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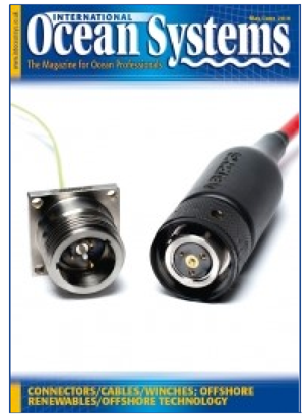

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Great advancement for pH monitoring in the Baltic Sea

"The optical pH measurement method newly adapted for brackish waters, including a prototype (the "Red Box'), was thoroughly tested - here in the engine room aboard the ferry 'Finnmaid'"

"The ferry 'Finnmaid', a voluntary observing ship with scientific instruments on board,

Researchers adapt optical pH measurement method for brackish waters

Is the Baltic Sea acidifying? To better observe possible acidification trends in brackish waters, Jens Daniel Müller, marine chemist at the Leibniz Institute for Baltic Sea Research Warnemünde (IOW), Germany, together with several partners, adapted the highly precise optical pH measurement technique, previously only applicable for the high salinity levels of the open ocean, for use in regions with low salinities. This has led to the development of a ready-to-use device from the sensor technology company Kongsberg Maritime Contros, Germany. The newly adapted method is highly suitable for routine applications in the field, for instance as part of the Helsinki Commission's (HELCOM) environmental monitoring of the Baltic Sea as well as for the pH monitoring of other coastal seas with low salinities. The work is a result of the EU and nationally co-funded project BONUS PINBAL.

Excessive anthropogenic CO_2 emissions are not only a problem for the global climate, but also for the oceans: carbon dioxide dissolves in seawater, forms carbonic acid and thereby releases hydrogen ions, which leads to acidification. Since the Industrial Revolution, the average pH of the oceans has dropped from 8.2 to around 8.1. Also known as "the other CO_2 problem", this pH decrease affects almost all biogeochemical processes in the ocean. Mussels, crustaceans and corals, for example, react very sensitively because the formation of their calcareous shells and skeletons is impeded in an acidifying environment.

Although scientists started to investigate ocean acidification about two decades ago, it remains difficult to follow the current dynamics of the phenomenon: long time series measurements in the open ocean show that the pH value decreases on average by about 0.002 units per year. To detect such small changes, highly accurate measurement methods are required. The optical pH measurement method was established as the de facto standard for this purpose. It is based on the addition of the dye m-Cresol purple to the water sample and its pH-dependent colour shift from purple to yellow. The colour can be determined very precisely with a photometer and converted into pH units depending on ambient salinity and temperature.

And what about the Baltic Sea? "We have analysed data from the last 20 years travels the route between Germany and Finland almost every two days. In 2019 it will be equipped with the optical pH measurement device CONTROS HydroFIA pH to provide precise pH data from the Baltic Sea in high spatial and temporal resolution ”

“ The CONTROS HydroFIA pH is a flow-through system for the automated determination of pH and is ideally suited for measurements in seawater or brackish water ”

and have not been able to detect a clear acidification trend – a rather remarkable result in view of the already proven acidification of the open ocean,” says IOW researcher Jens Müller, who has focused intensively on the CO_2 system of the Baltic Sea. There are several possible reasons for the observed lack of acidification; the marine chemist points out two as particularly important ones: 1) The data quality is inadequate with regard to measurement precision. 2) There is, in fact, no decreasing pH trend, as acidification is buffered by counteracting processes.

There are indeed processes in the Baltic Sea that counteract acidification, shown by extensive analyses of alkalinity, i.e. the acid binding capacity of seawater. Alkalinity has been increasing in the Baltic Sea since 1995, probably due to continental rock weathering, the products of which are washed into the semi-enclosed sea. How long alkalinity will continue to rise and buffer acidification, however, is unknown. “In order to understand what is happening in the Baltic Sea in terms of pH, it is important to rule out that the detection of acidification simply fails due to methodological shortcomings,” emphasises Müller. Currently, the routine determination of pH in Baltic Sea monitoring is based on glass electrode measurements on individual water samples. The measurement uncertainty of this method is too large for a reliable detection of acidification trends in environments like the Baltic Sea. Furthermore, Müller stresses that monitoring should be carried out with the highest possible temporal and spatial resolution, using the most accurate method available to ensure that the observation of such a key parameter is always up to date. Müller says: “We therefore have adapted the optical pH measurement method, which was previously only applicable at ocean salinities between 20 and 40, in such a way that it is ready for routine monitoring in brackish waters with a lower salinity of five to 20.”

Achieving this was the aim of the three-year EU project BONUS PINBAL (short for Development of a Spectrophotometric pH-measurement System for Monitoring in the Baltic Sea) headed by the IOW, which started in 2014. In a first step, Müller, in cooperation with Germany’s national metrological institute PTB (Physikalisch-Technische Bundesanstalt), traced optical pH measurements in buffered artificial seawater standards back to electrochemical pH measurements with Harned cells and systematically characterised the colour-shift behaviour of the indicator dye m-Cresol purple for low salinities. “With the aid of these data, we can now for the first time calibrate pH instruments for the low salinity range of the Baltic Sea and reliably convert the colour of the indicator dye into pH units,” he explains. Furthermore, the IOW scientist was able to experimentally rule out the possibility that hydrogen sulphide and larger amounts of dissolved organic material, both common in brackish waters, could interfere with the newly adapted method.

To round off the project and make the optical pH measurement method fit for routine use in the Baltic Sea and brackish water bodies in general, the BONUS PINBAL team – which, besides IOW researchers, included the sensor technology company Kongsberg Maritime Contros (KM Contros) and scientific partners from the University of Gothenburg in Sweden and the Institute of Oceanology of the Polish Academy of Sciences – developed, tested and characterised a field-ready device. The developments have now yielded a commercial product, providing a professional solution for various scientific applications as well as for any other monitoring purposes.

“The compact box contains everything you need for spectrophotometric pH measurements. It can be easily used on any research vessel for measurement of pH in discrete water samples as well as for continuous underway measurements. It can also be deployed autonomously on so-called voluntary observing ships,” says Peer Fietzek, manager science and research at KM Contros. Voluntary observing ships (VOS) are vessels that are not primarily used for research – such as freighters or ferries – but still carry instruments on board to collect scientific data.

“Nothing stands in the way of routinely using the adapted method for a much more precise, high-resolution and widespread pH monitoring in the Baltic Sea. We therefore are campaigning for it as an official new standard within the framework of HELCOM's environmental monitoring," concludes Gregor Rehder, head of the IOW working group Trace Gas Biogeochemistry and coordinator of the BONUS PINBAL project.

Further information on the BONUS PINBAL project can be found online at www.bonusportal.org/pinbal and www.io-warnemuende.de/pinbal-home.html.

Further questions and scientific exchange can be directed to Dr Jens D. Müller (jens.mueller@io-warnemuende.de) or Professor Gregor Rehder (gregor.rehder@io-warnemuende.de).

Dr Steffen Aßmann (steffen.assmann@km.kongsberg.com) or Peer Fietzek (peer.fietzek@km.kongsberg.com) can be contacted concerning the CONTROS HydroFIA pH and related application opportunities.

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