Draft guidelines for sampling and 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 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

Water samples are collected from discrete depths and analyzed.

Samples are treated with an oxidizing agent to transfer all organic and inorganic nitrogen compounds to nitrate. Previously pressure cookers and autoclaves were used, now microwave ovens are usually preferable.

2.2 Time and area

Monitoring of total nitrogen 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 soon after sampling.

For determination of total nitrogen, well-established wet chemistry methods are available (see section 2.3.3).

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. Samples from 2.5 m might be collected if relevant, e.g. in shallow waters or waters influenced by river runoff.

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 method(s) and equipment

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

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, if requirements for sample storage times and conditions can be met.

2.3.3 Sample handling and analysis

Samples should be kept refrigerated and protected from light.

Avoid unnecessary manipulation of samples to prevent contamination.

A subsample is transferred from a well-homogenised sample into an autoclave/microwave oven-resistant bottle (preferably Teflon) before the oxidizing reagent is added.

Freezing is recommended if samples have to be stored more than 12 hours before pre-treatment. Transfer the aliquot required to analyse total nitrogen into autoclave resistant flasks (Teflon, or SCHOTT or DURAN flasks). Samples are stored at -18 – -20°C (temperature should be maintained within the specified interval, and recorded with a digital data logger, e.g. Testo 174).

Methods for sample pre-treatment (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 sulphide, or adjusting sample to oxidizing reagent ratio.

2.4 Data analysis

Results need to be corrected for dilution by the oxidizing reagent.

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 analysed 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. ISBN 3-527-29589-5

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. ISBN 87-7482-021-4

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