Spring 2021

Estimating the Denitrification Rate in Hood Canal using Water Circulation

Spencer Johnson
Western Washington University

Estimating the Denitrification Rate in Hood Canal using Water Circulation

Spencer Johnson
Advised by Dr. David Shull
Western Washington University
June 2021

Abstract:

Hood Canal is a long, fjordal estuarine inlet. Because of a sill near its mouth, Hood Canal experiences regular low oxygen in its bottom water; recently, dissolved oxygen has been even lower than usual, leading to fish kills and other ecosystem damage. Anthropogenic nutrients, particularly nitrogen, may be the cause, so it is important to quantify the components of the nitrogen cycle, like denitrification. To my knowledge, there is only one estimate of denitrification from Hood Canal in the literature. This study sought to supplement that data with an independent estimate of denitrification using water circulation along with N_2 concentrations from the bottom of the water column at 4 stations in Hood Canal. I used Matlab to calculate mean flow velocities from instantaneous velocities generated by the Salish Sea Model. I started by using a simple 2-layer flow model with perfect diffusion through the bottom layer, but a high estimate led me to transition to an advection-diffusion partial differential equation model. This model yielded inconclusive results; the high denitrification outputs suggested that maybe the diffusion constant found in the literature increased too much with depth. Future studies could measure N_2 concentrations at different depths to better fit the diffusion constant or change the mean flow velocity in the model to vary with time.

Introduction:

Estuarine circulation is driven by the density difference between freshwater input and higher salinity water entering the estuary at depth. Rivers are typically the primary source of fresh water, creating a low salinity surface layer with a mean current directed toward the ocean. This freshwater input also causes a baroclinic pressure gradient driving the flow of deeper, saltier bottom water into the estuary. As a large, river-influenced body of water with many smaller inlets, the Salish Sea experiences many variations of estuarine circulation (Thomson, 1994). One of these inlets is Hood Canal, a long fjord west of Puget Sound that enters into Admiralty Inlet (Figure 1). Hood Canal's regionally unique bathymetry creates a distinct circulation pattern. Because the canal has a sill at its northern end (Figure 1), its water circulation is better described by the fjordal variation of estuarine circulation, where an outward flowing surface layer and inward flowing intermediate layer both sit on top if a relatively stagnant deep layer with little mean flow and a long residence time (Figure 2). Babson et al (2006) calculated the bottom water residence time for southern Hood Canal to be about 3 months, far longer than other basins in the Salish Sea.

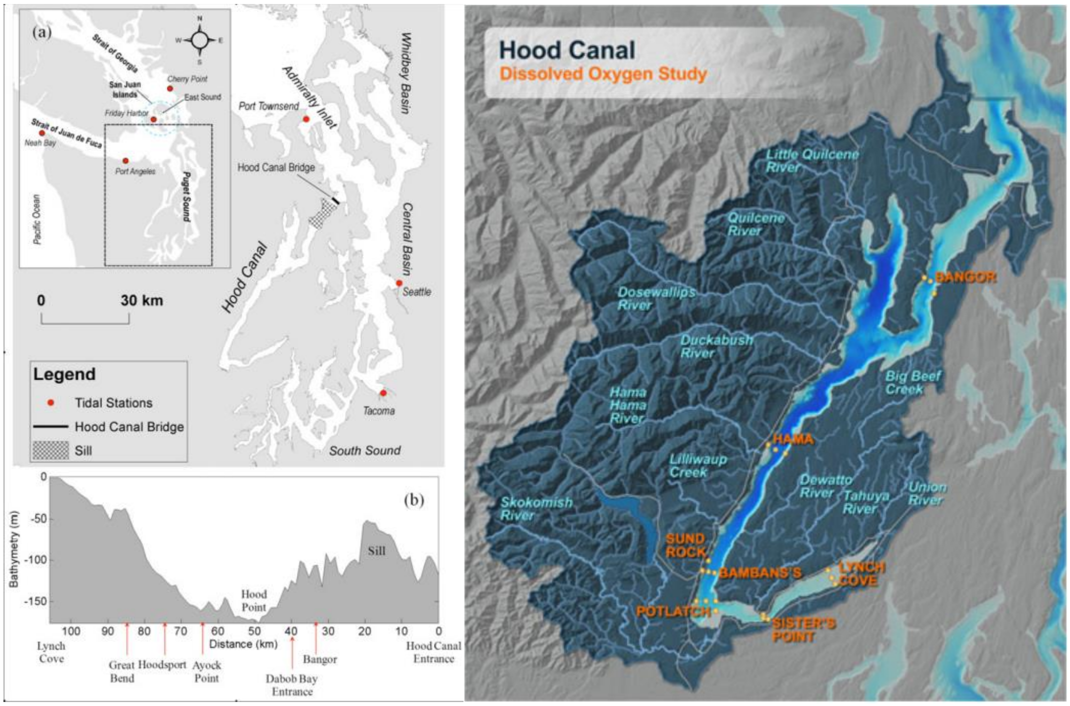

Figure 1. Location and bathymetry of Hood Canal from Khangaonkar and Wang (2013) (left), and illustration of the Hood Canal watershed from the Hood Canal Dissolved Oxygen Program (n.d.) (right).

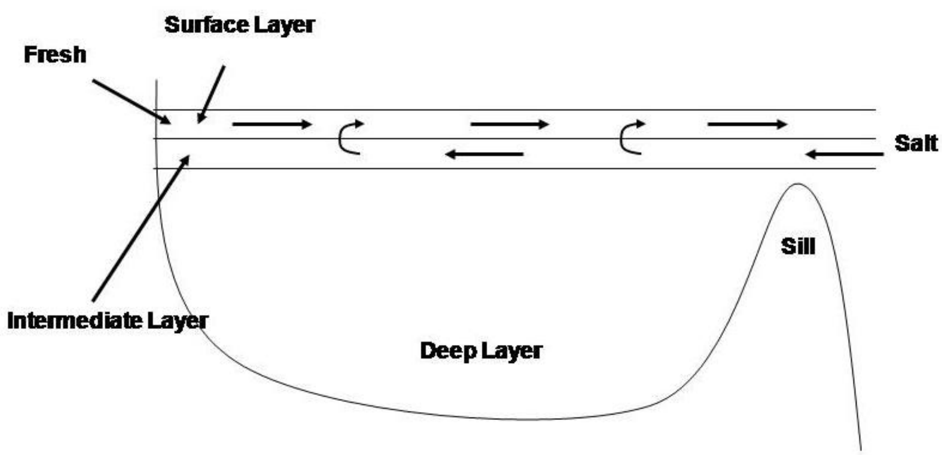

Figure 2. Fjordal circulation illustration. See Thomson (1994), pgs 13-14.

Because of this stagnant deep layer, Hood Canal is naturally susceptible to conditions like low dissolved oxygen (Feely et al., 2010). As organisms respire, the bottom water becomes rich in carbon dioxide and poor in oxygen. In extreme cases, this condition can lead to essentially anoxic conditions, killing fish, shrimp, and other members of the benthic community. Though chronic low oxygen is natural in southern Hood Canal, dissolved oxygen has been unusually low in recent decades, increasing the frequency of fish kills in the canal (*Hood Canal Dissolved Oxygen Program*, n.d.; see Figure 3). This development prompted the creation of the Hood Canal

Dissolved Oxygen Program (HCDOP) in 2005. The goal of this program was to further investigate the problem and bring together agencies and stakeholder groups that could play a role in solving it. One major concern in Hood Canal is overloading of nutrients, particularly nitrogen. Like in much of the ocean, primary productivity in Hood Canal seems to be nitrogen-limited in the summer (Newton et al., 2008), so nitrogen inputs could increase primary production in the surface water, leading to eutrophication and low dissolved oxygen in bottom water.

Figure 3. Fish and shrimp that washed up from a 2010 anoxic event in Hood Canal. The pictures were taken by Ron Figlar-Barnes, Skokomish Tribe Dept. of Natural Resources, on beaches from Potlatch to Hoodsport on the morning of September 21st (*Hood Canal Dissolved Oxygen Program*, n.d.)

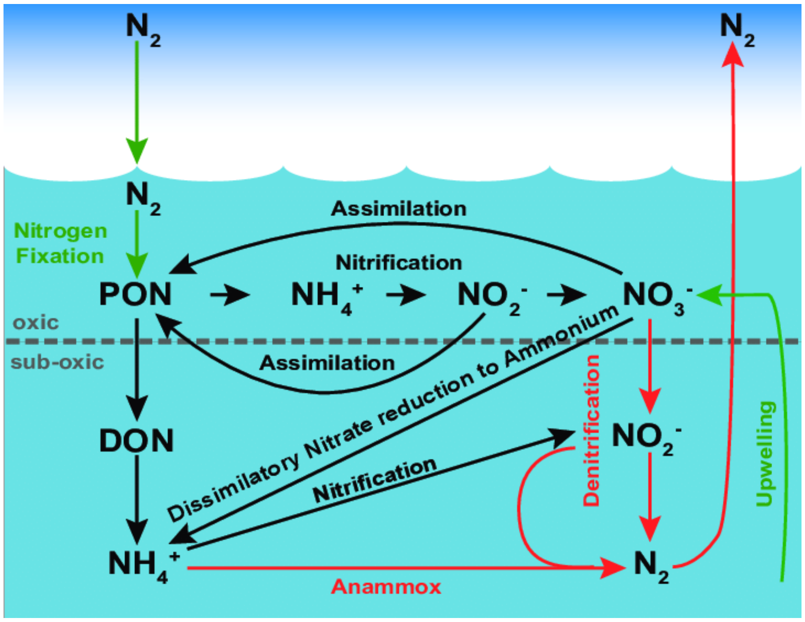

Figure 4. Marine nitrogen cycle. From Sollai et al. (2015), modified from Arrigo (2005).

To understand how nitrogen inputs are affecting Hood Canal, one must understand how nitrogen is cycled through marine ecosystems (Figure 4). Zooplankton grazers and decomposers like bacteria break down particulate organic nitrogen into dissolved inorganic nitrogen (DIN) – nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) – which can be taken up by marine autotrophs once again. However, DIN can also leave the system through denitrification. Denitrification occurs under anaerobic conditions, when certain bacteria ("denitrifying bacteria") use NO_3^- as an electron acceptor in cellular respiration, reducing it to nitrogen gas (N_2) in a multistep reaction. This reaction is the second step in the redox ladder, and it generally occurs from about 0.5 cm below the sediment surface (where O_2 runs out due to respiration and slow diffusion) to about 3 cm below the sediment surface (where NO_3^- becomes scarce) (Rigby, 2019). Additionally, N_2 can be created through anammox – anaerobic ammonium oxidation – where NO_2^- and NH_4^+ are the reactants (Dalsgaard et al., 2005). Denitrification and anammox are difficult to measure separately, so measurements of denitrification typically include both processes. Since these processes convert bioavailable DIN into an essentially inert gas – nitrogen fixation is minimal in bottom water (Marino and Howarth, 2016) – they are very important to measure, especially in the context of increased nutrient inputs and low-oxygen events. However, denitrification is difficult to measure, and although many methods have been used in various contexts (Groffman et al., 2006), each method comes with limitations. The only measurement of denitrification in Hood Canal from the literature is one from a 2018 masters thesis from Western Washington University. Santana (the author) used sediment core incubation, along with sediment C:N ratios, to calculate an average rate of 0.66 mmol N_2 m^{-2} d^{-1} across 5 cores from different locations in the canal. Based on this estimate, she calculated that denitrification and anammox should remove 10.9% of the DIN in Hood Canal (Rigby, 2019).

In this study, my goal was to estimate the denitrification rate in Hood Canal using water circulation. I began with the method outlined by Kana et al. (2006), but based on a likely violation of assumptions, I switched to a partial differential equation (PDE) model to better analyze the combined horizontal flow and vertical diffusion of N_2. Measuring denitrification using water circulation is a great way to obtain a broad spatial average, which is an improvement from using a few point estimates to extrapolate across an entire water body.

Methods and Results:

Kana et al. (2006) measured denitrification in Chesapeake Bay using a water circulation model. Their method assumed that the bottom water can be considered as a single water mass, separated from the surface layer, with perfect diffusion of N_2 throughout (Figure 5). If these assumptions are met, then the increase in nitrogen concentration ($[N_2]$) should be equal to the change in $[N_2]$ over distance (x) times the mean bottom water velocity in the direction of flow (Equation 1).

$$\frac{\Delta[N_2]}{\Delta x} * \frac{\Delta x}{\Delta t} = \frac{\Delta[N_2]}{\Delta t} \quad (1)$$

Because denitrification occurs in the sediment, the rate is usually measured in terms of seafloor area rather than volumetric concentration, e.g., mmol N_2 m^{-2} d^{-1}. To convert from $[N_2]$/time to areal units, one can simply multiply by the mean bottom water depth.

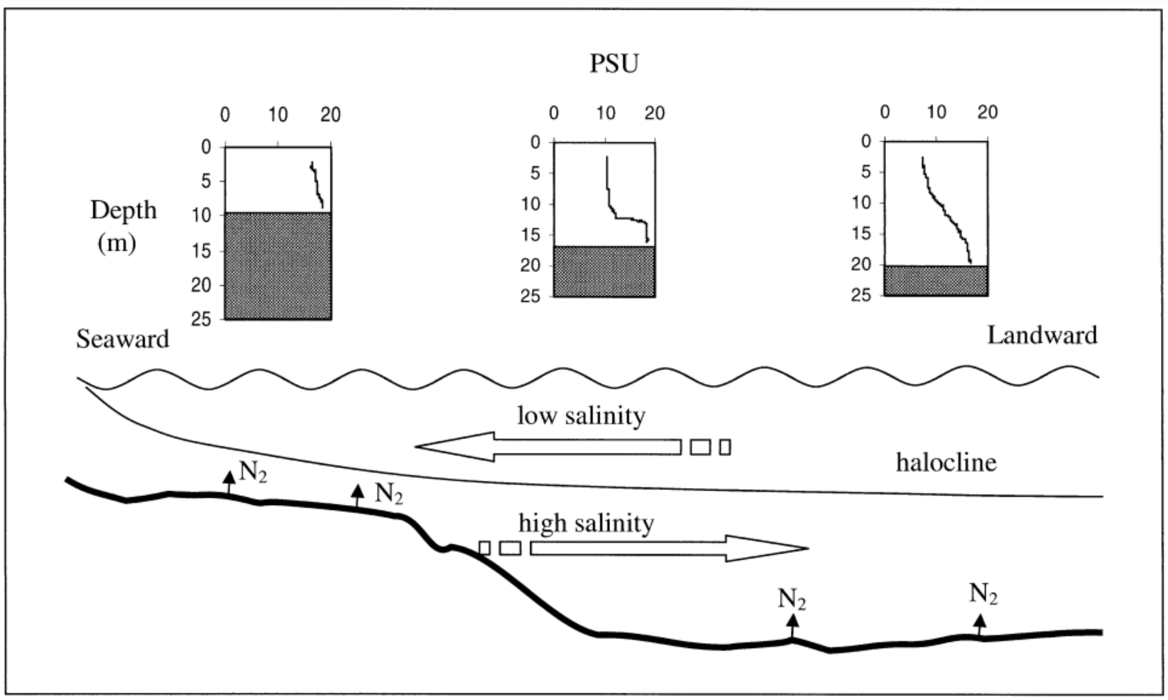

Fig. 1. Diagrammatic longitudinal cross section of the Chesapeake Bay two-layer flow with source of N_2 depicted. Plots are salinity profiles from three stations in October 2005. Left: km = 0, middle: km = 73, right: km = 144.

Figure 5. Schematic of Kana et al. (2006) model of water flow and N_2 release in Chesapeake Bay.

The Shull lab collected water samples at 5 stations along Hood Canal, ranging from near the north end, just south of the bridge, to near the beginning of the Great Bend. These samples were collected at the bottom of the water column on May 2nd, 2018. $[N_2]/[Ar]$ values were determined for each of these 5 stations using a membrane inlet mass spectrometer (MIMS). An anomalous salinity measurement at the second furthest south station suggested that the measurement there may not have been made in bottom water, so I did not consider the N_2 data from that station; consequently, only 4 stations were used for further modelling (Figure 7). These $[N_2]/[Ar]$ values were plotted by distance between stations, and linear regression was used to determine the average change in $[N_2]/[Ar]$ per km. The slope came out to 0.0283 km^{-1} and the relationship was quite linear, with an R^2 of 0.93 (Figure 6).

To convert from $[N_2]/[Ar]$ to $[N_2]$, I determined the saturation concentration of argon using the bottom water temperature and salinity (Weiss, 1970). Bottom water temperature and salinity were considered to be relatively stable along the canal, so I used the same estimates across all samples. These estimates came from the bottom measurement of a CTD profile taken at site 'HCB010' on May 10th, 2018. HCB010 is near station 2 in Figure 7.

To calculate mean water velocities, I used Matlab to analyze the output of the Salish Sea Model (SSM), developed by a team led by Tarang Khangaonkar at the Pacific Northwest National Laboratory (PNNL) in partnership with the Department of Ecology (Khangaonkar and Wang, 2011). I used the model output from 2014. The SSM consists of a spatial grid of points, each containing 10 depths (sigma layers) and timepoints every hour for a period of over 1 year. The sigma layers represent constant proportions of the water column, scaled to the depth of any given site. For each location/depth/timepoint (or relevant combination), the model gives outputs for geographic coordinates, site depth, east-west current velocity, north-south current velocity, vertical velocity, tidal fluctuation, temperature, and salinity. I averaged current velocities for each relevant location (the grid points in Figure 7) over a 3-month timespan ending on May 2nd, as 3 months is the estimated residence time for bottom water in southern Hood Canal (Babson et al., 2006). To determine what direction to calculate the current in for each location, I used PCA with the north-south and east-west currents at each site; the first principal component was the direction of flow along the canal, while the second principal component was the direction perpendicular to the canal. I used the first principal component for calculating average current velocity, and I used the line $y = -x$ to separate out positive velocity vectors from negative velocity vectors. I defined flow south along the canal as positive and north along the canal as negative. Given this definition and shape of Hood Canal, I defined any vector below $y = -x$ as positive and any vector above $y = -x$ as negative. Bottom water velocity is mostly positive in Region 1, the northernmost region. However, in Regions 2 and 3, the bottom water becomes stagnant, with average velocities straddling 0 m/s (Figure 8). Given this situation, it was unclear how to proceed with the Kana et al. (2006) method, so I ran a simpler test of the denitrification calculation using a mean water velocity from Cokelet et al. (1990), taken from a cross section of north-central Hood Canal.

Combining [Ar] at saturation with $\frac{\Delta[N_2]}{\Delta x}$, the mean water velocity from Cokelet et al. (1990), and a rough average bottom water depth, I calculated a denitrification rate of $20\ mmol\ N_2\ m^{-2}\ d^{-1}$ (Equation 2).

$$\frac{0.0283\ (\frac{[N_2]}{[Ar]})}{km} * \frac{14.3912\ mmol\ Ar}{m^3} * \frac{1.166\ km}{day} * 50\ m\ bw\ depth = 20\ mmol\ N_2\ m^{-2}\ d^{-1} \quad (2)$$

This rate is unrealistic. Santana calculated that denitrification and anammox should remove 10.9% of the DIN from the system when the denitrification rate is 0.66 $mmol\ N_2\ m^{-2}\ d^{-1}$ (Rigby, 2019), so a rate more than 20 times as high would imply that denitrification and anammox are removing virtually *all* of the DIN input in the system, leaving none for organisms to use. This result suggested that the assumption of perfect N_2 diffusion throughout the bottom layer was wrong. That assumption inflates the denitrification rate far above what one would calculate from assuming more limited vertical diffusion from the sediment-water interface. For this reason, I used an advection-diffusion model instead.

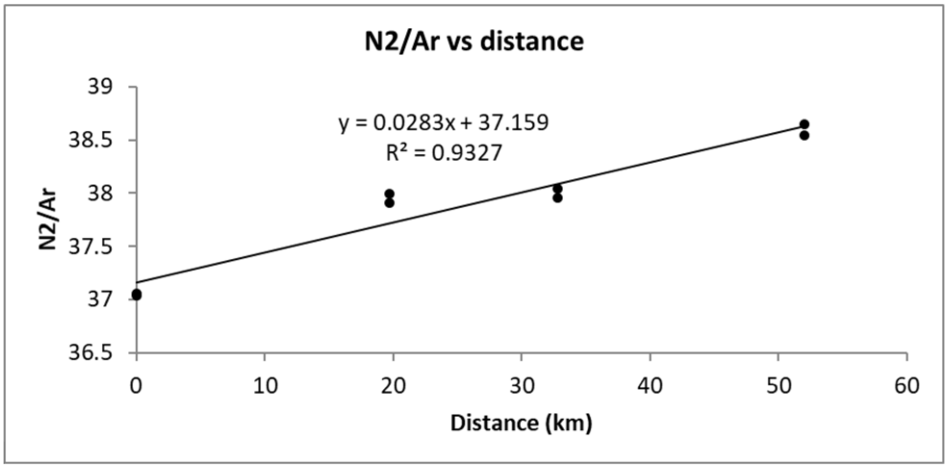

Figure 6. Change in bottom $[N_2]/[Ar]$ over distance. The regression line slope ($0.0283\ km^{-1}$) represents the average change over the length of the canal.

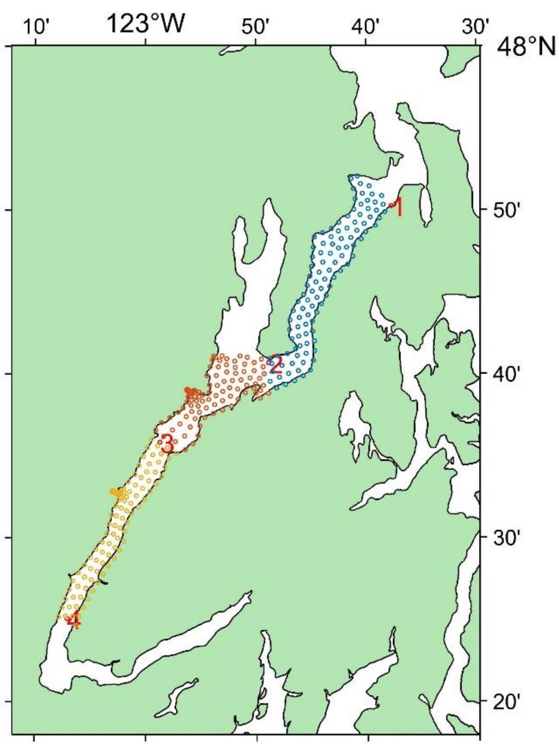

Figure 7. Hood Canal study region, with the N_2 measurement stations (numbered 1 to 4) and the SSM grid points within each region between measurement stations. Region 1 is blue, Region 2 is red, and Region 3 is yellow.

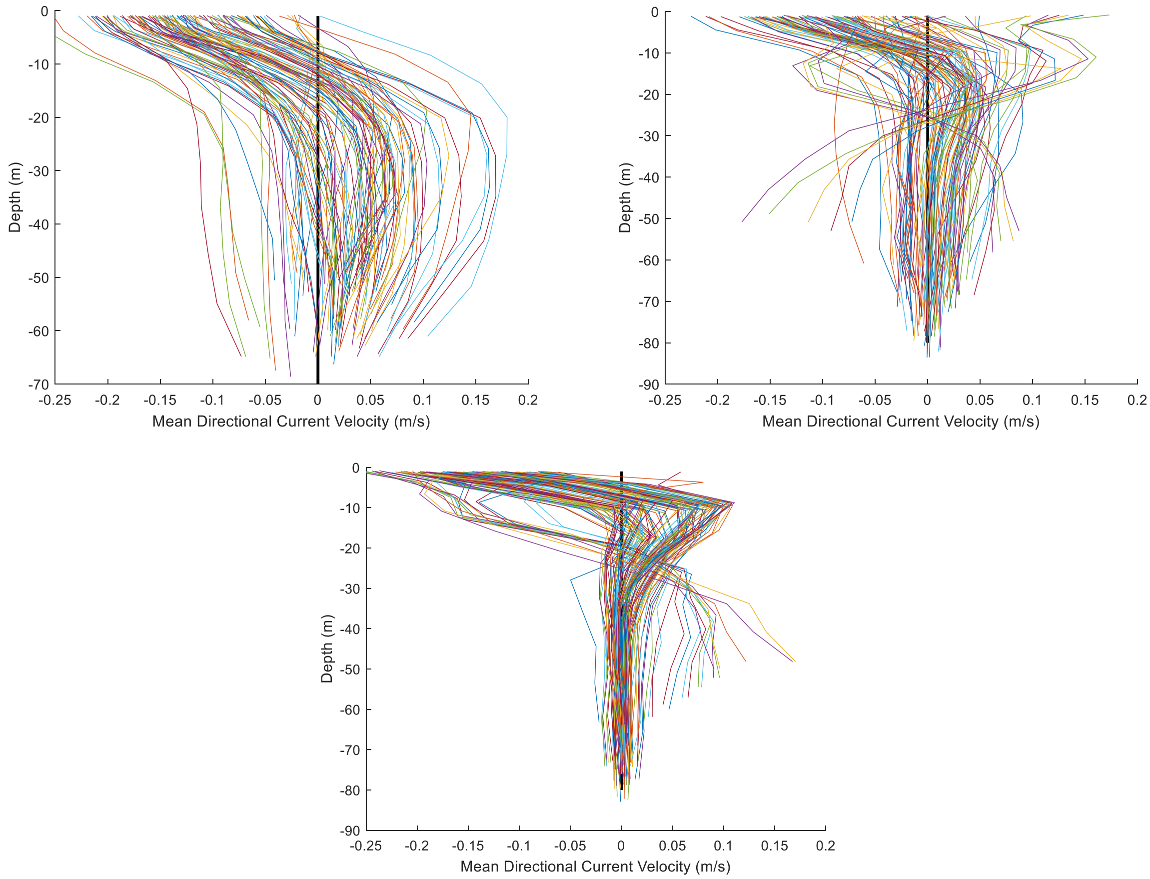

Figure 8. Average currents by depth along the canal axis at each SSM site, using PCA. Top left is Region 1 (northernmost), top right is Region 2 (middle), bottom is Region 3 (southernmost). South is positive and north is negative. The black line represents 0 m/s (no mean flow).

Advection means flow, while diffusion for this model meant vertical mixing, so the goal was to model the combined horizontal flow and vertical diffusion of N_2 in the bottom water of Hood Canal. Like with the rest of the calculations, Matlab was used to create this model. Equation 3 shows the partial differential equation that defined the model. Here, C is the concentration of N_2 (mmol/m^3), z is the depth (m), x is the horizontal position (m), u is the mean velocity (m/s), and K_z is the vertical diffusion constant (m^2/s). To simplify, I used a steady state assumption ($\frac{\partial C}{\partial t} = 0$) to get to Equation 4.

$$\frac{\partial C}{\partial t} = K_z \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial x} \quad (3)$$

$$\frac{\partial C}{\partial x} = \frac{K_z}{u} \frac{\partial^2 C}{\partial z^2} \quad (4)$$

This model was bounded at the pycnocline, which was defined as a depth of 18.5 m based on the CTD profile from HCB010 on May 10th, 2018. The pycnocline is where water density changes rapidly, so it should represent the upper boundary of the bottom water layer. The boundary condition at the pycnocline was that N_2 was at saturation (based on the same temperature and salinity I used to find [Ar] at saturation and the equations from Weiss (1970)). The boundary condition at the northern end of the model (station 1) stated that [N_2] increased linearly from the pycnocline to the measured concentration at station 1. The bottom boundary layer incorporated the flux of N_2 from the sediment – in other words, the denitrification rate. This flux was set equal to $\frac{\partial c}{\partial z} * K_z$.

For u, I used a matrix of currents derived from the methods described above that produced Figure 8. After finding 63 SSM points that trace a path along the canal, these currents were further refined to averages among the six SSM points closest to each of the 63 points along the 'horizontal transect' of the canal (removing points with depths less than 30 m). This transect extended a few SSM model points beyond the southernmost N_2 measurement site. At the southernmost point in the model, I forced all velocities to be positive to avoid modelling irregularities. With average currents by sigma layer in place for this horizontal representation of the canal, I used the 'pchip' function in Matlab to interpolate the data at equal intervals for however many depths or horizontal positions I wanted to try. To simplify the model, I built the grid as if depth were the same at each point along the canal (in reality, average cross-sectional depth varied from just over 50 m to over 80 m). This simplification maintained a rectangular grid shape. The matrix for K_z had the same dimensions. I used an estimate from Khangaonkar and Wang (2013), which says that K_z = 10^{-6} at the surface and increases exponentially with depth, so that K_z at depth d = $e^{10*(\text{d/total depth})}$. This equation implies that K_z at the bottom of Hood Canal should equal $10^{-6} * e^{10} = 0.022$.

To solve the partial differential equation, I used the method of lines. The code ran method of lines for different iterations of N_2 flux, using the Levenberg-Marquardt algorithm for nonlinear least squares regression. The model used different flux estimates at stations 2, 3, and 4, with the assumption that those flux values held for the regions surrounding the stations. The model then minimized the sum of squares between the model output N_2 concentrations and the measured N_2 concentrations.

Unfortunately, this model never quite worked the way that I wanted it to work. I continued to get denitrification estimates that were far too high. Simplifying the current matrix to just a simple bottom water velocity average for northern and southern Hood Canal helped the code to run faster and to reach steady state more consistently. I also tried manipulating the interpolation in various ways to make sure the number of horizontal and vertical intervals was not the issue. But the denitrification values were still far too high to be realistic. The left panel of Figure 9 shows a result from this model setup.

The one idea I had that seemed to maybe explain the situation was to bring the bottom diffusion constant, K_z, way down. The box model from Babson et al (2006) uses a constant K_z with depth, although that is more a function of how box models work than how the physical reality works. I found that bringing the exponential increase factor down from 10 to 1, or even 0 (eliminating the exponential growth altogether), yielded denitrification rates on the order of magnitude of what Santana calculated. The right panel of Figure 9 shows the N_2 concentrations calculated in this scenario.

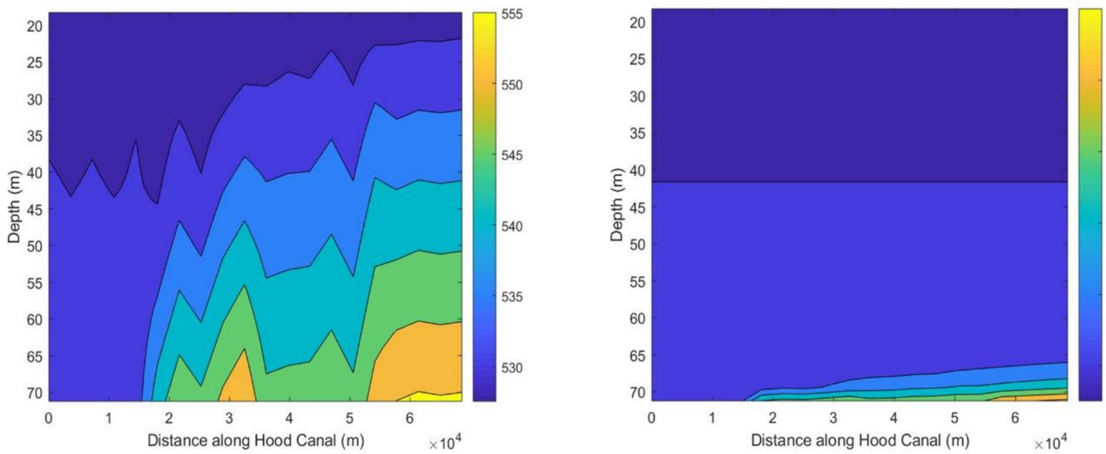

Figure 9. Example results from the advection-diffusion model. The left panel shows a result that suggested far too high of a denitrification rate, while the right panel shows a result when K_z was set constant with depth, which suggested a much more reasonable denitrification rate. The colors represent [N_2] in mmol/m^3.

Discussion:

The results of this study are inconclusive. It is possible that the diffusion constant, K_z, varies relatively little with depth in Hood Canal, in which case the advection-diffusion model results seem reasonable. However, the ultimate goal with creating the advection diffusion model was to obtain an independent estimate of denitrification rather than using the previous estimate of denitrification to fit the diffusion constant. If nothing else, the magnitude of the diffusion constant clearly has a huge impact on the model results, which makes sense given that this constant is what tells the model to what extent N_2 is mixed into the bottom water above the sediment surface. Future studies could determine nitrogen concentrations from many depths within the bottom water at a few representative sites, then fit these concentrations to the correct diffusion constant(s) within an advection-diffusion model.

There may be other issues with the model as well. For example, I modelled flow using a constant velocity along the flow axis of the canal. The reality is that the majority of the flow is back-and-forth tidal fluctuation. A more complex model could consider the flow velocity u as a function of time rather than as a matrix of constant mean velocities. This model formulation would be able to incorporate tidal fluctuation.

Despite the inconclusiveness of this study, we can still consider how a denitrification estimate based on water circulation can effectively supplement point-based estimates. Every estimate of denitrification requires assumptions, so comparing different estimates with different assumptions is a great way to confirm results. One of the biggest advantages of a flow-based estimate is that it would provide a broad spatial average of denitrification, rather than simply providing a few point estimates that must be assumed to be representative of the whole canal. Flow-based estimates also eliminate the need to physically disturb the sediment, as you can just measure [N_2] from bottom water samples. This noninvasiveness is preferable to a method like Santana's sediment core incubation (Rigby, 2019), where the sediment inevitably faces at least a small level of disturbance. A flow based estimate also does not require assumptions about where in the sediment denitrification is happening; the C:N rations that Santana used in her calculation required this assumption (Rigby, 2019). On the other hand, a flow-based estimate does require assumptions about the flow, namely that the two-layer flow model is accurate, and that diffusion is being modelled accurately.

Although an advection-diffusion model may not turn out to be the best approach for estimating denitrification in Hood Canal, obtaining more estimates of the denitrification rate is important. Santana's study suggested that denitrification removes 10.9% of the nitrate inputs from the system, which is a much higher percentage than in other parts of the Salish Sea (Rigby, 2019). Thus, denitrification is an important piece of the nitrogen cycle in Hood Canal. Given the dissolved oxygen problem that Hood Canal faces, and the potential role of anthropogenic dissolved inorganic nitrogen in this problem, quantifying the components of the nitrogen cycle is critical to understanding the system and mitigating human impacts.

References:

Babson, A. L., Kawase, M., & MacCready, P. (2006). Seasonal and interannual variability in the circulation of Puget Sound, Washington: a box model study. *Atmosphere-Ocean*, *44*(1), 29–45. https://doi.org/10.3137/ao.440103

Cokelet, E. D., Stewart, R. J., & Ebbesmeyer, C. C. (1990). *The annual mean transport in Puget Sound* (Technical Memorandum ERL PMEL-92). National Oceanic and Atmospheric Administration.

Dalsgaard, T., Thamdrup, B., & Canfield, D.E. (2005). Anaerobic ammonium oxidation (anammox) in the marine environment. *Research in microbiology*, *156*, 457-464.

Feely, R. A., Alin, S. R., Newton, J., Sabine, C. L., Warner, M., Devol, A., Krembs, C., & Maloy, C. (2010). The combined effects of ocean acidification, mixing, and respiration on pH and carbonate saturation in an urbanized estuary. *Estuarine, Coastal and Shelf Science*, *88*(4), 442–449. https://doi.org/10.1016/j.ecss.2010.05.004

Groffman, P. M., Altabet, M. A., Böhlke, J. K., Butterbach-Bahl, K., David, M. B., Firestone, M. K., Giblin, A. E., Kana, T. M., Nielsen, L. P., & Voytek, M. A. (2006). Methods for measuring denitrification: diverse approaches to a difficult problem. *Ecological Applications*, *16*(6), 2091–2122. https://doi.org/10.1890/1051-0761(2006)016[2091:MFMDDA]2.0.CO;2

Hood Canal Dissolved Oxygen Program. (n.d.). Retrieved May 26, 2021, from http://www.hoodcanal.washington.edu/index.jsp

Kana, T. M., Cornwell, J., & Zhong, L. (2006). Determination of denitrification in the Chesapeake Bay from measurements of N_2 accumulation in bottom water. *Estuaries and Coasts, 29(2)*, 222-231.

Khangaonkar, T. and Yang, Z. (2011). A high resolution hydrodynamic model of Puget Sound to support nearshore restoration feasibility analysis and design. *Ecological Restoration*, *29*(1-2), 173-184.

Khangaonkar, T., & Wang, T. (2013). Potential alteration of fjordal circulation due to a large floating structure — numerical investigation with application to Hood Canal basin in Puget Sound. *Applied Ocean Research*, *39*, 146–157. https://doi.org/10.1016/j.apor.2012.11.003

Marino, R., & Howarth, R. W. (2016). Why is planktonic nitrogen fixation so rare in coastal marine ecosystems? Insights from a cross-systems approach. In Aquatic Microbial Ecology and Biogeochemistry: A Dual Perspective (pp. 127-139). Springer International Publishing.

Newton, J., Bassin, C., Devol, A., Kawase, M., Ruef, W., Warner, M., Hannafious, D., & Rose, R. (2008). Hypoxia in Hood Canal: an overview of status and contributing factors. In: Proceedings of the 2007 Georgia Basin Puget Sound Research Conference.

Rigby, E. (2019). *Springtime benthic fluxes in the Salish Sea: Environmental parameters driving spatial variation in the exchange of dissolved oxygen, inorganic carbon, nutrients, and alkalinity between the sediments and overlying water* [Master's Thesis]. Western Washington University.

Sollai, M., Hopmans, E. C., Schouten, S., Keil, R., & Sinninghe-Damste, J. (2015). Intact polar lipids of Thaumarchaeota and anammox bacteria as indicators of N-cycling in the Eastern Tropical North Pacific oxygen deficient zone. *Biogeosciences Discussions* (Vol. 12). https://doi.org/10.5194/bgd-12-4833-2015

Thomson, R. E. (1994). Physical oceanography of the strait of Georgia-Puget Sound-Juan de Fuca strait system. *Review of the marine environment and biota of Strait of Georgia, Puget Sound and Juan de Fuca Strait*.

Weiss, R. F. (1970). The solubility of nitrogen, oxygen and argon in water and seawater. *Deep Sea Research and Oceanographic Abstracts*, *17*(4), 721–735. https://doi.org/10.1016/0011-7471(70)90037-9