Guidelines for sampling and determination of ammonium

1 Background

1.1 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.

1.2 Purpose and aims

Monitoring of nutrients in seawater is carried out to identify and quantify the amount of nutrients, which may cause eutrophication. The aim is to provide spatiotemporal information for detection of short-term status and long-term trends and to ensure that the data is comparable for the HELCOM core indicator ‘Dissolved inorganic nitrogen‘. The indicator description, including its monitoring requirements, is given in the HELCOM core indicator web site: http://helcom.fi/baltic-sea-trends/indicators/nitrogen-din.

2. Monitoring methods

2.1 Monitoring features

Ammonium is determined from samples collected from discrete depths. Samples need no pretreatment, besides filtration; details and storage options are described in section 2.3.3.

2.2 Time and area

Monitoring of ammonium is carried out by all HELCOM contracting parties, and the monitored area covers the entire Baltic Sea area, both the open sea and coastal areas.

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.

2.3 Monitoring procedure

2.3.1 Monitoring strategy

Water samples are collected from discrete depths, and analysed. Samples need to be analysed or prepared for storage immediately after sampling.

Samples are collected at depths of 1, 5, 10, 15, 20, 25 (Kattegat and the Belt Sea only), 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 225, 250, 300 and 400 metres; and as close to the bottom as possible.

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 Kérouel and Aminot (1997).

2.3.2 Sampling method(s) and equipment

For general requirements for sampling, preservation, handling, transport and storage of water samples, see 5667-3 and EN ISO 5667-9.

Samples are collected from sampling bottles attached to a CTD rosette, or clamped to a hydrographic wire.

Bottles for storage of samples must be thoroughly cleaned and rinsed, and kept capped when not in use.

2.3.3 Sample handling

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

Samples should be analysed as soon as possible after sampling (preferably within an hour), and should not be refrigerated for any length of time. According to EN ISO 5667-3, samples can be stored in plastic bottles up to one month in freezer at below -18°C. Experiences (from the BSH Laboratory Germany) suggest that samples could be stable for up to 4 months when stored between -18 – -20°C (temperature should be maintained within the specified interval, and recorded with a digital data logger, e.g. Testo 174, in particular if samples are also used to determine silicate). Before determination if ammonium, samples should be allowed to defrost slowly, preferably overnight, in darkness Before freeze storage, samples must be filtered as described below.

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 fibre 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 Kérouel 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 analysed.

2.4 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.

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.

An internal reference material (IRM) should be analysed working 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 testings for nutrients in seawater are provided by e.g. QUASIMEME or SYKE. More proficiency testing schemes are listed at www.eptis.bam.de.

Contracting parties should follow the HELCOM monitoring guideline but minor deviations from this are acceptable if the method achieves comparable results. Validation of the adopted method needs to be performed on the relevant matrix and concentration range e.g. by taking part in intercomparison studies or proficiency testing schemes.

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.

Collected data should be checked for consistency between sampled variables (e. g. dissolved inorganic nitrogen and total nitrogen).

5. Contacts and references

5.1 Contact persons

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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
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 5667-9* Water quality – Sampling – Part 9: Guidance on sampling from marine waters

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

5.3 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