New autonomous sensors for underway measurements

Steffen Aßmann, Carsten Frank, Jochen Wollschläger, Wilhelm Petersen

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Helmholtz-Zentrum Geesthacht
Centre for Materials and Coastal Research

Motivation

Topics of interest

- Marine Strategy Framework Directive (MSDF)
  - → Eutrophication — Nutrients
  - → Harmful algae blooms (HABs) — Identification of algae
- Primary production — O_2, pCO_2, Chl-a
- Ocean acidification — pH
  - → Alkalinity transport — Total alkalinity (TA)
  - → Sinks / sources for CO_2 — pCO_2, pH
  - → Feedbacks to the rising atmospheric CO_2 concentration — pCO_2, pH, TA

→ From physical parameters to biogeochemistry

FerryBoxes as platforms

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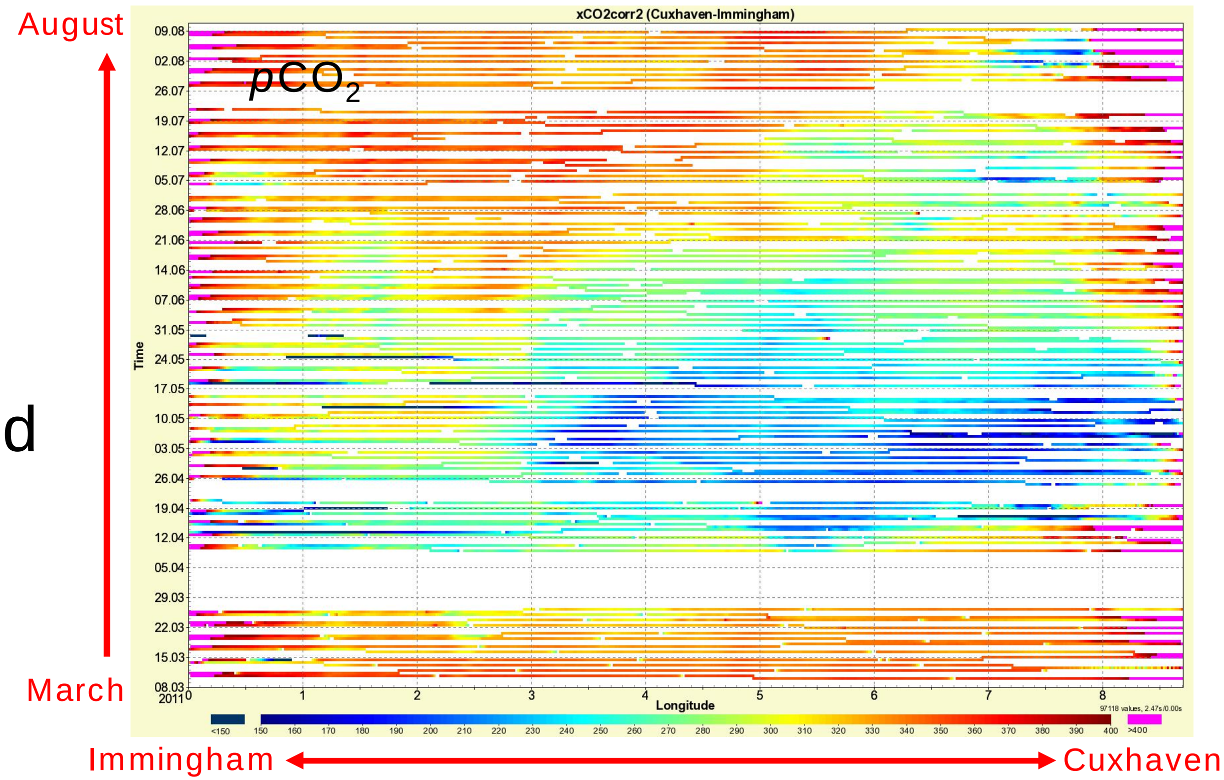
- cost effective and good to handle on SOO
- reduced demands on autonomy for new sensors developments
- high spatial and temporal resolution
- long-term records and seasonally resolution
- tracking of short-term biological processes



Sensors

pH – Principle

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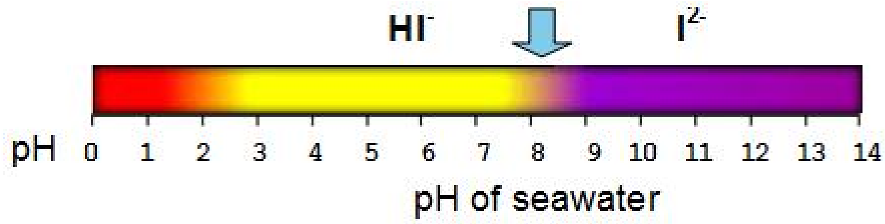
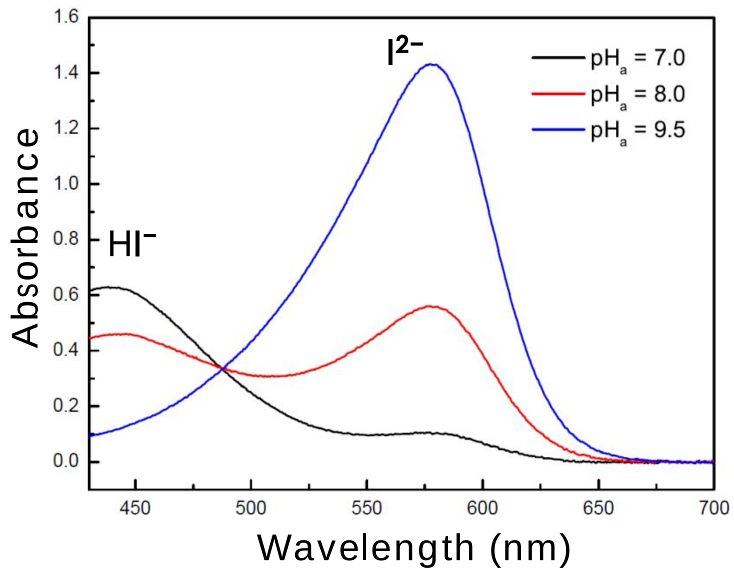
- FIA system using an indicator dye *m*-Cresol purple



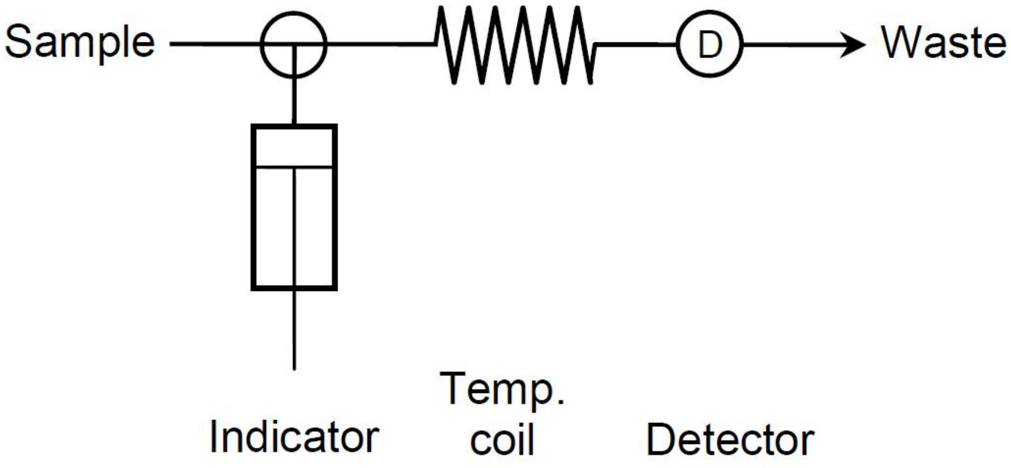
- Determination of the concentration of the indicator acid (HI^-) / base (I^{2-}) due to different absorption spectra

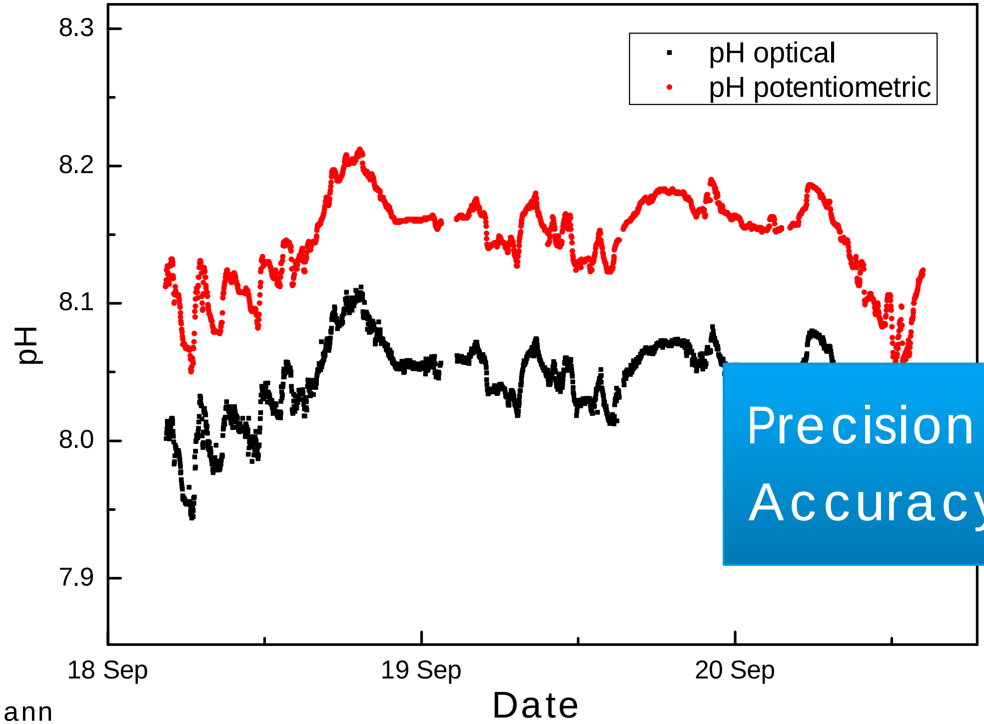


- Calculation of the pH value using Henderson–Hasselbalch equation

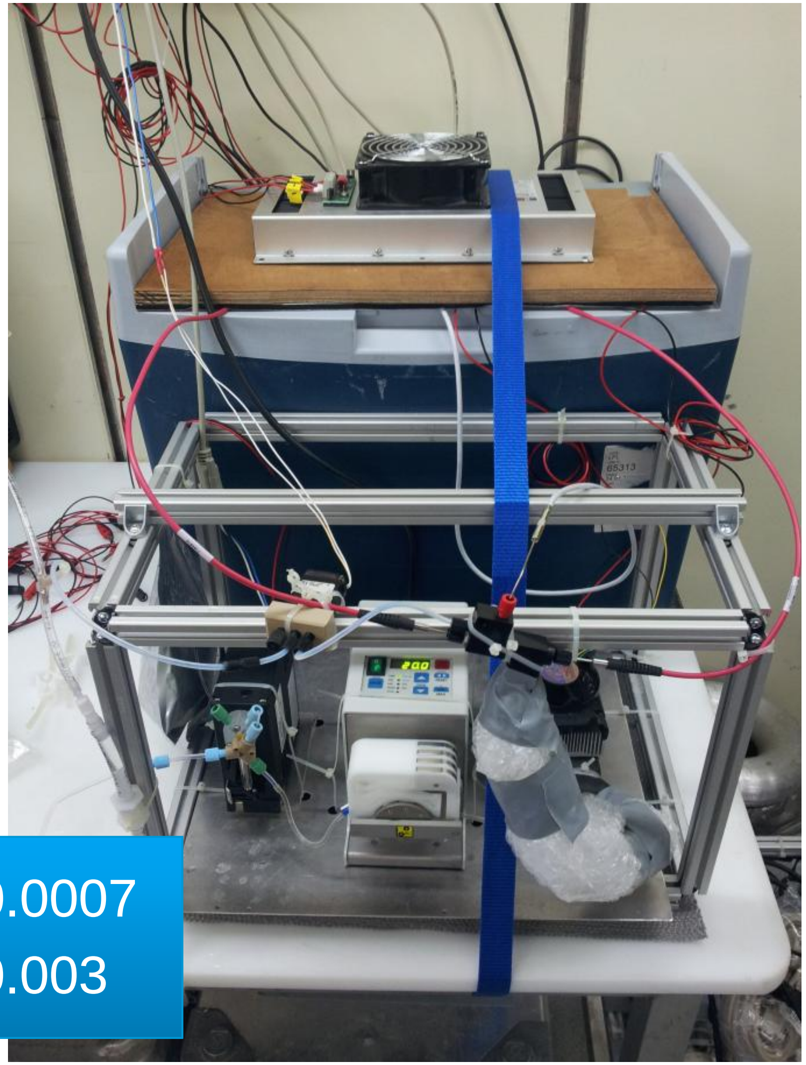
$$pH = pK_a + \log_{10} \frac{[I^{2-}]}{[HI^-]}$$

pH – Setup





Precision ± 0.0007
Accuracy ± 0.003



Aßmann et al., 2011

Total alkalinity (TA)

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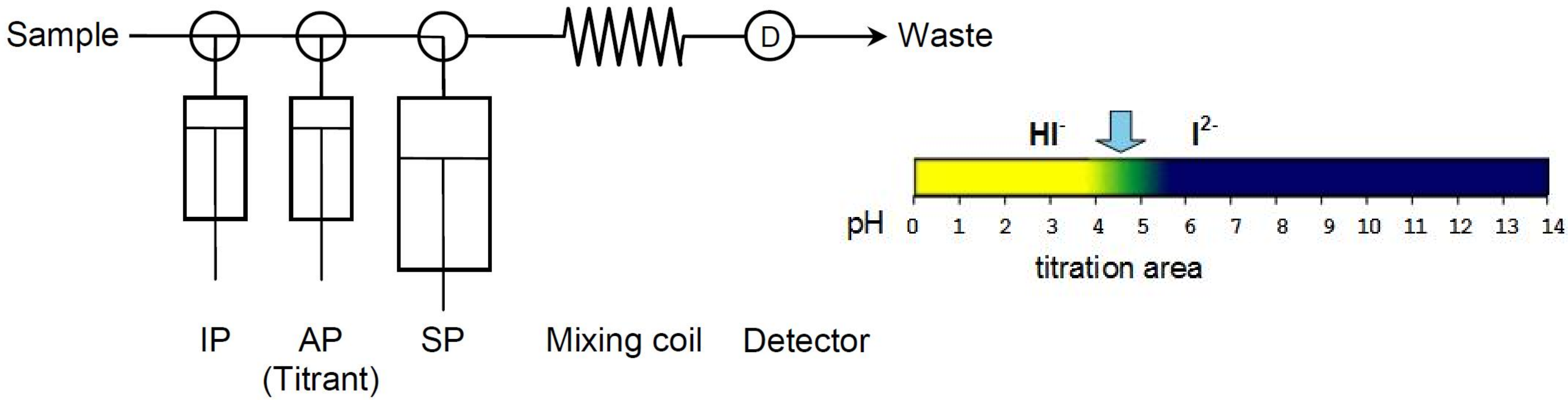
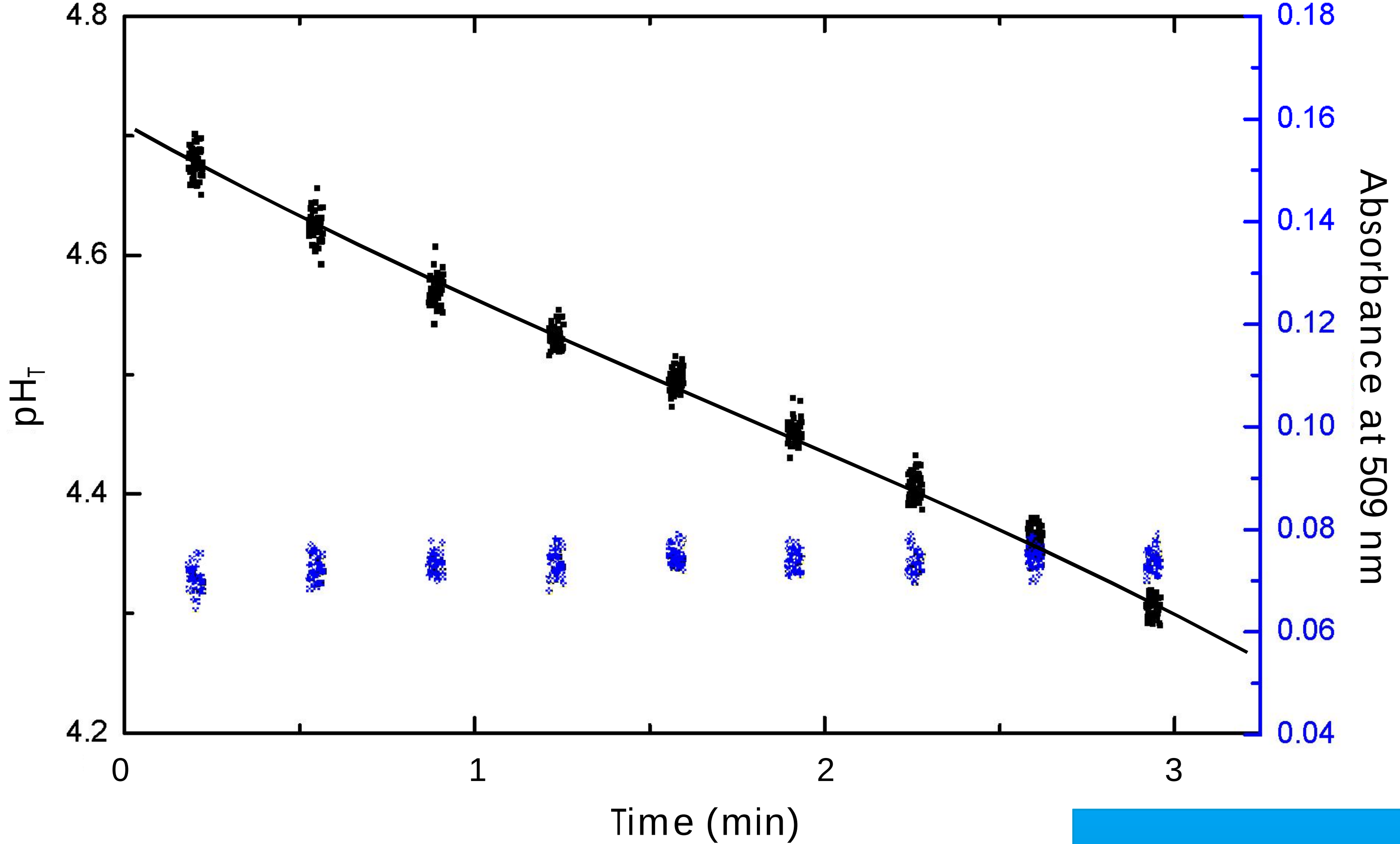


- Closed-cell titration with HCl (syringe aspirates simultaneously sample water, indicator dye and HCl)
- Monitoring of the titration curve (pH range of 3.5 to 5.5) by the acid-base indicator dye (Bromocresol green)
- Calculation of TA by a least-squares procedure based on a non-linear curve fitting approach

Aßmann, 2012

Total alkalinity (TA)



$$TA = \left[HCO_3^-\right] + 2\left[CO_3^{2-}\right] - \left[H^+\right] - \left[HSO_4^-\right]$$

$$0 = TA - DIC\left(\frac{K_1\left[H^+\right]_T + 2K_1K_2}{\left[H^+\right]_T^2 + K_1\left[H^+\right]_T + K_1K_2}\right) + S_T\left(\frac{1}{1 + K_S/\left[H^+\right]_F}\right) + \left(\frac{M_{SW} + M_A}{M_{SW}}\right)\left(\frac{\left[H^+\right]_T}{Z} - \frac{K_W}{\left[H^+\right]_T}\right) - \frac{M_A}{M_{SW}}N_A$$

Precision ± 5 µmol/kg

Accuracy ± 1 µmol/kg

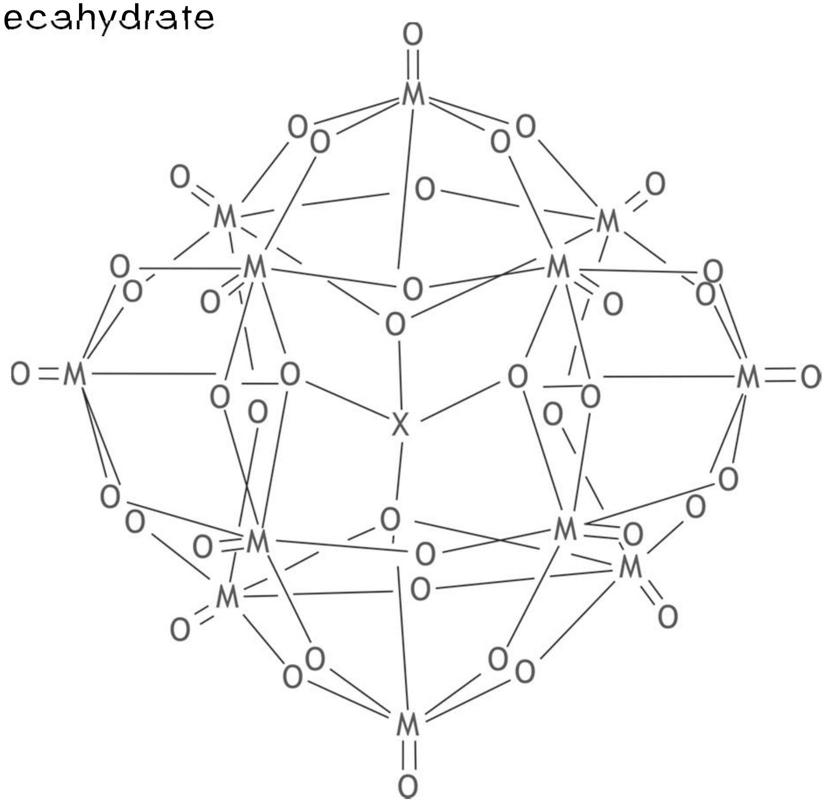
Phosphate – Principle

$$H_3PO_4 + 12(MoO_3) \rightarrow H_3PMo_{12}O_{40}$$

Phosphate + Molybdate → 12-Molybdophosphate hexadecahydrate

– Fluorescence quenching of Rhodamine 6G

– Excitation at 470 nm
Emission at 550 nm



Keggin structure

Phosphate – Setup / Data

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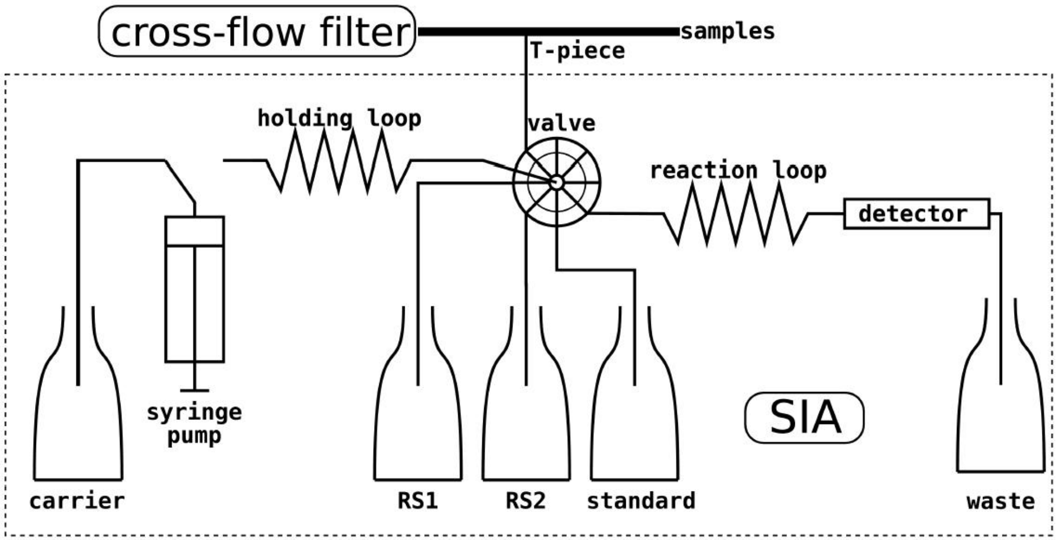

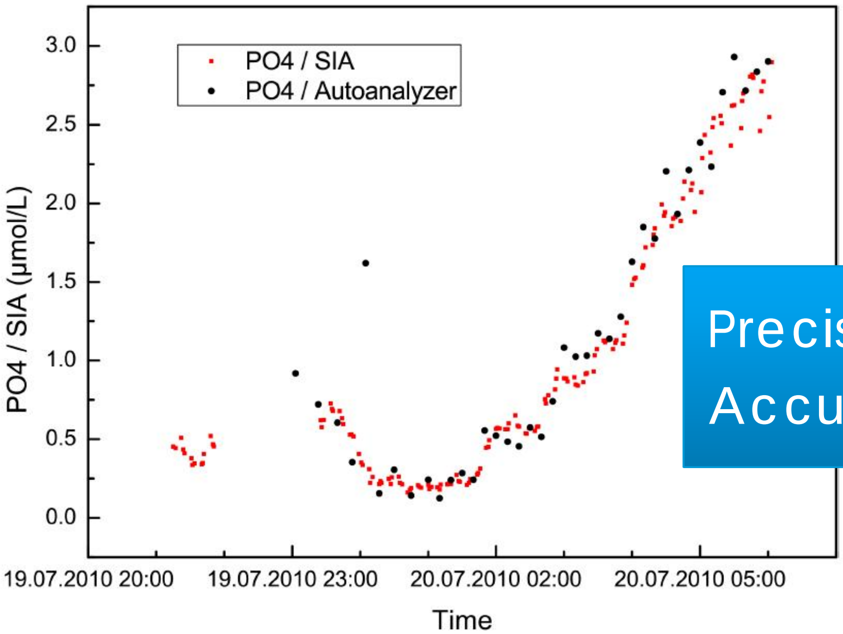

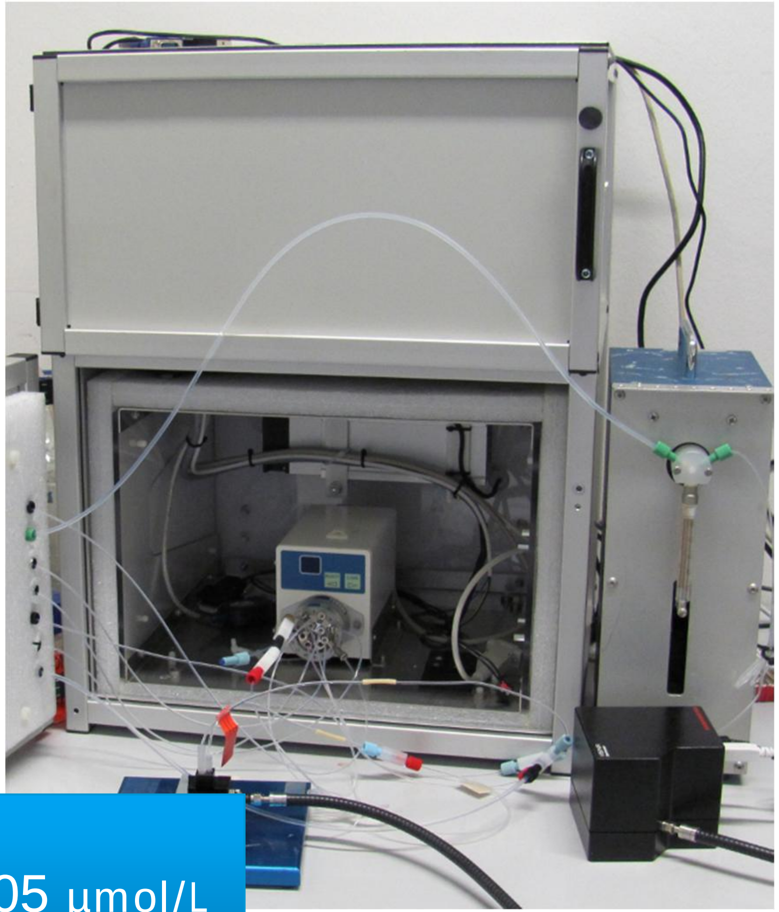

Precision
Accuracy
± 0.05 µmol/L

Frank & Schroeder, 2007
Frank et al., 2006

ft-PSICAM – Principle

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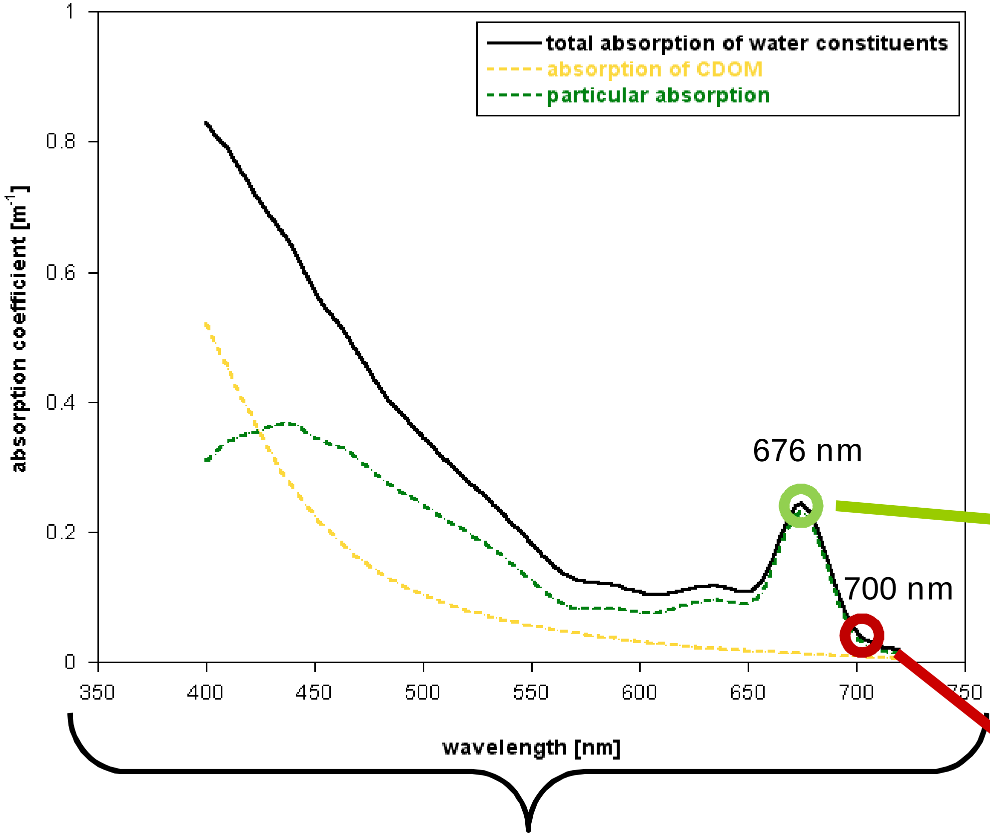


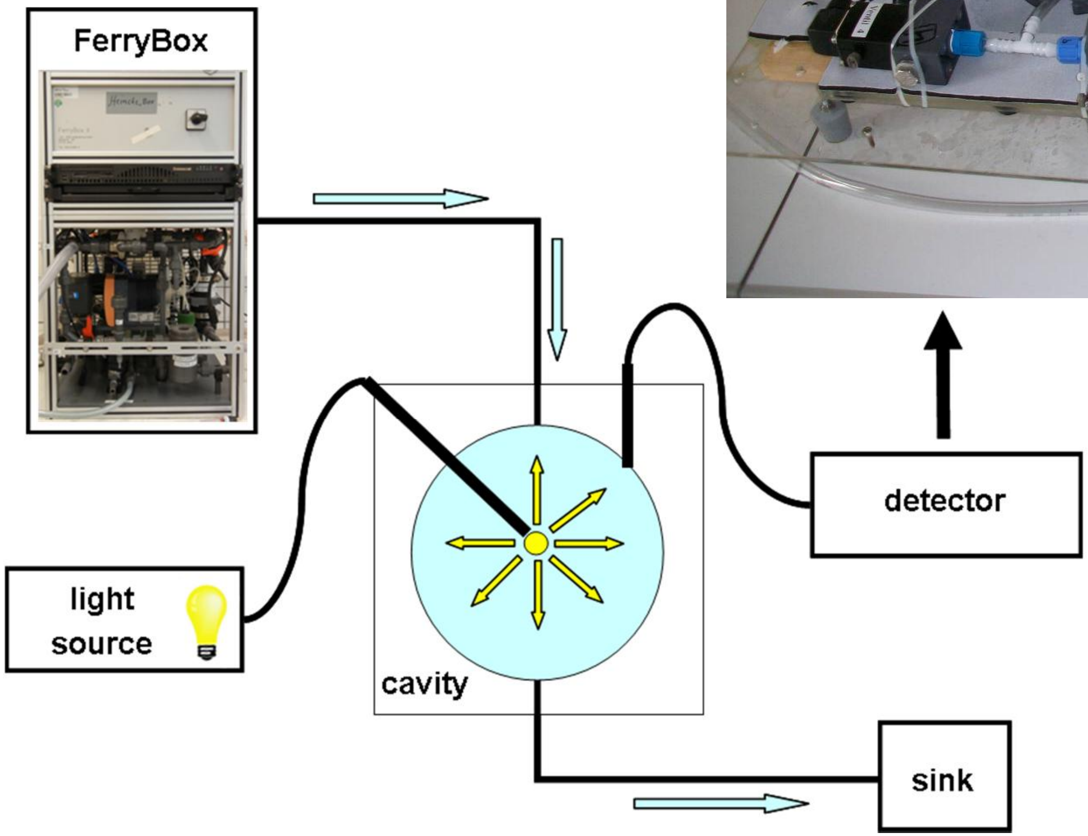
flow through –
Point Source Integrating
Cavity Absorption Meter

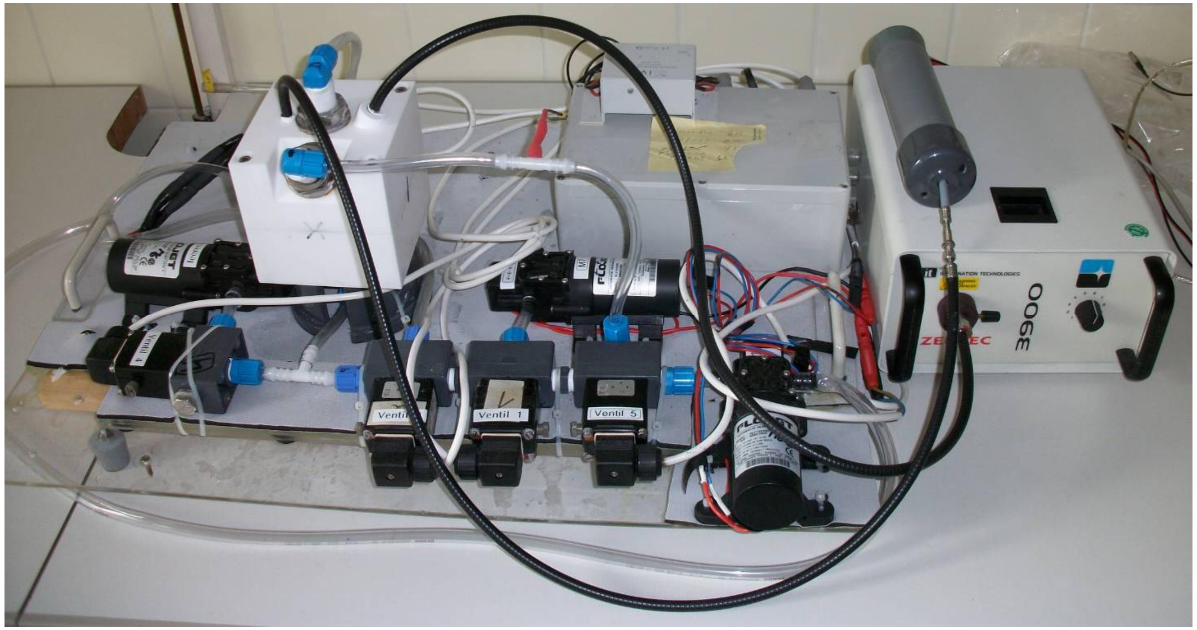
Absorption of chlorophyll-a

Total suspended matter (TSM)

Identification of algae groups

PSICAM – Setup





Precision ± 0.001 m^{-1}*

Accuracy ± 5 %*

*for TSM absorption at 700 nm

Röttgers et al., 2007

Wollschläger et al., 2012

PSICAM – Data

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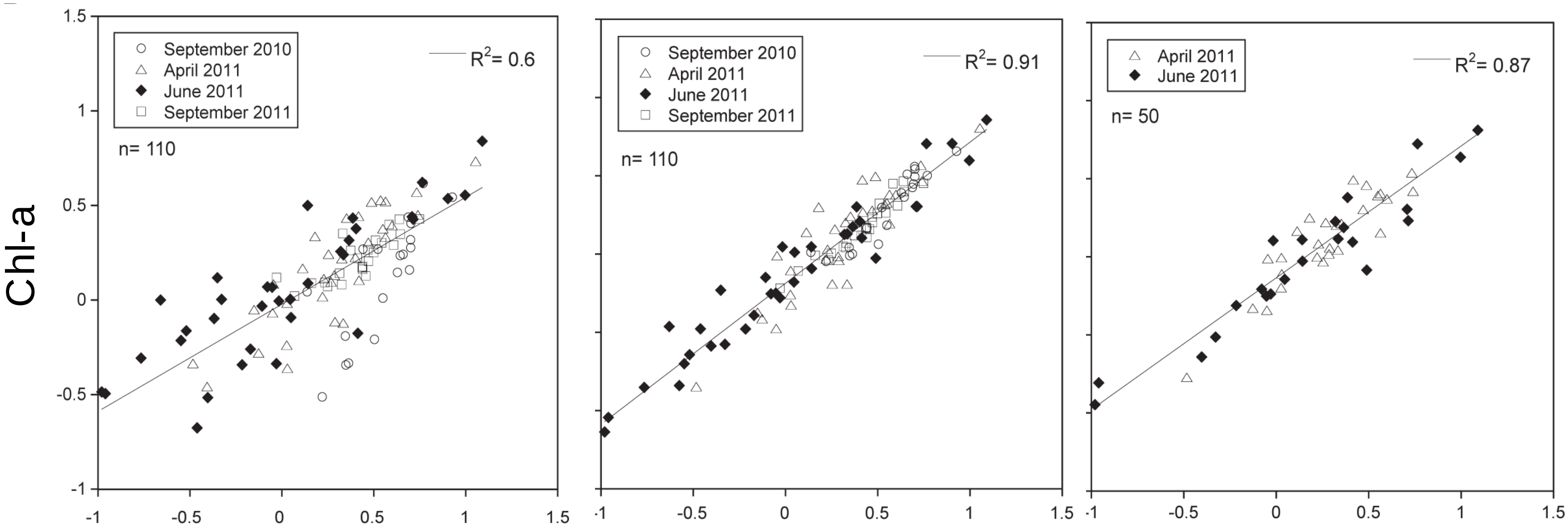
Chl-a Fluorescence | Chl-a PSICAM | Chl-a ft-PSICAM



Chl-a from HPLC

Summary

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	pH	TA	PO_4^{3-}	Absorption (PSICAM, 700 nm)
Accuracy	± 0.003 (with CRM)	± 1 µmol/kg	± 0.05 µmol/kg	± 5 %
Precision	± 0.0007	± 5 µmol/kg		± 0.001 m^{-1}
Meas. Cycle	1 min	5 min	1 min	1 min
Range	7.5–9.0	1.8–2.5 mmol/kg	0.1–10 µmol/kg	0.001–10 m^{-1}
Method	absolute	absolute	relative	absolute

Summary

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FerryBoxes are suitable platforms for sensor development and their final application.

Biochemical sensors are needed for monitoring and understanding the changes of the oceans.

- Nutrients for evaluation of the trophic status
- CO_2 parameters for assessment of ocean acidification
- Absorption measurements for tracking and identification of algae

Outlook

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- Fully characterized carbonate system
- Alkalinity transport between sediment and seawater into the ocean
- CO_2 air-sea fluxes (sinks / sources for CO_2)
- Quantification of production rates
- Comparison of productivity with estimates derived from diferent parameters (CO_2, O_2, Chl-a, winter nutrient stocks ...)
- Phytoplankton dynamics (e.g. seasonality ...)
- More reliable chlorophyll-a and turbidity data
- Differentiation of major algal groups by optical absorption signatures

New autonomous sensors for underway measurements

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Thank you

5th FerryBox Workshop

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