Document title	Draft guidelines for determination of nitrate
Code	2MA-8
Category	CMNT (LATE)
Agenda Item	2MA – Revision of HELCOM monitoring
Submission date	23.3.2016
Submitted by	Sweden
Reference	

Background

HELCOM guidelines for hydrography and hydrochemistry are currently being revised. In accordance with STATE & CONSERVATION 2-2015 (para 2MA.3), Lead Country Sweden submits draft guidelines for determination of nitrate in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. The draft has been revised by Co-lead country Poland, as well as representatives from Estonia, Finland and Germany.

Measurements of nitrite are currently described in Annex B-9 in the COMBINE manual. The draft for new guidelines includes updates on procedure. The QA/QC section is expanded and a procedure for estimation of measurement uncertainty has been added.

Action requested

The meeting is invited to

- consider and amend as needed the draft guidelines for analysis of nitrate.

Guidelines for determination of nitrate

1 Background

1.1 Introduction

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

1.2 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. Nitrogen is a HELCOM Core indicator: http://helcom.fi/baltic-sea-trends/indicators/nitrogen-din

2 Monitoring methods

2.1 Monitoring features

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

2.2 Time and area

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

2.3 Monitoring procedure

2.3.1 Monitoring strategy

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

2.3.2 Sampling method and equipment

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.

Samples are easily contaminated, and all unnecessary handling should be avoided. 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 or poisoning with mercury(II) chloride are necessary to increase stability. Poisoned samples are stable only for a limited time, up to 1-2 weeks.

Samples stored in freezer should first be filtered through 0.4 µm polycarbonate or 0.45 µm filters, and frozen as rapidly as possible. In temperatures below -20°C, samples are stable for at least a few weeks.

2.3.3 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 12 hours prior to analysis.

If samples must be stored for longer times, freezing samples or adding mercury chloride as a preservative increases.

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 sulfide.

2.4 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 is reported annually to the HELCOM COMBINE database, hosted by ICES.

4 Quality control

4.1 Quality control of methods

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

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 proficiency testing programs. Proficiency tests for nutrients in seawater are provided by e. g. QUASIMEME and 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 11352:2012. Estimation should be based on within-laboratory reproducibility, data from proficiency testsings, 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

5.2 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

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

Water quality – Estimation of measurement uncertainty based on validation and quality control data
ISO 11352:2012

5.3 Additional literature

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