

# pH optodes for CO<sub>2</sub> leakage detection

<u>Sergey M Borisov</u>, Hannah Wright, Rudi Hanz, Socratis Loucaides, Birgit Ungerböck, Bernhard J Müller, Christoph Staudinger, Jan Fischer, Dirk de Beer, Moritz Holtappels



# Optodes



Optical sensors (optodes) are sensors measuring a certain parameter with help of an optical chemical transducer

EMM-CCS

- Oxygen optodes are state-of-the-art: PreSens, PyroScience, Aanderaa etc.

 pH optodes are less established particularly for oceanographic applications



# **General advantages of optodes**



- simple fabrication and potentially low cost
- no electrical interferences
- multi-analyte sensing
- contactless sensing
- versatility of formats





# **pH Optodes**



pH 9







# Sensors for CO<sub>2</sub> release experiment

I. Optodes for measurements in water column





- Length: 270 mm (with protective cap), Ø 63 mm
- Aluminium/Titanium housing
- Integrated battery and logger
- Resistance thermometer for T compensation
- Can be used in combination with pH or O<sub>2</sub> sensors

Screw-able cap with sensing material (pH or O<sub>2</sub>)







#### **Fiber-optic sensor type**

- Plastic optical fiber (core  $\varnothing$  1 mm) with SubPort connector
- 25 cm stainless steel sleeve to prevent bending in sediments
- Logger designed by MPI Bremen



### **Challenges in material development**



**a** and **b** – before and after 12 h exposure to the sediment

EMM-CCS

Some of the sensor materials showed drastic performance decrease in Sediment from Goldeneye  $\Rightarrow$  new particle-based material for both water column and sediment measurements



# III. Fast microoptodes for eddy covariance



Tapered 430 µm glass fiber



#### **Characteristics**

- Small size
- ③ Very fast response
- Time consuming manufacture procedure
- No referencing yet, more difficult to calibrate
- Much faster drift due to photobleaching
- The sensors have not been used during the release experiment
  Promising analytical tools if the performance is further improved



# **Release experiment: detection in water column**



#### Optode bundle operated by ROV



# 3 pH and 2 oxygen optodes deployed simultaneously





- noise of the pH optodes  $\pm 0.002$  pH units
- abrupt pH increase is up to 0.05 pH units during CO<sub>2</sub> release
- oxygen optode does not show significant variations of C(O<sub>2</sub>)

Response of 3 pH optodes during 10I/min gas flow



This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 654462



EMM-CCS





# 30I/min gas flow



# **Release experiment: detection in sediment**









- Two closest sensors show drop of pH accompanied by temperature change
- Both effects are stronger for the 1.4 m sensor
- No change in parameters for the 4.0 and 7.0 m sensors, slow change may be due to drift of the pH sensors
- $\ensuremath{\mathfrak{S}}$  damage of fibers during recovery  $\Rightarrow$  no recalibration and drift correction



# **Conclusions and perspectives**

- pH optodes are promising tools for detection of CO<sub>2</sub> leakage
- Versatility of formats enables monitoring in water column and in sediment
- Further miniaturization and multiplexing is desirable and technologically is feasible











Multi fiber optode: J. Fischer, K. Koop-Jakobsen, Sens. Actuators B, 2012, 168, 354-359 SDR SensorDish<sup>®</sup> from PreSens



# Acknowledgements



Technical support in TU Graz (Anna Walcher, Matthias Schwahr, Eveline Maier) Crews and operators of the RRS James Cook and RV Poseidon People involved in preparation of the release experiment

