

Oxygen and hydrogen sulfide concentration of Nootka Sound bottom water

Senior thesis

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5/31/15

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Acknowledgement:

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Dr. Kathy Newell

Ashley Maloney

Abstract:

Nootka Sound is a narrow fjord located at the west side of the Vancouver Island that have little investigation been done. It has a large sill that could potentially trap ocean water. Along with steep salinity and other geological reasons, Nootka Sound is susceptible to oxygen depletion in water, which is detrimental to benthic communities and fisheries. In this study, oxygen concentrations were measured with oxygen probe on CTD instrument. Oxygen data was calibrated with titration of water sample from CTD, with Winkler Method. Water samples was analyzed to show its nutrient concentration, specifically nitrate, nitrite and ammonia concentrations. Results shows that at the time of the study, water below 350 meters in depth is oxygen depleted. At one of the station, water sample had a strong rotten egg smell, which means there was a lot of dissolved hydrogen sulfide. Hydrogen sulfide is a great indicator of sulfate reduction, which only happens when no oxygen and nitrate exists. The condition of Muchalat Inlet is similar to Sannich Inlet and Hood Canal in terms of the mechanisms that causes oxygen depletion.

Introduction:

Nootka Sound is a significant body of water in the Pacific Northwest. However, it has not been studied much. Oxygen profile of a body of water gives a lot of information about the health of its natural environment. Muchalat Inlet of the Nootka Sound is a straight inlet with a deep valley about 350 meters in depth. Heavy rainfall during the winter flushes a lot of fresh water into the fjords and traps the ocean water at the bottom. This gives the Inlet a high salinity gradient. While the bottom water is not getting much oxygen from mixing or photosynthesis, respiration continues. So the oxygen level keeps getting lower and lower. Over the course of winter, the bottom water might reach anoxic conditions. Continuous respiration might even produce hydrogen sulfide, which is an important environmental factor and potentially toxic.

The oxygen profile of a body of water is produced and influenced by a wide range of processes including physical, chemical, biological, and anthropogenic. The biggest influence that brings oxygen into the water is surface mixing because the water is constantly exchanging gas with the atmosphere. The major source of freshwater for Muchalat Inlet is the Gold River. During winter, Gold River inputs a large amount of freshwater into the inlet due to seasonal heavy rainfall. Since river water does not mix well with salty water, freshwater will be floating on top of salty water, making the water column very stratified. Even though during winter, weather is going to be windier, which will increase mixing in the surface ocean, the stratification will isolate the bottom salty water from exchanging gas with the atmosphere. Another possible source of oxygen is from phytoplankton doing photosynthesis. Primary production during winter in Muchalat Inlet is limited primarily by sunlight. So even though nutrient in the winter is high, there shouldn't be a high oxygen production from photosynthesis due to the lack of sunlight. Bacteria communities in the bottom water will continue to respire, using up oxygen, thus

lowering oxygen concentration. These processes all indicate that concentration of oxygen is likely to be low and there might be regions exist that have zero oxygen.

Bacteria in the benthic communities does not stop respiring when there is no oxygen. It continues to respire with other oxidant and dumps electrons to the oxidant. Other oxidant includes sulfate and nitrate. Sulfate will be reduced to hydrogen sulfide, and nitrate will be reduced to ammonium ion. It would be beneficial for our understanding of chemistry of the low oxygen zone if we can have nutrient data of the water. Especially the concentration of sulfate, nitrate, ammonium and H₂S. We would expect the sulfate and nitrate concentration to decrease and ammonium and H₂S concentration to increase as depth of water increases. The reason for this prediction is that the deeper the parcel of water is in the water column, the longer it had stayed at the bottom without being replenished with oxygen. And so the more respiration it had been experienced. Saanich Inlet is anoxic during summer and spring. It will be interesting to compare and contrast the conditions of Saanich Inlet and Nootka Sound (Anderson and Devol 1973; Ward and Kilpatrick 1989). Hood canal has similar natural environment as Nootka Sound. And its hypoxia condition have dramatic impact on fisheries (Palsson et al. 2008).

Hydrogen sulfide is a potential environmental factor and toxicant (Bagarinao 1992). Past studies have shown that Anoxic condition is potentially detrimental to benthic communities (Diaz and Rosenberg 1995). It raises mortalities for Echinoderms, Bivalves and Crustaceans (Garlo et al. 1979; Llanso 1992). Anoxic conditions are bad for fisheries, however, different organisms have different tolerance level to low oxygen. Scientist has investigated the influences and tolerance level of different types of organisms. ((Rabalais and Turner 2013)) Study shows that nektons and demersal invertebrates are absent when oxygen concentration is low. In rarely occasion, low oxygen level will lead to fish kills. But generally they will be safe. However, Benthic organisms, larger and macro infauna are at risk of stressed and death

when oxygen level is lower than 1 mg/L. So oxygen concentration measurements are very useful in answering the spatial distribution of fisheries and microorganisms.

Nootka Sound is a fjord that have very little human population. The most important industry in the area is sport fishing since Gold River is an important salmon spawning ground. Other than that, area around Nootka Sound is mostly undeveloped. So there is very little anthropogenic perturbation to oxygen and H₂S levels in Muchalat. Anoxic condition of Nootka sound have not had a report of fish kills due to low oxygen. However, with global warming continue to make the ocean water more acidic, health of estuary will be threatened. This is a abundant communities of benthic species including bivalves, shrimps and benthic worms. Even though these species are well adapted to cycles of anoxic environment and flushing, with global warming rapidly acidifying the ocean in geologic time, they might not adapt fast enough to keep up with change. Similar effect has happened at Hood canal. Hood canal is one of the four main basins of Puget Sound, Washington. This long narrow fjord has a lot of similarities with Muchalat Inlet. They both are narrow straight fjords with a major fresh water source. The biggest fresh water input for hood canal is Skokomish inlet. Hood canal has very low oxygen level year round and dead zone seasonally due stratification and low mixing rate. What's interesting about Hood canal is that the largest dead zone of Hood canal was discovered on 2006, even though most of the processes that created the dead zone have been stable in many years, except for climate change due to global warming. So it is interesting to compare and contrast Muchalat Inlet and Hood Canal to see the effect climate change have made to the oxygen concentrations.

Senior thesis method:

Measurement of this study was taken during the Senior Cruise of UW Oceanography department, on board RV Thompson from December 12 to December 22 2014. I collaborated with Una Miller, Julie Ann Koehlinger on collecting data and making measurements. Since Muchalat Inlet is the most likely place to find hypoxia in Nootka Sound, I focused my effort in Muchalat Inlet. In order to investigate the oxygen concentration and Hydrogen sulfide condition of Muchalat Inlet, I performed CTD casts starting from gold river mouth and end at Nootka Sound area, taking measurements along the channel equally separated, for a total of 11 stations. From the CTD cast, I expected to get oxygen profiles (to show oxygen concentration), salinity profiles (to see stratification), water samples (to do analysis). With the water samples, I did Winkler titrations, H₂S measurements. CTD casts, oxygen titrations and H₂S measurements was performed during Senior Cruise. Water samples was saved to do nutrient analysis after the cruise.

For every CTD cast, I took a total of 4 water samples. I took the first water sample right at the bottom of the mix layer according to the salinity profile of the CTD sensor. For the last water sample, I took at the bottom of the water column, as deep as the CTD can get. This way I can have a water sample of the very bottom of the water column. For the remaining two water samples, I separated them evenly between the first and last water sample. This sampling method allowed me to have a water sample that is well separated so that later I can produce a profile that is most useful.

For oxygen concentration, I used Winkler titration. For Hydrogen sulfide, I used a Hydrogen Sulfide Test Kit developed by Hach Company. To achieve the most accurate results, H₂S was tested with the Cline Method (Cline et al. 1969). Oxygen profile generated by the oxygen sensor on the CT was calibrated with Winkler titration results.

The majority of my CTD sampling stations fall in a straight line. So constructed a oxygen cross section along this line, with x axis being the run of the sampling route, y axis being depth, and third dimension being the oxygen concentration that is indicated with a color scale.

The 11 Stations are indicated by map of the Nootka Sound (Figure. 1) below.

Coordinates are also indicated by Table. 1.

Data was analyzed by Ocean Data View and Excel to support or reject my hypothesis.

Results

Figure 1 is a map of showing the stations of CTD casts. Stations are distributed long the inlet.

Figure 2 shows CTD oxygen measurements. Oxygen concentration appears to be decreasing as depth increasing. It reaches dysoxic condition at 55-60 meters. It reaches anoxic condition at 300 meters.

Oxygen concentration was correlated with depth. Oxidic layer (oxygen concentration > 2 ml/L) ranges from 0 meters in depth to 50 meters in depth. Dysoxic layer ($0.2\text{ml/L} < \text{oxygen concentration} < 2$ ml/L) ranges from 50 meters to 300 meters. Anoxic layer (oxygen concentration < 0.2 ml/L) ranges from 300 meters to 350 meters.

Figure 3 shows Winkler titration of water sample results of samples from different stations. Oxygen concentration reaches 0 at the depth of 350 meters. Mix layer and concentration gradient is clearly visible from the plot. At the top 100 meters, oxygen concentration drops drastically. Below 100 meter, oxygen concentration decreases not as fast as the top 100 meters. There are a obvious concentration slope.

Figure 4 shows nutrient measurements at station M08, where dissolved hydrogen sulfide is found. Nitrate concentration decreases significantly with depth, ammonia increases slightly. From the nutrient concentration profile, we can see that nitrate concentration decreases as a function of depth. It decreases from 20 mM to about 0 mM. Nitrite concentration increases from 0 to 300 meters in depth, and decreases from 300 meters to 350 meters. At depth of 200 to 300 meters, ammonium concentration increases.

Figure 5 shows nutrient measurements plotted on the same graph to show relative change. Nitrate drop is significantly higher than nitrite rise. That means there are more sinks nitrate other than nitrite.

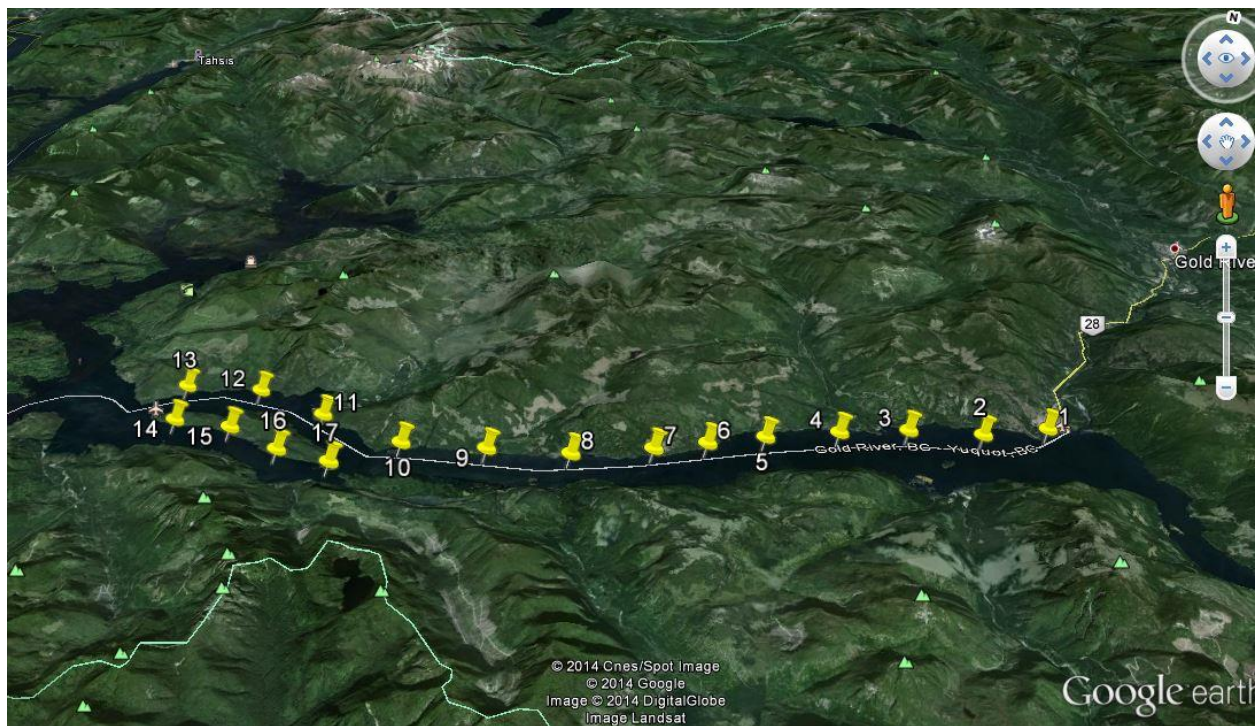


Figure. 1 Map of Muchalat Inlet of Nootka Sound, Vancouver Island BC, Canada. Pins showing the locations of sampling.

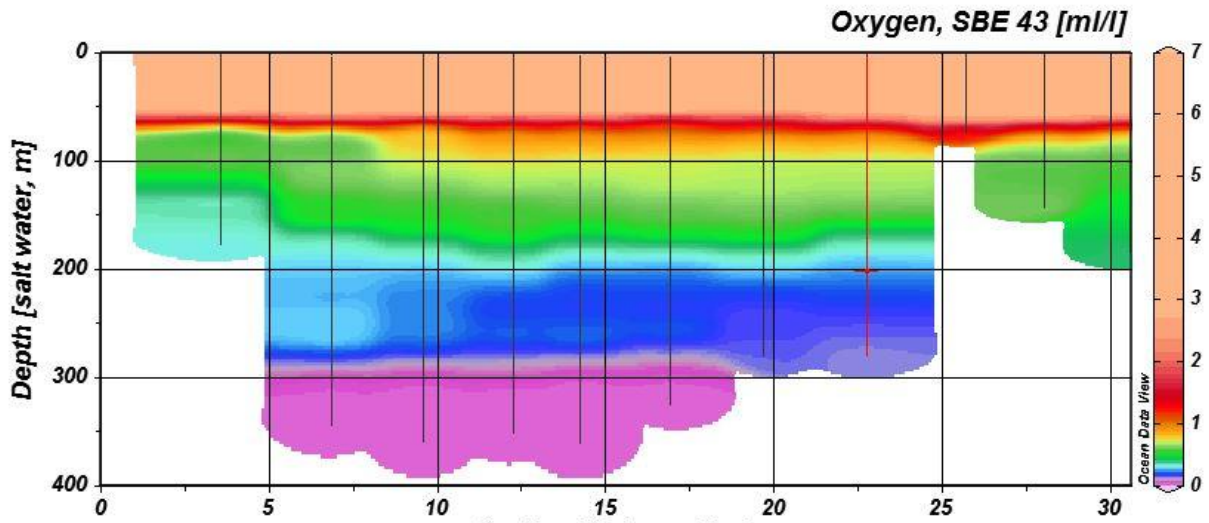


Figure 2. Oxygen concentration measurement from Muchalat Inlet taken by oxygen sensor on CTD. Y axis shows depth, X axis shows distance of stations. Color shows oxygen concentrations in ml/L unit. Purple regions shows anoxic regions, blue and green regions shows dysoxic region.

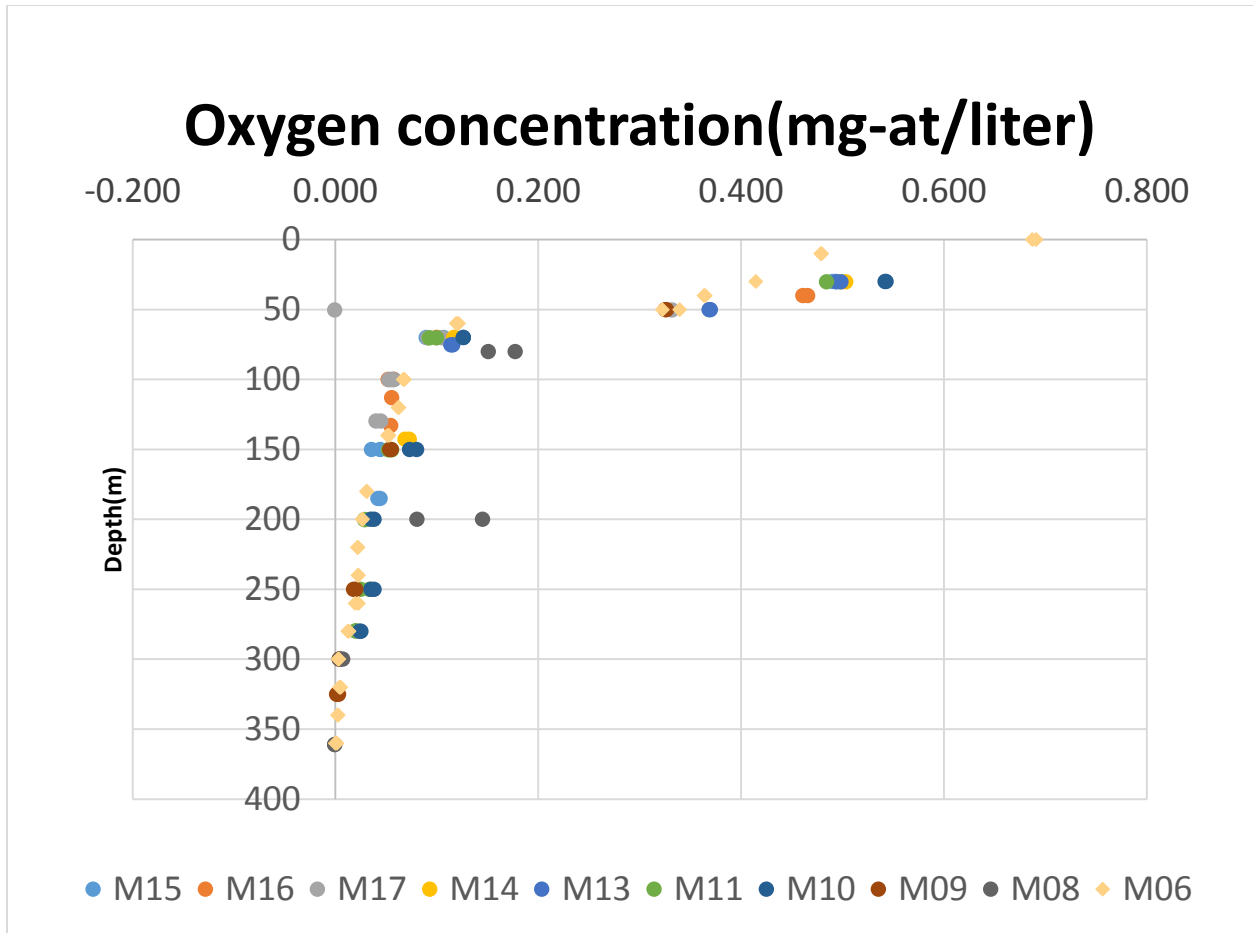


Figure 3. Oxygen titration of water samples from different depths of different stations. Different stations are denoted by different colors. Y axis shows depth where the water samples are taken.

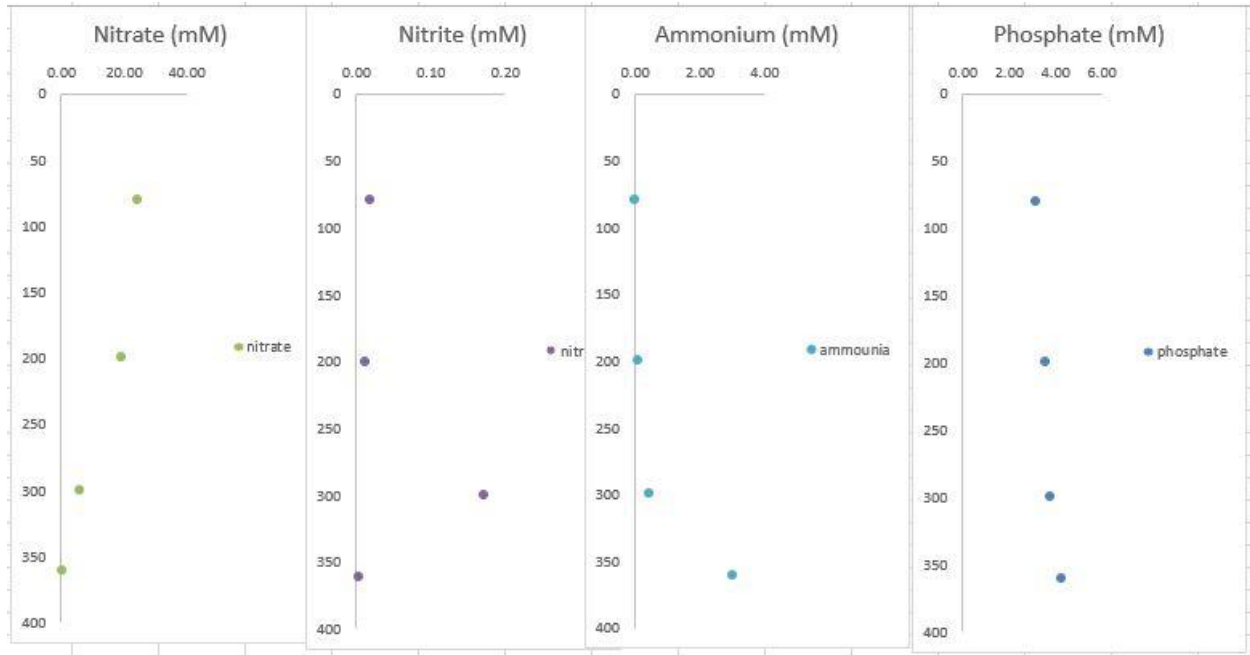


Figure 4. Nutrients concentrations of water samples from Station M08. Stations M08 is where water samples that has strong smell of Sulphur and test positive of hydrogen sulfide comes from. Each nutrients are plotted individually to show qualitative relationship between different species of nutrients.

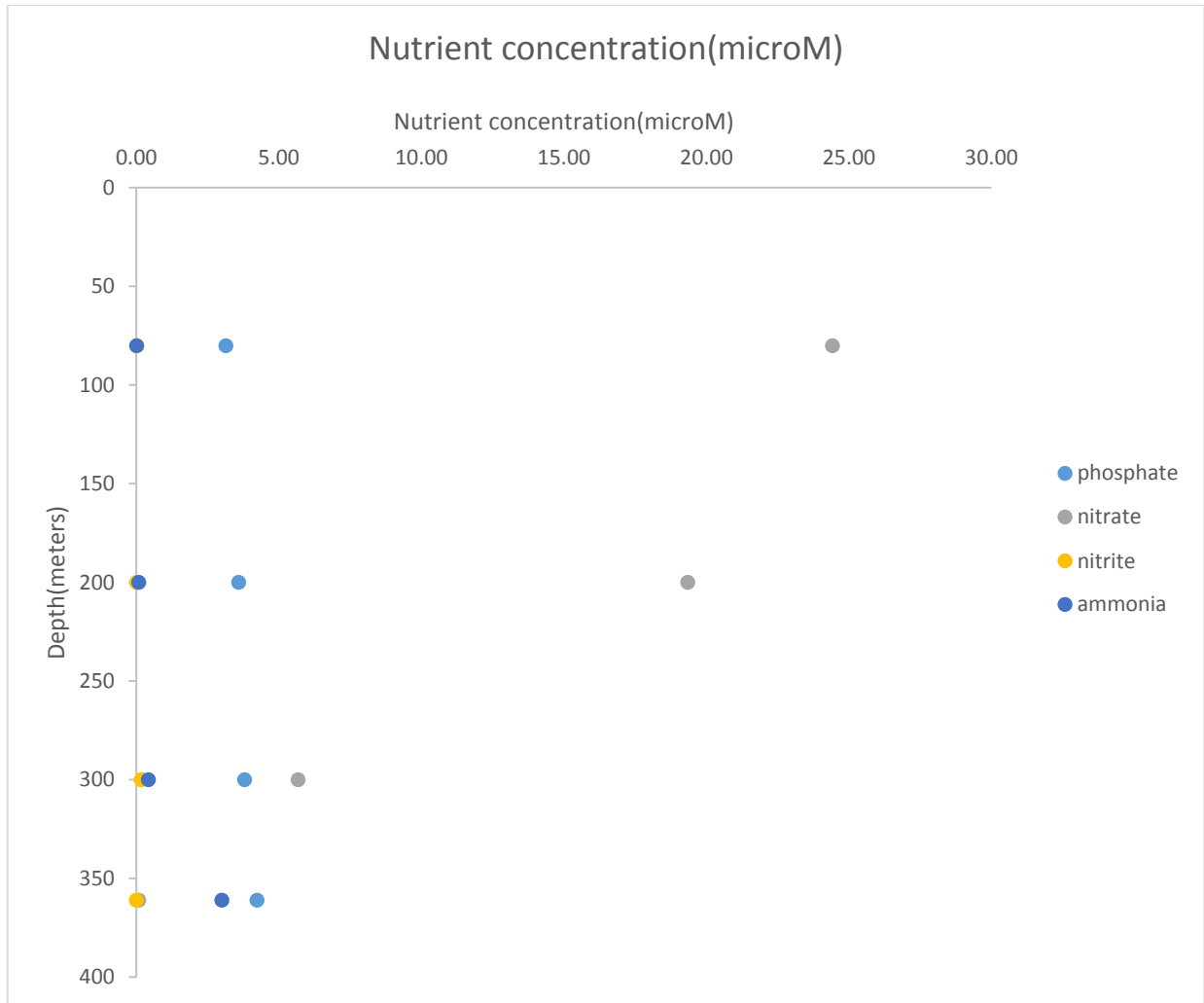


Figure 5. Nutrient concentrations from station M08 are plotted on the same graph to show the relationships between them quantitatively. This is useful for us to understand anaerobic respiration better. Y axis shows depths of water samples. X axis shows concentrations in mM.

Discussion

The decrease of nitrate and increase of nitrite could be explained by anaerobic respiration. At the top 100 meters, organisms respire aerobically, with oxygen and exhale carbon dioxide. Below 100 meters, oxygen concentration is low enough that it is more favorable to use other species of oxidant as an electron pool for respiration. Nitrate is the more favorable choice in this case because of the high concentration and chemical property. During anaerobic respiration, nitrate turns into nitrite. That explains why nitrite increases where nitrate decreases in the water column. The increase of ammonia concentration is due to the fact that ammonium ion is a product of anaerobic respiration. The oxygen profile shows two distinct layers with two slopes. The top layer has a steeper slope than the bottom layer. This is because the top layer consists of mostly fresh water input from Gold River, which is well mixed. The salinity gradient is too steep to mix down with the saline water. So the upper slope is controlled by wind vertical mixing while the lower slope is controlled by respiration. This makes sense since anaerobic respiration is a slower process. So the slope is less steep compared to the upper slope.

As we can see from the oxygen profile, oxygen concentration decreases to almost zero at about 350 meters. Low oxygen concentration in Muchalat Inlet has many reasons and causes. First of all, as a fjord, Muchalat Inlet has both seawater and fresh water input. Gold River is the primary fresh water input. During winter, especially from October to January, heavy rainfall greatly increases the freshwater input from Gold River. Since freshwater is less dense than seawater, it will float on top of the saline water. The two water sources with two contrasting salinities create a steep salinity gradient. This steep salinity gradient is characteristic of a highly stratified system. This steep salinity gradient prevents fresh water, with high oxygen concentration, from mixing down to the bottom, so new oxygen cannot travel to the water below. Besides these big reasons, other physical conditions also aggravated the condition. During winter, there is less lighting, which means there is little photosynthesis that produces oxygen. While photosynthesis is lessened, respiration remains. So the water gets more and more anoxic over the course

of winter. At the bottom layer, away from the photic zone, bacteria and virus metabolizes aerobically or anaerobically, using oxygen and other oxidants. Respiration used up oxygen at about 300 meters in depth, making water anoxic. The geographic location of Muchalat also contributes to the low oxygen concentration. Nootka sound locates at the pacific northwest, where oldest ocean water upwells after about 1000 years of traveling in deep ocean. So this source of ocean water is naturally more anoxic. Also the shape of the basin traps the deepest part of ocean water from circulation, making the water near the bottom oxygen depleted. These reasons all contribute to the low or no oxygen at the bottom of Muchalat Inlet, which is shown by the oxygen titrations and CTD casts data.

Sannich inlet is an inlet on the other side of the Vancouver island that has been studied more about its geological and chemical condition. (Anderson and Devol 1973) Sannich inlet also has deep basin shape that traps ocean water with a large sill. So we might expect that Sannich Inlet and Muchalat Inlet to be quite comparable in terms of process that leads to anoxic condition. The most anoxic condition in Sannich Inlet occurs during spring and summer according to the Anderson and Devol studies. Our study was conducted during winter, and we already tested positive of hydrogen sulfide in one of our stations. The nitrate concentration in that station, Station M08, goes to zero at about 350 meters in depth. Sannich Inlet's nitrogen concentration goes to zero at a much shallower depth, about 150 meters. This is due to the fact that Sannich Inlet is a shallower inlet with a maximum depth of about 250 meters while Muchalat Inlet has a maximum depth of close to 400 meters. This depth difference could also explain why the seasonality of Sannich Inlet is so prominent. Although we have no data in Muchalat Inlet that shows the oxygen concentration in other seasons, the much deeper basin would predict a less dramatic seasonality.

Conclusion

This study shows that oxygen concentration was very low at depth in Muchalat Inlet and there was dissolved hydrogen sulfide in some part of the deep basin. More studies can be conducted to show the seasonal variability of the oxygen depletion condition. El Nino and La Nina have effects on a lot of oceanographic phenomenon. Changes in upwelling rate, annual temperature and wind strength are all potential factor that changes the seriousness of hypoxia in Muchalat Inlet. More stuidies are needed to investigated whether extreme weather could be a potential factors.

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