Geological Survey Ireland

Reanalysis of Tellus stream water samples collected in 2012 and 2016

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Executive Summary

The Tellus programme of Geological Survey Ireland (GSI) has been collecting stream water samples since 2012. To date, almost 7000 sites have been sampled. At each site two samples are taken, one unacidified sample for anions and non-purgeable organic carbon (NPOC) analysis (30 ml), and another acidified sample for inorganic elements (60 ml). It is the practice of Tellus to store excess sample material remaining after preparation and analysis. This material now forms a sample archive that is available for further research. Continued storage of these samples would only be warranted if it could be demonstrated that the samples have not degraded chemically since original analysis. In the case of the acidified samples, stabilization by acid might be expected to preserve the samples indefinitely. For the unacidified samples, there is no comparable expectation, particularly in respect of analytes such as nitrate or NPOC.

In order to test the chemical integrity of the samples, two half batches of samples were selected for reanalysis at the British Geological Survey's Inorganic Geochemistry laboratory, the same laboratory responsible for the original analyses. The half batches included one from 2012 and one from 2016. Both were selected, based on the original analyses, in order to include a wide range of concentrations for as many elements as possible.

Reported data from the reanalyses suggest that the acidified samples are chemically stable, with no significant variation observed between the original and the new analyses. For the unacidified samples there is tentative evidence to suggest that older samples may have begun to degrade, at least for nitrate and NPOC.

It is recommended that samples be tested again in several years to verify the conclusions from this initial study.

Disclaimer

1. Introduction

The Tellus programme of Geological Survey Ireland (GSI) has been collecting stream water samples since 2012. To date, almost 7000 sites have been sampled. At each site two samples are taken, one unacidified sample for anions and NPOC analysis (30 ml), and another acidified sample for inorganic elements (60 ml). Acidification is carried out using concentrated nitric acid (1 % v/v). Each field batch of 100 ideally contains 88 field samples and 12 control samples, including duplicates, replicates, blanks and monitor site samples. Thus the total number of sample bottles each for unacidified and acidified samples is closer to 8,000, giving a total of nearly 16,000 bottled samples. These bottled samples are currently stored in c. eight large-capacity double-door fridges in GSI. Relatively little of the original sample (4.5 mL of acidified sample, c. 7 mL of unacidified sample) was consumed during analysis.

Completion of stream water sampling over the remainder of the country at a similar sampling density would entail collection of approximately 26,000 more samples from 13,000 sites. When control samples are included, this would imply storage of almost 30,000 sample bottles in addition to those already in storage in GSI, to give a grand total of c. 46,000 bottles.

It is the practice of Tellus to store all excess soil, sediment and water sample materials that remain after preparation and analysis. This material now forms a sample archive that is available for further research. There have been numerous draw-downs of soil and stream sediment material from the archive since 2012 but there have been no requests surface water samples in the same period.

Regardless of the interest to date, or lack thereof, of researchers in the surface water archive, continued storage of these samples would only be warranted if it could be demonstrated that the samples have not changed chemically since original analysis. In the case of the acidified samples, stabilization by acid might be expected to preserve the samples indefinitely. For the unacidified samples, there is no comparable expectation, particularly in respect of analytes such as nitrate or organic carbon.

In order to test the chemical integrity of the samples, two half batches of samples were selected for reanalysis at the British Geological Survey's Inorganic Geochemistry laboratory, the same laboratory responsible for the original analyses. The half batches included one from 2012 and one from 2016. Both were selected, based on the original analyses, in order to include a wide range of concentrations for as many elements as possible.

A summary of the results of these analyses is presented below.

2. Review of reanalyses

The data for the 2020 reanalyses have been compared directly to the original data from 2012 and 2016 by calculating the % relative difference (= [(new-old)/old)*100]) between each original analysis and the corresponding reanalysis for each sample and analyte. Thus, a positive % relative difference indicates that the concentration reported for the new analysis exceeds that for the old analysis. These calculations are presented in a conditionally formatted spreadsheet where % relative differences in excess of 20 % and 50 % are highlighted. In addition, for anions and NPOC only, the original analyses have been plotted against the reanalyses on both X-Y plots and box –plots.

While variation in reported concentrations between original analyses and subsequent reanalyses potentially may arise because of time-dependent compositional changes to the stored water, variations owing to analytical changes, such as calibration changes or instrumentation changes, may also be present. BGS laboratory reports indicate that the IC instrument is unchanged since 2012 but both ICP and TIC/TOC

analysers have changed since 2016. In the case of ICP-MS analyses this has led to significantly reduced detection limits for some analytes. The potential impact of calibration changes on IC, NPOC or ICP-MS analyses are not known although it is possible that at least some of the observed variation between original analyses and reanalyses for 2012 and 2016 samples may reflect calibration changes since 2012.

2.1 Anions and NPOC

The IC analyses included seven anions – Cl^-, Br^-, F^-, NO_3^-, SO_4^{2-}, HPO_4^{2-} and NO_2^-. Of these, only the first five are consistently detected in Tellus samples and so HPO_4^{2-} and NO_2^- are not considered further. The reanalysed samples included four blanks – these have been removed as most of the analytes were below the limit of detection.

Chloride (Cl^-)

Chloride demonstrates a strong coherence between the original analyses and reanalyses. Notable exceptions are two samples from 2016, 602320W and 602324W. The reported concentration for the former was 19.8 mg/L in 2016 and "<DL" in 2020. Setting the "<DL" to half the detection limit results in a calculated % relative difference of c. -100 %. For 602324, the concentration reported in 2020, 31.1 mg/L, is c. 46 % higher than that reported in 2016 (21.2 mg/L). Chloride is considered to be a conservative species with low reactivity as well as low involvement in chemical and biological processes thus analytical variability could potentially be a contributor to these deviating results. However, without detailed follow-up analyses it is not possible to exclude other possibilities such as contamination, precipitation or complex formation.

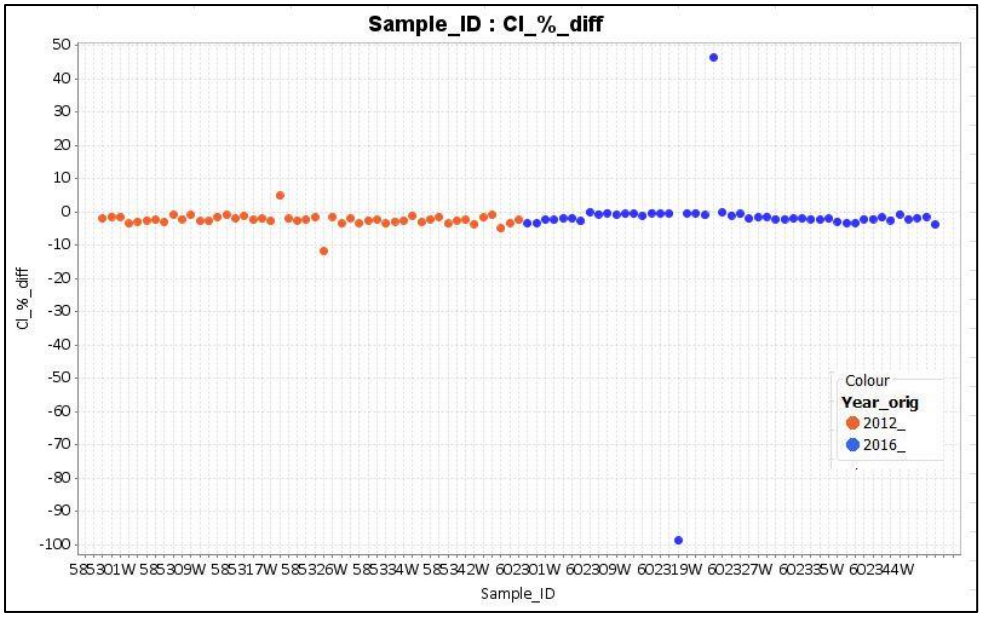

Figure 1 Chloride (Cl^-): % relative difference between original analyses and reanalyses

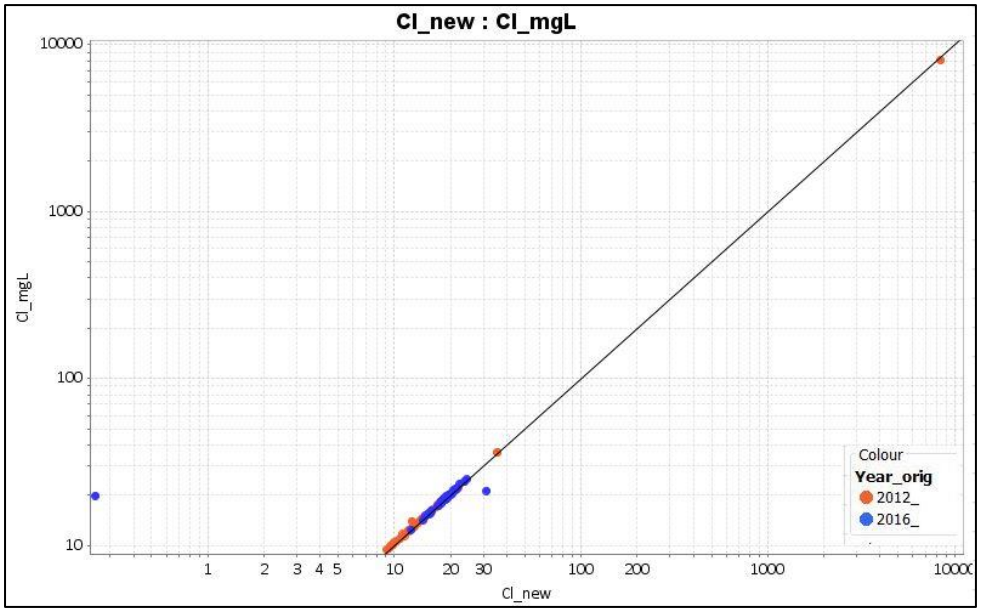

Figure 2 Chloride (Cl^-): original analyses v reanalyses

Bromide (Br^-)

Reported concentrations of bromide in the new analyses are typically lower than those in the original analyses, as illustrated in Figures 3 and 4. The reported variation between original and new analyses is somewhat more pronounced for the 2012 samples, suggesting the possibility that the observed variation may be time-dependent to some extent. Caution is needed however – as shown in Figure 4, much of the poor correlation observed between the original analyses and reanalyses occurs at the lower end of the range of reported Br concentrations, close to the detection limit (0.01 mg/L in 2020, 0.02 mg/L in 2012).

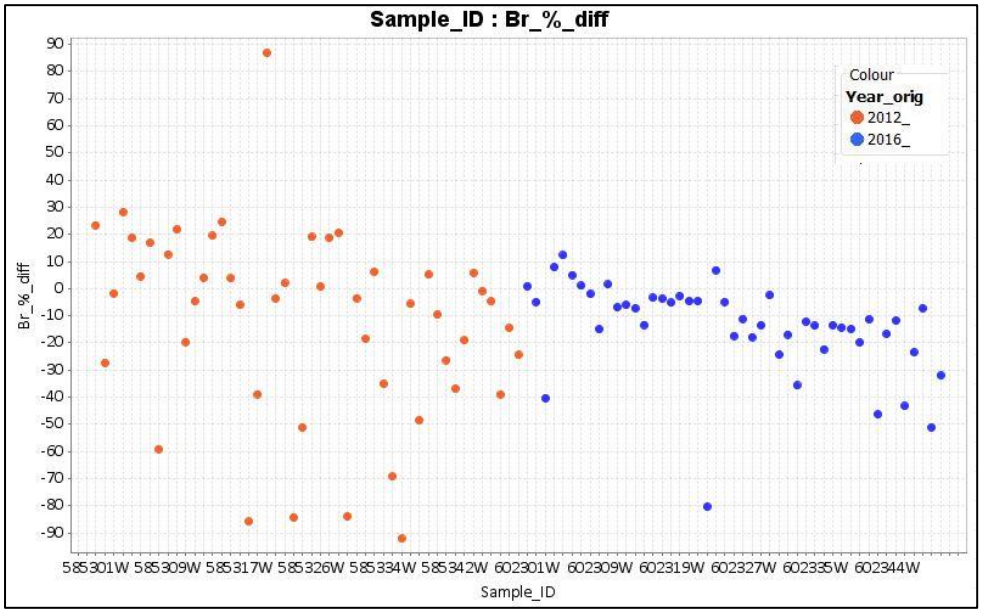

Figure 3. Bromide (Br^-): % relative difference between original analyses and reanalyses

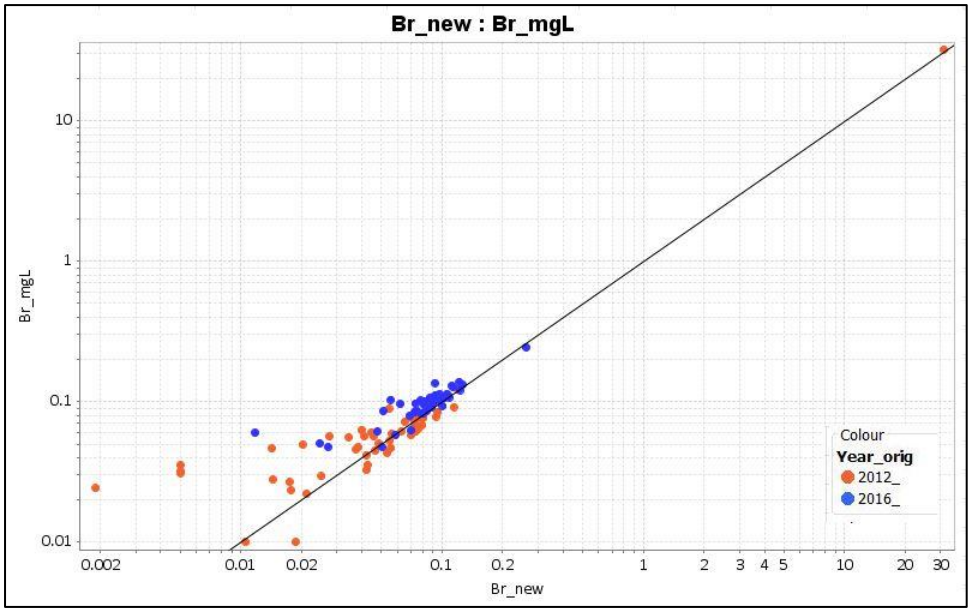

Figure 4. Bromide (Br^-): original analyses v reanalyses

Fluoride (F^-)

There is a considerable contrast between the reported concentrations of fluoride for reanalysed samples from 2012 and 2016, with the former showing a strong deviation from the original reported concentrations while the latter are broadly consistent with the original data. For the 2012 samples, the reported concentrations of fluoride are generally lower for the reanalyses than for the original analyses. The observed discrepancy may be due to analytical variation, but sample change cannot be ruled out. Similarly, as in the case of bromide, poor correlation is mainly observed at the lower end of the range where variability is expected to be higher.

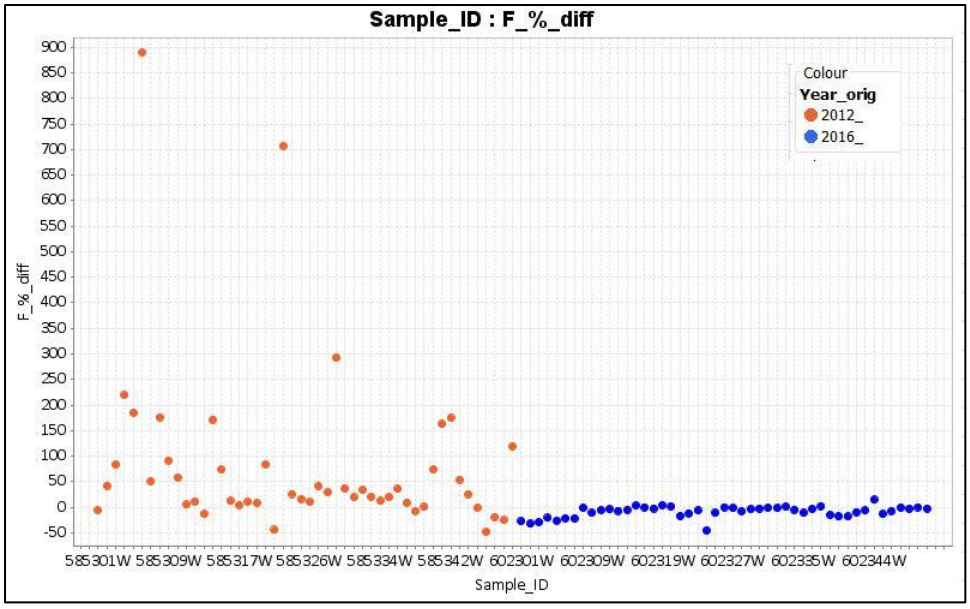

Figure 5. Fluoride (F^-): % relative difference between original analyses and reanalyses

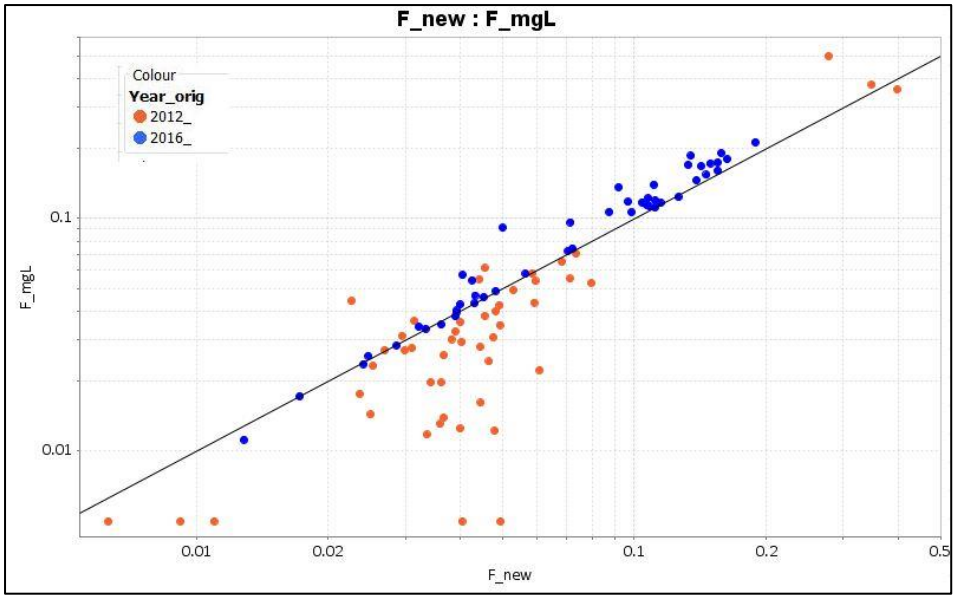

Figure 6. Fluoride (F^-): original analyses v reanalyses

Nitrate (NO_3^-)

Reported nitrate concentrations for reanalysed samples are generally lower than corresponding original analyses for both 2012 and 2016 samples, although the effect is somewhat more pronounced for the 2012 samples. The nitrate anion is generally considered to be relatively stable in aqueous solutions but the observed fall in reported concentrations for the reanalysed samples, from both 2012 and 2016, may indicate nitrate reduction over time. Again, it is noted that the greatest variation occurs at lowest reported concentrations so analytical uncertainty may also be a factor. Nitrate reduction to nitrite and further to other nitrogen species can be indicative of gradual microbial mediated degradation processes. This is particularly plausible when increase in organic carbon concentration, potentially interpreted as biomass growth, is also observed (see below).

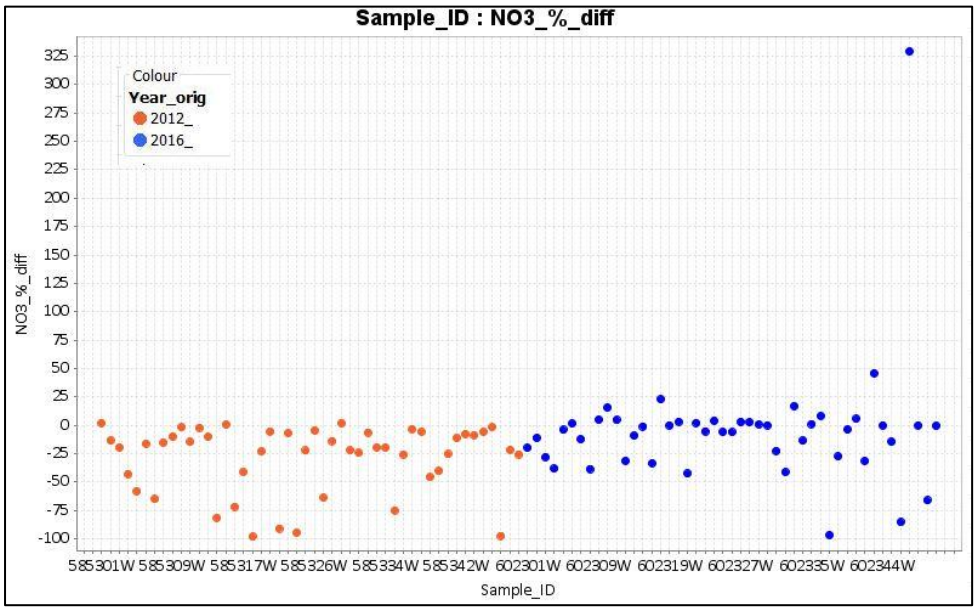

Figure 7. Nitrate (NO_3^-): % relative difference between original analyses and reanalyses

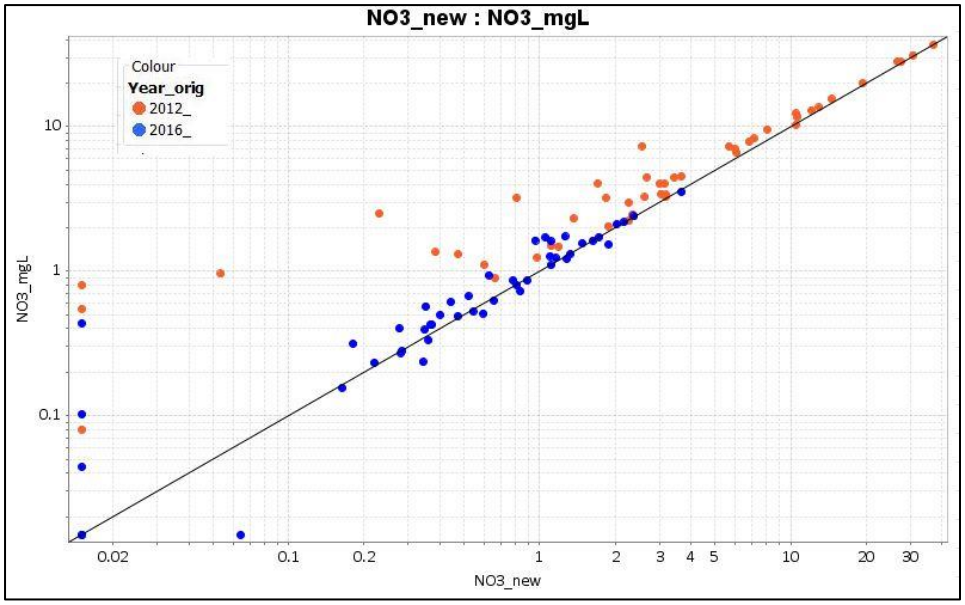

Figure 8. Nitrate (NO_3^-): original analyses v reanalyses

Sulphate (SO_4^{2-})

The sulphate anion is highly soluble and stable in aqueous solutions. Reported concentrations for reanalysed samples show little variation from concentrations previously reported in 2012 and 2016. Only one sample, 602324W, shows a significant deviation from the original result for sulphates (2.64 mg/L for reanalysis v 0.61 mg/L in 2016). This sample also has very high reported Fe (c. 25,000 ug/L).

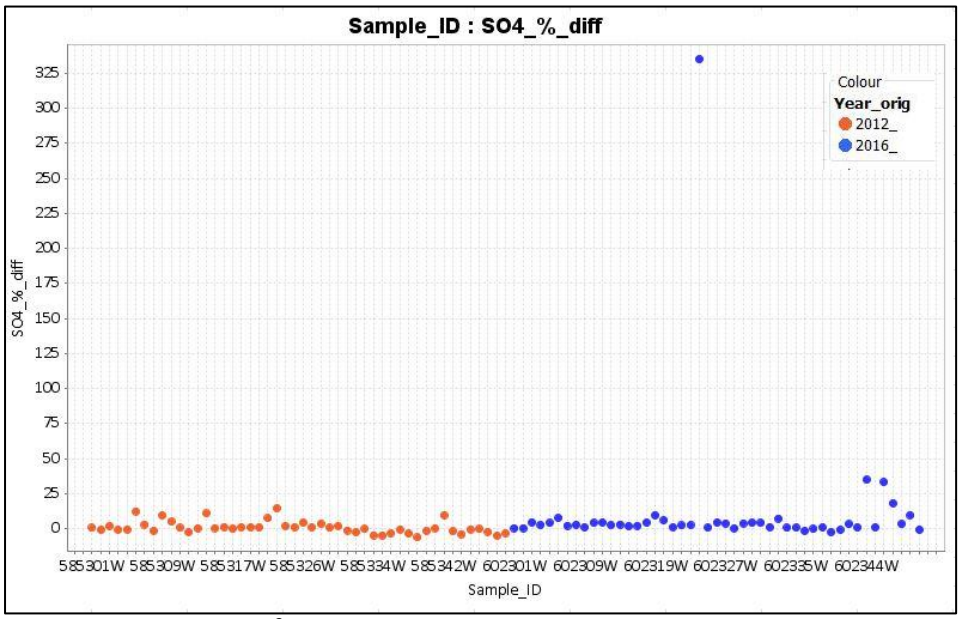

Figure 9. Sulphate (SO_4^{2-}): % relative difference between original analyses and reanalyses

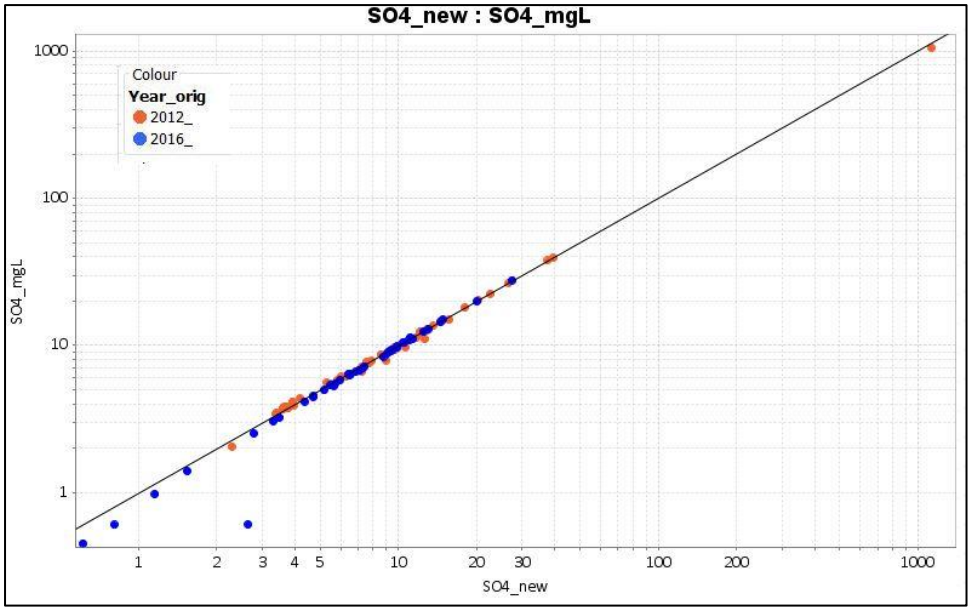

Figure 10. Sulphate (SO_4^{2-}): original analyses v reanalyses

Non-Purgeable Organic Carbon (NPOC)

There is a large degree of scatter in the % relative difference between reported NPOC values for original and reanalysed 2012 samples (Figure 11). Most of the reanalyses have higher reported NPOC concentrations and this holds across the range of reported NPOC values. In contrast the reported results suggest little variation between data for original and reanalysed 2016 samples. This may suggest a time-dependent change in the chemistry of the 2012 samples. Increase of non-purgeable organic carbon can result from plastic contaminant leaching of various additives such as antifogging agents, antioxidants, stabilizers, plasticizers and other plastic residues or alternatively can be a result of microbial activity. Further studies would be required to discern whether the observed increase in NPOC is due to analysis or sample degradation processes.

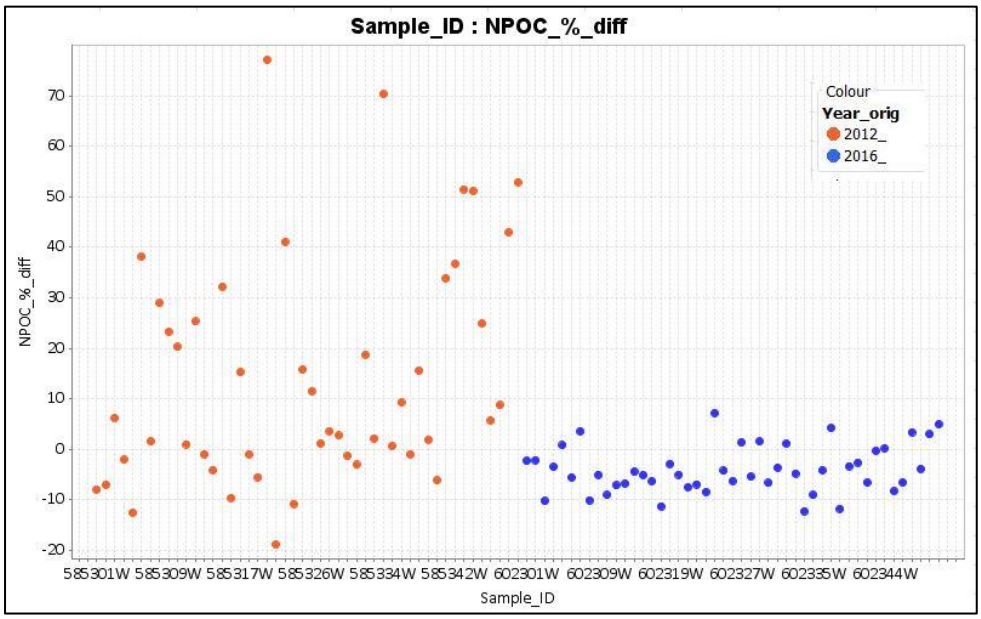

Figure 11. NPOC: % relative difference between original analyses and reanalyses

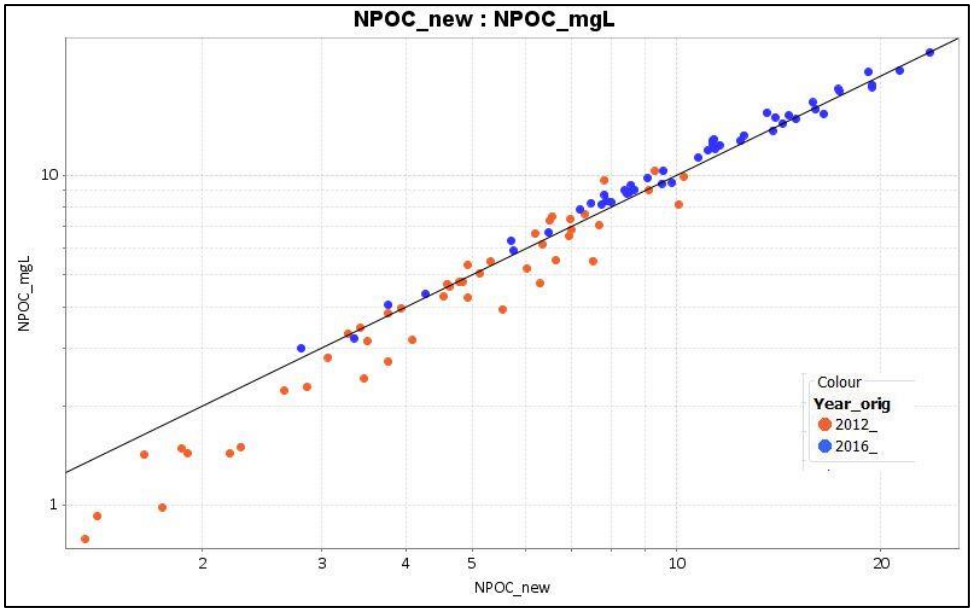

Figure 12. NPOC: original analyses v reanalyses

2.2 Major and trace elements by ICP-MS

Reported data for the reanalysed samples indicate that for majority of elements analysed by ICP-MS there is good agreement with the previous analyses. Significant systematic variations are typically observed only close to detection limits and also in the case of two particular samples (585336W, 585337W) where there is some suspicion of sample misidentification. Several elements of interest are plotted below (Figures 13 – 20) as examples of the data. Data for these plots were censored to half the batch detection limit.

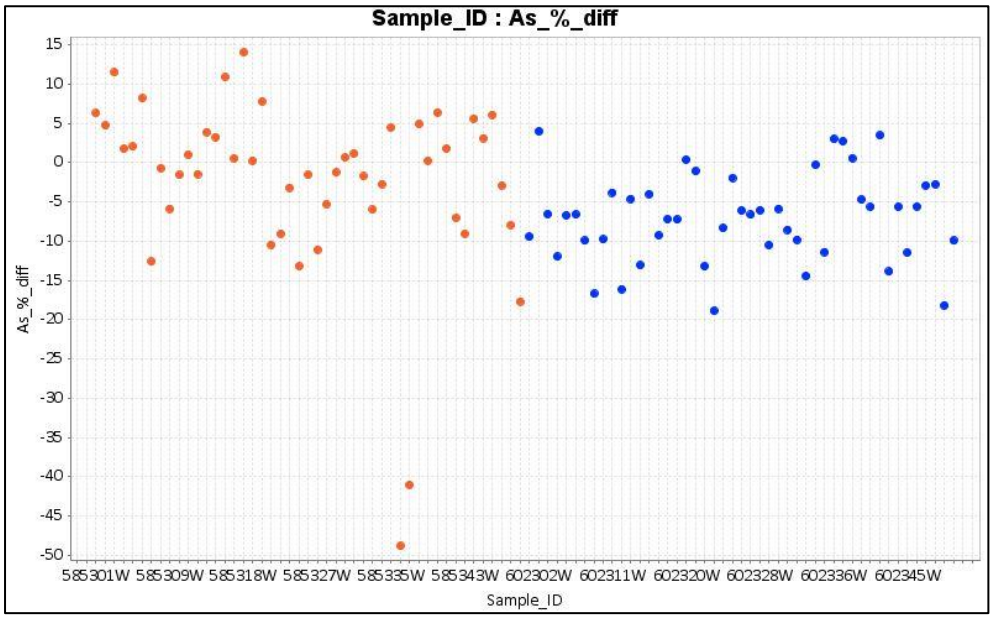

Figure 13. As: % relative difference between original analyses and reanalyses

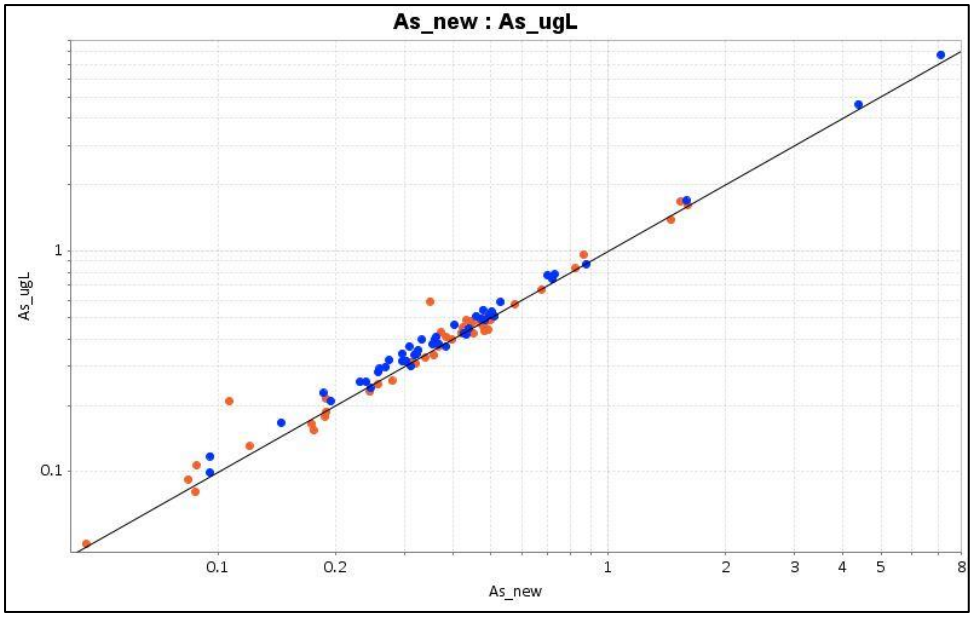

Figure 14. As: original analyses v reanalyses

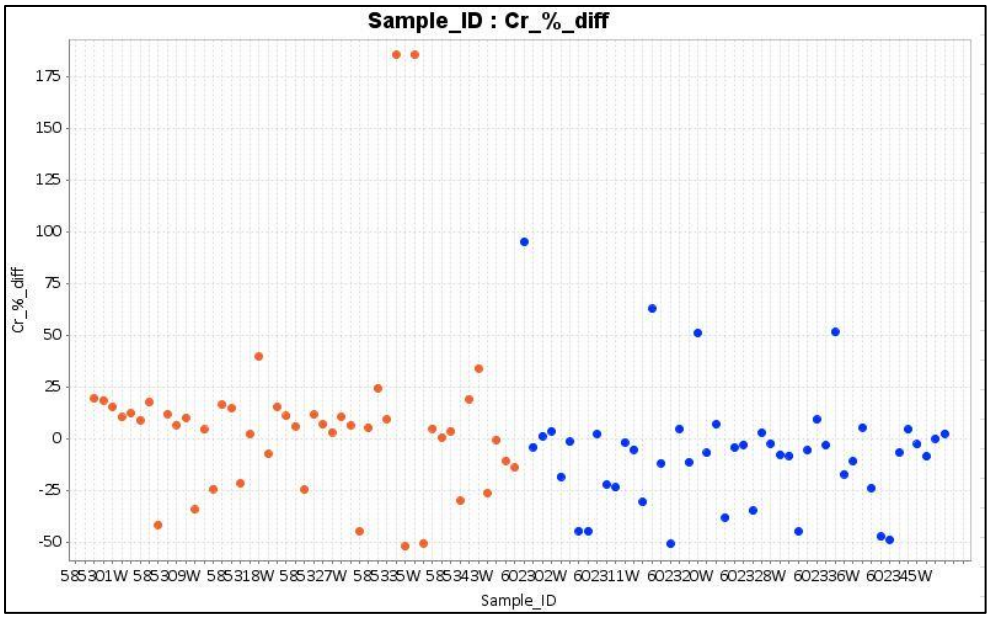

Figure 15. Cr: % relative difference between original analyses and reanalyses

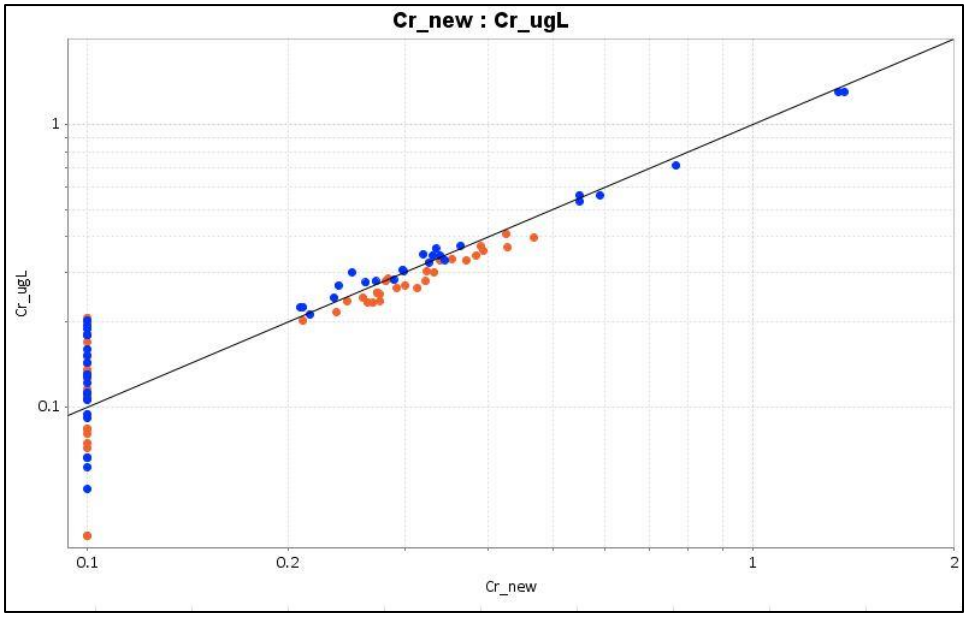

Figure 16. Cr: original analyses v reanalyses

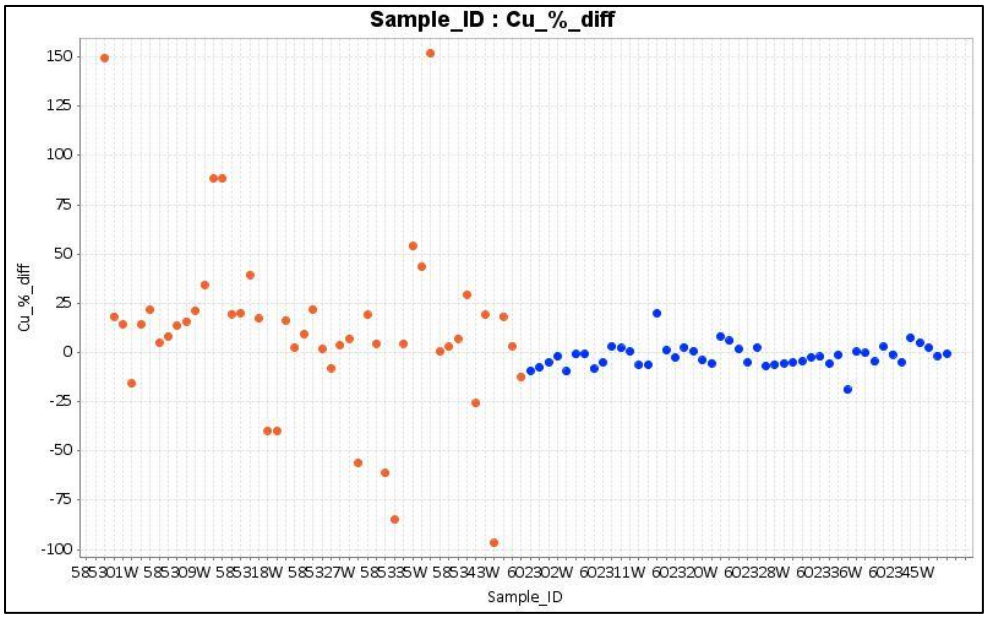

Figure 17. Cu: % relative difference between original analyses and reanalyses

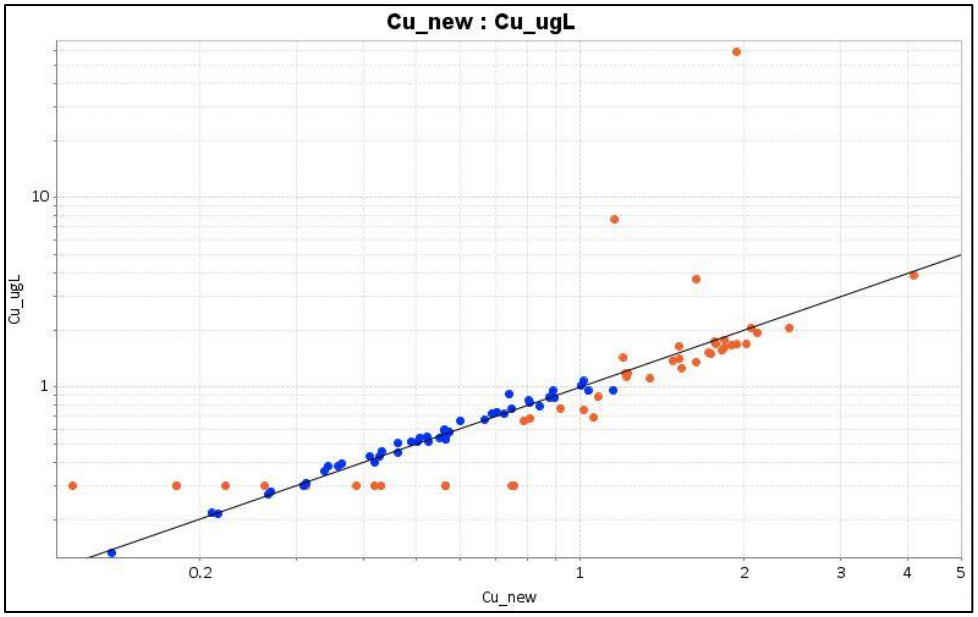

Figure 18. Cu: original analyses v reanalyses

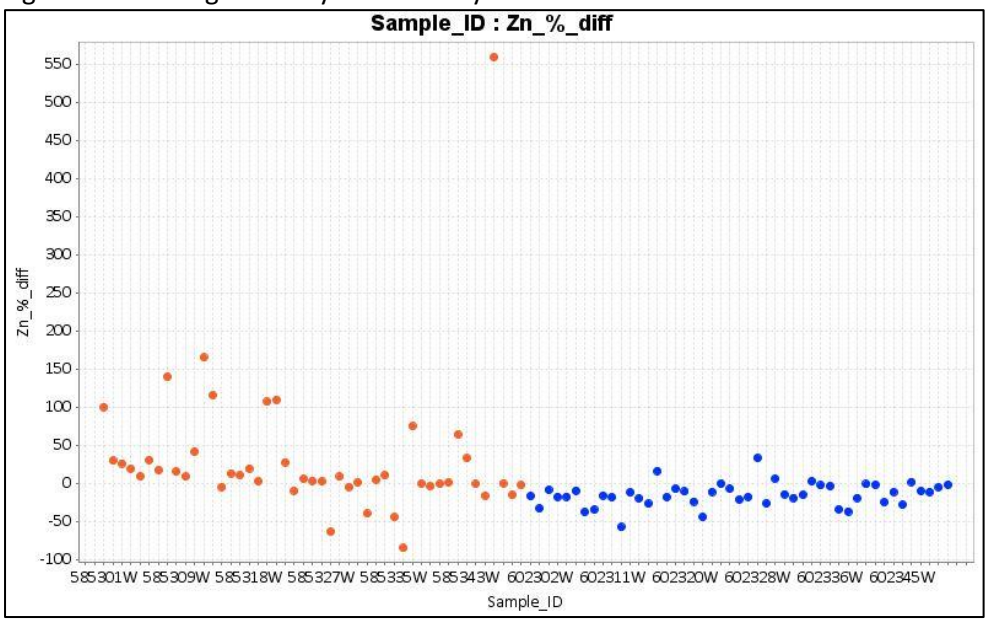

Figure 19. Zn: % relative difference between original analyses and reanalyses

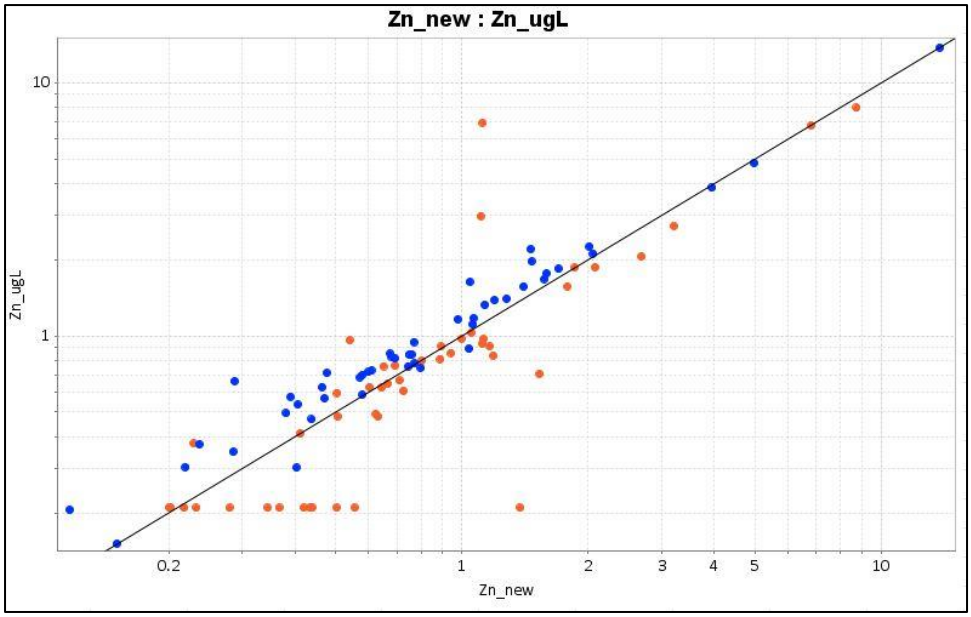

Figure 20. Zn: original analyses v reanalyses

2.3 Charge Balance

The charge balance of the major cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (HCO_3^{-}, Cl^{-}, SO_4^{2-}, NO_3^{-}) has been calculated, as per the methodology outlined by Knights *et al*. (2020). Figures 21, 22 and 23 display the data. The biplot of original v new analyses shows a pronounced difference between calculated charge balance for the original analyses and reanalyses of 2012 samples, suggesting the possibility of sample degradation. The boxplots of relative difference also show the older 2012 samples displaying generally higher relative difference between original and new analyses.

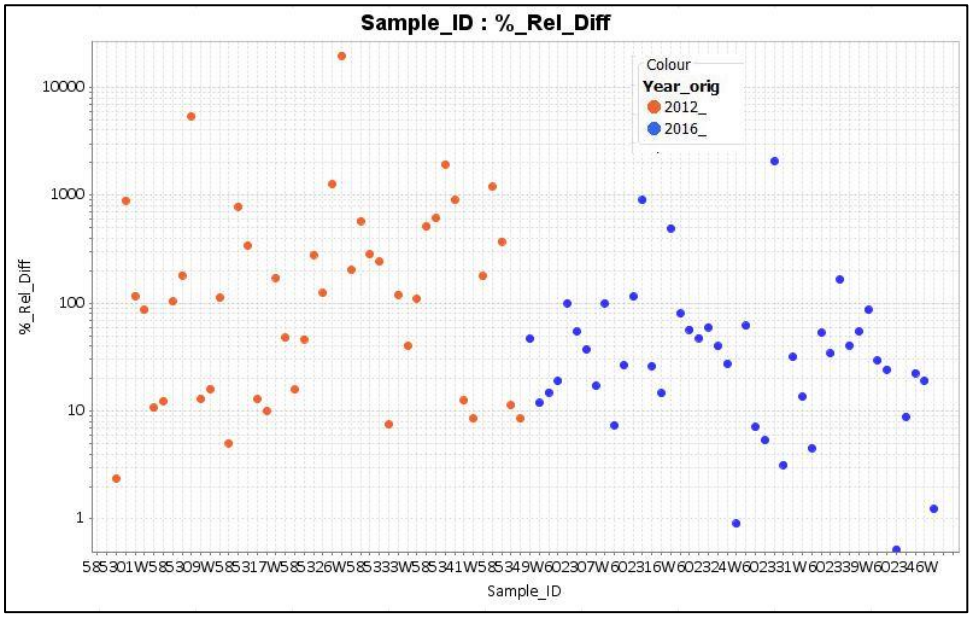

Figure 21. Charge Balance: % relative difference between original analyses and reanalyses

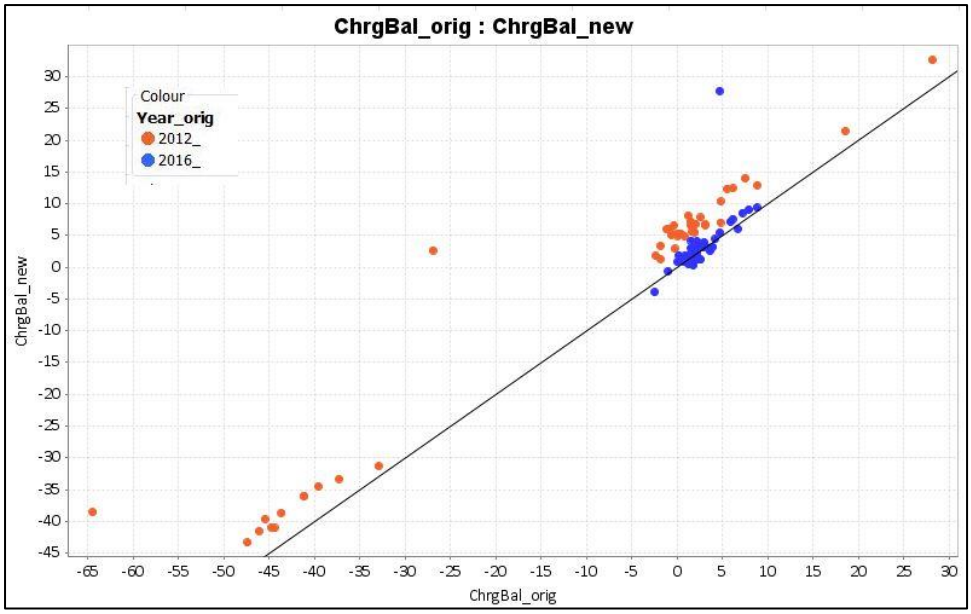

Figure 22. Charge Balance: original analyses v reanalyses

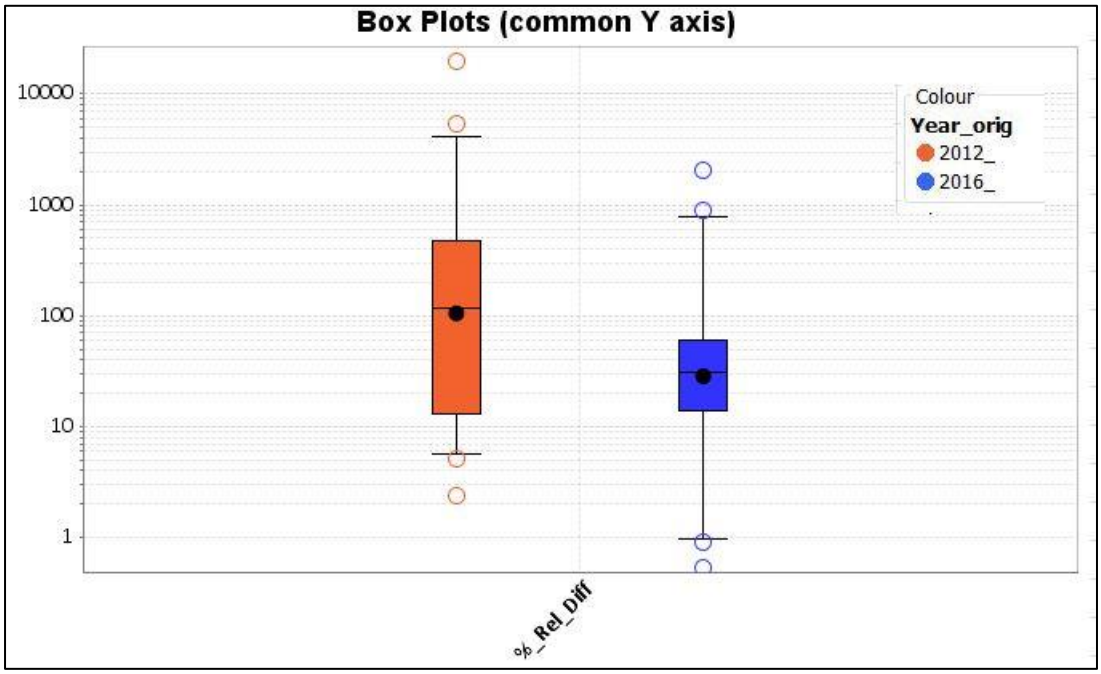

Figure 23. Charge Balance: Boxplots of relative difference, original analyses v reanalyses

3. Some observations on the data

A number of observations can be made on the reanalysis of archived Tellus surface water samples.

1. Multielement ICP-MS analysis suggests that acidified samples are highly stable, with significant variation between original and new analyses observed only close to limits of detection.
2. Therefore, ongoing refrigerated storage of these samples in their current state appears to pose no threat to their chemical integrity and they continue to have potential value as archive material.

3. IC analysis of unacidified samples suggests that the concentrations of most anions in solution have changed little since the samples were collected.
4. The differences between **nitrate** concentrations newly measured in 2012 and 2016 samples points to the possibility that the older samples may have undergone chemical change, with an observed reduction in nitrate concentration in the older samples.
5. Similarly, the differences between **NPOC** concentrations newly measured in 2012 and 2016 samples may also indicate that the older samples have begun to change chemically, with an observed increase in NPOC concentration in the older samples.
6. Charge balance calculations for the original and new analyses also point to possible sample degradation among older samples.
7. Both **bromide** and **fluoride** concentrations do appear to demonstrate a shift between 2012 and 2016 samples, the former apparently falling and the latter appearing to increase over time. Concentrations of both anions are generally quite low so caution is required interpreting these results. They may reflect analytical uncertainty, time-dependent changes or calibration effects.

4. Conclusions and Recommendations

Current recommended maximum holding times for water samples (ISO 5667-3:2018), preserved and stored as per Tellus protocols, range from four days (NO_3^-, NO_2^-) to 30 days (other anions and cations). Such recommendations would suggest that Tellus samples should not be considered for use as part of future research. However, as the reanalyses reported above show, Tellus surface waters samples collected in 2012 and 2016 and stored under refrigeration have been demonstrated to be chemically quite stable. As such they may continue to have potential value in a research context. On this basis the following recommendations can be made:

1. Acidified samples under refrigeration may be retained as archive material indefinitely.
2. Older unacidified samples demonstrate possible time-dependent changes in chemical composition. Therefore unacidified samples from 2012 and 2016 should be reanalysed again in several years.
3. If reanalysis confirms changes in the chemical composition of samples over time then consideration should be given to (a) setting a time limit for retention of unacidified samples or (b) discarding unacidified samples after original analysis is complete.

5. References

Knights, K.V>, Szpak, M., Mather, J. and Collins, L. (2020). Tellus geochemical survey: stream water data from the border and west of Ireland. Geological Survey Ireland. https://www.gsi.ie/en-ie/data-and-maps/Pages/Geochemistry.aspx

ISO 5667-3:2018 Water quality — Sampling — Part 3: Preservation and handling of water samples. https://www.iso.org/standard/72370.html