Guidelines for sampling and 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 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 phosphorus‘. The indicator description, including its monitoring requirements, is given in the HELCOM core indicator web site: http://helcom.fi/baltic-sea-trends/indicators/phosphorus-dip.

2 Monitoring methods

2.1 Monitoring features

Phosphate 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 phosphate 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.

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

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 fibre 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 between -18 – -20°C, samples are stable for up to four months (temperature should be maintained within the specified interval, and recorded with a digital data logger, e.g. Testo 174, in particular if samples are also used to determine silicate). Before determination if phosphate, samples should be allowed to defrost slowly, preferably overnight, in darkness (experiences from the Laboratory of BSH, Germany).

Acidification with sulphuric 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.

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 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 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 and 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 regularly at 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 phosphate and total phosphorus).

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 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