

Level up ocean carbon observations:

Successful implementation of a novel autonomous total alkalinity (A_T) analyzer on a commercial Ship of Opportunity (SOOP)

Katharina Seelmann¹, Tobias Steinhoff¹, Arne Körtzinger¹

¹GEOMAR Helmholtz Centre for Ocean Research Kiel



Contact: kseelmann@geomar.de

The ship



- M/V *Atlantic Sail* operated by Atlantic Container Line (ACL) between Europe and North America

The A_T analyzer

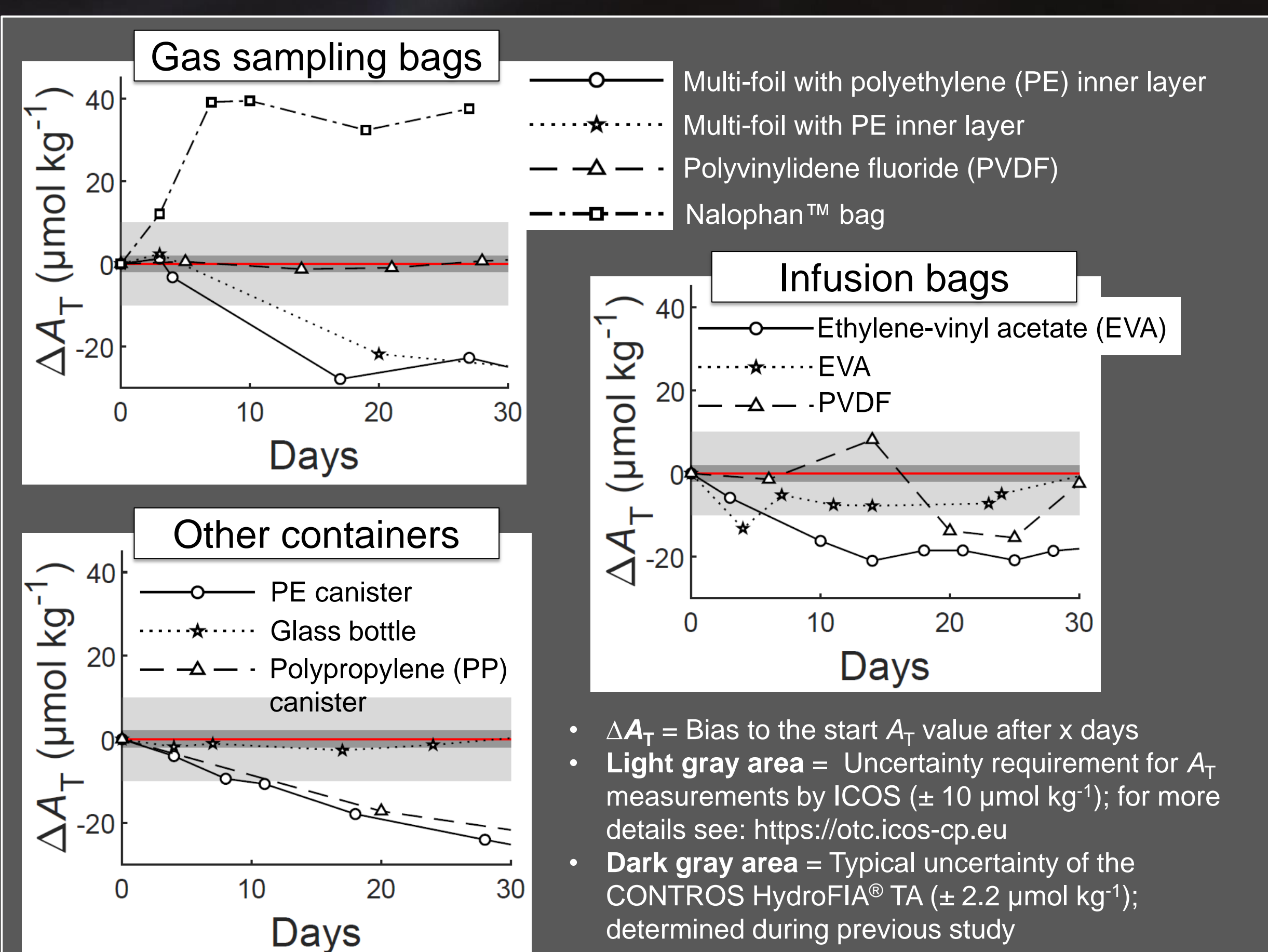
CONTROS HydroFIA® TA
(-4H-JENA Engineering GmbH, Germany)



- Measurement principle:** Single-point open-cell titration of the seawater sample with subsequent spectrophotometric pH determination (indicator dye = bromocresol green)
- Measurement interval:** 15 min
- Daily reference measurements for drift correction and quality assurance (à 5 consecutive measurements)

High-volume reference seawater storage tests

- Standard Certified Reference Material (CRM) bottles (500 mL) are not sufficient for long-term deployments
- Testing several high-volume (5 L) container types and materials with respect to their suitability to stably store seawater over a long time (max. 30 days)



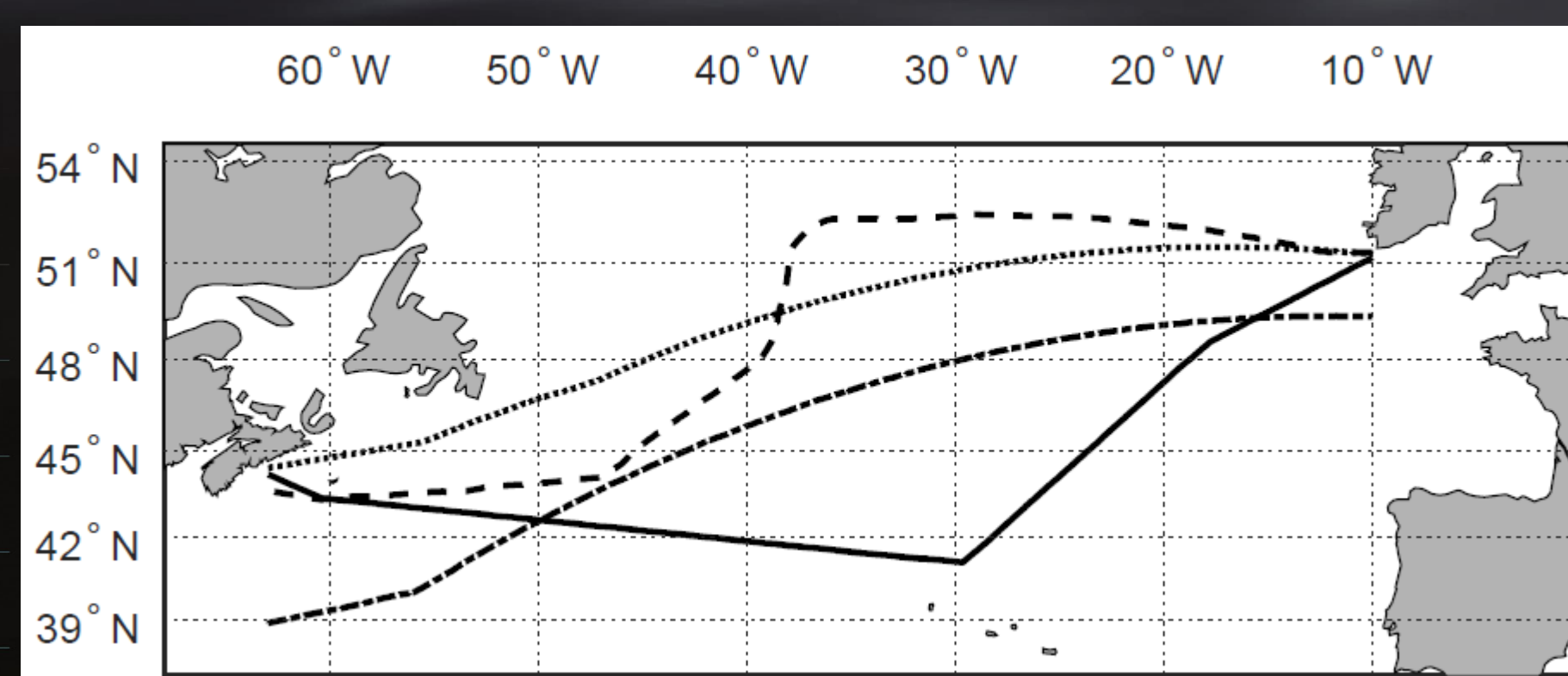
- Stability requirements:**
 - ✓ Must: All Δ A_T within $\pm 10 \mu\text{mol kg}^{-1}$
 - ✓ Ideal: All or most Δ A_T within $\pm 2.2 \mu\text{mol kg}^{-1}$
- Only the **gas sampling bag made of PVDF** fulfills the requirements (average bias = $0.2 \pm 1.3 \mu\text{mol kg}^{-1}$)
- All reference measurements on the ship were conducted out of a 5 L PVDF gas sampling bag

Installation in the ship's engine room



- CONTROS HydroFIA® TA system
- Crossflow filter device (-4H-JENA Engineering GmbH, Germany) for A_T measurements (0.2 μm filter)
- SBE 21 SeaCAT Thermo-salinograph (Sea-Bird Electronics, USA) and seawater manifold
- Electric box (containing the main electrical management and the control computer)
- General Oceanics (GO) underway $p\text{CO}_2$ system 8050 (USA) for autonomous $p\text{CO}_2$ measurements

First four measurement campaigns



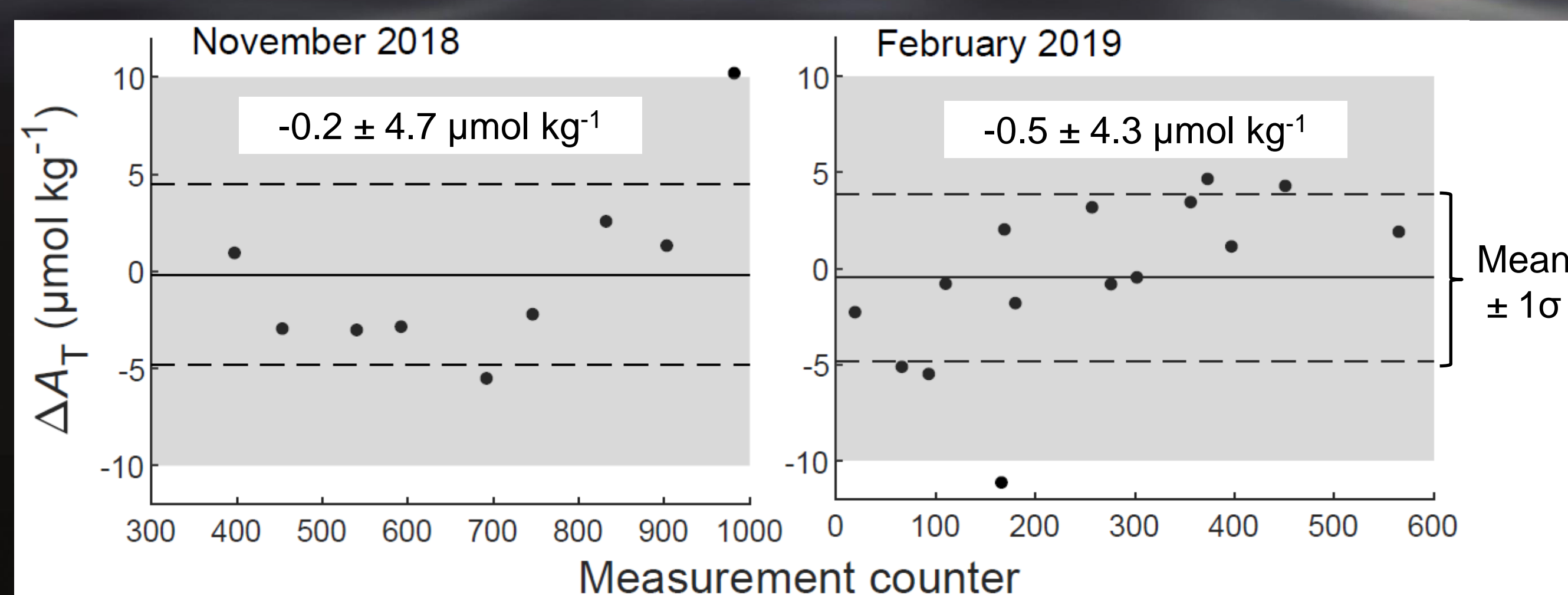
With one of our working group onboard (with discrete sampling):

— 30 October 2018 - 06 November 2018 (Towards West)
- - 05 February 2019 - 11 February 2019 (Towards East)

Entirely unattended:

- - 25 February 2019 - 05 March 2019 (Towards West)
- - 15 March 2019 - 20 March 2019 (Towards East)

Intercomparison with discrete samples



Bias (Δ A_T) between autonomously measured A_T (drift corrected) and A_T values of discrete samples

Conclusion

- ✓ Stable high-volume CRM storage for regular reference measurements during campaigns was found → 5 L PVDF gas sampling bag
- ✓ After installation → four measurement campaigns with autonomous A_T measurements were conducted (two of them with discrete sampling)
- ✓ Comparison between autonomous A_T values (drift corrected using CRM out of PVDF gas sampling bag) and A_T values of discrete samples
 - Slight deterioration compared to previous field characterization ($-0.3 \pm 2.8 \mu\text{mol kg}^{-1}$ with freshly opened CRM bottles for each reference measurement)
 - But: Entire fulfillment of uncertainty requirements for SOOP lines given by ICOS ($\pm 10 \mu\text{mol kg}^{-1}$)
- ✓ Implementation of autonomous A_T measurements was successful