Enabling responsible offshore well abandonment with real-time methane monitoring sensors

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Requirements for a sensor

- Post-abandonment and plugging, monitoring of wells is essential for environmental protection.
- Regulatory requirement.
- Requires a sensing system that can operate continuously, remotely and provides a rapid response.

Ideal sensor

- ✓ *Functions in water*
- ✓ *Minimal operational oversight*
- ✓ *Fast response time*
- ✓ *Enables continuous monitoring*
- ✓ *Cost efficient*

Existing sensing methods

Detection of bubbles/plumes

Photo - Zhang et al., Applied Ocean Research 2024

Satellite surveillance

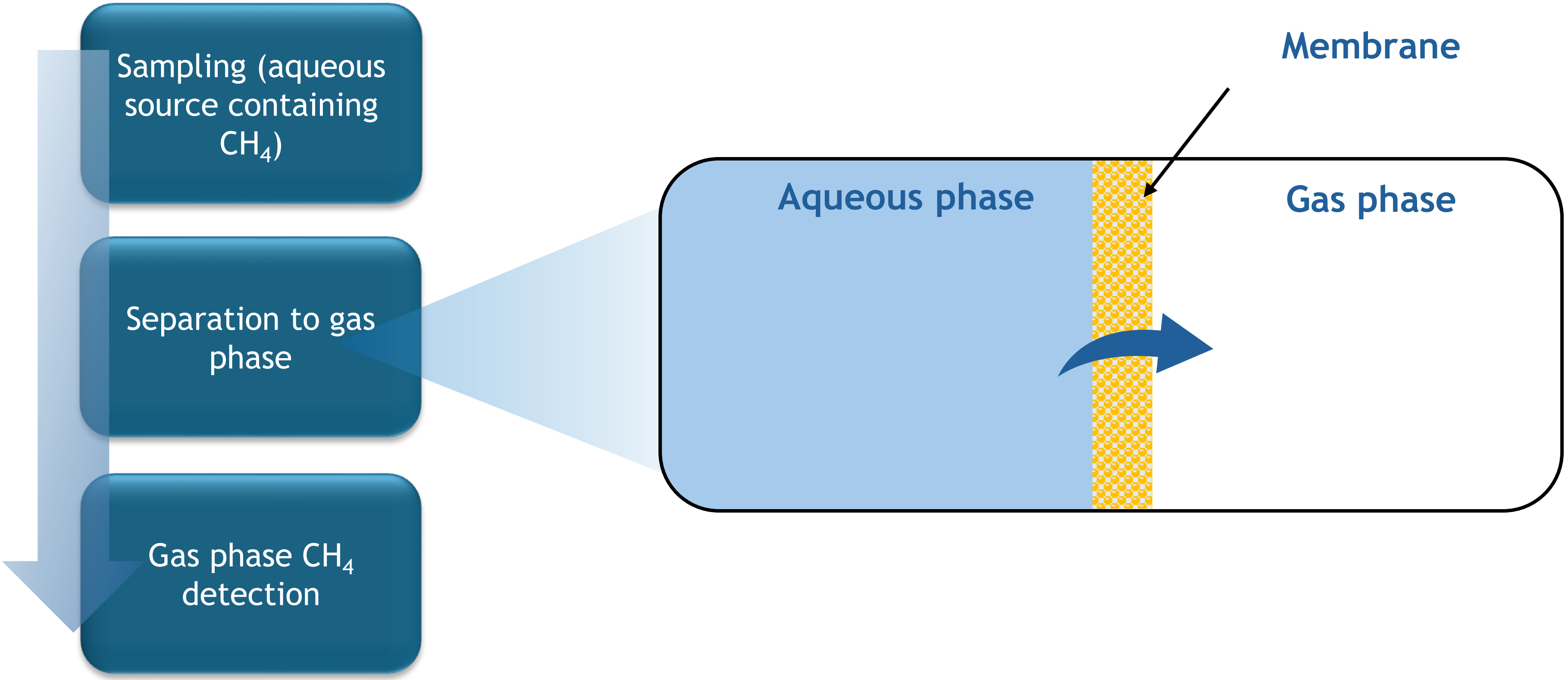
Photo - Danish Defence Command, 2022

Dissolved methane

Solubility **~24 ppm** at standard 1 atm, 23°C

Photo -
Solu-Blu™ CH_4, Pro-Oceanus
CONTROS HydroC® CH_4, 4H-JENA

Existing methods (dissolved CH_4)



- Slow extraction (10-60 minutes)
- Fast flow rates (1-10 L/min)
- Power hungry pumps
- Membrane saturation/hysteresis

There is room for improvements by developing new sensors capable of direct sensing of dissolved CH_4 without the need of extraction to gas phase.

Existing methods – limitations

- Bubble/plume detection.
- Even for dissolved methane, rely on gas phase extraction.
- Delay in detection hinders quick response.
- Small fugitive leaks go undetected but increase methane concentration in nearby waters.

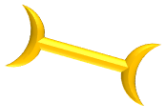
Nord Stream leak, captured by Planet Dove

A new approach towards sensors

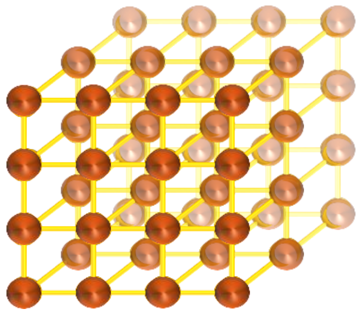
Can we design materials that have strong interactions selectively with methane in complex aqueous environments?

Advanced adsorbent materials – MOFs

Metal

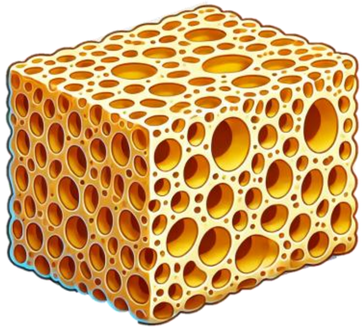


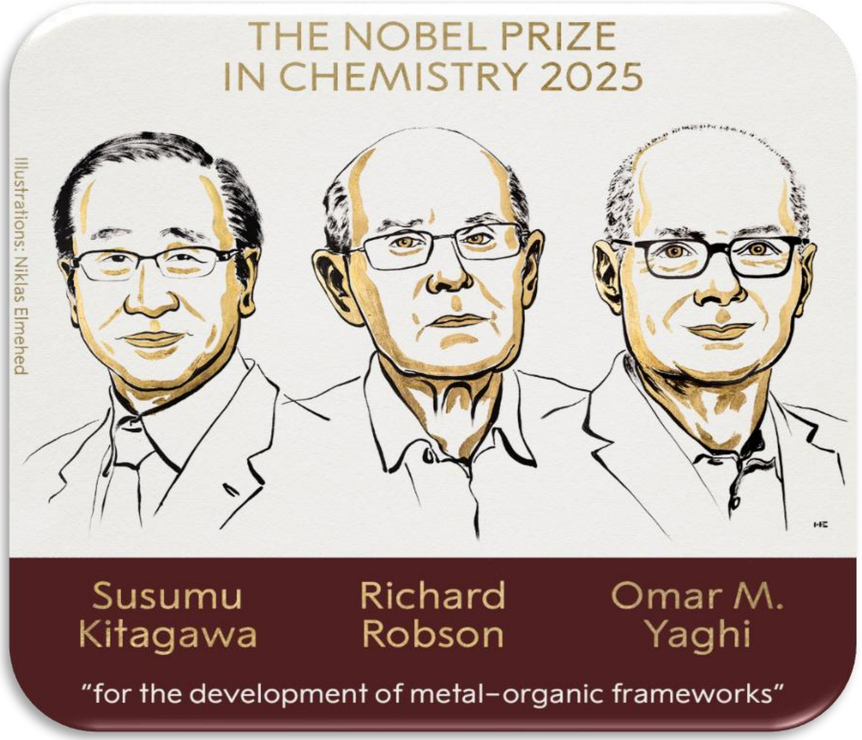
Organic linker

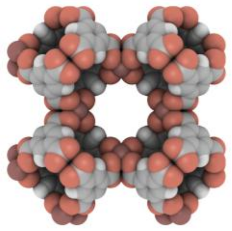


Metal-organic framework (MOF)

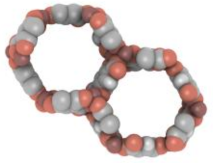
A selective molecular sponge





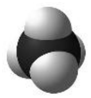
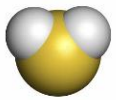


HKUST-1



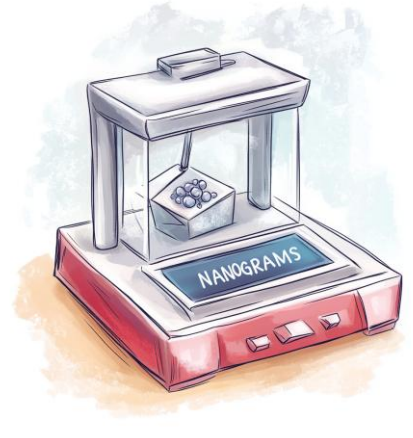
Zn-MOF-74

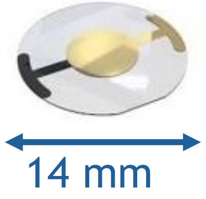
- ✓ *Porous materials (pores ~0.1 to 50 nm)**
- ✓ *Tuneable pore design*
- ✓ *High surface area (500-10000 m^2/g)*
- ✓ *Chemical selectivity*

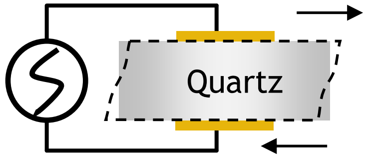
			
CH_4 0.36 nm	*CO_2* 0.33 nm	*H_2S* 0.36 nm	*C_6H_6* 0.59 nm

Sensing platform – QCM

A sensitive mass balance



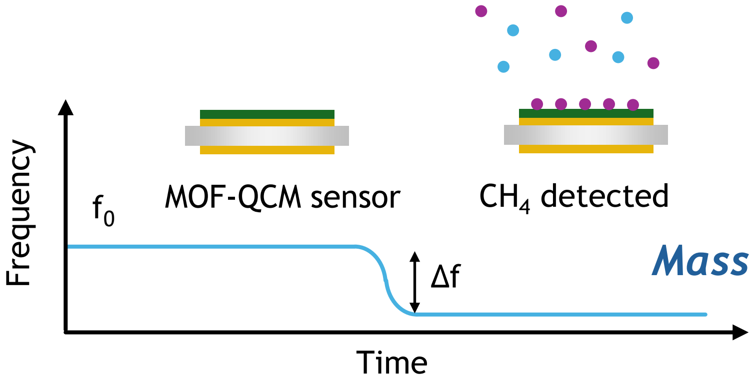




Quartz Crystal Microbalance (QCM)

- ✓ *Mass sensing technology (~4.4 ng/Hz)*
- ✓ *Continuous operation*
- ✓ *Compact measurement device*
- ✓ *Low power requirements (5V DC)*
- ✓ *Gold electrode surface for functionalization (e.g. with a MOF)*

OpenQCM NEXT
(measurement device)

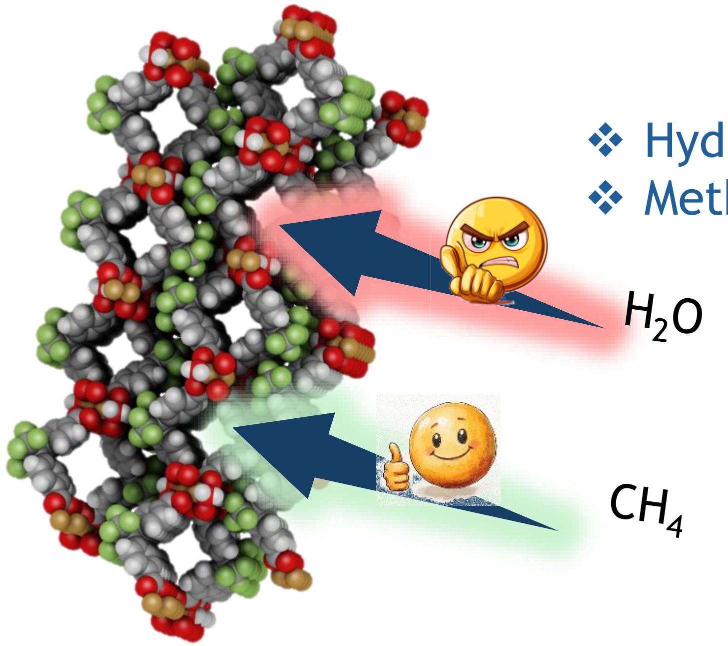


Mass ∝ frequency

1 crystal of salt ~ 0.1 mg

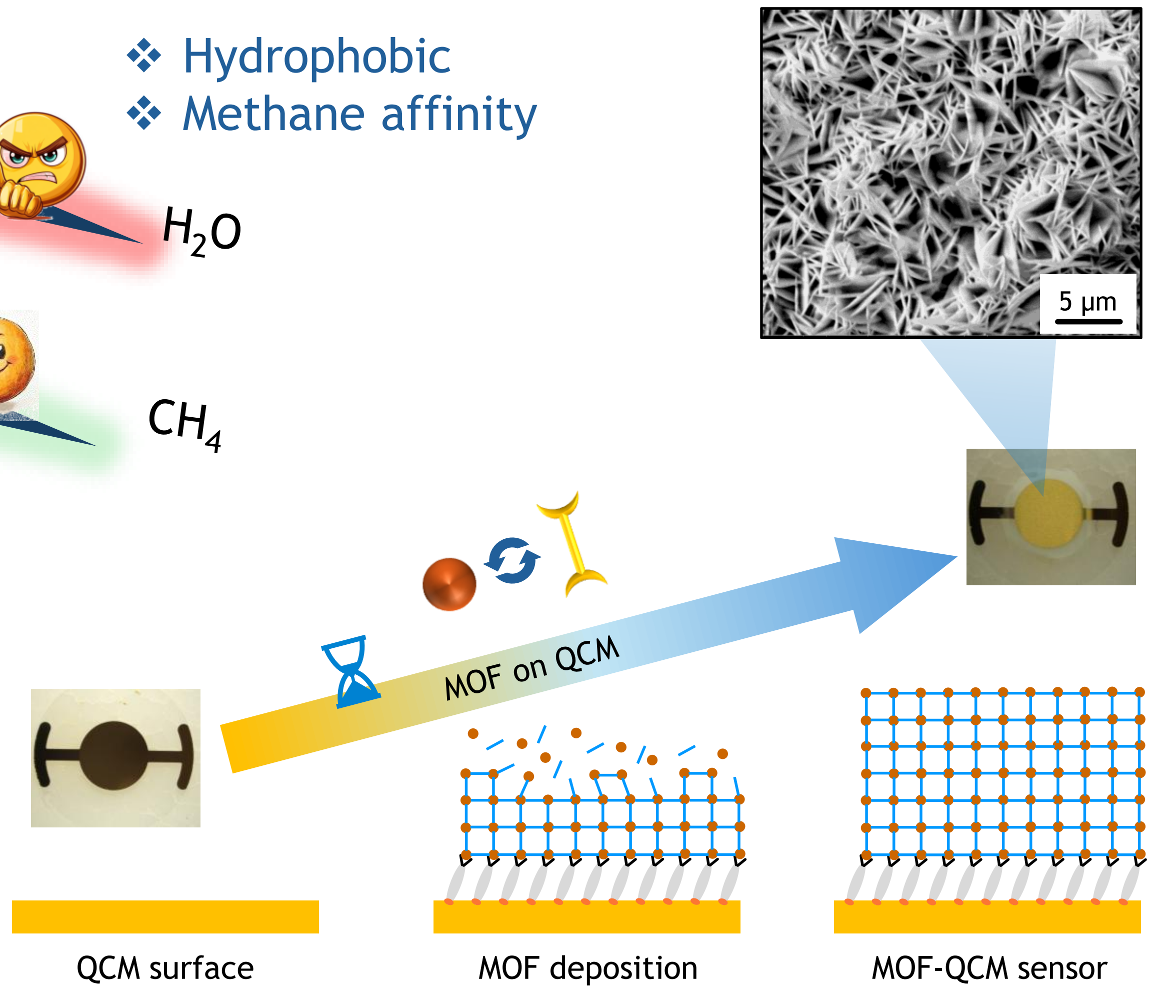
QCM sensitivity ~ 1/10000 of a salt crystal

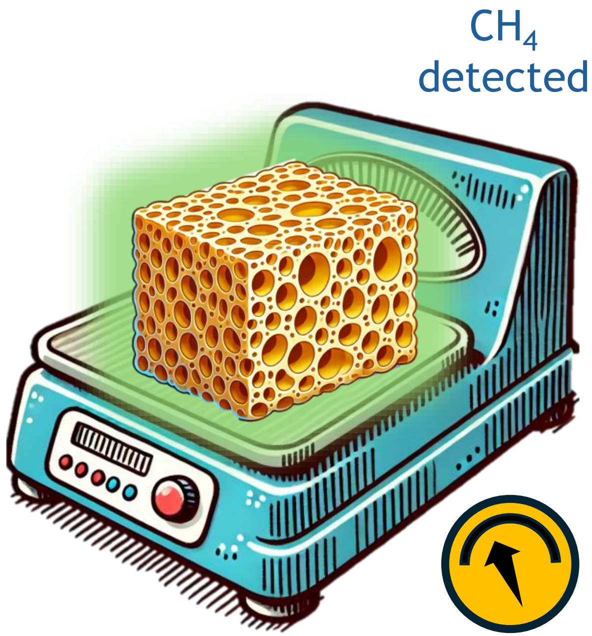
Combining the two – MOF-QCM sensor



Cu-MOF
$[Cu(hfipbb)(H_2O)]$

- Hydrophobic
- Methane affinity

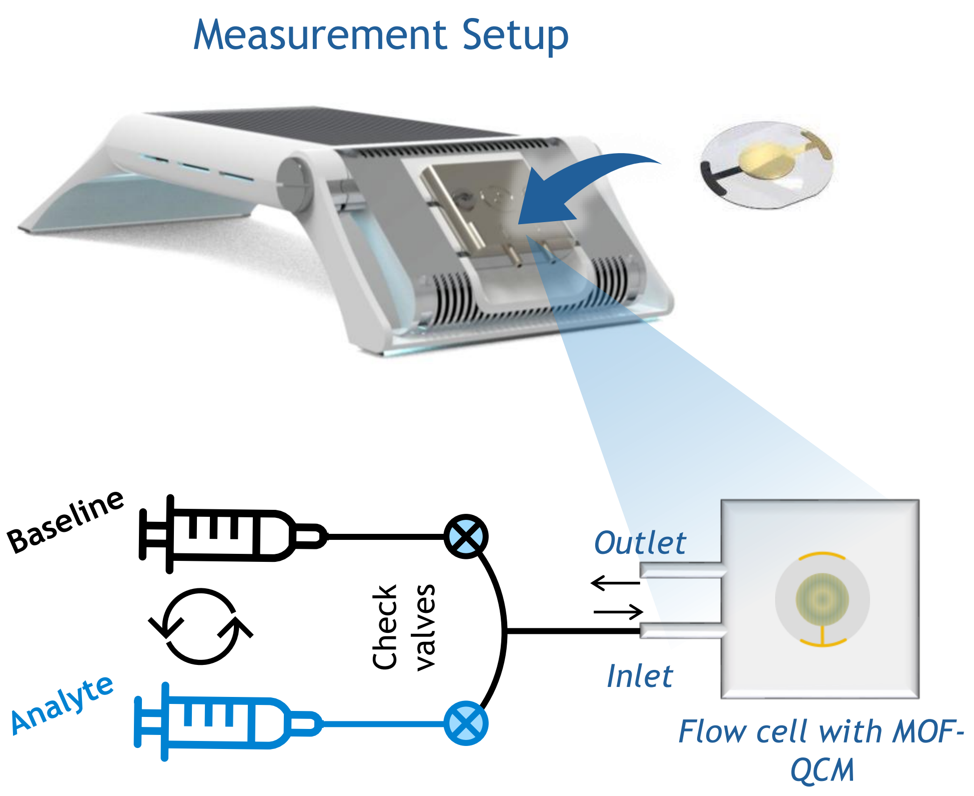




Sensor - MOF + QCM

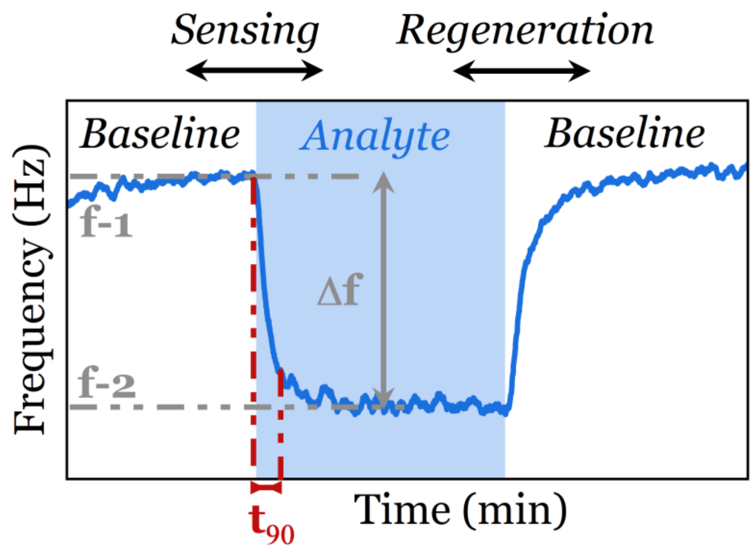
- ✓ *High selectivity of MOF*
- ✓ *High sensitivity of QCM*

Sensor performance



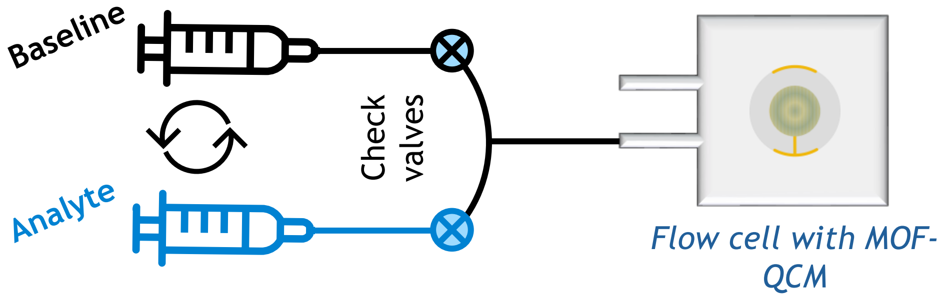
Baseline = Water

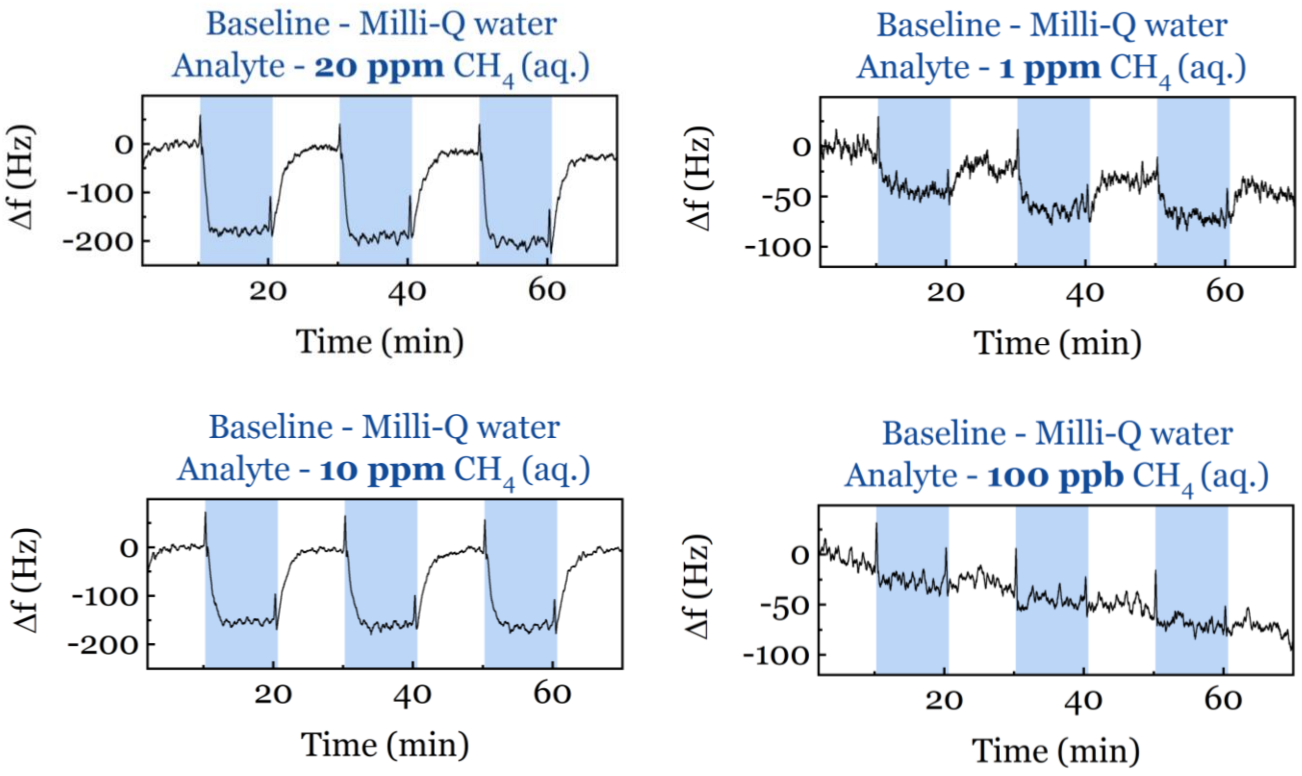
Analyte = Various concentrations of CH_4 in water



- *Fixed physical conditions (temperature 25 °C, flow 0.5 mL/min)*
- *Baseline acts as a frame of reference*
- *Response (Δf) corresponds to a fixed concentration*
- *Response time (t_{90}) corresponds to time taken to reach 90% of response*

Sensor performance

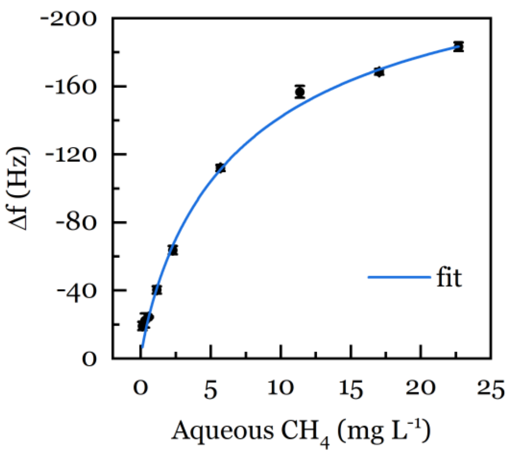




**20 ppm is used as an approximation for 22.7 mg L^{-1}*

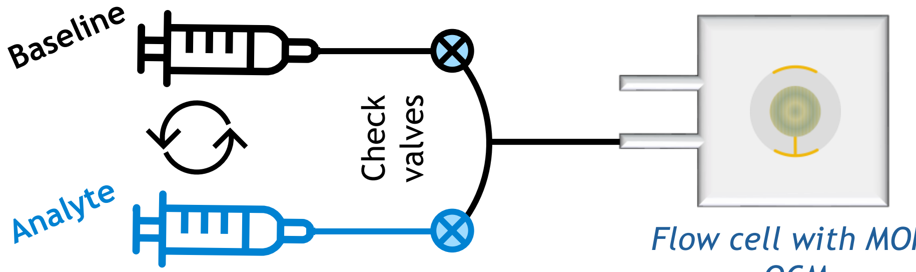
ppm = parts per million　　*ppb = parts per billion*

Calibration curve

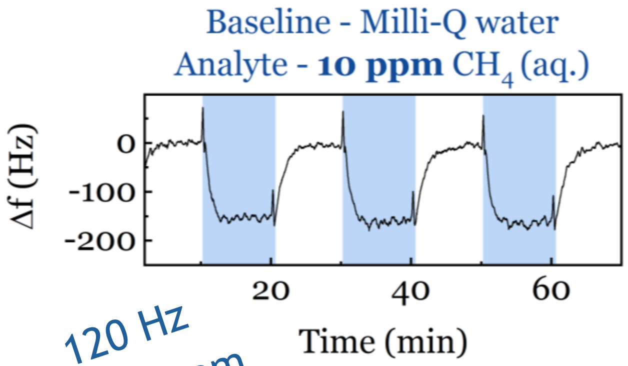


- ✓ *Quantifiable response (from the calibration curve)*
- ✓ *Detection limit - 100 ppb*
- ✓ *Quantification limit - 500 ppb*
- ✓ *Fast response time - 40 s*
- ✓ *Regenerative response*

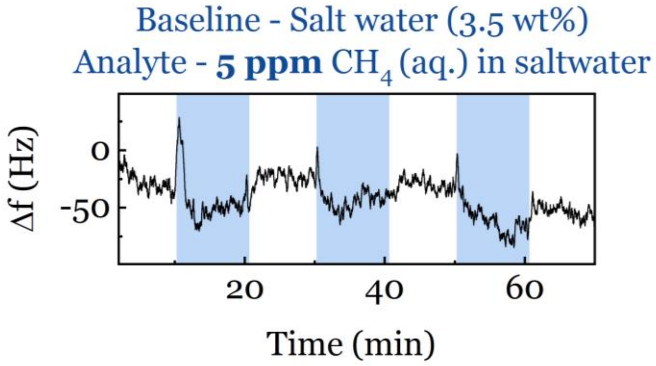
Sensor performance

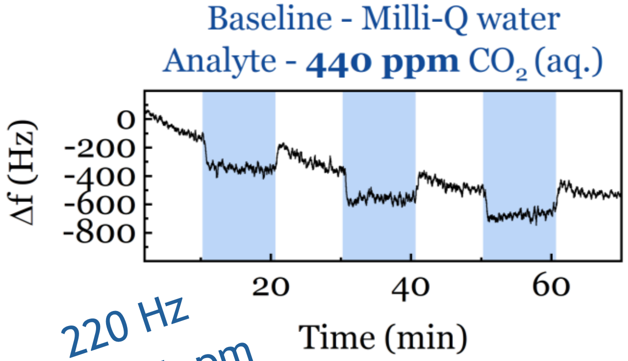


Flow cell with MOF-QCM

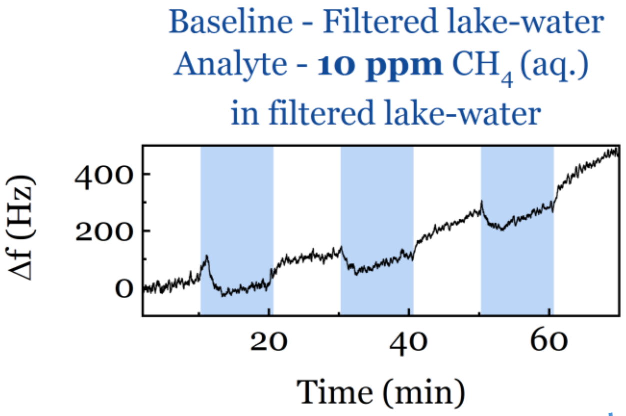


120 Hz
12 Hz/ppm





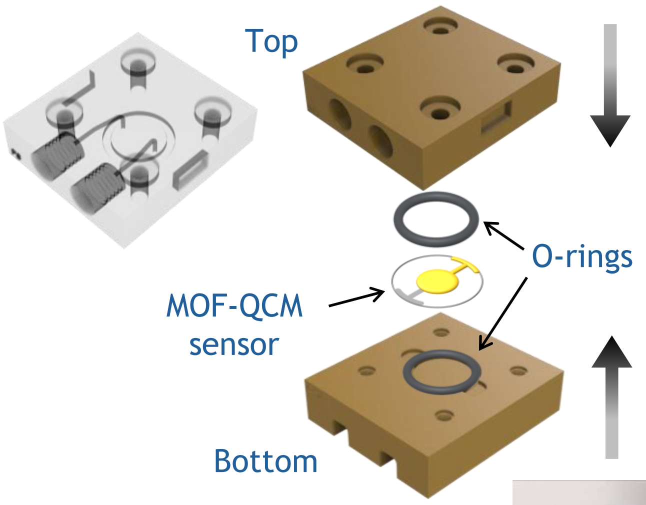
220 Hz
0.5 Hz/ppm



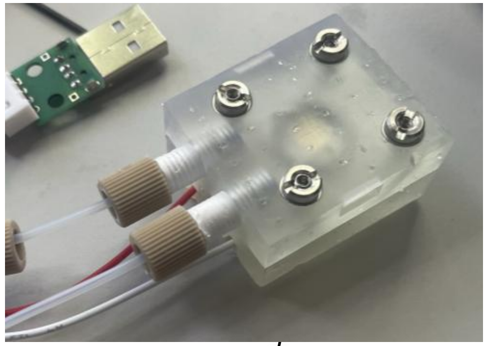
- ✓ *Higher sensitivity for dissolved CH_4 (over CO_2)*
- ✓ *Works with complex solutions - synthetic seawater, filtered lake-water*
- ✓ *Regenerates itself as the methane-free water is sampled*

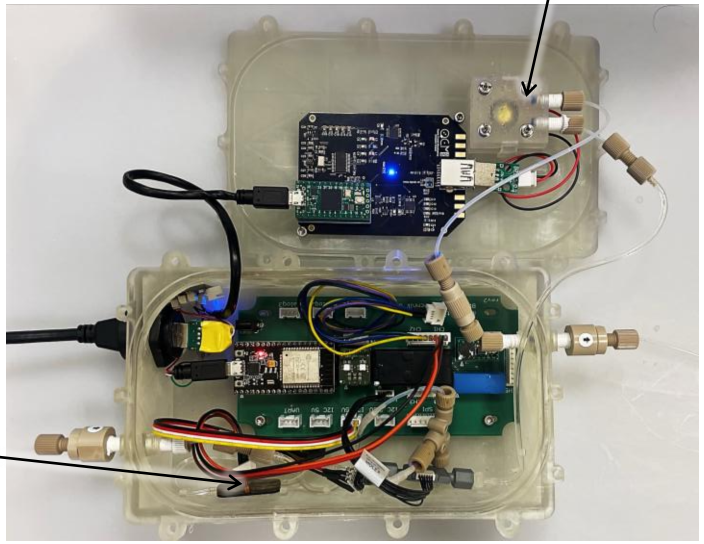
It drifts!!!!!
Challenge to be solved in the next iteration of the sensor.

Sensor prototype



Computer Aided Design
Stereolithography

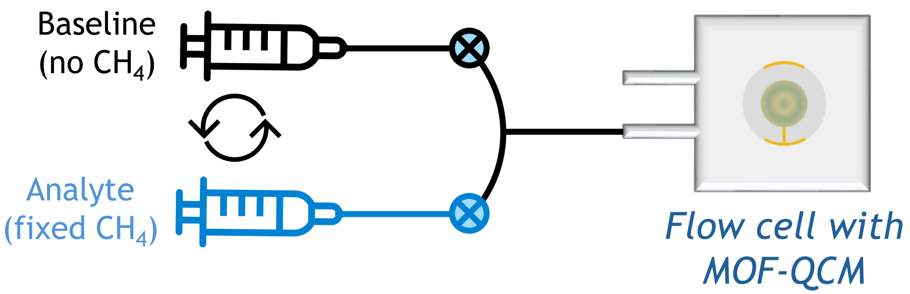




Current prototype

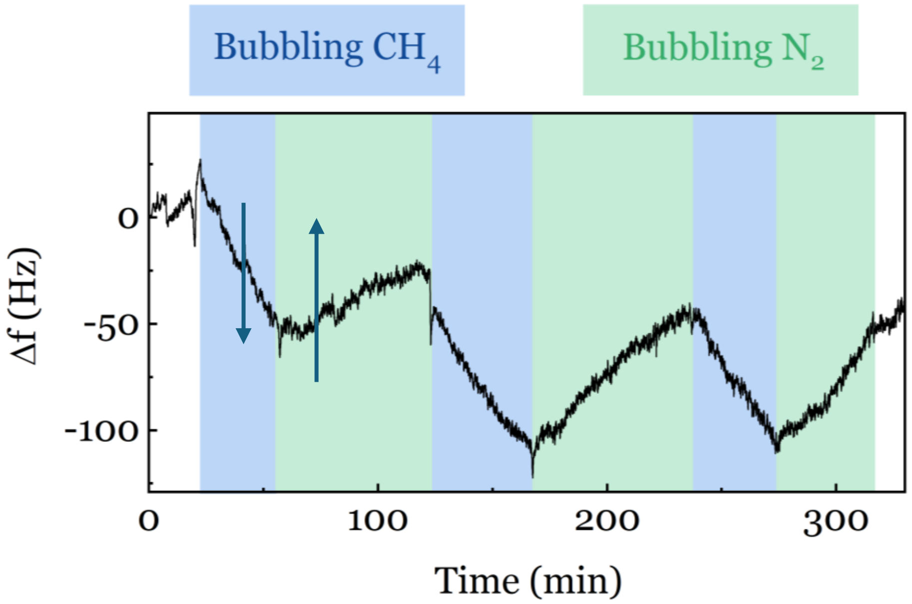
- ✓ *Developed via 3D printing in our lab*
- ✓ *Lightweight prototype (~500g)*
- ✓ *Operational via 5V DC power source*
- ✓ *Compact (19cm x 11cm x 5cm)*
- ✓ *Costs ~ 2000 € (bill of materials)*
- ✓ *Micropump for sampling (operational at low flow rates ~0.5-1 mL/min)*

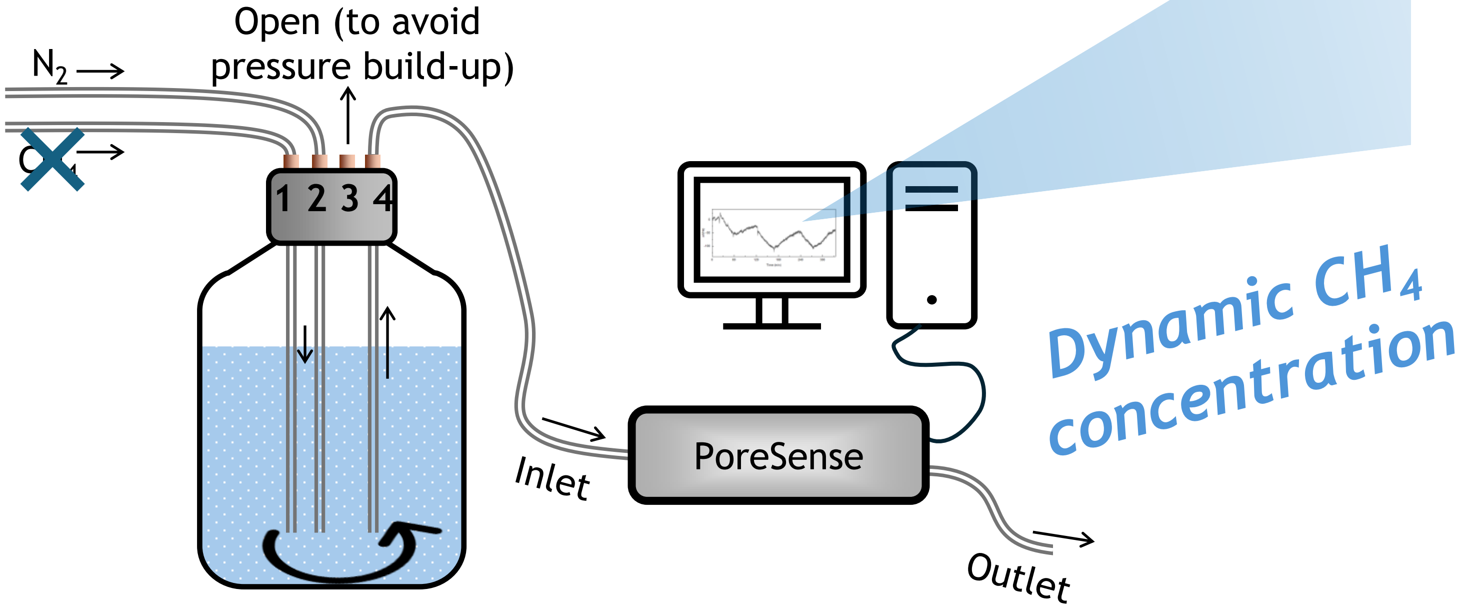
Sensor prototype – testing



Fixed CH_4 concentration

Goes from 0 (no methane)
to 1 (fixed methane concentration)





Dynamic CH_4 concentration

Monitoring of dissolved CH_4 concentration in real time

What is achieved so far?

- Demonstration of MOF-QCM platforms as chemical sensors.
- A prototype sensor validated to TRL 6 for detection of aqueous methane.
- Detection of dissolved methane, i.e. before bubble formation (essential for early leak detection).
- Fast (60 seconds), self-regenerating response with a limit of detection – 100 ppb.
- Multiple publications, ongoing patent application, founding of a company (for commercialization).

ACS SENSORS
pubs.acs.org/acssensors Article

Room-Temperature Monitoring of CH_4 and CO_2 Using a Metal–Organic Framework-Based QCM Sensor Showing Inherent Analyte Discrimination

Jaskaran Singh Malhotra, Mariusz Kubus, Kasper S. Pedersen, Simon I. Andersen, and Jonas Sundberg*

Cite This: ACS Sens. 2023, 8, 3478–3486 Read Online

ACS APPLIED NANO MATERIALS
www.acsanm.org Article

Quantification of Methane in Water at Parts Per Billion Sensitivity Using a Metal–Organic Framework-Functionalized Quartz Crystal Resonator

Jaskaran Singh Malhotra, Clara Dávila Duarte, Per Reichert, Deepthy Krishnan, and Jonas Sundberg*

Cite This: ACS Appl. Nano Mater. 2025, 8, 4542–4552 Read Online

RESEARCH ARTICLE
ADVANCED MATERIALS TECHNOLOGIES
www.advmattechnol.de

Surface-Mounted Metal-Organic Framework for the Adsorption and Sensing of Monoaromatic Pollutants in Water Using Quartz Crystal Microbalance

*Per Reichert, Jaskaran Singh Malhotra, Deepthy Krishnan, Sinem Evli, Srihari Yamunan, Clara Dávila Duarte, Mariusz Kubus, and Jonas Sundberg**

Further development

- Further funding secured for SEAL project (The Energy Technology Development and Demonstration Programme).
- Aims to mass produce MOF-QCM sensors, develop prototype, interface and advance signal processing (e.g. for drift correction).
- Commercialization via our start-up (PoreSense I/S)
- Develop a robust prototype and planned pilot testing in an offshore setting (by 2027)

EUDP

DTU Offshore and DTU EngTech develop the technology with support from Danish Technological Institute

PoreSense I/S holds the IP and supports commercialization in collaboration with DTU Skylab

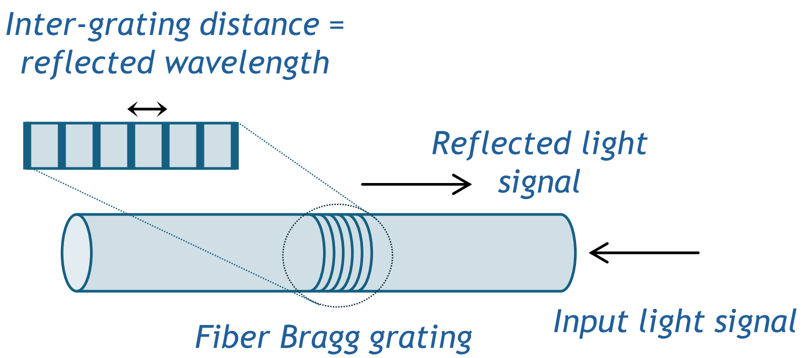
DUC (TotalEnergies, BlueNord and Nordsofonden) benefit from the technology as end users

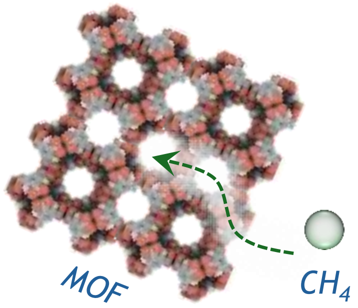
DEVELOPMENT → **COMMERCIALIZATION** → **MARKET**

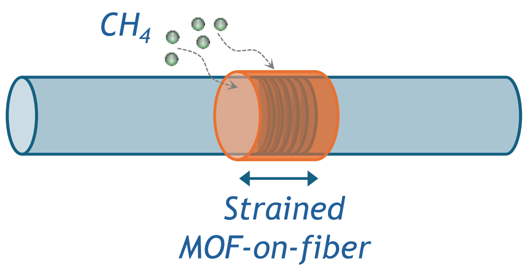
More sensor concepts?

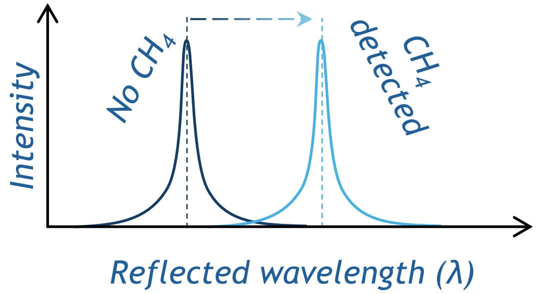
Can we use these materials to design sensor systems capable of covering large spatial regions at the seabed?

Distributed sensor network (fiber optics)

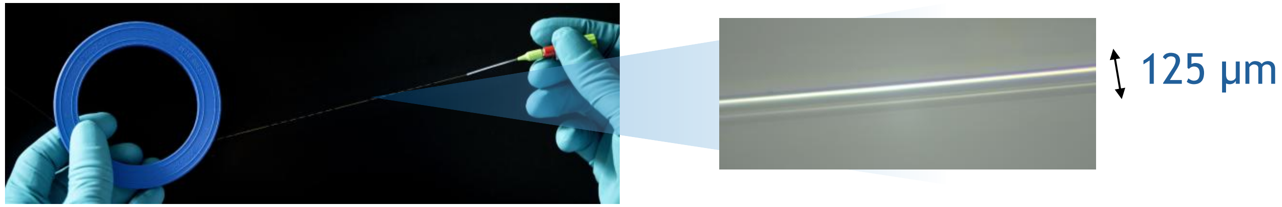


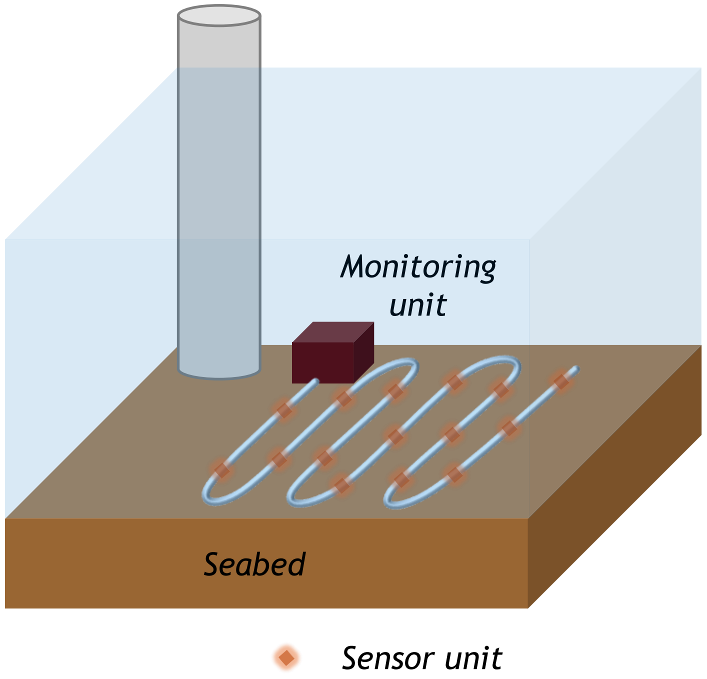






Can sense picometer (pm) strains





- *Distributed sensor network*
- *Multiple sensor units on one fiber*
- *Large spatial coverage*
- *Precise location of the leak*

Thank you

Our team

Simon

Charlotte

Monica

Clara

Nishchitha

Jonas

Jaskaran

Our poster girl