

The decomposition of the Faroe Shetland Channel circulation: application of POMP to a 20-year time series

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Within the sub-polar North Atlantic, the Faroe Shetland Channel (FSC) is an important region for the transfer of heat and salt from the North Atlantic to the Nordic Seas. The water mass properties and circulation have been monitored in the area for the past 20 years, and recently, the average heat transport (relative to 0 °C) of Atlantic water was estimated to be 107 ± 21 TW and the average salt import to be $98 \pm 20 \times 10^6$ kg s⁻¹ (Berx et al., 2013). These recent estimates, however, failed to include the deeper water masses of the FSC, which form the cold, fresh bottom waters of the North Atlantic basin; and, to decompose the contributions of different water masses.

The recent application of a novel method to estimate the mixing of water masses in the FSC (McKenna, 2014), allows a more detailed decomposition of the volume, heat and salt transport in temperature and salinity classes; and therefore, the contribution by each of the five discernable water masses in the FSC.

Parametric Optimum Multi-Parameter analysis objectively quantifies the distribution of water masses in the channel, by using a combination of temperature and salinity measurements, as well as recently available nutrient and $\delta^{18}\text{O}$ measurements. Results based on observations in May 2013 showed that there is significant mixing between the deep, intermediate and surface waters, which may impact these transport estimates. Mixing fractions determined by POMP will be combined with geostrophic velocity estimates (constrained by satellite altimetry) to estimate the volume, heat and salt transport through the FSC.

We will present an overview of the POMP analysis method, as well as highlight its application in quantifying the volume, heat and salt transport for each water mass in the FSC. The existing 20-year

dataset allows us to explore the variability of these quantities to the different seasons and years, and initial results of this analysis will be presented.

Acknowledgements

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Priming effects and microbial interactions during lignocellulose degradation in marine sediments

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Current oceanic C budgets suggest that more than half of the terrestrially-derived organic matter (OM_{terr}) flux to the ocean is mineralised despite its high refractivity^{1,2,3}. The efficient degradation of OM_{terr} in the marine environment could be fuelled by labile marine-derived material, a phenomenon commonly known as “priming effect”^{4,5} but experimental data to confirm this mechanism is lacking. We tested this hypothesis by treating coastal sediments with ¹³C-labelled lignocellulose, as a proxy for OM_{terr}, and following its degradation for 28 days with and without simultaneous addition of unlabelled marine diatom detritus that served as a priming inducer. At the same time we were able to follow the dynamics of the lignocellulose-degrading microbial population by means of the ¹³C enrichment of phospholipid fatty acid (PLFA) biomarkers. Our results suggested the involvement of activated diatom degraders in the decomposition of accessible polysaccharide components within the lignocellulose complex which explained the higher lignocellulose mineralisation in diatom-amended treatments during the first week of incubation. Between days 7 and 28, the activity of diatom degraders slowed down and lignocellulose mineralisation did not differ consistently between diatom treatments and control (lignocellulose addition only). Overall, our results did not support

the occurrence of significant priming on lignocellulose degradation due to diatom enrichment at least for the time frame considered here. This was further exemplified by the non-significant differences in bacterial PLFA enrichment between treatments. Fungal enrichment was negatively correlated to diatom quantity and maximised at the absence of diatoms suggesting possible competitive interactions with diatom-degrading bacteria.

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Linking carbon and iron cycles by investigating transport, fate and mineralogy of iron-bearing colloids from peat-draining rivers - Scotland as model for high-latitude rivers

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Motivation: The biogeochemical iron cycle interacts with the global carbon cycle in multiple ways. For example, the scarcity of dissolved iron in the open ocean limits primary productivity. The contribution of individual pools of iron input into the ocean is a matter of ongoing research. There is growing recognition that atmospheric inputs have been overestimated while river inputs have been underestimated because they were calculated on the basis of average composition and total water discharge by major world rivers, most of which exhibit extensive removal of iron by flocculation and sedimentation during mixing with seawater. Humic-rich, high latitude rivers with much higher iron-carrying capacity (Batchelli et al. 2010; Krachler et al. 2010; Pokrovsky et al. 2014) are underrepresented in these calculations. A much greater amount of iron may actually escape estuarine removal and be transported to the open sea.

Scotland provides good analogues for globally significant high-latitude river-ocean systems in North America and Eurasia. Short distances between peatlands and the coastal ocean offer potential for source-to-sea research investigating transport, fate and mineralogy of iron-bearing colloids. Their investigation is challenging because of particle sizes in the nanometer range, and the increasingly smaller sample volumes when dispersed in the ocean. Here we show preliminary results obtained with a new SEM-EDXA protocol, which helps to 'visualise' aquatic colloids and get information on their elemental composition. Information on iron speciation and oxidation states was obtained using the ⁵⁷Fe synchrotron Mössbauer source at the European Synchrotron Radiation Facility (ESRF) in Grenoble, France (Potapkin et al. 2012).

Preliminary results: The Environmental Research Institute (ERI) in Thurso provides easy access to sampling the Thurso and Halladale rivers and their ocean plumes. SEM images of colloidal matter isolated from the Thurso River and the high-salinity region of its plume revealed a series of very similar, almost spherical particles with diameter

smaller than 0.4 µm, confirming that no significant aggregation of the organic colloids had taken place during seaward transport. EDX analyses revealed an elemental composition (C, O, Si, Fe) typical of complexes formed between iron and humic substances. Mössbauer spectra showed that suspended particulate matter from the Thurso and Halladale rivers looked identical and contained exclusively ferric iron, most likely superparamagnetic iron (oxyhydr)oxides. A coastal seawater sample (Brough) contained 40% of ferrous iron, most of it in the calcium-iron carbonate ankerite.

Outlook: Combining SEM-EDXA, Mössbauer spectroscopy, and easy access to sampling sites we aim to (i) gain not-yet-achieved insight into the speciation and mineralogy of iron in colloids coupled with morphology and elemental composition; (ii) identify and quantify the main classes of surface-active terrestrial and marine colloids across the full salinity gradient, i.e. from the mouth of Rivers Thurso and Halladale to the open waters of Thurso Bay; (iii) describe the transformations undergone by river-borne colloids as the river plume mixes with ocean water; and (iv) assess whether bioavailable iron is effectively transported to the open ocean.

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Detecting ice- or snow-derived freshening of the North Atlantic

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Dramatic climate disruptions of the last glacial period have received considerable attention, however, relatively little resource has been directed toward climate variability in the Holocene (last 10,000 years). The marine red coralline algae, *Lithothamion glaciale* (maerl), will be used as an archive to reconstruct Holocene runoff; freshwater runoff influences the strength of the thermohaline circulation (THC) and over the Holocene it is thought to have caused the Younger Dryas cooling event, 8,200 yr. event, and the little Ice Age (Kamenos et al., 2012; Clark et al., 2002; Grove, 1988). Although multiple temperature proxies have been developed, means of reconstructing runoff from regions of freshwater influence (ROLFS), e.g. ice sheets and glaciers, remain problematic. Prior to historic reconstruction using maerl, contemporary oxygen isotope analysis was used to refine the detection of freshwater inflow into the North Atlantic. The isotopic fractionation between stable isotopes of oxygen ($\delta^{18}\text{O}$) in different sources of freshwater to the ocean, e.g. snowmelt, ice melt, rainfall, was investigated over the 2013-2014 melt season at Glencoe and Loch Etive, Scotland. Snow, ice and associated runoff were collected to determine; 1) If the melt water entering Loch Etive was derived from ice rather than snow leading to a differing isotopic baseline concentration at any maerl collection site and 2) changes of the oxygen signature through pathways to the ocean. Melt generated from ice and snow shows a 0.25 ‰ difference with snow being more enriched in $\delta^{18}\text{O}$ than ice. En route from the melt source to the ocean $\delta^{18}\text{O}$ values enrich 3.24 ‰ and increase to 5.86 ‰ at the end of the season. Thus by refining $\delta^{18}\text{O}$ pathways of freshwater inflow it is now possible to determine between snow and ice derived freshwater during a $\delta^{18}\text{O}$ maerl reconstruction (allowing for temperature), enabling detection of fluctuation in runoff from these sources over the recent Holocene.

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Spectral dependence of phytoplankton light harvesting and its implications for primary productivity modelling in Scottish West Coast waters.

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The waters off the west coast of Scotland contain variable, but optically significant, concentrations of coloured dissolved organic matter (CDOM). As a result, the blue and red wavelengths of the solar spectrum are rapidly attenuated with depth, and the underwater light field is largely composed of photons in the 470-550 nm waveband. Since absorption by chlorophyll a is minimal in this spectral region, it might be expected that phytoplankton cells have to rely on absorption by accessory pigments to drive photosynthetic processes. It is possible to demonstrate this using Gaussian reconstruction to identify the role of accessory pigments in the absorption spectra of natural phytoplankton populations, and to quantify the significance of these pigments using a depth- and spectrally-resolved primary production model which has been parameterised using data from Scottish Sea Lochs. The results support the hypothesis that phytoplankton taxa which contain light-harvesting carotenoids have an advantage in waters which are coloured by CDOM, and this may be a factor in the frequent dominance of diatoms in the spring bloom in these regions. These observations in local waters gain wider interest from the fact that CDOM concentrations in high-latitude fjords and arctic seas are expected to rise in response to increased river flows and thawing of the permafrost. Consequently, bio-optical models developed in sea lochs can be applied to investigate the likely impact of darker and greener waters on phytoplankton populations in northern seas.

Cold-water corals: a previously unknown sulphur pool?

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Dimethylsulphide (DMS), a volatile sulphur gas, is a major component of the marine sulphur cycle, and may be involved in a number of atmospheric processes once emitted from the oceans. The precursor to DMS, dimethylsulphoniopropionate (DMSP) is a secondary metabolite produced by most marine algae to provide resilience against environmental change.

Tropical corals (and their associated symbionts) are known to be a major source of benthic DMSP in shallow, low-latitude waters. However, the role of asymbiotic invertebrates in the global marine sulphur cycle is poorly understood. This includes cold-water corals despite their global distribution and ecological and economic importance. Here, we present the first study investigating DMSP content in cold-water corals.

Cold-water corals may be particularly susceptible to projected climate changes such as ocean acidification (OA). OA is projected to cause a shoaling of the carbonate saturation horizon, exposing cold-water corals to waters which favour the dissolution of their aragonitic skeletons. Recently, it has been suggested that, in benthic species, intracellular DMSP concentrations may be up-regulated under high CO₂ conditions. The mechanistic trigger for this is currently unknown but may be related to the putative antioxidant function for DMSP and its breakdown products.

We exposed the cold-water coral *Lophelia pertusa* to high CO₂ and high temperature conditions and measured the DMSP content of the coral tissue and the surrounding water column. Tissue DMSP increased under high CO₂, whilst water column DMSP reduced, suggesting an increased uptake and accumulation of DMSP by *L. pertusa* under high CO₂ conditions, potentially for use as an antioxidant. This effect was, however, mediated by high temperature, perhaps due to the increased metabolic rate of the coral.

These results provide a new insight into the biotic control of deep-sea biogeochemistry and challenges our understanding of the role of benthic ecosystems in the global sulphur cycle. The physiological benefits of accumulating DMSP may also help to better understand the future survival of cold-water corals under projected climate change.

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Effects of seawater $p\text{CO}_2$ on calcification and metabolism in the massive tropical coral, *Porites* sp.

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Ocean acidification, resulting from rising atmospheric CO_2 , poses a serious threat to marine calcifying organisms. Coral reefs are of particular concern as declining seawater pH reduces the concentration of carbonate ions required for skeletal calcification. However, the effects of ocean acidification on massive corals, which support tropical reef ecosystems, are poorly understood. Using the state-of-the-art culturing facility at the University of St Andrews (photographed here), we have acclimated small heads of massive *Porites* corals over a period of > 6 months to four different $p\text{CO}_2$ scenarios that range from the last glacial maximum (180 ppm) to levels projected by the end of this century (750ppm). We have measured calcification, photosynthesis and respiration rates in each treatment over a four-week period following this long acclimation. Further, we are quantifying the differences in internal energy reserves (lipid, protein and carbohydrate) in response to changes in seawater carbonate chemistry, and we will determine their role in calcification. Corals precipitate aragonite from an extracellular fluid (ECF) by actively increasing the fluid pH, which drives carbonate to higher concentrations and so raises the saturation state of CaCO_3 . This is an energetic process that may be more costly as the pH of seawater declines. We will use boron isotope

geochemistry to reconstruct the ECF pH in corals from each treatment, enabling us to compare the energetic cost of calcification between high and low seawater $p\text{CO}_2$. Understanding the relationship between coral metabolism, physiology and calcification is likely to be important in predicting the ability of *Porites* to adapt to future climate change.



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Coralline algae change their skeletal composition to counteract marine carbon dioxide enrichment

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Marine pCO₂ enrichment via ocean acidification (OA), upwelling and carbon capture and storage facility releases is projected to have impacts on marine biomineralisers. While evidence from short-term laboratory investigations indicates the many species will be negatively affected by pCO₂ enrichment, at naturally acidified field sites, several of those same species exist naturally. This indicates those species may be able to survive natural acidification. We used red coralline algae growing naturally at CO₂ venting sites (Ischia, Italy) over 14 months to determine how sessile species grow in pCO₂ enriched environments in which lab studies suggest they should struggle to calcify. Raman spectroscopy was used to investigate changes in their skeletal polymorph, composition and molecular bonding strength. Coralline algae at venting sites continued to lay down calcite but reduced the Mg composition of their skeleton, making it less sensitive to reduced pH and allowing them to grow at a similar rate, and to the same size, as algae at non-venting sites. While Mg-O bonds were weaker in algae from venting than control sites when they began to grow, after 6-9 months the bond strength of individuals at both sites was similar. We suggest that given multiple months, newly recruited coralline algae can change their skeletal composition and structure enabling them to survive in naturally pCO₂ enriched environments. If CO₂ venting sites are used as analogues for OA, certain species of coralline algae may be able to cope with projected changes in marine carbonate chemistry by changing the composition of their skeleton.

Ocean acidification alters the material properties of *Mytilus edulis* shells.

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Ocean acidification and resultant changing carbonate saturation states is threatening the formation of calcium carbonate shells and exoskeletons of marine organisms that inhabit the oceans. The production of biominerals in such organisms relies on the availability of carbonate, and the ability of the organism to biomineralise in changing environments. To understand how such organisms will respond to ocean acidification the common blue mussel, *Mytilus edulis*, was cultured at projected levels of $p\text{CO}_2$ and increased temperatures (380, 550, 750, 1000 μatm at ambient temperature and 380, 750, 1000 ambient plus 2°C).

Nanoindentation was used to assess the material properties of the shells. Young's modulus of elasticity, (E) and hardness, (H) was measured in mussel shells grown in control and ocean acidification conditions. Ocean acidification caused mussels to produce shell calcite that is less elastic (stiffer) and harder than shells grown in control conditions. Thus the outer shell (calcite) is more brittle in ocean acidification conditions than in control conditions. In contrast, the inner shell comprising aragonite is softer and more elastic in shells grown under ocean acidification conditions than in control conditions. Combining increasing ocean $p\text{CO}_2$ and temperatures as projected for future global ocean appears to reduce the impact of increasing $p\text{CO}_2$ alone on the material properties of the mussel shell by returning to ancestral evolutionary mechanisms.

Ocean acidification may cause changes in shell material properties that could prove problematic under environmental changes and predation. This study highlights the need for the synergistic study of ocean global change.

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The Importance of Phytoplankton Diversity on Marine Nitrogen and Phosphorus Cycles

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Abstract

Nitrogen and phosphorus are key nutrients for marine phytoplankton. In reaction to environmental changes, phytoplankton show species-specific dynamic responses that ultimately alter the relative cell-level concentration of these elements. Therefore, understanding these responses at the level of the phytoplankton cell, population, and community is essential to understand and predict how the global cycles of nitrogen and phosphorus will be affected by challenging future scenarios such as those related to global warming.

In this presentation, we will discuss about the emergent uptake functional responses for nutrient-limited phytoplankton at the taxon and community levels. The main focus will be recent novel observations that show emergent responses very different from the expected saturating uptake-rate curves measured in the lab, and modelling approaches aiming to replicate those observations. These new models necessarily consider both acclimation and adaptation: at the ecological timescale, phytoplankton cells acclimate by modifying the number of uptake proteins used to take up each nutrient; in turn, this regulation is deeply affected by the cell's physiological ranges and trade-offs, which are shaped by evolution. We will also introduce a novel model for phytoplankton regulation of the cellular nitrogen:phosphorus ratio, and current efforts to implement such a dynamic stoichiometry model at a global level. As we will argue here, these models considering species-specific reactions at the ecological and evolutionary timescales for both nutrients will contribute to make reliable predictions about the role of phytoplankton on the cycles of nitrogen and phosphorus.
