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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 total alkalinity in the HELCOM area as a contribution to the ongoing revision of HELCOM monitoring guidelines. Measurements of alkalinity are currently described in Annex B-15 in Manual for marine monitoring in the COMBINE program.

The draft for new guidelines includes updates on procedure, and stresses the importance of monitoring of alkalinity, which has not been indicated in the monitoring programme on hydrochemistry in the HELCOM Monitoring Manual.

Action requested

The meeting is invited to

- consider including total alkalinity in the Water column chemical characteristics subprogramme of the HELCOM Monitoring Manual,
- consider and amend as needed the draft guidelines for determination of total alkalinity.

Determination of total alkalinity

1 Background

1.1 Introduction

Increasing atmospheric levels of carbon dioxide raise the need for monitoring how the carbonate buffer system in seawater is affected. As more carbon dioxide is dissolved in seawater, biological and chemical processes are likely to be affected.

Although not listed among HELCOM Core Indicators, alkalinity must be monitored to provide information of changes in the carbonate buffer system induced by carbon dioxide emissions.

Total alkalinity and pH are also monitored as co-factors for primary production measurements.

1.2 Purpose and aims

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

2 Monitoring methods

2.1 Monitoring features

Total alkalinity (A_T) is defined as amount of protons required to neutralize proton acceptors in 1 kg of seawater. For a full definition and an overview of contributing ion species, see Dickson (1981).

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

When studies of the carbonate buffer system are performed, four variables are considered: total alkalinity (A_T), pH, dissolved inorganic carbon (DIC) and partial pressure of carbon dioxide (pCO_2).

Theoretically, when two of these components are accurately determined, the remaining two can be calculated. These calculations, while valid for oceanic water, does not take into account contributions from dissolved organic material. The conditions in the Baltic Sea with relatively high levels of humic matter and other dissolved organic components are more complex (Kuliński *et al* 2014, Ulfsbo *et al* 2015). A calculated A_T value is lower than a measured sample due to the conditions in the Baltic Sea

Measurements of DIC would provide good data for monitoring purposes, but demands expensive and complex equipment.

While not ideal, A_T is still a relevant parameter for monitoring purposes. Alkalinity should be determined by potentiometric titration, with endpoint determination or endpoint evaluation.

2.3.2 Sampling method and equipment

Samples should be collected into Pyrex glass bottles with gas-tight stoppers. Bottles should be rinsed with sample water before filling. Leave a headspace of about 1% of the total volume, just to allow room for thermal expansion without trapping excessive air in the bottle. Ground-in stoppers sealed with grease are suitable when samples have to be stored before analysis. If grease is used to seal sample bottles, take care not to transfer any of it to the equipment used for titration. Store bottles in upright position, refrigerated and protected from light.

2.3.3 Sample handling and analysis

2.3.3.1 Sample handling

Samples can be stored for up to two weeks in gas tight bottles as described above. For long-time storage, addition of mercury(II) chloride is necessary to increase stability of samples. However, health implications and environmental regulations make it necessary to use this procedure with extreme care.

2.3.3.2 Analytical procedure

A known amount of sample is titrated with a solution of hydrochloric acid until the equivalence point can be calculated. Titration procedure is monitored with a pH glass electrode. Titration is continued until a final pH of approximately 3.0 for a complete depletion of the carbonate buffer system.

pH meter should be calibrated daily when in use. Follow manufacturer's instructions for a 2-point calibration (pH 4 and pH 7 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.

In a controlled laboratory environment, an analytical balance is used for determination of sample size. If the analytical procedure is performed on board a vessel during a sampling cruise, it is better to use a volumetric method. Density of the sample water is calculated from temperature and salinity.

Automated burettes are commercially available, as well as software for data collection and processing. Hydrochloric acid, 0.01 – 0.05M is used for the titration. The titer of the hydrochloric acid needs to be correctly determined; ampoules of hydrochloric acid with certified concentration are commercially available.

2.4 Data analysis

When density of seawater is used for calculations, equation of state of seawater (Millero and Poisson1981) should be used.

3 Data reporting and storage

Data should be reported as $\mu\text{mol kg}^{-1}$. 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).

Equipment used (analytical balance, pH electrode, thermometer probe) must be calibrated and their accuracy monitored.

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

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

A certified reference material (CRM) is provided by Scripps Institute of Oceanography of the University of California, San Diego.

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

Anna Willstrand Wranne, SMHI

Johan Håkansson, SMHI

5.2 References

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An exact definition of total alkalinity and a procedure for estimation of total alkalinity and total inorganic carbon from titration data
Deep Sea Research Vol 28A p 609-623

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Deep Sea Research Vol 44 p 2031-2044

Millero F. J. and Poisson A 1981
International one-atmosphere equation of state of seawater
Deep Sea Research Vol 28, p 625–629

Water quality – Estimation of measurement uncertainty based on validation and quality control data
ISO 11352:2012

5.3 Additional literature

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The influence of dissolved organic matter on the acid–base system of the Baltic Sea
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