Comparability of oceanic nutrient data :
Use of CRMs in the French intercalibration program

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Context

Coastal nutrient concentrations are key parameters for the management of eutrophication, since they can be directly linked to nutrient inputs, which can be addressed by abatement measures.

In relation with the EU Water Framework Directive (WFD) implementation, Ifremer organizes interlaboratory exercises for the French oceanographic community in the framework of its quality assurance program. In the context of using nutrient concentration in the assessment of ecological status, it is indeed important that all French laboratories set consistent and comparable analytical performances.

Eleven exercises, each with two lots of samples for the five main nutrients (ammonium, nitrite, nitrate, phosphate and silicate), were proposed between 2006 and 2015, each exercise involving about 25 independent laboratories.

Test material preparation

Test material need to be homogeneous, to be stable over relative long periods (> 6 months), to enable simple storage and shipping

1- Filtration of depleted seawater
to remove phytoplankton cells

2- Addition of high purity salts
choice of the concentration of the samples

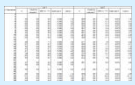
3- Pasteurization process
80 +/- 3°C during 2 h

4- Homogeneity test
Nanomolar variation for NO_2 and PO_4
Tens nanomolar variation for NH_4, NO_3, $Si(OH)_4$

5- Shipping of test material
25 participants in France and overseas

6- Stability test (40 months)
Low concentrations : variation comparable to homogeneity test
High concentrations : 0,3 – 0,5 %

7- Statistical process of dataset to calculate the laboratories performance



Use of Certified Reference Material (CRM) to calculate the laboratories performance

The performance of individual laboratory is usually determined by the z-score value calculated as :

$z = (x_i - X)/\hat{\sigma}$ where x_i is the measured value, X is the assigned value, $\hat{\sigma}$ is the standard deviation for proficiency assessment

$\hat{\sigma}$ is set at a value required to be compliant with a performance level adapted to marine water concentrations (ex : 5 % for NO_3 and $Si(OH)_4$)

X can be determinated by several ways as suggested by the ISO 13528 international standard :

1- *Consensus value* *from participants* : equal to the robust average of the results reported by all the participants of the proficiency test

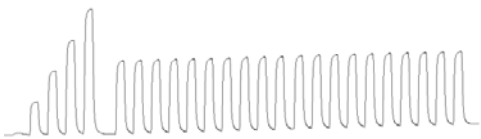
2- *Consensus values from expert laboratories* : the test material samples are analysed by a group of expert laboratories

3- *Certified reference value* : when the material used in the proficiency test is a CRM

4- *Reference value* : a number of the test material samples are tested along with CRMs. The assigned value is then derived from a calibration against the certified reference values of the CRMs.

	Advantages	Disadvantages
1 - Consensus value from participants	/	some results can bias the consensus value
2 - Consensus value from expert laboratory	/	who are the experts?
3 – Certified reference value	certified proficiency test	quite expensive , same sample concentrations at each proficiency test
4 – Reference value	**easy to operate**	/

Determination of the certified consensus value from 20 replicates of the test material calibrated against CRMs



CRM calibration — Test material replicates

Conclusion

The use of CRMs to certify the consensus value allows us to produce z-scores not biased by the performances of laboratories which use analytical methods not suited for coastal and marine waters.

This test material samples can also be regarded as a stable internal reference material for daily use.

It would be now desirable to have a CRM production for NH_4 analysis.

Référence Daniel A., Kérouel R., Aminot A. (2012). Pasteurization : a reliable method for preservation of nutrient in sea water samples for inter-laboratory and field applications. Marine Chemistry, 128-129, 57-63

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