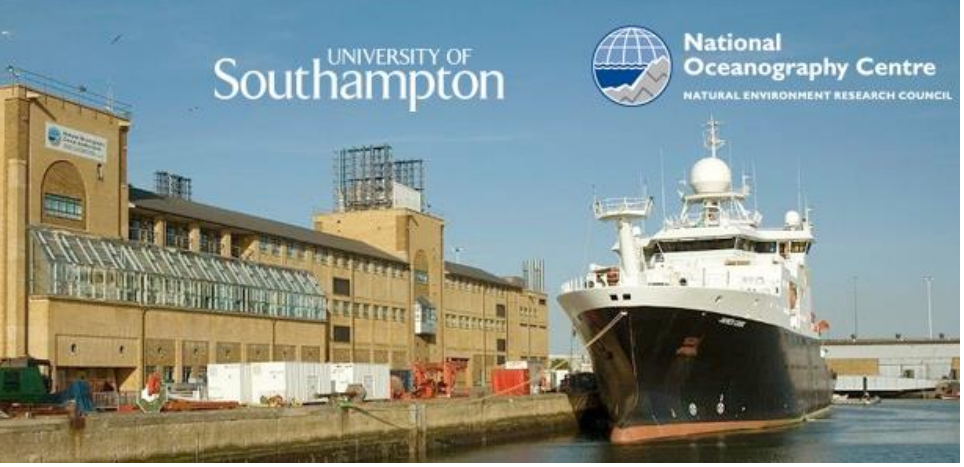


Sensor development at NOC

Dr Alex Beaton

a.beaton@noc.ac.uk

Ocean Technology and Engineering Group

National Oceanography Centre, Southampton

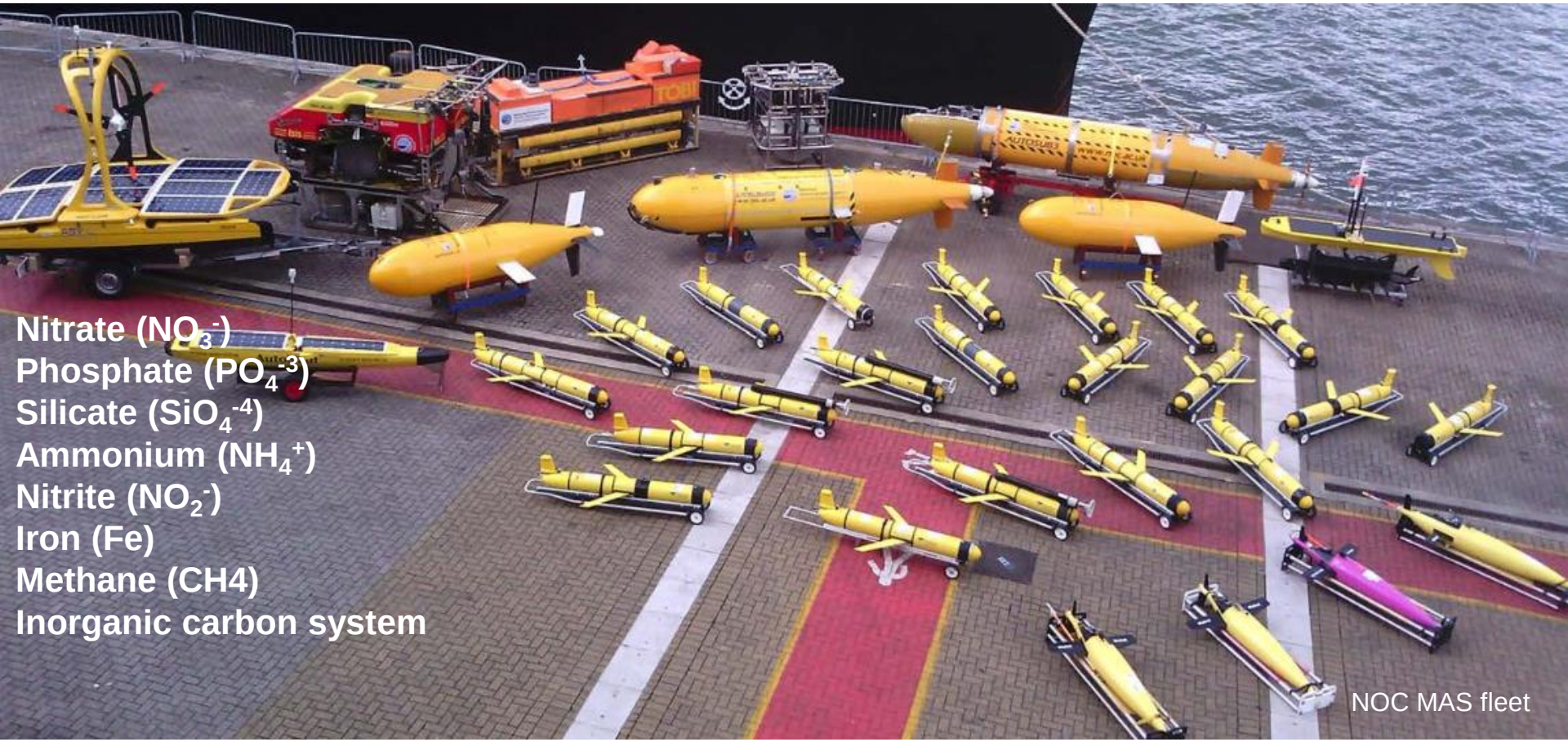
NOC: research, technology

Ocean Technology and Engineering Group (OTEG)

Mission (***"To develop novel technology and engineering resulting in the greatest impact for environmental and marine science"***)

Goal

Enable multi-parameter chemical sensing across autonomous marine platforms



NOC MAS fleet

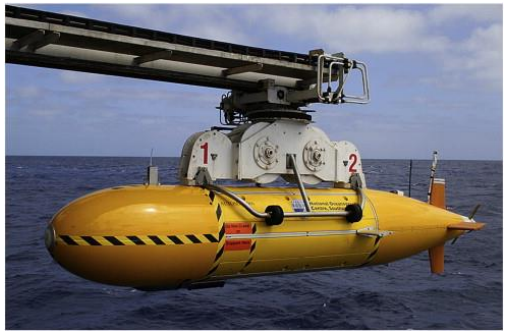
Chemical sensors in marine autonomy

High

Sensor size and power

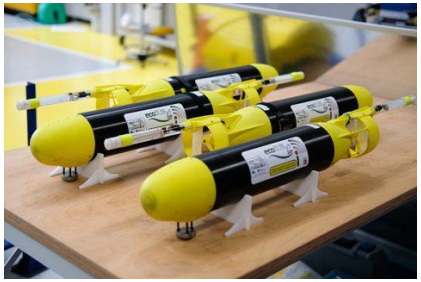
Low

Large AUVs



Underwater gliders

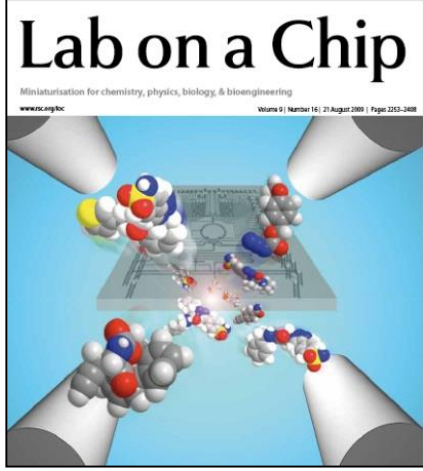
Micro AUVs



Talk focus

- Lab-on-chip sensor platform (multiple parameters)
- STEMM project (CCS leakage monitoring)
- Miniaturised optical methane sensors
- MAPS – Marine Autonomous Particle Sampler

Lab-on-chip technology

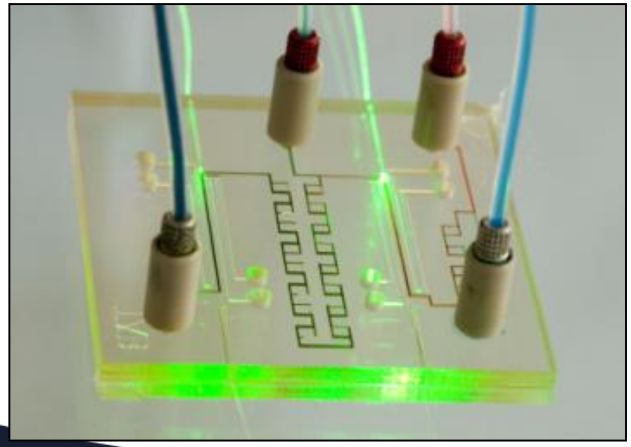


"Microfluidics"

Complex lab-based chemical analysis process

Lab-on-chip

Miniaturisation and automation



Lab-on-chip device

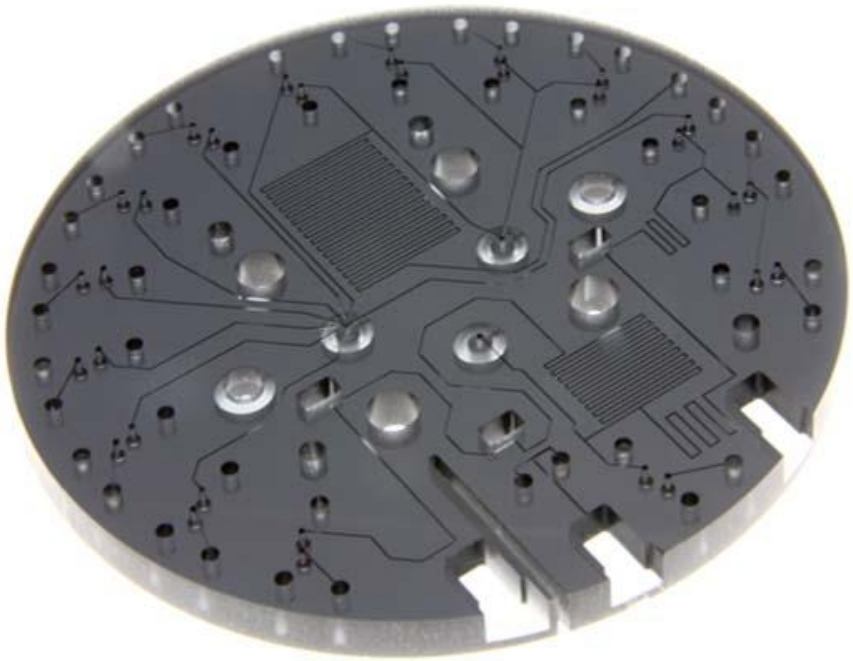
Advantages:

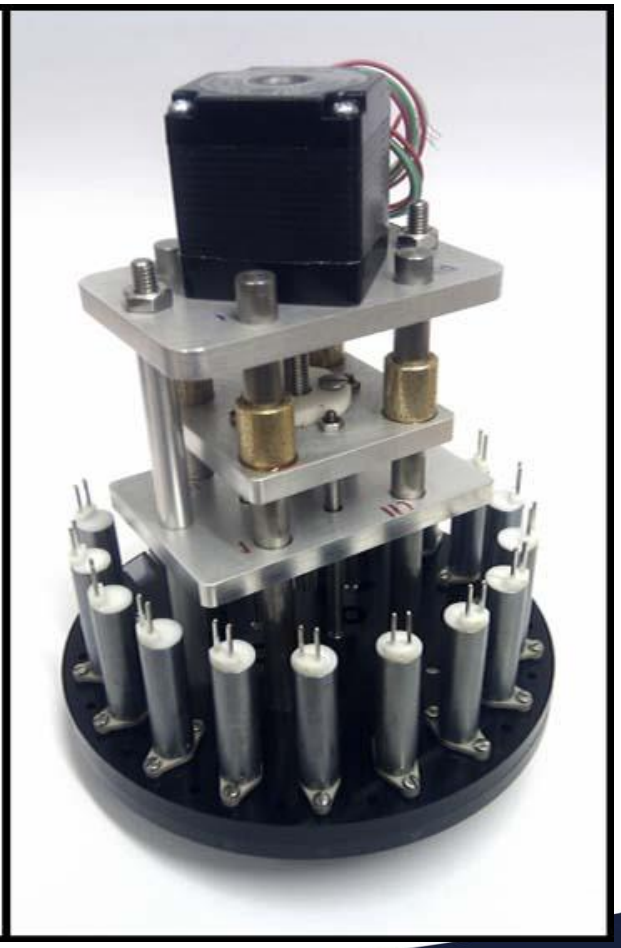
- Rapid prototyping
- Small sample size required
- Lower reagent usage
- Many parameters

LAB

CHIP

100 mm

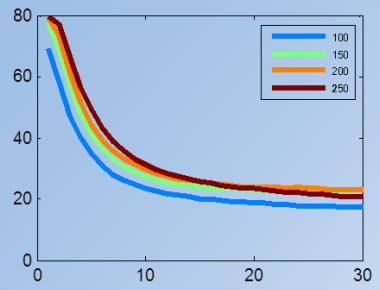




Lab-on-chip for nitrate and nitrite analysis

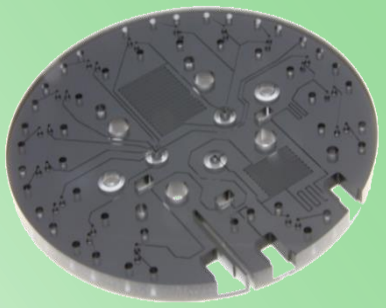
150 µm width channels milled into a polymer substrate

LOC Sensor	Analytical method	Measurement type	LOD/precision*
Nitrate + nitrite	Griess assay (with Cd reduction)	Colourimetry (absorbance)	20 nM
pH	Thymol blue	Dual wavelength absorbance	0.001 pH units*
Phosphate	Molybdenum blue (modified)	Colourimetry (absorbance)	20 nM
Iron (II), Iron (III)	Ferrozine (with ascorbic acid reduction for Fe (III))	Colourimetry (absorbance)	1 nM
Silicate	Silicomolybdic acid	Colourimetry (absorbance)	100 nM
Ammonium	OPA + membrane	Fluorescence	(1 nM)
Total alkalinity	BCG with TMT or single step	Dual wavelength absorbance	2 µM
DIC	Membrane+ EC of NaOH	Conductivity	10 µM
Organic N and P	UV digester + inorganic system	Colourimetry (absorbance)	(20 nM)

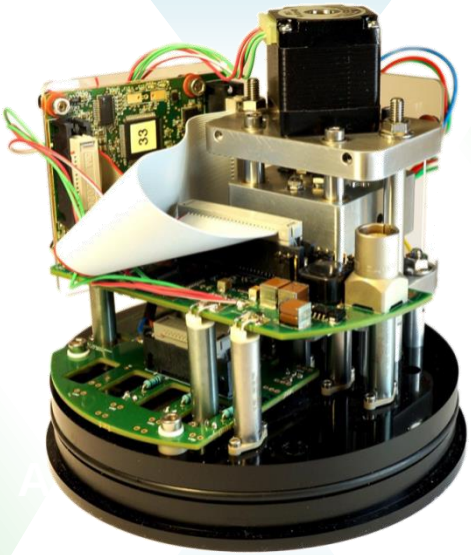


State of the art analytical assays

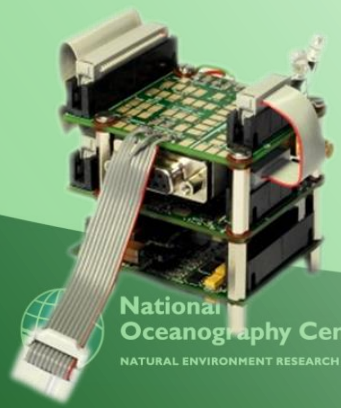
Microfluidics



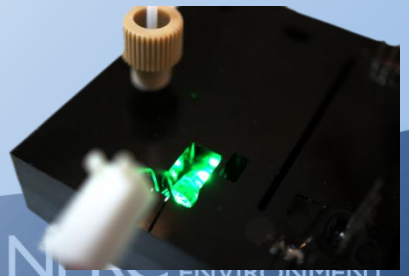
Lab on a chip



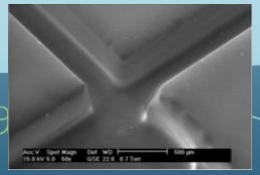
Pressure tolerant electronics



High performance low-cost optics



Low-cost manufacturing

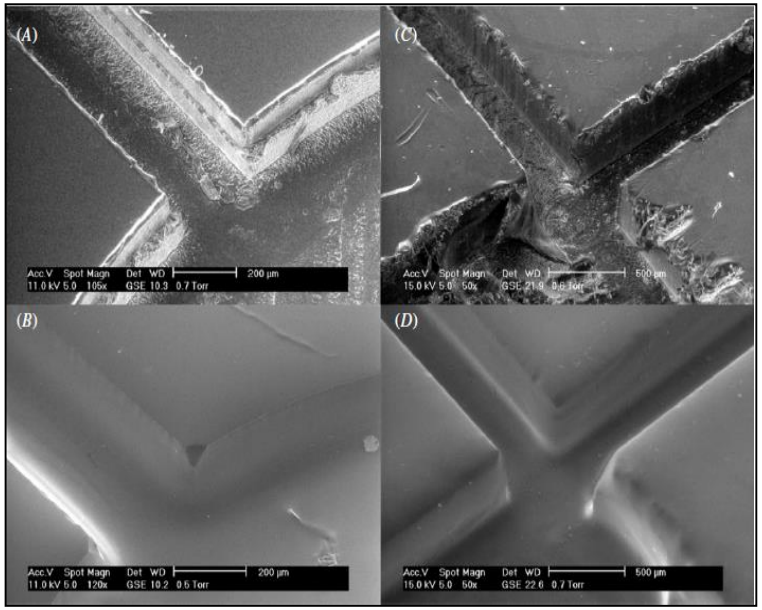


National Oceanography Centre
NATURAL ENVIRONMENT RESEARCH COUNCIL

NERC ENVIRONMENT

Lab-on-chip production

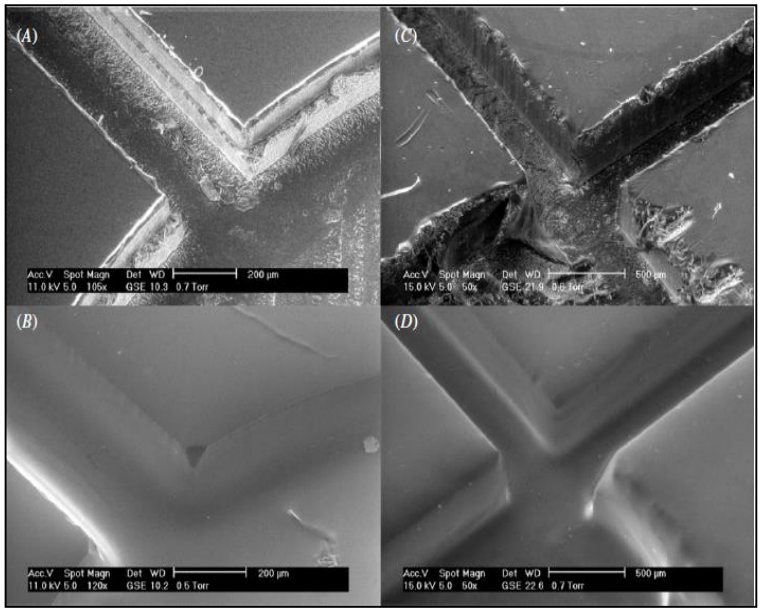
Datron Neo CNC machine



Optical quality channels

Micromilling PMMA, followed by solvent vapour bonding procedure

Lab-on-chip production



IOP Publishing — Journal of Micromechanics and Microengineering
J. Micromech. Microeng. **20** (2010) 065016 (8pp) — doi:10.1088/0960-1317/20/6/065016

Reduction of surface roughness for optical quality microfluidic devices in PMMA and COC

I R G Ogilvie[1], V J Sieben[1,2], C F A Floquet[2], R Zmijan[1], M C Mowlem[2] and H Morgan[1]

[1] Nanoscale Systems Integration Group, University of Southampton, Southampton, SO17 1BJ, UK
[2] National Oceanography Centre, University Of Southampton, Southampton, SO14 3ZH, UK

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journal homepage: www.elsevier.com/locate/talanta

Short communication

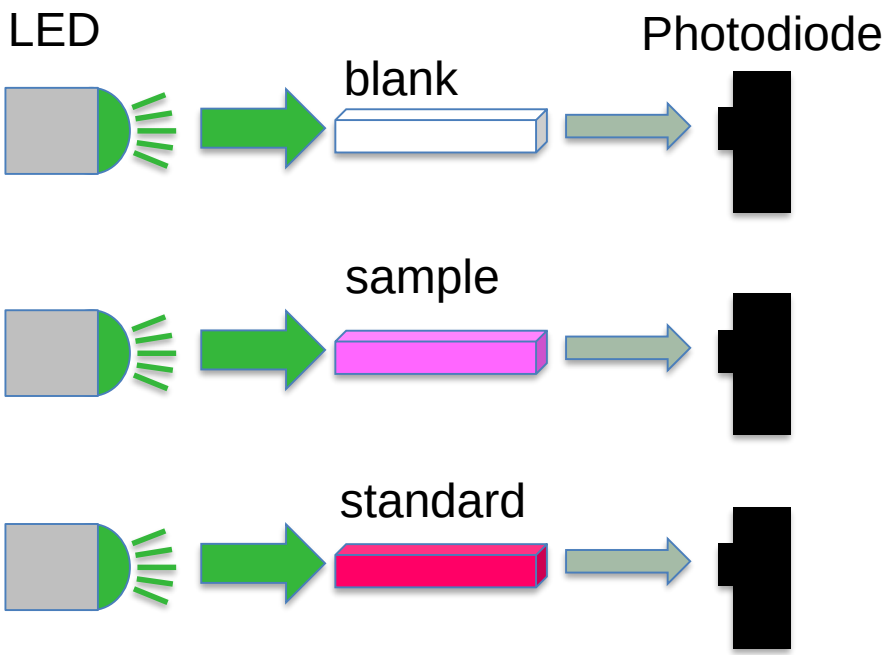
Nanomolar detection with high sensitivity microfluidic absorption cells manufactured in tinted PMMA for chemical analysis

Cedric F.A. Floquet[a,*], Vincent J. Sieben[a,b], Ambra Milani[a], Etienne P. Joly[a,3], Iain R.G. Ogilvie[a,b], Hywel Morgan[b], Matthew C. Mowlem[a]

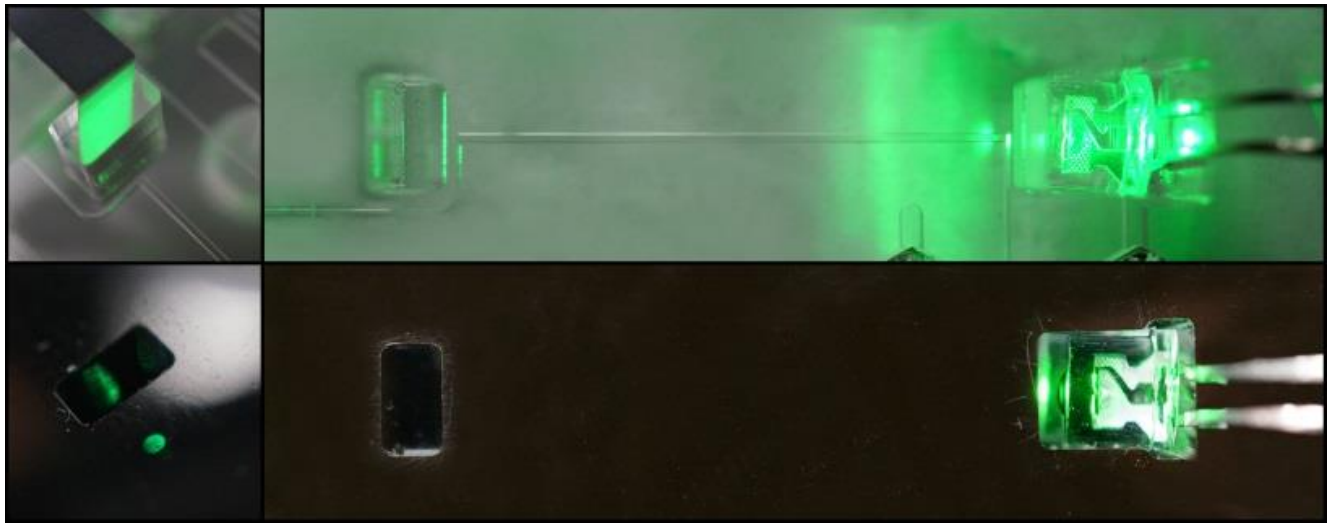
[a] National Oceanography Centre, University of Southampton, Southampton SO14 3ZH, UK[1]
[b] Nanoscale Systems Integration Group, University of Southampton, Southampton SO17 1BJ, UK[2]

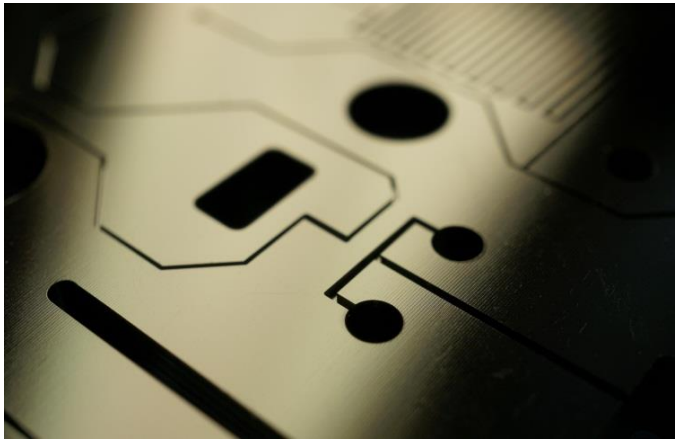
How the platform operates

- Colour-forming chemical reaction
- followed by a colourimetric optical absorbance measurement
- Optical blanks, analytical blanks and standard measurement can be taken for each sample measurement
- Stopped-flow measurement



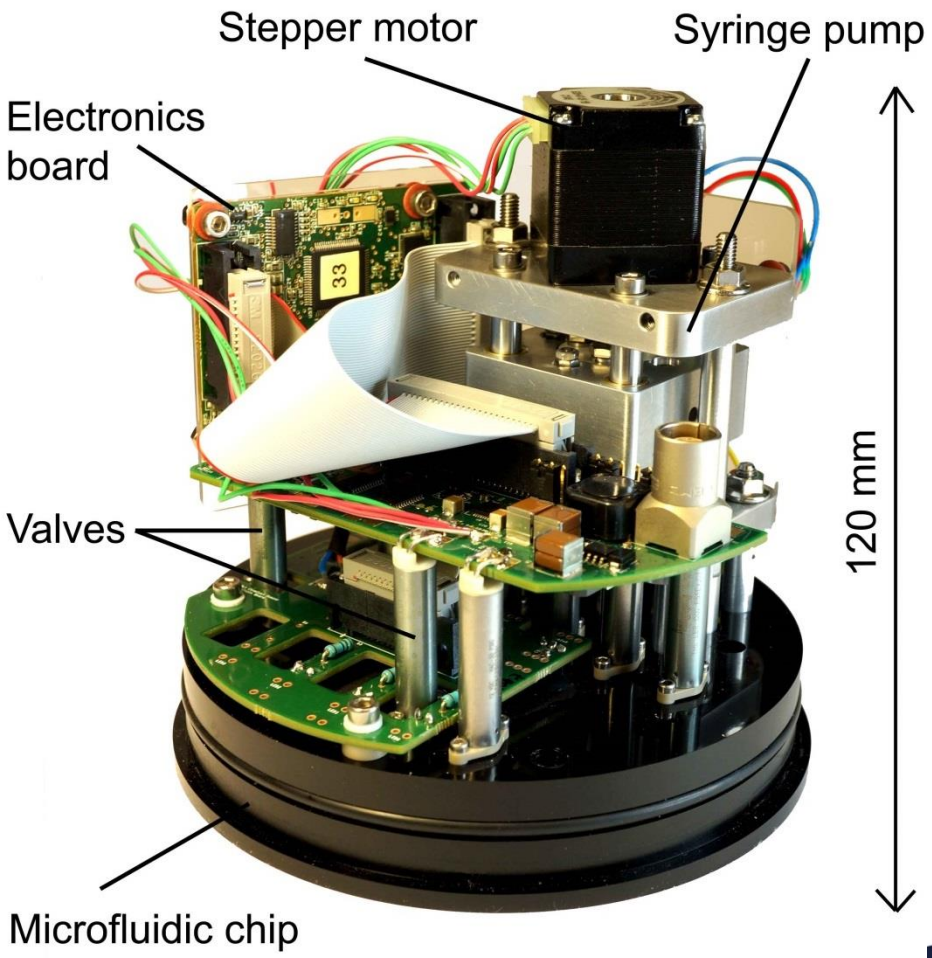
Tinted PMMA optical absorbance cell





Lab-on-chip chemical sensor platform

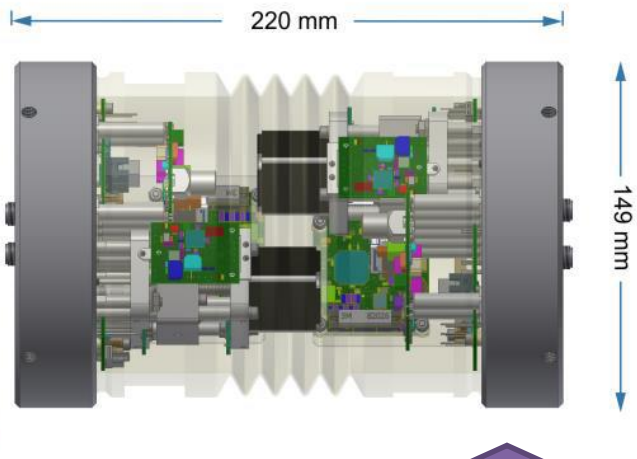
- Microfluidic colourimetric analyser
- Limit of detection: 0.025 µM (nitrate), 0.04 µM (phosphate), 0.1 µM (silicate)
- Range: up to 1000 µM (nitrate)
- Low sample volumes (~320 µL per sample)
- Low power consumption (~1.5 W)
- Has been adapted to several parameters:
- Works in the deep sea (deepest deployment to date: 4800 m)



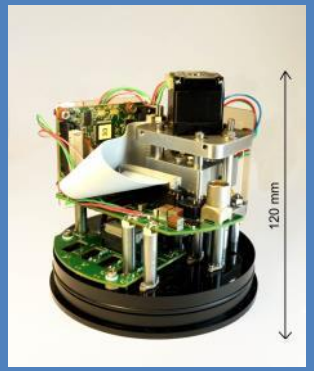
LOC Carbonate Chemistry Autonomous Sensor System

DIC

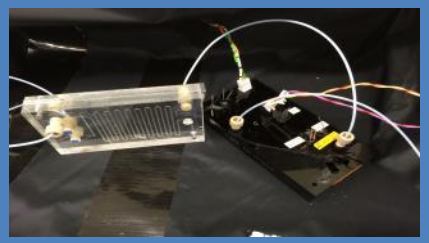
TRL4

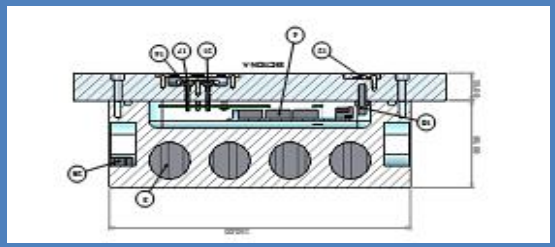


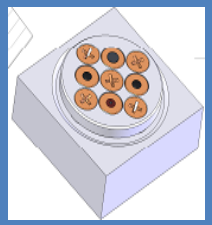
pH_{SPEC} TRL6



TA TRL4







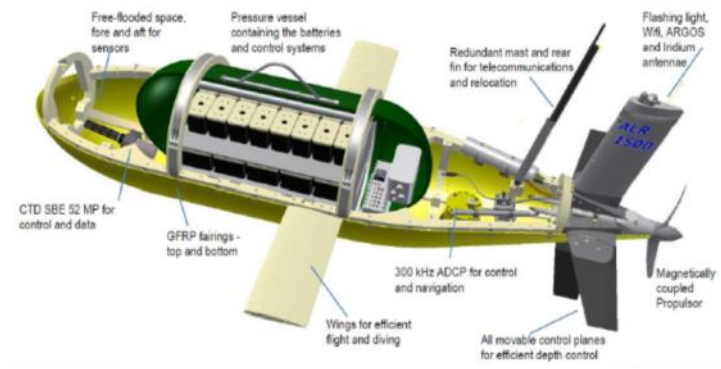
TRL6

pHIMS

How do they get deployed?

Integration with autonomous vehicles

Seaglider



Autosub LR

AutoNaut

ASV C-Enduro

Slocum

Waveglider

LOC sensor Seaglider integration

Measures every 5-6 minutes

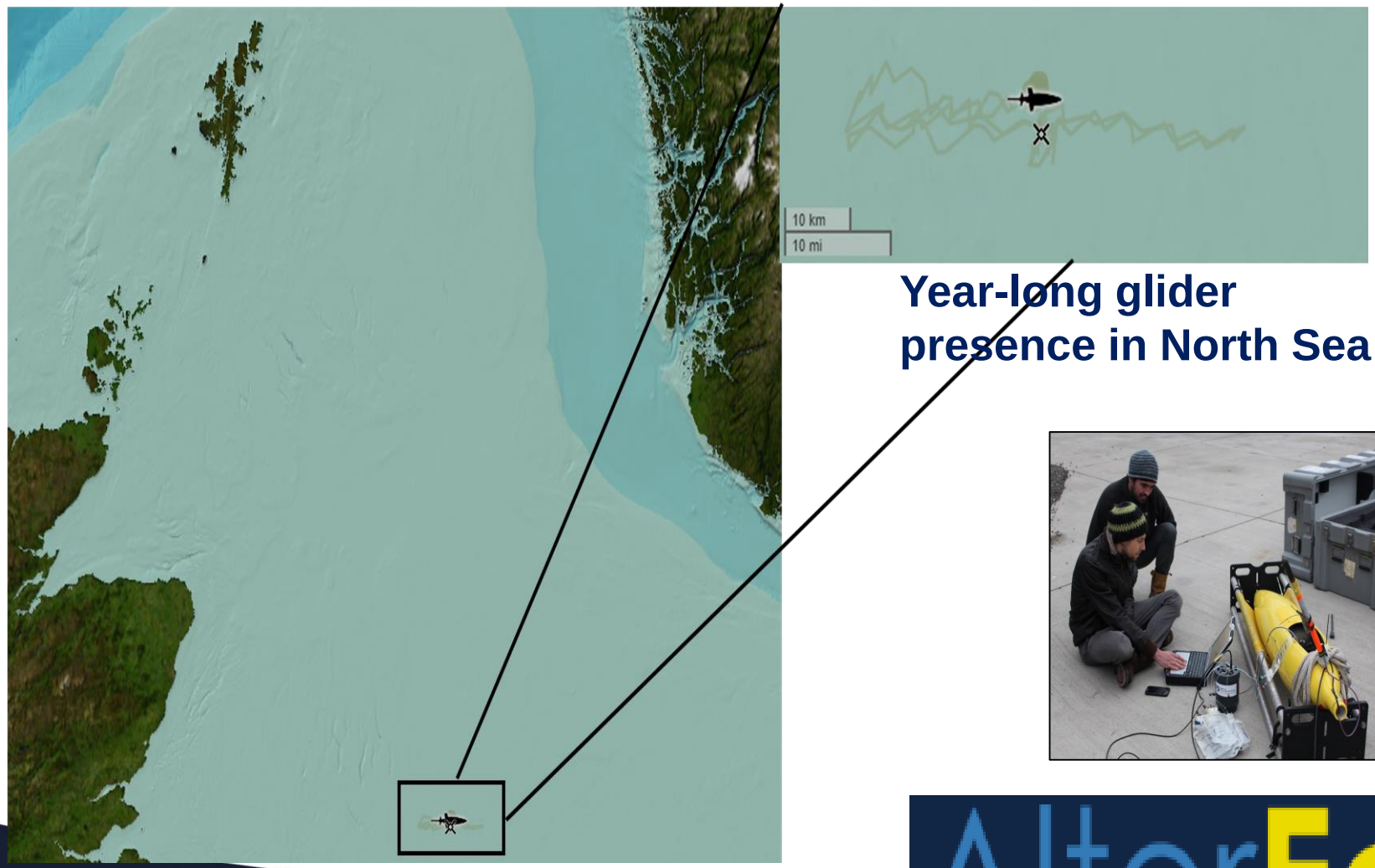
Capable of 1000 m deep dives containing 22 discrete chemical measurements per dive

3 month deployments

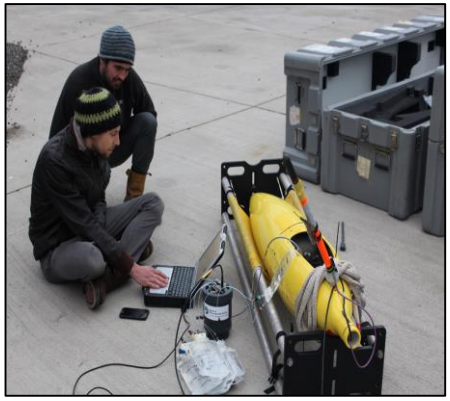
320 µL sample volume

Data storage communication via Iridium

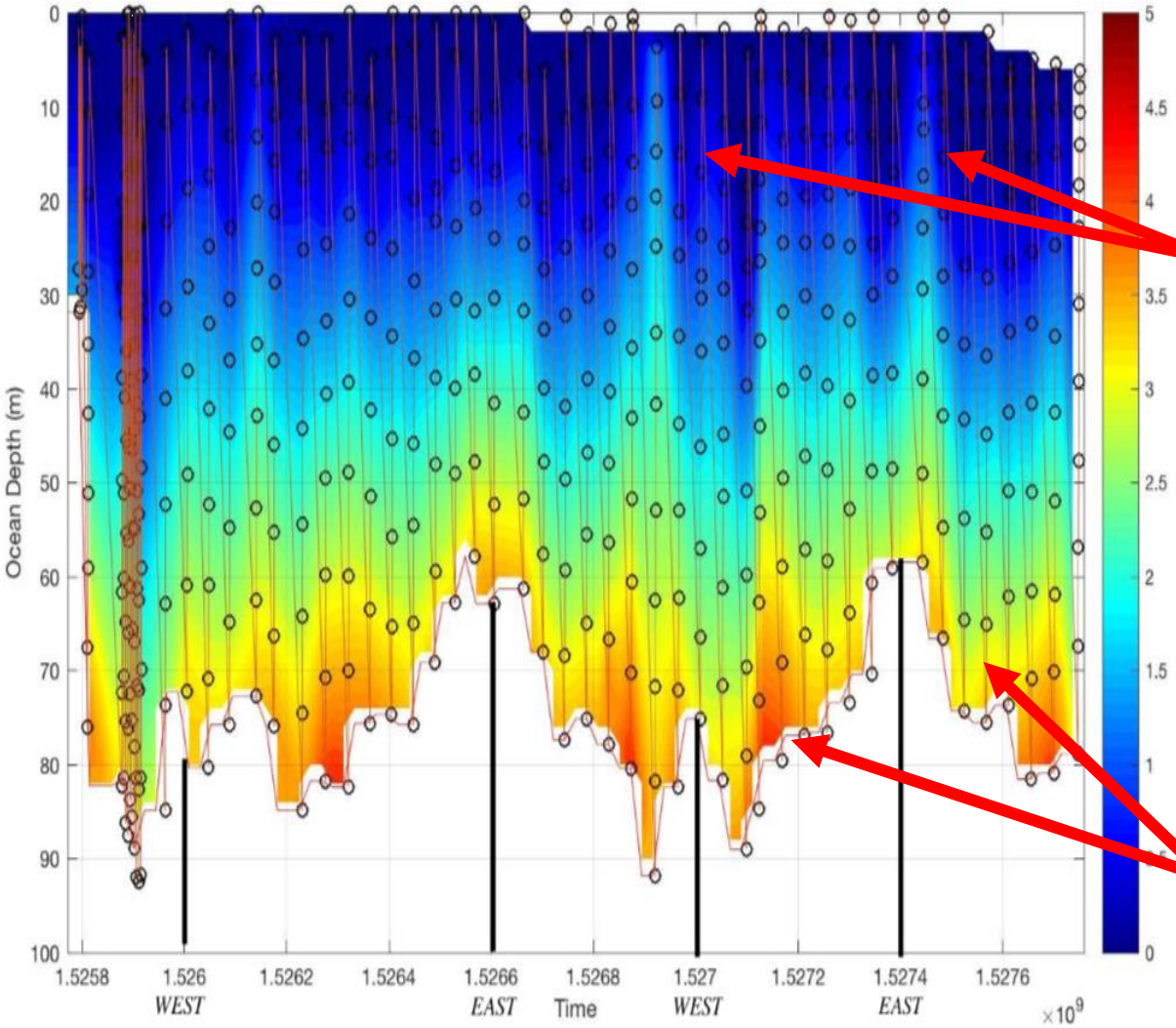
Nitrate and phosphate sensors on a glider in the North Sea



Year-long glider presence in North Sea



Seaglider in North Sea – nitrate sensor



6th May to 31st May 2018

Evidence for 'pulses' of nitrate to surface waters.

Spatial variability in bottom water nitrate concentrations revealed by autonomous sampling approach.

NERC SCIENCE OF THE ENVIRONMENT

STEMM-CCS

Strategies for Environmental Monitoring of Marine Carbon Capture and Storage

- Funded by H2020 CALL FOR COMPETITIVE LOW-CARBON ENERGY (LCE-15-2015) “Enabling decarbonisation of the fossil fuel-based power sector and energy intensive industry through CCS”
- Total Budget €15.9 M
- March 2016 – February 2020
- Coordinator: Prof. Doug Connelly, National Oceanography Centre
- Industrial Partner - Shell

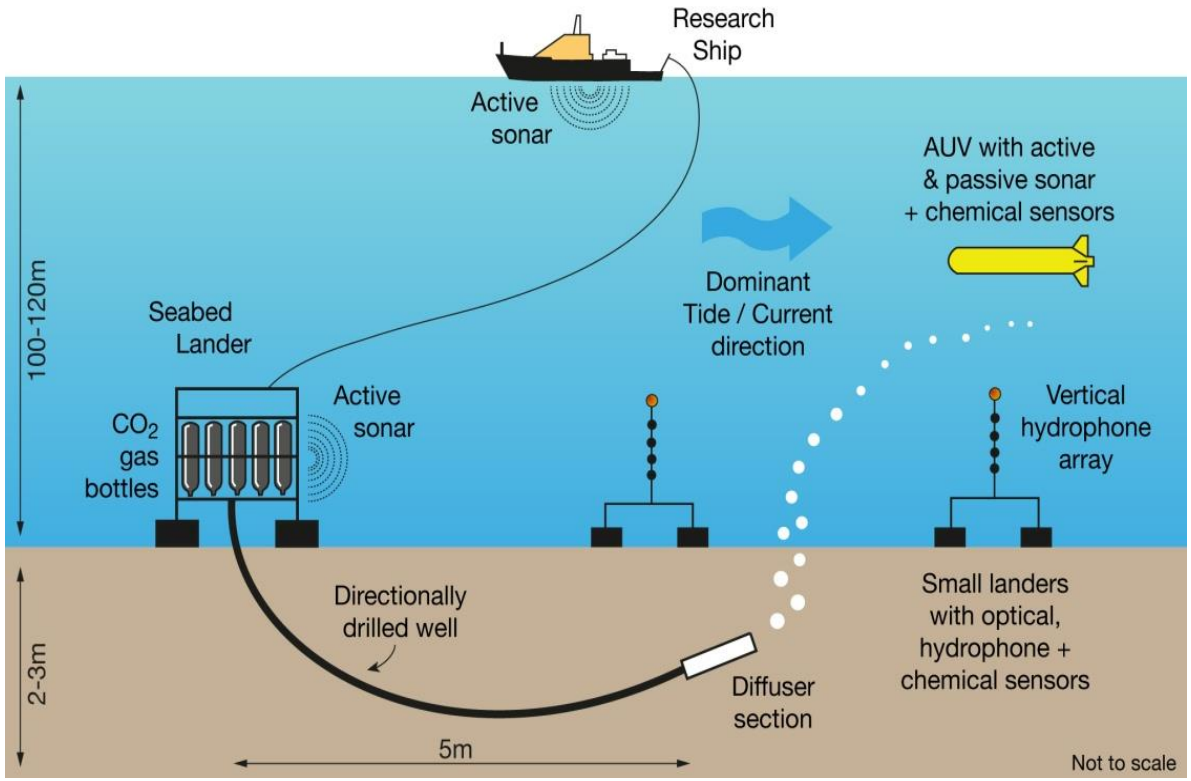
Partners

National Oceanography Centre, NERC, UK
University of Southampton, UK
GEOMAR Helmholtz Centre for Ocean Research, Kiel, Germany
Shell, Netherlands
Plymouth Marine Laboratory, UK
Seascape Consultants Ltd, UK
Heriot Watt University, UK
University of Tromsø, Norway
Max Planck Institute for Marine Microbiology, Germany
Technical University Graz, Austria
University of Bergen, Norway
NIVA, Norwegian Institute for Water Research, Norway
NORCE, Bergen, Norway

Objectives of STEMM-CCS

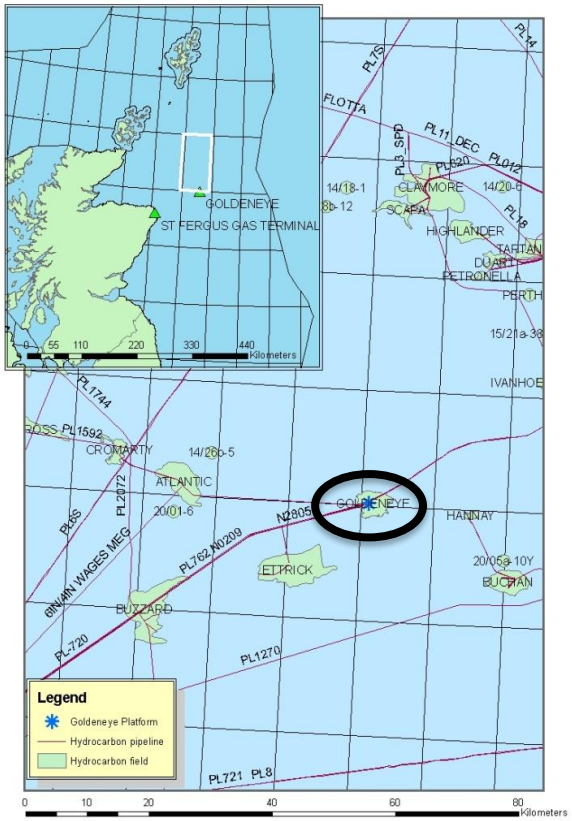
- Develop tools to identify, detect and quantify CO_2 leakage
  - LOC pH, DIC, Total Alkalinity sensors (monitoring of inorganic carbon system)
  - LOC nitrate and phosphate sensors (constrain biological effects on carbon system)
- Constrain natural and anthropogenic induced CO_2 permeability
- Assess artificial and natural tracers for detection, quantification and attribution of leakage.
- Model and assess impacts of different reservoir leak morphologies and provide decision support tools for monitoring, mitigation and remediation action.
- Document best practice.

Main Experiment - 2019



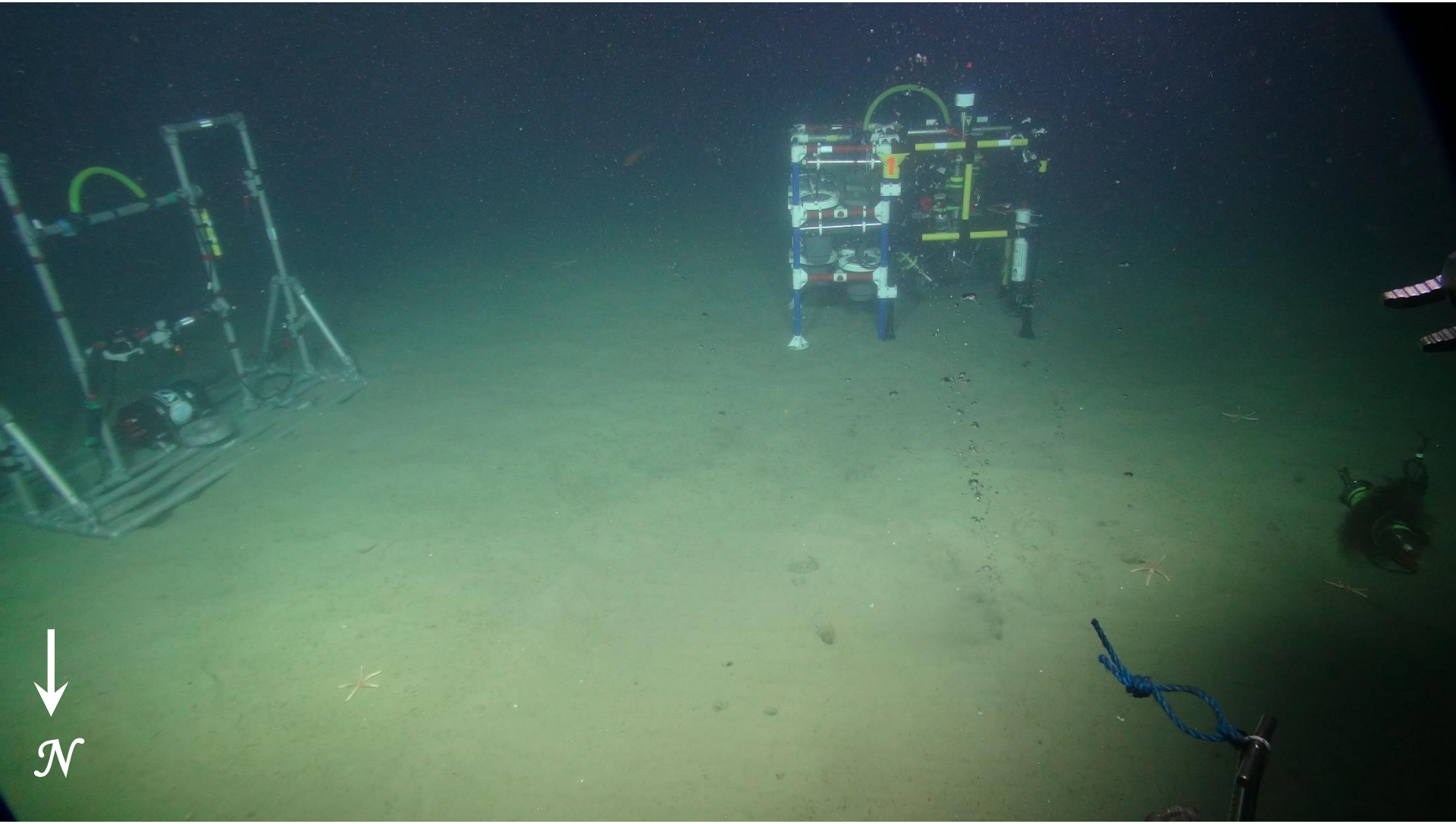
Schematic of the shallow sub-surface release of CO_2 gas in sediments (< 5 m depth) was conducted at the Goldeneye field in the North Sea.

Goldeneye Field Location



GANTRY BLOCKS
LIQUID
CARBON DIOXIDE
STEMM-CCS
Oceanography Centre

Experimental site layout



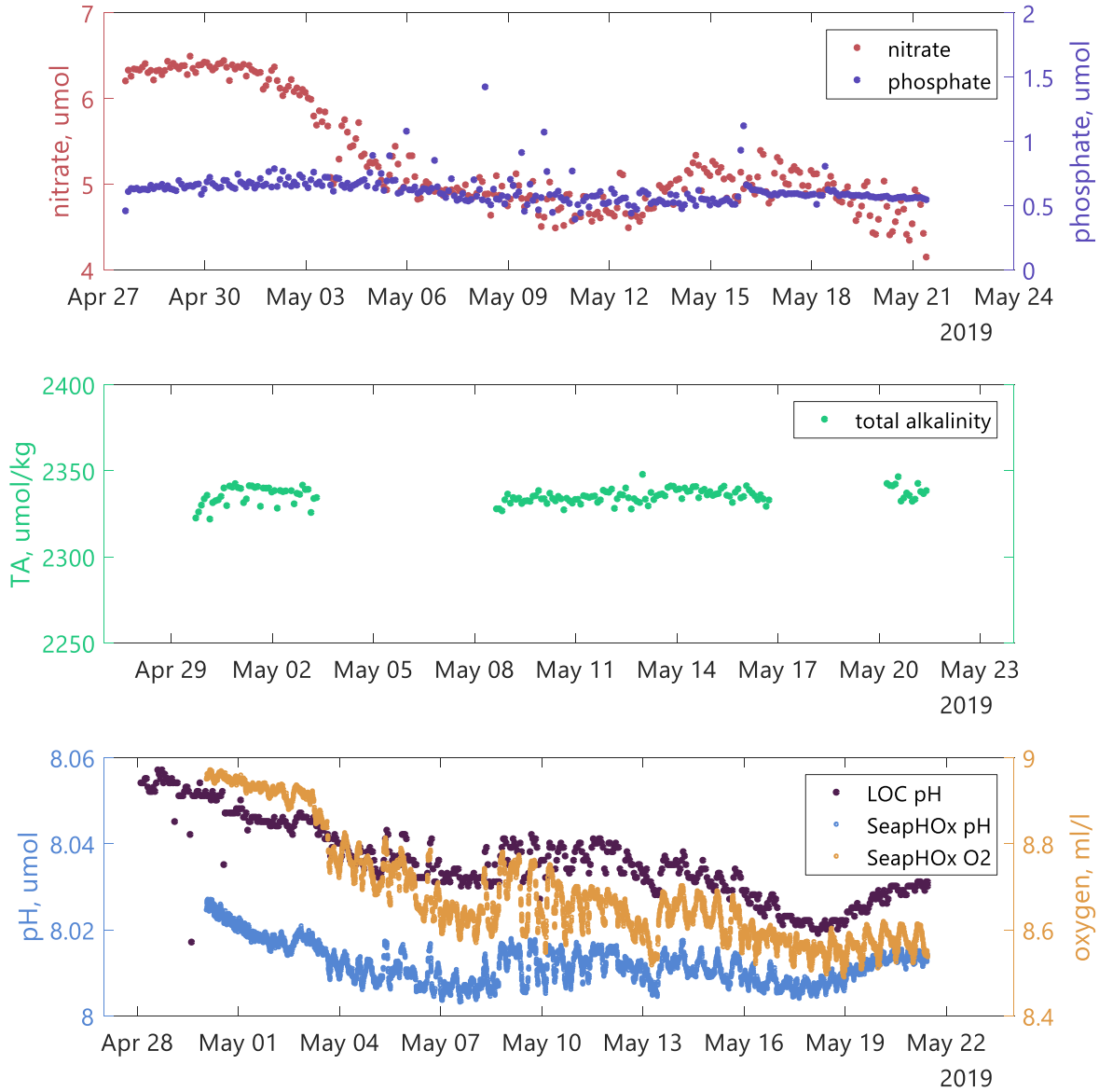
LOCs on replacement baseline lander

Deployed for 25 days (pre-gas to post-gas)
Battery-powered, mostly measuring 2 hourly (pH hourly)

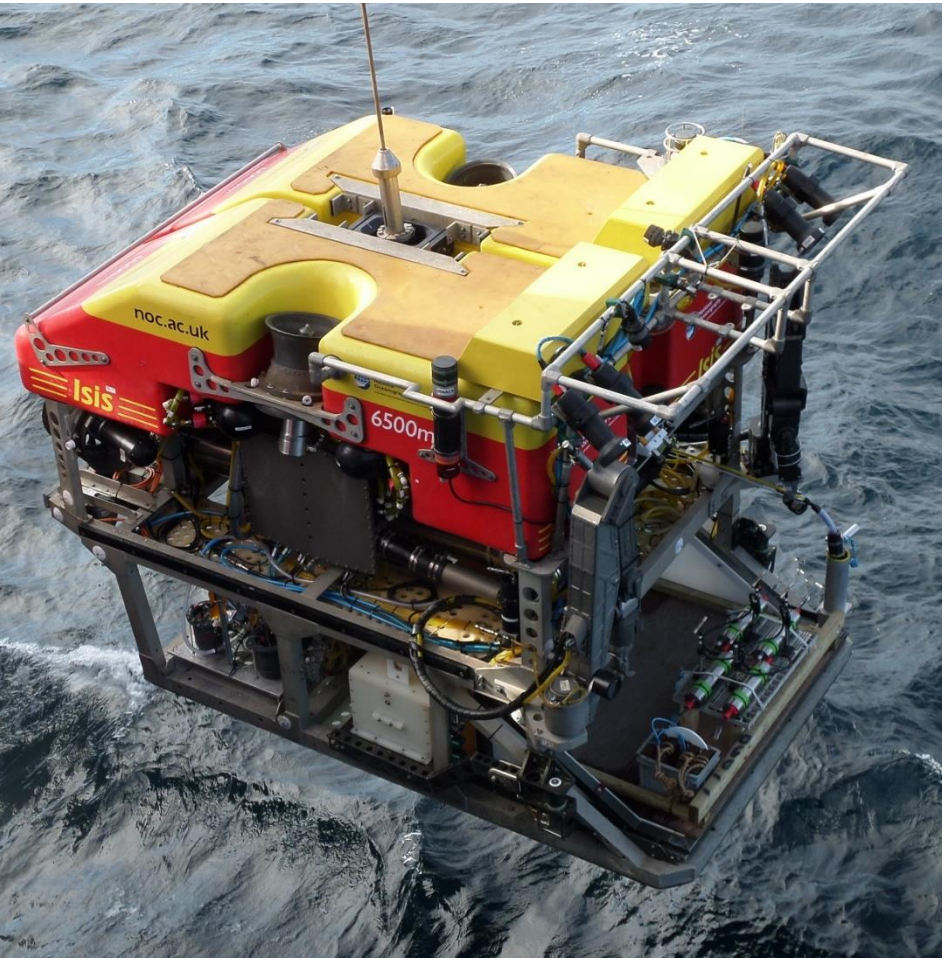
LOCs on replacement baseline lander

Sensor	Sampling frequency	Calibration frequency
pH	Hourly	n/a
Nitrate	Every two hours	Every sample
Phosphate	Every two hours	Every sample
TA	Every two hours	4x per day
DIC	Every two hours	6x per day

Preliminary data from the LOC sensors & SeapHOx on the (new) baseline lander



LOCs on ISIS



Real-time data back in the lab on the ship
Limited turn-around time between dives
Sensors turned on/off by ROV team – usually at around 20 m depth

Miniature optical methane sensors for microsubs

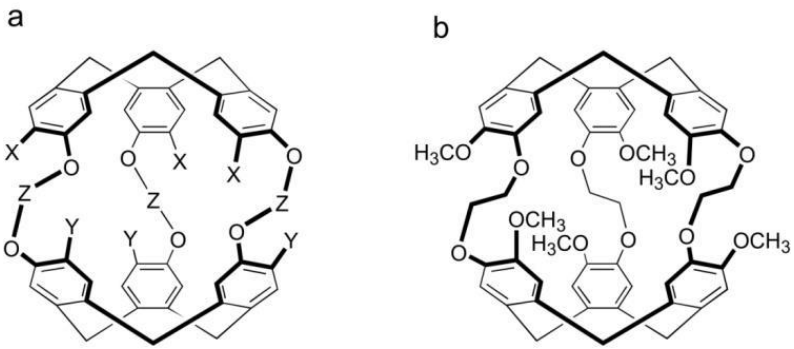
ecoSUBm25

Length: 1000 mm
Diameter 146 mm
Weight in air: 12 kg
Depth rating: 2500 m
Endurance: 28 hours

Optode with polymer sensitive layer

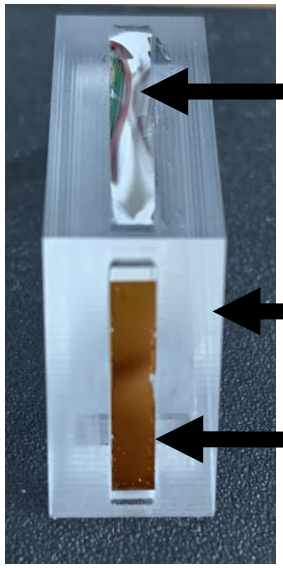
UNIVERSITY OF Southampton

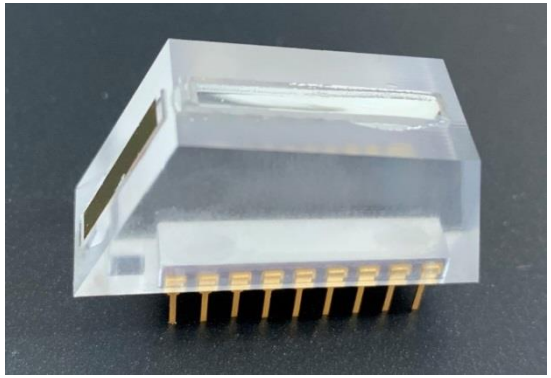
- Cryptophanes are host molecules that can bind reversibly with a guest molecule, with Cryptophane-A showing strong affinity towards methane.
- Interaction with methane causes change in refractive index of sensitive layer
- Two technologies under development at NOC to detect this: SPR and fibre



New optimised SPR chip

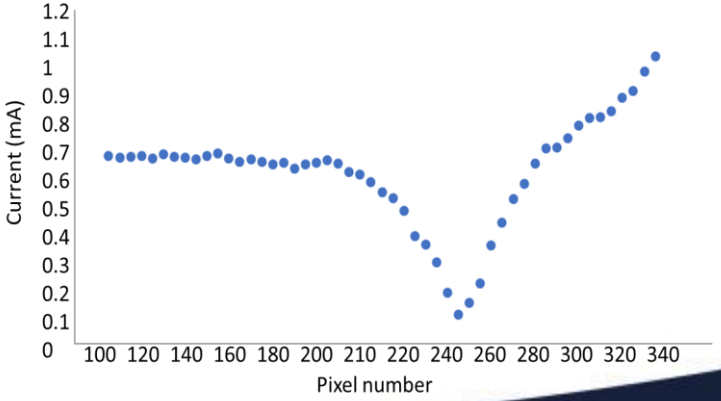
(photos prior to fitting of light-excluding cover)





Photodiode array

SPR curve from new SPR chip
The minimum point on this curve shifts as the refractive index (RI) of the sensitive layer changes.

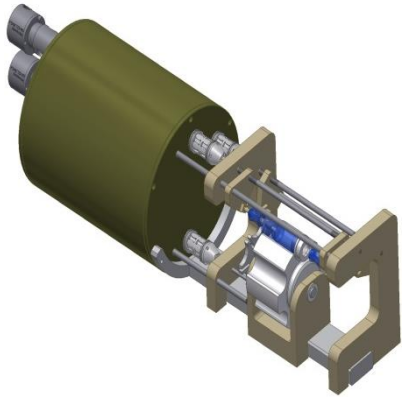


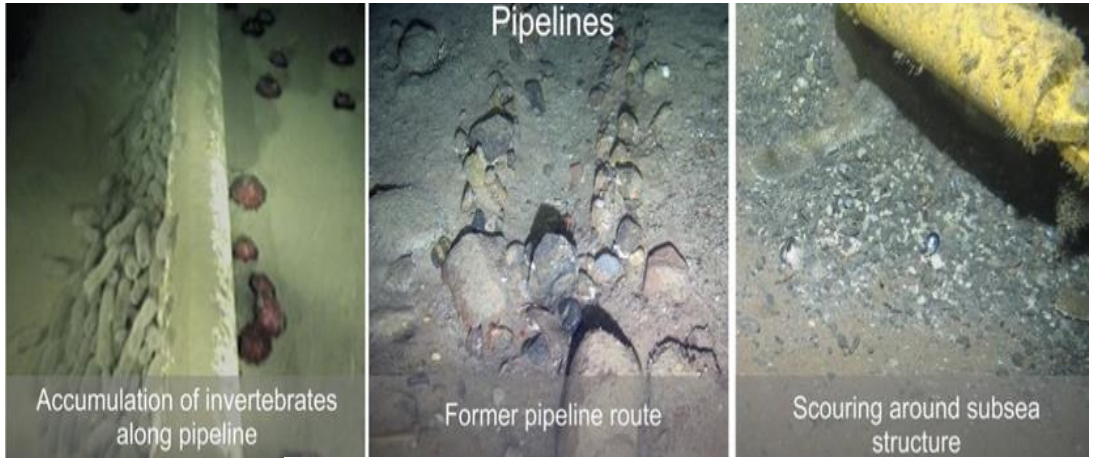
Integration with ecoSUB

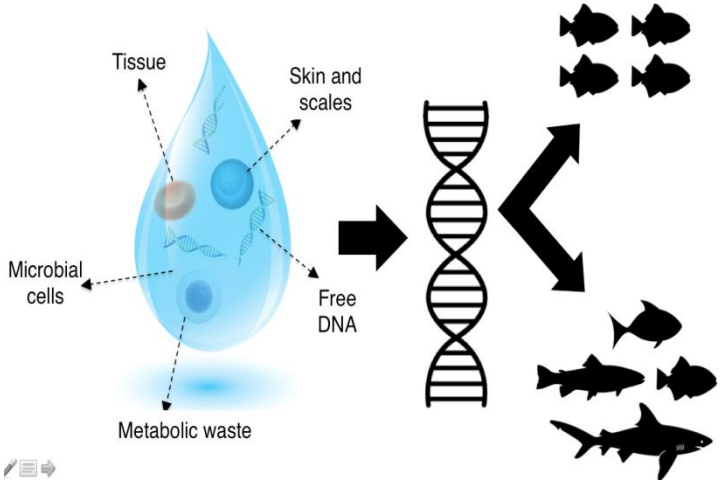
- Integrated into the nose cone of ecoSUB

Marine Autonomous Plankton Sampler (MAPS)

Autonomous monitoring of environmental DNA or eDNA (“marine forensics”) informs species-level biodiversity, dispersal, biogeography, etc.







Jones et al., 2019

Opportunities

- Large portfolio of sensor projects in OTEG (many more not mentioned here!)
- Many based on platform technology available that can be adapted to multiple parameters
- Open to future funded projects and collaborations