6th FerryBox Workshop

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Determination of Total Alkalinity and pH in Seawater

Steffen Aßmann, Carsten Frank, Peer Fietzek, Wilhelm Petersen, Arne Körtzinger, Peter Linke

CONTROS Systems & Solutions GmbH

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Centre for Materials and Coastal Research

Outline

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- Carbonate System
  - Parameters
  - Cross Calculations
- Parameter: pH
- Parameter: Total Alkalinity
  - Closed-Cell Titration
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- Summary

Dr. Steffen Aßmann, sassmann@geomar.de

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Introduction

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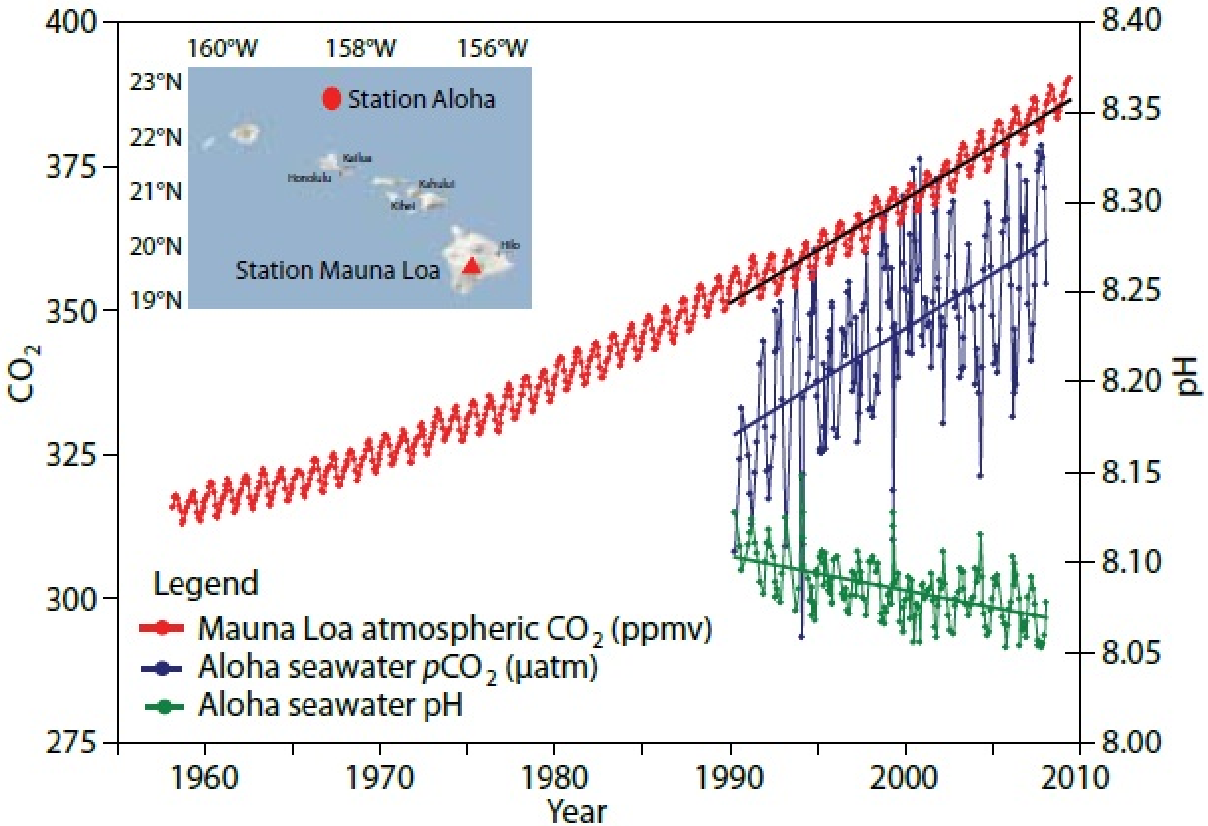
Temporal Variability of CO_2

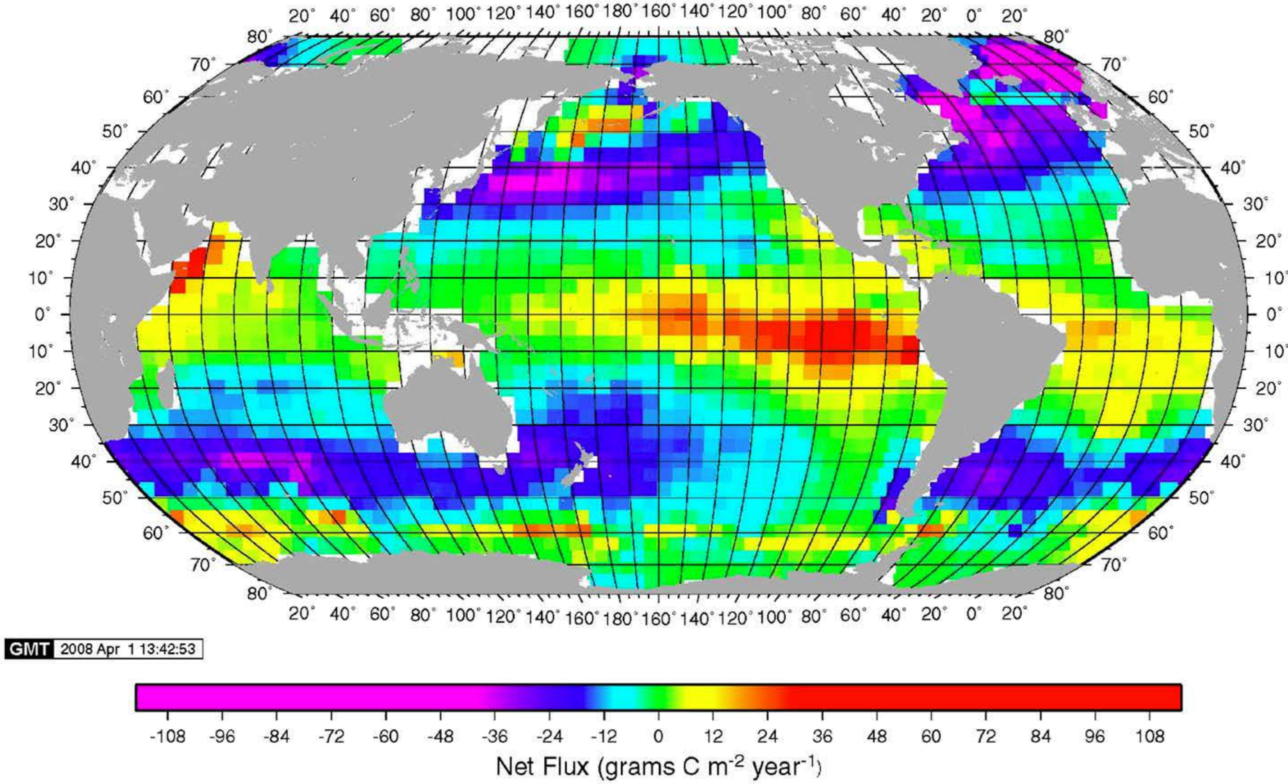


- Rising CO_2 concentration in the atmosphere
- Increasing pCO_2 and decreasing pH in the surface ocean
- High temporal variability
- Measured at one spot on earth
- Good for monitoring trends

Doney et al., 2009

Dr. Steffen Aßmann, sassmann@geomar.de

Spatial Variability of CO_2



- Most data from voluntary observing ships (VOS)
- Averaged over decades
- Only pCO_2 measured
- No access to the carbonate chemistry
- More parameters are needed

Takahashi et al., 2009

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Carbonate System

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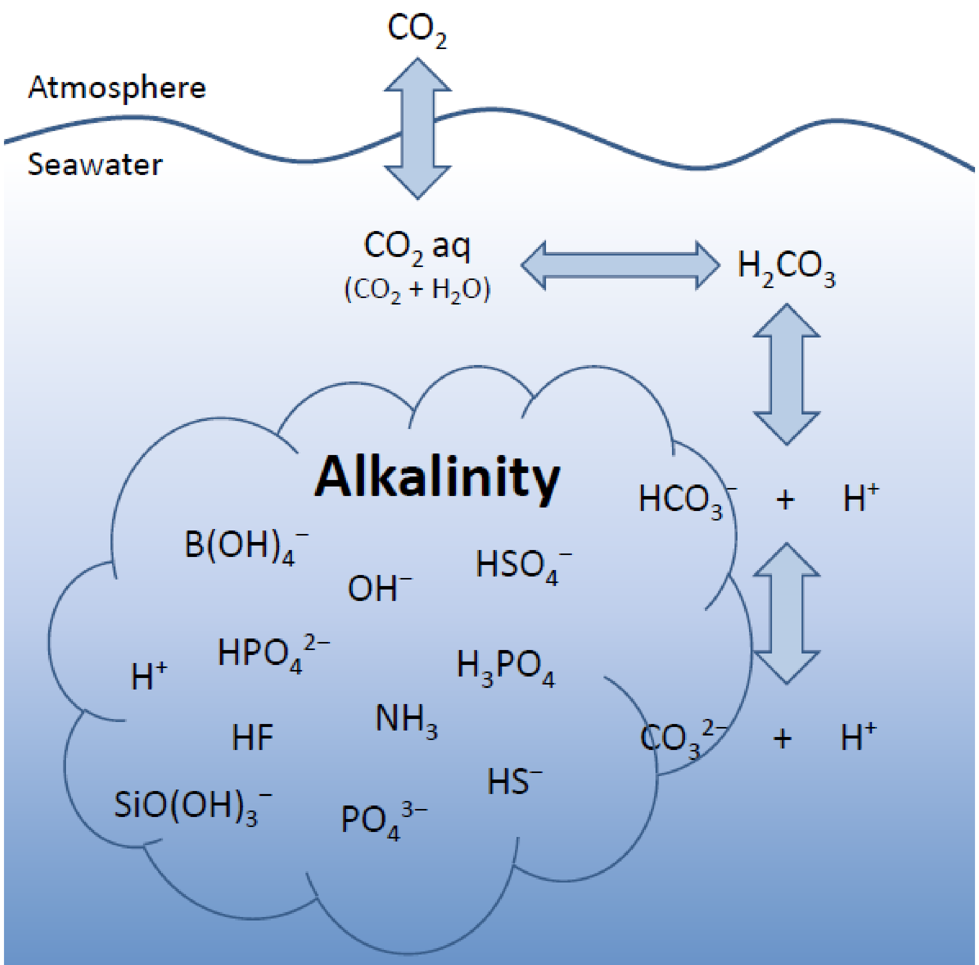
Carbonate System



Four measureable parameters:

- **pH** (hydrogen ion concentration)
- ***p*CO₂** (partial pressure of CO_2)
- **DIC** (dissolved inorganic carbon)
- **TA** (total alkalinity)

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Calculation of the Carbonate Parameters

Input	ΔpH	ΔTA ($\mu mol\ kg^{-1}$)	ΔDIC ($\mu mol\ kg^{-1}$)	ΔpCO_2 (µatm)
Value	8.045	2300	2000	397
Error	± 0.002	± 3	± 2	± 2
pH – TA			± 3.8	± 2.1
pH – DIC		± 2.7		± 1.8
pH – pCO_2		± 21	± 18	
pCO_2 – DIC	± 0.0025	± 3.4		
pCO_2 – TA	± 0.0026		± 3.2	
TA – DIC	± 0.0062			± 5.7

Millero et al., 2007

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Spectrophotometric Determination of pH

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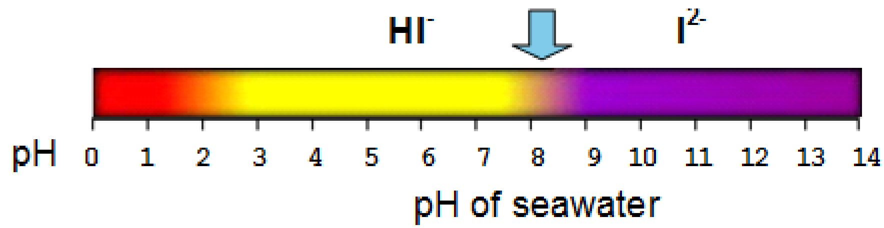
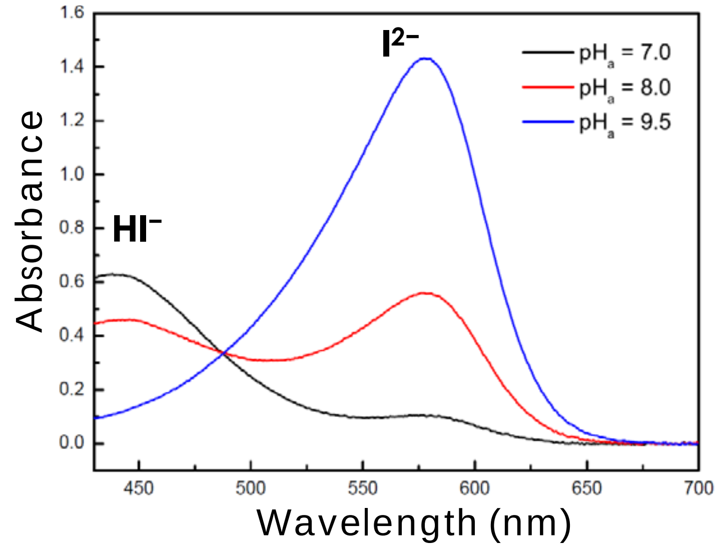
pH System – Principle

- FIA system using an indicator dye *m*-Cresol purple
- Determination of the concentration of the indicator acid (HI^-) / base (I^{2-}) due to different absorption spectra using a CCD spectrometer
- Calculation of the pH value using Henderson–Hasselbach equation





$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{I}^{2-}]}{[\mathrm{HI}^{-}]}$$

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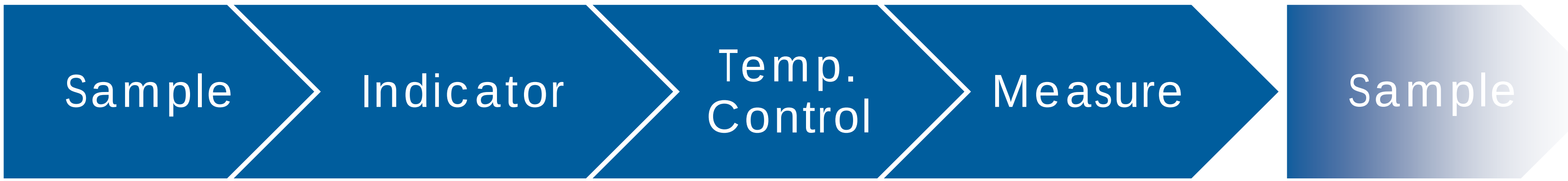
Measurement Intervals for pH



Sample → Continuous sample stream

Indicator → Injection of the indicator

Temp. Control → Steadily controlled sample stream

Measure → Spectrophotometric pH detection in the cuvette

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pH Setup

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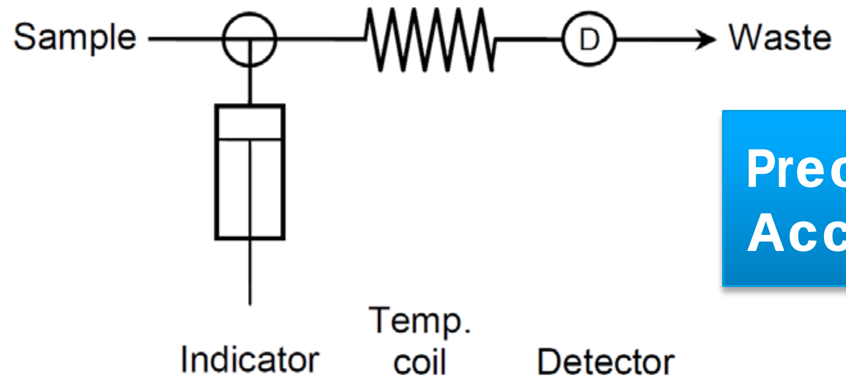
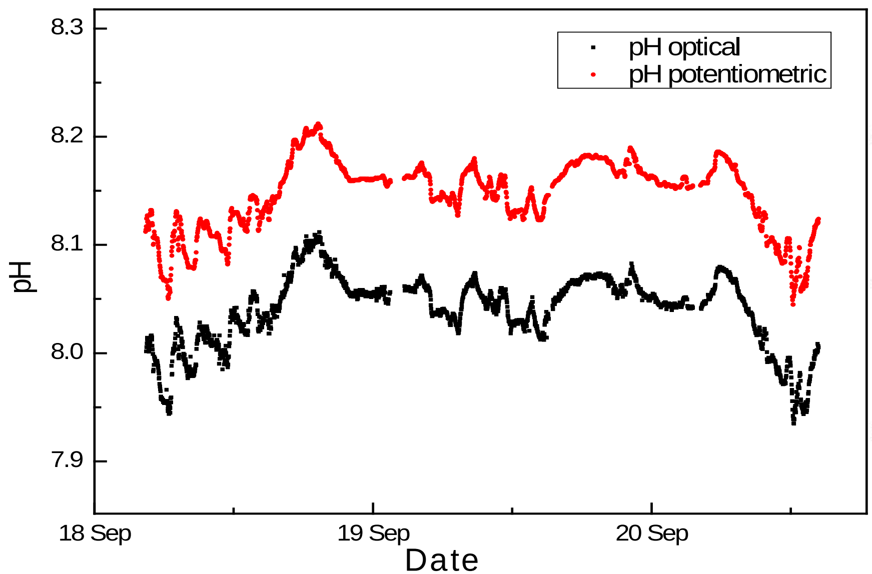
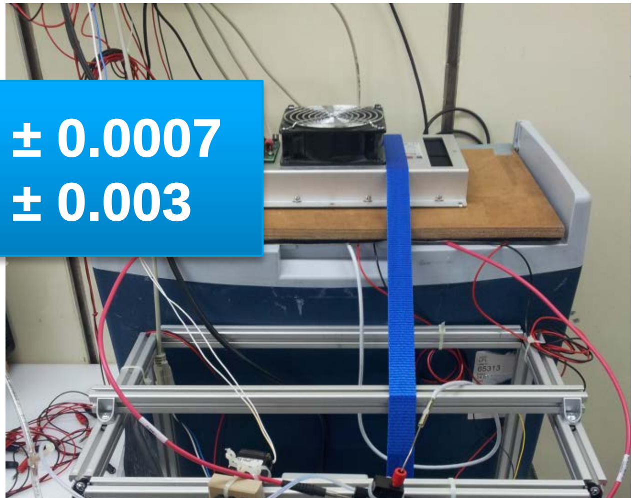
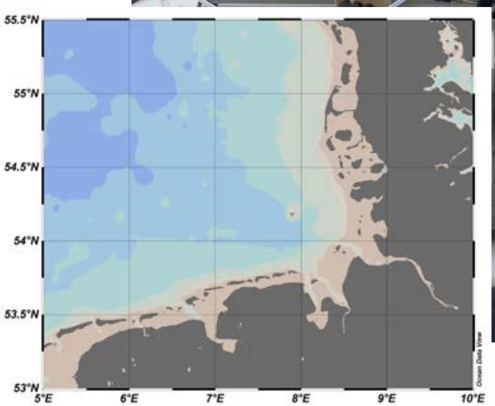






Precision ± 0.0007
Accuracy ± 0.003



Aßmann et al., 2011

Dr. Steffen Aßmann, sassmann@geomar.de

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Spectrophotometric Determination of TA

Total Alkalinity

Why TA?

- TA is a conservative quantity
  → independent of T- and p-changes like salinity
- Less susceptible to the prevailing biological perturbations/effects (=all processes involving CO_2) than DIC, but it is influenced by various biogeochemical processes
- Least correlated with pH, DIC and pCO_2
- A good water mass tracer that can be used to parameterize important TA/S relationships
- Opposed to DIC an accurate, technically ready measuring principle is available that can serve as the basis for an autonomous TA analyzer (wet chemical, sample acidification with subsequent optical pH-measurement).

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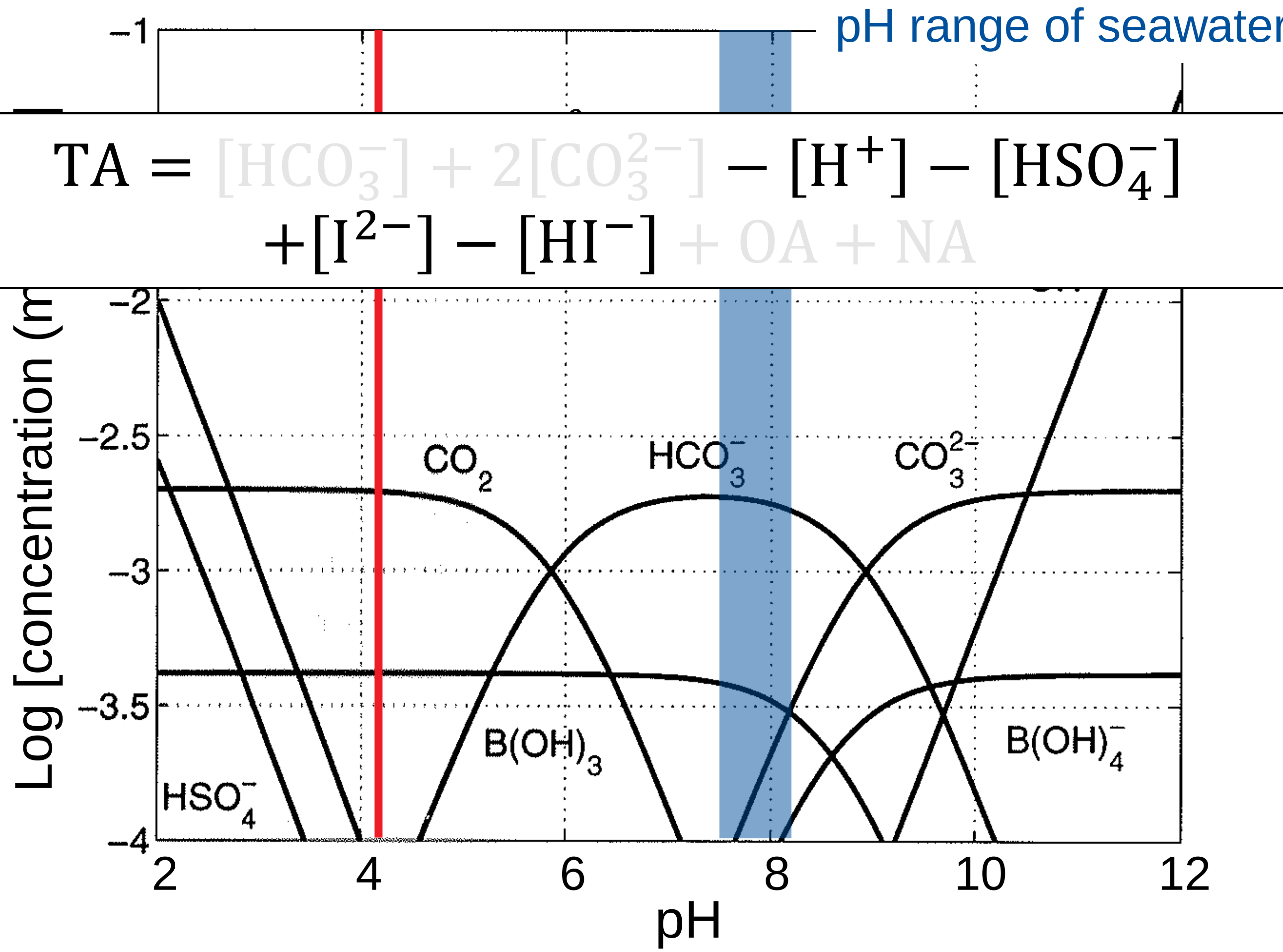
Bjerrum Plot & TA



$$\mathrm{TA} = [\mathrm{HCO_3^-}] + 2[\mathrm{CO_3^{2-}}] - [\mathrm{H^+}] - [\mathrm{HSO_4^-}] \\ +[\mathrm{I^{2-}}] - [\mathrm{HI^-}] + \mathrm{OA} + \mathrm{NA}$$

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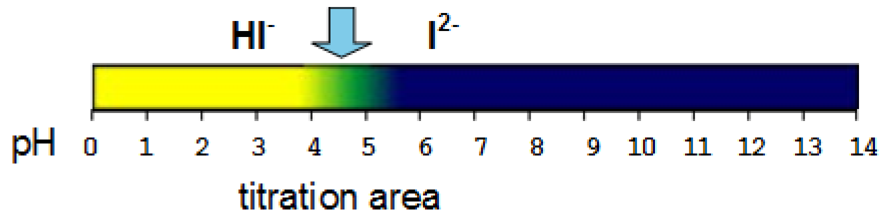
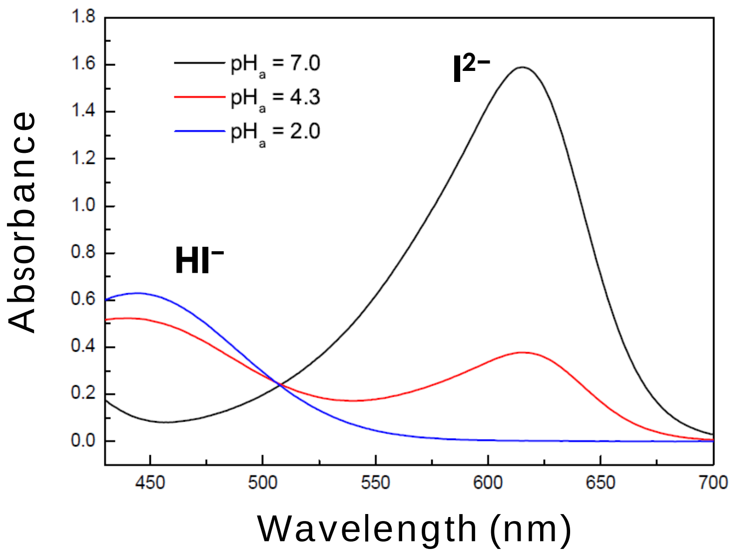
TA – Principle



- Acidification of a seawater sample using HCl



- Addition of the indicator dye Bromocresol green
- Determination of the concentration of the indicator acid (HI^-) / base (I^{2-}) due to different absorption spectra using a CCD spectrometer
- Calculation of the pH value using Henderson–Hasselbach equation

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\frac{[\mathrm{I}^{2-}]}{[\mathrm{HI}^-]}$$

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Closed-Cell Titration Measurement Intervals

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Flush → Full replacement of the sample solution

Sample/Acid/Indicator → Aspiration of sample water together with indicator and acid

Mixing/Kinetics → Homogenous solution and reaction

Measure → Spectrophotometric pH detection

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Closed-Cell Titration
Field Data (preliminary)

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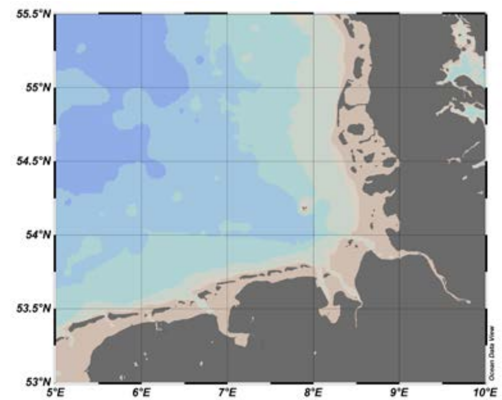
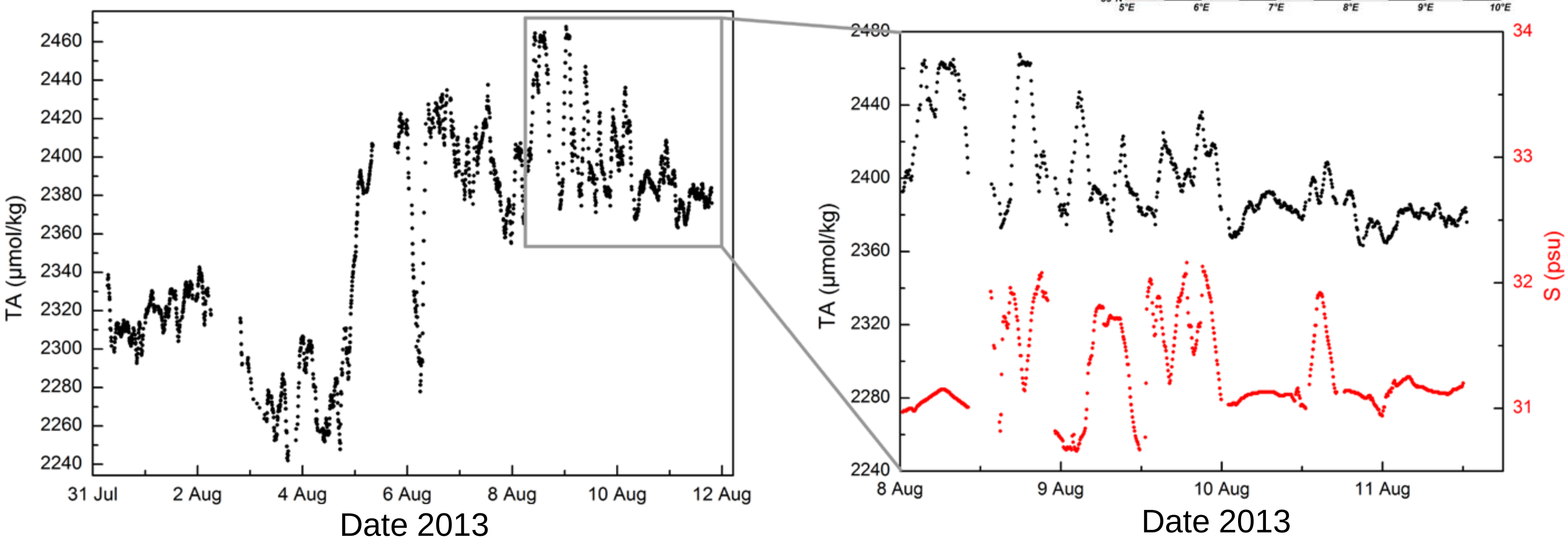
- Measurements in the North Sea (Waddensea)
- Measured range: 2240 µmol/kg to 2470 µmol/kg
- Measurement Cycle: 7 minutes
- Period: 12 days → ~ 2100 values





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Closed-Cell Titration
Reference Measurements (preliminary)

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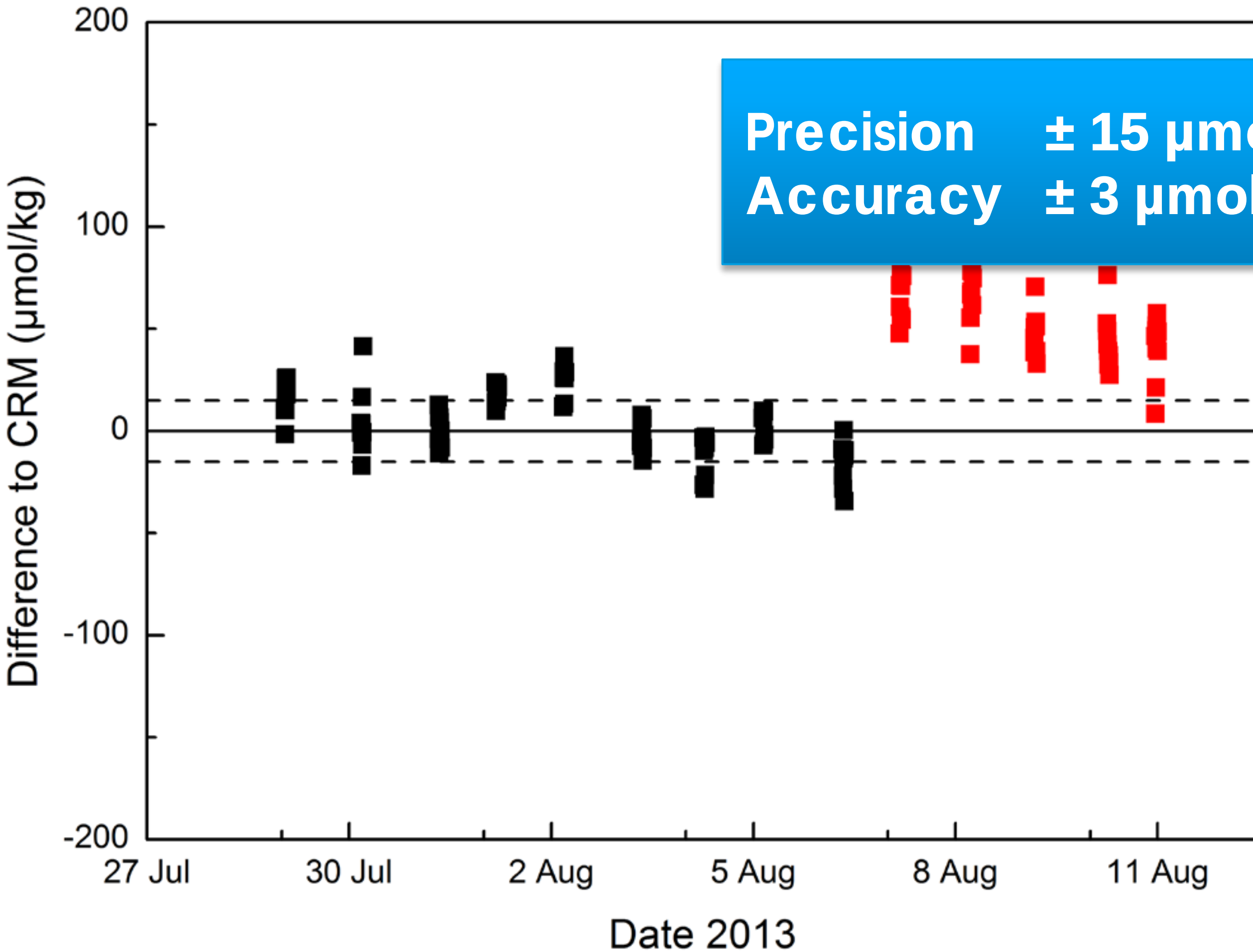

Precision ± 15 µmol/kg
Accuracy ± 3 µmol/kg

Dr. Steffen Aßmann, sassmann@geomar.de

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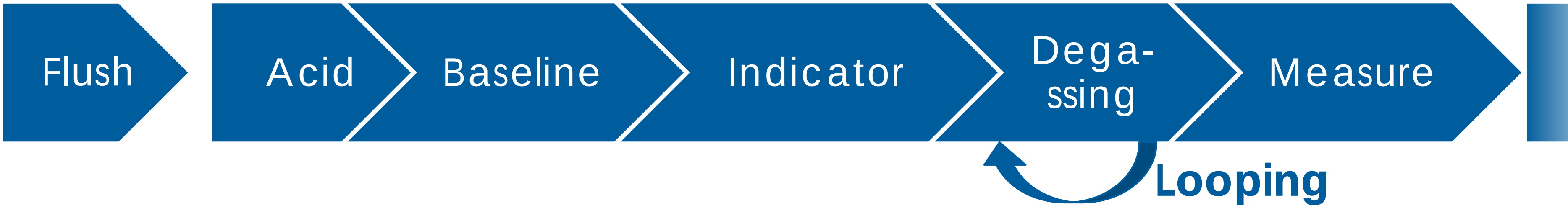
Open-Cell Titration
Measurement Intervals



Flush	→	Full replacement of the sample solution; water intake closed and subsequent sample treatment
Acid	→	Injection of hydrochloric acid into the sample loop
Baseline	→	Detection of the baseline
Indicator	→	Injection of the indicator
Degassing	→	Full removal of the DIC (pCO_2); *Looping of acidified, indicator-added sample until complete removal of DIC*
Measure	→	Spectrophotometric pH detection

Dr. Steffen Aßmann, sassmann@geomar.de

Open-Cell Titration
Figure of Merit

- Only one titration point needed
- Short measuring cycles (~5 min)
- Low reagent consumption
  - Acid (HCl) (0,3 mL)
  - Indicator (BCG) (0,3 mL)
  - Sample (100 mL)
- No perturbation of the carbonate equilibrium constants due to low pH values and high pCO_2

Dr. Steffen Aßmann, sassmann@geomar.de

Open-Cell Titration
HydroFIA™ TA

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Flow-through application

Discrete sample measurements

RS232
USB
Ethernet

Dr. Steffen Aßmann, sassmann@geomar.de

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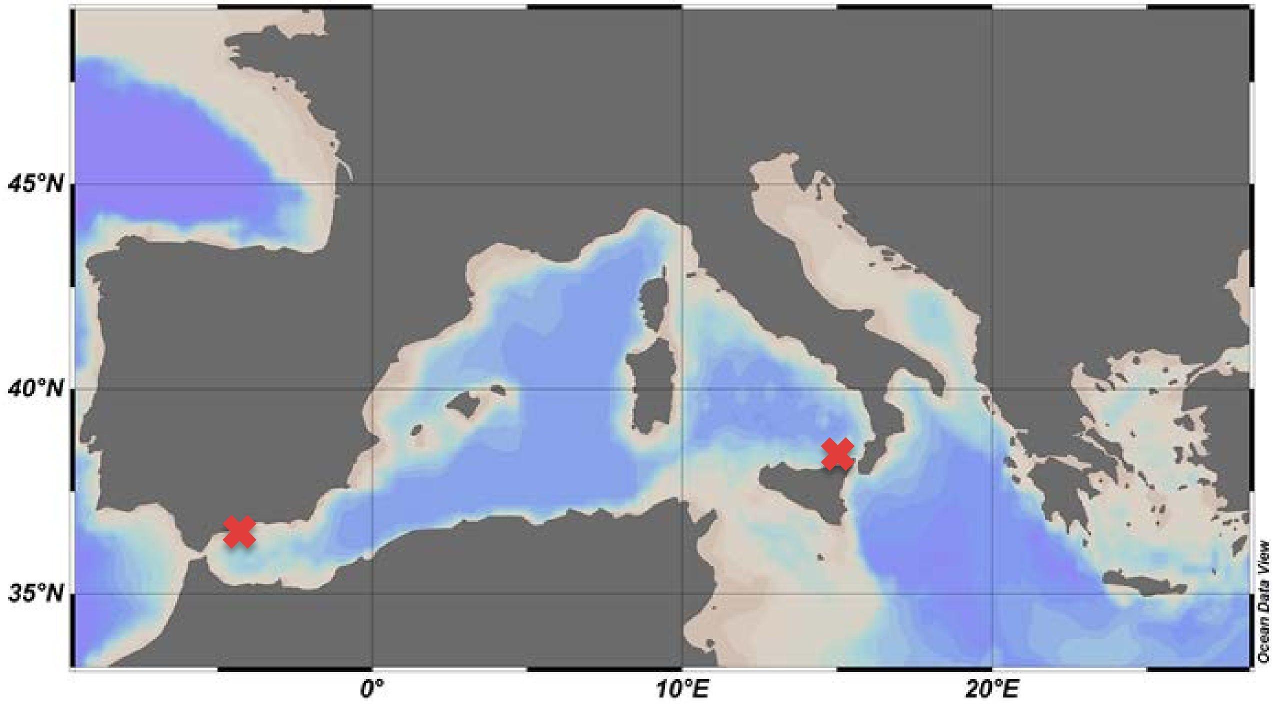
Open-Cell Titration Field Data (preliminary)

- Measurements in the Mediterranean Sea: Transit Panarea-Malaga
- Measurement Cycle: 5 minutes
- Period: 5 days
- ~ 1500 values



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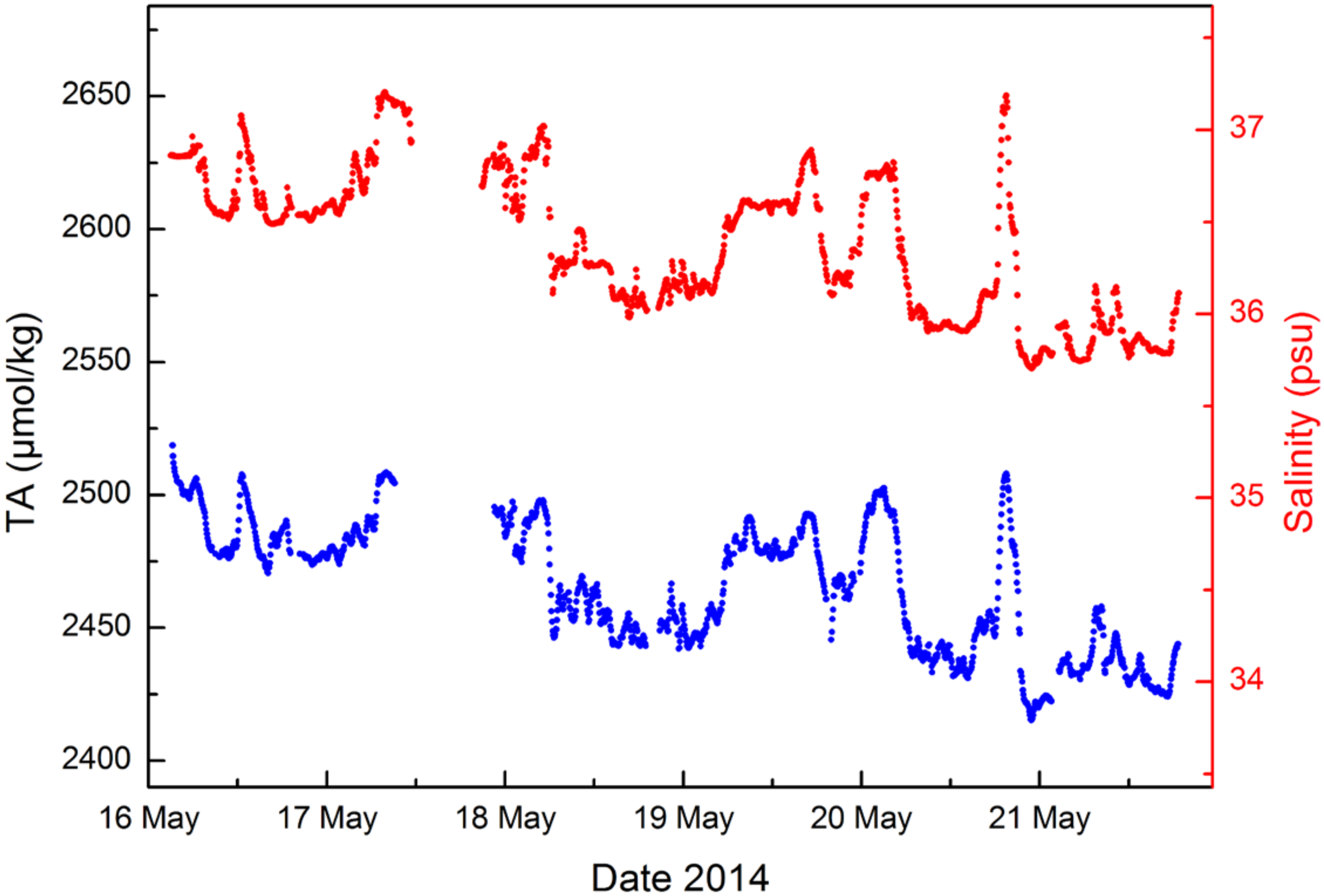
Open-Cell Titration
Field Data (preliminary)



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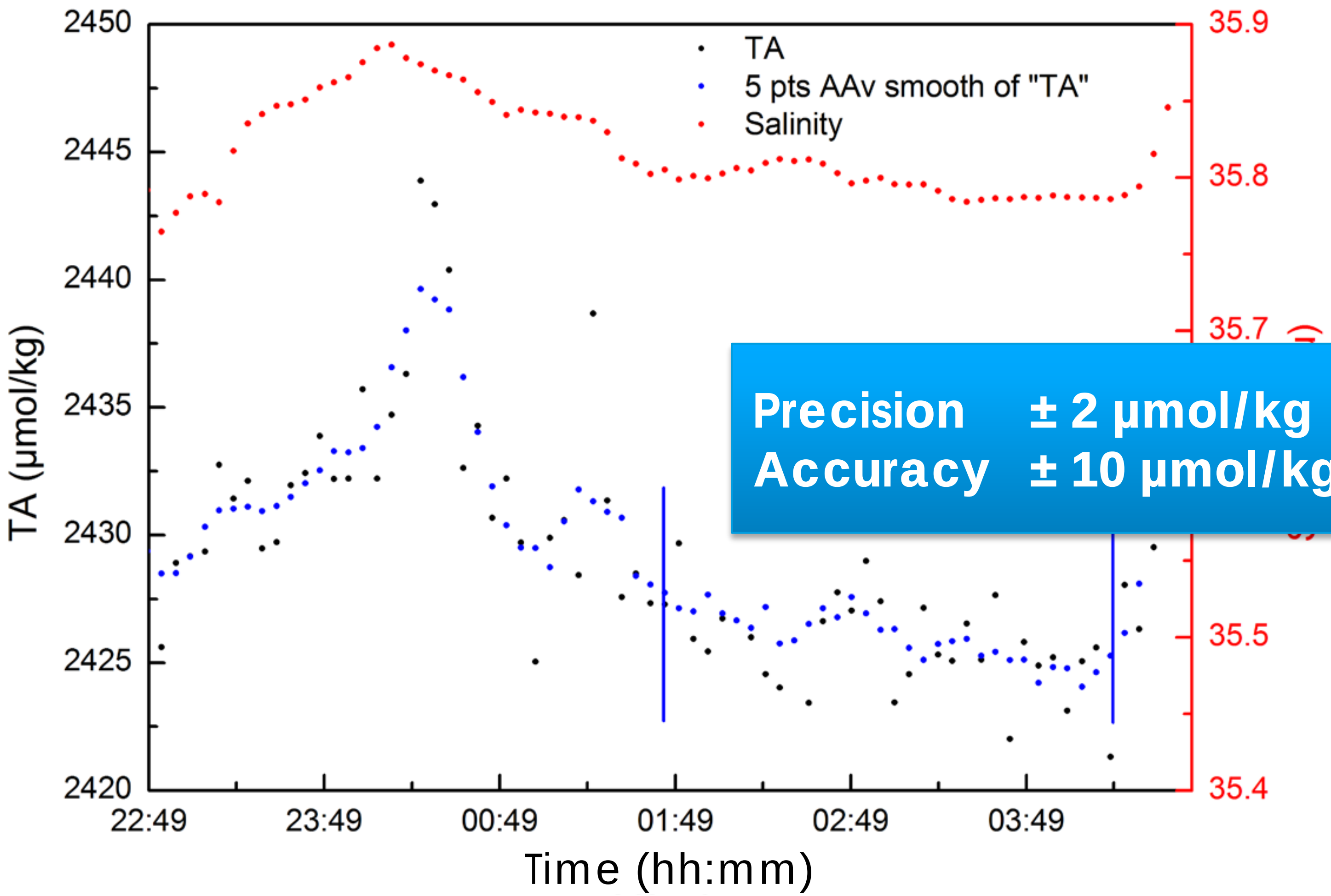
Open-Cell Titration
Field Data – Zoom (preliminary)



Precision ± 2 µmol/kg
Accuracy ± 10 µmol/kg

Summary

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Summary

- Knowledge about the **carbonate system** is mostly gained from **bottled data** and a view time series stations.

- There is a **need for autonomous, continuously measuring sensors** providing the parameters of biogeochemical cycles, especially for the carbonate system:
  - understanding and monitoring **Ocean Acidification**,
  - giving a picture of the **carbonate system in coastal areas**.

- **New systems** are developed **for pH and TA** providing adequate quality for a characterization of the carbonate system and experience ongoing optimization.

	pH	Closed-Cell	Open-Cell
Accuracy	± 0.003	± 3 µmol/kg	<± 10 µmol/kg
Precision	± 0.0007	± 15 µmol/kg	± 2 µmol/kg

Thank You

Cooperation Partners

Contact

Dr. Steffen Aßmann

GEOMAR Helmholtz Centre for Ocean Research Kiel
email: sassmann@geomar.de

CONTROS Systems & Solutions GmbH
email: s.assmann@contros.eu