Guidelines for sampling and determination of pH in seawater

1 Background

1.1 Introduction

Since ocean acidification is a growing concern, monitoring of pH is necessary for studies of acidification and its effects on the carbonate buffer system. As many important biological processes are likely to be affected by rapid changes in pH, it is important to include accurate determination of pH among monitoring parameters.

pH is operationally defined, and a number of pH scales are used in environmental monitoring. The NBS (National Bureau of Standards) scale is suitable for waters of low ionic strength, and used for freshwater monitoring. The total hydrogen ion scale is often used for pH determinations in oceanic waters. The salinity gradient from the Bothnian Bay to Skagerrak, or from surface to deep water in the Baltic Proper, makes it difficult to select a pH scale that would be suitable for the entire Baltic area.

pH is also used in marine environmental monitoring as a co-factor in measurements of primary production.

1.2 Purpose and aims

The aim of monitoring is to identify spatial variations and temporal trends in pH.

2 Monitoring methods

2.1 Monitoring features

2.2 Time and area

Monitoring covers the entire Baltic area, and is performed throughout the whole year.

2.3 Monitoring procedure

2.3.1 Monitoring strategy

Two different principles are available, based on potentiometric and spectrophotometric detection. Potentiometric detection has the advantages of being fast and simple, and requires no advanced or expensive equipment. Buffers used for calibration should ideally have an ionic strength matching that of the samples, which is challenging when an area with a large salinity gradient is monitored. A number of pH meters, electrodes and buffers are commercially available.

Spectrophotometric detection is more accurate, has a higher precision, but requires expensive equipment. It is widely used in measurements under oceanic conditions, but less in estuarine waters. Since commercial applications for the spectrophotometric methods are not widely used; users must assemble instruments and software for data processing. Methods based on spectrophotometric detection are therefore not yet recommended for monitoring purposes.

pH is measured using a glass/combined electrode. The NBS pH scale should be used (although not ideal, the NBS scale has to this day been considered to be the best option for the wide range of salinity in the monitored area). Temperature is measured and recorded both during pH measurement and at sampling depth.

Water samples are collected from discrete depths, and analysed. Samples can be stored a limited time 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.

2.3.2 Sampling method(s) and equipment

Subsamples for pH should be drawn from sampler bottles as early as possible (after samples for oxygen and hydrogen sulfide, but before samples for nutrients and salinity) to avoid gas exchange between water and air.

Samples should be collected in gas-tight bottles. Bottles should be rinsed thoroughly with sample water before filling. Bottles are filled with a laminar flow of sample water, allowing 2-3 bottle volumes to overflow before capping. Bottles should be completely filled, leaving no headspace. Avoid trapping bubbles of air when capping bottles.

Samples should preferably be analysed as soon as possible directly after sampling.

2.3.3 Sample handling and analysis

Determination of pH using a glass electrode is described in ISO 10523.

Temperature must be monitored and controlled during calibration of instrument and analysis, preferably by use of a tempered water bath. Make sure temperature of buffers and samples is constant (±1°C) during the process. To maintain constant temperature, select a bath temperature slightly above ambient temperature (for normal room temperature, set bath temperature to 25°C – in a cooler environment 20°C may have to be used). pH analysis can also be made in + 15C in a cooling bath which has been shown to produce comparable results.

pH meter should be calibrated daily when in use. Follow manufacturer's instructions for a 2-point calibration (pH 7 and pH 9 are recommended). Use NBS buffers for calibration. Observe expiry dates of buffers.

Rinse electrode and temperature probe with deionized water and wipe between buffers/samples.

Allow electrode to equilibrate in sample water for 15 minutes before first measurement. Make sure equilibrium is reached for each sample before recording a reading.

Open-cell measurements allow gas exchange between sample and air during the time of measurements. Closed-cell measurements eliminate the interferences.

Follow manufacturer's instructions for handling and storage of electrodes. Electrodes may require cleaning and conditioning when exposed to samples from intense plankton blooms. Anoxic water containing high concentration of hydrogen sulfide may shorten the life of electrodes.

2.4 Data analysis

A correction for *in situ* pH (Gieskes 1969) is sometimes applied, but the correction is not determined for Baltic Sea conditions. A better option is to report measured pH, temperature from pH measurement and *in situ* temperature.

3 Data reporting and storage

pH values from potentiometric detection should be reported with two decimals. Temperature from measurement and sampling depth should also be reported.

Information on which pH scale is used must be included in metadata.

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 pH should have established a quality management system according to EN ISO/IEC 17025.

Data for samples for estimation of measurement uncertainty (repeated measurements from a sample, multiple subsamples from different samplers closed at same depth).

An internal reference material (IRM) should be analysed daily.

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 pH in environmental waters are provided by e.g. 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, IRM, and, if available, data from proficiency testings and CRM.

Collected data should be checked for consistency between sampled variables (e.g. total alkalinity and pH).

5 Contacts and references

5.1 Contact persons

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5.2 References

Gieskes J M 1969. Effects of temperature on the pH of seawater. Limnology and Oceanography Vol 14 Issue 5, p 679-685

Wedborg M, Turner D R, Andersson L G and Dyrssen D 1999. Determination of pH. Chapter 7, p 109-128 in Grasshoff K, Kremling K and Erhardt M (ed). *Methods of Seawater Analysis* 3rd ed. Wiley-VCH. ISBN 3-527-29589-5

ISO 10523*: Water quality – Determination of pH

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

Carter B R, Radich J A, Doyle H L and Dickson A G 2013

An automated system for spectrophotometric seawater pH measurements. *Limnology and Oceanography*: Methods 11, p 16-27

Hammer K, Schneider B, Kuliński K and Schulz-Bull D E 2014. Precision and accuracy of spectrophotometric pH measurements at environmental conditions in the Baltic Sea. *Estuarine, Coastal and Shelf Science* 146 p 24-32

Dickson A G, Sabine C L, Christian J R (ed) 2007. Guide to best practices for ocean CO2 measurements. PICES Special Publication 3. IOCCP Report No 8