



Comparability of Oceanic Nutrient Data:

Using an Approved Silicate Standard and Good Lab Practice doesn't Automatically Imply Good Inter-Comparison Results.

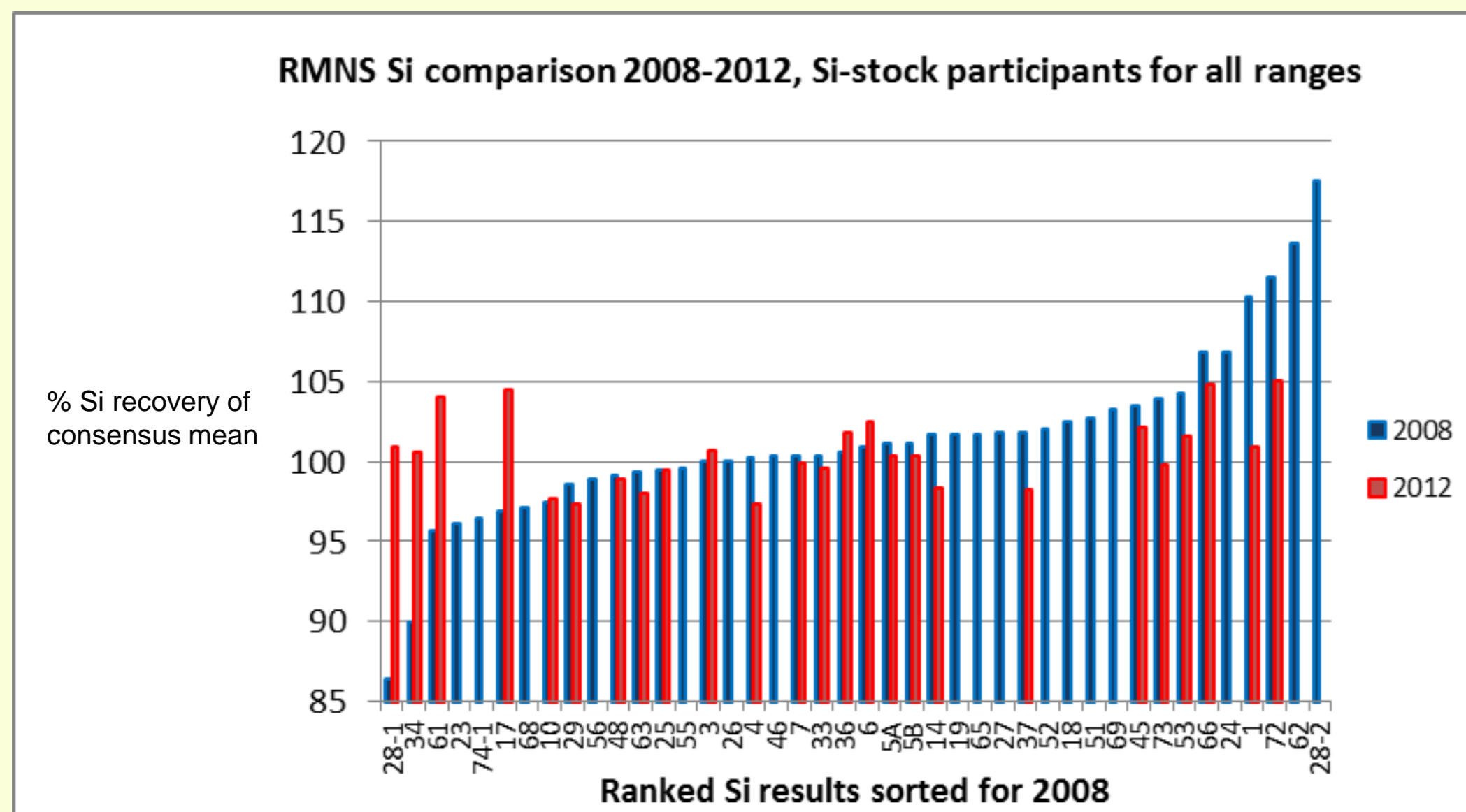
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(SCOR Working Group #147: Towards comparability of oceanic nutrients)



Introduction

The 2008 and 2012 Inter Comparison Study of Reference Material for Nutrient Standards (IC RMNS) showed a large standard deviation (5.3%) in the silicate data reported by the different participating laboratories.



Si data of the 2008 & 2012 IC RMNS study showing the large variability of results.

From the pre SCOR #147 working group called SGONS (Study Group on Nutrient Standards 2008-2012) a study was organised in 2009 to investigate the different silicate standards used in the global nutrient analytical community.

Question & Aims in 2009

Is the variance due to the difference in silicate stocks used for making standards? All participants to send their stock silicate solution to one laboratory in The Netherlands for analysis on one single instrument.

Results 2009

Standard recoveries showed that the stock standards were more or less 100% with only a small variance of 2%. The high variance of the RMNS 2008 results could presumably be explained by the methods and accuracy in diluting samples to the proper calibration range by some participants which led to the need for a further study.

(‘Comparability of nutrients in the world’s ocean’ ISBN 978-4-9904863-0-3).

Follow-up study in 2014

This study was conducted to further investigate the comparability of silicate standards and the methods of dilution. A single homogeneous silicate stock solution made from sodium silicate fluoride (Na_2SiF_6) in ultra pure water (UPW) was sent to the participating labs of the IC RMNS 2014/2015 study.

Na_2SiF_6 is used as the standard by 70% of participants.

Weighed 9.0052g Na_2SiF_6 (MW 188.06 g/Mol) in 5000 ml UPW.

Sample sent to 31 participants.

Guideline: use this stock by diluting 100 times in the same matrix and in the same procedure as the calibration standards.

Na_2SiF_6 purity certificate: 99.0 % = 9.50 mM/kg

If purity 98-100%, then concentration range = 9.41 - 9.60 mM/kg

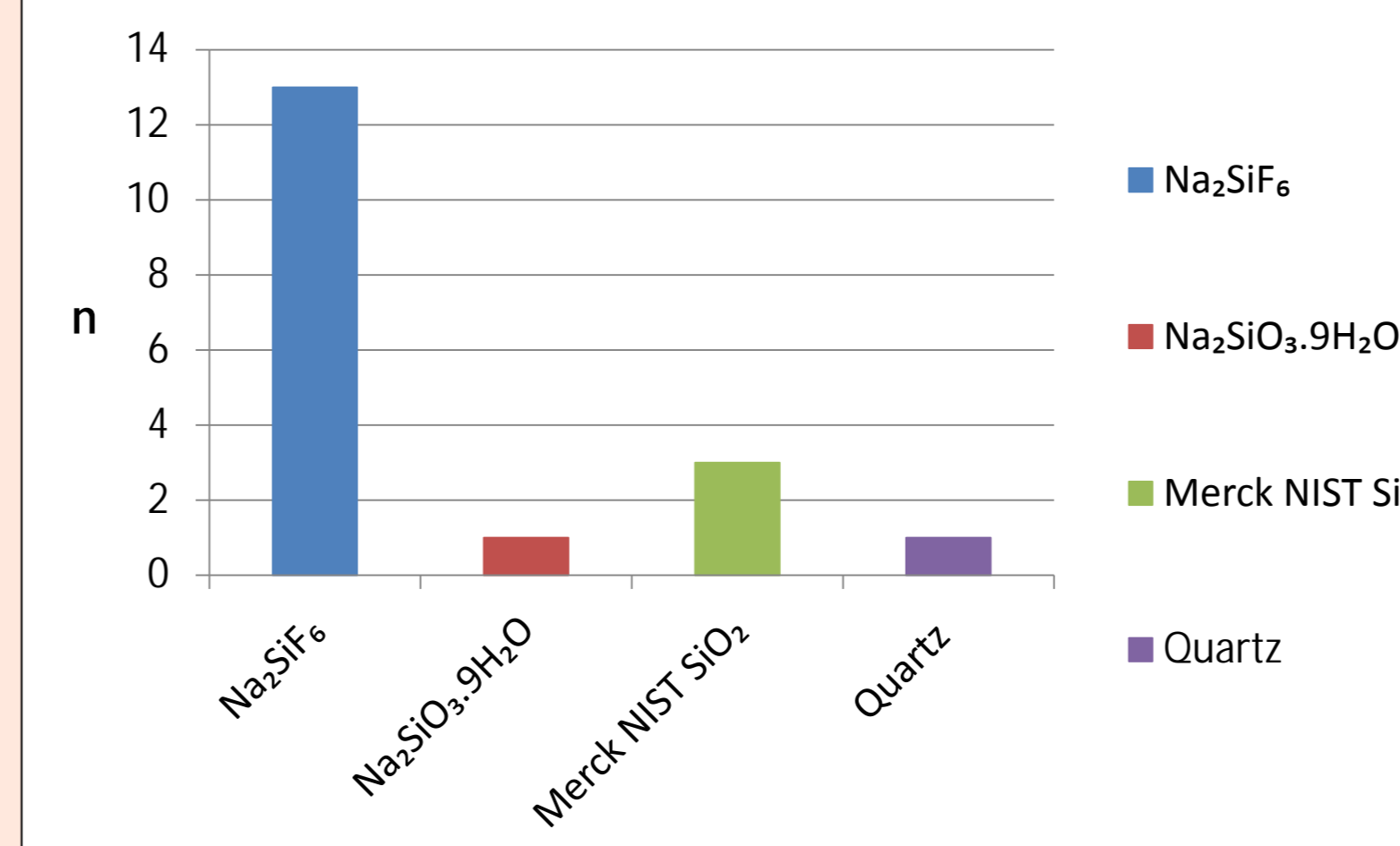
Add estimated errors from all steps of analysis $\pm 1.5\%$
Calculated target range = 9.26 - 9.74 mM/kg (96.5% - 101.5%).

18 reported results:

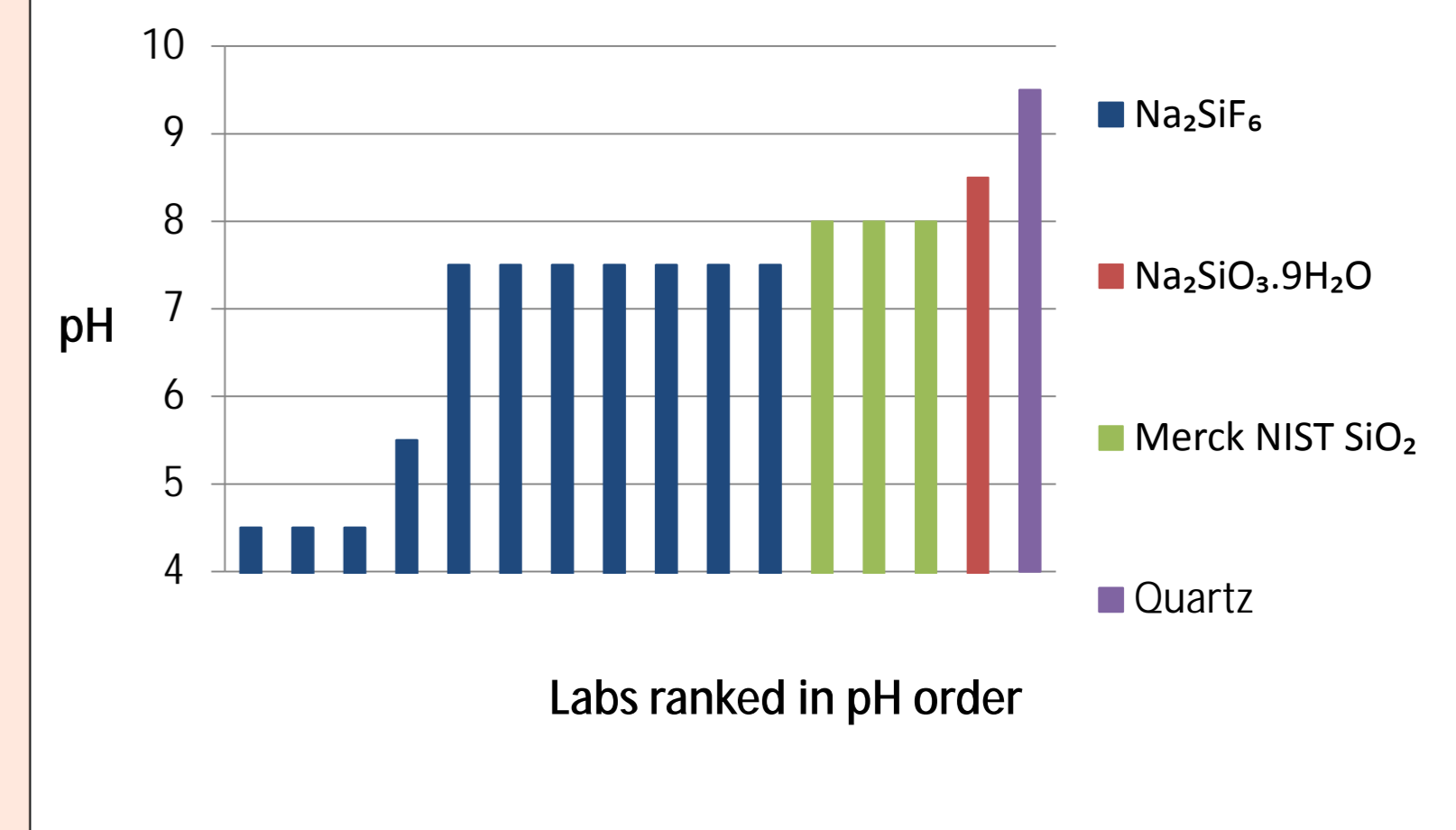
Reported results range: 9.25 – 10.21 mM/kg (96.4% - 106.4%)

Different Si materials used by participants for calibration during the Si stock exercise 2014:

Si material used for calibration

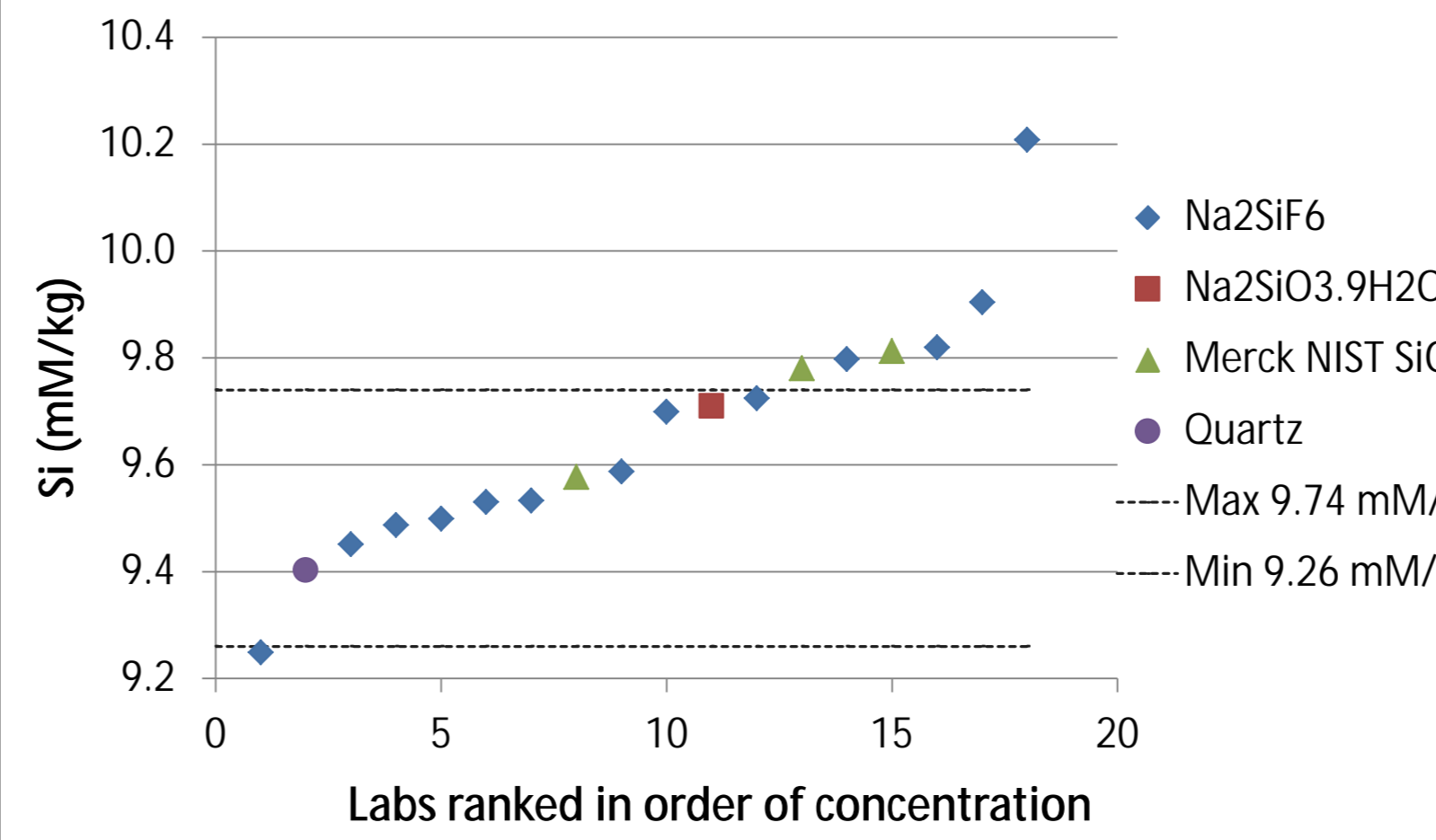


pH at calibration

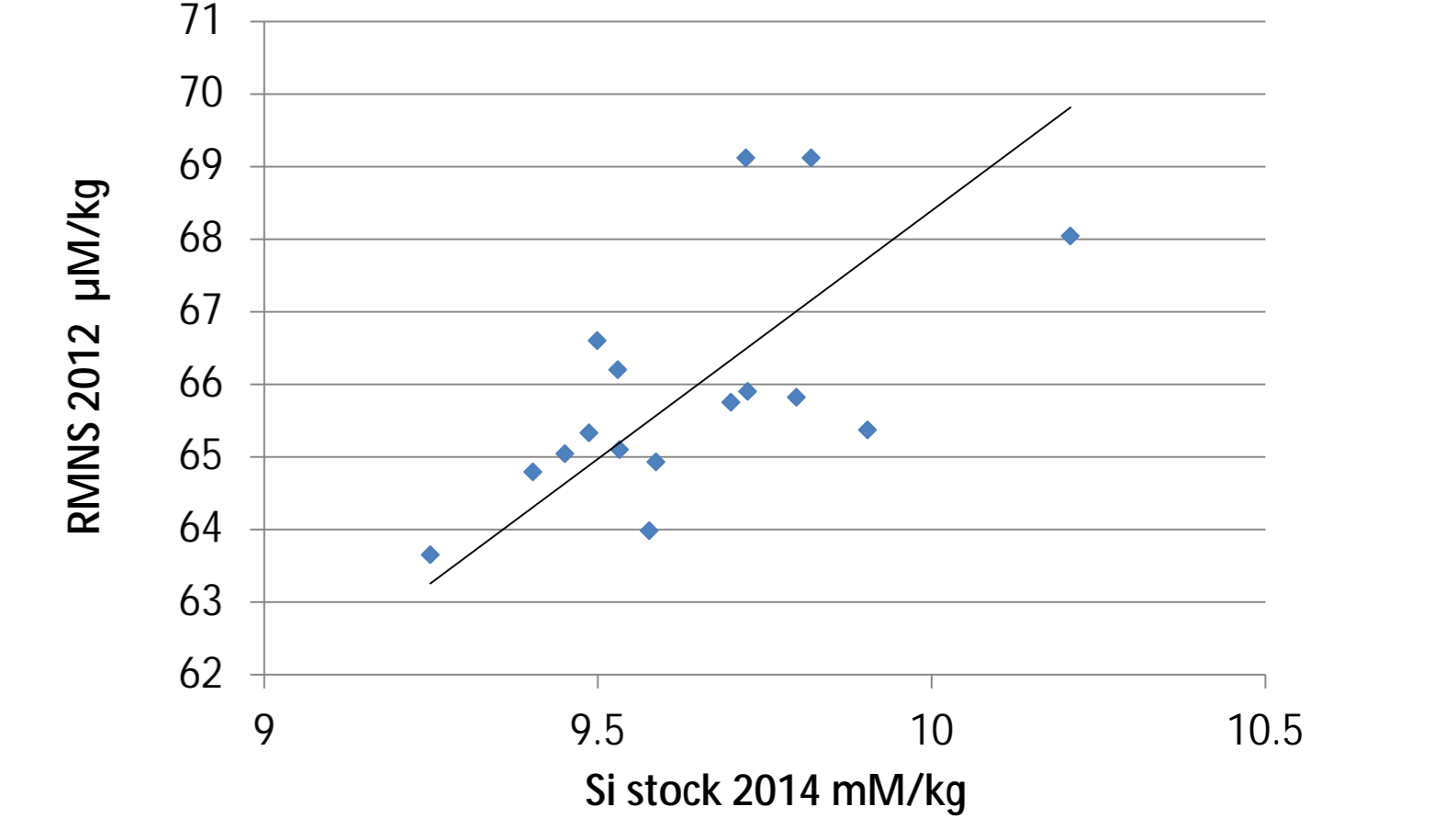


Reported Data from the 2014 Si stock exercise :

Reported data of Si Stock



Data comparison RMNS 2012 vs Si stock 2014



Discussion and Conclusions

The reported concentration after diluting the sample under the participants standard operating procedure gave a standard deviation of 2.6% suggesting that there are still inconsistencies in the global analytical procedures.

During the 2014 Si stock exercise, some labs reported concentrations above 9.74 mM/kg, suggesting purity values above 102% for the Na_2SiF_6 standard.

Suggestion

It may be important for the global community to have one silicate material used for preparing a stock solution. This stock should have no effects on any of the diluents LNSW, ASW, UPW used for calibration and shouldn't interfere if used simultaneously in mixed nutrient standards.

To overcome a salinity decrease from dilution when preparing the working standards the strength of the Si stock solution should be approximately 15mM.

Future

The recommendation would be to order one and the same batch of Na_2SiF_6 from one manufacturer as this material is in favour by 70% of the labs and make a uniform method to prepare a stable stock from this in UPW. The purity is no longer an issue by using the same standard batch worldwide.

Good comparability of data is not only dependent on good laboratory practice but also on its chemistry.

