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Background

HELCOM guidelines for hydrography and hydrochemistry are currently being revised. In accordance with STATE & CONSERVATION 2-2015 (para 2MA.3), Lead Country Sweden submits draft guidelines for determination of pH in seawater in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. Measurements of pH are currently described in Annex B-14 in the Manual for marine monitoring in the COMBINE program.

The draft for new guidelines includes updates on procedure, and introduces determinations based on spectrophotometric measurements. This new principle for analysis introduces the use of a pH scale new to monitoring in the Baltic area.

Action requested

The meeting is invited to

- consider and amend as needed the draft guidelines for determination of pH.

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. Commercial applications for the spectrophotometric methods have not yet been developed; users must assemble instruments and software for data processing.

2.3.1.1 Potentiometric determination

pH is measured using a glass/combined electrode. The NBS pH scale should be used. Temperature is measured and recorded both during pH measurement and at sampling depth.

2.3.1.2 Spectrophotometric determination

pH is determined by spectrophotometric measurement using an indicator dye (m-cresol purple). The total hydrogen ion scale is used. The indicator used must be well characterized; dissociation and extinction coefficients have to be determined for the range of temperature and salinity in the monitored area.

2.3.2 Sampling method 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 analyzed as soon as possible after sampling. Preservation by poisoning samples with mercury chloride keeps samples stabilized for a limited time.

2.3.3 Sample handling and analysis

2.3.3.1 Potentiometric measurement

Temperature must be monitored and controlled during calibration of instrument and analysis, preferably by use of a tempered water bath. Make sure temperature of calibrants and samples is constant ($\pm 1^\circ\text{C}$) 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 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 calibrants/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.

2.3.3.2 Spectrophotometric measurement

A method for spectrophotometric pH measurements is described by Hammer et al (2014).

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. pH values from spectrophotometric detection should be reported with three 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

Collect and analyze 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 analyzed daily.

4.1.1 Potentiometric measurement

Use a calibrated temperature probe with the pH electrode.

Make sure emf value of electrode for each calibrant is within range recommended by manufacturer.

4.1.2 Spectrophotometric method

Use a calibrated temperature probe to monitor temperature during measurements.

4.2 Quality control of data and reporting

Measurement uncertainty should be estimated using ISO 11352:2012. Estimation should be based on within-laboratory reproducibility, IRM, and, if available, data from proficiency testings and CRM.

5 Contacts and references

5.1 Contact persons

Kristin Andreasson, SMHI

Johan Håkansson, SMHI

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

Hammer K, Schneider B, Kuliński K and Schulz-Bull D E

Precision and accuracy of spectrophotometric pH measurements at environmental conditions in the Baltic Sea

Estuarine, Coastal and Shelf Science 146 p 24-32

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

Water quality – Determination of pH

ISO 10523:2008

Water quality – Estimation of measurement uncertainty based on validation and quality control data

ISO 11352:2012

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

Dickson A G, Sabine C L, Christian J R (ed) 2007

Guide to best practices for ocean CO₂ measurements

PICES Special Publication 3

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