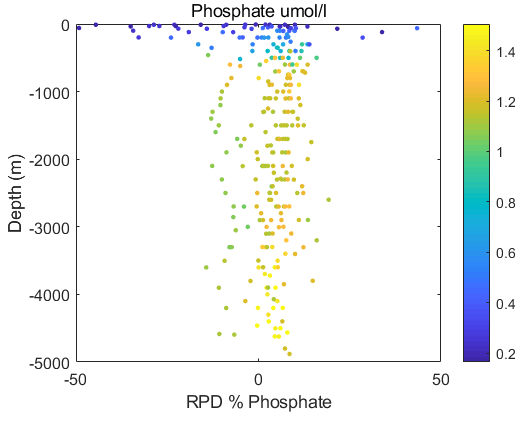

Figure 5e

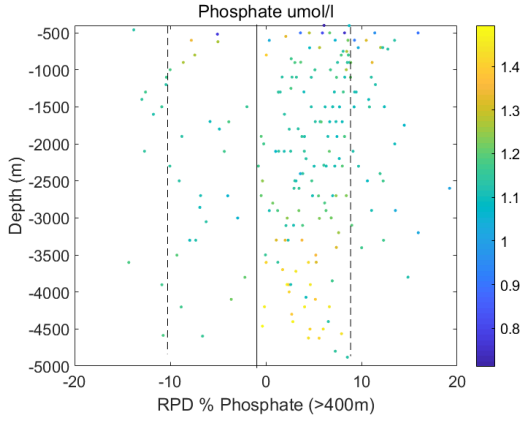

Figure 5f

Figure 5 Relative percentage difference (RPD) calculated as (MI conc - Dal conc)/average conc * 100% for each nutrient for the whole water column and for depths > 400m. The colour bar for each plot is the average concentration (µmol/l) of each nutrient (i.e. the average concentration from both systems) at that depth.