



Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature
Conservation

STATE & CONSERVATION
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Document title	Determination of total nitrogen – proposed monitoring guidelines
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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 total nitrogen in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. Draft guidelines for nitrite 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 total nitrogen 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 total nitrogen.

Draft guidelines for determination of total nitrogen

1 Background

1.1 Introduction

Total nitrogen includes all organic and inorganic forms of nitrogen, dissolved as well as suspended or particulate. The results are an estimation of the total amount of nitrogen, not only the dissolved bioavailable fraction.

1.2 Purpose and aims

Monitoring of total nitrogen is carried out to identify and quantify the amounts of total nitrogen which may result in eutrophication. The aim is to provide information for detection of long-term trends, as well as studies of short-term events.

2 Monitoring methods

2.1 Monitoring features

Water samples are collected from discrete depths and analyzed. Samples are treated with an oxidizing agent to transfer all nitrogen compounds to nitrate. 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. Simultaneous determination of total phosphorus and total nitrogen is recommended.

2.3.2 Sampling methods and equipment

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

Samples are collected from sampling bottles attached to a CTD-rosette, or clamped to a hydrographic wire. Collection from ferrybox (on research vessel, or ship of opportunity) is also possible.

2.3.3 Sample handling and analysis

Samples should be kept refrigerated and protected from light.

Avoid unnecessary manipulation of samples to prevent contamination.

Freezing is recommended if samples have to be stored more than 12 hours before pretreatment.

Transfer the aliquot required to analyze total nitrogen into autoclave resistant flasks (Teflon, or SCHOTT or DURAN flasks). Samples are stored at -18°C.

Methods for sample pretreatment (a digestion step where organic and inorganic nitrogen compounds are oxidized to nitrate) as well as colorimetric determination of nitrate are described by Hansen and Koroleff in Grasshoff (1999).

2.3.3.1 Interferences

High levels of oxygen-consuming material (sulphide, or organic material) will limit the ability to oxidize all organic nitrogen compounds to nitrate. Interferences must be removed prior to oxidation, by pre-oxidation of sulfide, or adjusting sample to oxidizing reagent ratio.

2.4 Data analysis

(n/a)

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

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 (for reduction of nitrate to nitrite) 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-ydelsler/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 testings 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

Johan Håkansson, SMHI

5.2 References

Filtration and storage
Kremling K and Brüggeman 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

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

5.3 Additional literature

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

Lysiak-Pastuszek 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.