Exxon Valdez Oil Spill
Final Report

Gulf Watch Ocean Acidification Monitoring

Exxon Valdez Oil Spill Trustee Council Project 22200127
Final Report

Maile Branson, Jacqueline Ramsay, Dale Hubbard, and Jeff Hetrick

Chugach Regional Resources Commission, Alutiiq Pride Marine Institute
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Study History:

Chugach Regional Resources Commission is an inter-tribal fish and wildlife commission certified by the Internal Revenue Service as a 501 (c)(3) nonprofit organization. The seven tribes of the Chugach Region located in South-central Alaska established Chugach Regional Resources Commission in 1984 to address environmental and natural resources issues of concern to their members. Chugach Regional Resources Commission assists its member tribes in developing their technical capacity to be more meaningfully involved in the environmental and natural resource decisions and regulations that affect their traditional use areas and resources.

The Alutiiq Pride Marine Institute in Seward, Alaska is a division of Chugach Regional Resources Commission, which houses and operates an Ocean Acidification Research Laboratory. This connection links Chugach Regional Resources Commission closely with coastal villages through an ocean acidification sampling project funded by the Bureau of Indian Affairs Landscape Conservation Program in 2016. The goal of this program is to make a region-wide assessment of ocean acidification in southcentral Alaska, specifically lower Cook Inlet and Prince William Sound. All the communities within Chugach Regional Resources Commission's service area participated in collecting ocean acidification samples including Chenega, Tatitlek, Eyak, Valdez, Qutekcak, Port Graham, Nanwalek. We have also included Seldovia due to their proximity to our member tribes of Port Graham and Nanwalek. Chugach Regional Resources Commission also partnered with the Prince William Sound Science Center, the Kasitsna Bay Laboratory, and the Kachemak Bay National Estuarine Research Reserve during these initial efforts.

The Bureau of Indian Affairs funding described above ended in 2018, but Chugach Regional Resources Commission has continued to collect ocean acidification samples at the sites listed above through a water quality program funded by the Environmental Protection Agency and its Indian General Assistance Program. Each of the villages in the Chugach Region has tribal environmental personnel funded through Indian General Assistance Program or other sources who participate in this sampling. The environmental staff members are Chugach Regional Resources Commission's vector for information exchange with villages. Funding from the *Exxon Valdez* Oil Spill Trustee Council to enable the collection and processing of samples in areas adjacent to current collection sites by Prince William Sound Science Center and Kachemak Bay National Estuarine Research Reserve has enabled Chugach Regional Resources Commission to continue with the original goal of a region-wide sampling program and provide ocean scientists with valuable near-shore ocean acidification data.

Abstract:
Chugach Regional Resources Commission operates the Alutiiq Pride Marine Institute, and its Ocean Acidification Research Laboratory in Seward, Alaska. This project collects dissolved inorganic carbon sampling for the purposes of characterizing parameters that might exacerbate ocean acidification. The Prince William Sound Science Center and the Kachemak Bay National Estuarine Research Reserve are current partners in Council-funded Gulf Watch Alaska program and routinely conduct vessel-based marine sampling transects in the *Exxon Valdez* Oil Spill affected region on a time series. Through its routine sampling in Prince William Sound and lower Cook Inlet, the Gulf Watch Alaska program added the collection of ocean chemistry samples to several of its sampling sites for this project. This addition of ocean chemistry parameters, including dissolved inorganic carbon measurements, to the current data sets from these locations offers a broader understanding of ocean acidification in Prince William Sound and lower Cook Inlet.

Key Words:
Cook Inlet, dissolved inorganic carbon, Gulf of Alaska, monitoring, oceanography, ocean acidification, Prince William Sound

Project Data:
The data for this project consist of 328 dissolved inorganic carbon samples, collected in Prince William Sound and lower Cook Inlet, Alaska from 2020-2022. Sample counts are as follows:

2020:
Lower Cook Inlet (n = 48)
Prince William Sound (n = 44)

2021:
Lower Cook Inlet (n = 133)
Prince William Sound (n = 28)

2022:
Lower Cook Inlet (n = 75)

All project data can be found on the Alutiiq Pride Marine Institute website (www.alutiiqprideak.org/oar). Final project data and metadata are published in the GOA Data Portal here: https://gulf-of-alaska.portal.aoos.org/#metadata/97356fe3-2403-45d5-b380-6db9810a9880/project and will be archived with DataOne: https://doi.org/10.24431/rw1k7dj.

The data custodians are:
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There are no limitations on the use of the data, however, it is requested that the authors of this report be cited for any subsequent publications that reference this dataset. It is strongly recommended that careful attention be paid to the contents of the metadata file associated with these data to evaluate data set limitations or intended use.

Citation:

Branson, M. A., J. Ramsay, D. Hubbard, and J. J. Hetrick. 2023. Gulf Watch Ocean Acidification Monitoring. Long-Term Monitoring Program (Gulf Watch Alaska) Final Report, (*Exxon Valdez* Oil Spill Trustee Council Project 22200127), *Exxon Valdez* Oil Spill Trustee Council, Anchorage, Alaska.

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EXECUTIVE SUMMARY

Changing levels of dissolved inorganic carbon have been observed in the coastal waters of southcentral Alaska for several years. Chugach Regional Resources Commission and its subsidiary, the Alutiiq Pride Marine Institute developed the Ocean Acidification Research Laboratory in 2013 in response to academic and industry leaders recognizing the impacts of ocean acidification on shellfish. The Ocean Acidification Research Laboratory at the Alutiiq Pride Marine Institute has achieved the goal of providing high quality data to tribal partners, researchers, and community stakeholders alike. These data adhere to strict measurements of quality developed by the ocean acidification research community and agency partners. Data generated provide insight into local oceanographic trends and identify relative spatial patterns and short-term variations in oceanographic conditions.

Since 2013, Alutiiq Pride Marine Institute has developed a continuous monitoring program of intake water from Resurrection Bay. This program is funded in part by the Alaska Ocean Observing System and is distributed nationally through the Integrated Ocean Observing Systems Partner Across Coasts database. The Alutiiq Pride Marine Institute also runs an extensive discrete sampling program with 15 partners, including several tribal communities in Prince William Sound and lower Cook Inlet.

The Prince William Sound Science Center and the Kachemak Bay National Estuarine Research Reserve are current partners in Council-funded Gulf Watch Alaska Program (program 21120114) and routinely conduct vessel-based marine sampling transects in the *Exxon Valdez* Oil Spill affected region on a time series. Through its routine sampling in Prince William Sound and lower Cook Inlet, the Gulf Watch Alaska program added the collection of ocean chemistry samples to several of its sampling sites for this project. In this project, the Alutiiq Pride Marine Institute supported Gulf Watch Alaska partners by providing analyses for dissolved inorganic carbon (including partial pressure and total CO_2 concentrations), pH, aragonite saturation state, calcite saturation state, total alkalinity, and concentrations of bicarbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}).

INTRODUCTION

Ocean acidification is a result of anthropogenic carbon dioxide emissions being absorbed by the ocean and changing the seawater chemistry that marine life depends on. The rate of change observed in dissolved inorganic carbon profiles has dramatically increased and the colder ocean temperatures of the Gulf of Alaska have been found to take up carbon dioxide faster than warmer climate oceans (Evans et al. 2014, 2015).

Changing levels of dissolved inorganic carbon have been observed in the coastal waters of southcentral Alaska for several years (Evans et al. 2015). Through regular sampling activities

under previously funded opportunities, Chugach Regional Resources Commission (CRRC) and its subsidiary, the Alutiiq Pride Marine Institute (APMI) have observed a significant breadth of changing ocean chemistry parameters throughout the *Exxon Valdez* Oil Spill (EVOS) affected region. This phenomenon has raised particular concern with regards to the growth, development, and general physiology of a wide variety of marine organisms. Many of these species are included in the list of those affected by EVOS. Several species under this list are the subjects of existing EVOS Trustee Council (EVOSTC) funded programs and projects.

The Gulf Watch Alaska Program (GWA, EVOSTC Program 20120114) was funded with the goal of supporting research efforts throughout the EVOS affected region. As part of this activity, regular research and monitoring cruises are conducted on several vessels by GWA partners. The project targets of this program are diverse, and the research and monitoring efforts conducted during these cruises support a multitude of nearshore and pelagic species. CRRC and APMI maintain an extensive network of discrete sample sites across the spill affected region through tribal, academic, and agency partners. This project enabled CRRC to continue with its original goal of region-wide ocean acidification monitoring program in southcentral Alaska, specifically in lower Cook Inlet and Prince William Sound. GWA partners at Kachemak Bay National Estuarine Research Reserve (KBNERR) and the Prince William Sound Science Center (PWSSC) supported our data collection efforts aboard vessels and APMI provided analyses for inorganic carbon chemistry. These data may provide valuable insight into the marine ecosystem conditions, including documenting temporal and spatial changes in ocean chemistry, driven mainly by increased carbon dioxide uptake and changes in temperature and salinity over time.

OBJECTIVES

The objective of the proposal is to extend the sampling coverage of CRRC's ocean acidification sampling program to utilize EVOSTC's existing investments in the GWA program to generate more complete datasets from GWA cruises by providing inorganic carbon chemistry analyses. For each sample analyzed, the data returned are dissolved inorganic carbon (DIC), including total carbon dioxide and partial pressure of dissolved carbon dioxide, pH, aragonite saturation state, calcite saturation state, total alkalinity, and concentrations of bicarbonate ions, carbonate ions.

METHODS

Study area

This study took place in Lower Cook Inlet and Prince William Sound, Alaska within the EVOS affected area from 2020-2022 (Figure 1). KBNERR conducted vessel-based water sampling under the GWA program as it surveyed transects across Kachemak Bay. KBNERR selected two transects (4 and 9) to be included into this ocean acidification monitoring program (Table 1, Figure 2). PWSSC also conducted vessel-based water sampling as part of the GWA program, in Prince William Sound during March, May, June, August, October, and November of each year.

Three sites in this region were selected for ocean acidification sampling (Table 2, Figure 2). The Naked Island site was the central profile site selected for the PWSSC sampling program, Simpson Bay was selected as a representative of eastern Prince William Sound, and Whale Bay was selected as a representative of western Prince William Sound.

Figure 1. Samples were collected in Prince William Sound and lower Cook Inlet during the Gulf Watch Alaska program research and monitoring cruises.

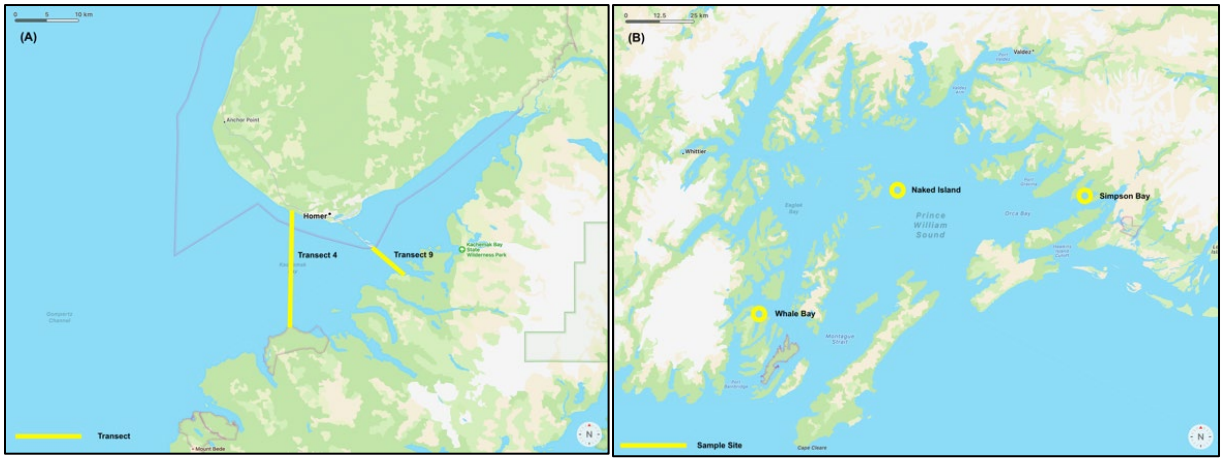

Figure 2. Line transects and sites at which sampling was conducted by (A) the Kachemak Bay Estuarine Research Reserve and (B) the Prince William Sound Science Center.

Table 1. Prince William Sound sample sites and number of samples (n = 72) collected by the Prince William Sound Science Center.

Sample Site	Latitude	Longitude	2020 (n = 44)	2021 (n = 28)	2022 (n = 0)
Naked Island	60.61000	-147.20000	22	15	0
Whale Bay	60.23000	-148.17000	20	13	0
Simpson Bay	60.61000	-145.91000	2	0	0

Table 2. Lower Cook Inlet samples sites and number of samples (n = 256) collected by Kachemak Bay Estuarine Research Reserve.

Sample Site	Latitude	Longitude	2020 (n = 48)	2021 (n = 133)	2022 (n = 75)
AB-06	59.582	-151.38500	0	20	24
AB-10	59.658	-151.20800	0	25	29
4-1	59.49200	-151.65000	0	0	0
4-2	59.50500	-151.65000	0	0	0
4-3	59.52500	-151.65000	24	34	2
4-4	59.54200	-151.65000	6	0	0
4-5	59.55800	-151.65000	0	0	0
4-6	59.57500	-151.65000	0	0	0
4-7	59.59200	-151.65000	0	0	0
4-8	59.60800	-151.65000	0	0	0
4-9	59.62500	-151.65000	0	0	0
4-10	59.64200	-151.65000	0	0	0
6-2	59.205	-151.95200	0	6	12
6-3	59.197	-151.98000	0	6	0
6-4	59.19	-152.00700	6	6	0
9-1	59.56900	-151.35012	0	0	0
9-2	59.57241	-151.36669	0	0	0
9-3	59.57241	-151.37129	0	0	0
9-4	59.57508	-151.36669	0	0	0
9-5	59.57720	-151.37129	0	0	0
9-6	59.57998	-151.37727	12	36	8

Field sampling

Through collaborations with researchers, APMI developed an easy-to-use field kit designed for community members to collect shelf stable sea water samples. This method of collecting samples was adapted primarily from the National Oceanic and Atmospheric Administration's Pacific Marine Environmental Laboratory protocols (Dickson et al. 2007, Bockmon and Dickson 2015). The sample acquisition protocol was modified to apply to vessel-based collection at remote Alaskan sites by collaboration between Wiley Evans (Hakai Institute), Burke Hales (Oregon State University), and Jacqueline Ramsay (APMI). In the field, 350 mL seawater samples were collected from Niskin bottles and aliquoted to amber glass bottles; some samples were collected in replicate and triplicate. The depths sampled were 0, 5, 10, 15, 25, and 50 meters. The

temperature of the samples was captured with a sensor record during collection. Samples were preserved with 80 µL of saturated mercuric chloride on board ship prior to capping and shipping to the APMI Ocean Acidification Research Laboratory (OAR Lab) in Seward.

Wet lab analysis

At APMI, each sample is analyzed for DIC, including partial pressure of dissolved carbon dioxide (pCO2), total carbon dioxide (TCO_2), the saturation state of aragonite (Ωarag) and calcite (Ωcalc), total alkalinity (TA), pH, and concentrations of bicarbonate ions (HCO_3^-), and carbonate ions (CO_3^{2-}) using a *Burke-O-Lator* (Dakunalytics). Each analytical session requires calibration with three gas and three liquid standards of known concentrations, providing a standard curve for each. Liquid standards are prepared gravimetrically from analytical grade sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), and 0.1N hydrochloric acid (HCl). Certified reference materials (CRMs), produced by Andrew Dickson at University of California San Diego, are used to provide a correction factor for the liquid standards (Dickson et al. 2007). Gas standards, liquid standards, and CRMs are analyzed at the beginning and end of each set of samples analyzed in a day to correct for drift over analysis time (changing temperature or atmospheric pressure) during a sample analysis session.

Data analysis

Data acquired during sample analysis through LabView software (National Instruments) are input into an excel spreadsheet designed to integrate the liquid, gas, and CRM standard values and return data ready to be processed through CO2SYS software (Lewis 2023) using the temperature at collection to obtain finalized pCO2, TCO_2, Ωarag, TA, pH. Additionally, Ωcalc, HCO_3^-, and CO_3^{2-} were also calculated for a subset of the data. The data generated at the OAR Lab received a secondary review and analysis by external data management contractor Hydrophilia, LLC before sharing with the partner institutions (Co-Investigators) and prior to release to the public. Upon successful QA/QC, finalized data were provided to GWA program collaborators directly via email, through Research Workspace and through the publicly available APMI website.

Protocols, standards, and QA/QC

All the laboratory processes at APMI, from liquid bag construction and glassware preparation to data finalization, were adapted from both Oregon State University (OSU) and Hakai Institute protocols for analyzing similar samples with identical equipment. The methods used for analyzing discrete bottle samples using the *Burke-O-Lator* were developed at OSU and written into protocol by the Hakai Institute. The complete protocol detailed specific instrumentation and analysis parameters to be followed to acquire acceptable data utilizing a *Burke-O-Lator*, within the standards set forth by the research community (Pimenta and Grear 2018). Additionally, all system maintenance was performed according to manufacturer's suggestions for specific system components.

RESULTS

A total of 328 samples were obtained from Prince William Sound Science Center (PWSSC) and lower Cook Inlet (KBNERR) cruises from 2020-2022. The number of samples includes replicate and triplicate samples. PWSSC provided samples in 2020 (n = 44) and 2021 (n = 28) and KBNERR provided lower Cook Inlet samples in 2020 (n = 48), 2021 (n = 133), and 2022 (n = 75). For the cruise data we present here all the listed carbonate parameters were recorded for samples from July 2021 through 2022. For samples acquired before July 2021 the parameters recorded are pCO_2, TCO_2, pH, TA, and Ωarag. Data include Ωcalc, HCO_3^-, and CO_3^{2-} after July 2021. TCO_2 was selected for modeling at sites with adequate data collection as an indicator of ocean acidification, and the primary parameter of interest.

Prince William Sound

APMI received a total of 72 samples from Prince William Sound across three sites (Table 1). Samples collected at the Simpson Bay site were analyzed, however, the limited sample number proved insufficient for oceanographic analysis. Samples collected at both the Naked Island site (Table 1; Figure 3) and the Whale Bay site (Table 1; Figure 4) provided the most data coverage and included one year of data with adequate spatial and temporal coverage for modeling.

Lower Cook Inlet

APMI received a total of 256 samples from lower Cook Inlet across 21 sites (Table 2). Data collections were insufficient for modeling along transect 4, and a single site along transect 9 (site T9-6) yielded sufficient data with adequate spatial and temporal coverage for modeling (Figure 5). Data analyzed by APMI from collections at T9-6 from 2017 – 2020 and funded by the National Oceanic and Atmospheric Administration were also included in this dataset to provide more robust analyses for the T9-6 site (Figure 5).

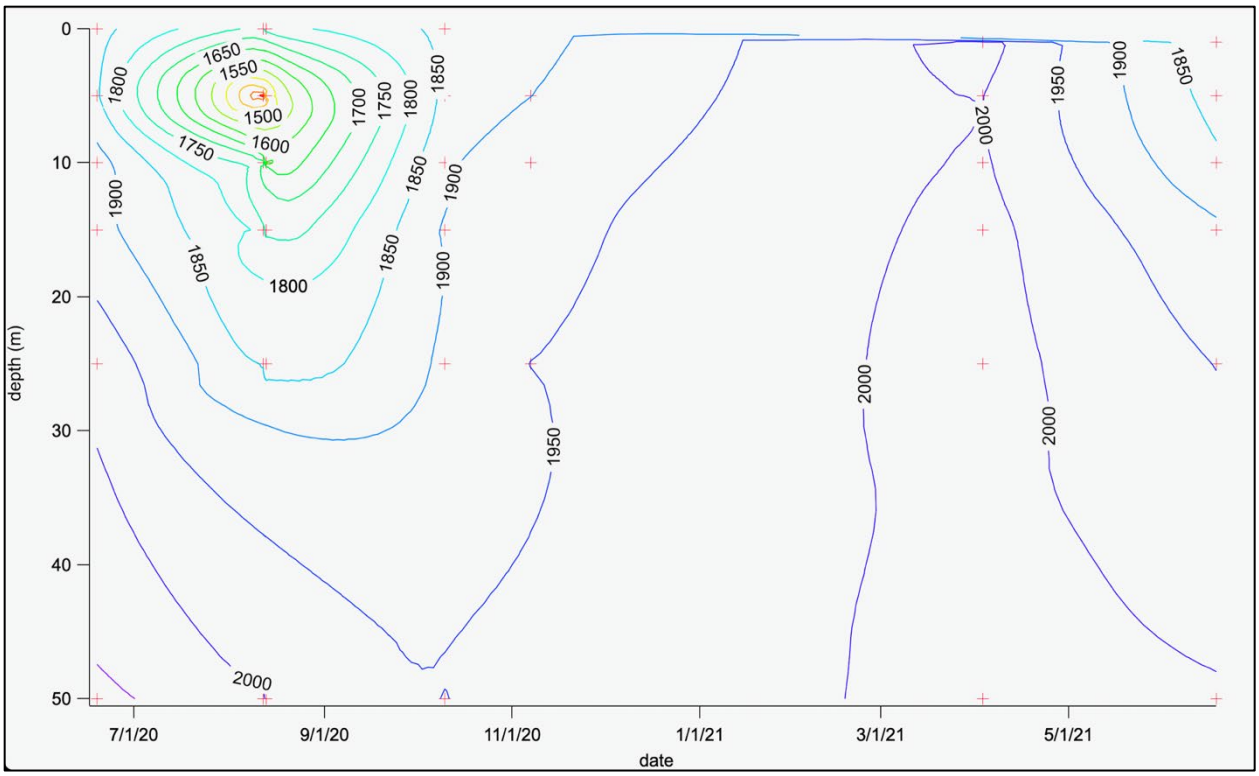

Figure 3. Total CO_2 profiles (µmol/kg) across depth and time for the Naked Island sample site in Prince William Sound, July 2020 - 2021.

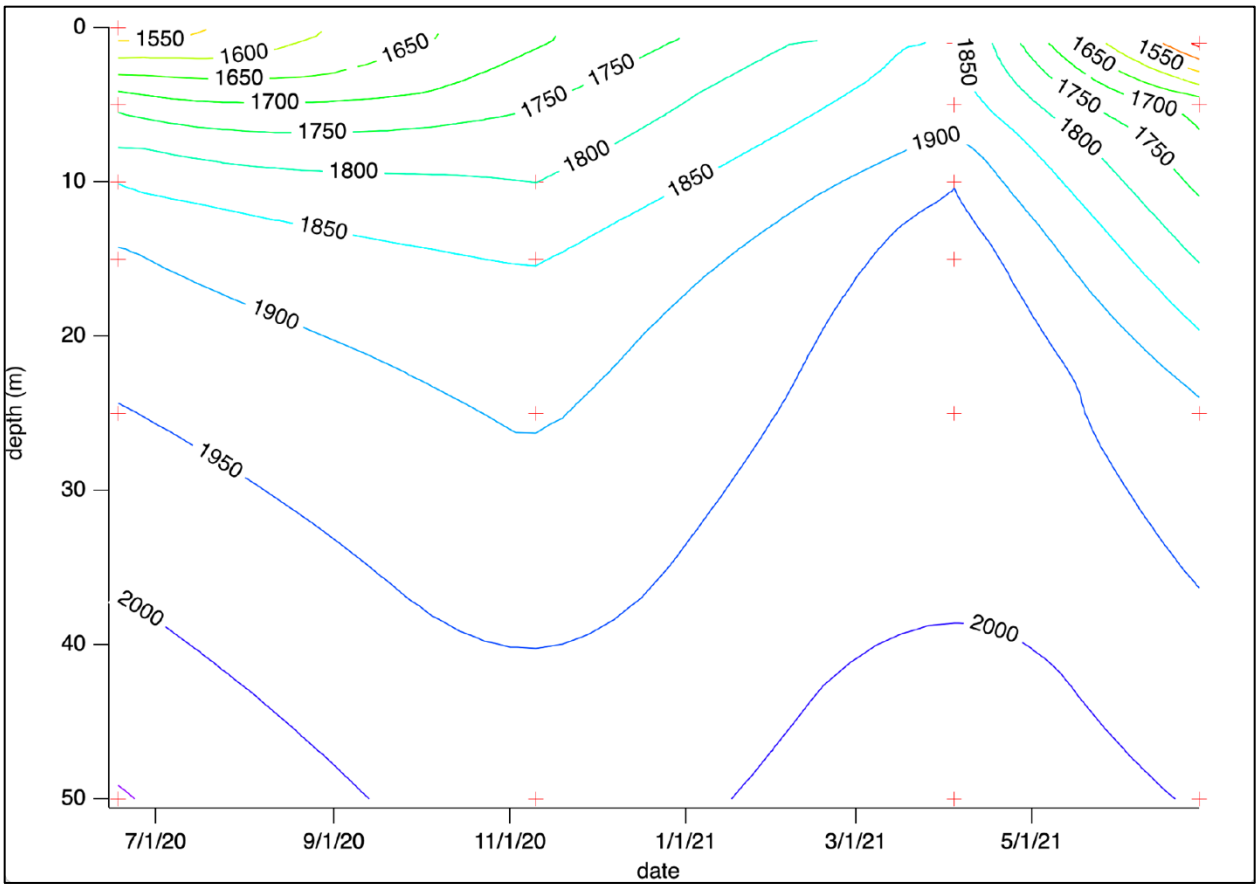

Figure 4. Total CO2 profiles (µmol/kg) across depth and time for the Whale Bay sample site in Prince William Sound, July 2020 - 2021.

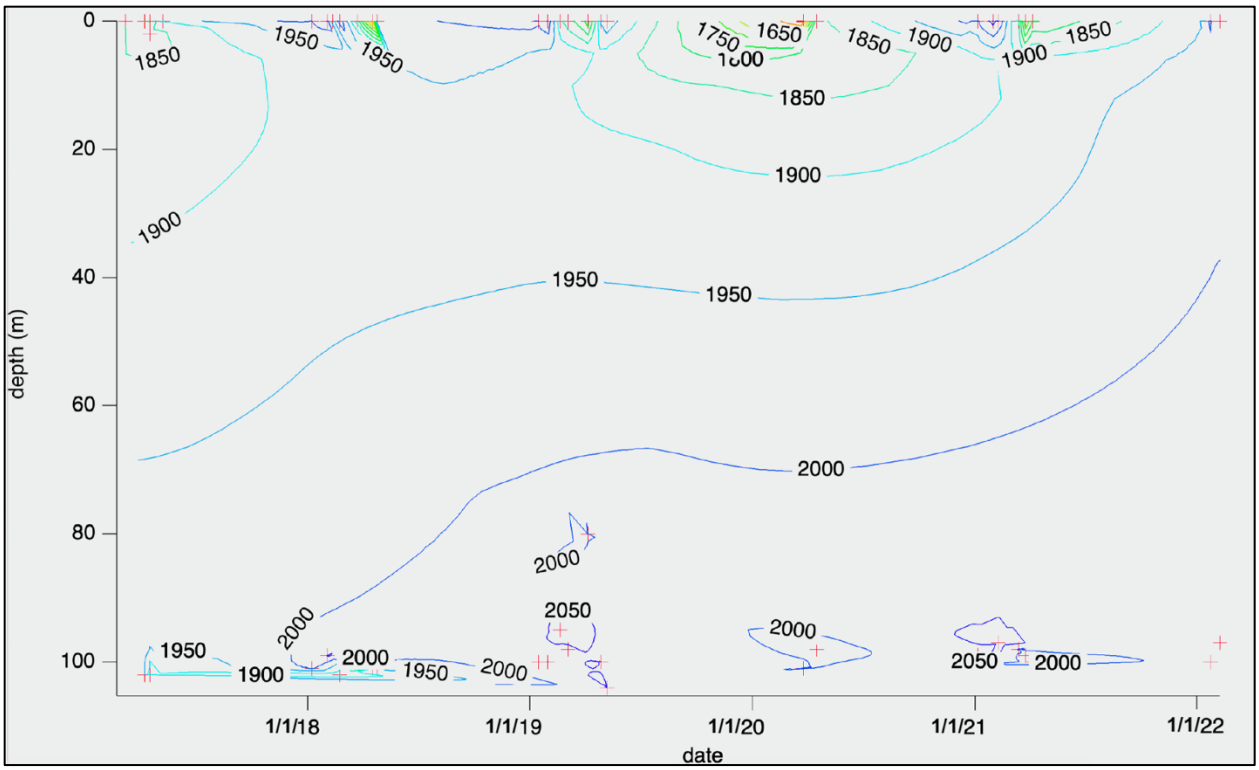

Figure 5. Total CO_2 profiles (µmol/kg) across depth and time for the transect 9 sample site 6 location in lower Cook Inlet, February 2017 – January 2022.

DISCUSSION

Prince William Sound

The sites at Naked Island (Figure 3) and Whale Bay (Figure 4) both yielded a year of data with adequate spatial and temporal coverage, and both demonstrate normal seasonal variations in hydrography associated with costal sample sites in Alaska. The water columns for both these sites are well-mixed in the winter due to storms, reduced freshwater input, and reduced biological activity. The water columns are much more stratified at both sites during the summer months. The low TCO_2 values apparent in the mixed layer (0-10 m depth) correlate with low salinity and cooler temperatures due to glacial meltwater, and in some cases, very low pCO_2 due to algal blooms and photosynthetic activity. The extent of seasonal stratification is most apparent at the Naked Island site (Figure 3), where there is the most sampling coverage. Whale Bay (Figure 4) appears to be more stratified during the winter months than Naked Island (Figure 3). This may be because Whale Bay is located in a protected region, which is exposed to less wind, wave, and current influence. Conversely, Naked Island is located in the middle of Prince William Sound, and likely receives more disruption to the water column due to wind, waves, and currents.

Lower Cook Inlet

The single site in lower Cook Inlet lies inside Kachemak Bay, just outside of the Homer Spit (Figure 2). The changes in TCO_2 profiles that accompany seasonality in Prince William Sound sites are also demonstrated in Kachemak Bay at site T9-6 (Figure 5). These dynamics remain relatively consistent across five consecutive summers, also likely due to the limited wind, wave, and current activity within the bay.

Limited data collected during this project was largely the result of the COVID-19 pandemic. Some planned research cruises were not conducted due to the pandemic, significantly reducing the amount of data collected from the original proposed efforts. Additionally, the absence of data for Ωcalc, HCO_3^-, and CO_3^{2-} on samples before July 2021 was due to a misunderstanding of reporting these parameters for this project. These time series are not comprehensive enough to make conclusions about long-term changes health of Prince William Sound and Kachemak Bay, but they do reveal the dynamic nature of these environments and the need to further monitor seasonal changes over a longer timeframe. Given ongoing and increasing ecosystem perturbations caused by climate events such as marine heat waves and terrestrial heat waves, and anthropogenic activities, long term monitoring is essential for assessing the status of these habitats after EVOS.

CONCLUSION

These data may serve to provide crucial information to a wide variety of both ecological and oceanographic research efforts conducted during GWA research programs and projects. While these data provide relevant information for concurrent research efforts occurring during the GWA cruises, more frequent sampling from a greater number of depths could improve efforts to capture oceanographic dynamics in both Prince William Sound and lower Cook Inlet. These data may be useful to the GWA-Long Term Research and Monitoring Program project 22220202 (Continuation and Expansion of Ocean Acidification Monitoring in the *Exxon Valdez* Oil Spill Area).

ACKNOWLEDGEMENTS

For the Prince William Sound sample collection, we would like to thank the crew of PWSSC; R. Campbell and C. McKinstry. For the lower Cook Inlet samples, we thank the staff at the NOAA Kasitsna Bay Laboratory; K. Holderied, D. Hondolero and M. Renner, who provided all the boat support and assisted with the field collection sampling in collaboration with the staff at KBNERR; C. Guo, and C. Walker for conducting sampling logistics. We also acknowledge the staff at CRRC/APMI; V. Verhey, H. Helen, and H. Rappleyea, for assisting with laboratory sample analyses, and E. Mailman for assistance with report preparation. Finally, we are grateful to B. Hales at OSU for support in data analyses and protocol development. The findings and conclusions presented by the authors are their own and do not necessarily reflect the views or position of the *Exxon Valdez* Oil Spill Trustee Council.

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