Baltic Marine Environment Protection Commission

Working Group on the State of the Environment and Nature Conservation

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Document title	Determination of total phosphorus – 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 total phosphorus 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 total phosphorus 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 total phosphorus.

Draft guidelines for determination of total phosphorus

Background

Introduction

While determination of dissolved phosphate gives information on the bioavailable pool of phosphorus, an assessment of the total amount of phosphorus is also essential.

Total phosphorus includes all organic and inorganic forms of phosphorus present in seawater, particulate as well as dissolved. The dissolved organic phosphorus is also partly bioavailable, mainly when phosphate is exhausted. Also the particulate fraction can be used in part.

Purpose and aims

Monitoring of nutrients is carried out to identify and quantify the amount of 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

Monitoring methods

Monitoring features

Water samples are collected from discrete depths and analyzed.

Samples are treated with an oxidizing agent to transfer all phosphorus compounds to phosphate. Previously pressure cookers and autoclaves were use, now microwave ovens are usually preferable. Well established wet chemistry methods for determination of phosphate 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

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

Sampling methods 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. Collection from ferrybox (on research vessel, or ship of opportunity) is also possible.

Sample handling and analysis

Samples should be kept refrigerated and protected from light.

Avoid unnecessary manipulation of samples to prevent contamination.

Freezing is recommended if samples have to be stored more than 12 hours before pretreatment. Transfer the aliquot required to analyze total phosphorus into Teflon flasks. Samples are stored at -18°C.

Phosphate free detergents must be used for all laboratory equipment.

Methods for sample pretreatment (a digestion step where organic and inorganic phosphor compounds are oxidized to phosphate) as well as colorimetric determination of phosphate are described by Hansen and Koroleff in Grasshoff (1999).

For determination of total phosphorus contents by flow analysis (FIA and CFA) see EN ISO 15681-1 and 15681-2.

Interferences

In high saline waters, release of chlorine gas during the digestion step will interfere with phosphate determination.

High levels of oxygen-consuming material (sulphide, or organic material) will consume the added oxidizing agent, and limit the ability to oxidize all organic phosphor compounds to phosphate. Interferences must be removed prior to oxidation, by pre-oxidation of sulfide, or adjusting sample to oxidizing reagent ratio.

In presence of iron, there is a risk of precipitation of phosphate as iron-(III)-phosphate during oxidation. Any precipitated phosphate must be re-dissolved before determination.

Data analysis

Interferences mentioned in 2.3.3.1 will result in an underestimation of total phosphorus. Phosphate levels slightly higher than total phosphorus indicate interferences during sample pretreatment, and that total phosphorus results are unreliable.

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 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

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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

K Grasshoff, K Kremling and M Erhardt
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 15681-1*: Water quality - Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) - Part 1: Method by flow injection analysis (FIA)

EN ISO 15681-2*: Water quality - Determination of orthophosphate and total phosphorus contents by flow analysis (FIA and CFA) - Part 2: Method by continuous flow analysis (CFA)

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. 149 pp, ISBN 87-7482-021-4.

Wurl O (ed)
Practical Guidelines for the Analysis of Seawater
CRC Press 2009

ISBN 978-1-4200-7306-5

Ichinose N, Kanai H and Nakamura K
A problem in the spectrophotometric determination of dissolved total phosphorus in brackish anoxic waters
Analytica Chimica Acta, 156 (1984) pp 345-349