Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature Conservation

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Document title	Determination of nitrate – proposed monitoring guidelines
Code	2MA-8
Category	DEC
Agenda Item	2MA – Revision of HELCOM monitoring
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Submitted by	Sweden

Background

HELCOM guidelines for hydrography and hydrochemistry are currently being revised. Lead Country Sweden submits proposed guidelines for determination of nitrate in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. Draft guidelines for nitrate were discussed at STATE & CONSERVATION 4-2016 (para 2MA.22). The guidelines have been amended based on reviews by Co-lead country Poland, as well as representatives from Denmark, Estonia, Finland and Germany.

Determination of nitrate is currently described in Annex B-9 in the *Manual for monitoring in the COMBINE programme in HELCOM*. The revised guidelines include updates on procedure. The QA/QC section is expanded and a reference for estimation of measurement uncertainty has been added.

Action requested

The Meeting is invited to endorse the monitoring guidelines for determination of nitrate.

Guidelines for determination of nitrate

1 Background

Introduction

Dissolved inorganic nitrogen is present in seawater both as nitrite, nitrate and ammonium. As a complement to the overall assessment of nutrient status, detailed information on the distribution of different species must be obtained.

Purpose and aims

Monitoring of nutrients is carried out to identify and quantify the effects of eutrophication. The aim is to provide information for detection of long-term trends, as well as studies of short-term events. Dissolved inorganic nitrogen is a HELCOM Core indicator: http://helcom.fi/baltic-sea-trends/indicators/nitrogen-din

2 Monitoring methods

Monitoring features

Water samples are collected from discrete depths and analyzed. Well established wet chemistry methods are available.

Time and area

Monitoring should be carried out in the entire Baltic Sea area. Winter pool of nutrients must be assessed.

2.1 Monitoring procedure

Monitoring strategy

Colorimetric methods described by Hansen and Koroleff (Grasshoff et al 1999) are considered sufficient.

Sampling method and equipment

For general requirements for sampling, preservation, handling, transport and storage of water samples see EN ISO 5667-3

Subsamples should be collected without unnecessary exposure to air. Rinse bottles with sample water before filling them. Avoid trapping bubbles of air when filling and capping bottles.

Seawater contains microorganisms and other suspended particles, which may have to be removed prior to analysis, since turbidity caused by suspended matter interferes with colorimetric measurements.

Filters used should be free of contaminants, and have an appropriate pore size, e. g. 0.40 µm polycarbonate filters or Whatman GF/F filters. Glass fiber filters, if used, should be combusted at 450°C for at least 4 hours before use.

If samples are not filtered, a turbidity blank can be used to correct for interferences from turbidity or colour.

The procedure selected for removing interference from turbidity must be validated.

Unnecessary handling of samples should be avoided to prevent contamination.

Samples must be protected from airborne contamination from tobacco smoke or engine exhaust fumes.

Samples should be analyzed as soon as possible after sampling, preferably within a few hours. If samples must be stored for longer periods, storage in freezer at temperatures between – 18 °C and – 20 °C are necessary to increase stability.

Samples stored in freezer should first be filtered as described above, and frozen as rapidly as possible. In temperatures below -20°C, samples are stable for at least a few weeks.

Sample handling and analysis

Samples should be analyzed as soon as possible after sampling. When samples need to be stored they must be kept refrigerated and protected from light, and not stored for longer than 10 hours prior to analysis.

The colorimetric method described by Hansen and Koroleff (Grasshoff et al 1999) is recommended.

The efficiency of the cadmium coil used for reduction of nitrate to nitrite is strongly reduced by hydrogen sulphide.

2.2 Data analysis

The method described above determines sum of nitrite and nitrite (TOxN, Total Oxidized Nitrogen); nitrate is calculated as difference between TOxN and nitrite.

3 Data reporting and storage

Data are reported annually to the HELCOM COMBINE database, hosted by ICES.

4 Quality control

4.1 Quality control of methods

Laboratories carrying out analyses of nutrients should have established a quality management system according to EN ISO/IEC 17025.

Immediate analysis of samples is always preferable to preservation and prolonged storing. If samples are stored in freezer, temperature must be monitored and recorded.

Methods for preservation must be validated since results can be affected by biological activity, seasonal cycle, salinity or other matrix effects.

Efficiency of cadmium coil must be monitored and recorded.

An internal reference material (IRM) should be analyzed daily.

Certified reference materials (CRM) are available from VKI/Eurofins: http://www.eurofins.dk/dk/milj0/vores-ydelser/reference-materialer

It is strongly recommended that all laboratories participate in interlaboratory comparisons and proficiency testing programs, to provide external verification of laboratory performance. Proficiency tests for nutrients in seawater are provided by e. g. QUASIMEME or SYKE. More proficiency testing schemes are listed at www.eptis.bam.de.

4.2 Quality control of data and reporting

Measurement uncertainty should be estimated using ISO 11352. Estimation should be based on within-laboratory reproducibility, data from proficiency testings, IRM, and, when available, CRM.

Data must be flagged if normal QA routines or recommended storage conditions cannot be followed.

5 Contacts and references

5.1 Contact persons

References

Filtration and storage
Kremling K and Brügman L
Chapter 2 p 27-40;

Determination of nutrients
Hansen H P and Koroleff F
Chapter 10 p 159-228 in

Grasshoff K, Kremling K and Erhardt M
Methods of Seawater Analysis 3rd ed
Wiley-VCH 1999
ISBN 3-527-29589-5

EN ISO 5667-3*: Water quality - Sampling - Part 3: Preservation and handling of water samples

EN ISO 11352*: Water quality – Estimation of measurement uncertainty based on validation and quality control data

EN ISO/IEC 17025*: General requirements for the competence of testing and calibration laboratories

* For undated references, the latest edition of the referenced document (including any amendments) applies

5.2 Additional literature

Lysiak-Pastuszak E. and Krysell M (eds)
Chemical measurements in the Baltic Sea: Guidelines on quality assurance.
ICES Techniques in Marine Environmental Sciences, No. 35. 149pp, ISBN 87-7482-021-4.

Wurl O(ed)
Practical Guidelines for the Analysis of Seawater
CRC Press 2009
ISBN 978-1-4200-7306-5