Towards Accurate, long-term traceable pH-measurements in the Baltic Sea

Rationale, Progress, and Vision of the BONUS PINBAL Project

Gregor Rehder, Jens D. Müller, Bernd Schneider, Leif Anderson, David Turner, Steffen Aßmann, Peer Fietzek, Frank Bastkowski, and Karol Kuliński

BONUS PINBAL

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

Within PINBAL, … we 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.*

Work Package	Task	Lead
WP1	Coordination, Communication, and Dissimination	IOW
WP2	Chemical Parameter Characterization	IOW
WP3	Theoretical Evaluation of Perturbations and Uncertainties	UGOT
WP4	Prototype and System Development	CONTROS
WP5	Lab and field testing of prototype instrumentation	IOPAN

Rationale

Requested indicator explicitly mentioned in the Marine Strategy Framework Directive (MSFD), Annex 3, Indicative list of characteristics, pressures, and impacts

„pH, pCO_2 profiles or equivalent information used to measure marine acidification“

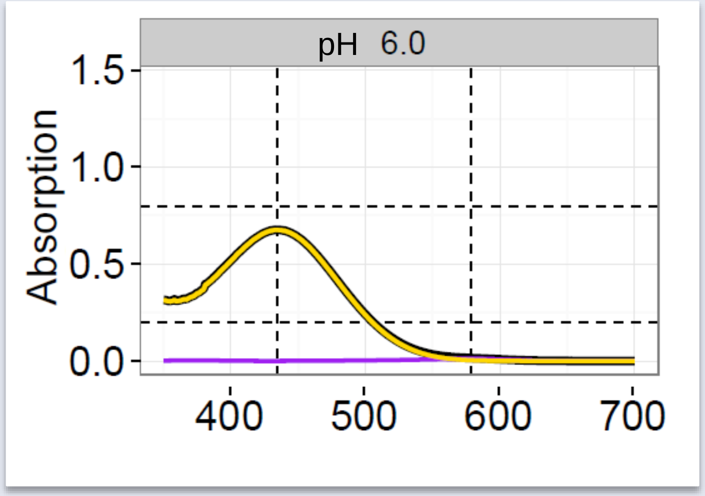
- **Different pH-scales**
- **Standards and calibration issues**
- **Long-term traceability**
- **Very high precision and accuracy needed**

?? **Why is that so difficult**

Litmus paper

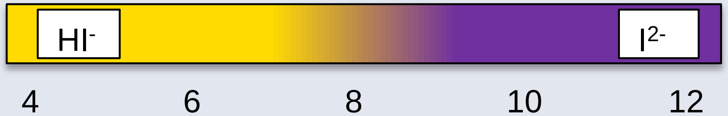
pH-electrode

Spectrophotometer



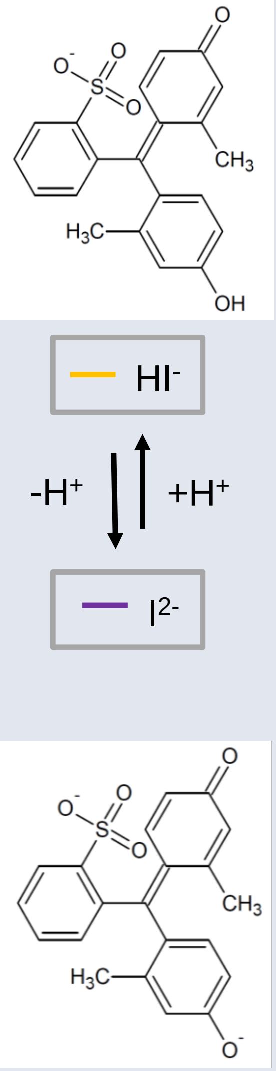
Spectrophotometric pH-measurement ???

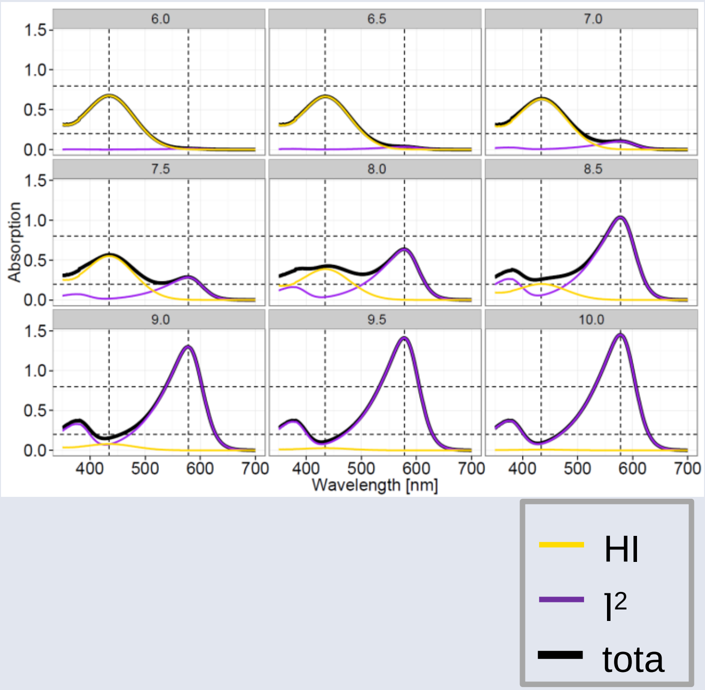
pH m-Cresol Purple (mCP)

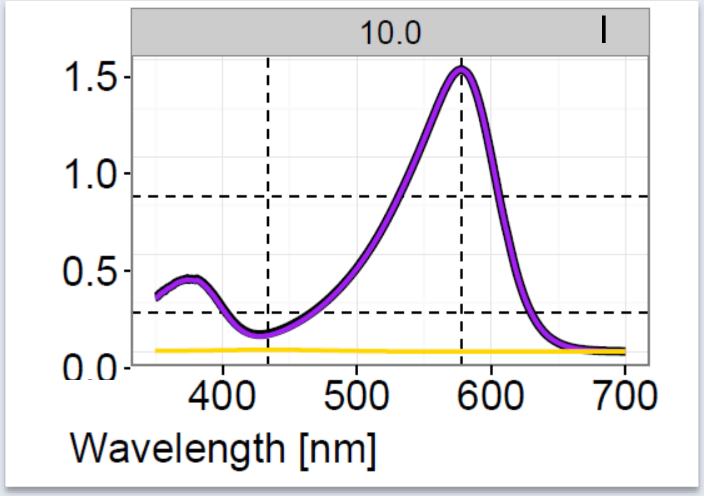


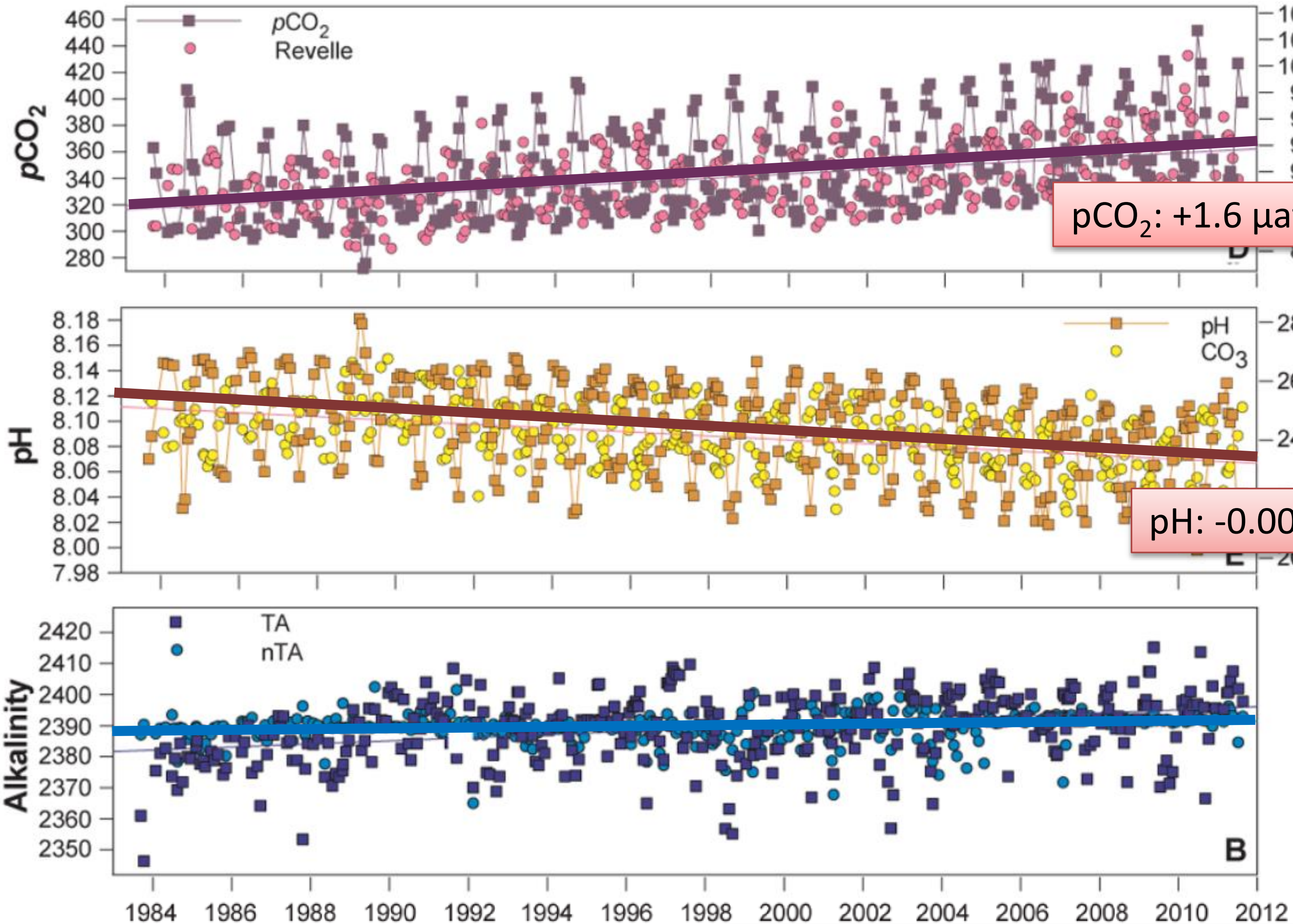
$$pH = pK(\mathrm{mCP}) + \log\left(\frac{\varepsilon_{434}(\mathrm{HI}^-) * R - \varepsilon_{578}(\mathrm{HI}^-)}{\varepsilon_{578}(\mathrm{I}^{2-}) - \varepsilon_{434}(\mathrm{I}^{2-}) * R}\right)$$

- R ensures long-term traceability
- pK and ε's need to be characterized









pCO_2: +1.6 µatm yr^{-1}

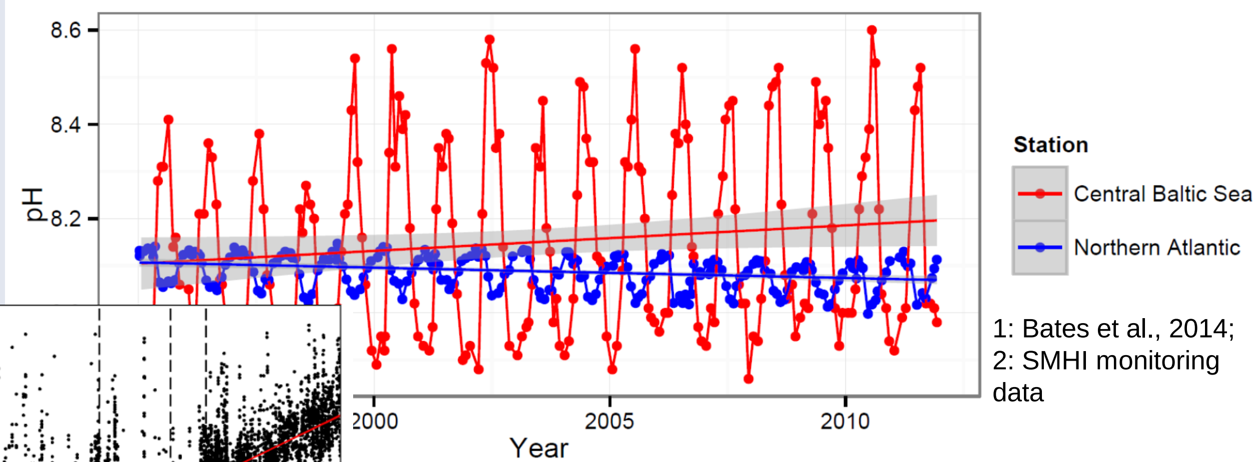
pH: -0.0016 yr^{-1}

AT: No significant trend

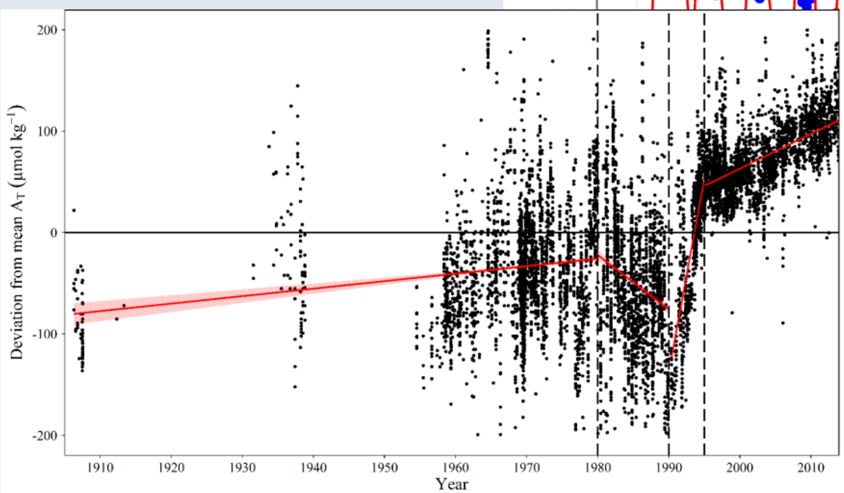
BATS time series, Bates et al., 2012

Situation for the Baltic Sea is far more complex

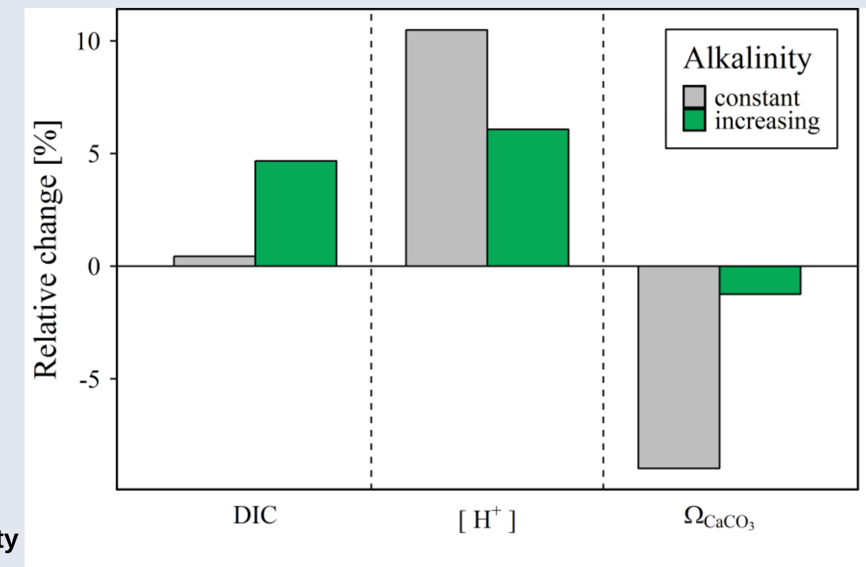
Larger dynamics, larger spatiotemporal variability



1: Bates et al., 2014;
2: SMHI monitoring data



... largely counterbalancing potential acidification, or change in calcite saturation



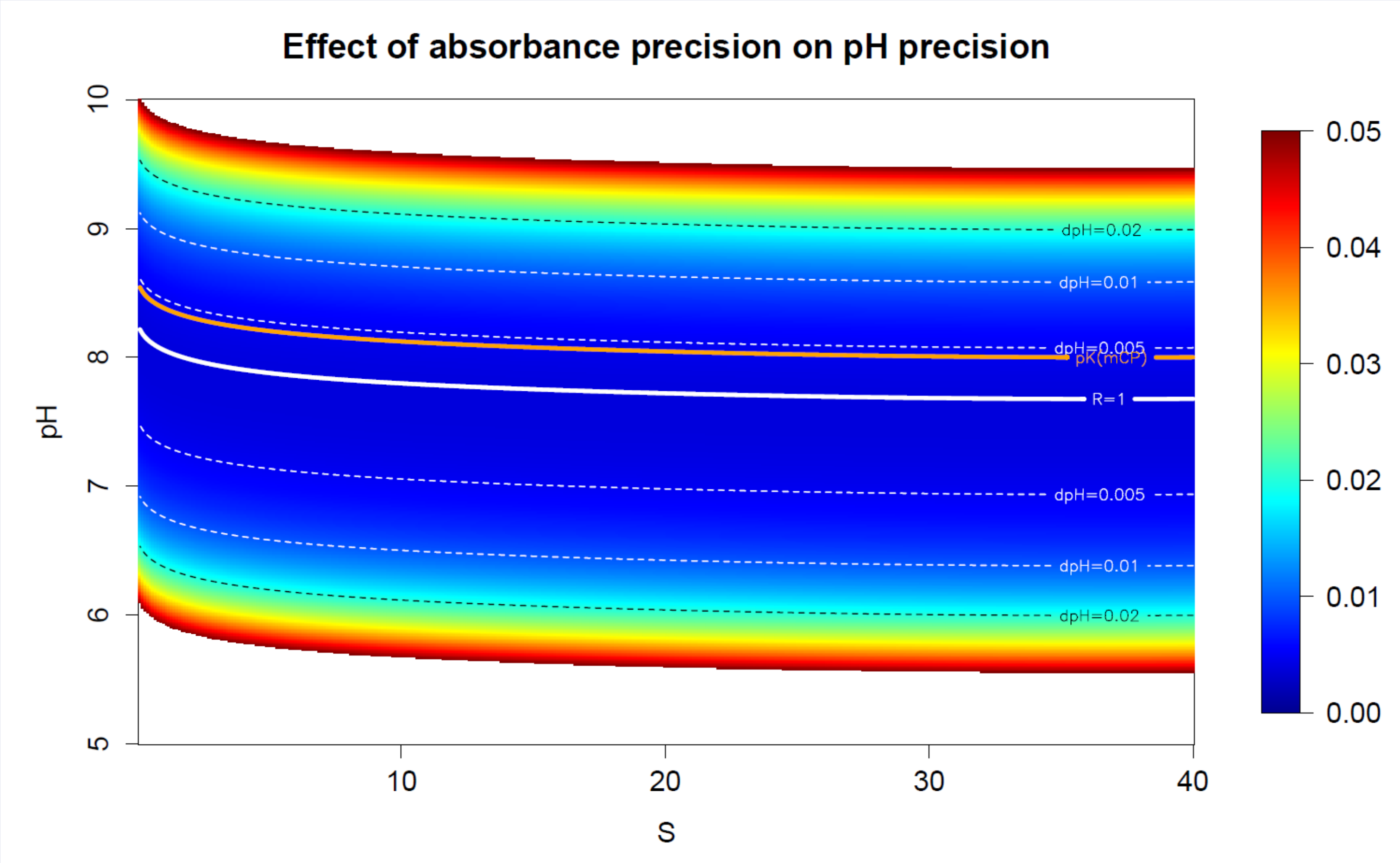
Müller, J. D., B. Schneider and G. Rehder (2016). Long-term alkalinity trends in the Baltic Sea and their implications for CO_2-induced acidification. Limnol. Oceanogr. 61: 1984-2002

Challenges of mCP-based pH measurements for the Baltic Sea (and other coastal systems)

- Extended pH range
- Interference of spectral properties by interaction with DOM or H_2S
- Perturbation of the acid-base balance (pH) by the dye
- Knowledge of $pK_{(mCP)}$ as f(T,S)

Challenges of mCP-based pH measurements for the Baltic Sea (and other coastal systems)

- **Extended pH range**

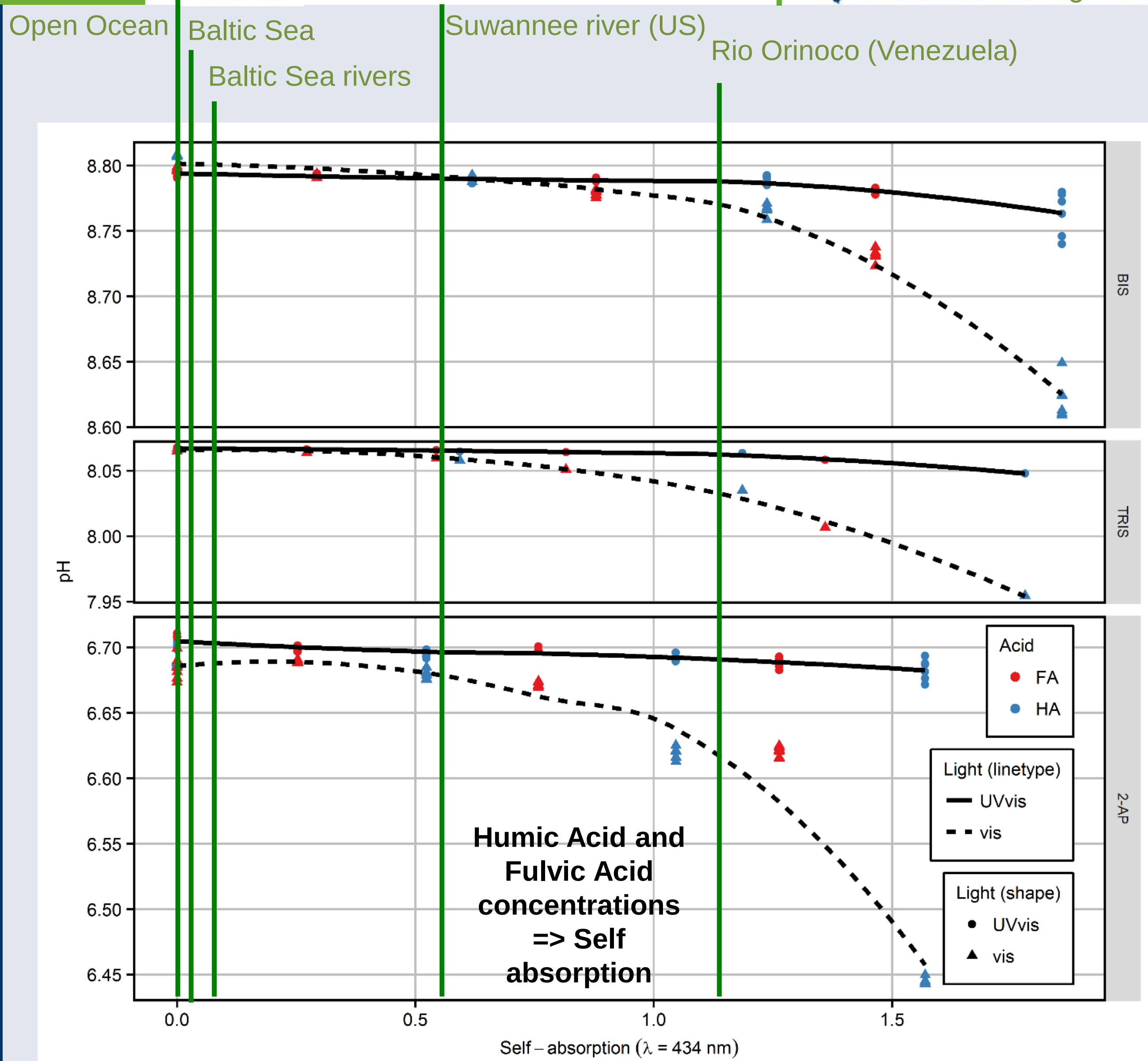


pK from Mosley, 2004 | Temperature: 298 K | Cuvette length: 10 cm | mCP concentration: 5 µM

Challenges of mCP-based pH measurements for the Baltic Sea (and other coastal systems)

- Extended pH range
- **Interference of spectral properties by interaction with CDOM or H_2S**
- Perturbation of the Acid-Base balance (pH) by the dye
- Knowledge of $pK_{(mCP)}$ as f(T,S)

Pore and ground waters



Nelson et al. (1998); Ferrari et al, (1996); Stedmon et al. (2000); Yacobi et al. (2003); Battin (1998)

No detectable perturbation by H_2S

Recommendations

If self-absorption > 0.3, use:

1. **Intense light source**
2. (Alternativ R*-ratio)
3. **Shorter cuvette length**
4. (Spectrophotometrically calibrated glass electrodes)

"Spectrophotometric pH measurements in the presence of dissolved organic matter (DOM) and hydrogen sulfide (H_2S)"
Submitted to *Limnology and Oceanography: Methods* on Jan 6, 2017

Leibniz-Institut für Ostseeforschung Warnemünde

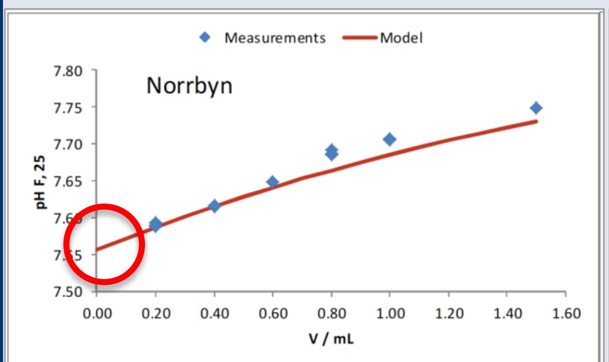
CONTROS Systems & Solutions GmbH

BONUS
Science for a better future of the Baltic Sea region

Challenges of mCP-based pH measurements for the Baltic Sea (and other coastal systems)

- Extended pH range
- Interference of spectral properties by interaction with CDOM or H_2S
- **Perturbation of the Acid-Base balance (pH) by the dye**
- Knowledge of $pK_{(mCP)}$ as f(T,S)

The elegance of a Flow Injection Analyser (FIA)



D. Turner and L. Anderson
BONUS PINBAL Deliverable Report 2.3

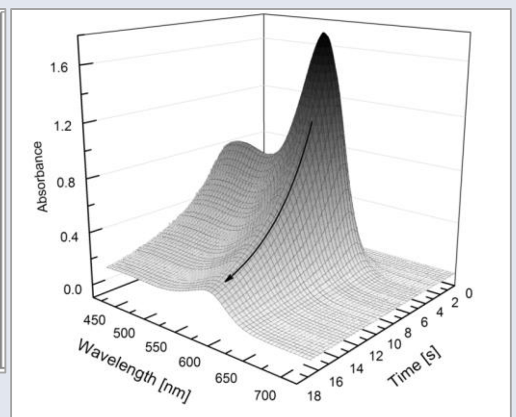
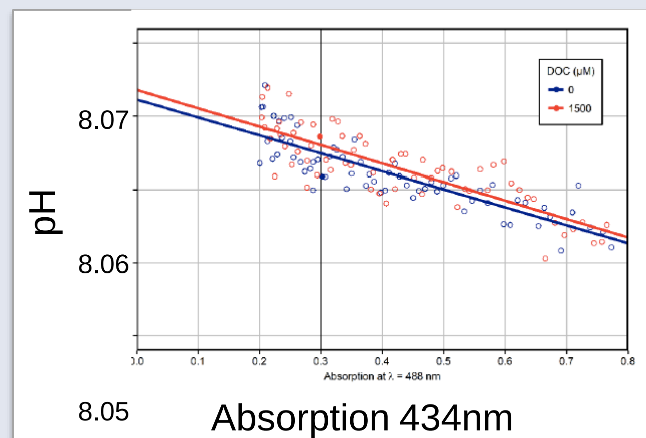


Fig. 5. Dilution curve passing the cuvette after indicator injection into a continuous sample flow and the recorded spectra. The smooth backward flank of the concentration peak is used for calculation of the perturbation-free pH value. For this more than 200 spectra are available (compare Fig. 6).

Aßmann et al., 2011



Müller et al., L&O methods, submitted (Supplement)

Challenges of mCP-based pH measurements for the Baltic Sea (and other coastal systems)

- Extended pH range
- Interference of spectral properties by interaction with CDOM or H_2S
- Perturbation of the Acid-Base balance (pH) by the dye
- **Knowledge of $pK_{(mCP)}$ as f(T,S)**

On the chemical characterization front ...
pK$_{(mCP)}$ as f(T,S)

Some really fundamental chemical **work beyond the original scope – and our ability** within the project has been required

<u>Expected outcome of Harned cell measurements:</u>

Well characterized TRIS buffer solutions at:

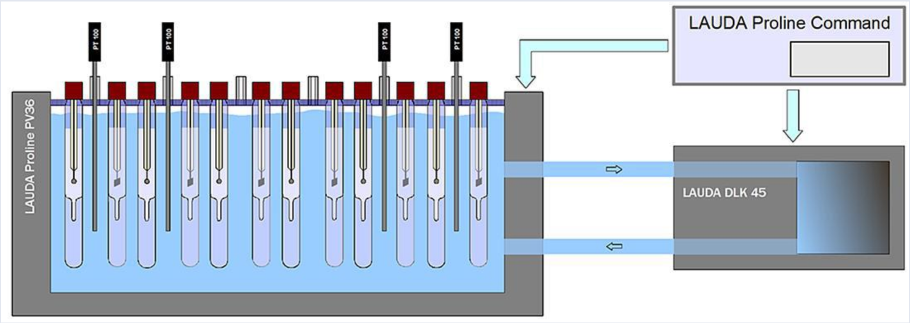
-salinity levels: 5, 10, 15, 20, 35

-temperature range: 5-30 ºC

-variable TRIS concentrations

PTB Braunschweig

Frank Bastkowski



SCRIPPS

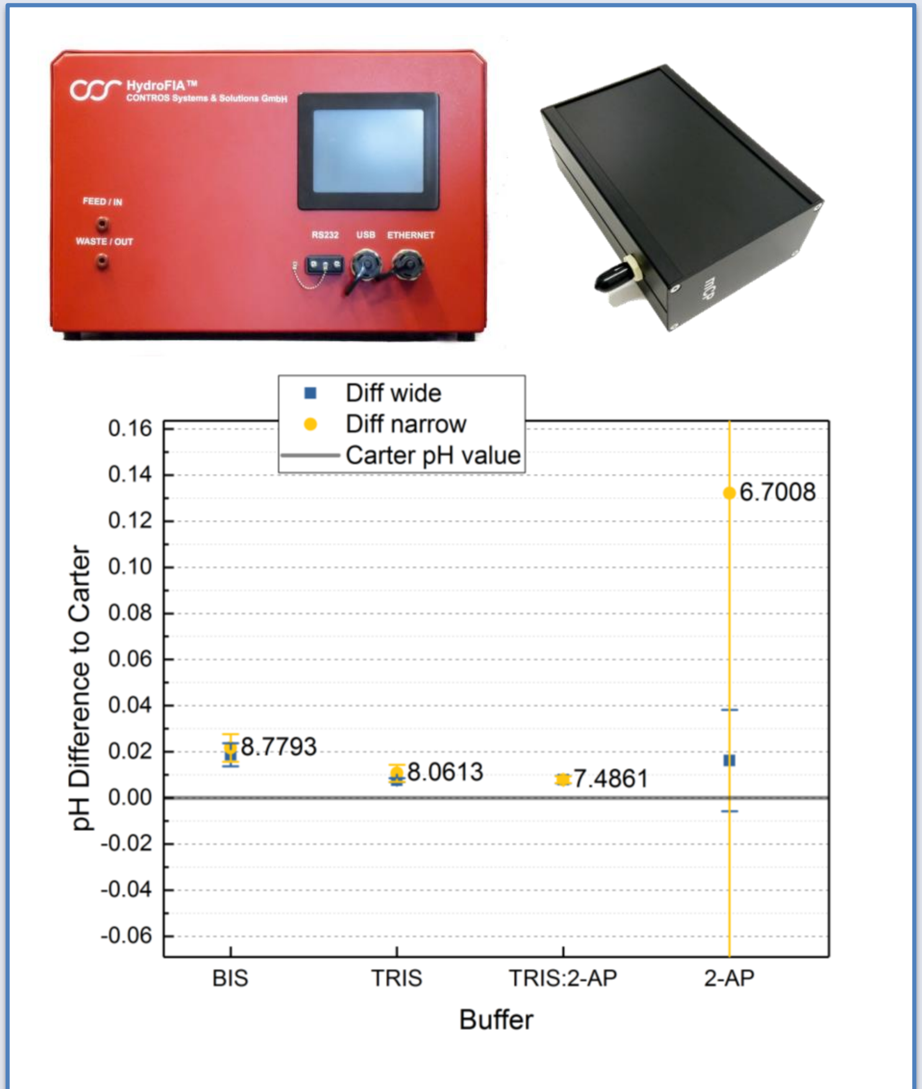
Andrew Dickson

The Instrument

3 prototypes developed within different stages of BONUS PINBAL

Strong interaction with results from theoretical work and lab and field tests

- FIA Approach
- User Friendly dye cartridges provided by manufacturer
- Continuous and discrete sample mode
- Precision ~0.002 pH-units (pH 7-8.5)
- Accuracy Offset to reference sys about 0.008 pH-units (same order as reference system itself)



Rationale revisited (Why we really do it)

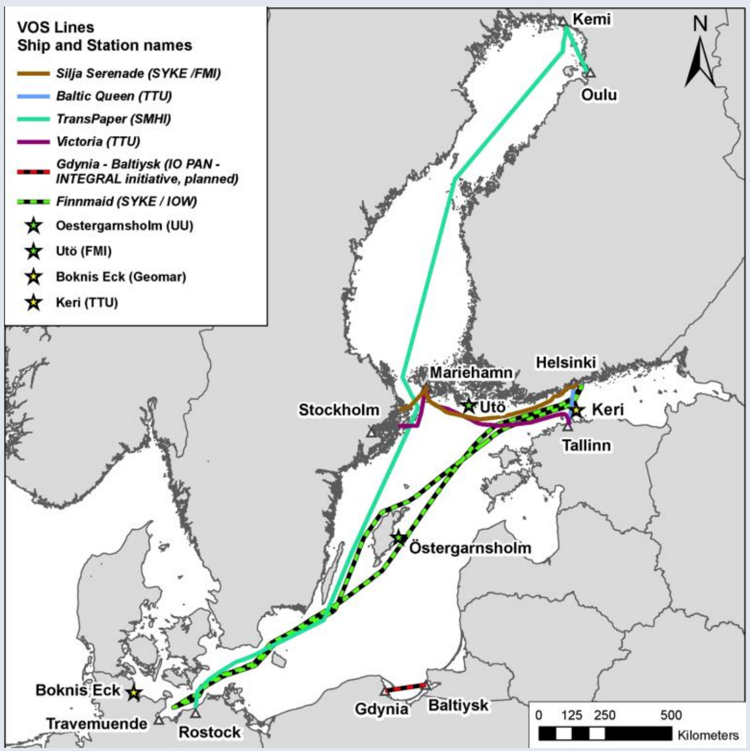
Advertisement

- Genuine interest in the carbon system, based on the belief that it is the key variable to assess productivity (and its triggers and controls), refined CNP-stoichiometries, eutrophication, and its link to hypoxia
- pCO_2 and pH could both be measured in high frequency from e.g. a VOS

Announcement – BONUS INTEGRAL to come

- Currently under Negotiation after successful application to the Blue Baltic call, expected 7/2017 to 6/2020

(IOW, GEOMAR, UU, SMHI, TTU, IO PAN, FMI, UExeter)



- Integrate the different data streams of ICOS and related infrastructure in the pan-Baltic area,
- Provide best charts of seasonal carbon dioxide and GG flux over the Baltic Sea, including advanced remote sensing approaches,
- Integrate the carbon system into a high resolution 3D-model, which will allow for a better description of the biogeochemical coupling of eutrophication and deoxygenation
- Demonstrate the added value for a better biogeochemical ecosystem status description of the Baltic Sea

On the chemical characterization front ...

pH of buffer solutions at low salinities

Poster P227 by Bastkowski et al.

Thursday

Also today at **Kongsberg/PINBAL Exhibit**

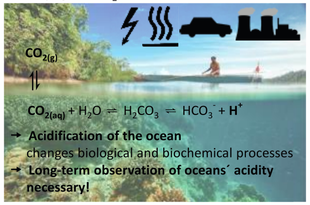
Electrochemical pH_T measurements of TRIS buffered artificial seawater samples in the salinity range 5-20

Physikalisch-Technische Bundesanstalt
National Metrology Institute

Frank Bastkowski, Jens Daniel Müller, Beatrice Sander, Steffen Seitz, Gregor Rehder

Motivation and Background

Anthropogenic CO_2 emission:



Acidity is expressed by the „**pH**" of an aqueous solution:

$pH = -lg(a(H^+))$ internationally accepted, IUPAC definition, activity $a(H^+)$ measured potentiometrically, valid only for dilute solutions of ionic strength ≤ 0.1 mol·kg⁻¹ (salinity 5) ➔ this pH value is not yet measurable in seawater media

➔ Instead: $pH_T = -lg(c(H^+) + c(HSO_4^-))$, commonly measured in oceanography.

pH_T scale is based on the total H⁺ concentration including HSO_4^- also contributing to H⁺

pH_T is frequently determined spectrophotometrically e.g. on ships using an indicator dye like *m*-cresol purple

➔ traceability of pH_T measurement results to an internationally agreed standard or to the SI is not established in the middle salinity range (5-20) up to now

➔ no comparability of pH_T measurement results

Objective

Determination of pH_T values of equimolal TRIS/TRIS·H⁺ buffered artificial seawater solutions enabling traceability of spectrophotometrically measured pH_T values to a primary (Harned cell) pH_T measurement procedure

Interlaboratory collaboration between PTB and IOW

1. Potentiometric measurement of pH_T of equimolal TRIS/TRIS·H⁺ buffered artificial seawater solutions of salinity 5-20 at three different total TRIS molalities (0.02, 0.05 and 0.08 mol·kg⁻¹) using Harned cells at **PTB** (completion of the works of Bates & Hetzer 1961 at salinity ≤ 5 and DelValls & Dickson 1998 at salinity 20-40)

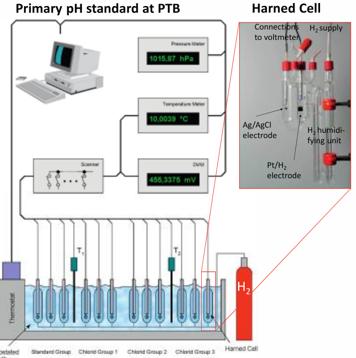
Measurement equation (equivalent to the above mentioned pH_T definition according to DelValls & Dickson, 1998):

$$pH_T = \frac{(E - E^{0*})F}{RT \ln 10} + lg(b_{Cl^-}) - lg(\omega_{H_2O})$$

E: Electric potential of the Harned cell filled with artificial seawater
E^{0*}: Standard potential of the Ag/AgCl electrode in artificial seawater (to be determined in an extra experiment)
b_{Cl^-}: Molality of chloride of the artificial seawater
ω_{H_2O}: Water content of the artificial seawater

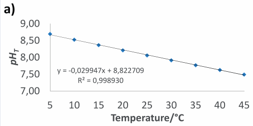
2. Determination of the dissociation constant of spectrophotometric dye *m*-cresol purple at **IOW** in the framework of the Innovation Project BONUS PINBAL using the same buffered artificial seawater solutions characterised at PTB. See poster of Müller *et al* (P228) and talk by Rehder *et al*)

Primary pH standard at PTB / **Harned Cell**



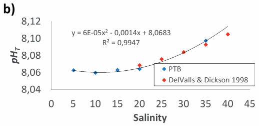
Results

a)



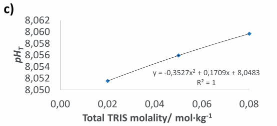
Temperature dependence of pH_T values at salinity 10 and 0.08 mol·kg⁻¹ total TRIS molality

b)



Salinity dependence of pH_T values at 25 °C and 0.08 mol·kg⁻¹ total TRIS molality measured at PTB (blue) and by DelValls & Dickson 1998 (red)

c)



TRIS dependence of pH_T values at salinity 10 and 25 °C

Acknowledgements

We gratefully thank Andrew Dickson (University of California) and David Turner (University of Gothenburg) for fruitful discussions and the interpretation of the measurement results

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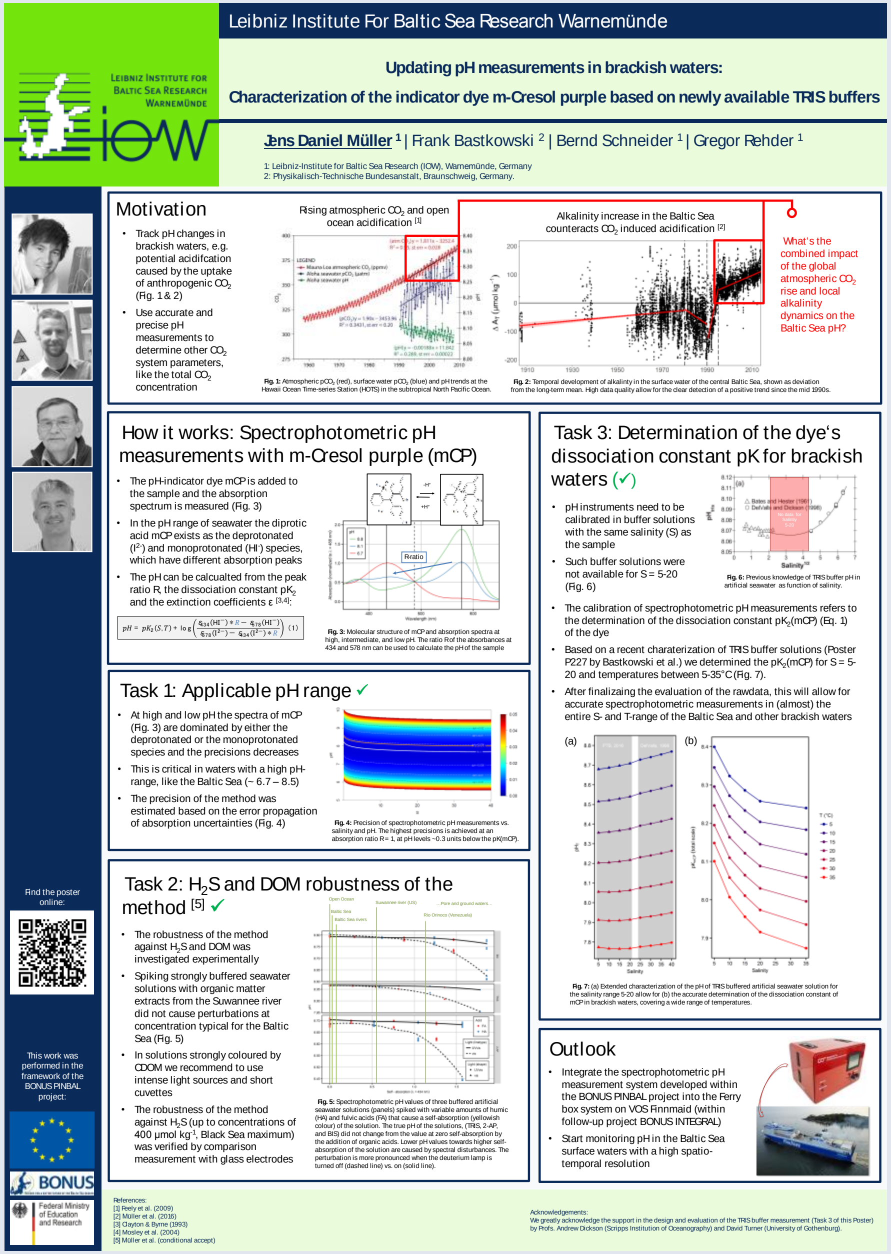
On the chemical characterization front ...

pK$_{(mCP)}$ as f(T,S), pH-range, DOM and H2S perturbation

Poster P228 by Müller et al.

Thursday

Also today at Kongsberg/PINBAL Exhibit



Leibniz Institute For Baltic Sea Research Warnemünde

Updating pH measurements in brackish waters:

Characterization of the indicator dye m-Cresol purple based on newly available TRIS buffers

Jens Daniel Müller [1] | Frank Bastkowski [2] | Bernd Schneider [1] | Gregor Rehder [1]

1: Leibniz-Institute for Baltic Sea Research (IOW), Warnemünde, Germany
2: Physikalisch-Technische Bundesanstalt, Braunschweig, Germany.

Motivation

- Track pH changes in brackish waters, e.g. potential acidifcation caused by the uptake of anthropogenic CO_2 (Fig. 1 & 2)
- Use accurate and precise pH measurements to determine other CO_2 system parameters, like the total CO_2 concentration

Rising atmospheric CO_2 and open ocean acidification [1]

Fig. 1: Atmospheric pCO_2 (red), surface water pCO_2 (blue) and pH trends at the Hawaii Ocean Time-series Station (HOTS) in the subtropical North Pacific Ocean.

Alkalinity increase in the Baltic Sea counteracts CO_2 induced acidification [2]

Fig. 2: Temporal development of alkalinty in the surface water of the central Baltic Sea, shown as deviation from the long-term mean. High data quality allow for the clear detection of a positive trend since the mid 1990s.

What's the combined impact of the global atmospheric CO_2 rise and local alkalinity dynamics on the Baltic Sea pH?

How it works: Spectrophotometric pH measurements with m-Cresol purple (mCP)

- The pH-indicator dye mCP is added to the sample and the absorption spectrum is measured (Fig. 3)
- In the pH range of seawater the diprotic acid mCP exists as the deprotonated (I^{2-}) and monoprotonated (HI^-) species, which have different absorption peaks
- The pH can be calcualted from the peak ratio R, the dissociation constant pK_2 and the extinction coefficients ε [3,4]:

$$pH = pK_2(S,T) + \log\left(\frac{\varepsilon_{434}(HI^-) * R - \varepsilon_{578}(HI^-)}{\varepsilon_{578}(I^{2-}) - \varepsilon_{434}(I^{2-}) * R}\right) \quad (1)$$

Fig. 3: Molecular structure of mCP and absorption spectra at high, intermediate, and low pH. The ratio R of the absorbances at 434 and 578 nm can be used to calculate the pH of the sample

Task 1: Applicable pH range ✓

- At high and low pH the spectra of mCP (Fig. 3) are dominated by either the deprotonated or the monoprotonated species and the precisions decreases
- This is critical in waters with a high pH-range, like the Baltic Sea (~ 6.7 – 8.5)
- The precision of the method was estimated based on the error propagation of absorption uncertainties (Fig. 4)

Fig. 4: Precision of spectrophotometric pH measurements vs. salinity and pH. The highest precisions is achieved at an absorption ratio R = 1, at pH levels ~0.3 units below the pK(mCP).

Task 2: H_2S and DOM robustness of the method [5] ✓

- The robustness of the method against H_2S and DOM was investigated experimentally
- Spiking strongly buffered seawater solutions with organic matter extracts from the Suwannee river did not cause perturbations at concentration typical for the Baltic Sea (Fig. 5)
- In solutions strongly coloured by CDOM we recommend to use intense light sources and short cuvettes
- The robustness of the method against H_2S (up to concentrations of 400 µmol kg^{-1}, Black Sea maximum) was verified by comparison measurement with glass electrodes

Fig. 5: Spectrophotometric pH values of three buffered artificial seawater solutions (panels) spiked with variable amounts of humic (HA) and fulvic acids (FA) that cause a self-absorption (yellowish colour) of the solution. The true pH of the solutions, (TRIS, 2-AP, and BIS) did not change from the value at zero self-absorption by the addition of organic acids. Lower pH values towards higher self-absorption of the solution are caused by spectral disturbances. The perturbation is more pronounced when the deuterium lamp is turned off (dashed line) vs. on (solid line).

Task 3: Determination of the dye's dissociation constant pK for brackish waters (✓)

- pH instruments need to be calibrated in buffer solutions with the same salinity (S) as the sample
- Such buffer solutions were not available for S = 5-20 (Fig. 6)

Fig. 6: Previous knowledge of TRIS buffer pH in artificial seawater as function of salinity.

- The calibration of spectrophotometric pH measurements refers to the determination of the dissociation constant pK_2(mCP) (Eq. 1) of the dye
- Based on a recent charaterization of TRIS buffer solutions (Poster P227 by Bastkowski et al.) we determined the pK_2(mCP) for S = 5-20 and temperatures between 5-35°C (Fig. 7).
- After finalizaing the evaluation of the rawdata, this will allow for accurate spectrophotometric measurements in (almost) the entire S- and T-range of the Baltic Sea and other brackish waters

Fig. 7: (a) Extended characterization of the pH of TRIS buffered artificial seawater solution for the salinity range 5-20 allow for (b) the accurate determination of the dissociation constant of mCP in brackish waters, covering a wide range of temperatures.

Outlook

- Integrate the spectrophotometric pH measurement system developed within the BONUS PINBAL project into the Ferry box system on VOS Finnmaid (within follow-up project BONUS INTEGRAL)
- Start monitoring pH in the Baltic Sea surface waters with a high spatio-temporal resolution

Find the poster online:

This work was performed in the framework of the BONUS PINBAL project:

References:
[1] Feely et al. (2009)
[2] Müller et al. (2016)
[3] Clayton & Byrne (1993)
[4] Mosley et al. (2004)
[5] Müller et al. (conditional accept)

Acknowledgements:
We greatly acknowledge the support in the design and evaluation of the TRIS buffer measurement (Task 3 of this Poster) by Profs. Andrew Dickson (Scripps Institution of Oceanography) and David Turner (University of Gothenburg).

Thanks for listening !

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