Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature Conservation

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Document title	Determination of silicate – 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 silicate 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 silicate 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 silicate.

Draft guidelines for determination of silicate

Background

Introduction

Silicate is introduced to the Baltic Sea as a result of natural geological processes, as opposed to nitrogen and phosporus, 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.

Purpose and aims

Purpose and aims of monitoring of silicate are identical to monitoring of nutrients.

Monitoring methods

Monitoring features

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

Water samples are collected from discrete depths and analyzed. Well established wet chemistry methods for determination of silicate are available.

Time and area

Monitoring should be carried out in the entire Baltic Sea area. Winter pool of nutrients must be assessed.

Monitoring procedure

Monitoring strategy

Methods for determination need to include all biologically relevant species of silica. Colorimetric method described by Hansen and Koroleff (Grasshoff et al 1999) are considered to be sufficient.

Sampling methods and equipment

Samples can be 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.

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.

Freezing of samples has been known to induce polymerization of dissolved silicate. Allow sufficient time for thawing (48 h in refrigerator, or 24 h 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).

Data analysis

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.

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.

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-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.

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.

Contacts and references

Contact persons

Johan Håkansson, SMHI

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 Kand 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 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-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.