CANON2014: Experimental Plan & Scientific Background

For the 2014 Fall experiment the CANON team will follow a subsurface patch infused with two tracers, Rhodamine and SF_6. The patch will also be marked with drifters, floats and an AUV and will be followed over multiple (1-3 weeks) days with a combination of AUVs, wave gliders and ships (Fig. 1). The location of the experiment will be inshore of M1 where we know the processes of interest occur and the physical dynamics are weak and conducive to patch following. The scientific focus will be on the nitrogen cycle and specifically on the remineralization of organic matter to nitrate in the pycnocline where the patch and the assets will be deployed. Primary, new and export production will be measured using a variety of methods in an attempt to balance the inputs and outputs of nitrogen to and from the primary producers. The science is detailed below, courtesy of Jason Smith who synthesized the background material and generated the initial questions.

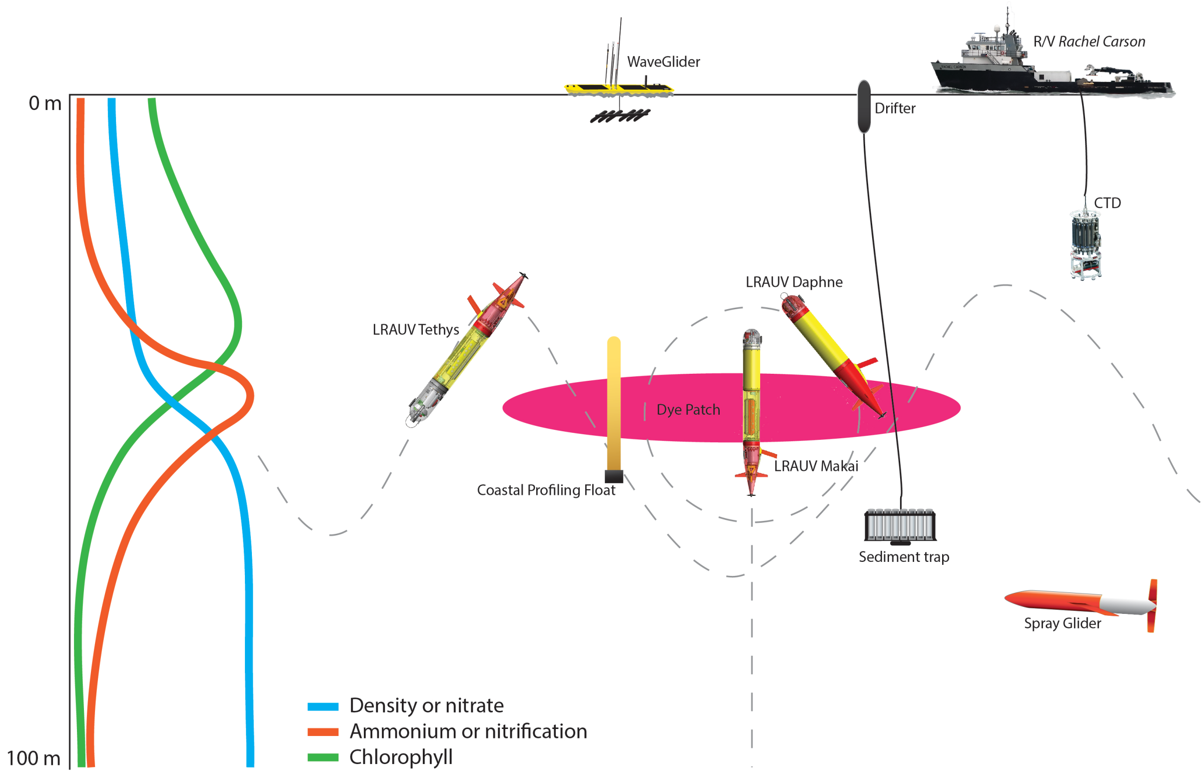

Figure 1. Schematic of the experiment proposed for Fall 2014. The experiment focuses on the zone of maximum remineralization observed at the base of the euphotic zone in the pynocline around the 25.5 kg m^{-3} (sigma theta) isopycnal level. At the site of the proposed experiment, inshore of the M1 mooring, this level is found between 30 and 50 meters depth. This region will be infused with two tracers, Rhodamine and SF_6. Drifters, a float and an AUV will also be deployed at this depth and passively drift with the tracer patch. A wave glider and another AUV will communicate acoustically with the drifting float and AUV and provide information to the scientists on a research vessel for sampling purposes. A third AUV will monitor the patch growth and decay. Drifting sediment traps will collect particulate flux.

Background & Science Questions

The biological pump: Phytoplankton fix carbon dioxide and inorganic nitrogen (either NO_3^- or NH_4^+) using energy generated from sunlight. The resultant particulate organic matter that is produced is grazed by zooplankton (and transferred up the food web), consumed by heterotrophic microbes or sequestered in the seafloor. Exactly where the first two processes occur, either in the euphotic zone or below it, is of great interest since it determines the general biogeochemical balance of elements. The majority of the organic matter is recycled or regenerated in the euphotic zone but between 1 and 40% is exported vertically and exponentially attenuates to the seafloor. Microbes remineralize the organic matter in the water column converting it back to carbon dioxide, NO_3^- and other elements. Only about 1% of the primary production in the sunlit layers reaches the sea floor.

Sediment trap data suggests that particulate organic carbon flux towards the ocean's interior follows a simple power law rule of the form:

$$Flux = F_{100} \times \left(\frac{z}{100}\right)^{-b}$$

The parameter F_{100} indicates the particulate organic carbon flux at 100 m depth, and z is the depth of the sediment trap. The unit less parameter *b* determines the transfer efficiency of the particles and, more generally, reflects the rate and path length of remineralization, or the rate at which organic carbon is converted back to CO_2, in the deep sea.

Originally it was assumed that there was little spatial variability in the flux of particles to the seafloor in the open ocean. However, a number of studies have since reported up to an order of magnitude range in *b* between different oceanic provinces. **Knowledge of the magnitude of export at the base of the euphotic zone is key to estimates of particle flux attenuation.**

What can intensive studies of nitrogen cycling tell us about the functioning of the biological pump?

Throughout much of the ocean, nitrogen (N) limits primary production. Phytoplankton may use the available N in the euphotic zone to grow. When they die, N used to support their metabolism is liberated for use by other phytoplankton. Because the amount of N available to support primary production does not change by this mechanism, phytoplankton growth supported by the 'recycled' N pool represents 'regenerated' production (Fig. 2).

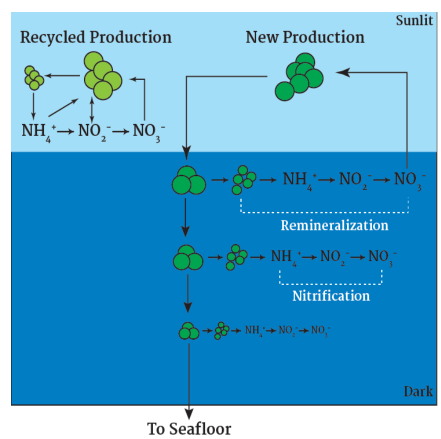

Figure 2. Mechanisms supporting new and regenerated primary production and how they relate to carbon export and nitrogen cycling in the deep ocean.

The net transport of carbon to the deep ocean is related to the quantity of N that enters the euphotic zone from places outside of it (so-called new production). Most commonly, this N enters from the dimly lit depths immediate below it in the form of nitrate (NO_3^-), all of which was generted via the process of nitrification – the oxidation of ammonium (NH_4^+) to nitrate (NO_3^-), via nitrite (NO_2^-). Nitrification is mediated by two groups of chemoautotrophic microorganisms that couple energy generation to the oxidation of inorganic N compounds (either NH_4^+, NO_2^-).

The first step in nitrification is the oxidation of NH_4^+ to NO_2^-, carried about by ammonia oxidizing archaea and bacteria. Requiring NH_4^+ to make energy means their growth is largely constrained by the rate at which it is produced via recycling of organic matter in the ocean. In the dark ocean, the flux of ammonium is directly related to how much organic material escapes the euphotic zone (the export flux). As these particles sink deeper into the ocean's interior the flux of NH_4^+ from them decreases in a predicable manner – according to the power-law function originally described by John Martin in 1987.

Do nitrification rates decrease with depth in the ocean according to a power-law function? Is so, do they fit the equation put forth by Martin during the Vertical Transport and Exchange (VERTEX) experiments conducted offshore of Central California? When we analyzed nitrification rate data obtained during several cruises along CalCOFI lines 60 and 67, we confirmed that **nitrification rates decline with depth below the euphotic zone according to a power-law function**, with a *b* of 0.8; while this value is not far from the average of 0.85 from the VERTEX experiments, the spread in the data suggest there to be some variability in the transfer efficiency of carbon between stations in the CCS (Fig. 3).

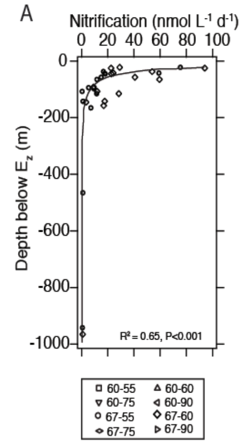

Figure 3. Nitrification rates with depth at stations along lines 60 & 67 in the northeast Pacific Ocean.

The depth of the euphotic zone varies with pycnocline depth, being shallower when the pynocline (and nutrients) are closer to the surface. The pycnocline slopes off Central California, being shallower near the coast and deepening offshore. For this reason, we also analyzed our data using density as the vertical coordinate (Fig. 4). **The emergent point from this analysis is that nitrification rates measured at different stations/times were consistent within an isopycnal but less so with depth;** with the highest rates occurring near the 25.5 kg m^{-3} density layer (Fig. 4A).

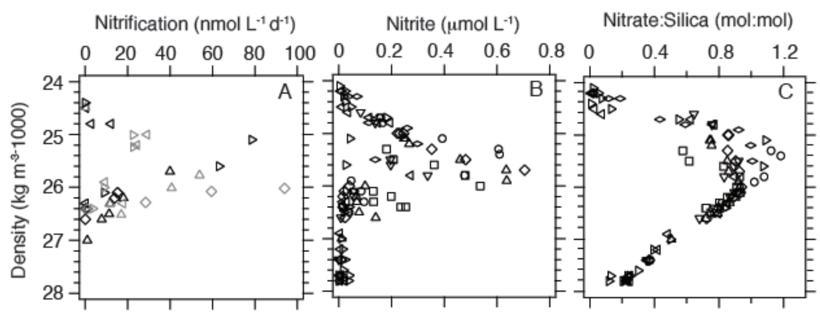

Figure 4. Lines 60 and 67 data plotted using density as the vertical coordinate. A) Nitrification rates; B) nitrite concentrations; C) ratio of nitrate to silica. Symbols are defined in the legend in Fig. 2.

It was surprising to see that discrete nitrification rate measurements appear to be maximal within, or in proximity to, a specific isopycnal surface. Even more so, the observed co-location of these high nitrification rates with the highest concentrations of NO_2^- (4B) – an intermediate product of nitrification – and an excess of nitrate, relative to silica (Fig. 4C) indicate there to be some agreement between 'instantaneous' process measurements and the geochemical record.

The ratio of NO_3^- to SiO_4^{4-} was consistently low in both shallow (<25 kg m^{-3}) and deep (>26 kg m^{-3}) density layers, but a pronounced 'bulge' was observed near where nitrification rates were highest (Fig. 4A,C). These observations support the general belief that sinking or suspended materials are first depleted of N, enriching them in Si going deeper into the ocean's interior. Nitrification, sustained from the enhanced N flux, would cause the nitracline to begin at shallower depths/isopycnals than the silicicline (hence, higher NO_3^-:SiO_4^{3-}; Fig. 4C).

Analysis of 1 m resolution downcast data from M1 shows the nitrification zone to be positioned at the steepest part of the pycnocline (or thermocline), a place where the sinking rate of particles is believed to decrease due to a stronger density gradient, which increases the time that they are exposed to decomposition and remineralization (Fig. 5). In further support of this idea is that the 25.5 kg m^{-3} isopycnal most commonly occurred at depths where there was an excess of nitrate relative to silica in data generated every month since 1988 at station M1, as part of the Monterey Bay Time Series (Fig. 6).

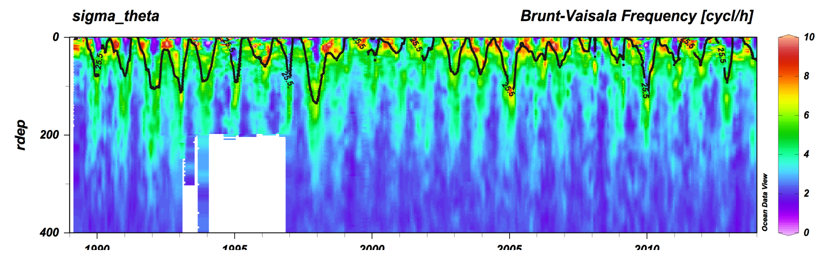

Figure 5. Brunt-Vaisala Frequency at MBTS station M1, between 1988 and 2013. The black line shows the position of the 25.5 kg m^{-3} isopycnal over time.

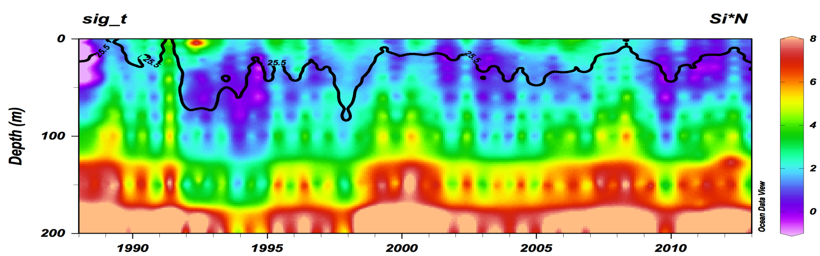

Figure 6. The distribution of Si*N with depth, based on data generated during near monthly samplings at station M1 between 1988 and 2013. The black line shows the position of the 25.5 kg m^{-3} isopycnal over time

Finally, to determine whether our small set of cruise observations were relevant on broader spatiotemporal scales, long-term average conditions on density surfaces (at 0.1 kg m^{-3} resolution) in the central CCS were determined by averaging all hydrocast data collected by BOG between M1 and 67-90 since 1997 (Fig. 7). Overall, these data support our initial observations made within the same 200 km band of coastal ocean. Most notably, concentration maxima of NO_2^- and NH_4^+, both products of organic matter remineralization, occur at or on

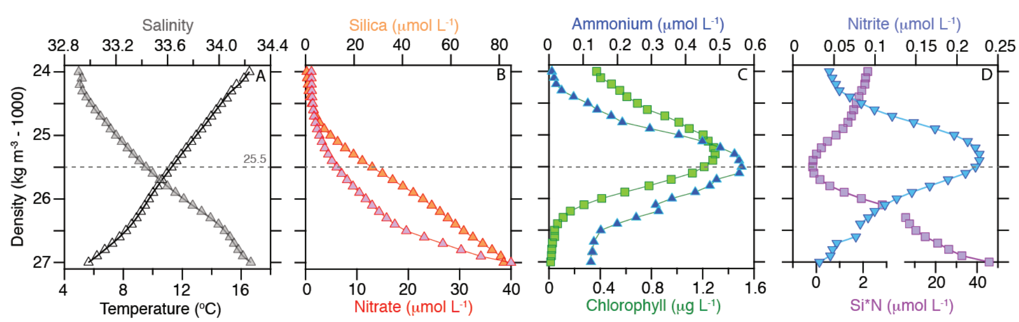

Figure 7. Long-term average conditions along the pycnocline in the central CCS.

density surfaces directly adjacent to the 25.5 kg m^{-3} isopycnal (Fig. 7C,D), where there is also an excess of nitrate relative to silica (Fig. 7D). Highest average chlorophyll concentrations occur within the less dense isopycnals immediately adjacent to the 25.5 kg m^{-3}, which suggest that the ‘nitrification zone’ is positioned near the base of the euphotic zone, where the flux of sinking organic matter is highest, and the materials freshest – both of which could support high rates of remineralization.

What does this mean for CANON?

Phytoplankton blooms: First, close to coast the isopycnal of interest resides within the 30 to 50 m depth interval, which is the range that is typically upwelled during the spring-summer upwelling season. **This means that the gross amount of N produced here during the non-upwelling periods sets the upper bound for the size of the spring phytoplankton bloom, which has cascading impacts on pH and oxygen content of surface waters** in MB & the central CCS.

Phytoplankton community structure & HABS: The relative availability of N compared to Si is an important factor in determining phytoplankton community structure. Since our evidence points toward the fact that N is remineralized at shallower depths than Si, the rate at which N is remineralized at the depths closest to base of the euphotic zone is going to set the ratio at which these two important macronutrients are upwelled to surface waters. **Water bearing more N than Si might favor the growth of dinoflagellates versus that of centric or pennate diatoms. It also might favor the production of domoic acid by diatoms. Oscillations between the amount of diatom versus dinoflagellate growth that can be supported by upwelled waters has important implications for:**

- Sinking rate of marine particles
- Diurnal cycle of nutrients (diatoms are diurnal, dinoflagellates are not)
- Quantity of domoic acid produced

The biological pump: In carbon equivalents, an export flux of 106 g C m^{-2} yr^{-1} is required to support the nitrification rates observed in the upper 1000 m of the CCS (Fig 2). In their carbon budget, Pennington & Chavez estimated new primary production in the central CCS to be 169 g C m^{-2} yr^{-1}, of which 93 g C m^{-2} yr^{-1} are expected to sink below the euphotic zone. **The striking agreement between annual export flux estimates introduces the potential to use depth-integrated nitrification rate measurements to study spatiotemporal variability in carbon flux to the ocean’s interior, an effort that would be technically easier, less costly and much higher throughput compared to deploying sediment trap arrays.**

Second, remineralization rates in the upper 1000 m of the dark ocean, termed the upper mesopelagic zone, have the most influence over the amount of carbon that reaches the seafloor. Meaning, in order to build better models, we should focus on characterizing the variability in remineralization rates at these depths, and how it relates to new and exported production and the delivery of carbon to the seafloor. However, like any process or flux, knowledge of where to make the most important measurements is paramount to arriving at the best estimates.

Oceanographers have a very good understanding of where highest rates of photosynthesis are occurring in the euphotic zone, because there are clearly defined relationships between it and concentrations of nutrients, chlorophyll and light intensity. These relationships are lacking for the dark ocean, which is also orders of magnitude larger in size, so there is less assurance that a limited set of measurements made there are capturing the most important (read: largest) component of any given flux. From a technical perspective, **our density-based analysis yielded several easily measured parameters by which we can**

track the physicochemical and biological variability at a point in the dark ocean. These parameters are easily detectable by autonomous systems, allowing for adaptive or targeted sampling and experimentation at what appears to be a critical interval in the water column.

How does a Lagrangian approach get us closer to understanding the potential impacts of N remineralization on the 25.5 kg m^{-3} isopycnal?

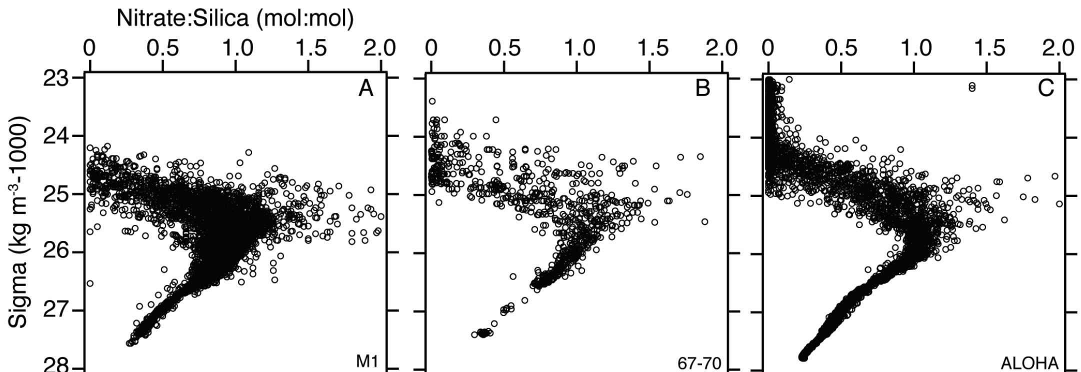

Figure 8. Ratios of NO_3- to SiO_4^{4-} at stations M1, 67-70 and ALOHA in the North Pacific Ocean. Data were collected between 1988 and 2012. Station ALOHA data courtesy of the Hawaii Ocean Time Series Program.

Nearly 25 years of hydrographic data were mined while exploring this idea, and no matter how it is cut up, there is always evidence of accelerated N remineralization within the 25.5 kg m^{-3} isopycnal – from the MBTS to L67 to Station ALOHA (Fig. 8). This is a highly stable and potentially very important interval of the ocean. The fact that this feature is non-ephemeral in nature means that it is almost certain to be present during the fall experiment. Therefore, the intensive efforts to label and then track a path of water in the coastal ocean will help us to draw important parallels between the physical, chemical and biological characteristics of the waters within, above and below this interval.

Initial Hypotheses:

H1: The 25.5 kg m^{-3} isopycnal represents the nitrogen remineralization maximum.

H2: This interval represents the start of the particle flux attenuation curve. If this is the case, variability in the rates of remineralization in the 25.5 kg m^{-3} density layer, and those immediately adjacent to it, has considerable influence over the amount and quality (lability) of the organic matter that makes it to the sea floor.

H3: The remineralization that occurs here is important for sustaining new primary production. In the absence of mixing, sustained nitrification would cause there to be a NO_3^- maximum at the depths where the 25.5 kg m^{-3} isopycnal occurs (30 – 50 m), much like that observed for NH_4^+ and NO_2^- (Fig. 6C,D); this isn't the case because a fraction of the NO_3^- produced is most likely transported to the layers adjacent to it via mixing. The fact that this particular isopycnal occurs at the base of the euphotic zone, near the deep chlorophyll maximum, means that a fraction of the NO_3^- produced is quickly mixed back into the euphotic zone to support new primary production over sub-annual time scales. If waters from these layers reach the surface during upwelling, the concentration of NO_3^- in these layers would also set an upper boundary for the amount of new production that results from wind-driven upwelling (rather than that sustained by smaller scale transport from the thermocline).

Specific Objectives:

1) Measure rates of new primary production using multiple methodologies (^{15}N, triple oxygen, O2:Ar).

2) Determine the rates of particle delivery and decomposition (both N and C based) in the remineralization zone as well as the intervals adjacent to it, including the lower euphotic zone.

3) Quantify the flux of suspended and dissolved organic materials to identify the substrate pool with the most immediate effects on remineralization over hourly to daily timescales.

4) Measure the vertical and horizontal diffusivity to determine the rates at which nutrients are physically transported away from the remineralization zone (and into the euphotic zone).

5) Determine the degree to which biological (cells, biogeochemistry), chemical, physical and molecular (DNA, RNA, protein) signals vary over periods of hours to days and whether these relate to one another or the metabolic state of the water mass.