Guidelines for sampling and determination of silicate

1 Background

1.1 Introduction

Silicate is introduced to the Baltic Sea as a result of natural geological processes, as opposed to nitrogen and phosphorus, which levels are affected by human activities.

Although it is not listed among the HELCOM Core Indicators, silicate is still biologically significant. Since diatoms are dependent of dissolved silicate for growth, monitoring of silicate is essential for evaluation and modelling of nutrient status, and assessment of conditions for phytoplankton growth.

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.

2 Monitoring methods

2.1 Monitoring features

Dissolved silicon is present in seawater as dissolved silicate or silicic acid, and as suspended particles of silicon dioxide.

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

2.2 Time and area

Monitoring of silicate 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.

For determination of silicate, 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.

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

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.

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

2.3.3 Sample handling and analysis

For general requirements for sampling, preservation, handling, transport and storage of water samples, see EN ISO 5667-3.
Samples should be kept refrigerated and protected from light, and should not be stored for longer than 12 hours prior to analysis.

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 or colour.

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

Unnecessary handling of samples should be avoided to prevent contamination.

If samples need to be stored for longer than 12 hours freezing is the suggested preservative method. Prepare samples for freezing by filtering as described above. In temperatures between -18 and -20°C, samples are stable for several weeks (temperature should be maintained within the specified interval, and recorded with a digital data logger, e.g. Testo 174).

Freezing of samples has been known to induce polymerization of dissolved silicate. Allow sufficient time for thawing (24 hours in room temperature) to allow depolymerization of silicate.

Quality of deionized water used in the laboratory needs to be monitored, since silicate ions are among the most common ions to escape through purification steps. The efficiency of water purifiers is usually monitored through measurements of water conductivity, but since silicate ions have low specific conductivity, contamination can go unnoticed.

Avoid use of glass containers for samples, standards or reagents.

Colorimetric methods for determination of silicate are described by Hansen and Koroleff in Grasshoff et al (1999).

ISO 16264:2002 (Water quality. Determination of soluble silicates by flow analysis (FIA and CFA) and photometric detection)

2.4 Data analysis

No conversions or corrections of data are necessary.

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.

Methods for preservation must be validated since results can be affected by biological activity, seasonal cycle, salinity or other matrix effects.

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.

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. 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