

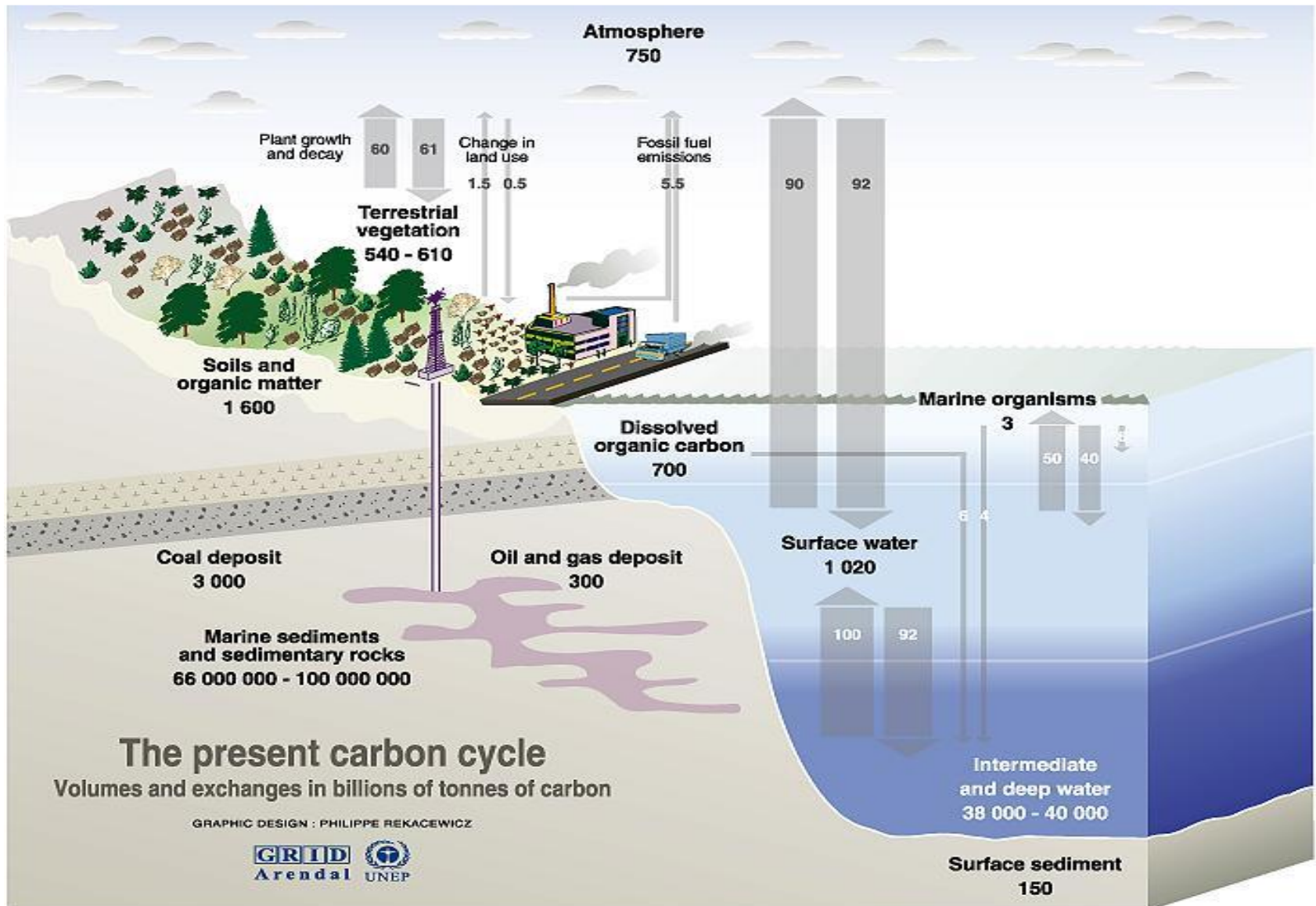
Some challenges and opportunities in our quest to understand and monitor carbon cycling

Are we responsible for current global warming??



Even if climate change is not anthropogenic, should we still monitor carbon?

CARBON CYCLING KNOWN KNOWNS:



Sources: Center for climatic research, Institute for environmental studies, university of Wisconsin at Madison; Okanagan university college in Canada, Department of geography; World Watch, November-December 1998; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.

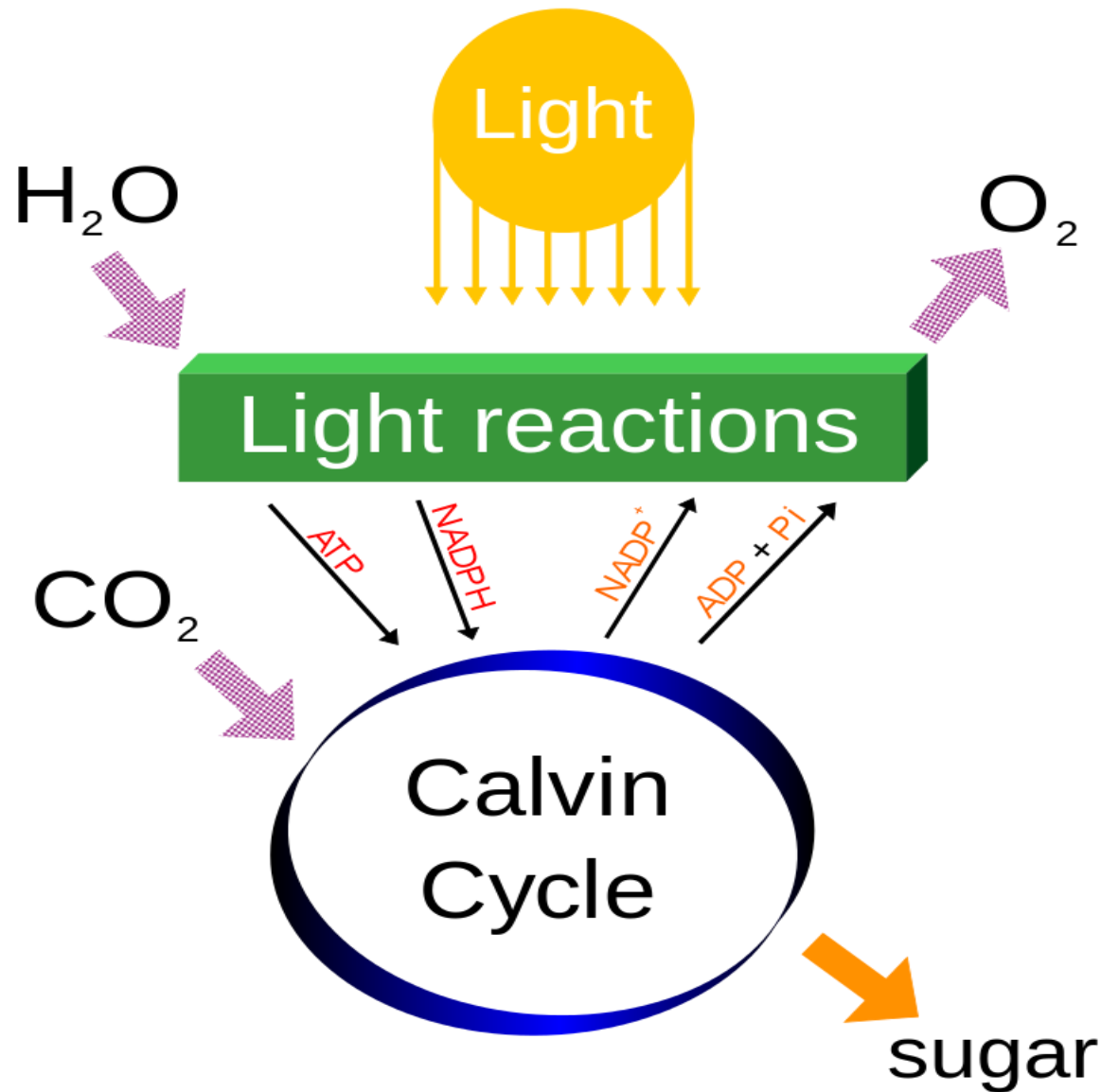
CARBON CYCLING KNOWN UNKNOWNS:

~ 25% of anthropogenic CO₂ is “missing”!

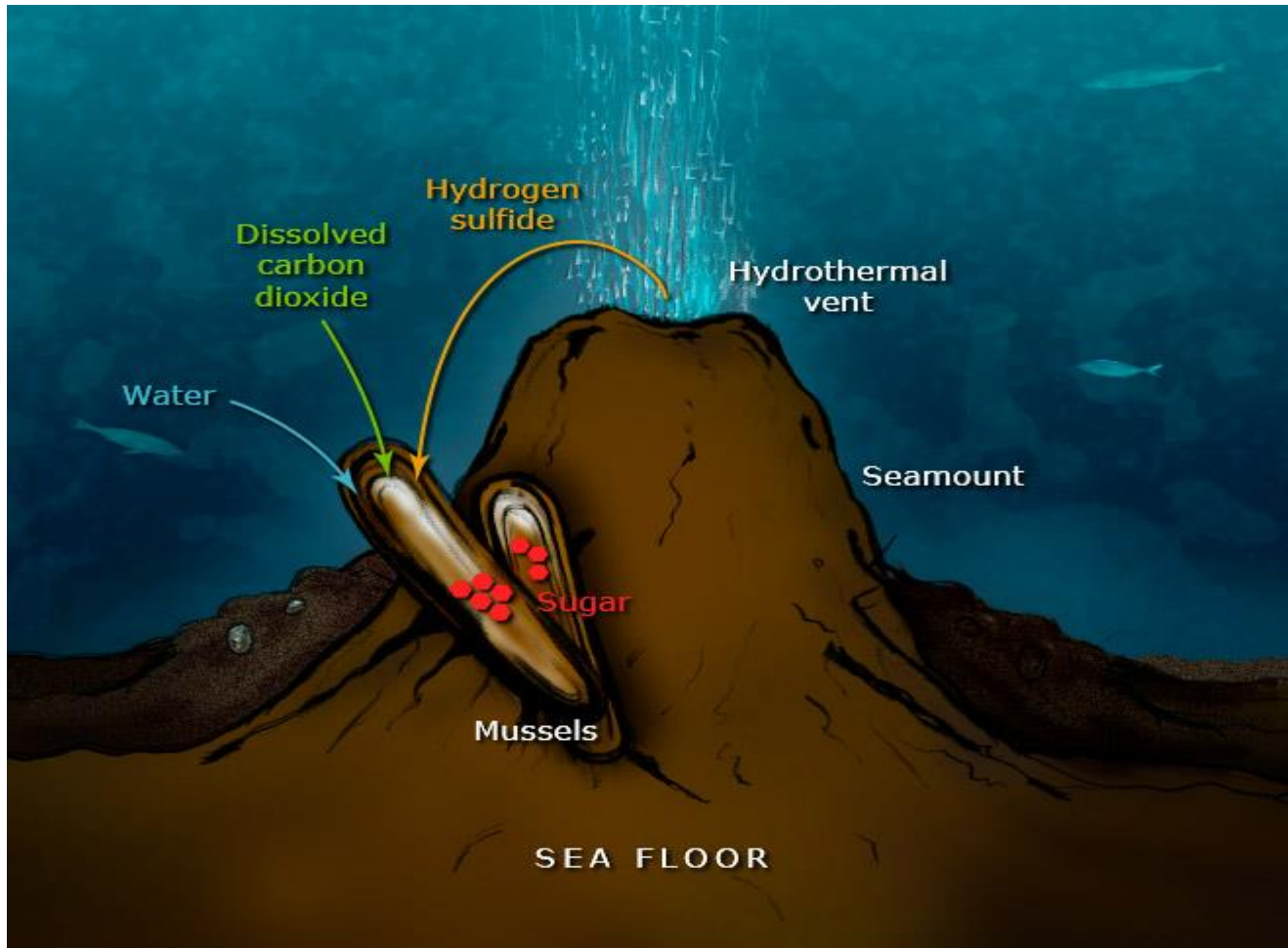
CARBON CYCLING UNKNOWN UNKNOWNNS:

????????????????????????????????

A major component of the carbon cycle: **Photosynthesis**



Chemosynthesis



Chemosynthesis is not everywhere, it's only found deep in the ocean, near thermal vents!!!!!!!!!!!!!!!!!!!!!!



The Grand Prismatic Spring, Yellowstone National Park

“we know more about the movement of celestial bodies than the soil underfoot”. **Leonardo Da Vinci**

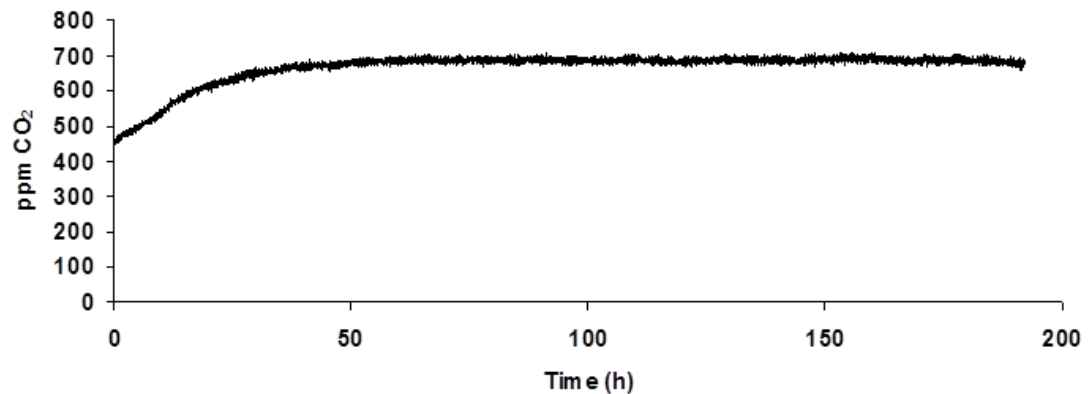
Soil Chemosynthesis??

- We investigated how the addition of elemental sulfur (S^0) affects an agricultural soil by incubating both an unaltered and an S^0 amended arable soil.
- The incubations were carried out in both $^{12}CO_2$ and $^{13}CO_2$ atmospheres under close to natural CO_2 concentrations (400ppm).
- The efflux (CO_2 production through respiration and degradation), CO_2 uptake and net change in atmospheric CO_2 caused by the incubated soils was continuously measured.
- The $^{13}CO_2$ experiments facilitated the combination of Stable Isotope Probing (SIP), Nuclear Magnetic Resonance (NMR) and phospholipid fatty acid (PLFA) analysis with compound specific stable isotope mass spectrometry that we use to track the fate of atmospheric CO_2 .

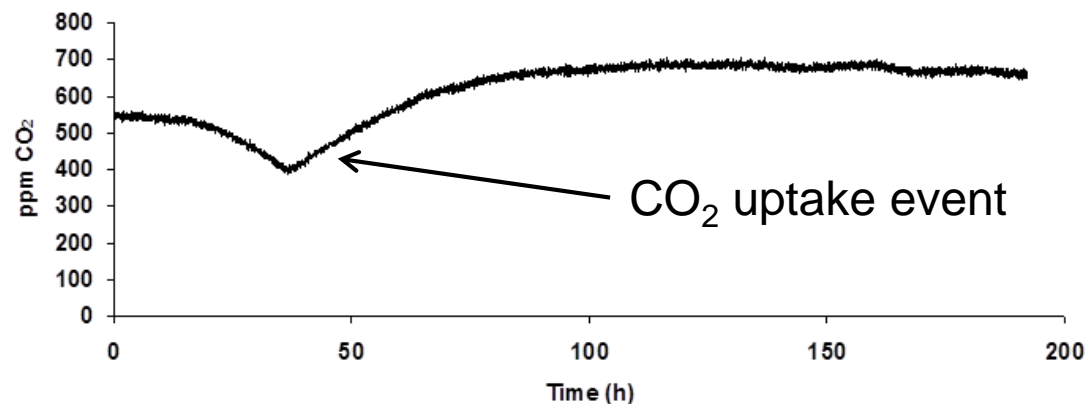
CO₂ uptake Investigations

An order of magnitude increase in CO₂ assimilation in soil occurred when conditions for chemosynthesis existed.

No electron donor



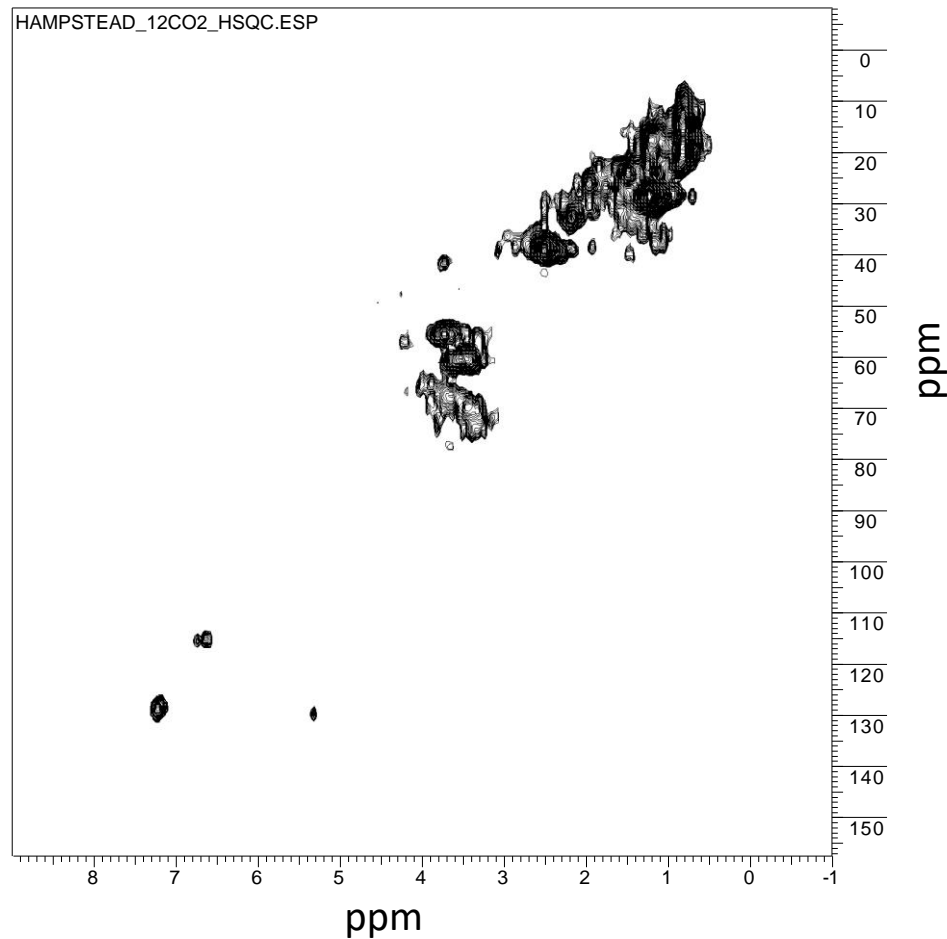
Sulfur added as an electron donor



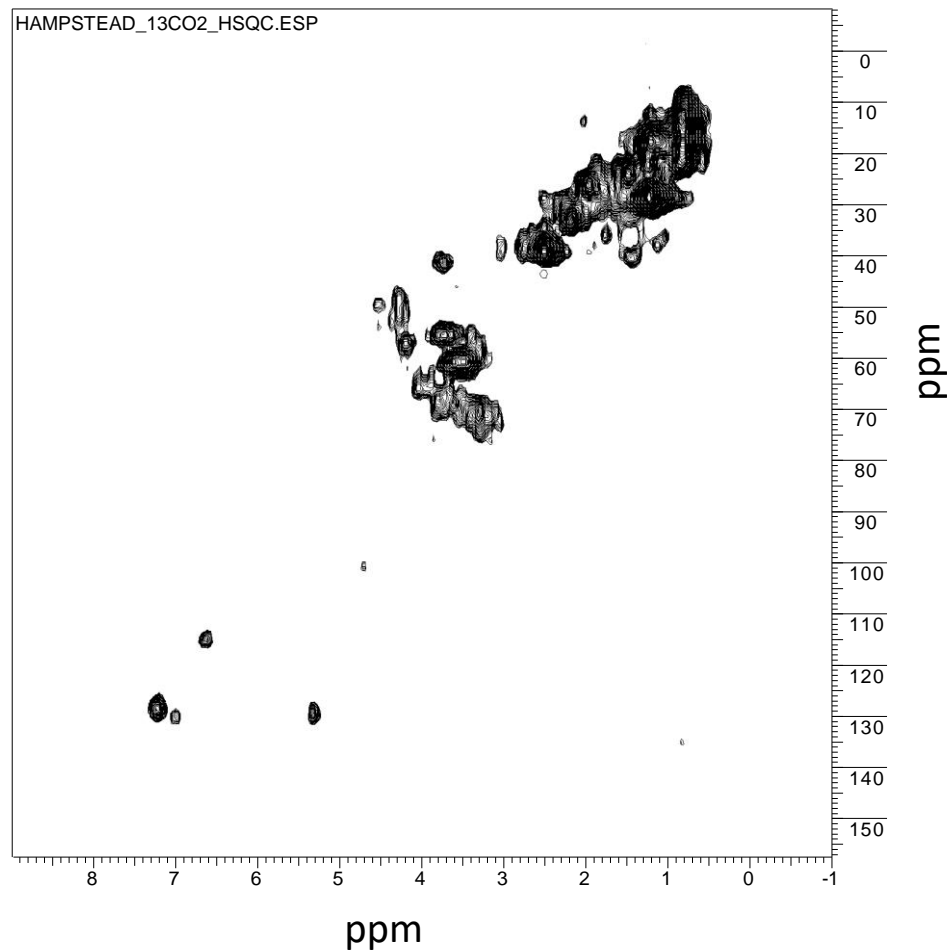
Tracking the fate of chemosynthetic uptake of atmospheric CO₂ in soil:

- NMR analysis of soil organic matter before and after the application of electron donor in atmosphere enriched with ¹³CO₂
- Comparison of the 1D solid phase CP-MAS ¹³C NMR spectra before and after labeling allows us to quantify the increase in total carbon signal in the soils due to uptake of ¹³CO₂.
- By subtracting the NMR spectra of the ¹²CO₂ from the ¹³CO₂ incubations we can see carbon incorporated into soil as a result of chemosynthesis.

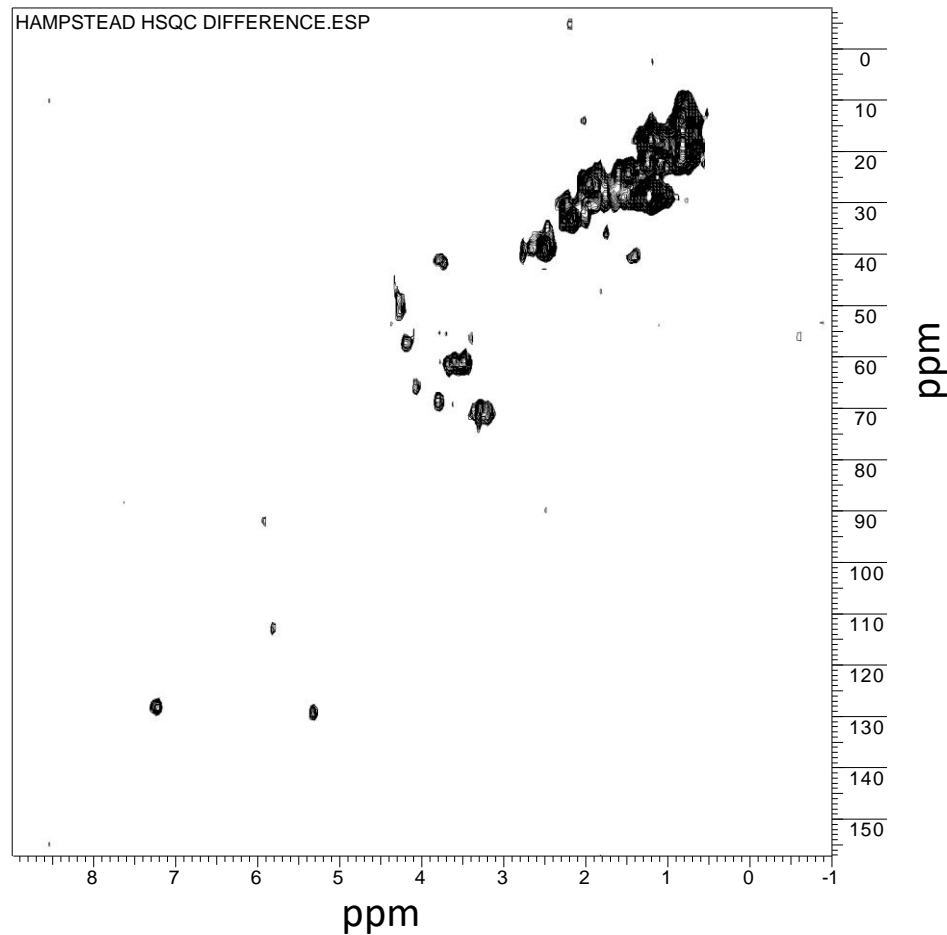
^1H – ^{13}C HSQC NMR analysis of soil organic matter before the application of electron donor in atmosphere enriched with $^{13}\text{CO}_2$



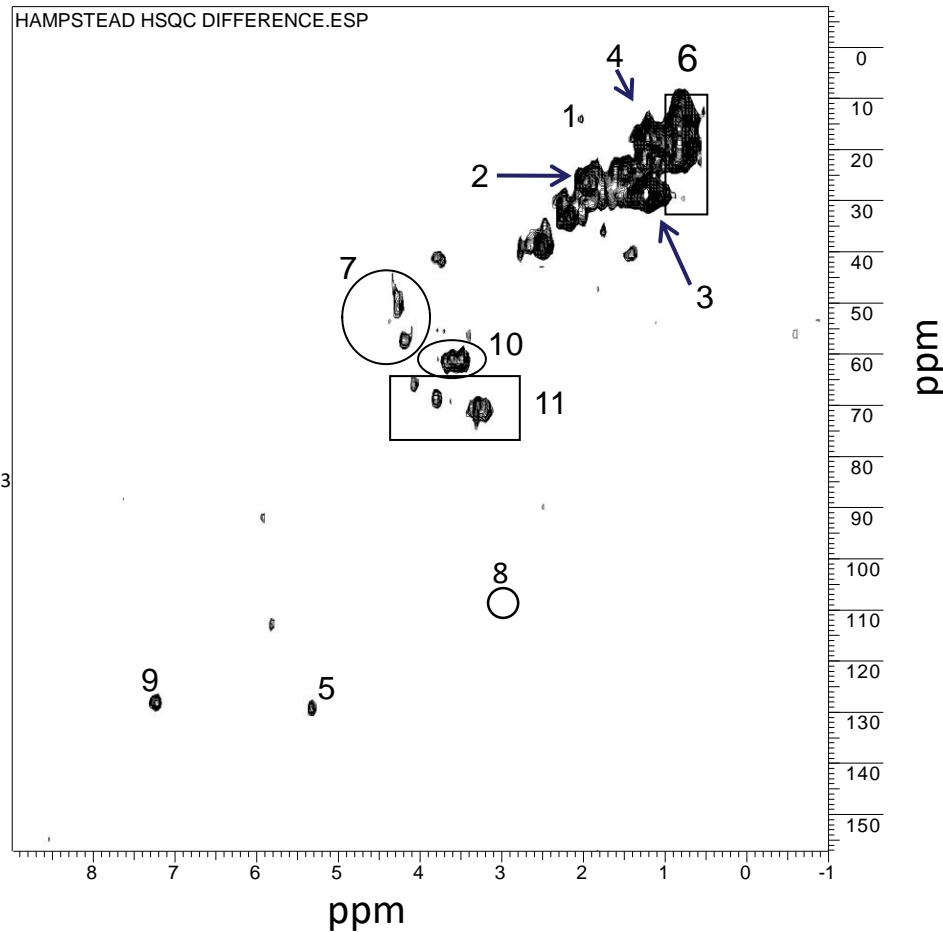
^1H – ^{13}C HSQC NMR analysis of soil organic matter after the application of electron donor in atmosphere enriched with $^{13}\text{CO}_2$



By subtracting the NMR spectra of the $^{12}\text{CO}_2$ from the $^{13}\text{CO}_2$ incubations we can see carbon incorporated into soil as a result of chemosynthesis.



^1H - ^{13}C HSQC Difference – I.E. soil that has been ^{13}C enriched



Latest experiments show that soil organic matter increases by approximately 64% over 12 weeks as a result of the addition of an electron donor, in this case sulfate, to soil.

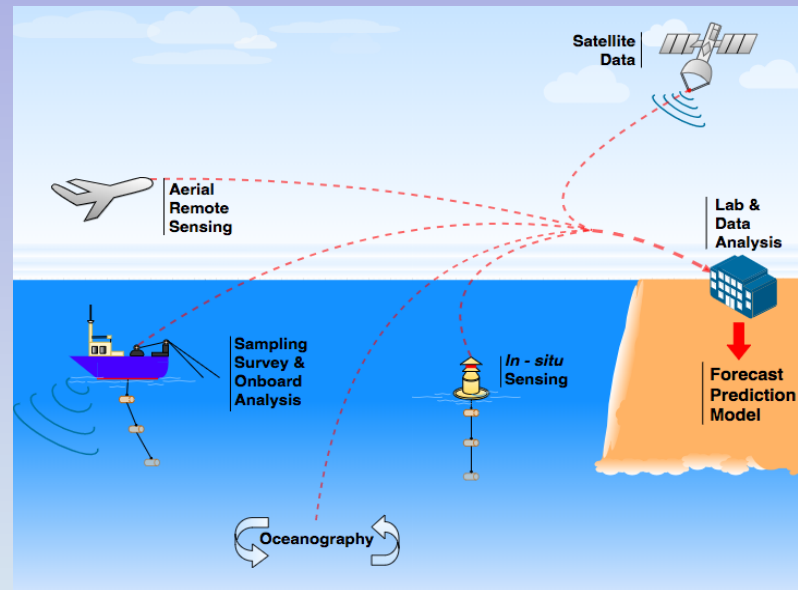
If we underestimate chemosynthetic contributions to soil organic matter, do we also underestimate its contribution to carbon cycling??

- We now know that ~50% of all the Earth's biomass is present in soils and sediments as bacteria,
- It is certain that much of this biomass is comprised of CO₂ fixing potential.



Prediction of Irish Coastal Transformations.

Integrating multidisciplinary geoscientific data into forecasting models to monitor and predict coastal change: Proof of concept in Dublin Bay.



Academic Partners:



Background:

- **Satellite-based environmental data is an important asset** and a major tool that we can use to address societal challenges such as coastal flooding, port security or marine pollution.
- **However, extensive validation is required** not only for improvement of model performance but also for accurately quantifying the errors and consistency of the predictions.

Objectives:

- **A coordinated program of coastal ocean observations** that will be used to validate, calibrate and extract as much information as possible from satellite earth observation data
- We will **integrate these datasets to generate models** that can be used to predict environmental change.
- The project aims to provide experimental proof-of-concept in Dublin Bay that can be extrapolated to a range of environments.

- All data and models produced will be made publicly available.
- The project is multidisciplinary and will integrate mathematical modelling, remote and in-situ sensing, physical and chemical oceanography and seabed mapping.

Funded through SFI
IvP:



Geochemical mapping of inner Dublin Bay and Bull Island

Introduction

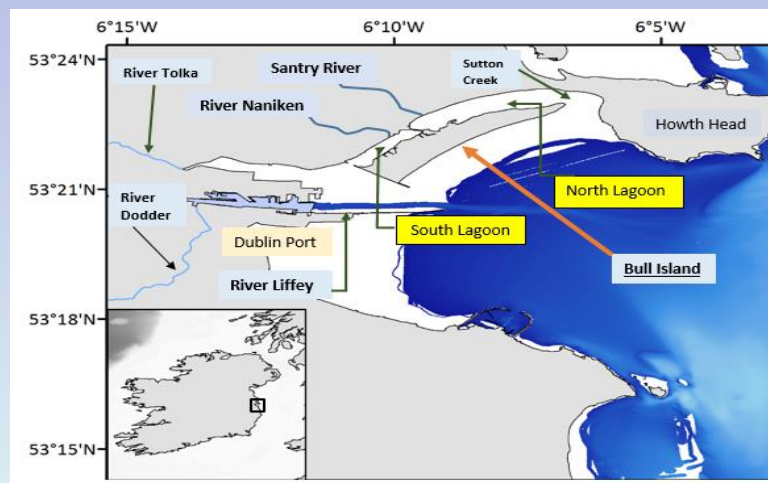
- Bull Island (BI) is situated in Dublin Bay on the east coast of Ireland (Figure 1).
- man-made island as it formed in response to the construction of the Great South Wall in the 1700s and North Wall in the 1800s.
- Special Area of Conservation under the EU Habitats Directive

Objectives

- Provide baseline information for future studies that investigate environmental change over time.
- Use data to validate, calibrate and extract information from satellite earth observation data.
- long-term provision of such datasets is required to generate models that can be used to predict environmental change.

Physical analysis	Chemical analysis
<ul style="list-style-type: none"> Particle Size Analysis (PSA): <ul style="list-style-type: none"> % Clay % Silt % Sand Average Particle Size 	<ul style="list-style-type: none"> Total nitrogen content (%TN) Electrical conductivity (EC) PAHs Total organic carbon content (%TOC) Fe, Cr, Al, Cr, Pb, Ca pH Organic matter content (%OM)

Table 1: Analysis carried out in this Bull Island study



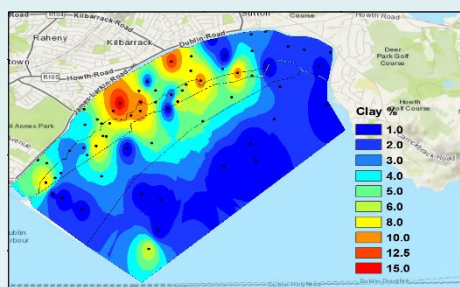
Map of Dublin Bay and Bull Island with sampling zones and points.

Sampling, mapping and analysis

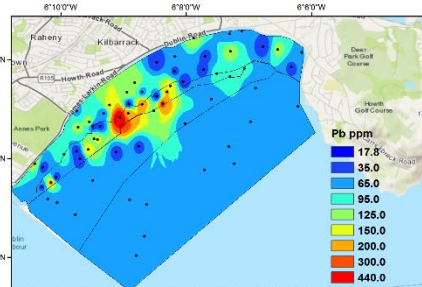
- The sampling plan was produced using R Statistics and ArcGIS software.
- The sampling area was divided into; salt marsh, bull mudflats, Bull island and intertidal.
- ArcGIS was used to map results

RESULTS

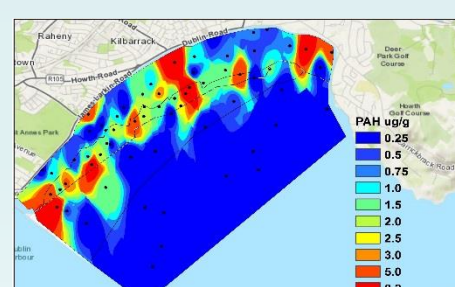
- depositional zone in the salt marsh/mud flat area where PAHs, lead and chromium concentrate.
- primary source of PAHs is the combustion of fossil fuels
- C:N ratios show that high pollutant concentrations are mainly due to terrestrial anthropogenic activity.
- Principal component analysis (PCA) indicates strong linear relationships between PAH and lead with TOC.



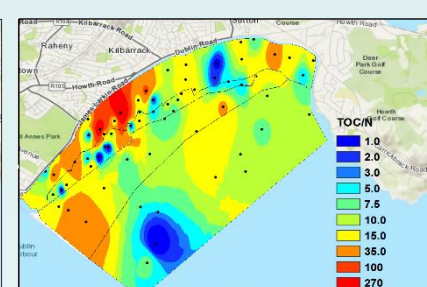
Interpolated map of clay distribution in Bull Island



Lead distributions

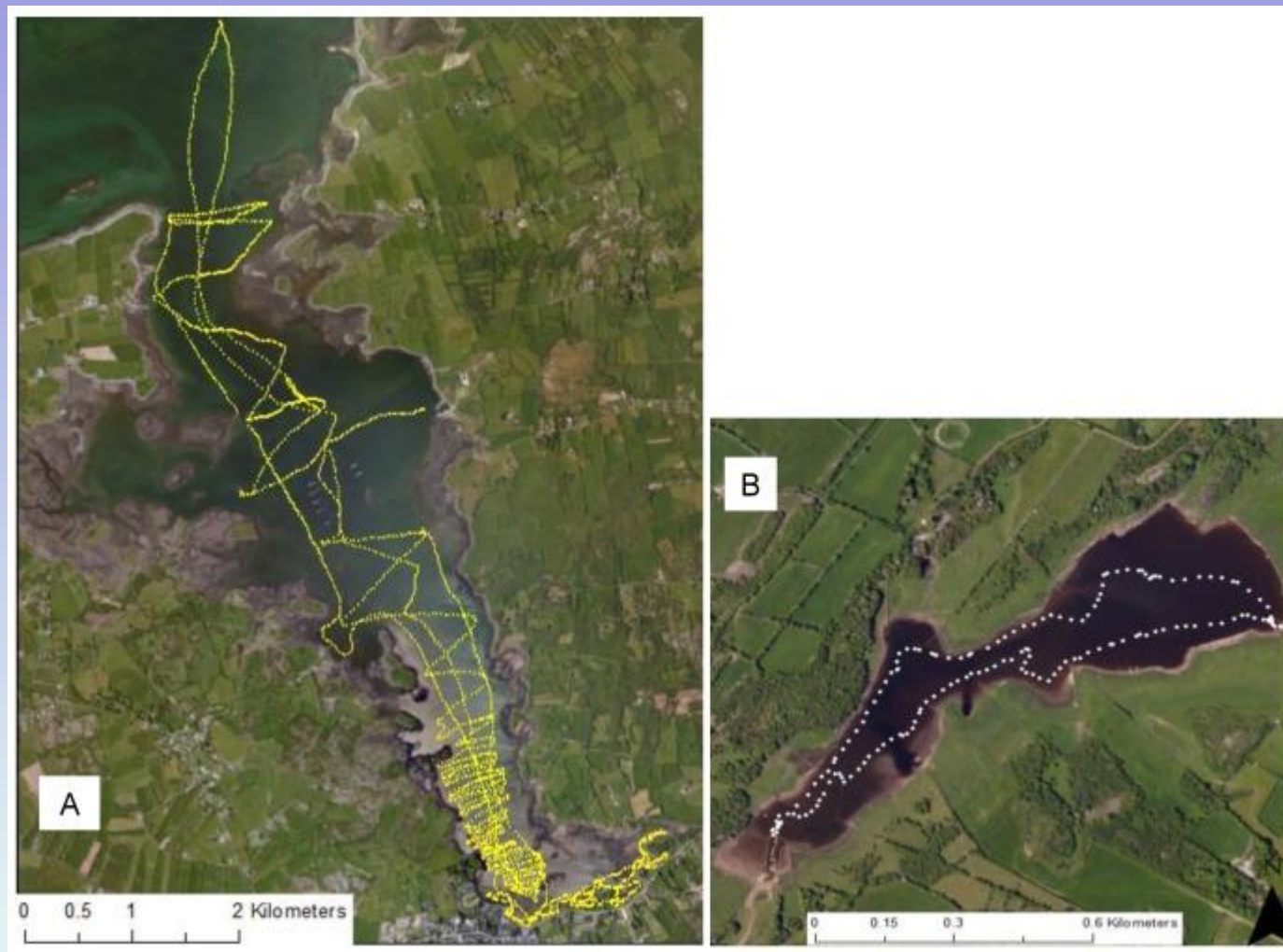


PAH distributions

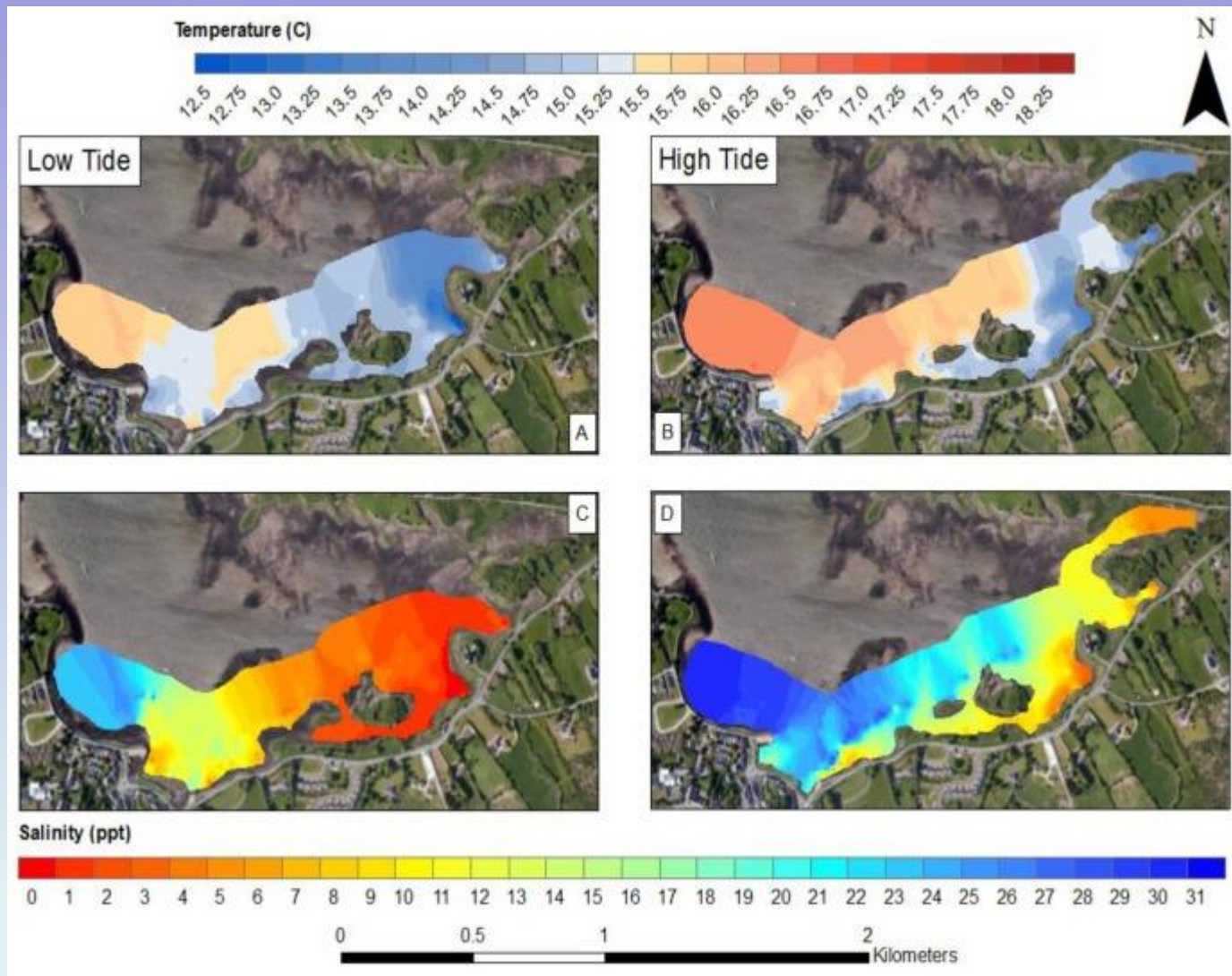


C:N ratio distribution

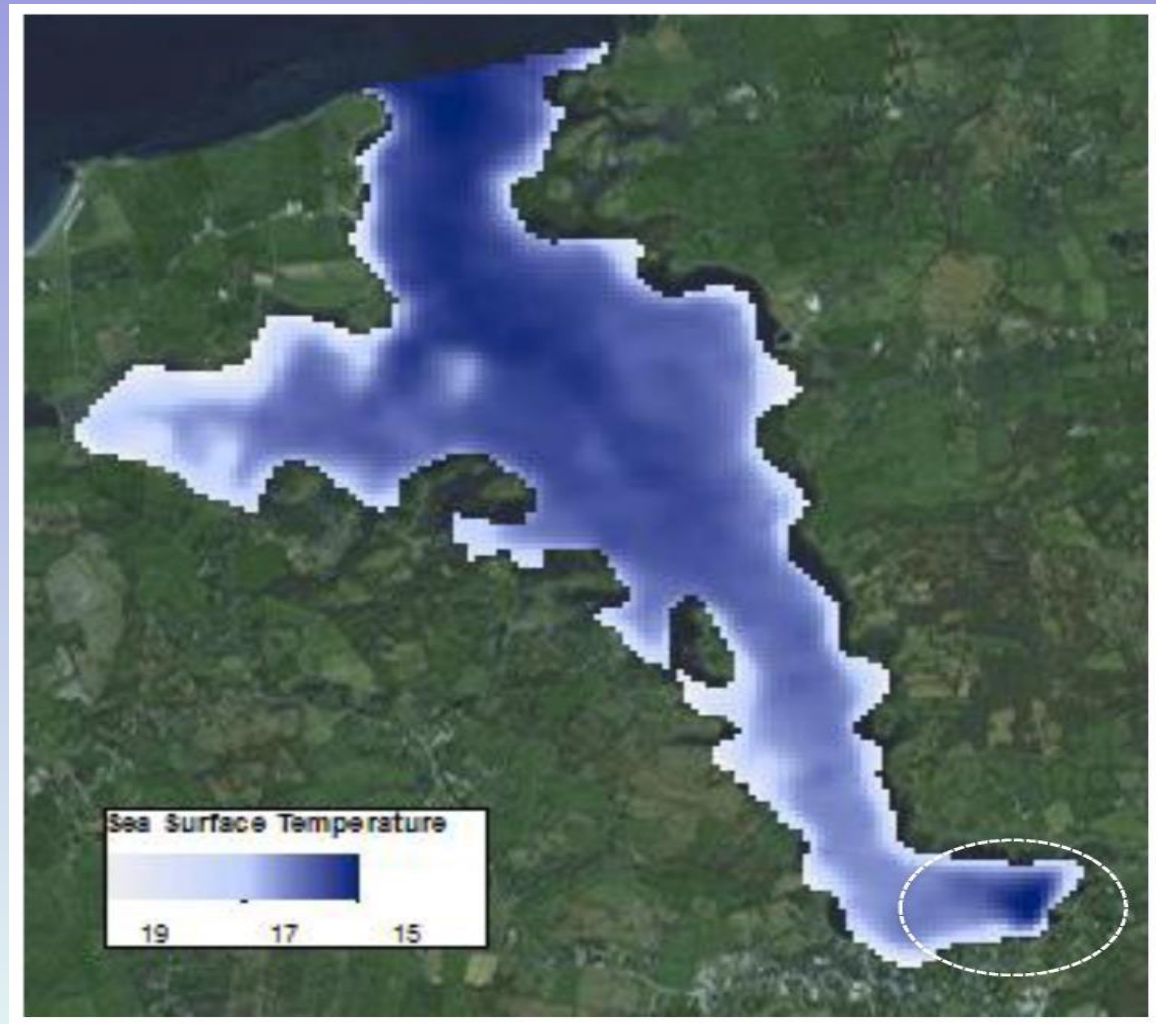
Combining Remote with in-Situ Sensing



Location of in-situ data points collected over a four-day sampling campaign in (A) Kinvara Bay and (B) Cahergruassuan Turlough (25–28 August 2015).

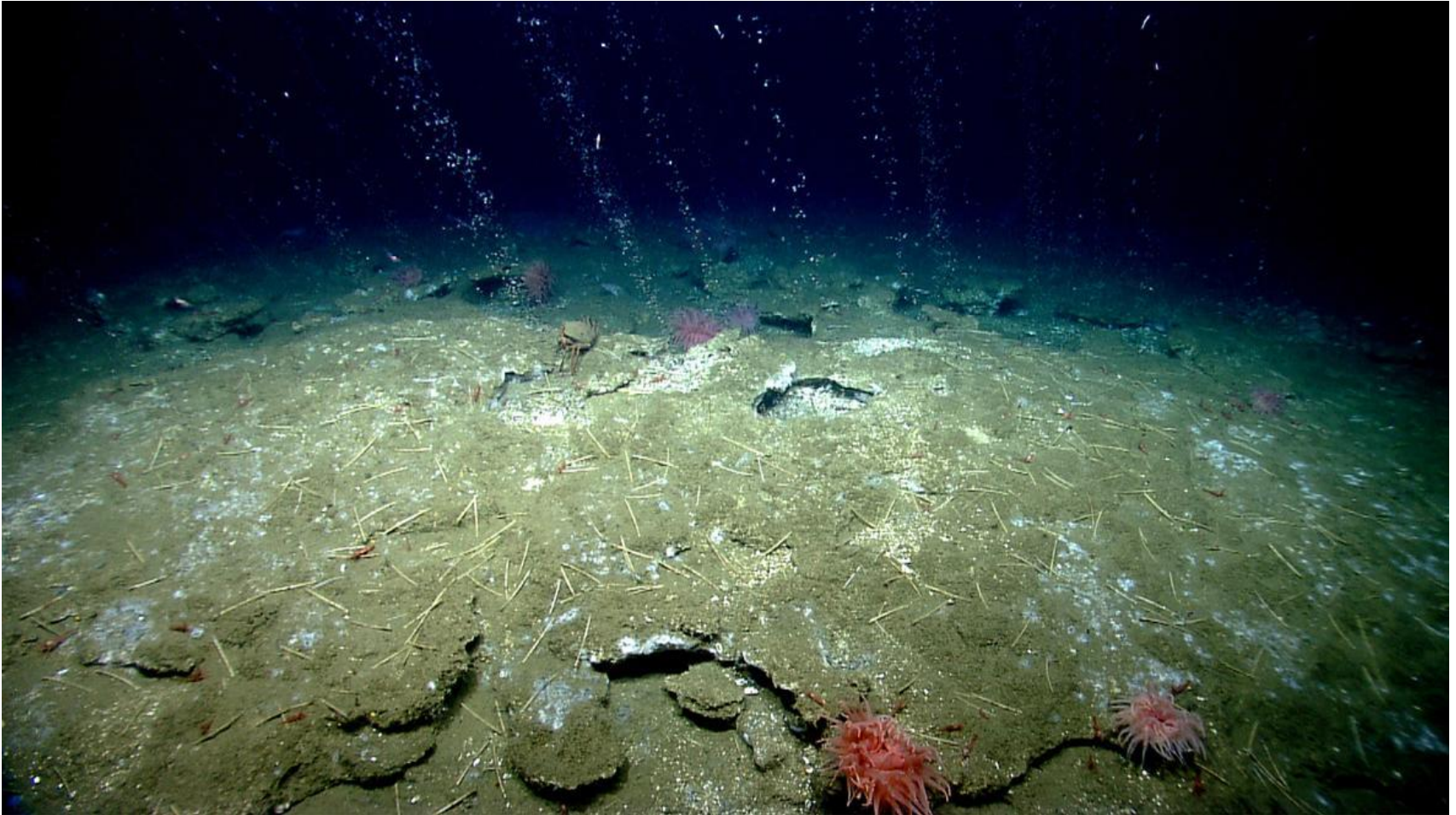


Sea surface temperature and salinity maps of southern Kinvara Bay interpolated from in-situ data (**D**).



Sea surface temperature map of Kinvara Bay generated from Landsat 8 satellite imagery

Marine Methane.



[Widespread methane leakage from the sea floor on the northern US Atlantic Margin](#)

Skarke et al, Aug 2014 · Nature Geoscience

Methane Seepage Features in Irish Waters

Recent discoveries:

Irish Sea

- Codling Fault MDAC mounds
- Irish Sea pockmarks,

Malin Sea:

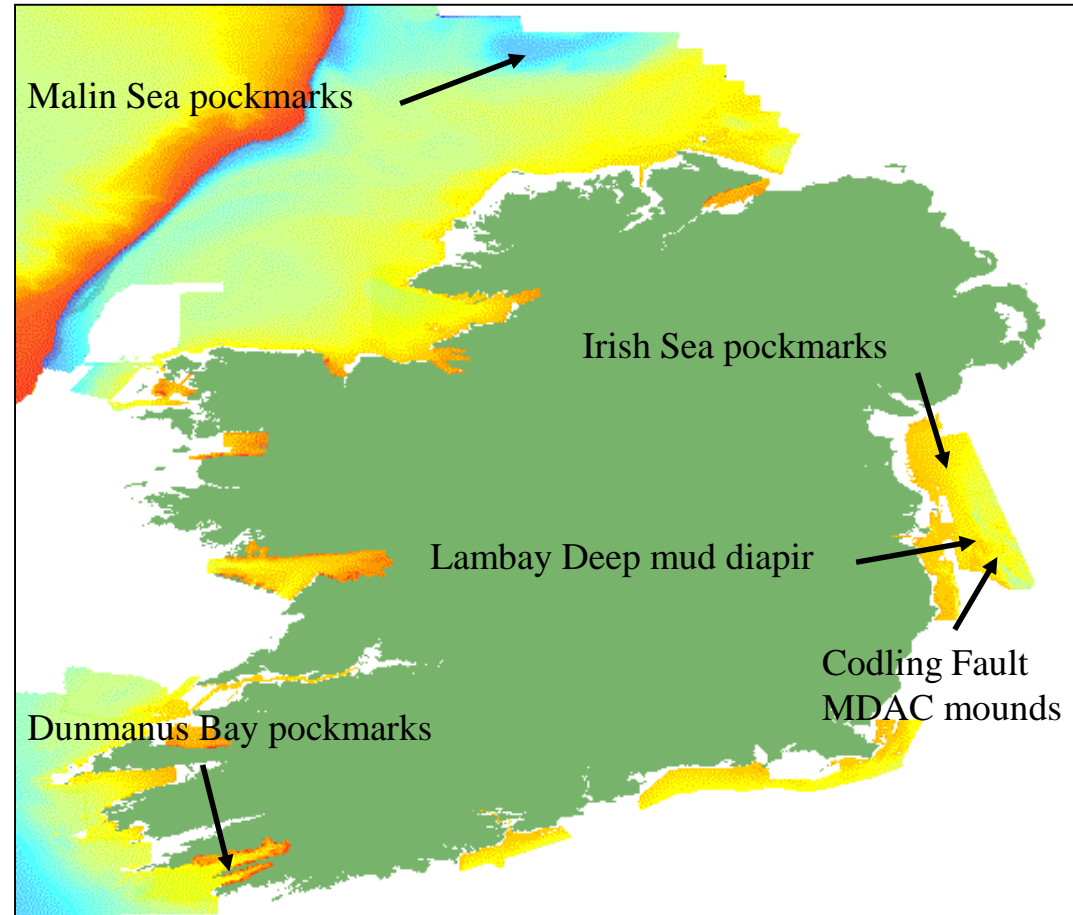
- Malin Shelf Giant Pockmark,

Dunmanus Bay:

- Dunmanus Bay micro-Pockmarks.

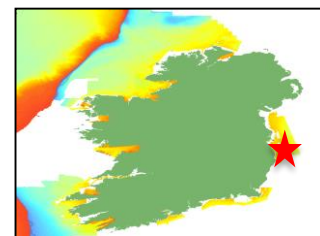
Bantry Bay:

- Pockmarks,
- Constant gas seepage

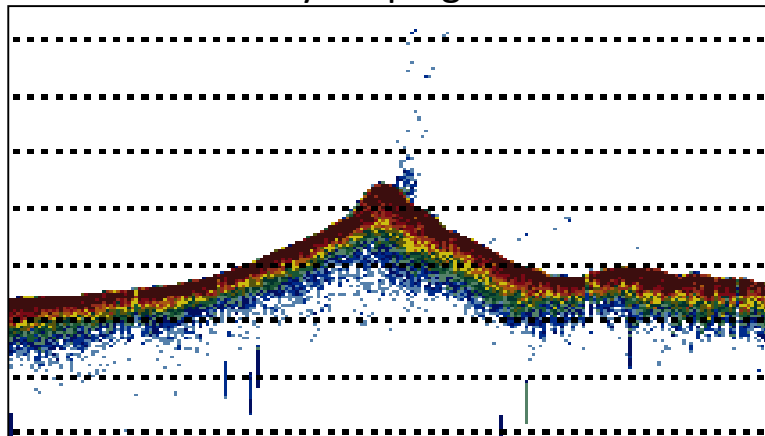


- Szpak, M. T., et al Geophysical and geochemical survey of a large marine pockmark on the Malin Shelf, Ireland. *Geochemistry, Geophysics, Geosystems*. 2012. 3, Q01011, doi:10.1029/2011GC003787.
- Szpak, M. et al. Occurrence, characteristics and formation mechanisms of methane generated micro-pockmarks in Dunmanus Bay, Ireland. *Continental Shelf Research*. 2015, 103, 45-59.
- Shane S O'Reilly, et al. *Estuarine, Coastal and Shelf Science*. 136, 157-171, 2014.
- S. S. O'Reilly, et al. *Continental Shelf Research*, 113, 1-9, 2016.

Codling Fault Methane Derived Authigenic Carbonate mounds (MDAC)



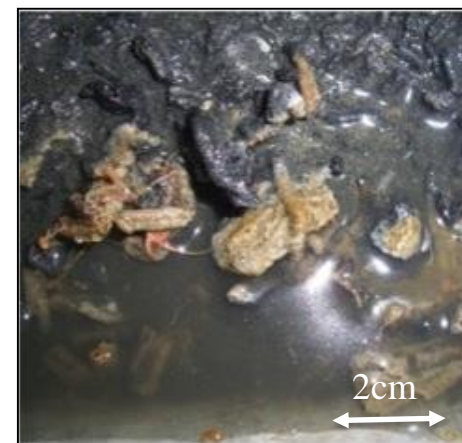
Actively seeping mound



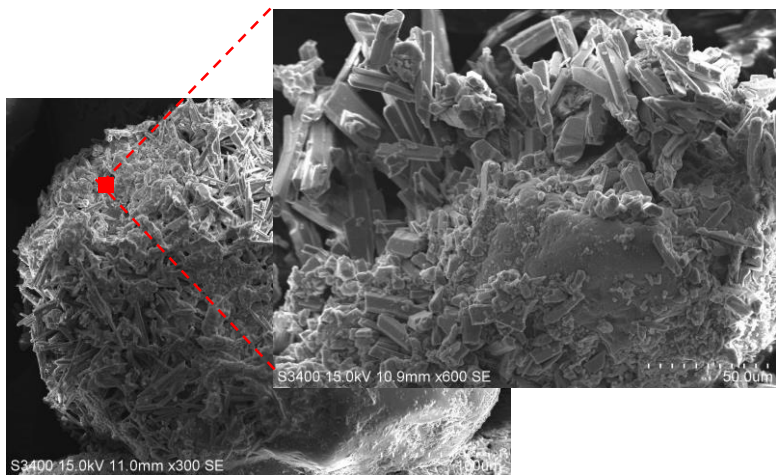
Pavement stacking



Anoxic surface sediment



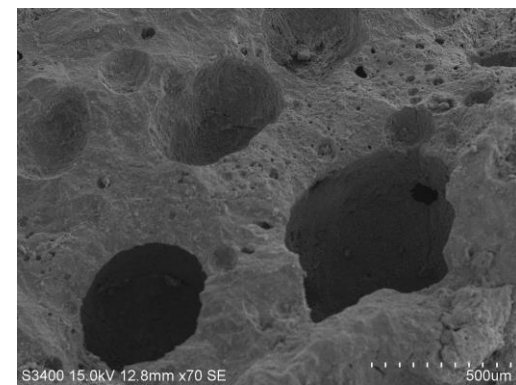
Carbonate & pyrite encrusted quartz grain



Microbial structures



Fluid flow pores



Thank you

Past & Present PGs and PDs:

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Paul Flanagan,
Anthony Grey,
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Suman Kharel
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Andre Simpson (University of Toronto),

DCU School of Chemical Science technicians.

