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# Temporal and spatial variability of carbonate chemistry in a Tillamook Bay tributary: Tracing acidification from the river to the bay

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## Abstract

Coastal acidification from rising atmospheric carbon dioxide can be exacerbated by local factors such as land inputs of inorganic carbon and nutrients. In Tillamook Bay, OR, the possibility of local factors enhancing acidification and impacting oyster aquaculture in the bay is a concern due to extensive agriculture in the watershed. The US EPA has been monitoring water conditions in Tillamook Bay tributaries since the summer of 2016, and preliminary findings showed increased dissolved inorganic carbon (DIC) downstream of agricultural areas. To determine the causes of elevated DIC, changes attributed to land-based inputs must be distinguished from natural temporal variability and in-stream processing. We initiated a study to assess temporal variability by conducting a day-long time series of DIC and partial pressure of CO<sub>2</sub> (pCO<sub>2</sub>) at locations upstream and downstream of agricultural areas along the Trask River. To quantify in-stream processing (periphyton photosynthesis and respiration), stream rocks were placed in sealed microcosm chambers for 7 hours, and changes in dissolved oxygen and carbonate chemistry were measured. Initial and final concentrations of dissolved oxygen (DO), DIC, and pCO<sub>2</sub> in each container were compared to the conditions in the stream itself. Time series data show that DIC was lower upstream and decreased more throughout the day. In chambers, the  $\Delta$ DIC :  $\Delta$ DO ratio is consistent with stream photosynthesis-respiration stoichiometry at both sites, while in streamwater, the  $\Delta$ DIC :  $\Delta$ DO ratio is much lower downstream. In-stream processing can account for most of the changes in DIC in the chambers, but not in the streamwater, suggesting that elevated DIC levels can be attributed to inputs of inorganic carbon from land-based sources.

## Introduction

Ocean acidification is occurring on a global scale from increasing levels of carbon dioxide in the air. Coastal acidification from rising atmospheric carbon dioxide can be exacerbated by local factors such as land-based inputs of nutrients and inorganic carbon, which are also increasing over time. Nutrient inputs can increase the production of organic matter, and thus increase the rate of respiration in aquatic ecosystems. This can result in accumulation of dissolved carbon (Figure 1) and thus enhanced acidification (Van Dam et al., 2018; Sunda and Cai, 2012). This process of increased  $\text{CO}_2$  from nutrient inputs (Figure 1) can account for a third of the measured acidification at the surface in coastal waters (the other two thirds being anthropogenic carbon), and up to 5 times the anthropogenic carbon levels at depths of 50 – 100 m (Feely et al., 2016). Additionally, atmospheric  $\text{CO}_2$  inputs and DIC inputs associated with respiration can interact to cause even greater amounts of acidification than each factor would cause individually (Sunda and Cai, 2012; Pacella et al., 2018), and as climate change increases, so can the variability in the streamwater and estuarine processes that cause acidification (Mulholland et al., 1997b). The greatest respiratory increases in DIC occur at low salinities (Sunda and Cai, 2012), so streams and estuaries such as the Trask River and Tillamook Bay could be more susceptible to pH changes than other coastal areas or the open ocean.

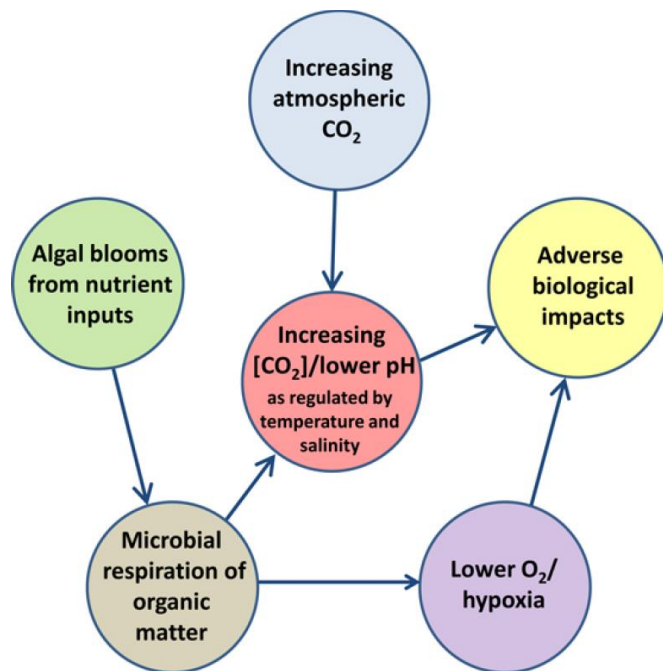


Figure 1. Relationship of increasing atmospheric  $\text{CO}_2$  and nutrient inputs to pH and DO levels, from Sunda and Cai (2012).

Tillamook, Oregon supports a large agriculture industry, especially dairy. In 2012, there were 280 farms in Tillamook County and around 45,000 cows, 55 percent of whom were dairy cows (USDA/NASS Census of Agriculture, 2012). Many farms collect the manure and store it to be sprayed on fields. Other areas leave the manure or store it less permanently, allowing for runoff to carry some of the nutrients and carbon into the watershed. As an indirect result of both of these methods, much of the nutrients and carbon from the manure may indirectly end up in the groundwater and rivers in Tillamook Valley. Tillamook Bay, which supports many important industries including recreation and oyster aquaculture, is directly downstream of this agriculture and is therefore at risk of negative effects from ocean acidification.

Effects of acidification in Netarts Bay, just south of Tillamook, have already been heavily felt by the Pacific oyster shellfish industry. Commercial oyster farming in Netarts Bay has existed since the late 1800s (Waldbusser and Salisbury, 2014). In 2007, large amounts of oyster larval mortality in the Whiskey Creek Shellfish Hatchery (Waldbusser and Salisbury, 2014; Gouldman et al., 2011) caused researchers to investigate the causes. While they originally attributed the oyster seed die-off to bacterial pathogens, they later found a significant relationship between DIC increases and decreased larval survival (Waldbusser and Salisbury, 2014; Barton et al., 2015). They subsequently implemented a more comprehensive monitoring system with collaboration between the shellfish growers and the US Integrated Ocean Observing System (Gouldman et al., 2011).

The Pacific Coastal Ecology Branch of the US Environmental Protection Agency (EPA) in Newport, Oregon monitored water conditions in Tillamook Bay and the five rivers that run into the bay approximately monthly between July 2017 and September 2018 as part of its research program. There are five main rivers in Tillamook Valley: the Miami, Kilchis, Wilson, Trask, and Tillamook. Preliminary findings show increased total dissolved inorganic carbon (DIC) downstream of agricultural areas in each of the four rivers where upstream and downstream locations were compared. However, during the field sampling trips, time constraints restricted sampling to once per day at each location, with different locations sampled at different times. To accurately make comparisons of water conditions between sites, it is necessary to know the variability in conditions at each site over the course of a day to put the differences between sites in the context of temporal variability.

Determining the causes of elevated downstream DIC in the river also requires understanding which changes can be attributed to land-based inputs versus in-stream processing (the photosynthesis and respiration of periphyton and suspended organisms). This necessitates isolating the in-stream processing from the overall changes taking place. The purpose of this study was to examine the effects

of short-term temporal variability and in-stream processing on water conditions, specifically carbonate chemistry, at locations upstream and downstream of agricultural inputs along the Trask River to better understand causes of acidification in Tillamook Bay.

## Methods

### *Study locations*

Measurements were taken in the Trask River, which is one of five tributaries to Tillamook Bay. This river was chosen because it is the only one of the tributaries that has a portion upstream of all agricultural inputs before any major forks occur. Two locations along the Trask River were chosen for comparison (Figure 2). Nips' Landing, the upstream location, is in a primarily forested area and is upstream of all agricultural activities. Steiner Boat Launch is near the center of Tillamook Valley, and has around 5000 cows in Concentrated Animal Feeding Operation (CAFO) farms upstream of it (USDA data provided to EPA), plus an unknown number of cows outside of the CAFOs. Nips' Landing was more highly shaded from the forest foliage as compared to Steiner Boat Launch, but both locations were similar in width, depth, sediment structure, and turbulence.



Figure 2. Map of Tillamook Bay and tributaries, with Nips' Landing and Steiner Boat Launch marked.

### *Time series*

Time series measurements were conducted on three days: June 29, July 26, and August 8, 2018. On two of these days, June 19 and August 8, a pre-programmed YSI multi-parameter data sonde was left at both Nips' Landing and Steiner Boat Launch to automatically take measurements of pH, temperature, conductivity, depth, in situ fluorescence (a proxy for chlorophyll a), and dissolved oxygen every 15 minutes for 50-56 hours.

On all three of these dates, water samples were collected for laboratory analysis of carbonate chemistry parameters (DIC and partial pressure of CO<sub>2</sub>) and nutrient concentrations. For these nutrient and carbonate samples, each location was sampled several times between 8:00 and 16:30 local time (7:00 and 15:30 Pacific Standard Time) depending on the day (5 samples were taken at each location on June 29, 3 samples at Nips and 4 at Steiner on July 26, and 7 samples at Nips and 5 at Steiner on August 8). Additionally, a hand-held YSI 6600 Multiparameter data sonde was used to take the same measurements as the pre-programmed data sonde. This was done to have these measurements at the exact same time as the manual water samples were collected, and to serve as quality control for the measurements from the pre-programmed YSI data sonde.

Water for nutrient measurements was filtered using a 0.45- $\mu$ m syringe filter that was rinsed with 5 ml of sample, and then 30-35 ml of sample was filtered into a plastic centrifuge tube. Samples were placed on ice in the field, then frozen upon return to the laboratory in Newport. These samples were later shipped frozen to the University of Washington for analysis.

For the carbonate chemistry samples, a dark brown glass bottle was rinsed with unfiltered sample water and then filled with 300ml of unfiltered sample water using a plastic tube to minimize mixture with the air. During filling, the bottle was allowed to overflow to reduce bubbles. The sample was poisoned with 30 $\mu$ l of saturated mercuric chloride to preserve the samples, and then the bottles were sealed. The pCO<sub>2</sub> and DIC concentrations were measured at the EPA laboratory in Newport using a carbonate chemistry analyzer (designed and built by Burke Hales, Oregon State University; Figure 3), which uses microporous hydrophobic membrane contactors to make high-frequency and high-accuracy measurements of partial pressure and total concentration of carbon dioxide (Hales et al., 2004). Post-processing corrections were made to account for instrument drift using Burke Hales' method (Hales et al., 2004; Bandstra et al., 2006). Concentrations were then corrected for the change in alkalinity due to the addition of mercuric chloride to the sample. This correction is not usually made because the effect of mercuric chloride is negligible in high-salinity ocean water, which is normally the type of water measured. However, with these low-salinity samples, this correction was necessary for maximum

accuracy. The corrected pCO<sub>2</sub> and DIC concentrations were used to calculate the rest of the carbonate chemistry parameters including total pH, alkalinity, carbonate and bicarbonate concentrations, and the saturation states of calcite and aragonite using CO<sub>2</sub>SYS version 2.3, an internationally-used calculations spreadsheet written by Ernie Lewis of the Brookhaven International Laboratory.

### *In-stream processing*

To assess whether the elevated downstream DIC observed in the time series measurements could be attributed to land-based agricultural inputs or to in-stream processing, it was necessary to investigate the effects of in-stream processing on the water chemistry. To do this, in-stream processing was isolated from the inputs by using clear containers as sealed microcosm chambers (Figure 4) at both Nips' Landing and Steiner Boat Launch. This allowed us to measure changes in DO and carbonate chemistry due only to in-stream processing (photosynthesis and respiration of periphyton and suspended organisms), and then compare these conditions to those in the open streamwater.

Shortly after sunrise, a small metal quadrat the area of the container lid was placed on the streambed. The top layer of rocks was removed and temporarily placed on the lid to ensure that the layer of rocks with the most periphyton stayed on top. Approximately 2 cm of the sediment under the top layer was removed and placed in the container. Then, the top layer of rocks was placed in the container upright. The chambers were filled with streamwater and closed underwater to avoid bubbles. At the same time they were closed, an initial measurement of the DO in the stream was taken right next to the container using a YSI sonde, and an initial measurement of DIC in the stream was taken using a Van Dorn bottle to capture a water sample and then preserved as described previously. Half of the chambers were covered with foil for a dark treatment, and half left uncovered as light treatments. At each of the two sample locations, there were 4 light treatments, 2 light controls (only streamwater; no rocks), 4 dark treatments, and 2 dark controls.

The chambers were left in the stream for approximately 7 hours, depending on the container. Final DO measurements were taken with an optical DO probe that had been calibrated within 0.2 μmol/kg of the YSI sonde. Two carbonate chemistry bottles were filled from each enclosed container and taken to the lab to measure final DIC and pCO<sub>2</sub> concentrations, and an additional two carbonate chemistry bottles were filled from the stream for comparison. All chambers had a hole drilled in the lid the same diameter as the glass stoppers for BOD (Biological Oxygen Demand) bottles and were plugged with these stoppers in the stream so the DO could be easily measured with a BOD probe with minimal air exposure. Hourly production and respiration rates were calculated using these measurements.

Carbonate chemistry parameters from the microcosm chambers were measured and calculated in the laboratory using the same methods as described in the time series portion of the experiment. Sampling was first done on July 26, 2018 with light treatments and light controls only; the experiment was repeated on August 8, 2018 to include dark treatments and controls in addition to the light treatments and controls, so that changes in water conditions due only to respiration and not photosynthesis could be observed. The effects of location and treatment on DIC concentrations were tested using a two-way omnibus ANOVA test with an alpha value of 0.05, and then simple main effects were used to compare the ratio of changes in DIC and DO between the two locations.



Figure 3. Analysis of carbonate samples on the Burke-o-lator, a carbonate chemistry analyzer.



Figure 4. Sealed microcosm chambers (light treatment) placed in the Trask River to measure in-stream processing

## Results

### *Time series*

DIC concentrations were consistently lower upstream (Nips' Landing) than downstream (Steiner boat launch) of agricultural areas even with substantial change in concentrations over the course of a day (Figure 5), with a difference between locations ranging from approximately 100 to 275  $\mu\text{mol}/\text{kg}$ . DIC concentrations decreased throughout the day due to drawdown of  $\text{CO}_2$  via photosynthesis. The amount of drawdown was fairly consistent with respect to the time of day for each of the three sample days in June, July and August, with slightly more drawdown earlier in the season. However, there was much more drawdown at the upstream location (approximately 200  $\mu\text{mol}/\text{kg}$  over 7 hours) than the downstream location (approximately 50  $\mu\text{mol}/\text{kg}$  over 7 hours), causing increasing differences in DIC concentrations between locations as each sample day progressed (Figure 5).



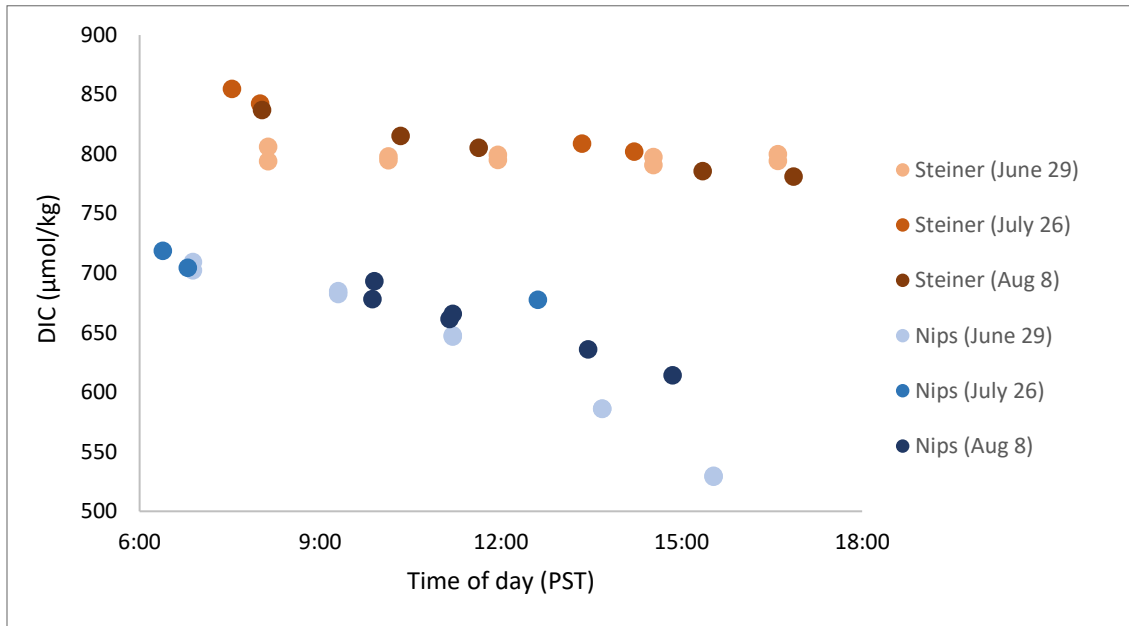


Figure 5. Time series of DIC concentrations throughout the course of a day at two locations along the Trask River. Times are in Pacific Standard Time, which was one hour earlier than local time during the dates sampled.

Time series data show that the pH was consistently higher upstream (Nips' landing) than downstream (Steiner boat launch) even against a background of high temporal variability (Figure 6), with the difference between locations ranging from 0.4 to 1.2. The pH was more variable upstream than downstream and was more variable in the early summer than later in the season, with Nips' Landing ranging from 7.6 to 9.4 in June and 7.5 to 8.7 in August and Steiner boat launch ranging from 7.1 to 7.3 in June and 7.1 to 7.5 in August. Downstream pH was less variable, both hourly and seasonally.

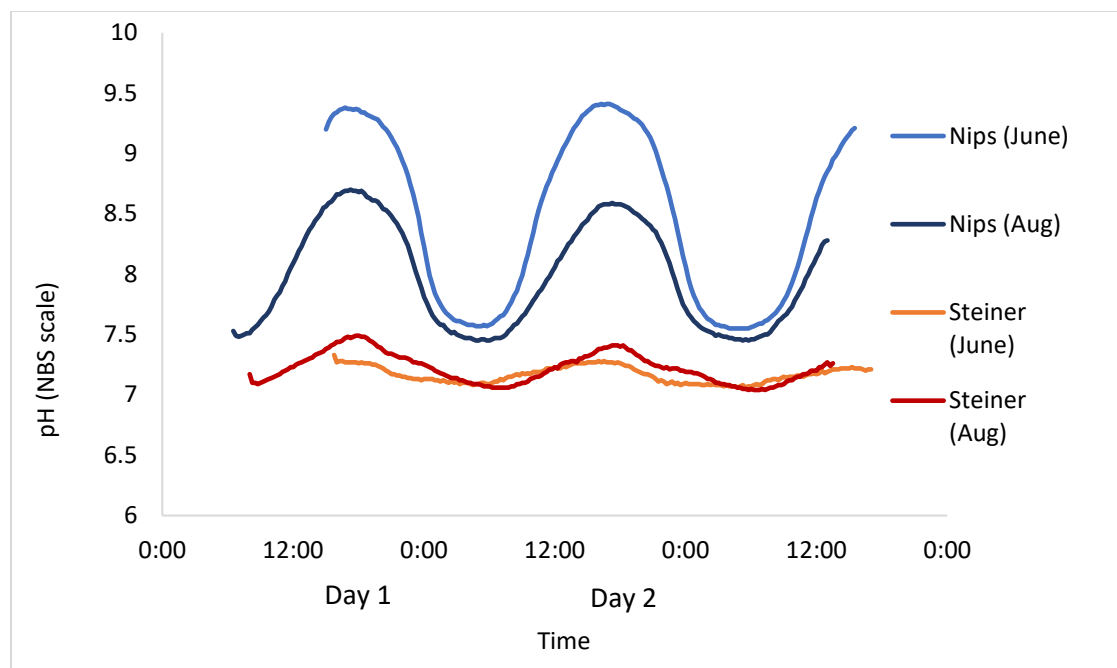


Figure 6. 48-hour time series of pH at two locations along the Trask river. Times in Pacific Standard Time.

### *In-stream processing*

In the sealed chambers, changes in dissolved oxygen in both light and dark treatments were matched by approximately equal and opposite changes in DIC at both locations along the Trask River (Figure 7), which is consistent with the assumption that the only changes occurring in the chambers were due to photosynthesis and respiration. The light and dark control treatments showed very little change in DO and DIC, except for the control treatment  $\Delta$ DIC at Steiner. The minor changes that did occur can be attributed to respiration of organic material suspended in the water column, though lack of corresponding changes in DO can likely be attributed to error. In the streamwater, there was a greater decrease in DIC per hour than the increase in DO, which indicates that factors other than photosynthesis and respiration were affecting the concentrations.

The effects of location and treatment on DIC concentrations were tested using a two-way omnibus ANOVA. Since ANOVA is robust to non-normality, the assumption of normality was not a concern. A Levene test for homogeneity of variance of location\*treatment on DIC showed that the assumption of equal variance was not met ( $p < .05$ ), and even after transforming the data via square root, log, and  $-1/y$  transforms, the assumption was still not met. This reflected the higher variability in the stream treatment compared to the other treatments. To account for the unequal variance, the alpha value of 0.05 was reduced to 0.025 to account for any possible inflated F values from the unequal

variance (Gamst et al., 2008). A two-way omnibus ANOVA did not show a significant interaction between location and treatment ( $F_{4,18}=1.1$ ,  $p = .38$ ) on DIC concentrations, but did show a significant effect of both location ( $F_{1,18}=7.16$ ,  $p = .015$ ) and treatment ( $F_{4,18} = 14.2$ ,  $p <.01$ ). Despite a relatively low sample size, there is a comparatively high F value for both location and treatment ( $F = 7.16$  and  $14.2$ , respectively), whereas the F value for the interaction of location and treatment was small ( $F = 1.1$ ), further indicating no significant interaction of location and treatment.

For the ratio of changes in DO to changes in DIC, an omnibus ANOVA with an alpha value of .025 showed no significant effect of location or treatment or an interaction, which makes sense given that the ratio should remain relatively constant across treatments in the chambers. However, since the omnibus test did not make comparisons between locations for each specific treatment, I chose to additionally make these comparisons using simple main effects to compare the ratio of changes in DIC and DO between the two locations. A Levene test for homogeneity of variance of the effect of location on ratio showed that the assumption of equal variance was met ( $p >.05$ ), so there was no need to adjust the original alpha value of 0.05. For the four treatments in the chambers (light, dark, light control, and dark control), there was no significant difference between the two locations (light  $F_{1,3} = 1.27$ ,  $p = .27$ ; dark  $F_{1,3} = .034$ ,  $p = .86$ ; light control  $F_{1,1} = .0088$ ,  $p = .93$ ; dark control  $F_{1,1} = .0004$ ,  $p = .98$ ). While the small sample size may have limited the ability to find a significant difference between treatments even if there was one, the small effect size values (F) indicate that there was very little difference between locations, so this further confirms that there is very little effect of location on the DIC to DO ratio in the chambers. However, there was a significant difference in the streamwater between the ratio at the upstream location ( $F_{1,3} = 5.05$ ,  $p = .037$ ). So, in the chambers, there was no statistically significant difference between the upstream and downstream locations in the ratio of changes in DO and DIC, but in the streamwater, there was a significant difference between locations, which indicates that these changes cannot be accounted for by in-stream processing alone.

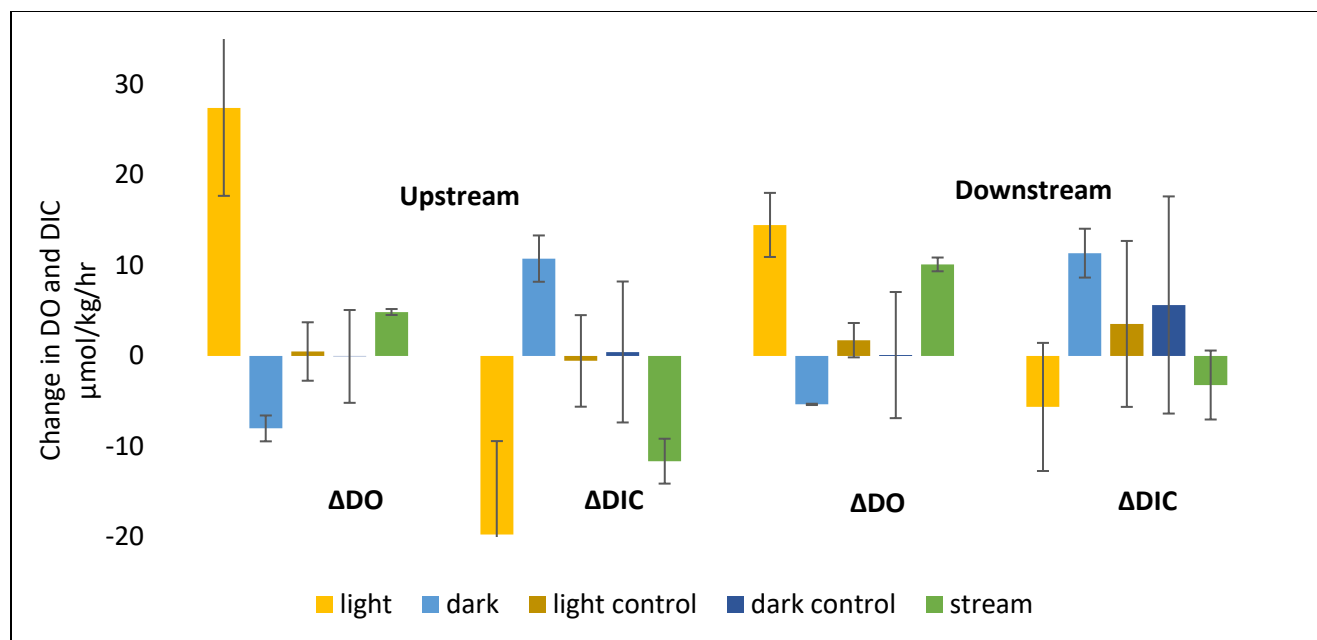


Figure 7. Production and loss of DO and DIC in chambers (blue and yellow) compared to streamwater (green) at the upstream location (left) and downstream location (right). Error bars show standard error.

A graphical comparison of the ratios of DIC and DO concentrations allows more quantitative comparisons to be made between the chambers and open streamwater in the upstream and downstream locations. Ordinary Least Square Regression lines were used to calculate the ratio of changes in DO to DIC and the fit of this line to the data. In enclosed chambers, the  $\Delta\text{DIC} : \Delta\text{O}_2$  ratio was almost exactly the same at upstream (Nips) and downstream (Steiner) sites, and is consistent with photosynthesis-respiration stoichiometry (Figure 8, left). Both locations had slope values around the expected value of 1.0 due to the 1:1 ratio of changes in DIC and DO in photosynthesis (slope = -0.90 at Nips and -0.82 at Steiner), and this relationship was highly linear ( $R^2 = 0.99$  at Nips and  $R^2 = 0.95$  at Steiner) (Figure 8, left). In the open streamwater, the  $\Delta\text{DIC} : \Delta\text{O}_2$  ratio is much lower at the downstream site (slope = -0.41) than at the upstream site (slope = -2.05), and the relationship is much less linear downstream ( $R^2 = 0.24$ ) than upstream ( $R^2 = 0.77$ ) (Figure 8, right). This suggests that inputs from land-based sources are causing increases in respiration, which adds inorganic carbon to the system and offsets the uptake of DIC via photosynthesis.

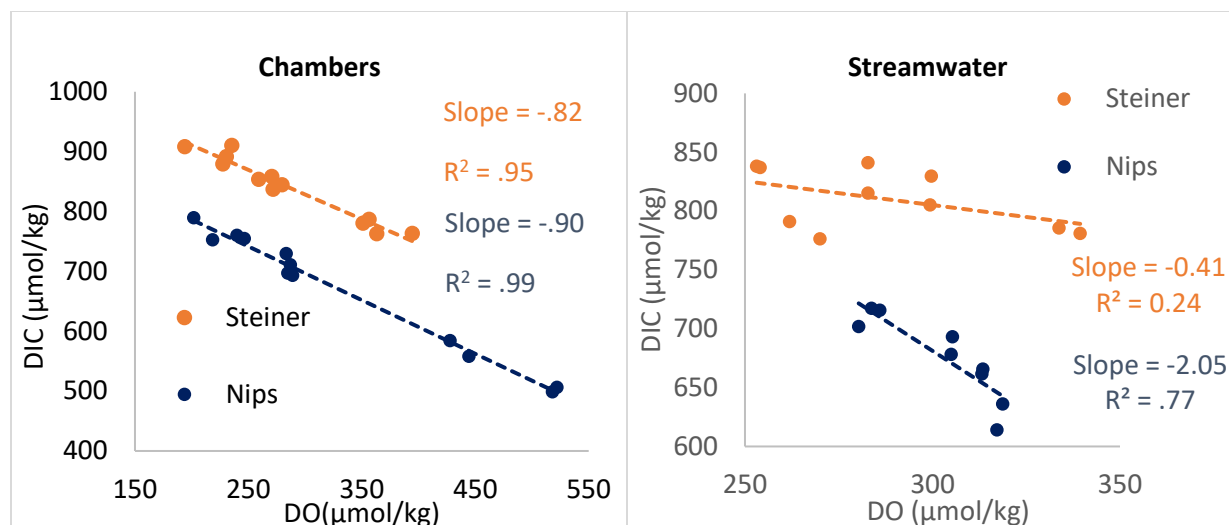


Figure 8. Changes in dissolved organic carbon (DIC) and dissolved oxygen (DO) in enclosed microcosm chambers (left) and open streamwater (right). Changes were measured at upstream (Nips) and downstream (Steiner) locations along the Trask River in August of 2018. Trendlines were calculated using Ordinary Least Squared (OLS) Regression.

Another way to look at these results is to model the concentrations of DIC that would be observed in the streamwater without inputs, and compare these modeled concentrations to actual observed concentrations. Similar to Bott et al. (1978), DIC concentrations that would be seen via in-stream processing were modeled using the change in DO concentration in the streamwater over each 15- minute interval. The ratio of changes of DO and DIC measured in the chambers was used to calculate the expected change in DIC for the each 15- minute interval. Then, an air-stream exchange coefficient was calculated using the method described in Izagirre et al. (2007), and used to correct the modeled DIC concentration for air-stream exchange.

At the upstream location, the modeled and observed DIC concentrations were similar (Figure 9). The difference between modeled and observed can most likely be explained by a low estimate of the air-stream exchange coefficient, resulting in not all of the air-stream exchange to be accounted for. If all of the air-stream exchange were accounted for, the modeled DIC concentration would fall lower because greater amounts of DO accounted for correspond with greater decreases in DIC, so the modeled and observed concentrations would likely be closer to each other. At the downstream location, the actual downstream DIC was higher than the modeled DIC. If more of the air-stream exchange were accounted for, this would cause the modeled DIC concentrations, again, to be lower. In this case, the modeled and observed concentrations would then be even further apart. Thus, inaccuracy in the air-

stream exchange coefficient cannot account for the difference between modeled and observed DIC concentrations at the downstream location. The large differences between modeled and observed DIC levels at the downstream location can only be accounted for by land-based inorganic carbon inputs, illustrating the impact of these inputs on streamwater conditions.

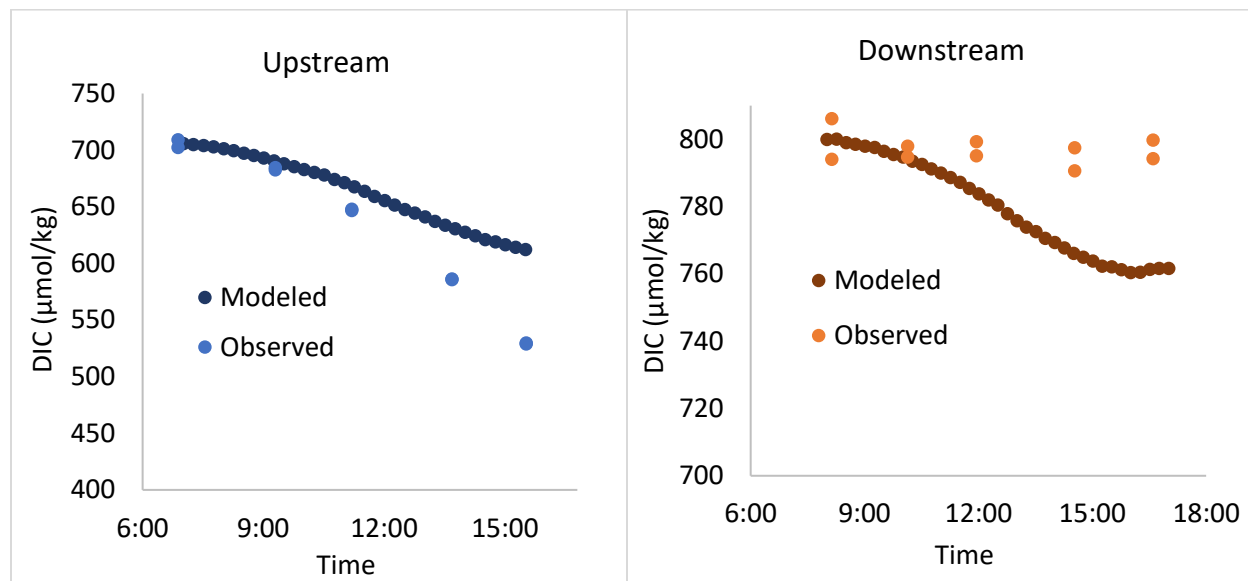


Figure 9. Modeled (without inputs) and observed (with inputs) DIC concentrations over the course of a day at upstream (Nips) and downstream (Steiner) locations on the Trask River.

## Discussion

Data from this study confirmed earlier observations of elevated levels of dissolved inorganic carbon in Tillamook tributaries downstream of agricultural areas. By analyzing temporal and spatial variability and isolating the in-stream processing from the inputs for comparison, it can further be concluded that these elevated levels of DIC cannot be accounted for by temporal variability or in-stream processing alone. This indicates that the elevated downstream DIC can be attributed to inputs, likely from nearby agriculture, that are contributing inorganic carbon to the system. As the water from the Trask River drains into the bay, this can, in turn, play a significant role in ocean acidification in Tillamook Bay.

The time of day had a strong influence on the pH and the DIC concentrations in the streamwater. In fact, at Nips landing, there was more variability in pH and DIC over the course of the day on June 29 than was observed over the course of a year in preliminary longer-term EPA data. Although there are no preliminary longer-term data from Steiner boat launch, a similar downstream location on

the Trask river showed variability in pH and DIC over the course of a year similar to variability exhibited at Steiner boat launch over the course of a day. This indicates that daily and yearly temporal variability may be on similar scales, so the time of day at which sample is taken is critical when comparing the pH levels or DIC concentrations between locations over longer time scales.

Daily variability of pH can be explained by photosynthesis and respiration. During the night, respiration is the only process occurring, so there is a buildup of DIC that lowers the pH. During daylight hours, photosynthesis occurs alongside respiration, so some of the DIC that is produced via respiration is uptaken during the process of photosynthesis and pH becomes higher. The upstream and the downstream locations likely had similar rates of uptake of DIC via photosynthesis, considering that the closed microcosm chambers showed similar changes in DIC and DO at both locations. In the open streamwater at the upstream location, DIC decreased throughout the course of the day as the DIC that had built up overnight from respiration was uptaken via photosynthesis. However, at the downstream location, higher levels of nutrients and/or organic matter from agricultural runoff likely caused increased rates of cellular respiration, concurring with the process described in Van Dam et al. (2018). Thus, the uptake of DIC via photosynthesis is exceeded by these higher respiration rates, and the net DIC in the water does not decrease as much throughout the day. This, alongside buffering from higher alkalinity, explains the consistently higher DIC concentration downstream and increasing differences in DIC concentrations between locations observed throughout the day. These differences between the upstream and downstream locations observed in the streamwater were not observed in enclosed chambers, which further indicates that the elevated DIC observed downstream can be attributed to agricultural inputs.

Water flowing from the Trask River into Tillamook Bay can contribute to the acidification already occurring, especially combined with other factors including nutrient and bacteria loading (Sullivan et al., 2005). The other tributaries to Tillamook Bay may have even greater DIC loading, considering that of the five tributaries, the Trask River's flow-weighted average pH of 7.0 is as high or higher than the other tributaries (Sullivan et al., 2005). In terms of the impact of temporal variability, short-term variations in water conditions are less likely to be as relevant or noticeable once they reach the bay, but they could still affect some processes and are an important part of understanding and contextualizing longer-term variability.

While this study is a good starting point for observing temporal variability, further studies are needed to more comprehensively quantify and account for these effects. Lack of night-time carbonate data limited the ability of this study to quantify respiration rates in the stream. Considering the high

variability in DIC fluxes observed in other studies over many time scales including large day-to-day variability (Roberts et al., 2007), seasonal variability (Roberts et al., 2007; Uehlinger and Naegeli, 1998; Uehlinger et al., 2000; Uehlinger, 2006) and interannual variability (Van Dam et al., 2018; Roberts et al., 2007; Uehlinger, 2006), the short-term data collected in this experiment may have limited potential for extrapolation. A 24-hour time series of carbonate chemistry at both locations and sample dates during multiple seasons and over multiple years would allow for a more comprehensive understanding of the temporal variability of carbonate chemistry and thus the potential for extrapolation of smaller datasets.

Looking at the in-stream processing, an increased overall sample size and a balanced sample size between treatments would allow for a higher level of confidence in the results, which is concurrent with the observations of Bott et al., 1978, who suggested that 12 measurements are necessary to characterize metabolic parameters. While this study allowed for a comparison of the ratio of the changes in the chambers to the changes in the stream, the specific rates of photosynthesis and respiration were impossible to quantify because the chambers were left long enough for supersaturation of the dissolved oxygen to occur (Bott et al., 1978). Future studies should take this into consideration when conducting similar experiments; a shorter time span and a reduced initial DO concentration may allow for photosynthesis rates to be more exactly quantified. It would also be useful to measure solar radiation at both locations to have a greater understanding of potential confounding factors causing differences in photosynthesis and DIC uptake between locations; public data of hourly solar radiation are available for the general Tillamook area, but not for specific locations. Finally, it may be useful to study microcosm chambers that are open on the top to allow natural air-stream exchange to occur, as this would minimize the need to account for air-stream exchange with imperfect calculations.

A map of groundwater and direct agricultural inputs would also help to better understand the whole system. This would allow for direct observation of the inputs into the stream rather than the indirect measurement of changes in streamwater chemistry due to these inputs. It would also facilitate collaboration between multiple parties including scientists and landowners in order to gain access to streamwater outside of public areas, though this complication is the reason that no such data have been collected so far. Useful areas of future work might include similar short-term studies of temporal variability and in-stream processing on the other four tributaries to Tillamook Bay, and looking at loading of organic matter (dissolved and/or particulate) from land-based sources. This would add to a more holistic understanding of the Tillamook tributary-estuarine system.



The issue of acidification in estuaries is a complicated problem to address. It involves the livelihoods of many local people, including dairy farmers and those working in the shellfish aquaculture industry. Those working in the oyster industry and other industries in nearby bays and Tillamook Bay are concerned about economic impacts from acidification, but minimizing these impacts is a nuanced issue. The Tillamook Cheese Corporation is a co-op of independent farms in Tillamook County, and though there are many CAFOs, most of these are family owned. In many places, the farmers have been independently implementing conservation practices. Some farms have been storing the manure so that it can be sprayed at a better time to minimize contamination from fecal coliform bacteria (US Environmental Protection Agency Office of Water, 2015), and this technique could potentially be used to lessen the amount of nitrogen and other nutrients that end up in the groundwater. Thus, there are already some conservation practices that exist in Tillamook County, and there are many other ways to decrease the amount of agricultural contamination reaching the streams. Even after these conservation measures, a certain extent of this watershed contamination is just unavoidable with around 46,000 cows. In the future, as minimizing acidification and other effects of agricultural runoff becomes more and more difficult and necessary, there is a possibility that the discussion of solutions will include, in addition to smaller-scale mitigation measures, scaling down the scope of the dairy industry in the area.

Because of the multi-faceted nature and complexity of this issue, looking at the interactions of both local and global factors is important when studying acidification. In a similar manner, the search for solutions will likely need to include a combination of small, short-term measures and larger systemic changes, and involve communication and collaboration of all stakeholders including scientists and the community.

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