Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature Conservation

Tallinn, Estonia, 7-11 November, 2016

STATE & CONSERVATION 5-2016

Document title	Determination of phosphate – proposed monitoring guidelines
Code	2MA-11
Category	DEC
Agenda Item	2MA – Revision of HELCOM monitoring
Submission date	14.10.2016
Submitted by	Sweden

Background

HELCOM guidelines for hydrography and hydrochemistry are currently being revised. Lead Country Sweden submits proposed guidelines for determination of phosphate 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 phosphate 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 phosphate.

Draft guidelines for determination of phosphate

1 Background

1.1 Introduction

Phosphate is in many cases in the Baltic Sea the limiting factor for phytoplankton growth. Monitoring of phosphate levels is essential for evaluation of the effects of eutrophication.

1.2 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 phosphorus is listed as a HELCOM Core indicator: http://www.helcom.fi/baltic-sea-trends/indicators/phosphorus-dip

2 Monitoring methods

2.1 Monitoring features

Water samples are collected from discrete depths, and analyzed. Well established wet chemistry methods are available.

2.2 Time and area

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

2.3 Monitoring procedure

2.3.1 Monitoring strategy

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

2.3.2 Sampling methods and equipment

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

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

2.3.3 Sample handling and analysis

Samples should be kept refrigerated and protected from light, and should not be stored for longer than 6 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 must be stored for longer times, freezing will increase shelf life of samples. Samples should be filtered as described above before freezing, and frozen as rapidly as possible. In temperatures below -20°C, samples are stable for several weeks.

Acidification with sulfuric acid is often recommended in standard methods for water analysis, but this procedure is not suitable for marine waters. Addition of acid will dissolve and release phosphate from biological material present in samples.

Phosphate free detergents must be used for all laboratory equipment.

Avoid unnecessary manipulation of samples to prevent contamination.

2.4 Data analysis

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 determination of nutrients should have established a quality management system according to 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 and SYKE. More proficiency testing schemes are listed at www.eptis.bam.de.

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.

5 Contacts and references

5.1 Contact persons

Johan Håkansson, SMHI

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 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 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