Advances in Marine Biogeochemistry Conference

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Appendix of abstracts

Oral presentations (in order of appearance)

KEYNOTE

Mechanisms of mussel biomineralisation under climate change: what we know and what we need to find out

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Global climate change threatens the oceans as anthropogenic carbon dioxide causes ocean acidification and warming. The amount of carbonate available in the oceans under ocean acidification will be reduced. Calcifying organisms, such as shellfish, are those at most risk from such ocean acidification, as carbonate is vital in the biomineralisation of their calcium carbonate protective shells. This study examines the mineral specific carbon source and route for shell production or 'biomineralisation pathway' under ocean acidification and warming for three mollusc species. Here I present data for the mussel, *M. edulis,* which suggests that ocean acidification can implement a fundamental shift in the carbon source utilised for biomineralisation. Projections for ocean acidification and reduced carbonate saturation levels may prove detrimental to mussel shell production. Knowledge of the mineral specific biomineralisation pathways, in combination with the shell physical properties, will enable accurate predictions of the vulnerability of these mollusc species to future climate change.

Vulnerability to climate change: exposure, sensitivity and adaptive capacity of molluscan shellfish aquaculture

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Human-induced climate change is changing the physical and biological processes within the marine environment from local to global scales. The shellfish aquaculture industry is an important contributor to the economy of many coastal nations worldwide. Changes in environmental variables such as pH, temperature, primary productivity, and extreme weather events that are directly linked to climate change will have direct effects on aquaculture. We compared the vulnerability of mollusc shellfish aquaculture industries to climate change using an indicator-based approach on a global scale. We used a vulnerability assessment (VA) that was composed of equally-weighted layers: exposure (E), sensitivity (S) and adaptive capacity (AC). Exposure to future changes in sea surface temperature, ocean acidification, extreme weather events, and primary productivity was modelled to the year 2100. Of the countries that scored an overall vulnerability of 5, all scored 5 for adaptive capacity. This indicates that the greatest risk to a nations' vulnerability is the country's own ability to adapt to climate changes. In Asia, top-producing nations were vulnerable in the large part due to high exposure to climate changes. In America and Europe, top-producers were mainly vulnerable due to low adaptive capacity and high sensitivity. Vulnerability increases as exposure to climate change becomes more severe over time. Exposure is largely determined by location and increases in severity each decade to 2100 with the largest changes happening in this study beginning in 2070 and worsening again in 2080, perhaps representing "tipping points" for shellfish aquaculture production.

Seasonality of Coccolithophore populations & calcification rates within a temperate shelf sea system (Celtic Sea)

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Coccolithophores are single celled phytoplankton which dominate pelagic calcite production, however, little is currently known of their importance in shelf seas regarding productivity and role in carbon cycling. Measurements of coccolithophore populations, rates of calcification and cellular calcite quotas were made during fall, spring and summer cruises within the Celtic Sea (NW European Shelf). Samples were taken at the central Celtic sea and shelf edge sites. Coccolithophore populations ranged from <1 cell ml^{-1} to 150 cells ml^{-1} at the central site and 31 to 114 cells ml^{-1} at the shelf edge. Cruise averaged coccolithophore abundances were 69, 55 and 39 cells ml^{-1} for fall, spring and summer respectively. Rates of calcification (measured from ^{14}C uptake) ranged from 0.3 – 135.7 µmol C m^{-3} d^{-1}, with cruise average rates of 17.8, 36.9 and 10.3 µmol C m^{-3} d^{-1} for fall, spring and summer respectively. Cell normalised calcification rates ranged from 0.1 – 7.8 (pmol C cell^{-1} d^{-1}) throughout all seasons due to the composition of coccolithophore communities. These observations demonstrate the temporal and spatial variability of coccolithophore populations and calcite production. We also provide evidence for environmental drivers of coccolithophores, along with the role of species specific growth rates in influencing biogeochemical cycles.

KEYNOTE
Shifts in deep-sea food webs linked to climate and food supply

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Shifts in deep-sea benthic communities detected in time-series data (> 20 years) in the NE Atlantic (Porcupine Abyssal Plain) have been linked to climate-driven variation in particulate organic matter (POM) fluxes[1]. The effect of climate-driven variation in POM flux on food web dynamics over decades in the deep sea is unclear. We investigated the trophic structure of the benthic megafaunal food web using stable nitrogen isotope analysis at the PAP-SO from 1989-2005. The δ^{15}N composition of 6 key species was determined and included: 4 deposit-feeding holothurians, *Amperima rosea*, *Oneirophanta mutabilis*, *Pseudostichopus aemulatus, Psychropotes longicauda,* the predatory anemone *Iosactis vagabunda*, and the mud-ingesting asteroid *Hyphalaster inermis*. Bulk δ^{15}N isotopic compositions ranged from 7.8‰ in *A. rosea* to 16.3‰ in *H. inermis* and revealed clear differences between the species, reflecting different feeding strategies. Significant inter-

annual differences were noted for *A. rosea*, *P. aemulatus* and *H. inermis* but not for *O. mutabilis*. This suggests a change in either the quality or δ^{15}N composition of POM through the time-series coupled to differences in feeding strategy of consumers at the PAP-SO. Compound-specific stable isotope analysis of amino acids (δ^{15}N -AA) allows us to disentangle the relative effects of $\delta^{15}N_{baseline}$ (i.e. $\delta^{15}N_{POM}$) over trophic fractionation on a consumers' δ^{15}N composition. $\delta^{15}N_{Phenylalanine}$, an amino acid representative of the base of the food web was relatively consistent across the 6 species throughout the time series, being ~5‰. Conversely, $\delta^{15}N_{Glutamic}$, an amino acid representative of trophic position varied between different consumers and across the time-series, ranging from 15 to 30‰. These data show that deep-sea food webs do show significant variation in trophic status over decadal time-periods. However, this appears to be primarily driven by changes in community composition, which in turn is linked to climate-driven variation in POM.

1. Billett, D.S.M., Bett, B.J., Reid, W.D.K., Boorman, B. & Priede, I.G.. *Deep-Sea Res II* **57**, 1406–1417 (2010).

Deep transfer of copepod faecal pellets in the Southern Ocean in spring: the role of deep zooplankton communities

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Zooplankton faecal pellets (FP) can be important vehicles for the transfer of particulate organic carbon (POC) to the deep ocean, however, the routes by which these FP reach the deep ocean have yet to be fully resolved. To address this, we present a comparison of copepod FP production to measurements of copepod FP size, shape and number, in the upper mesopelagic (175-205 m) using Marine Snow Catchers, and in the bathypelagic using sediment traps (1,500-2,000 m). We focus on the Scotia Sea, which contains some of the most productive regions in the Southern Ocean, where epipelagic FP production is likely to be high. Although the size distribution of the copepod community suggests that high numbers of small FP are produced in the epipelagic, small FP are rare in the deeper layers, implying that they are not transferred efficiently to depth. Consequently, small FP make only a minor contribution to FP fluxes in the meso- and bathypelagic, particularly in terms of carbon. The change in FP morphology, as well as size distribution, points to the repacking of surface FP in the mesopelagic and *in situ* production in the lower meso- and bathypelagic, which may be augmented by inputs of FP via zooplankton vertical migrations. The flux of carbon to the deeper layers within the Southern Ocean is therefore strongly modulated by meso- and bathypelagic zooplankton, meaning that the community structure in these zones has a major impact on the efficiency of FP transfer to depth.

Increased warming reduces carbon export in the Southern Ocean

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Microbial respiration of particulate organic carbon (POC) is one of the key processes controlling how much POC is exported from the surface ocean and potentially stored on long time scales in the deep. Century-old ecological theory predicts respiration scales with temperature, hence rising sea temperatures would increase microbial respiration and likely reduce POC export. We tested this theory in the sub-Antarctic Southern Ocean by collecting and forming large sinking particles from the mixed layer and measured microbial oxygen uptake with time over a 10 °C temperature range. The study occurred when *in situ* temperature was at its annual maximum, so our extended temperature range is beyond the norm for sub-Antarctic microbes. Applying metabolic theory of ecology (MTE) our novel results suggest net export could decrease by 9 (± 2) or 34 (±10) % before the end of the century, depending on which Representative Concentration Pathway is applied. This is much higher than predicted by simple mechanistic models due to the high temperature sensitivity of the Southern Ocean. The estimated decrease in exported POC would likely reduce carbon storage in the deep oceans and increase the amount of CO_2 that could be re-exchanged with the atmosphere.

Hadal trenches: evidence for particulate-matter dynamics on short time scales

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With regards to marine biology and biogeochemistry, hadal trenches (water depths >6000m) are amongst the least understood seafloor features of the ocean. For instance, qualitative and quantitative aspects of food supply to the hadal benthos remain largely unclear. Recent studies revealed that, despite the great hadal water depths, amounts of 'fresher' organic material can be higher and rates of aerobic respiration of the benthic community can be increased in comparison to nearby plain sites. These results indicate that there can be processes that concentrate nutritious organic matter towards the trench axis. Material input through downslope mass wasting is probably too infrequent and the transported organic matter too refractory to meet the demand of the benthic community for more easily degradable organic matter. Therefore, more subtle and more continuous transport processes are likely to play an important role in controlling qualitative and quantitative aspects of organic-matter supply into the trenches. The nature of these processes and their characteristic time scales has remained largely unclear though. Here, we present the results of the first measurements of the naturally occurring radioactive and short-lived (half life: 24.1 days) particle tracer thorium-234 (^{234}Th) that were carried out in four hadal trenches in the Northwest Pacific (Mariana, Japan, Tonga, Kuril-Kamchatka) to

further constrain time scales and processes that affect particle - and, hence, food - supply into hadal trenches.

New insights into abyssal-hill biogeochemistry

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Current estimates suggest that more than 60% of the global seafloor (>40% of the Earth's surface) are covered by millions of abyssal hills and mountains. These features introduce spatial fluid-dynamic 'granularity' whose influence on deep-ocean sediment biogeochemistry is largely unknown. Here, we present results from a tall, fluid-dynamically well characterised abyssal hill on the Porcupine Abyssal Plain in the Northeast Atlantic and compare biogeochemical surface-sediment properties from the hill and upstream plain. The study revealed two main results. (1) In hill sediments, organic-carbon and nitrogen contents are only about half as high as on the plain while proteinaceous material displays evidence for a reduced extent of degradation. That is, while the flow/hill interactions reduce the overall amount of organic matter in surface sediments, the organic matter that is deposited appears to have a lower extent of degradation. (2) On the hill, sediments were more coarse-grained (reducing particle surface area) and displayed very variable calcite contents (influencing particle surface charge), potentially influencing the extent and compound-specificity of sorptive organic-matter preservation. Given the high number of abyssal hills and mountains, their integrative influence on formation and composition of deep-sea sediments warrants more attention.

'Lab-on-Chip' sensors for *in situ* determination of macronutrients in natural waters

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In situ sensors are attractive alternatives to discrete sampling of natural waters, offering the potential for sustained long term monitoring in remote locations, and eliminating the need for sample handling. Microfluidic technology miniaturises bench-top assay systems into portable devices, known as a 'lab on a chip' (LOC) sensors. The Ocean Technology and Engineering Group at the National Oceanography Centre has been developing state-of-the-art microfluidic sensors, designed to autonomously perform *in situ* measurements down to full ocean depths. In this presentation I will provide an overview of the current state of the technology, including the current suite of nutrients we can detect down to the nM range. In this presentation I will show some laboratory development data on our newer silicate sensor in addition to recent deployment data using the nitrate and phosphate sensors. We have recorded for the first time nutrient concentrations and pH in Seychelles waters, which is now part of an on-going deployment. I will be showing some initial data collected over 4 days to highlight this work. I will also present high resolution P data collected over a 2 month deployment in a chalk river to demonstrate how these sensors allow access to unprecedented high resolution data.

A seasonal comparison of high-resolution nitrate fluxes into the euphotic zone in the Celtic shelf sea, using a Lab-on-Chip nutrient and microstructure sensors deployed on gliders

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Seasonally stratified temperate shelf seas act as important carbon sinks, where primary production is controlled by the availability of nutrients such as nitrate. Spring phytoplankton blooms reduce nitrate concentrations within the euphotic zone, with primary production being confined to the sub-surface chlorophyll maximum during the summer. Diapycnal nitrate fluxes from replete bottom layer water can drastically result in increased primary production, happening on temporal scales from hours to days, with current sampling methods unable to capture high frequency events leading to an underestimation of nutrient fluxes and hence new production. Autonomous underwater vehicles (AUV) allow the simultaneous collection of physical and biogeochemical parameters on both extended spatial and temporal scales. Here, we describe for the first time, the use of a novel Lab-on-Chip nutrient sensor and MicroRider microstructure package deployed on an autonomous underwater gliders that collected high-resolution nitrate and turbulence data (> 1500 profiles per deployment), over both the spring bloom (April 2015) and summer (July 2015) periods in the central Celtic Sea. We highlight the ability of sensors and AUV deployments to improve our understanding of biogeochemical cycles within the dynamic temperature shelf seas.

Next generation sensors for marine microbiology using Lab on a Chip

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Ocean microbes are essential to many of the processes that sustain life on earth. In contrast, some species can also cause serious disease in humans and animals, as well as contaminate drinking water and food supplies. Thus, there is an increasing requirement to make accurate, high resolution measurements of ocean microbial communities, even more so as the oceans respond to changing climatic and anthropogenic pressures. New innovations in engineering and biotechnology mean that complex bio-analytical methods, once restricted to the centralised, highly resourced laboratory, can now be implemented on portable or deployable, low power and low cost instrumentation. The Ocean Technology and Engineering Group (OTEG) at the National Oceanography Centre (NOC) are developing a new suite of samplers and sensors for ocean microbiology, offering new possibilities in marine metrology. These include field-portable and deployable instruments for detecting small molecule marine contaminants and harmful microorganisms *in situ*, obviating the need for a centralised lab, bulky equipment and trained personnel. Core technologies include aptamer-based sensors for small molecules, eco-genomic sensing platforms for nucleic acid analysis and multi-wavelength and multi-parametric fluorescence-impedance micro-cytometers. This presentation will provide an overview of current OTEG sensing capabilities with emphasis on new sensing platforms, and their applications for marine microbial science.

What microbes can tell us about nutrient mixing in the open ocean

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Blooms occur in the oligotrophic open ocean despite strong stratification in the warm summer months, but the nutrient sources fuelling these blooms remain unknown. The potential for vertical advection of deep nutrients was addressed using a combination of experimental manipulations and high-resolution *in situ* sampling in the North Pacific Subtropical Gyre. The surface (25m) microbial community associated with an anticyclonic eddy was sampled and preserved *in situ* with an ecogenomic sensor (the Environmental Sample Processor). Metatranscriptomic patterns recovered from 3 days of *in situ* samples were extremely similar to patterns 24h after simulated diapycnal mixing in deck board incubations, but distinct from the no-mixing control conditions and simulated isopycnal mixing treatments. These "mixing signature" metatranscriptomic patterns were dominated by photosynthesis and nutrient response genes, despite no indication of nutrient advection *in situ* from frequent ship-based density, chlorophyll and oxygen water column profiles. In the context of previous literature including mixing experiments at Station ALOHA, we find that while the stimulation of photosynthetic organisms is immediate, oxygen production and chlorophyll increases are undetectable until 3-4 days after mixing in the summer months. Therefore, metatranscriptomic profiles may serve as more sensitive indicators of photosynthetic stimulation due to nutrient advection.

In situ chemical sensors based on droplet microfluidics

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In situ chemical sensors can deliver large data sets of useful biogeochemical information in real time. Microfluidic sensors (which automatically sample the environment, add an analyte-specific reagent to produce an optical response which is measured and recorded) can be used to measure a huge range of potential analytes and offer high sensitivities and excellent long-term stability. Here I will describe a prototype field-deployable chemical sensor that, in contrast to all previous microfluidic-based sensors, utilises a droplet flow regime. In droplet flow, aqueous samples are carried as discrete droplets within a stream of oil, which gives reduced carry-over between samples and allows for improvements in temporal resolution as well as in fluid and power economy. Furthermore as sample droplets can be interleaved with droplets of known standards, internal calibration can be continuously performed. Here I will explain the mode of operation of the sensor platform and describe its application to the measurement of nitrate, including laboratory characterisation and results from an in situ deployment in a tidal river (River Itchen) to characterise the variation in nutrient levels over the tidal cycle.

KEYNOTE
Coupling and decoupling of Zn and Si in the global ocean

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The remarkable similarity of the oceanic distributions of Zn and Si has been puzzled over by oceanographers for decades. While Si is dominantly cycled by diatoms, which use it to build their opaline frustule, Zn is associated with the organic parts of phytoplankton, co-occurring with P [1]. Zinc is also regenerated from sinking phytoplankton with P, at shallow depths, while Si is released at greater depths through the slower dissolution of opal [2]. A recent study proposed a solution to this Zn-Si paradox: the elevated uptake of Si and Zn compared to P by diatoms growing in the well-mixed Southern Ocean, followed by the transport of the resulting Zn:Si 'fingerprint' to the global ocean by the ocean circulation [3]. A 3-d ocean model that simulates such elevated Zn/P uptake ratios reproduces the global Zn:Si relationship even without any explicit coupling between the two elements [3]. We present an analysis of the systematics of the Zn-Si relationship in the subarctic northeast Pacific [data from 4], a region distal from the Southern Ocean influence. Here, 1-d vertical cycling processes, including the differing length scales of regeneration of Zn and Si, may play a more dominant role in setting dissolved nutrient profiles. Indeed, Zn and Si are decoupled in this region, with a notable shallow Zn excess. We attribute this decoupling to the aforementioned shallow remineralisation of Zn relative to Si, providing corroborating evidence that there is no mechanistic link in their vertical cycling. We thus contend that whilst the subarctic north Pacific is unique in the decoupling of Zn and Si distributions, this decoupling comes about through the same mechanisms that lead to their coupling at the global scale.

[1] Twining, B. S., & Baines, S. B. (2013). *Ann. Rev. Mar. Sci. 5*, 191-215. [2] Twining, B. S. et al. (2014) *Limnol. Oceanogr*. 59, 689-704. [3] Vance D., et al. (2017). *Nature Geoscience* 10(3), 202-206. [4] Janssen D. J. & Cullen J. T. (2015). *Mar. Chem.* 177, 124-133.

The Impact of Upwelling on the DIC-Temperature Relationship in the Surface Global Ocean

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The release of the Global Ocean Data Analysis Project Version 2 (GLODAPv2) database presents an opportunity to improve our understanding of the controls on the dissolved inorganic carbon (DIC) distribution in the global ocean. Of particular interest in this study is what controls the latitudinal gradient (of up to 310 µmol kg^{-1}) in surface open ocean nDIC. In this study, we specifically study the impact of upwelling in the subpolar oceans on surface DIC and aqueous CO_2, where CO_2-rich water is brought to the surface from depth in both the Southern Ocean (meridional overturning circulation) and subarctic regions (deep winter mixing). Our study finds that upwelling, which has not traditionally been considered as a major driver, can be responsible for a majority of the surface nDIC latitudinal gradient (40-280 µmol kg^{-1} out of 310 µmol kg^{-1} in the high-latitude Southern Ocean, depending on how calculated). The relationship between CO_2(aq) and temperature also further demonstrates the role of upwelling: CO_2(aq) in the Southern Ocean and North Pacific fall above their saturating values (up to 5 µmol kg^{-1}), reaching their highest values in winter, consistent with the calculated upwelling effects. Whereas CO_2(aq) in the North Atlantic (observations only in summer) falls below their saturating values (up to 15 µmol kg^{-1}), probably due to the biological production.

Comparison of Latitudinal Distributions of Macronutrients, Alkalinity and Carbon

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We used the new high-quality dataset GLODAPv2 to examine the latitudinal distributions of several biogeochemical variables in each of the three ocean basins (Atlantic, Pacific, Indian). Similarities and differences are instructive in showing how different biogeochemical processes play out on the global scale. As well as the macronutrients (nitrate, phosphate and silicate), an alkalinity-based tracer (Alk*; Fry et al 2015) and salinity-normalised DIC were plotted. All five are seen to exhibit increases from low latitudes to high latitudes, attributed to upwelling and/or winter mixing of iron-deficient deep water at high latitudes (Moore, 2016), and, for nDIC, also to temperature-related changes in CO_2 solubility. For all variables, the elevation from low to high latitudes is less pronounced in the subarctic North

Atlantic than in the subarctic North Pacific or Southern Ocean, attributed to the young age of the deep water entrained in the North Atlantic during winter. Increases in nDIC, nitrate and phosphate in the north Indian Ocean and Equatorial Pacific Ocean are not matched by increases in either Alk* or silicate, attributed to the source waters for the upwelling coming from depths that are shallower than the dissolution depths of calcium carbonate and opal.

Fry, Claudia H., et al. "Analysis of global surface ocean alkalinity to determine controlling processes." *Marine Chemistry* 174 (2015): 46-57.

Moore, C. M. (2016), Diagnosing oceanic nutrient deficiency, *Philosophical Transactions of the Royal Society A*, *374*, 20152090, doi: 10.1098/rsta.2015.0290.

Temporal variability in the biogeochemistry of the surface North Atlantic - more than a decade of Ship of Opportunity data

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The biological carbon pump is important for the carbon sink potential of the North Atlantic and must be sustained by an adequate supply of nutrients. Here we analyse the evolution of surface inorganic nutrients across the low and mid-latitude North Atlantic, the mechanisms supplying these nutrients as well as the consequences of their variability. We present the results of an 11-year time series of samples collected onboard voluntary observing ships. Our results show an increasing trend of 0.024 ± 0.003 μmol L^{-1} yr^{-1} in nitrate in the subtropical North Atlantic. The trend is not observed in silicate or phosphate. For a large area in the mid-latitude North Atlantic, the winters of 2009/2010 and 2010/2011 are characterized by nitrate values more than 1 μmol L^{-1} higher than the average for the data coverage period (2002-2013). This translates into larger values of new production. New production in the region between 31° and 39° N was 20.6 g C m^{-2} in 2010, which is over 260% higher than the average value of the other years. Our results provide a unique collection of data that increases our observational footprint of Atlantic biogeochemistry.

NERC KNOWLEDGE EXCHANGE: MARINE POLICY AND MANAGEMENT

From marine biogeochemistry to marine management and policy, and back again

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As a NERC Knowledge Exchange Fellow working with management and policy organisations, such as Marine Scotland and the Marine Management Organisation, I often notice that the marine science and marine management communities don't always communicate well, resulting is lost chances for scientists to further support effective, evidence-based marine management, and lost opportunities for potential "impact" from research. In this presentation I will explore some ways in which researchers like yourselves can improve the chances of your research being picked up by the right people – it's probably simpler and less time consuming than you think it might be. It could be as simple as coming to talk to me, or contacting me after this meeting, if you would like to know more about "knowledge exchange", or if you carry out research you think would be useful to marine managers.

KEYNOTE

Isotopic insights into the marine biogeochemical barium cycle

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Studying the marine biogeochemical barium (Ba) cycle can provide valuable insights into the export of organic carbon to the deep ocean and marine sediments. In particular, suspended particulate Ba inventories in mesopelagic waters have been used as a proxy for organic carbon remineralisation rates, while Ba accumulation rates in marine sediments are considered to be a robust paleo-proxy for export production. The basis of these proxy applications stem from the dominant sink of Ba in the ocean being through the precipitation of barite ($BaSO_4$), which is thought to occur within decaying organic aggregates. However, aspects of the marine Ba cycle are still poorly understood compromising the reliability of these proxy applications. In this talk, we investigate the potential of novel stable isotope composition variations to study the marine Ba cycle. Specifically, how can Ba isotope compositions variations in the water column be used to better constrain the internal cycling of Ba in the ocean? What can the Ba isotope compositions of marine sediments tell us about the cycling of Ba in the modern and paleo-oceans?

Lessons learned from modelling SSB benthic observations in the Celtic Sea

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Results from the European Regional Seas Ecosystem Model (ERSEM) biogeochemical model are compared with new observations collected under the UK Shelf Seas Biogeochemistry (SSB) programme to assess model performance and clarify elements of shelf-sea benthic biogeochemistry and carbon cycling. Differences between modelled and observed quantities of organic carbon in the bed were interpreted to suggest that a large part (>90%) of the observed benthic organic carbon is biologically relatively inactive. Results from modelling oxygen dynamics suggest that modelled oxygen uptake is rather insensitive to the relative biomasses of the biological components (macrofauna, meiofauna and bacteria), being ultimately controlled by total input of organic material to the bed. Also, results of including permeable sediment effects will be presented.

Composition and size structure of plankton communities across the North Atlantic

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The ocean environment is changing rapidly in response to global climate change, especially in higher latitudes with increased pressure from rising temperatures. Marine plankton are highly sensitive indicators of change due to their size and dependence on the physical environment but also hold important roles in the marine ecosystem, such as forming the base of the marine food web. The Continuous Plankton Recorder (CPR) survey simultaneously collects both phytoplankton and zooplankton. Temporal and spatial analysis has previously been completed using abundance measures and biomass proxies such as the Phytoplankton Colour Index from the survey; however, such studies have lacked important taxonomic information about the community. In this study, taxonomic data from the CPR survey and cell size information from literature was used to examine changes to the composition and size structure of the plankton community across the North Atlantic between 1958 and 2013. These observations reveal large-scale spatio-temporal changes in species dominance and complex interactions within the community composition. The relationship of the plankton community was also explored in the context of changes to the physical environment, highlighting the complexity of top down and bottom up interactions.

Using dissolved inorganic carbon (DIC) $\delta^{13}C$ and $\Delta^{14}C$ ratios to characterise organic matter respiration and blue carbon stability within an East Coast US salt marsh

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The low-oxygen, high-salinity environments found within intertidal salt marshes facilitate the long-term vertical accretion of organic matter (OM) such that the formation of peaty, organic-rich sediments produces a significant long-term carbon store. In the context of the global carbon cycle and climate change mitigation, this ranks them amongst the most important natural carbon sinks on the planet. Indeed, the concept of a 'blue carbon' economy which leverages the carbon storage capacity of the marine environment for its own protection has been in development for some time, with saltmarshes representing ideal candidates for such a scheme. However, a lack of certainty surrounding the stability of marsh carbon stores in the face of increasing temperatures, rising sea levels, large-scale land use change and coastal nutrient enrichment has thus far inhibited its realisation. Here, we assess the stability of a marsh carbon store on the US East Coast (Sage Lot Pond (SLP), Cape Cod, MA). Using dissolved inorganic carbon (DIC) $\delta^{13}C$ and $\Delta^{14}C$ isotope ratios, we identify a DIC component produced via the respiration of stored OM (DIC_{MR}) of 0 - 16% of

total DIC (DIC_{total}) within surface waters, and of 12 - 100% within porewaters. These values occurred alongside exclusively modern $\Delta^{14}C$ values of 13 - 22‰. Modelling based upon OM age dating at this site is indicative of DIC_{MR} produced via the respiration of OM which is modern in nature, likely having been laid down within the last 13 years. Whilst tidal stage was seen to influence DIC_{MR}, it did not significantly influence the age of OM being respired. We conclude that the SLP marsh blue carbon store is stable.

KEYNOTE

The changing nature of marine biogeochemistry: past, present and future

Peter J Statham

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The talk will provide a personal view of how modern marine biogeochemistry has evolved over the last 40 years. I will focus on how some factors, such as technological innovations, and inspirational individuals underpin the field and have moved the science rapidly on. A key development has been the move from isolated sub-disciplines in ocean sciences (including marine chemistry) to the modern interdisciplinary field of marine biogeochemistry. I will draw on some examples from my own experiences, ranging from determination of dissolved organic carbon in the ocean to metal cycles to illustrate the ups and downs of a career in this field. I will end by giving my view of some of the exciting and important science waiting for the new generation of marine biogeochemists emerging now.

Stability of dissolved and soluble Fe(II) in shelf sediment porewaters and release to an oxic water column

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This study presents the findings on the benthic iron (Fe) cycle and release of dissolved Fe (dFe) from cohesive shelf sediments to the overlying water column over two seasons, late spring and late summer, in oxygenated waters of the Celtic Sea (Klar et al., 2017). Our findings indicate that dissimilatory iron reduction is an important mechanism of dFe formation, and porewater dFe was predominantly in the soluble and reduced Fe(II) form. We observed higher concentrations of dFe in cohesive surface sediments after the spring bloom, following the deposition of large amounts of phytodetritus to the seafloor. In addition, we detected Fe(II) in oxic seawater overlying sediments and bottom waters, hence a significant fraction of Fe(II) resists oxidation, thus suggesting that some additional mechanism must account for the stabilisation of reduced Fe. Measured oxidation rates of Fe(II) in waters overlying sediments were substantially slower than empirical predictions. In addition, model calculations show that the diffusive efflux of Fe(II) from porewaters may be enhanced 30% in late spring and 8% in late summer in the presence of Fe(II)-stabilising organic ligands.

Klar, et al. (2017) *Biogeochemistry*, DOI 10.1007/s10533-017-0309-x

Iron isotopes track the uptake and exchange of iron across an oxic shelf sea

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Iron (Fe) supply to the surface ocean dictates levels of primary productivity where macronutrients are replete. Continental shelves are a source of Fe to ocean basins however, mechanisms that control its supply are poorly understood. Fe isotopes trace the transfer of Fe from shelf sediments to the water column and the cycling of Fe within the water column. Oxic shelf seas represent a large fraction of ocean continental shelves but the importance of its benthic Fe supply is poorly constrained. Water column profiles of dissolved iron (dFe) and iron isotopes (δ^{56}dFe) in the Celtic Sea are presented from across the shelf. The on-shelf site was sampled during pre-bloom, bloom and post bloom conditions. As the bloom develops δ^{56}dFe becomes lighter in surface waters due to biological uptake of Fe. Bottom waters on shelf showed little variation between bloom (-0.22 ± 0.04 ‰) and post bloom (-0.26 ± 0.03 ‰). These values are indicative of benthic Fe supply to the water column. The isotopic composition of dFe in the water column allows the processes of dFe-particle exchange, biological uptake, and sedimentary sources to be disentangled. This improves our understanding of dFe supply on the shelf and export to the open ocean.

Trace metal supply from the western Antarctic Peninsula Shelf to the open ocean

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The offshore waters of the Antarctic Circumpolar Current (ACC) are very low in iron (Fe), but the shelf waters of the western Antarctic Peninsula (WAP) are Fe rich below the mixed layer. Circumpolar Deep Water (CDW) intruding onto the WAP shelf becomes enriched in Fe due to interaction with multiple sources (sediments, (sub)glacial melt, etc.). On-shelf CDW flux via deep canyons and eddies has the potential to be offset locally by export along the central WAP shelf, which may bring Fe-replete shelf water into the high-nutrient ACC and stimulate off-shelf primary production. However, little is known about the distribution, mechanisms, magnitude or frequency of off-shelf transport along the central WAP. We present full water-column trace metal distributions along the WAP shelf to investigate the potential for this region to supply Fe to the ACC. Our data suggest that both cross-shelf eddies and formation of intermediate nepheloid layers at the slope can transfer Fe and other metals to the open ocean, with the greatest component in the particulate phase. Understanding the influence of the WAP shelf on adjacent ACC waters is crucial to our ability to accurately predict how productivity and C drawdown in this region may change in the future.

KEYNOTE

Glaciers deliver nutrients to coastal waters?

Martyn Tranter

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This talk will summarise current thinking about the generation of bioavailable macro-(N, P, Si) and micro-nutrient Fe in glacial environments, and their potential fluxes to coastal waters in runoff and ice bergs. The generation and export of glacial DOC will also be covered. A key theme is that glacial erosion produces silt-sized debris, covered in micro-particles and amorphous zones, which have greater reactivity than the bulk mineral. Glacial comminution also liberates trace reactive components from the mineral lattice in which they are embedded, so enhancing the bio-utilisable potential of the debris. The potential of the glacial flour is hard to dispute. What is more controversial at present is the quantity of the reactive debris that escapes from fjords into the surrounding coastal ocean, and the time scales over which this happens. There is a correspondence between certain periods of potential elevated glacial inputs to coastal waters, and phytoplankton blooms, suggesting that significant quantities can be transferred over relatively short timescales. This area of research is likely to be a growth area in the coming years.

Mineralogy of reactive iron species: Combining sequential extractions and Mössbauer spectroscopy

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Bioavailable iron minerals are crucial components of the ocean's biogeochemical cycles[1]. However, they are difficult to quantitatively characterise using standard tools (e.g. XRD), since they generally assume amorphous, colloidal, or nanoparticulate forms. Sequential extraction procedures[2] that rely on reagent-specific mineral solubility are used to separate operationally-defined pools of reactive iron minerals. Although these procedures are fundamental for mineral separation (e.g. investigating isotopic fractionation), mineral solubility is affected by grain size, complexation, degree of crystallinity and organic matter content, which can lead to the incomplete or premature dissolution of some mineral phases[2-4]. ^{57}Fe Mössbauer spectroscopy (MBS) probes the hyperfine interactions between next-nearest neighbouring atomic nuclei in the crystal lattice and is consequently useful for colloidal and nanoparticulate analysis. MBS can discriminate between individual iron minerals and determine iron oxidation state, which offers a time-saving, non-destructive, mineral specific alternative for iron mineral identification that can also be used in-situ[4]. We report the results of a cross-calibration of sequential iron extraction and MBS methods using a suite of natural and synthetic iron minerals to optimise sequential extraction procedures for more accurate isotopic fractionation studies, and advance the analytical accuracy of bioavailable iron mineral characterisation.

[1] Tagliabue *et al.* (2017) *Nature* **543**, 51-59. [2] Poulton and Canfield (2005) *Chem. Geol.* **214**, 209-221. [3] Henkel *et al.* (2016) *Chem. Geol.* **421**, 93-102. [4] Schröder *et al.* (2016) *Hyperfine Interact.* **237**, 85.

Fe colloids and nanoparticles in aquatic environments: towards a mineralogical understanding

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Iron plays an integral role in ocean biogeochemistry, the regulation of ocean primary productivity, and the carbon cycle [1]. Particulate phases control dissolved iron concentrations in the ocean [2]. These particulate phases range in sizes below the traditional dissolved operational filter cut-off size (0.45 μm), where they are difficult to characterise and not well understood [3]. Raiswell and Canfield stress the importance of a more mineralogical approach to characterising colloids and nanoparticles, defining their role in the iron biogeochemical cycle within aquatic environments [4]. Here we present an analysis of the iron-bearing particulates shown to be a source of bioavailable iron to coastal ocean waters in Northern Scotland: River Halladale and River Thurso [5]. Using a cascade of filtering techniques we collected and quantified iron particulates above and below the 0.45 μm threshold. Mineralogical information was gathered using the Synchrotron Mössbauer Source (SMS) at the European Synchrotron Radiation Facility in Grenoble, France [6,7]. The SMS enables the analysis of microscopic sample volumes, thus making it feasible to collect enough material for analysis from a few litres of seawater, compared to ~1000 L for conventional Mössbauer spectroscopy.

[1] Lalonde *et al.* (2012) *Nature,* **438**, 198-200. [2] Tagliabue *et al.* (2017) *Nature,* **543**, 51-59. **[3]** Milne *et al.* (2017) *Geophysical Research Letters,* **44**. [4] Raiswell and Canfield (2012) *Geochemical Perspectives,* **1**(1), 1-220. [5] Krachler *et al.* (2016) *Science of the Total Environment,* **556**, 53-62. **[6]** Potapkin *et al.* (2012) *Journal of Synchrotron Radiation*, **19**, 559-569. [7] Schröder *et al.* (2016) *Hyperfine Interactions*, **237**, 85.

Ecological and biogeochemical consequences of bentho-pelagic exchanges in shallow coastal ecosystems

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Exchanges between the sea floor and overlying water are important processes for many aspects of the marine ecosystem and as such, need to be understood in their entirety. While both the pelagic and the benthic system are well-studied individually, there are distinct gaps in the understanding of the connection between the two. This on-going study aims to supply some of these links through a combination of geophysical and ecological methods. By measuring a range of factors such as sediment properties and resuspension potentials, exchanges of organic matter, oxygen, carbon and nutrients as well the presence of organisms and their effects on the system, a holistic picture of the links between water and sea floor can be made. In the course of a seasonal study, bentho-pelagic exchanges of each of these parameters are investigated in situ at a coastal site within the Western English Channel. Data collected in this way is then put into temporal context using past data sets of the long-term time series of the Western Channel Observatory station.

Iron deficient waters over the Hebridean shelf break

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Due to the extremely low solubility of iron (Fe) in oxic seawater the concentration of dissolved Fe (dFe; <0.2 µm) is typically sub-nanomolar. Consequently, Fe availability regulates phytoplankton growth over 20-40 % of the world's ocean. In order to alleviate the conditions for Fe limitation external sources of Fe are required. Continental shelf sediments are a large source of Fe to the overlying water column, with shelf slope (200-2000 m) sediments alone estimated to supply 37 x 10^9 mol dFe yr^{-1} globally, ≈3-4 times larger than the global atmospheric aerosol flux of dissolvable Fe. In this study, the concentration of dFe and macronutrients were determined in water samples collected during an autumn field survey to the Hebridean and Malin shelf seas. Despite the proximity to shelf sediments, the concentration of dFe in surface waters overlying the shelf break was vanishingly low (typically <0.15 nM). Moreover, corresponding nitrate concentrations were in excess of 5 µM, suggesting that the conditions leading to seasonal Fe limitation in the high latitude north Atlantic (HNLA) persists to, and in some instances beyond, the Hebridean shelf break. Consequently, the spatial extent of seasonal Fe limitation over the HNLA may be greater than previously considered.

Behaviour of iron isotopes in hydrothermal systems: Beebe and Von Damm vent fields on the Mid-Cayman ultraslow-spreading ridge

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The micronutrient iron (Fe) is a key regulator of primary productivity in high nutrient low chlorophyll regions. However, the relative importance of different sources of Fe to the oceans is not well known, and flux estimates from atmospheric dust, hydrothermal vents, icebergs and ocean sediments vary by orders of magnitude. GEOTRACES studies have shown that as much as 46% of hydrothermal Fe may remain in the dissolved (<0.2 µm) phase and this Fe may be transported for thousands of kilometers away from the mid-ocean ridge. Recent work in the East Scotia Sea suggests that this hydrothermal Fe may have a distinct iron isotope signature, but this may change during plume dispersion (Klar et al., 2017; Lough et al., 2017). To better understand the causes of these changes, the iron isotopic composition of dissolved iron has been determined in both the near-field and far-field hydrothermal plume at two vent fields (Beebe and Von Damm) located along the ultraslow Mid-Cayman spreading ridge in the Caribbean Sea. Initial results suggest that the δ^{56}Fe signature of dissolved Fe in the near-field plume is lower than the hydrothermal fluids, but subsequently evolves to higher values.

Biogeochemical Mn, Fe and S cycling in Kemp Caldera sediments, south of the Antarctic Polar Front

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Hot, reduced fluids flow through metalliferous sediments at active hydrothermal vent sites and create steep redox gradients at the sediment-water interface, which stimulate microbial metabolism and support chemosynthetic consortia of subseafloor microorganisms. Here, we use a novel, interdisciplinary approach to discuss the impact of local hydrothermal venting [1] on sediment composition and the localisation of chemosynthetic, microbial consortia in two diverse sediment systems of the Kemp Caldera – a southern feature of the South Sandwich Arc: Toxic Castle and Tubeworm Field. Toxic Castle sediments are compiled from the episodic deposition of magmatic (crystalline S^0 with a δ^{34}S signature of +4.8 ‰ to +5.9 ‰) and hydrothermal (buoyant plume particles) components, while pore fluid composition is strongly influenced by diffuse, upwelling hydrothermal fluid. The original magmatic-hydrothermal signature is diagenetically altered (pore fluid Fe and Mn is typical of stratified marine sediments) in the solid phase Tubeworm Field sediments, likely initiated by dissimilatory sulfate reduction. Microbial cell counts are relatively consistent across the major Tubeworm Field redox boundaries, although there is a notable downcore shift in the microbial community structure towards δ-, ε-, and γ-proteobacteria (that host known S metabolisers), which confirms active, microbial S cycling in the deeper Tubeworm Field sediments.

[1] Hawkes *et al.* (2014) *Geophys. Res. Lett.* **41**, 942-947.

HIGH RESOLUTION MASS SPECTROMETRY

Beyond Bulk Isotope Ratios: Looking at Clumped and Position-Specific Isotopes in Light Alkanes

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The development of high resolution stable isotope mass spectrometry has broadened the field of possible investigation of position-specific and clumped isotopes. A few years ago the only common analytes were N_2O (for N-position-specific isotopic compositions) and CO_2 (for clumped isotopes). The main challenge was separating the isotopologues of interest from isobars, which can be contaminants (water from methane clumped isotopes), other isotopologues of the analyte or ions produced by source chemistry processes. We present the results of hardware and software development of the ThermoFischer Scientific 253 Ultra, a new double-focusing, multi-collection and high resolution IRMS, which was first installed in SUERC in July 2015. It can reach mass resolving powers of up to 48,000 and drifts in peak position over 30 minutes are below 1ppm. With those capabilities, it is possible to study the distribution of isotopes among the isotopologues of light alkanes, beyond the classical bulk isotopic ratios ($\delta^{13}C$ and δD). We will present the potential for geothermometry (clumped isotopes of methane), tracers of kinetic processes and inheritance from prior, larger biomolecules (clumped isotopes of methane and ethane, position-specific isotopic composition in propane).

Poster Presentations

Culturing *Serpula vermicularis* in a controlled manipulation experiment in search of palaeoclimate proxies

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The development of palaeoclimate proxies is essential for the reconstruction of past environmental responses to elevated atmospheric CO_2, and with which to improve projections of future high-CO_2 scenarios. Currently few such chemical proxies exist. Rare earth elements (REE) preserved in biogenic carbonate may be suitable proxies for the marine carbonate system, and hence atmospheric CO_2, because of their pH sensitivity when dissolved. Here we investigate the potential of the REE proxy by culturing three tanks of serpulid worms (*Serpula vermicularis*), which secrete calcite tubes, under controlled conditions for 12 weeks. In this poster we present our experimental set-up and some preliminary results. Each tank was held at different seawater pH (7.9, 7.7, 7.5) by manipulation with CO_2 gas to within ±0.1 pH units by using a coupled solenoid/pH computer. Weekly samples were collected to monitor the water chemistry (nutrients, DIC/TA, DOC, REE) and to calculate the parameters of the marine carbonate system in CO2SYS. The dissolved REE were analysed in two size fractions (<0.4 µm, <3 kDa) to evaluate complexation with humic substances (DOC), and the potential influence of this complexation on REE partitioning into biogenic carbonate. At the end of the culturing period, the serpulid tubes were analysed for their REE concentrations. The combined serpulid tube and water sample REE concentrations will be used to evaluate apparent partitioning behaviour and the pH dependence of REE abundances in biogenic carbonate, and therefore their viability as chemical proxies.

Iron BREW: The role of DOC in Iron Beyond River Etive Water

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The importance of Fe as an essential micronutrient in marine biogeochemistry is undisputed[1], and has driven many of the recent efforts to refine knowledge of Fe sources and fluxes to the ocean[2]. Riverine transport is typically considered a relatively unimportant source of dissolved Fe because estuarine processes remove ≥95%[3]. However, complexation to dissolved organic carbon (DOC) is gaining attention as a mechanism for Fe to survive flocculation across estuarine salinity gradients[4,5]. Recent efforts to quantify the riverine Fe flux have identified humic substances (HS) as the dominant transport vector[5], specifically fulvic acids[4], with observations of substantially increased HS-bound Fe fluxes (~4 times greater) in northern European rivers over the last 20 to 40 years[6] mirroring the general increase in DOC observed in Northern Hemisphere rivers[7]. Here we focus on the behaviour

of dissolved Fe in Loch Etive, a sea loch on the West Coast of Scotland supplied with river waters draining peat-dominated catchments. We carried out direct measurements and mixing experiments of dissolved Fe in two size fractions (<0.4 µm, <5 kDa) and DOC (<0.7 µm). We use these data to address two key questions: (1) How much dissolved Fe is maintained in suspension across the salinity gradient? (2) What is the dominant carrier phase of dissolved Fe? While the colloidal fraction carries greater absolute Fe concentrations across the salinity gradient, the <5 kDa fraction is more efficient at transporting Fe. It also has a constant Fe/DOC ratio, implying mainly organic complexation, compared to the decreasing trend in the <0.4 µm fraction. Further work is required to conclusively identify the nature of these organics.

1 Tagliabue, A. *et al. Nature* 543, 51-59, (2017). **2** Conway, T. M. & John, S. G. *Nature* 511, 212-215, (2014). **3** Sholkovitz, E. R. & Copland, D. *Geochimica et Cosmochimica Acta* 45, 181-189, (1981). **4** Krachler, R. *et al. Marine Chemistry* 174, 85-93, (2015). **5** Laglera, L. M. & van den Berg, C. M. G. *Limnology and Oceanography* 54, 610-619, (2009). **6** Neal, C. *et al. Aquatic Geochemistry* 14, 263-288, (2008). **7** Clark, J. M. *et al. Science of The Total Environment* 408, 2768-2775, (2010).

Dissolved Organic Matter Cycling at the West Antarctic Peninsula

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The Southern Ocean is critical for carbon and nutrient cycling, however, little is known about the processes controlling dissolved organic matter (DOM) cycling in this region. Most DOM in the Southern Ocean is introduced autochthonously by seasonally restricted primary production. While it is known that DOM concentrations and microbial activity are comparatively low, reasons behind this remain unclear. This makes it difficult to model Southern Ocean biogeochemical responses to ongoing changes in atmospheric CO_2 and climate. The West Antarctic Peninsula (WAP) contains a productive ecosystem and plays a biogeochemically important role. Most recently, it has been undergoing rapid climate change with increasing atmospheric and oceanic temperatures, widespread glacial retreat, and large reductions in sea-ice. This study aims to characterise DOM cycling processes under these physical and the resultant biological changes. Seawater samples from Rothera Research Station (UK) and the Palmer Antarctic LTER (US) annual research cruise are analysed for bulk C and N concentrations and N-isotopic composition of DOM. In combination with other ecological data available (e.g. primary and microbial production, nutrients, physical parameters), processes driving DOM cycling are reconstructed. Initial results of spatial and seasonal variability are presented and discussed in this poster.

Mesopelagic microbial community analysis of the Extended Ellett Line (EEL)

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Understanding the biogeochemistry of the North Atlantic between Scotland and Iceland is important because these highly productive waters are ecologically and economically crucial to life in and around this basin. Driving the biogeochemical fluxes in this region are a diverse array of auto- and heterotrophic microbes distributed throughout the water column. The mesopelagic microbes as especially important in controlling the mineralisation of nitrogen, as well as the biological carbon pump. Surprisingly, no study has examined the microbial community along the EEL. In this study, submersible autonomous pumps were used to sample seven stations during the JC86 (2013) occupation of the EEL. Archaeal and bacterial community analysis of the ≥1.2 µm particulate matter collected by the pumps was performed using Illumina 2x250 bp DNA sequencing. The data reveals the Rockall Trough to have greater taxonomic diversity compared with the Icelandic Basin. The microbial community at all stations were clearly structured by depth. A characteristic signature of the deeper waters (ca. 500-1200 m) was the presence of ammonia oxidising Archaea. Ongoing computational analysis is exploring the correlation of biogeochemical data with the distribution of various microbial taxa and to explore the extent to which the microbial populations of the two basins might be segregated.

Benthic microbial diversity influences biogeochemical cycling under future climate scenarios

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Marine sediments are important sites for global biogeochemical cycling, mediated by macrofauna and microalgae. However, it is the microorganisms that drive these key processes. There is strong evidence that coastal benthic habitats will be affected by changing environmental variables (rising temperature, elevated CO_2), and research has focused on the impact on macrofaunal biodiversity and ecosystem services. Despite their importance, there is limited understanding of how microbial community assemblages will respond to environmental changes. In this study, a manipulative mesocosm experiment was employed, using next-generation sequencing to assess changes in microbial community under future environmental change scenarios. Illumina sequencing generated over 11 million 16S rRNA gene sequences and revealed Bacteroidetes and Proteobacteria dominated the total bacterial community of each sediment sample. In this study, the sequencing coverage and depth revealed clear changes in species abundance within these phyla. Bacterial community composition was correlated with simulated environmental conditions, and species level community composition was significantly influenced by the mean temperature of the environmental regime ($p = 0.002$), but not by CO_2 and diurnal temperature variation. Species level changes were reflected in changing nutrient concentration as mean temperature increased, suggesting there is no functional redundancy in microbial communities for nitrogen and phosphate cycling. Marine coastal sediments are likely to undergo changes to biogeochemical cycling under future environmental changes.

Iron and phosphorus co-limitation in the sub-tropical North Atlantic

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Inorganic phosphate, the most bioavailable form of the vital nutrient phosphorus, is scarce in the sub-tropical North Atlantic. To maintain primary production, organisms can utilize the abundant dissolved organic phosphorus via enzymes of the alkaline phosphatase group in presence of iron. The strong natural gradient of iron from > 1.0 nM in the East to < 0.2 nM in the West, presents an ideal natural laboratory to examine the role of iron as regulator of phosphorus acquisition. Along this gradient, bioassays and upper water column profiles were conducted in summer 2017 to examine the impacts of trace metal limitation on phosphorus uptake. Dissolved and soluble iron species were measured using flow injection analysis with chemiluminescence detection on board and compared with alkaline phosphatase activity and primary production rates. Preliminary data on the iron gradient and insights from the bioassays will be presented to test the hypothesis that iron co-limits phosphorus uptake via alkaline phosphatase activity. Further analyses will investigate the relative importance of the physicochemical speciation of iron and other bioactive trace metals for alkaline phosphatase activity, especially in the light of predicted reduced subsurface supply of nutrients due to global change.

Comparing passive sampling, mussel caging and biomarkers for the evaluation of water quality for European Directives in Normandy coastal waters (France)

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In the scope of the Water Framework Directive (WFD, 2000/60/EC) implementation, the aim of this work was to compare the response of different emerging tools to evaluate the chemical status of water bodies in Normandy coastal waters (France). These tools included passive samplers foreseen in future evaluation campaigns in France as a replacement for bulk seawater sampling (*i.e.* Diffusive Gradient in Thin films (DGT), and Polar Organic Chemical Integrative Sampler (POCIS)). They were deployed at three contrasted sites in terms of pollution level along the Normandy coast, simultaneously to mussel caging, in which three common biomarkers were analysed at the end of the experiment. This work highlighted the operational challenge of deploying passive samplers and caging in open coastal waters of the Channel. The only POCIS that could be analysed from the bay of Veys

revealed the presence of metabolites of forbidden pesticides, and of several pharmaceutical substances. Results given by DGTs confirmed a gradient in metal concentrations between the three sites with a maximum at the Seine estuary, confirmed with organic and metal analyses in mussels, and with the lysosomal membrane stability biomarker which gives an indication of organisms' health status relative to their environment.

Scottish Blue Mussels <*Mytilus edulis*> - Evidence for Change down the Cultivation Rope

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The Scottish blue mussel industry reached record production values in 2016 of 7,732 tonnes being worth £10.1 million, supporting the local economy and employment. Mussel cultivation relies on natural spat fall in habitats with pronounced environmental variability, both on small and large temporal and spatial scales. We monitored fluctuations in key environmental drivers (temperature, salinity, food availability, seawater carbonate chemistry) and the corresponding quality of the cultured mussels (condition index, meat yield) over one year and at different depth of cultivation at a mussel farm on the west coast of Scotland, UK. Whilst both the environment and mussel product quality varied seasonally as expected, the most dramatic responses were with depth i.e. down the length of a mussel cultivation rope. The range in water salinity of near-surface grown mussels varied from 1.8 to 29.2 PSU within days, with far less variation for deeper grown mussels (27.0 ± 3.7 PSU at 7m). Seasonal and vertical fluctuations in temperature, salinity and food availability, in particular, were closely associated with the mussels' product quality with maximum meat yields achieved in the top meters of the water column and during summer months. In addition, the shape and strength of the mussels shells were found to differ down a cultivation rope, reflecting differences in species distribution (more fragile shelled M. trossulus in surface waters), stocking density (decreasing with depth) and prevailing habitat conditions (e.g. lower salinity in surface waters), allowing for the implementation of such data for farm management practices.

Calling all collaborators: clumped isotope paleothermometry at SUERC

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Clumped isotope geochemistry is the measurement of molecules with more than one heavy isotope and the interpretation of their abundances. In carbonates, "clumping" is thought to be controlled by the temperature of crystallization, and fixed afterwards in many tectonic settings. This removes the uncertainties with paleothermometry studies based on bulk $\delta^{18}O$, which requires knowledge of the $\delta^{18}O$ of the water. Our facility is nearing completion and looking for collaborators! Currently, we are setting up conventional paleotemperature studies with biogenic (foraminifera, molluscs, bivalves) and inorganic carbonates, and non-

conventional studies, such as examining chondrites to determine the temperature carbonate formation in the early solar system, and dinosaur teeth to investigate how dinosaurs regulated body temperature. Due to the variety of scientific questions we aim to consider, we have maintained the ability to analyse a variety of sample media. Preparation is completely in-house, beginning with a manual vacuum line with multiple traps for preliminary gas purification, in addition to a gas chromatograph for complete gas separation with a computer-controlled inlet to the mass spectrometer (Thermo Fisher MAT 253 IRMS). An automated line is now under construction to allow continuous sample processing, which will maintain our ability to process large or otherwise unconventional samples.

Long-term Puget Sound plankton dynamics: A comprehensive parameter – space exploration in a new model

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Wild salmon populations in Puget Sound, USA have undergone a long-term decline with their survival correlating with decadal climate patterns for reasons yet unknown. The search for bottom-up ecological explanations requires reconstructing interannual variation and trends in phytoplankton production and bloom timing. Despite a long history of studies of primary production in the region, long time series are rare, and information on nutrient and light sensitivity of primary production in the area is limited. This study presents an optimal plankton model for Puget Sound built by coupling a generalised NPZD-style model to a 1-D physical model of the Puget Sound Main Basin, which includes vertical mixing and advection processes caused by estuarine (river-driven) circulation. The 1-D simplification is possible because along- and cross-channel gradients of phytoplankton and nutrients are small in this deep fjord. Hundreds of thousands of variants of the model were investigated, with variation of both internal and physical drivers as uncertain parameters. The goodness-of-fit of parameter combinations were determined by matching to phytoplankton blooms' peak and timings, as well as seasonal cycles of nitrate, in a multi-year dataset. Unconstrained parameters and processes were systematically removed by conducting model reduction based on these observations. The ensemble model results allow testing of multiple hypotheses that have been proposed to link the continuously decreasing wild salmon pattern to phytoplankton dynamics.

Sediment biogeochemistry in Christchurch Harbour (UK): Diffusive fluxes and the role of resuspension events

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Estuaries are important regions for the biogeochemical processing of nutrients from both terrestrial and marine sources. These water bodies are typically shallow in nature but also highly dynamic. The sediment-water interface and processes controlling uptake/release of nutrients from the sediment are of particular importance to the local microbial communities. Christchurch Harbour (UK) is a shallow micro-tidal estuary fed by two rivers, the Hampshire Avon and the Stour, both of which are known to have elevated nutrient concentrations. As part of the Christchurch Harbour Macronutrients Project, the role of sediment resuspension events on estuarine biogeochemistry was investigated. Laboratory and in situ flumes were used along with assessing the changes in nutrient diffusive fluxes from different sediment types over a seasonal cycle. Initial results reveal widespread heterogeneity in the sediment biogeochemistry both within and across the three sites that ranged from anoxic silty sediment to consolidated mud to a sandbar. Responses to in situ resuspension events are also highly variable both within and across the sites. Diffusive flux and resuspension data are compared to elucidate the importance of each process on nutrient cycling within the estuary as well as the overall role of the sediments in the biogeochemistry of this anthropogenically-impacted estuary.

Biogeochemical cycling of permeable sediments in a shelf sea environment: Celtic Sea, a seasonal study

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Shelf-seas are globally important in contributing to the biogeochemical cycling of carbon and nutrients. Much of the benthic environment found in shelf seas comprise of relic permeable sands whereby advective pore-water flow processes govern the biogeochemical cycling. To further understand these processes, flow-through column reactors were employed during a field campaign as part of the NERC/Defra funded Shelf Sea Biogeochemistry programme. Three cruises took place in the southern Celtic Sea in 2015 and were timed to sample pre-bloom, post-bloom and late summer. Pre-bloom and late summer oxygen consumption rates ranged between 0.18 mmol O_2 m^{-3} d^{-1} and 0.15 mmol O_2 m^{-3} d^{-1} respectively. However, post-bloom oxygen consumption rates were 0.29 mmol O_2 m^{-3} d^{-1}. Iron (II) is removed during pre-bloom with significant releases of up to 137 nmol m^{-3} d^{-1} post-bloom. Silicate release was significant and comparable across all seasons. There was a consistent flux of phosphate (2-4 micromoles m^{-3} d^{-1}) over all seasons. Release of dissolved organics from the post-bloom and late summer incubations demonstrates the remineralisation of the fresh pelagic particulate organic matter. These findings demonstrate the seasonal variability and extent of the biogeochemical cycling of benthic permeable sediments and is evidence that permeable sediments are dynamic systems.

Controls of temporal and spatial variation in resuspension driven inorganic nutrient exchange in UK Shelf Seas

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Shelf seas are highly dynamic environments, undergoing frequent resuspension events as a result of wave and current action. They are also highly valued global ecosystems, with a recognized role in biogeochemical cycling. However, the interplay between resuspension events and biogeochemical exchange is not well understood. To address this, the relative importance of sediment type, seasonality and water depth on the flux of inorganic nutrients across the sediment water interface has been investigated in the North and Celtic Seas. Shipboard and in situ annular flume experiments were used to determine seabed stability, likelihood of resuspension, and flux of dissolved inorganic nutrients across different sediment types (ranging from mud to sands) under pre-bloom, post-bloom and late summer conditions. Data (from 2008 to 2015) indicates an increase in surface bed stability with increasing median grain size, and a seasonal relationship to surface sediment bulk density and organic matter. Sediment resuspension can lead to increased inorganic nutrient release to the water column, which is mediated by the overall depth of erosion, bed type and season, and water depth. These findings illustrate the complex variations in resuspension driven biogeochemical cycling within shelf seas highlighting the importance of understanding the controlling factors of resuspension.

Tidal mixing drives episodic spring-neap pulses of nutrients to the euphotic zone

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Tidal mixing-driven nutrient supply to the euphotic zone in the oligotrophic ocean is widely viewed as insignificant to sustain biological production. The vertical supply of nutrients from diapycnal diffusion to the euphotic zone is viewed as a weak, yet persistent flux over the oligotrophic gyres. Following a field campaign in the North Atlantic we measure episodic pulses of nutrients driven by internal tides over the mid-Atlantic Ridge, which are up to an order of magnitude higher than fluxes in the adjacent abyssal ocean. Nitrate fluxes over the ridge temporally vary from neap to spring tides by a factor of five. We explore the significance of spring and neap pulses of nutrients over the Atlantic and Pacific Gyres (40ºS-40ºN) where we identify large contrasts in vertical nutrient supply between regions of abyssal ocean and regions where internal tides are generated. Hence we view the vertical supply of nutrients to the oligotrophic ocean to be characterised by contrasting regimes, where there are regions of very low vertical nutrient supply and hot spots of tidally induced mixing and enhanced nutrient supply. The episodic pulses of nitrate will boost local new production and influence the community structure in the primarily nitrogen limited gyres.

Ammonium and Phosphate Excretion by Gelatinous Zooplankton in the Celtic Sea

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The Marine Strategy Framework Directive (MSFD) requires all EU member states to monitor their respective marine habitats and ensure that they achieve Good Environmental Status. Achieving this for zooplankton communities requires new information concerning the role of gelatinous animals in nutrient cycling and their potential impacts upon primary production. Excretion of ammonium and phosphate by gelatinous zooplankton was measured during a research cruise in the Celtic Sea in November 2014. Our results provide initial insights into the contribution of gelatinous zooplankton excretion to the nutrient demands of phytoplankton and aid the evaluation of their role in ecosystem functioning. They also serve to highlight the need for new techniques for quantifying the biomass of gelatinous organisms during routine monitoring surveys.

Development of custom assays for the autonomous detection and quantification of targeted marine microorganisms using Lab on a Chip

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Prokaryotic species cycle major greenhouse gases and underlie biogeochemical cycles but can only be differentiated using DNA or RNA signatures. Molecular methods have become an important tool in marine biological sciences because they can identify individual species and active biological processes. Many of these techniques are amenable to miniaturisation and deployment *in situ* however some hurdles remain. The goal of this study was to identify an optimal methodology for the long-term storage of enzyme mixtures for PCR and NASBA for use on a Lab on a Chip (LOC) device developed by NOC. The best-performing storage agents included 10% pullulan-encapsulation and lyophilisation, which successfully performed PCR for 5 and 8 weeks respectively, with little loss of efficiency. Both techniques appear to be viable methods for the storage of enzymes used in nucleic acid amplification. Further modifications will integrate these techniques onto a LOC platform for automated analysis. I will present the results of on-chip preservation and nucleic acid amplification, demonstrating nucleic acid quantification on targeted genes is possible using pre-manufactured chips with custom reagents combined with LOC analytics.

A 100-year record of changing toxic algae in Scottish coastal waters relating to climate change

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Globally, and in Scotland, the aquaculture industry is expanding but marine-based aquaculture is threated by toxic algae, which annually affects the industry through economic losses and risks to human health. Over the past 40 years, there has been much research on toxic algal cells, but little on the cysts that those cells form and which become the "seeds" for the next bloom. Cysts sink to the sea floor, where they lie dormant in the sediment. After a dormancy period, and when the right conditions coincide with resuspension in to the water column, new cells emerge from the cysts to create a new bloom. Most toxic blooms are caused by a group of microscopic algae known as dinoflagellates. Some species and strains of the dinoflagellate *Alexandrium* are potent producers of paralytic shellfish toxins (PSTs) worldwide. In Scottish waters, toxic and non-toxic strains of *Alexandrium* are now known to coexist (John, U. et al., 2003; Collins, C. et al., 2009; Brown, L. et al., 2010; Touzet, N. et al., 2010), and changes in the toxicity of Scottish shellfish have been observed (Bresnan et al., 2008). In this project, we are studying the cyst's role in the recurrence of local algal blooms and how, over time, changes in cyst numbers indicate changes in the environment, by examining sediment cores collected from Scottish sea lochs, which have an unique sediment archive of the recent past (Cage & Austin, 2011). We are also studying material caught in a sediment trap suspended in shallow, coastal waters because cysts collected there are the link between algal cells in the water column and benthic cysts; show the rate of encystment; and can indicate resuspension events that lead to the next generation of toxic algae.