

PINBAL

Development of a spectrophotometric pH-measurement system for monitoring in the Baltic Sea



Summary of the First Annual Report

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PINBAL Objectives

Within PINBAL, a consortium of the Leibniz Institute for Baltic Sea Research Warnemünde (IOW), the German SME 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 terrigenous 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).

Achievements of the first year of the project

A) Management

The PINBAL Kick-Off meeting took place in June 26 at IOW, with representatives of all institutions present. All relevant positions for the project were filled by mid-July. The webpage of the project (**Deliverable Report 1.1 filed**) was launched in October. Frequent communication between the partners assured information and clarification at interfaces between the duties of different partners. Several scientific contacts were used or established to raise international awareness of the project and seek input from experienced scientists in the field. The first annual meeting took place in Sopot (hosted and organized by partner IO PAN) from March 24th to 25th, 2015.



B) Scientific and Technological progress

The scientific tasks within PINBAL are organized within four work packages (WP 2-5), all of which have already been active within the first year of the project.

Within WP2 (Chemical parameter characterization), an assessment of the applicable pH-range based on formal error propagation calculation was performed (Task 2.1, **Deliverable Report 2.1 filed**). First investigations of the salinity dependence of the absorption of the indicator dye (Task 2.2) have been performed. The consideration of the results led to the start of a cooperation with the PTB (Physikalisch-Technische Bundesanstalt, Germany) because of an identified need for certified NBS buffer standards at varying salinities. Initial experiments as well as calculations based on a Pitzer approach were performed towards Tasks 2.3 (Experimental determination of pH perturbation by indicator addition) and 3.1 (Calculation and parameterization of the effect of indicator addition on the measured pH-value) based on samples covering a wide S-range, the calculations performed within WP3 (Theoretical evaluation of perturbations and uncertainties). Within WP4 (System development), a thorough evaluation of available components for the spectrophotometric system was executed (Task 4.1, Assessment of available components and materials to provide a basis of the sensor in development, **Deliverable Report 4.1 filed**), and the first prototype was finalized in time, already allowing continuous operation with a precision of 0.002 pH units under optimal conditions. The system allows for continuous measurements, has a user-friendly dye-addition unit and a rudimentary operating software (Task 4.2, Prototype (version I) ready for field test, **Deliverable Report 4.2 filed** and system handed over for field test, see also Fig. 1).



Fig. 1: Left – first prototype of the spectrophotometric pH-measurement system; Middle – cartridge containing the dye solution; Right – picture of the field test with the first prototype developed within PINBAL in front, IOW's permanent pCO₂-measurement system in the back, and PINBAL PhD-student Jens Müller, operating the system, on the right.

Within WP5 (Lab and field testing of prototype instrumentation), fundamental work on the impact of organic carbon to the acid base system was performed, which is essential for the best possible field testing plan for the instrument. Moreover, a first two week long field test campaign on board of the ferry ship *Finnmaid* was executed, showing encouraging results and allowing a comparison with the continuous pCO₂-record measured simultaneously from the same water supply by IOW's permanent instrumentation on the vessel.

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