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Working Group on the State of the Environment and Nature
Conservation

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Document title	Determination of ammonium – proposed monitoring guidelines
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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 ammonium in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. 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 ammonium 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 ammonium.

Draft guidelines for determination of ammonium

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 amount of inorganic nutrients which may cause 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 listed as a HELCOM Core indicator:

<http://helcom.fi/baltic-sea-trends/indicators/nitrogen-din>

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 in the surface layer; however, information about the annual cycle in the surface is also important. Furthermore, the vertical distribution has to be considered with respect to oxic/anoxic conditions.

Monitoring procedure

Monitoring strategy

Colorimetric method described by Hansen and Koroleff (Grasshoff *et al* 1999) are considered to be sufficient. A more recent method based on fluorometry is described by K  rouel and Aminot (1997).

Sampling method 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.

Sample handling and analysis

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 should be analyzed as soon as possible after sampling (preferably within an hour), and should not be stored for any length of time. It is important that the bottles used for the determination has to be heated at 180  C at least for 2 hours.

No preservative methods are available.

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

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.

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

Unnecessary handling of samples should be avoided to prevent contamination.

Indophenol method

The indophenol method, a photometric method, is described by Hansen and Koroleff in Grasshoff *et al* (1999).

OPA method

A method for determination based on fluorometry is described by K erouel and Aminot (1997).

Since the main reagent is sensitive to light, amber bottles must be used. When SFA/CFA instruments are used, analytical manifold and tubing must be protected from light.

Coloured organic matter when present in high concentrations might interfere. Humic material displays similar fluorescent properties as the ammonium-OPA complex. Validation is needed to confirm the insignificance of interferences if water rich in humic material is analyzed.

Data analysis

Corrections for salt effects may have to be applied if the indophenol method is used. Validation is needed if waters with a wide range of salinity are sampled.

Data reporting and storage

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

Quality control

Quality control of methods

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

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

Certified reference materials (CRM) are available from VKI/Eurofins:

<http://www.eurofins.dk/dk/milj0/vores-ydelse/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.

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.

Contacts and references

Contact persons

Johan Håkansson, SMHI

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

Kérouel R and Aminot A 1997

Fluorometric determination of ammonia in sea and estuarine waters by direct segmented flow analysis
Marine Chemistry 57 , p 265-275

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

Additional literature

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.

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Practical Guidelines for the Analysis of Seawater

CRC Press 2009

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