Establishing fluxes of carbon dioxide and a transect of pCO_2 during the late fall of precipitation driven Northern fjord

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Abstract

As atmospheric carbon dioxide (CO_2) continues to increase beyond 400 ppm, the concerns of how and where the anthropogenic CO_2 will cause drastic effects is under intense scrutiny. While the effects on oceanic biogeochemistry is well understood, the exchanges between the ocean and atmosphere are not, despite the understanding that the oceans are sinks of the anthropogenic CO_2. This study investigated the methodology of measurements and inter-annual variability of a high latitude, precipitation driven fjord on Vancouver Island, British Columbia, Canada. A map of carbon fluxes and gradients of Muchalat Inlet in Nootka Sound was developed using hand collected surface samples in combination with a CTD transect. This method combination better developed a picture of this fjord after a warm summer anomaly in the late autumn/early winter. The data revealed a variation of efflux and influx dependent upon both location within the fjord and the external forces acting on the circulation of fjordal waters.

Introduction

Since the industrial revolution and the utilization of coal, oil, and other fossil fuels the global atmospheric concentration of carbon dioxide (CO_2) has been increasing; due to this the oceans have been recognized as sinks of this anthropogenic carbon (Sabine et al. 2004). With the current atmospheric concentrations of CO_2 crossing 400ppm this year, oceanographers are focused on quantifying the ocean to atmosphere balance of carbon with hopes of determining the future impacts of anthropogenic carbon.

In conjunction with this atmospheric increase of CO_2, a subsequent change in the oceanic carbon chemistry is occurring. This is caused by the increase in partial pressure of CO_2 (pCO_2) then reacting with water to create carbonic acid (H_2CO_3). Which at oceanic pH (~7.9-8.1) dissociates into bicarbonate (HCO_3^-) and can dissociate again into carbonate (CO_3^{2-}), each time releasing a proton (Doney et al. 2009). This is the process that causes ocean acidification, an ongoing process that is altering the biogeochemistry of oceans by lowering the pH; this has the most pronounced effects on shell forming species but could have yet unknown effects on all oceanic species (Doney et al. 2009; Feely et al. 2010; Gruber 2011). Combined with other impacts of global warming (increased surface temperatures, stratification, and deoxygenation) the biogeochemistry of the oceans we currently understand is going to change globally, but will vary within regions. Important for this work is the increased acidification expected with higher latitudes, which implies an uptake of atmospheric CO_2 (Gruber 2011).

Coastal waters are considered one of the most productive areas of the global oceans and estuarine waters are recent focuses of both oceanographers and aquatic scientists alike due to their variability and unique biospheres (Elliott and Whitfield 2011). The dynamics of estuarine waters like fjords are complex and change on an hour scale; and these complex dynamics are

precisely why they are a recent focus of study. Attempting to characterize the carbon fluxes of high latitude estuarine waters is just one piece of the greater puzzle, but it is important in characterizing the drivers of waters that have the greatest influence on human populations. Understanding the drivers and dynamics of estuarine environments could yield previously unknown effects of anthropogenic influences or of estuarine drivers on populations.

Fjords are unique coastal waters that are glacially carved, steep sided, deep and narrow estuaries. They have a characteristic bathymetry of a shallow sill at the mouth and a deep basin with fresh water input defining the head. They are typically well stratified vertically and have unique estuarine exchanges due to the shallow sills at the mouth, the deep main basins, and the variance in freshwater inputs. Recent work has revealed that fjords are significant sinks of organic carbon, specifically into the sediments due to their deep basin and stratification leading to isolation of sediments from the oxygenated surface waters. This study estimated the global contribution of fjords at 11% due to the high quantities of organic carbon that reaches the sediment with being remineralized (Smith et al. 2015).

Temperate coastal waters, especially those at higher latitudes, have been shown to be sinks of atmospheric CO_2, but are an ongoing place of research in an effort to determine where this is true, the magnitude of the CO_2 flux, and the processes involved (Torres et al. 2011; Borges 2012). Other recent work has shown that coastal waters influenced by upwelling waters are sources of CO_2 to the atmosphere (Torres et al. 2011; Murray et al. 2015), because of the high pCO_2 upwelled waters mixing up to the surface results in a net flux out of the surface layer. While it was observed that high latitude, southern hemisphere fjords off Chile with cold, less saline surface waters and glacially driven fjord systems showed strong pCO_2 under saturation and are thus sinks of atmospheric carbon (Torres et al. 2011). This suggests that cold, upper

latitude fjords maybe sinks of atmospheric CO_2 into the surface waters while deeper waters contain high pCO_2 values and when mixed with surface waters may become sources of CO_2 to the atmosphere.

This is the unique dynamic being investigated at Muchalat Inlet of Nootka Sound. Previous work by Claire Knox from the 2014 UW Oceanography Cruise to Nootka Sound found a flux into the waters of Muchalat and Tahsis but stated concerns surrounding her sample technique and flux calculations as she did not have in-situ wind measurements (Knox 2015).

Nootka Sound is a fjord system on the northern end of Vancouver Island, British Columbia, Canada (~49.5º to 50º N) with freshwater input primarily driven by precipitation and affected during the winter months by strong storms and cold temperatures. Nootka is made up of three inlets, Muchalat to the east containing the largest river of the system, Tahsis to the NNW, and Tlupana to the northeast with the primary opening of the sound being in the southwest (Dodimead 1984; Knox 2015).

This study develops a map of ocean to air fluxes of CO_2 of Tahsis and Muchalat Inlets. Also, in collaboration with Gen Hinde, creates a transect of pCO_2 with depth for Muchalat Inlet to better understand the potential drivers of CO_2 within a cold, high latitude fjord during the beginning of winter.

Methods

Field Techniques

All samples for carbonate system measurements were collected on the UW Oceanography Cruise from the 10-20th of December 2015. Surface samples were collected during daylight hours from the *R/V Weelander* that was deployed from the *R/V Thomas G. Thompson*. Collection was done using a hand deployed 2 liter Niskin bottle that was held parallel

with the surface, with the center of the Niskin being 10 cm below surface, directly behind the sensor array for the YSI Datasonde. This was done to maximize the equality of the YSI and the collected sample. The YSI collected in-situ temperature, salinity, and oxygen concentrations and saturation, all of which were recorded.

Samples were drawn from the Niskin bottle into a 500 mL glass bottle using a long, flexible plastic tube. All bottles received a thorough rinse of the bottle followed by filling it from the bottom and allowing a minimum of 15s of overflow to occur so that all water was unexposed to the air. Upon returning to the *R/V Thompson* samples were fixed with 200 μL of saturated mercuric chloride solution, sealed with Apiezon grease, and stored for analysis upon return to the University of Washington. Samples were not fixed in the field to minimize potential exposure to toxic mercuric chloride. All samples were kept in the dark and cold, thus it is unlikely this led to any significant biasing.

In-situ wind speeds were collected using a cup anemometer mounted on top of the pilot house on the *R/V Weelander* and averaged over the time on station, which was ~ 3-5 minutes depending on the number people in the boat.

CTD samples were collected using the *R/V Thompson*'s CTD and bottle rosette system with bottles being closed remotely from the ship at depths chosen by the feedback from the device to capture deep water, the transition through the thermocline, and the surface layer. Samples were then drawn from the 10 liter Niskin bottles on the rosette were then drawn into 500 mL bottles using the same method as the surface samples.

Lab Analysis

Sample analysis for total dissolved inorganic carbon (DIC) was done using the Dickson standard operating procedure (SOP) 2 method (Dickson et al. 2007) in Alex Gagnon's lab on a

Vindta 3D and LabView™ software on a control PC. This method utilized phosphoric acid and filtered medical grade nitrogen gas to strip CO_2 from the titrated sample volume. Standards were run at the beginning of every day of sample processing and again with every ~10 samples processed (a single run counts as a sample process).

Total alkalinity (T_A) was determined using the open cell Dickson SOP 3b method utilizing hydrochloric acid as the titrant. The open cell titrations were run using a control PC and appropriate hardware to amplify the signal from an analytical pH probe. Titrations were done using a 5 mL Dosimat™ dispenser, stir plate, and medical grade nitrogen as a carrier gas. Cells were maintained at constant temperature using a cooler and pumping water through the cells. The cooler doubled as a sample cooling chamber as well to pre-cool the samples before the sample was drawn for a titration. Samples were dispensed to ~135 mL and analytically weighed to the hundredths for the analysis calculations.

Calculations

In order to calculate the flux of CO_2 across the air-sea interface, atmospheric concentrations of CO_2 were acquired from Environment Canada's Estevan Point station that has such a sensor. This data is preliminary and is subject to potential adjustments, but was used here as this is the same data site C. Knox used.

Carbonate system calculations were done using CO2Calc from the USGS on an Apple MacBook Pro running OS X 10.11.4 using Microsoft Silverlight™ . CO2Calc utilizes CO2Sys (Lewis and Wallace 1998; Robbins et al. 2010), which is the same system that C. Knox used in her 2015 thesis, thus results are comparable with minor changes due to calculations. DIC and T_A from lab analysis and temperature, salinity, wind speed, and pressure (set at 0) from in-situ

measurements were utilized to calculate pH, pCO_2, ΔpCO_2, and flux. The equations used by CO2Calc and CO2Sys are:

$$F = k \times S \times \Delta pCO_{2\ (sw-atm)}$$

$$\Delta pCO_{2\ (sw-atm)} = pCO_{2\ sw} - pCO_{2\ atm}$$

$$k = (0.222U^2 + 0.333U)\left({}^{Sc}/_{600}\right)^{-0.5}$$

Where $pCO_{2\ sw}$ is the surface water and $pCO_{2\ atm}$ is the atmosphere, ΔpCO_2 is the gradient of CO_2 between the air-water interface where the sign reveals the flux between the air-surface interface (negative is into the sea, positive is into the atmosphere), *S* is the solubility of CO_2 in the water at the given temperature and salinity, *k* is the gas transfer velocity of CO_2 and is dependent on the wind speed (*U*) and Schmidt number (*Sc*) (Nightingale et al. 2000; Knox 2015).

Results

Tahsis Inlet

Tahsis Inlet was collected entirely on December 15th and showed a consistent ΔpCO2 into the atmosphere with maximum of 764.12 μatm and a mean of 192.11 μatm. Temperature had a maximum of 7.54ºC and a min of 5.97ºC and salinity maxed at 18.93‰ and a min of 11.31‰. Fluxes for Tahsis showed a net efflux into the atmosphere with 0.86 mmol m^{-2} day^{-1} mean and a maximum of 2.71 mmol m^{-2} day^{-1}, in-situ wind speed averages had a mean of 1.19 m s^{-1} and had a maximum of 3.31 m s^{-1}.

Muchalat Inlet

Muchalat Inlet was sampled on two different days, December 16th and 18th with different stations sampled each day. Table 1 has the complete data of the what is summarized here.

December 16th had a minimum ΔpCO_2 of -93.6 μatm, a max of 610 μatm past the Gold River, and a mean of -50.8 μatm (without the 610 μatm sample) and 31.8 μatm (with the high sample). Temperatures showed less range with a max of 7.21ºC and a min of 5.03ºC and salinity (excluding the Gold River) ranged from 3.27‰ to 22.07‰. In-situ wind speeds ranged from 0 m s^{-1} to 29.6 m s^{-1} which resulted in fluxes ranging from 0 mmol m^{-2} day^{-1} to -16.83 mmol m^{-2} day^{-1}, which resulted in a mean of -5.01 mmol m^{-2} day^{-1} with average winds of 3.67 m s^{-1}.

December 18th showed a consistent efflux with a minimum ΔpCO_2 of 14.8 μatm, a maximum of 99.16 μatm, and a mean of 45.142 μatm. Temperatures ranged from a max of 9.32ºC to a min of 7.90ºC and salinities ranged from 33.67‰ to 27.67‰. In-situ average winds ranged from 15.8 m s^{-1} to 26.1 m s^{-1} resulting in CO_2 fluxes from 1.02 mmol m^{-2} day^{-1} to 4.72 mmol m^{-2} day^{-1} and a mean flux of 2.64 mmol m^{-2} day^{-1}.

Figure 1 shows salinity and temperature by station while figure 2 shows the magnitude of fluxes of CO_2 and ΔpCO_2 revealing the direction of the flux.

Discussion

The initial motivation of collecting this data set was to assess the methods and identified errors of Claire Knox's work from the previous year in Nootka Sound. Sampling methodology was altered to standardize the depth of sampling to 10cm by using a hand deployed 2 L, end-closing Niskin bottle. This method alteration removed any sample to sample variation potentially introduced by Knox's method. Additionally, an anemometer onboard the *R/V Weelander* was used to measure average wind speeds on station in place of using the *R/V Thompson's* anemometer; thus avoiding both temporal and spatial disparities in the flux calculations identified as a likely error source by Knox. The 'in-situ' anemometer increased the accuracy of each sample's flux calculation, as conditions around the time of sampling pertain most to the

concentrations in that sample. Recording in-situ winds also revealed a potential trend of higher flux magnitudes in Nootka Sound and lower Muchalat Inlet to lower magnitudes within upper Muchalat Inlet, near and beyond the Gold River. Tahsis showed fairly consistent fluxes throughout the inlet.

The sign of ΔpCO_2 defines the direction of the flux and there were more effluxes from Nootka Sound then was observed by Knox's work. The data also opposes the hypothesis for this study and hypotheses from other literature that cold, high latitude fjords are sinks of CO_2 in the winter months. When comparing with Knox's results Tahsis is a complete sign flip with samples from 2015 showing all efflux while samples from 2014 showed all influx. Muchalat showed more variability but still showed a significant sign inversion of ΔpCO_2 from Knox's work (Figures 3 & 4).

Muchalat was more thoroughly investigated in this study effort by collaboration with Gen Hinde in developing a transect of pCO_2 from outside of Nootka Sound up to the head of Muchalat Inlet (Figure 5). The transect enables further interpretation of the surface observations. Generally, surface samples inversed sign depending upon the date of sampling; which suggests that some fjord dynamics or other mechanisms must be at work within Nootka Sound. The transect reveals that high pCO_2 (> 400 ppm) water is close to the surface in Muchalat Inlet (Figures 6 & 7), observations vary between 10m to 30m depending on location. Note the C08 shows a spike in pCO2 levels to over 700 μatm near the surface. This maybe an error as the CTD rosette was momentarily on the bottom and despite repeating the cast for samples, it is possible that sediments and/or other contaminants were within the samples.

There are many possible reasons to explain the variation observed, but primarily discussed here is that mixing took place between the first and second day of sampling. This has

evidence within the transect itself as C05 and C06 were done 3 days after the other stations and reveal a raising of the density isopycnals. Additionally, the Gold River discharge observations (Figure 8) show a significant decrease in the volume of freshwater input into the system, which with fjord estuarine exchange dynamics may increase the amount of salt water entering the system and increase mixing over the sills. Further evidence that mixing is the primary driver of the observed variations of pCO_2 is Figure 9, which shows DIC and T_A along with a trend line. The slope of the trend line is 1.095 which suggests that mixing is the primary source of pCO_2 exchange.

Observing the tidal trends in Figure 2 and taking into account timing and direction of sampling for Muchalat, reveals that sampling was completed off-cycle enough to alter timing with tidal velocities. Sampling begun on the 16th just as the high-low tide was reached resulting in a majority of sampling taking place before, during, and after max ebb velocity; also sampling began in the Gold River, then beyond and ended back at C06 before returning to the *R/V Thompson*. The 18th began at C05 just after the high-high tide of the day and likely at max flood velocity, sampling for the day began at C05 and continued up inlet to SS4. Thus sampling on December 16th captured a primarily ebbing inlet while sampling on December 18th captured a primarily flooding in inlet. This makes it possible that the samples from the 16th captured the last day of influx and the 18th captured one of the first days of efflux. If this is true it suggests that Muchalat Inlet is actually switching to outgassing, possibly after a highly productive summer.

These observations combined with the unique dynamics within a fjord like Nootka Sound and Muchalat Inlet make grand assumptions about the net, long term affect fjords have on the carbon budget difficult to accept. The variation observed both within this data set and in an inter-annual comparison to Knox's 2014 work suggest that fjords are too variable to accept a net effect

they may have on the global carbon budget. While fjords effects on atmospheric carbon budgets are in question from this data, the transect of pCO_2 done with Gen Hinde actually adds evidence to Smith et al.'s (2015) work. As observed pCO_2 levels higher then 1000 μatm seen at depth, in likely stagnant waters within Muchalat Inlet are likely derived from the breakdown of particulate organic carbon reaching these depths.

The observed high concentrations of pCO_2 beyond C10, both at the surface and with depth casts, are likely signals of highly stagnate water. C11 had zero flux due to no observed winds and without winds a stagnate boundary layer model applies, which significantly reduces the rate of gas exchange as this model relies entirely on molecular diffusion (Emerson and Hedges 2008). It is possible that this same process is the driver behind the observations at the head of Tahsis with a ΔpCO_2 of 764.2 μatm and a flux of 0.663 mmol/m^3/day. These observations come with the caveat of capturing only a single moment of a dynamic system.

Overall this data set poses more questions than could be answered, but this project and collaboration create a unique template with how to study fjords. Further work using or building on the methodology introduced here could work to either expand the time scale of sampling or reduce the temporal error. To ideally capture the annual variability within a fjord a monitoring system should be utilized, this would expand the temporal scale of sampling. Future efforts could include moorings or structured ship time so no interruptions occur during the transect. Either of these could eliminate or better explain and capture the variations observed within this data set.

The remaining question of this data and project is if Muchalat Inlet is representative of global fjord systems. The Torres et al. (2011) paper focused on the Patagonian fjords of South America and all of them were ice-melt fed which drastically changes the dynamics. In addition to no glacial or ice melt feeding Nootka, there is a small population surrounding all the inlets that

utilize the area for industrial processes such as logging and fish farming, and are popular during the spring and summer for tourism. This study did not take into account any anthropogenic effects on the inlets and future studies should attempt to quantify these potential effects.

Conclusions

The methodology utilized for the collection of this data set allowed for speculation as to causes of the observed inter-annual and day to day variations by establishing both a surface to air map of ΔpCO_2 and fluxes along with a transect of depth pCO_2 concentrations in an attempt to reveal the processes at work within the fjord system. The results of this work in Nootka Sound, BC, Canada over the UW Senior Cruise from December 10^{th} to 20^{th} 2015 revealed an unclear picture as to the general trend of high latitude, cold fjords and their respective place in the global carbon budget. The observations put forward here suggest that they maybe a net source of CO_2 to the atmosphere, but this is likely dependent on variables not captured here. Including potential mixing by winds and/or tides or possibly when the deep, semi-stagnant layers within a fjord are mixed towards the surface. Overall this data set and collaboration with Gen Hinde offer a template to build from to potentially capture an ever more inclusive data sets in future studies.

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Table 1: Data from samples listed out by date of collection. Figures show locations of all stations.

Station	Date	DIC (μmol/kgSW)	TA (μmol/kgSW)	pCO_2 (μatm)	ΔpCO_2	T (˚C)	Sal (ppt)	Wind (m/s)	Flux (mmol/m^2/day)
T01	12/15/15	1029.72	974.94	1170.02	764.2	7.54	11.31	0.9	0.663
T02	12/15/15	1040.61	1037.79	469.96	64.1	6.45	12.93	4.1	0.423
T03	12/15/15	1175.24	1181.92	511.36	105.5	6.75	18.14	4.3	0.671
T04	12/15/15	1261.83	1278.93	480.19	74.3	7.06	18.93	0	0
T05	12/15/15	1083.95	1085.74	497.57	91.7	6.36	17.12	6.5	1.096
T06	12/15/15	858.68	847.64	489.17	83.3	5.97	13.35	11.9	2.707
T07	12/15/15	820.92	802.49	567.55	161.7	6.31	13.05	2.3	0.44
C06	12/16/15	1267.08	1309.78	370.47	-35.9	7.21	22.07	29.6	-5.223
C07	12/16/15	949.79	966.31	312.74	-93.6	6.16	15.5	21	-7.396
C08	12/16/15	905.06	908.27	377.11	-29.3	5.88	14.35	23.7	-2.574
C09	12/16/15	772.00	772.59	326.64	-79.7	5.77	11.65	19.2	-16.834
C10	12/16/15	607.29	589.51	408.84	2.5	4.7	7.5	0.6	-0.227
C11	12/16/15	420.64	357.84	1016.59	610.2	5.03	3.27	0	0
GR	12/16/15	205.05	153.78	788.60	382.2	4.51	0.02	0	0
GR-End	12/16/15	214.71	161.38	824.36	418.0	4.6	0.23	9.2	-9.013
SS5	12/16/15	707.97	700.78	360.12	-46.3	5.46	10.39	7.9	-5.85
SS6	12/16/15	702.61	697.28	332.98	-73.4	5.22	10.04	3.8	-1.981
C05	12/18/15	1796.30	1893.36	504.76	99.2	9.32	33.67	15.8	4.717
SS1	12/18/15	1594.66	1666.74	457.94	52.3	8.23	29.34	15.8	2.447
SS2	12/18/15	1587.98	1667.20	422.20	16.6	8.04	29.24	26.1	1.942
SS3	12/18/15	1624.67	1703.91	448.37	42.8	8.41	29.79	20.1	3.07
SS4	12/18/15	1518.70	1587.14	420.43	14.8	7.9	27.67	19.8	1.021

Figure 1: Map of surface samples from showing basic water properties of temperature and salinity along with date of sampling.

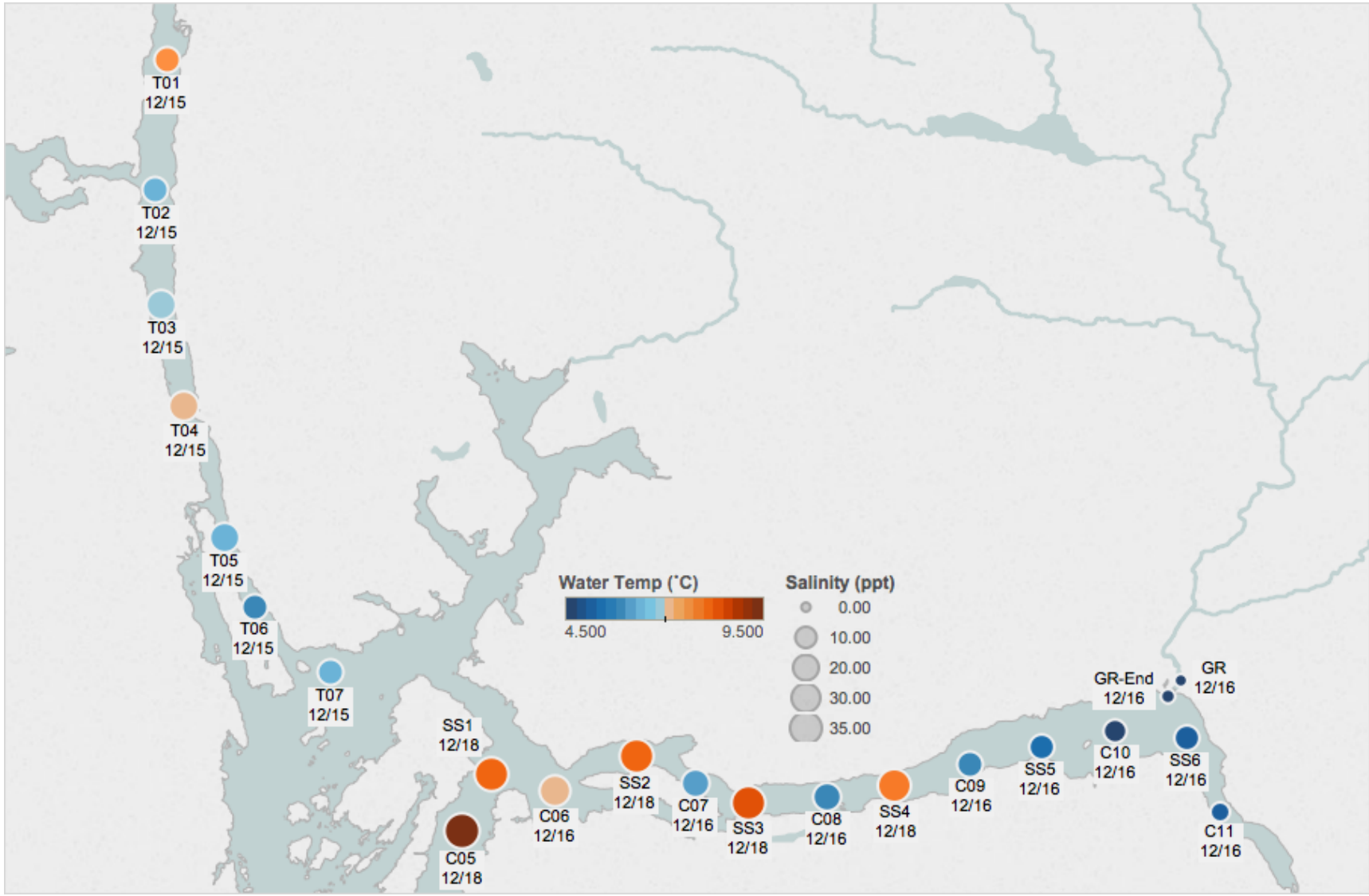

Figure 2: ΔpCO_2 and flux magnitude of surface samples along with approximate tidal stage based on Environment Canada info.

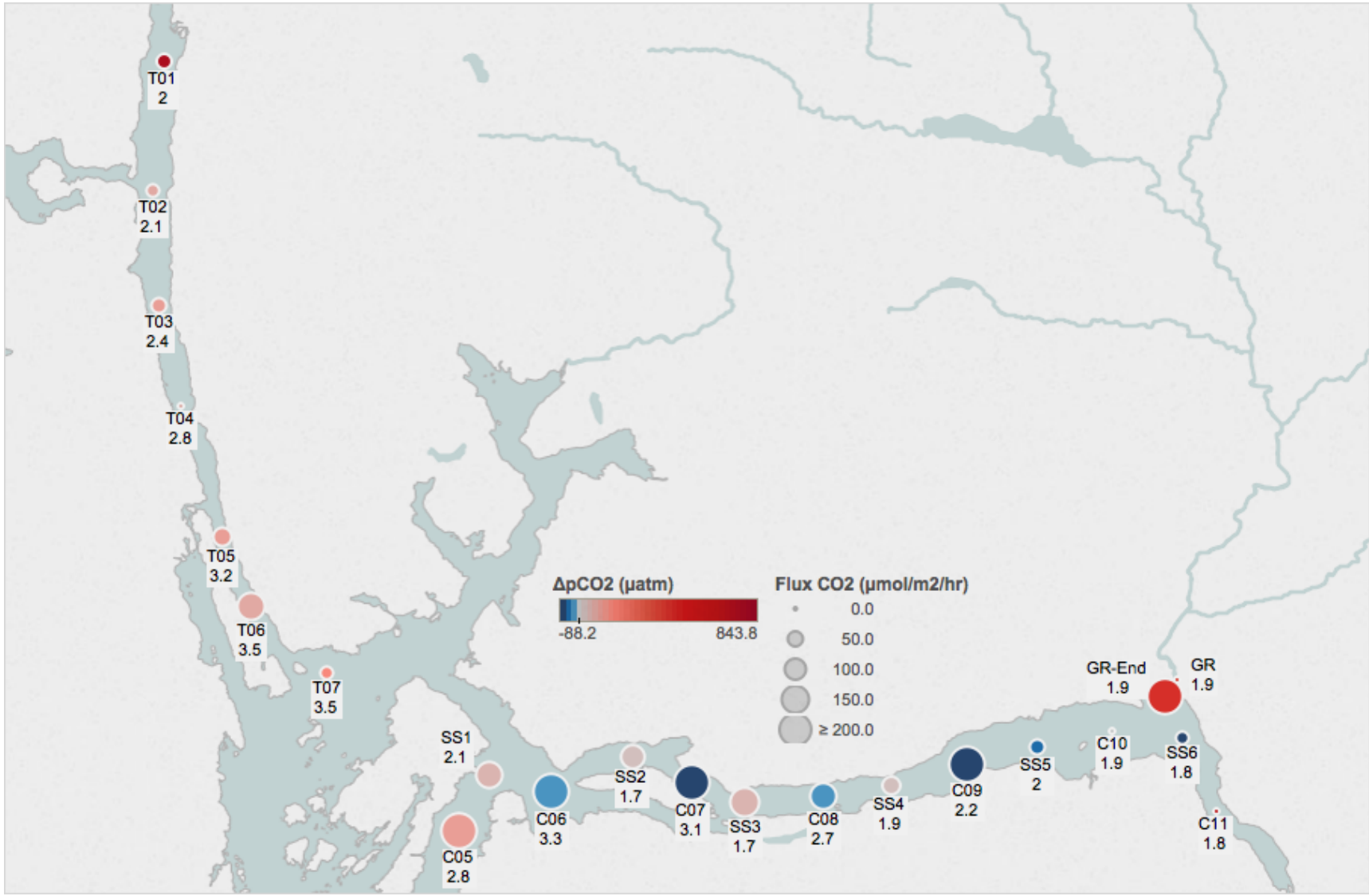

Figure 3: Similar plot of salinity versus ΔpCO_2 for a direct visual comparison with C. Knox's 2015 plot.

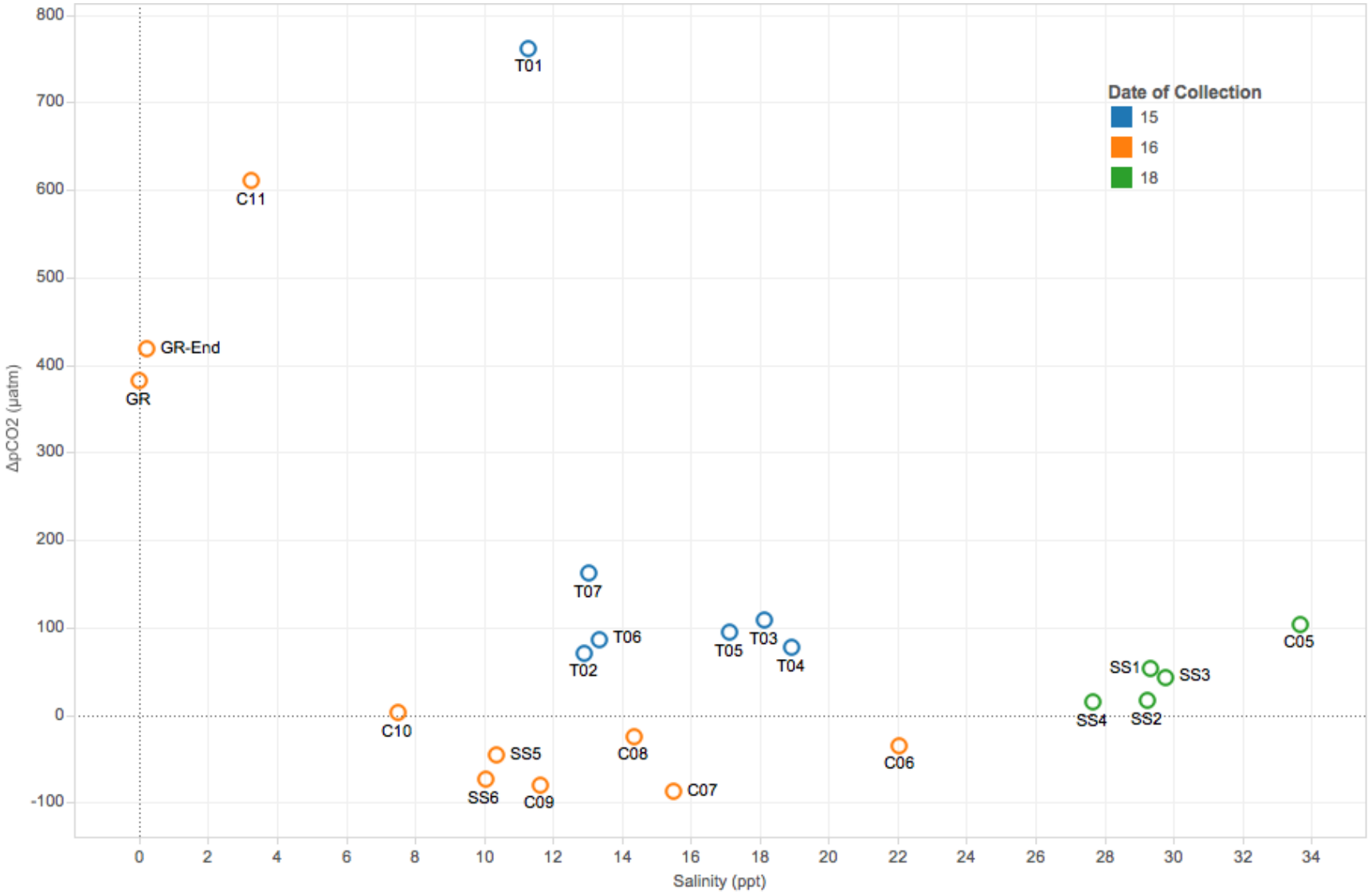

Figure 4: C. Knox's 2015 plot of salinity and ΔpCO_2.

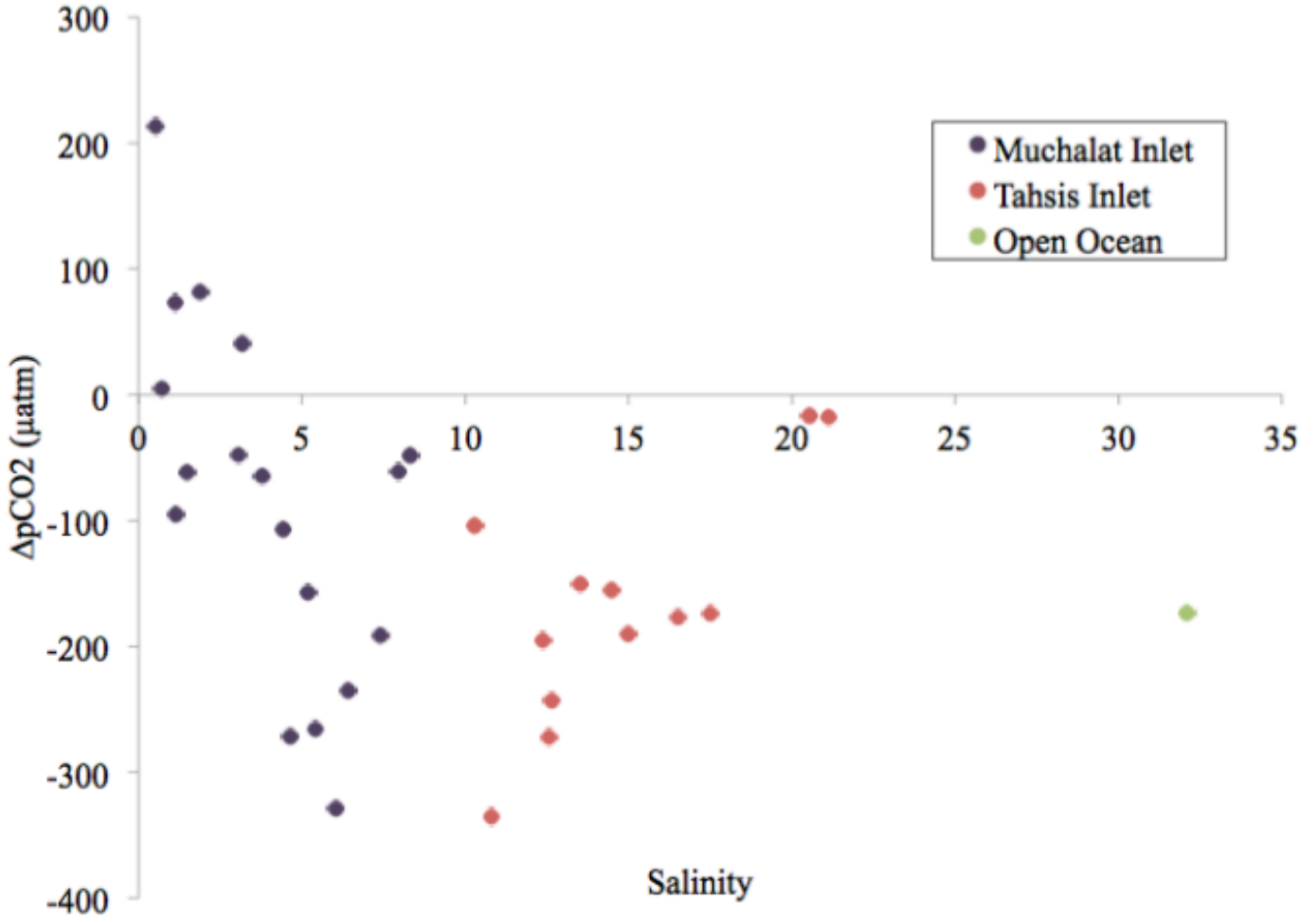

Figure 5: Transect of pCO_2 from Nootka Offshore to Uptain 01, capturing both the shelf and Nootka into Muchalat. Credit: Gen Hinde

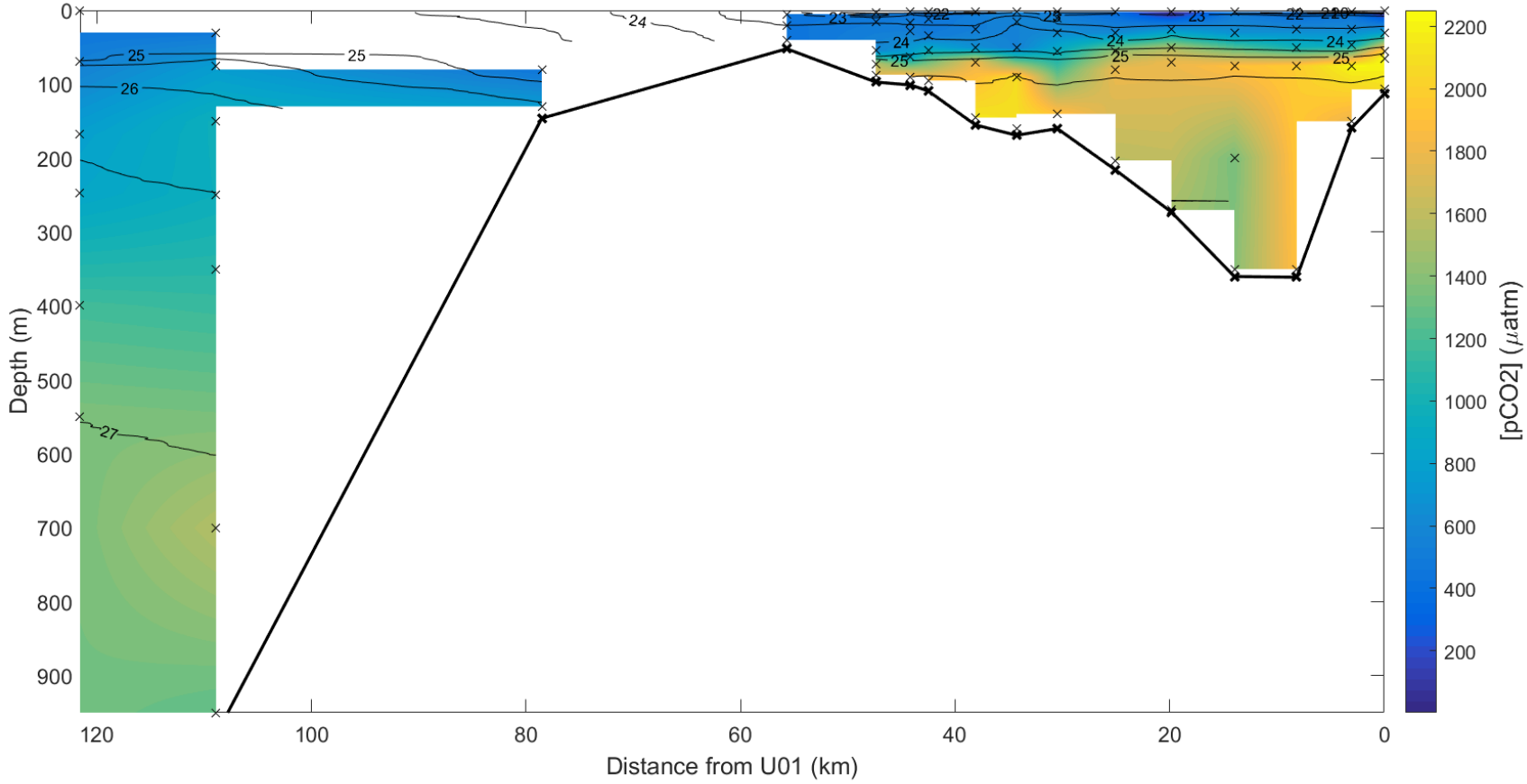

Figure 6: Transect focused only on Muchalat Inlet and Nootka Sound

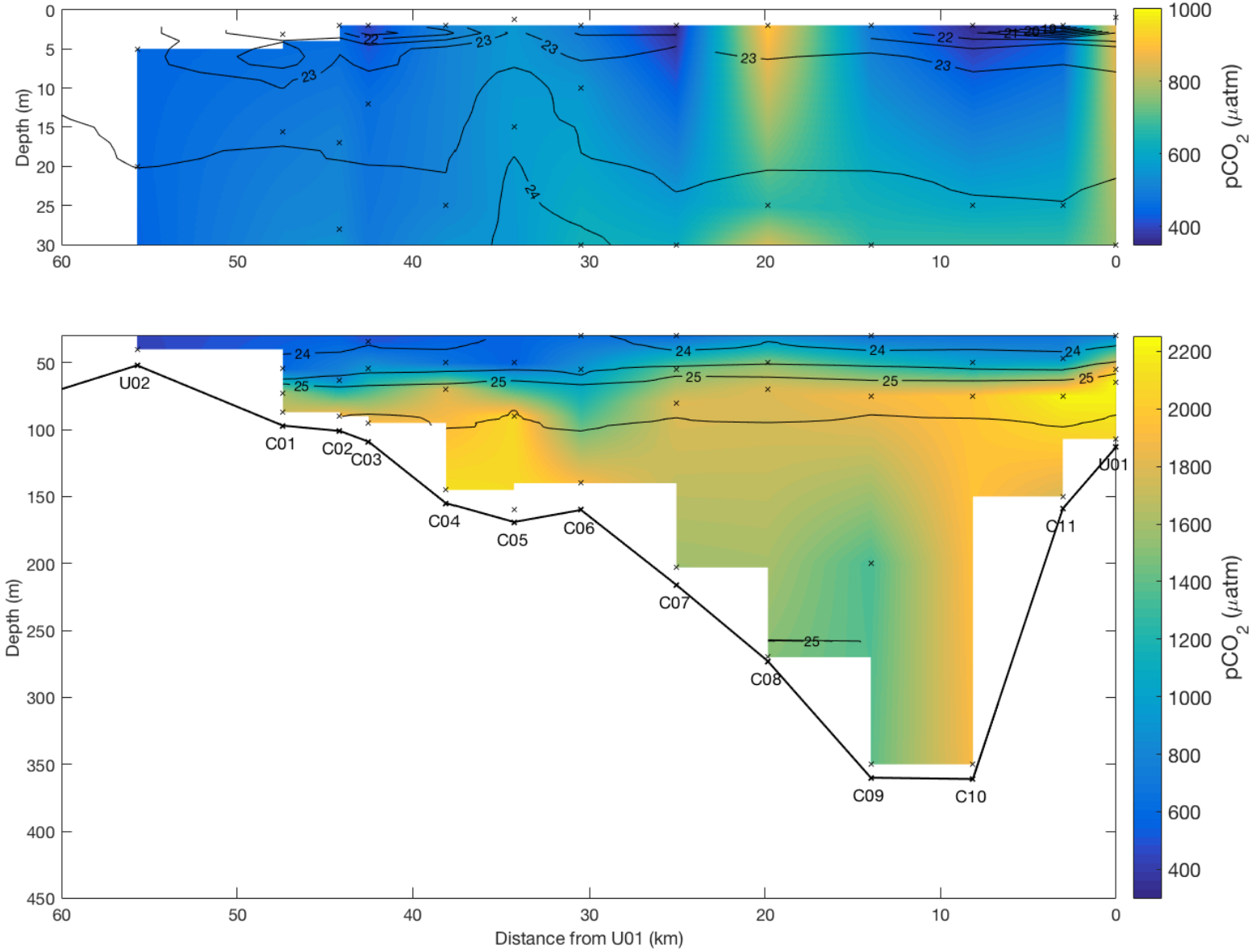

Figure 7: Transect from C05 to C11 of top 30m within Muchalat Inlet. Temporal variation between depth and surface samples may cause skewed interpolation.

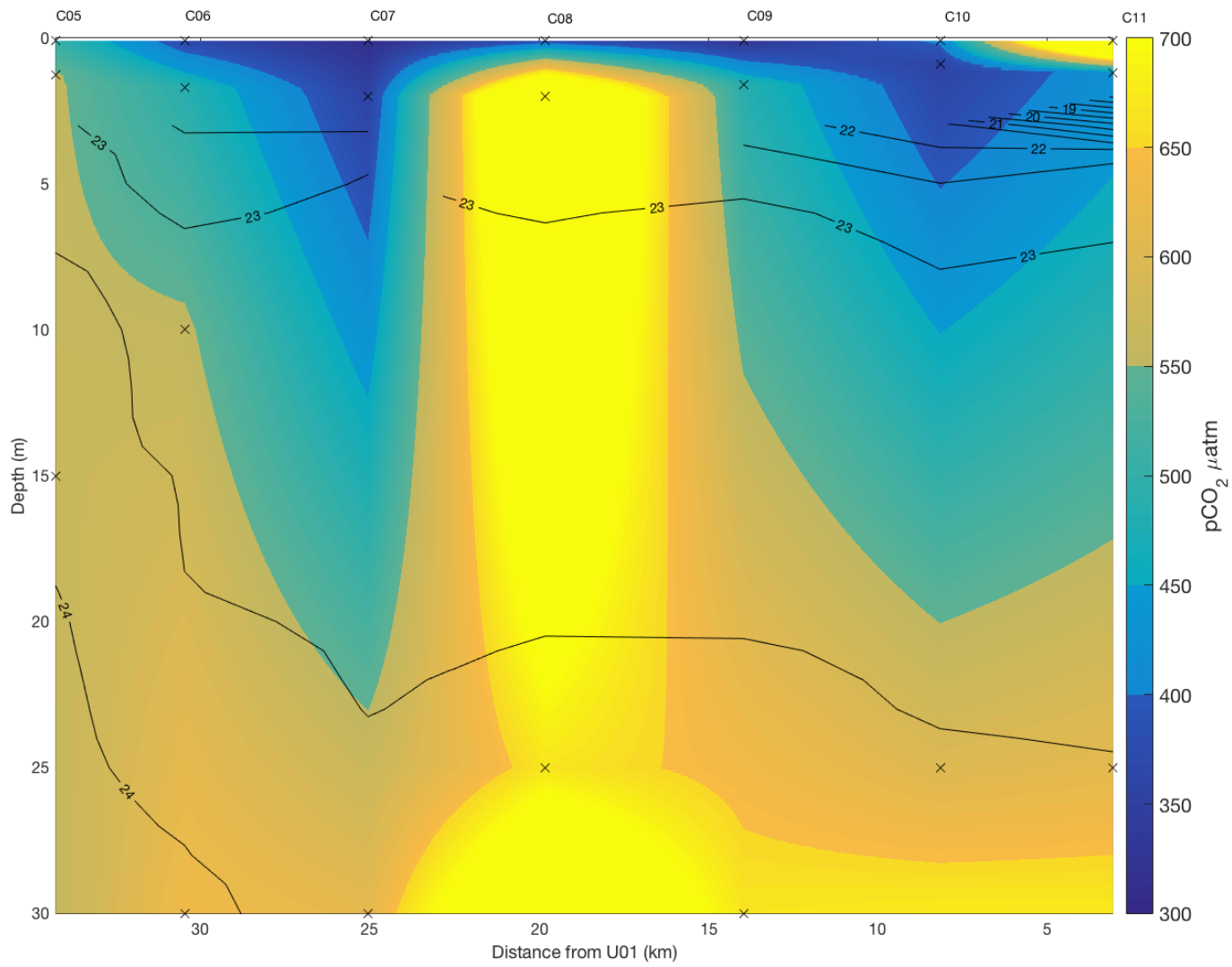

Figure 8: The Gold River output from Environment Canada's station upstream of the mouth into Muchalat Inlet.

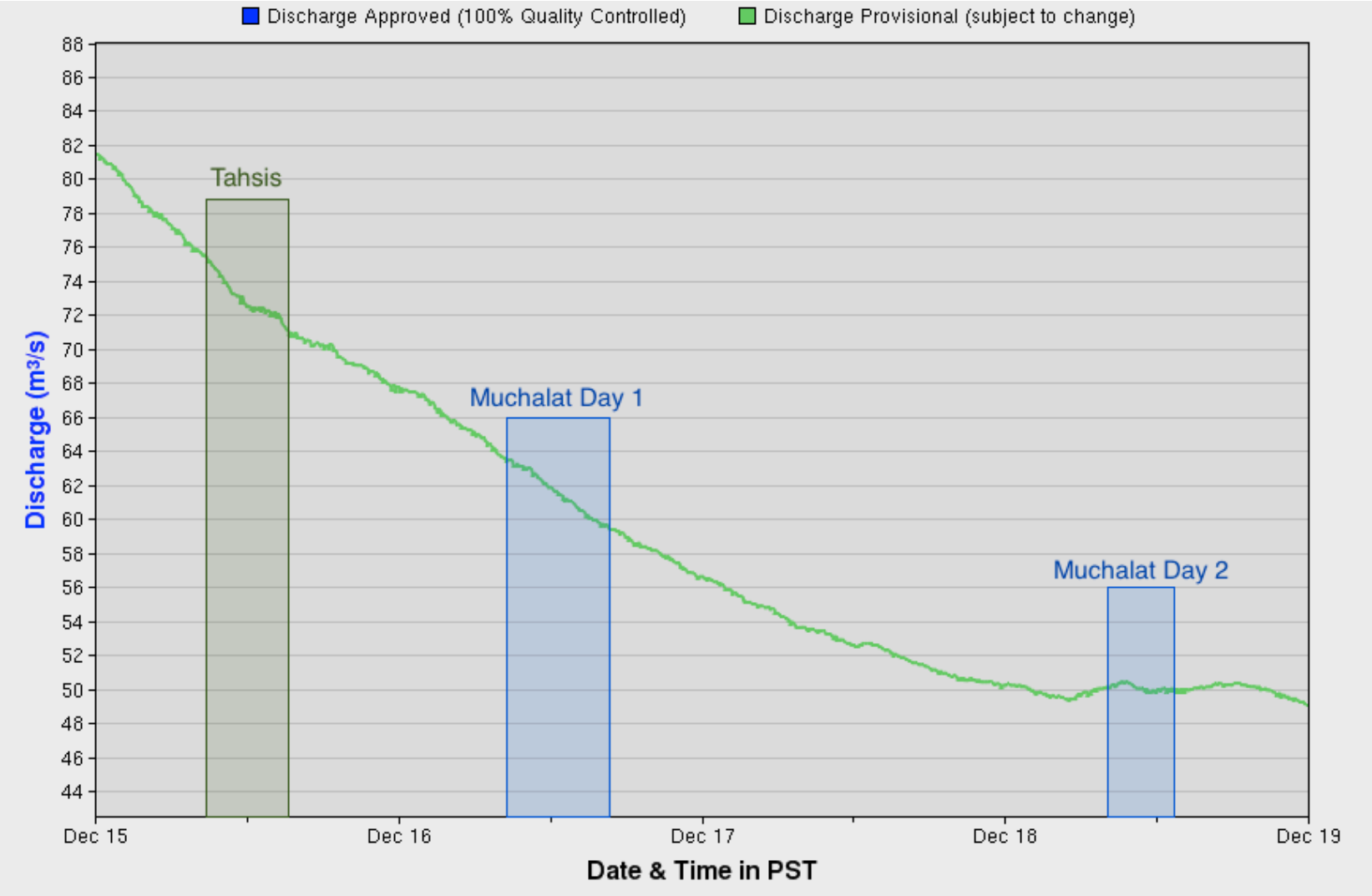

Figure 9: TA versus DIC plot with trend line suggesting only mixing as primary cause for increase, with T01 as the exception.

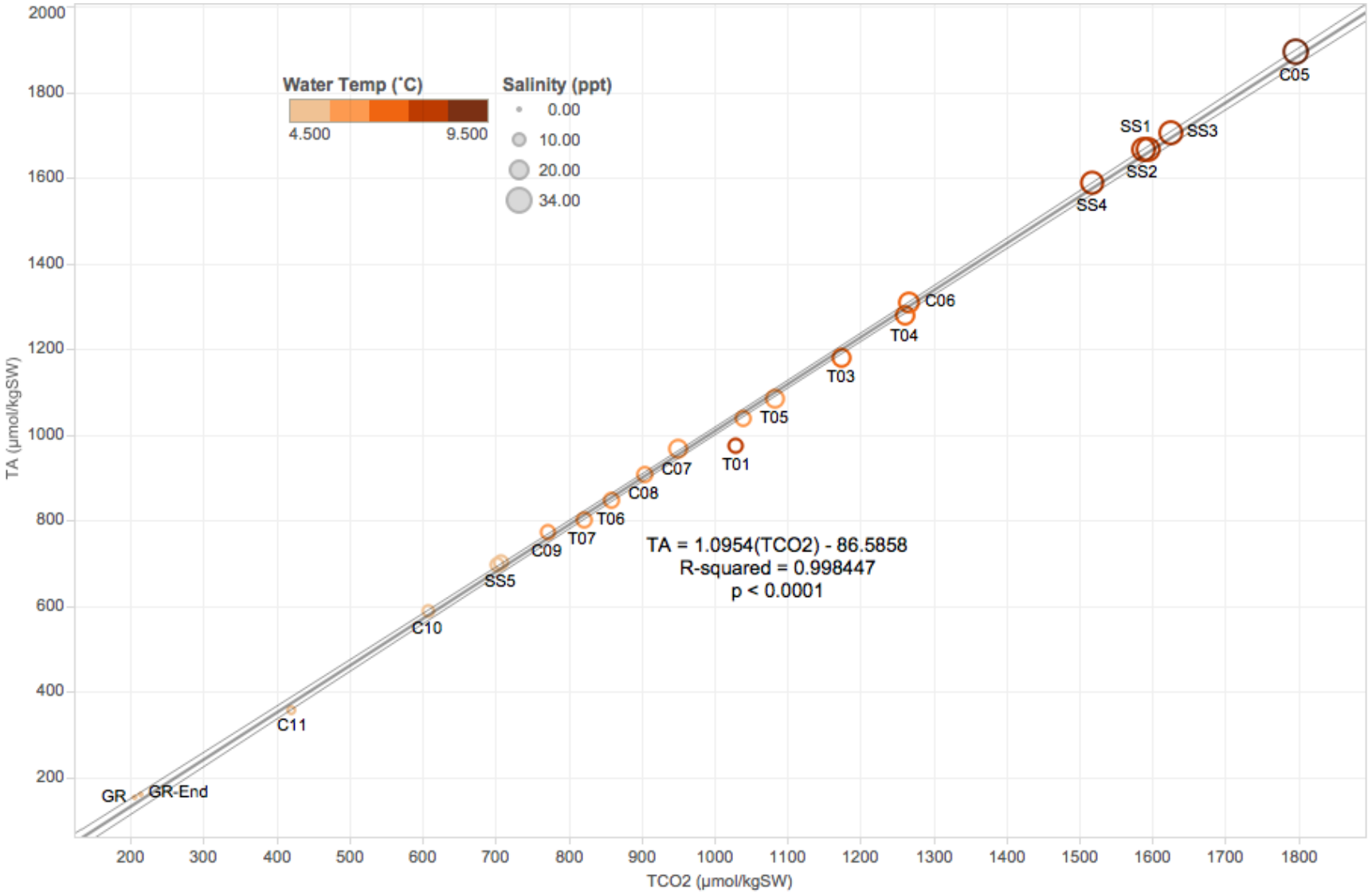

Figure 10: Temperature and salinity plot with total alkalinity (TA) and DIC (TCO2) showing general trends of surface samples.