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Updating pH measurements in brackish waters: Characterization of the indicator dye m-Cresol purple based on newly available TRIS buffers

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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]

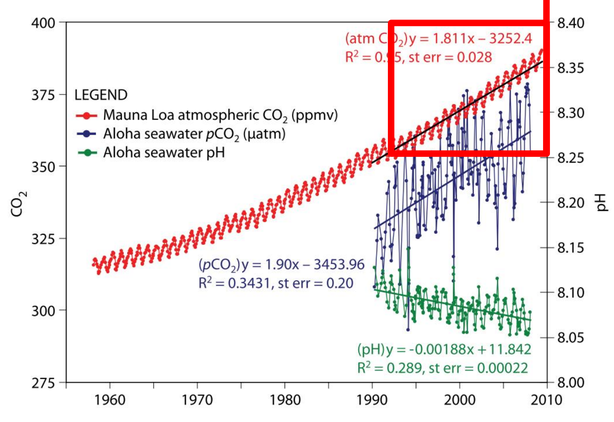

Fig. 1: Atmospheric pCO_2 (red), surface water pCO_2 (blue) and pH trends at the Hawaii Ocean Time-series Station (HOTS) in the subtropical North Pacific Ocean.

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

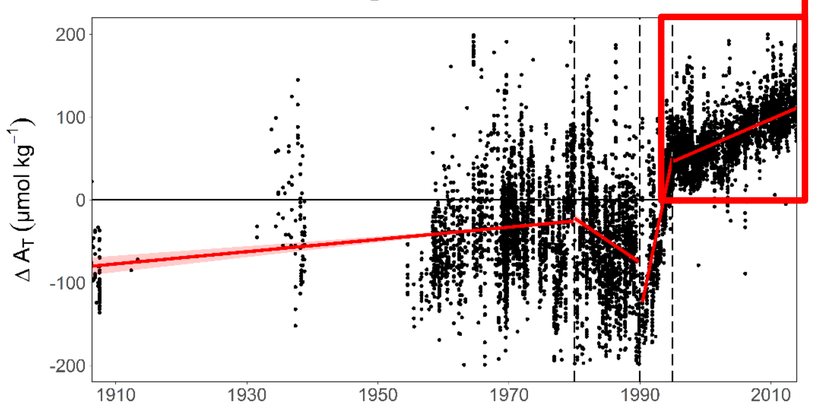

Fig. 2: Temporal development of alkalinity in the surface water of the central Baltic Sea, shown as deviation from the long-term mean. High data quality allow for the clear detection of a positive trend since the mid 1990s.

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]:

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

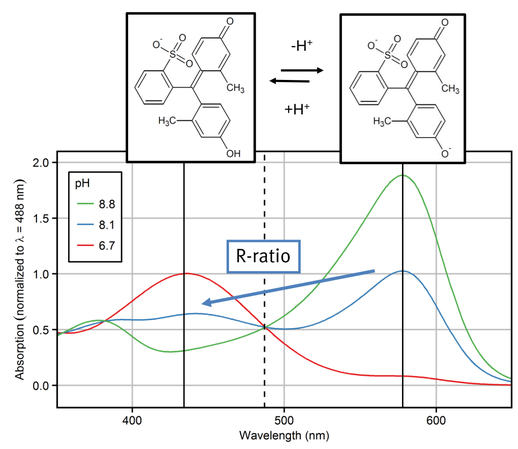

Fig. 3: Molecular structure of mCP and absorption spectra at high, intermediate, and low pH. The ratio R of the absorbances at 434 and 578 nm can be used to calculate the pH of the sample

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)

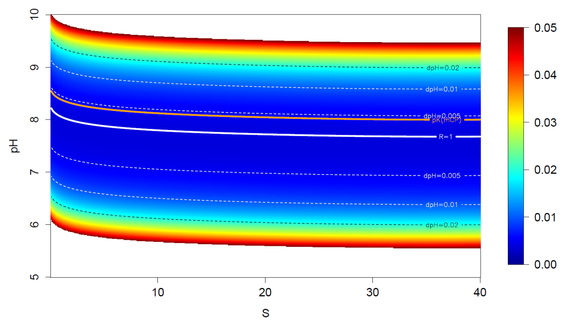

Fig. 4: Precision of spectrophotometric pH measurements vs. salinity and pH. The highest precisions is achieved at an absorption ratio R = 1, at pH levels ~0.3 units below the pK(mCP).

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

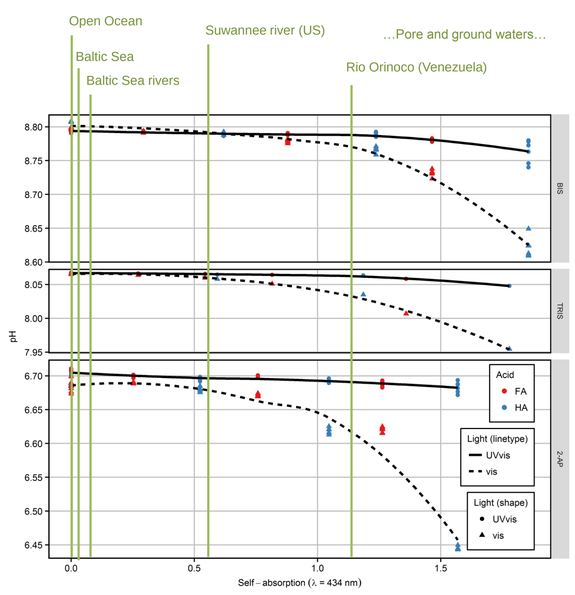

Fig. 5: Spectrophotometric pH values of three buffered artificial seawater solutions (panels) spiked with variable amounts of humic (HA) and fulvic acids (FA) that cause a self-absorption (yellowish colour) of the solution. The true pH of the solutions, (TRIS, 2-AP, and BIS) did not change from the value 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)

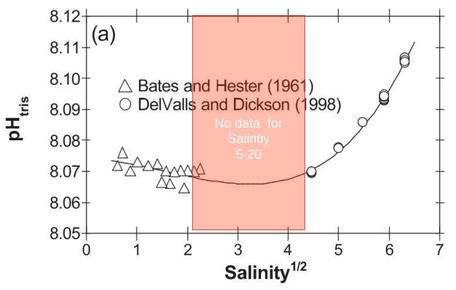

Fig. 6: Previous knowledge of TRIS buffer pH in artificial seawater as function of salinity.

- 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

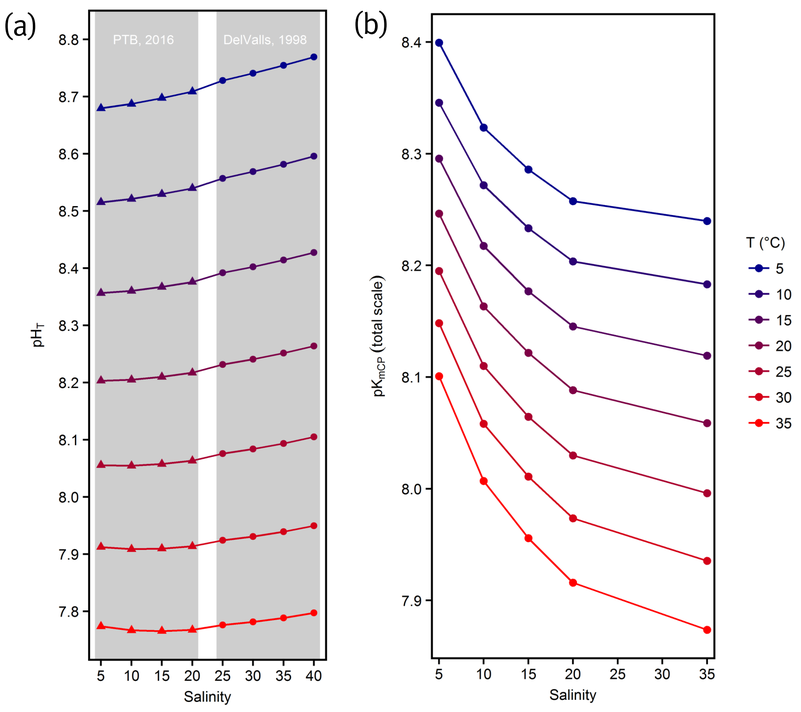

Fig. 7: (a) Extended characterization of the pH of TRIS buffered artificial seawater solution for the salinity range 5-20 allow for (b) the accurate determination of the dissociation constant of mCP in brackish waters, covering a wide range of temperatures.

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).