BONUS PINBAL

Development of a spectrophotometric **p**H-measurement system for monitor**ing** in the **Bal**tic Sea

Summary of the Final Report

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Project goals and results envisaged at the beginning of the project

Within BONUS PINBAL, a consortium of the Leibniz Institute for Baltic Sea Research Warnemünde (IOW), the German Kongsberg Maritime Contros GmbH, Kiel (CONTROS, formerly CONTROS Systems & Solutions GmbH), the University of Gothenburg (UGOT) and the Institute of Oceanology of the Polish Academy of Sciences, Sopot (IO PAN) cooperatively fulfilled the necessary fundamental chemical work, system/software design and field testing to realize a prototype of a spectrophotometric pH-measurement system for underway measurements from research vessels and ships of opportunity, as well as for the pH-determination of discrete samples. Special emphasis was placed on the identification of the measurable pH range and the determination of the effects of potential perturbations typical for the Baltic or other brackish water systems (salinity range, potential interference with hydrogen sulphide or organic material). The project aimed at the development of a robust, long-term stable and in particular traceable (i.e. open to recalculation if any changes to the indicator parameters would occur) method for the determination of pH in the Baltic to meet the requirements of the HELCOM Baltic Sea Action Plan (BSAP) and the EU Marine Strategy Framework Directive (MSFD). In a broader perspective, BONUS PINBAL is regarded as a major step towards the vision of a full carbon system monitoring in the Baltic Sea, providing a valuable state-of-the-art approach for the assessment of acidification as well as eutrophication.

Synthesis of the main results achieved during the project and its implications

Within BONUS PINBAL, some of the major uncertainties and unknowns with respect to using the spectrophotometric pH-measurement technique in brackish waters like the Baltic Sea have been considerably reduced or resolved, and a prototype of a spectrophotometric pH measurement system for the needs of pH-monitoring in the Baltic Sea has been developed.

To better constrain the potential for trends of seawater pH in the Baltic Sea, an assessment of all available alkalinity data for the entire Baltic has revealed that over the last 20 years, an increase of alkalinity has considerably counterbalanced the potential for coastal acidification, caused by the uptake of anthropogenic CO_2 from the atmosphere.

Potential limitations of spectrophotometric pH-determination due to the presence of high loads of organic material and/or hydrogen sulphide have been investigated and shown not to hamper application of the method in Baltic Sea waters. The perturbation of a sample's pH by addition of the indicator dye has been addressed experimentally and theoretically, resulting in improved strategies towards extrapolation to the undisturbed pH value of the sample, which has been implemented in the design of the system under development. Thorough error assessment has documented that the method is applicable over the vast majority of conditions encountered in the Baltic Sea. A collaboration between the Physikalisch-Technische Bundesanstalt (PTB) and IOW, which developed over the course of the project, seeks to extend the parameterization of the indicator dye mCP over the salinity range 5-20 (+35) and an extended temperature range (5-35°C), a fundamental work expected to be published within the next 12 months.

A close-to-market prototype of a pH measurement system for application in the widest range of conditions encountered in the Baltic Sea has been developed, with strong emphasis on the needs for an instrument allowing a long-term traceable, accurate and precise monitoring of pH in the Baltic Sea. The system determines pH by injecting a pH-sensitive dye into a continuous sample stream (FIA approach) and allows for the measurement of samples from a continuous water flow, as well as for discrete sample analysis. Market launch of the instrument is planned within the next year (Spring 2018).

Work carried out during the project

Structure

BONUS PINBAL was organized within five interacting work packages (WPs). WP1 assured the organization, management, and dissemination of the project. The main objective of WP2 was the systematic execution of chemical experiments needed for the application of the spectrophotometric determination of pH using m-cresol purple (mCP) over the widest possible range of conditions for the Baltic. WP3 was designed to derive model-based perturbations parameterizations caused by the addition of the indicator dye (mCP), as well as to theoretically address the impact of sulfidic waters and the total error of the method. WP 4 comprised the entire process of the experimental research related to the instrument prototype development including the realization of different stepwise-improved field-going analyser versions. The main objective of WP5 was to test all aspects of the performance (accuracy, precision, robustness to field conditions, user-friendliness, etc.) of the instrumentation developed within WP4 in the range of environmental conditions encountered in the Baltic Sea. This included lab experiments, test runs on platforms allowing continuous measurements, as well as a joint field experiment during a seagoing expedition on RV Oceania.

Long-Term alkalinity trends in the Baltic and impact on CO_2-induced acidification

The call of the Marine Strategy Framework Directive for measurements that allow tracing the impact of ocean acidification was one of the motivations for BONUS PINBAL. In order to better understand the magnitude of this problem, all available data on alkalinity were compiled and investigated within BONUS PINBAL. For the last 20 years, trend analysis unambiguously shows an increase of alkalinity and thus buffer capacity of Baltic Sea surface waters, most pronounced in the northern and central basins, which helps to counterbalance marine acidification in the Baltic Sea.

Experimental and theoretical work on fundamental chemical processes

The spectrophotometric determination of pH is now state-of-the art for open ocean applications due to its unprecedented precision and accuracy. In brackish waters, like the Baltic Sea, several obstacles hamper the application so far:

- A larger pH range encountered in the different parts of the ecosystem;

- Large gradients in salinity and total alkalinity;
- Higher impact of the perturbation by addition of the indicator dye in low alkalinity samples;
- Potential interferences by high organic loads (including coloured organic material, CDOM) and hydrogen sulphide (H_2S), which could be caused by interaction with the indicator dye's spectral properties, or, in the case of CDOM, by self absorption.

Within the project, all of these issues were addressed.

The applicable pH range was theoretically addressed, performing a proper error analysis according to Gauss' law of error propagation. This law was applied to uncertainties associated to the absorption measurement, which control the decreasing precision at high and low pH (Fig. 1). The same approach was also applied to the propagation of uncertainty associated to other parameters that have to be assessed (salinity, temperature, extinction coefficients). The main finding with importance towards the instrument development – and use - is that the uncertainty cannot be represented by a single number, but shows a strong dependency on salinity, temperature, and the actual pH.

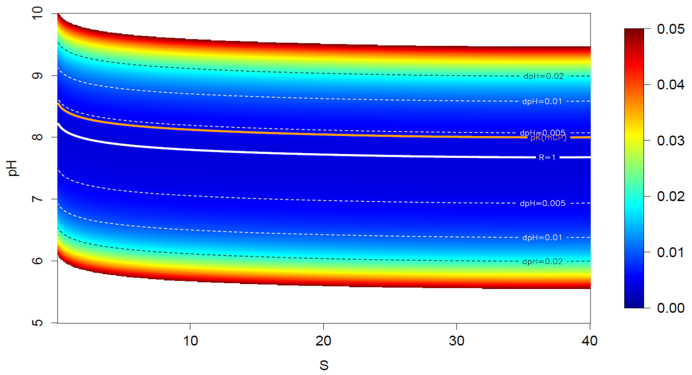


Figure 1: *pH precision that can be obtained by spectrophotometric pH measurements with m-cresol purple over a salinity range 0-40 and a pH range 5-10. The dashed lines represent isoprecision lines. The optimum conditions for spectrophotometric pH measurements correspond to an absorption ratio R = 1, which occurs at a pH value approximately 0.3 units below pK (mCP).*

Furthermore, the potential uncertainty of pH measurements performed at 25°C was assessed by a chemical speciation model for realistic conditions in the Gulf of Bothnia, the Gulf of Riga, and the Baltic Proper, in the pCO_2 range 100-600 µatm, reflecting the maximum range of the seasonal cycle of the carbonate system in surface waters in the Baltic Sea. These results show that where the sample pCO_2 is at atmospheric or supersaturated levels, significant uncertainties will be encountered only in the low salinity waters of the Gulf of Bothnia (and also in the Gulf of Finland). Strongly undersaturated samples present more of a problem, most particularly in the summer period where the water temperatures are high.

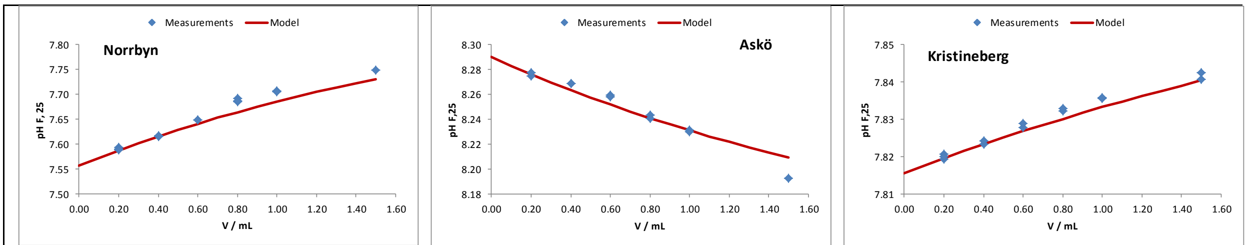
A comprehensive investigation of the impact of H_2S and CDOM on spectrophotometric pH measurements was performed, which were described in a manuscript currently under review. The main outcome of the study was:

- No impact on spectrophotometric pH measurements is expected by H_2S up to a concentration of 400 µmol kg^{-1}, which reflects high levels as reported from e.g. the Black Sea, far higher than what is typically encountered in the anoxic water bodies of the Baltic Sea.
- Natural DOM did not interfere with the spectrophotometric measurements at concentrations typical for oceanic environments and large estuarine systems.
- Strongly coloured river waters can cause spectral disturbance, resulting in calculated pH values that are up to several tenths of a pH unit too low. This result is most likely related to instrument-specific properties at high absorbances of the benchtop measurement system (with a 10 cm cuvette) rather than to interaction between DOM and the dye solution.
- Perturbations in strongly coloured samples can be reduced by using intense light sources, an absorption ratio at alternative wavelengths, a shorter cuvette length (e.g., 1cm cuvette as

applied in the instrument under development) or spectrophotometrically calibrated glass electrodes.

Oxidation of hydrogen sulphide results in proton release and thus pH decrease. This effect was addressed theoretically applying a kinetic model, using the data of Landsort Deep in winter 2014 as a realistic base case. The potential pH change depends both on the amount of sulphide present, and on the rate of oxidation, which has been shown to be dependent on the concentration of trace metals. As both oxygen invasion into the sample during measurement as well as the kinetics of oxidation will be instrument- and material-dependent, potential for gas transfer must be minimized, and the kinetics tested on the individual setting of the instrument. For the calculated case (25°C, oxygen saturation, 1µmol/L iron(II) and 40 µmol/L sulphide, the initial pH change was in the range of 0.002 pH units per minute.

The problem of perturbation of a sample's pH by addition of the indicator dye is by far more complex for measurements in brackish waters than in the open ocean, where variations in salinity and alkalinity are relatively small, and the buffer capacity is high due to the high alkalinity. Therefore, parameterization and extrapolation to zero indicator pH was tackled experimentally, theoretically, and considered in the instrumental design. For three contrasting waters of the Baltic sampled in Norrbyn, Askö, and, Kristineberg, pH measurements were performed using a series of well defined indicator volume additions. A speciation model was then developed which accurately reproduced the observed change in the measured pH (Fig. 2). Additional model runs were performed to specifically address the processes within the developed instrument prototype, which uses an injection flow through principle (see below). The theoretical approach thus allowed to scrutinize and optimize data fitting options such as the best fitting function and the fitting window used for the extrapolation to zero mCP concentration.



Norrbyn	Askö	Kristineberg

Figure 2: *Measured (dots) and modelled pH as a function of indicator addition for the three natural waters of the Baltic Sea covering a large salinity range, reported on the free pH scale.*

Extending the original work plan, TRIS pH buffer solutions in the salinity range 5-20 (+35) were characterized by Harned cell measurements in cooperation between the Physikalisch-Technische bundesanstalt (PTB), project partners IOW/UGOT, and under advice of Prof. A. Dickson (Scripps Institution of Oceanography, UCSD), These buffer solutions were used to determine the dissociation constant, pK, of the pH-indicator dye mCP by spectrophotometric measurements for the same S-range and temperature of 5-35°C. Finalization of this work is still ongoing

Field tests in support of system development

The main scope of the project was the development of a spectrophotometric pH measurement system for use in the Baltic Sea and other brackish water systems. A total of three prototypes with increasing maturity were constructed during the project. The prototypes were tested during field and lab studies to assess the performance and user-friendliness, directly supporting the further development of the instruments. Main field work included a test aboard the voluntary observing ship Finnmaid operated by Finnlines in April 2015, where the instrument was deployed in continuous mode in parallel to the pCO_2 underway system installed permanently on the ship. As both parameters are anti-correlated, the setting was perfect for a comparison of the newly developed pH-prototype with an established method for another parameter of the CO_2-system. Further field tests in 2015 comprised a 10 day expedition on RV Oceania in may 2015, including a long-term precision test and performance evaluation in the southern Baltic Sea, including the transect from Pomeranian

Bay to the mouth of the Odra River under a large range of salinity, alkalinity, and pCO_2 conditions, and a test at the Kristineberg field station in Sweden.

The main field test of two instruments set up to the technology of the second prototype took place on RV Oceania from November 14-20th, 2016, on a cruise entirely dedicated to BONUS PINBAL in the Gulf of Gdansk, the Szczecin Lagoon, the Pomeranian Bay and the coastal Baltic Sea waters in between. Valuable insights into the system's performance could be achieved through the availability of the two prototypes and the additional use of a benchtop spectrophotometric pH-measurement system for discrete samples provided by IOW. The report and analysis of the observations during the final field test guided further improvements, leading to the close-to-market prototype (version 3), the final hardware development of the project.

System description

The general principle of the instrument developed within BONUS PINBAL is the measurement of the pH value of a continuous sample stream through an injection of a concentrated indicator solution into the stream. The indicator injection leads to a concentration gradient of the dye in the sample water, which is needed for the subsequent detection and recording of the absorbance spectra at high frequency and decreasing dye concentration. These spectra are used for calculation of the pH value of the water sample. The starting point of the development was the scientific instrument and data processing described in Aßmann et al., Ocean Sciences, 7, 597 ff., 2011, and the know how from the development of an automated wet-chemical total alkalinity instrument by partner CONTROS.

The indicator is stored in user-friendly cartridges that allow for a fast and clean plug-and-play exchange of the reservoirs by the operator. The cartridges are placed within the system ensuring a stable temperature of the indicator solution. A second cartridge allows for a regular cleaning by flushing of the relevant parts such as the tubing and the optical path of the cuvette at defined intervals with diluted acid.

The instrument can be run on a continuous water supply as well as in a discrete sample mode. The measurement principle is identical in both cases, with a pre-set number of measurements foreseen in the discrete sample mode. In both cases, a dark and a blank spectrum is recorded before each injection of indicator dye into the sample water.

Figure 3: *Members of BONUS PINBAL on the final meeting in Warnemünde, with the latest version of the flow injection spectrophotometric pH measurement system in the centre .*

The prototype development has reached a high degree of maturity (Fig. 3) in terms of user-friendliness (touch screen, basic mission planner, different measurement routines), dye perturbation correction (optimized correction function), autonomy and interfacing (low maintenance while in operation, remote control via serial connection). The precision in the main pH working range for

Baltic Sea conditions (pH = 7…8.5) is within approx. ±0.002 pH units. The accuracy of the prototype (offset of 0.008 pH units compared to a separate reference system owned by IOW) is in the same order of magnitude as of the reference system itself, estimated to be approx. ±0.005 pH units (Carter et al., L&O Methods 11, 16-27, 2013). This performance results from several amendments made throughout the project and in particular in response to the final field experiment, addressing the time span between thermal equilibration, dye injection, and the measurement, as well as the range of dye concentrations used for the calculation of the pH of the measured solution.

Continuity plan for the future after the project has been completed

Evaluation of the experimental work on well-characterized TRIS buffer solutions at low salinities, and the proper characterization of the indicator dye at low salinities and over an extended temperature range will be continued and is expected to be finalized within one year. Some improvements and amendments of the instrument are planned before the market launch of the instrument envisaged for spring 2018, including the implementation of the new mCP characterization after its publication. Dissemination and protection of the new knowledge generated within BONUS PINBAL has been and will be further assured through publication in peer reviewed journals and filing of a patent, respectively. Further assessment of the instrument and start of its use for monitoring purposes in the Baltic Sea is envisaged within the Blue Baltic project BONUS INTEGRAL, which is currently under negotiation and expected to start July 1st, 2017. In this framework, a strong focus is on the introduction and promotion of new pH and carbon system monitoring strategies for the Baltic Sea towards HELCOM and national agencies in charge for the assessment of the Baltic Sea ecological state. The vision of BONUS PINBAL, and also BONUS INTEGRAL is to set the stage for a new start of carbon system monitoring to provide a valuable state-of-the-art approach for the assessment of acidification as well as eutrophication in the Baltic Sea.

Publications

Published

Müller, J.D., Schneider, B., Rehder, G., 2016. Long-term alkalinity trends in the Baltic Sea and their implications for CO_2-induced acidification. Limnol. Oceanogr. 61, 1984–2002. doi:10.1002/LNO.10349.

Submitted / under review:

Müller, J.D., Schneider, B., Rehder, G. (subm. To L&O Methods). Spectrophotometric pH measurements in the presence of dissolved organic matter (DOM) and hydrogen sulfide (H_2S).

Gallego-Urrea, J.A., Turner, D.R.(subm. To Mar Chem). pH Measurements in Estuarine and Brackish Water: Pitzer Model parameters for TRIS in Seawater and dissociation constants for m-cresol purple at 298.15K

Kuliński, K., Schneider, B., Szymczycha, B., and Stokowski, M. Structure and functioning of the acid-base system in the Baltic Sea, Earth Syst. Dynam. Discuss., doi:10.5194/esd-2017-39, in review, 2017.

For an update of publications arising from BONUS PINBAL, **please visit the project's web sites:**

https://www.bonusportal.org/projects/innovation_2014-2017/pinbal

https://www.io-warnemuende.de/pinbal-home.html

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