

BONUS PINBAL

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



Summary of the Second Annual Report

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Goals and expected results

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) will cooperatively fulfil 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 is 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 load of terrigenic organic material). The project aims 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).

Work performed since the last reporting period and main results achieved during the reporting period

A) Management

Frequent communication between the partners assured information and clarification at interfaces between the duties of different partners during the entire reporting year. The first annual report was submitted in time, and the minor changes requested were initiated **(Deliverable 1.2).** A scientific symposium on the acid-base system in the Baltic was organized by BONUS PINBAL and held in December, 2015. The occasion was used for an interim project meeting, which allowed for status analysis and planning of next steps, in particular with respect to technological implementations suggested for the next prototype version of the instrument.





B) Scientific and Technological progress

The scientific tasks within BONUS PINBAL are organized within four work packages (WP 2-5), all of which have been active within the second year of the project. Within WPs2&3 (Chemical parameter characterization, Theoretical evaluation of perturbations and uncertainties), additional experiments and theoretical studies addressing the uncertainty of the measurement were performed, with special emphasis on the perturbation of the pH by injection of the dye solution and possible ways to account for this effect, and on potential interferences of hydrogen sulphide (H₂S) and dissolved organic material (DOM) on the results of spectrophotometric pH-measurements. The submission of the **Deliverable Reports 2.2, 2.3, 3.1, 3.2, and 3.3** within the 2nd reporting period summarize this work.

The first prototype of the system under development was ready for testing in month 13 of the project (**Deliverable Report 4.2**), and after hands-on training for the scientists involved, was tested in the continuous operation mode during four field expeditions, most of them with simultaneous continuous measurement of pCO_2 . The majority of the field tests were successful, and measurement precision was already in the region the project is aiming for. A detailed summary of the results of the field tests in the continuous surface mode was compiled (**Deliverable Report 5.1**), and a list of suggested amendments and improvements on the hard- and software was created as the basis for the development of the 2nd prototype version of the instrument, due in month 25 of the project.

The identified lack of reference materials and pK-determination of the dye in the salinity range 5-20 lead to a cooperation with the Physikalisch-Technische Bundesanstalt, Germany, who are currently preparing the appropriate reference materials. This also initiated in the invitation of Prof. Andrew Dickson (SCRIPPS), one of the most renowned experts in the field, for the planning of the experiments needed to overcome this lack of basic indicator data.

A publication lead by Jens Müller (PhD student within BONUS PINBAL) was submitted, showing the trends of surface alkalinity in the Baltic over the last 100 years (main focus last 20 years), and discussing the effect on potential acidification due to rising atmospheric CO_2 -concentrations. The paper is currently in press.



Fig. 1: Left. "Mini-ocean used for spike experiments to detect cross-interference with H_2S and DOM; Right: Development of pH (upper panels) and pCO₂ (lower panels) during a field testing campaign on VOS Finnmaid, showing the effect of the onset of the productive period in April, 2015.

After the 2nd year, the project is perfectly on track and all deliverables are being met.

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