Exxon Valdez **Oil Spill Trustee Council**

Long-Term Research and Monitoring, Mariculture, Education and Outreach

Annual Project Reporting Form

Project Number: 24220202

Project Title: Continuation and Expansion of Ocean Acidification Monitoring in the *Exxon Valdez* Oil Spill Area 24220202

Principal Investigator(s): Claudine Hauri, International Arctic Research Center

Reporting Period: February 1, 2024 – January 31, 2025

Submission Date (Due March 1 immediately following the reporting period): March 1, 2025

Project Website: https://gulfwatchalaska.org/

Please check all the boxes that apply to the current reporting period.

☒ **Project progress is on schedule.**

☐ **Project progress is delayed**

☒ **Budget reallocation request.**

The late funding in FY22 resulted in the need to rebudget some categories for that year. The request did not make it to EVOSTC at that time. We would like to move $1,085 to Travel, from Commodities to support the cost of delivering sampling bottles to Seward. We would also like to move $9,620 to Contractual, from Commodities to support the cost of equipment maintenance and shipping. The Contractual costs include sending the alkalinity instrument in for repairs and the shipping costs of a loaner instrument to continue analysis. The grant included instrument refurbishment costs in the original budget, but these items were budgeted under Commodities as per of the cost per sample. There is no change in the scope of work for this project.

☐ **Personnel changes.**

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1. Summary of Work Performed:

With funding from the *Exxon Valdez* Oil Spill Trustee Council (EVOSTC), our team collected water samples for total alkalinity (TA), dissolved inorganic carbon (DIC), and pH during the spring and fall 2024 Gulf Watch Alaska Long-Term Research and Monitoring (GWA-LTRM) and Northern Gulf of Alaska Long-Term Ecological Research (NGA LTER) cruises along the Seward and Kodiak lines and in Prince William Sound.

Sydney Wade, an undergraduate chemistry student, was trained in our lab to analyze seawater samples and worked with Brita Irving to complete analyses of the samples collected on the spring (401 samples) and fall (214 samples) cruises. Sydney was trained in the collection of inorganic carbon samples and participated in the fall cruise as the lead ocean acidification (OA) sample collector, with assistance from the National Oceanic and Atmospheric Administration (NOAA) teacher at sea, Alexa Helm.

Consumables for the 2025 sample collection and lab analyses have been compiled and will be ordered this spring. All the sample bottles have been cleaned and are ready for the upcoming 2025 field season, which will consist of a spring, summer, and fall cruise. Cruise preparation will include reinforcing the peristaltic pump sampling rack and designing and building a stand to secure the mercuric chloride pipette during sampling.

OA samples collected during the 2022 and 2023 field season went through final quality control (QC) and were delivered to Axiom for archival on DataONE and the Gulf of Alaska Data Portal. Data from our 2024 cruises will be post-processed and undergo our routine QC this spring before submission to Axiom for archival.

Our 2018-2023 inorganic carbon dataset and metadata was submitted to the Sustainable Development Goal 14.3.1 Indicator with the goal of increasing the visibility of this work with our government and internationally.

After careful review of our DIC Analyzer analysis protocol, the protocol was updated to make instrument drift correction more straightforward during post-processing. As part of this review, gas-tight bags were tested and will be used moving forward for calibration and analyses of standard references for DIC and pH.

Graduate student Addie Norgaard defended her MSc thesis (http://hdl.handle.net/11122/15526) in early June. Her thesis and defense included data from this project, which are highlighted below. We are preparing a manuscript for publication based on this work.

We plan to recruit one or more undergraduate analytical chemistry students to join our team as sample collectors and lab analysts.

<u>Regional empirical pCO_2-based pH algorithm cross-validation and evaluation</u>

Our 2018-2023 data were used as part of a cross-validation dataset (pH^{disc}) for the pCO_2-based regional empirical pH algorithm, modeled after Hauri et al. (2024), and suggest that estimated pH (pH^{est}) in the Northern Gulf of Alaska are within the "weather" quality goal of 0.02 and therefore of sufficient quality to identify relative spatial patterns and short-term variability (Newton et al. 2015). pH^{disc} and pH^{est} compared well (r^2 = 0.999, RMSE = 0.004, Fig. 1a and Fig. 2b). Absolute differences between pH^{disc} and pH^{est} were within the weather goal for pH of 0.02 (Newton et al. 2015) 99% of the time (Fig. 1c); the exceptions occurred at depths greater than 500db (not shown). pH^{est} slightly overestimated pH^{disc} with a mean difference of 0.0008 (95% confidence interval of 0.0005 to 0.0012) and a median difference of 0.0020.

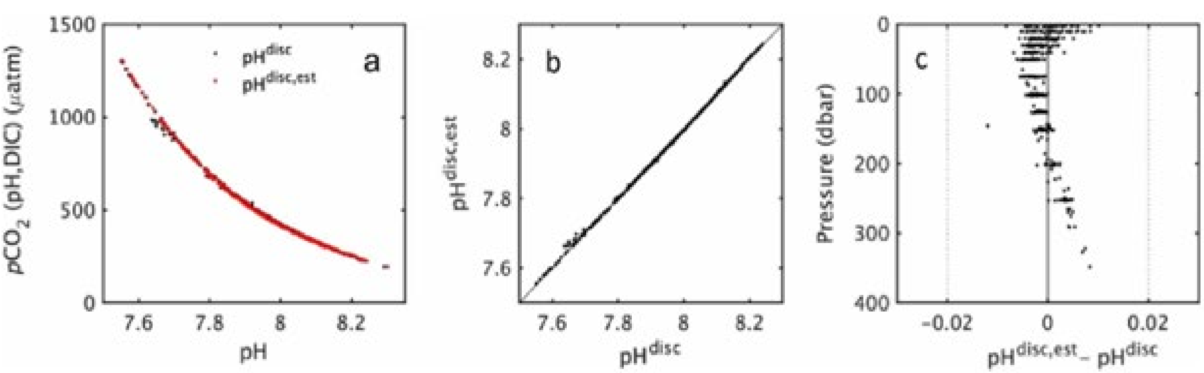

Figure 1. Cross-validation of pH algorithm with training dataset. From left to right, a) $pCO_{2}{}^{disc}_{(pH,DIC)}$ vs pH^{disc} (black) and $pCO_{2}{}^{disc}_{(pH,DIC)}$ vs. pH^{est} (red). b) $pH^{disc,est}$ vs. pH^{disc} with black line indicating 1:1 relationship. c) pressure (dbar) vs. residual pH ($pH^{disc,est}$ - pH^{disc}) with a black vertical line at 0, and dashed vertical lines at ± 0.02, indicating the weather-level uncertainty goal for pH (Newton et al. 2015). 515 discrete samples were used for evaluation (Hauri et al. 2021a and unpublished preliminary data).

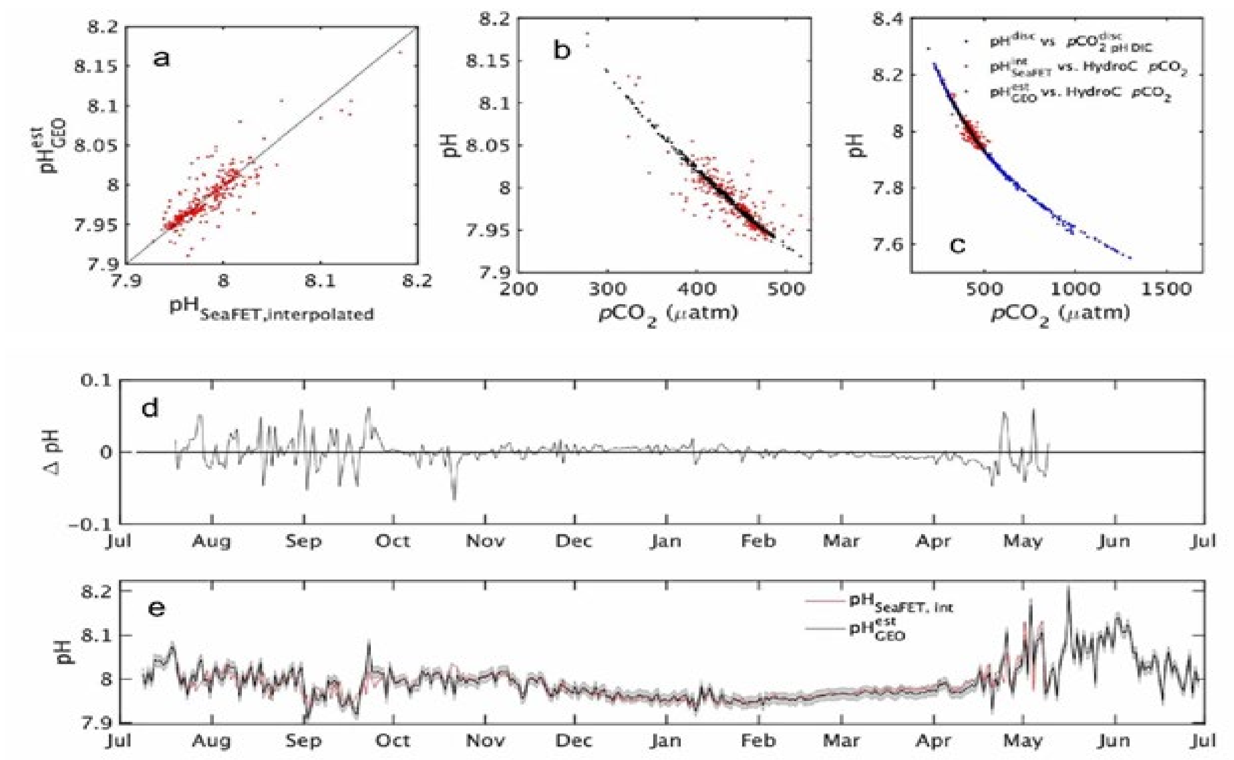

Figure 2. Evaluation of pH algorithm. pH^{est} evaluation with pH_{SeaFET} interpolated to pCO_2 timestamp from the Gulf of Alaska Ecosystem Observatory from July 2020 – July 2021. Top left to right to bottom, a) pH^{est} vs. pH_{SeaFET} with black line indicating a 1:1 relationship, b) HydroC pCO_2 vs. pH (pH_{SeaFET} in red and pH^{est} in black), c) pH^{disc} vs. $pCO_{2(pH,DIC)}^{disc}$ from the hydrographic test dataset, d) residual pH (pH^{est} - pH_{SeaFET}) over the pH_{SeaFET} timeseries, and e) pH_{SeaFET} (red) and pH^{est} (black) vs. time.

<u>*Future goals for improving and investigating data quality*</u>

We plan to review our data quality and the associated uncertainty we publish with our data, to ensure our uncertainty aligns with community standards (we believe we're over reporting uncertainty relative to peers). We will do this by comparing all triplicates collected since 2019 (includes the error associated with the collection, handling, as well as the analytical precision), looking into the available QC tools (e.g., Lauvset et al. 2015, Cacabelos et al. 2024), and standardizing/hard coding statistics and figures during post processing for quick reference and posterity. It is important to note, secondary level QC (a process in which data from one cruise are objectively compared against data from another cruise or a previously synthesized data set in order to quantify systematic differences) is difficult owing to the limited number of samples collected deeper than 1500 m in coastal regions such as the Northern Gulf of Alaska and is not recommended for cruise level data submission but will be used for our internal quality control (Jiang et al. 2021, Monacci et al. 2024).

Internal consistency

We plan to examine the internal consistency of the inorganic carbon system parameters in our region to further evaluate the accuracy of our data. This is possible because we analyze samples for three parameters and thus our carbon system is overdetermined. As part of this study, we plan to compare the available inorganic carbon data estimates with our data with special attention on the departure from a linear TA:S relationship at high salinity (Fig. 3), as well as the commonly recommended carbonic acid dissociation constants of Lueker et al. (2000) (the standard in synthesis data products; e.g., Jiang et al. 2021, Lauvset et al. 2022, Metzl et al. 2024) against the perhaps better suited coefficients of Sulpis et al. (2020) (Fig. 4; Hauri et al. 2024), and investigate potential offsets or biases by comparing estimates using different pairs of carbon measurements.

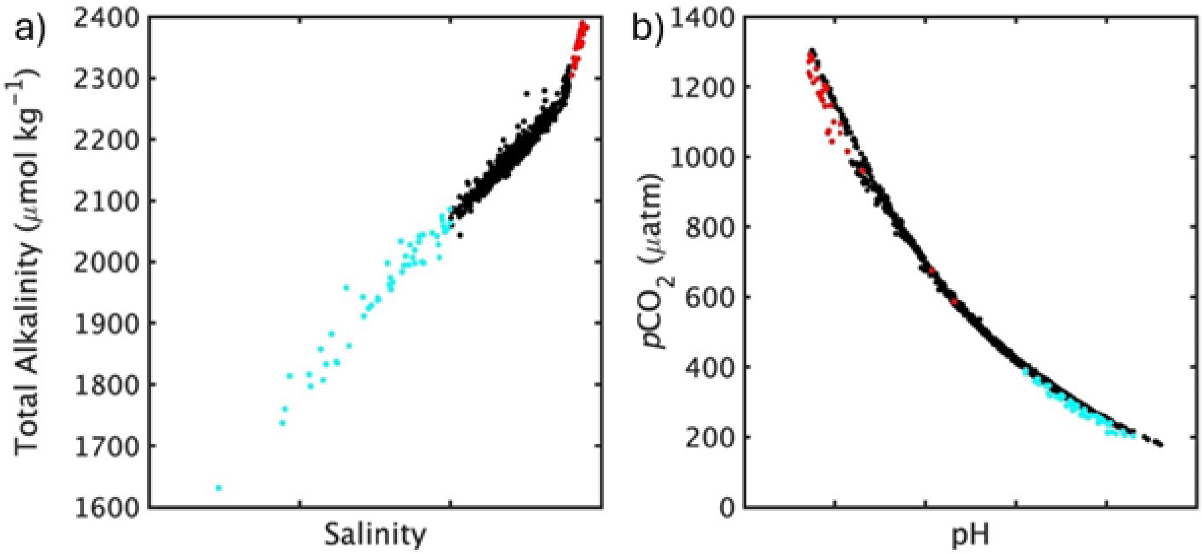

Figure 3. Salinity versus total alkalinity (TA) in the Northern Gulf of Alaska (a, left). Salinity < 30 in turquoise and salinity > 34 in red (approximately North Pacific Intermediate Water) in (a) and (b, right). Salinity > 30 and < 34 is used to approximate shelf water ambient to Gulf of Alaska Ecosystem Observatory. pH versus pCO_2 in (b) shows differing pH:pCO_2 ratio in the three water masses. (Supplemental Fig. 1 from Norgaard 2024.)

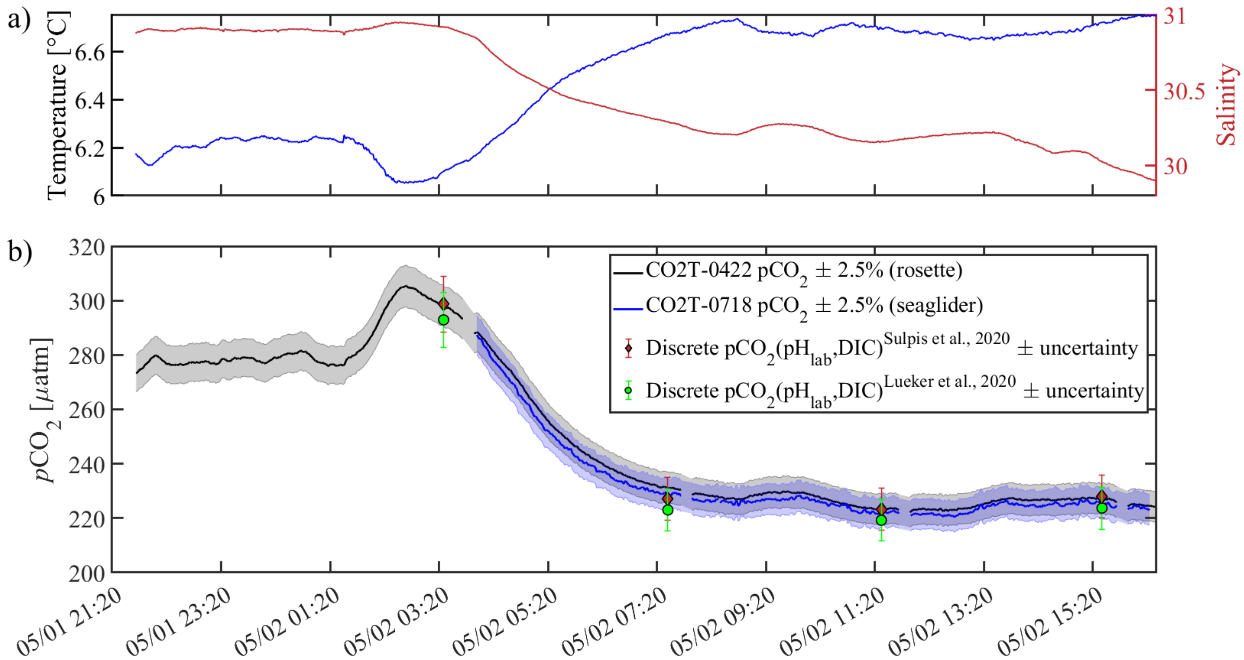

Figure 4. HydroC CO_2 sensor validation during a tank experiment at the Alutiiq Pride Marine Institute on 1-2 May 2022. a) Temperature (blue line) and salinity (red line) from a recently calibrated Sea-Bird Scientific SBE37. b) Black (blue) lines show pCO_2 in micro-atmospheres (µatm) from HydroC CO2T-0422-001 (HydroC CO2T-0718-001), with the shaded gray (blue) areas showing a relative uncertainty of 2.5 % (weather quality goal; Newton et al. 2015). Discrete pCO_2 are the average of triplicate bottles calculated with the carbonic acid coefficients of Sulpis et al. (2020) (black diamonds filled red) and calculated with the carbonic acid coefficients of Lueker et al. (2000) (black circles filled green), with error bars showing the combined standard uncertainty from errors (Orr et al. 2018). HydroC pCO_2 data are shown at 1 min resolution with a 2 min moving median filter applied and have not been corrected for response time, but differences were negligible (< 0.1 µatm). (Adapted from Hauri et al. (2024) Fig. 6.)

A closer look at "calibration" samples

Our data can theoretically be used as a calibration point or to establish an error envelope for our moored Seabird SeaFET pH sensors, given that they are collected after the sensor is conditioned. However, after reviewing the feasibility of this more closely (Figs. 5 and 6), we determined that none of our available samples were adequate due to differences in collection depth and distance from the moored sensor. To investigate the feasibility, we looked at the available discrete data collected at Gulf of Alaska Ecosystem Observatory (GEO) and the nearest station (GAK5 ~31 km away) to our moored sensor after the SeaFET had been deployed for ~14 days and was properly conditioned. Since we only collect a few samples at GEO, we wanted to see if we could interpolate pH to the moored depth using the GEO or GAK5 profile. Unfortunately, in both instances GEO discrete data (red circles with horizontal error bars Fig. 5a and Fig. 6a) were collected above the moored sensor depth (horizontal blue line in Figs. 5 and 6) and based on the departure in the temperature and salinity profiles (Fig. 5 and 6b, c) near the moored depth between the GAK5 and GEO profiles, it was not feasible to use our discrete data as either a calibration point for the SeaFET, or useful reference samples to generate an error envelope.

This large difference as a result of depth and distance is not unexpected, as Hauri et al. (2024) reported much higher differences in pCO_2 discrete samples and two HydroC CO2 sensors when discrete water samples were taken 1 km apart and within 4 h, relative to when discrete samples were taken directly next to the sensor in a tank (Fig. 4). Thompson et al. (2021) recommended collecting calibration or reference samples within 100 m (of a glider) and Bresnahan et al. (2014) recommended taking discrete samples alongside the sensor, both of which are beyond our scope.

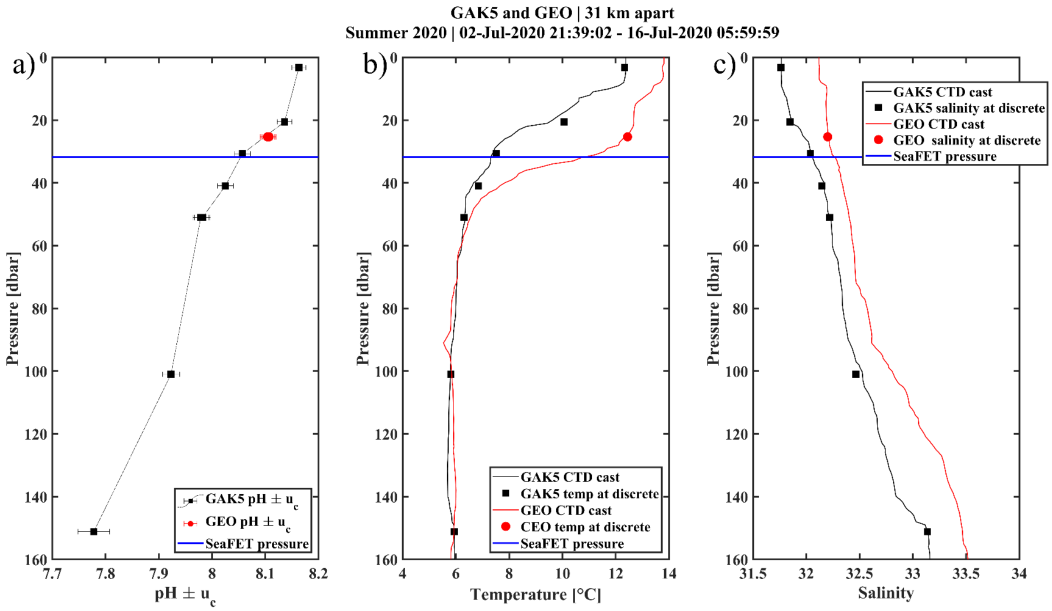

Figure 5. Summer 2020 Northern Gulf of Alaska Long-Term Ecological Research Cruise Gulf of Alaska Ecosystem Observatory (GEO) and GAK5 profiles versus pressure with discrete data. a) Discrete pH ± uncertainty at GAK5 (black squares) and GEO (red circles). b) Temperature at GAK5 (black line = conductivity and temperature at depth (CTD), black squares = T_{CTD} at time of the bottle fire) and GEO (red line = CTD, red circle = T_{CTD} at time of the bottle fire). c) Salinity at GAK5 (black line = CTD, black squares = S_{CTD} at time of the bottle fire) and GEO (red line = CTD, red circle = S_{CTD} at time of the bottle fire). Pressure of the moored SeaFET sensor is the blue horizontal line in all axes.

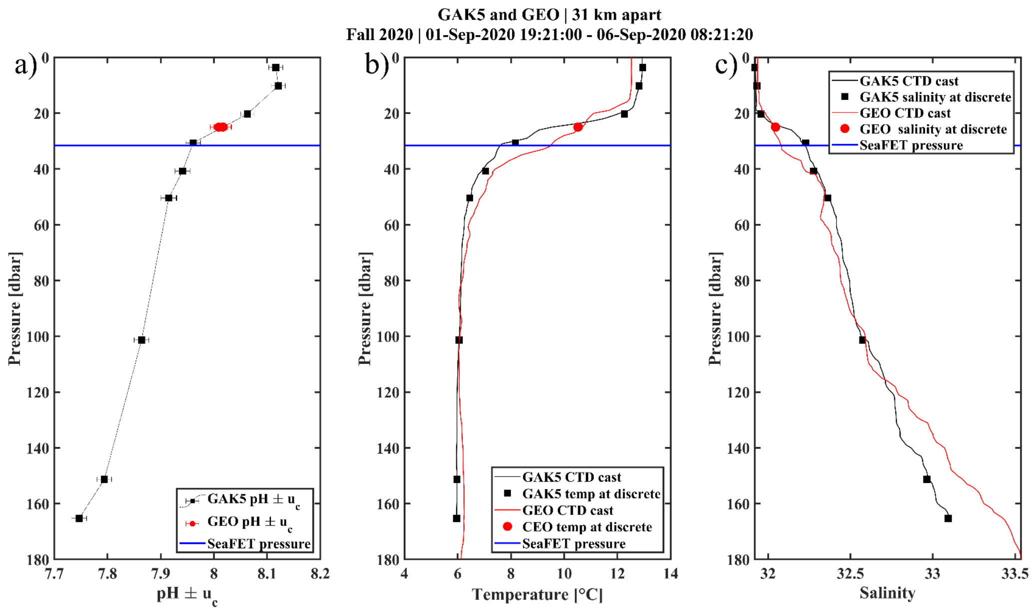

Figure 6. Fall 2020 Northern Gulf of Alaska Long-Term Ecological Research Cruise Gulf of Alaska Ecosystem Observatory (GEO) and GAK5 profiles versus pressure with discrete data. a) Discrete pH ± uncertainty at GAK5 (black squares) and GEO (red circles) with pressure of the moored SeaFET sensor (blue horizontal line). b) Temperature at GAK5 (black line = conductivity and temperature at depth (CTD), black squares = T_{CTD} at time of the bottle fire) and GEO (red line = CTD, red circle = T_{CTD} at time of the bottle fire). c) Salinity at GAK5 (black line = CTD, black squares = S_{CTD} at time of the bottle fire) and GEO (red line = CTD, red circle = S_{CTD} at time of the bottle fire). Pressure of the moored SeaFET sensor is the blue horizontal line in all axes.

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Sulpis, O., S. K. Lauvset, and M. Hagens. 2020. Current estimates of K and K appear inconsistent with measured CO_2 system parameters in cold oceanic regions. Ocean Science 16:847–862. https://doi.org/10.5194/os-16-847-2020.

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2. Products:

Peer-reviewed publications:

No new contributions for this reporting period.

Reports:

Norgaard, A. 2024. Seasonal marine inorganic carbon dynamics on the northern Gulf of Alaska continental shelf (Order No. 31487590). M. S. Thesis, University of Alaska Fairbanks, https://scholarworks.alaska.edu/handle/11122/15526.

Popular articles:

No new contributions for this reporting period.

Conferences and workshops:

No new contributions for this reporting period.

Public presentations:

No new contributions for this reporting period.

Data and/or information products developed during the reporting period:

No new contributions for this reporting period.

Data sets and associated metadata:

Hauri, C., B. Irving, and A. Norgaard. 2021. Inorganic Carbon data from water samples collected during CTD casts at stations during the Northern Gulf of Alaska LTER seasonal cruises, 2018-2021. Research Workspace. 10.24431/rw1k45g, version: 10.24431_rw1k45g_20230203T202101Z.

The 2022 and 2023 data have been submitted to Axiom and are in their pipeline for archival.

Additional Products not listed above:

No new contributions for this reporting period.

3. Coordination and Collaboration:

The Alaska SeaLife Center or Prince William Sound Science Center

This project is a subawardee of the *Exxon Valdez* Oil Spill Trustee Council (EVOSTC) NOAA grant award that is administered by the Prince William Sound Science Center (PWSSC). The principal investigator (PI) coordinates with PWSSC on invoicing, reporting, and meeting attendance.

EVOSTC Long-Term Research and Monitoring Projects

This project is part of the Gulf Watch Alaska Long-Term Research and Monitoring (GWA-LTRM) program funded by EVOSTC and is within the environmental drivers component. PI Hauri coordinates with PIs from the Seward Line project (24120114-L; Russ Hopcroft) and GAK1 project (24120114-I, Seth Danielson) for seasonal sampling in the Gulf of Alaska.

EVOSTC Mariculture Projects

Ocean acidification may be an important consideration for mariculture activities and the mariculture projects funded by EVOSTC. We are open to collaboration and data sharing.

EVOSTC Education and Outreach Projects

No new contributions for this reporting period.

Individual EVOSTC Projects

The ocean acidification project works with the Data Management program to ensure data collected are properly reviewed, have current metadata, and are posted to the GOA data portal within required timeframes. We will work with other individually funded EVOSTC projects if collaborative efforts make sense based on data collected.

Trustee or Management Agencies

No new contributions for this reporting period.

Native and Local Communities

Claudine Hauri and Brita Irving are in regular meetings with the Chugach regional Resources Commission to connect Traditional Ecological Knowledge with western science observations and models.

4. Response to EVOSTC Review, Recommendations and Comments:

September 2024 Science Panel Comments:

This new project delivers high-resolution inorganic carbon monitoring along the Seward Line and in Prince William Sound in May, July, and September, and adds monitoring along an additional transect off Kodiak. Some of the work is leveraged with funding from the NGA-LTER. The transect off Kodiak is near current and proposed mariculture sites and is of particular importance because it may include ocean acidification extreme events ("hot spots"). The PI responded positively to previous Science Panel comments, as well as those from external reviews. Delayed funding meant that there were no new data in 2022 (and hence in the FY23 annual report), but data from previous years were used to quantify potentially important spatial details in pH and pCO2. In 2023 all planned cruises were completed, and lab analysis of the spring and summer samples is complete. At the time of the FY24 annual report most of the preparatory work for the 2024 field work was completed. The SP was impressed by the insightful, mechanistic interpretation of data in the 2024 report, notably the linkages to known patterns of natural variability in the GOA ecosystem. In summary, the work to date is impressive and on course.

The Science Panel has no concerns about this project.

PI Response:

We appreciate the continued support of the *EVOSTC* Science Panel.

2024 Executive Director Comments

I concur with the Science Panel. Funding for this project is managed by NOAA. The expenses on the annual reports are well documented and easy to track. The Fiscal Manager is responsive to budget questions. Staff do not have any concerns at this time.

2024 PAC Comments

Whissel asked about deepwater intrusion and natural upwelling in the gulf. Hauri clarified there is natural upwelling in the gyre offshore and downwelling on the shelf all the time. Sometimes there is stronger upwelling in the middle of the gyre and weaker downwelling on the shelf, which allows for deep water intrusion. Sea surface height can help indicate the strength of downwelling or upwelling, which provides a better picture of environmental conditions. The strength may naturally vary between years, but with other climate change trends, it all can lead to extreme events.

Whissel introduced a motion to proceed with no concern. Stephens seconded, and there was no opposition. The motion passed unanimously.

5. Budget:

The late funding in FY22 resulted in the need to rebudget some categories for that year. The request did not make it to EVOSTC at that time. We would like to move $1,085 to Travel, from Commodities to support the cost of delivering sampling bottles to Seward. We would also like to move $9,620 to Contractual, from Commodities to support the cost of equipment maintenance and shipping. The Contractual costs include sending the alkalinity instrument in for repairs and the shipping costs of a loaner instrument to continue analysis. The grant included instrument refurbishment costs in the original budget, but these items were budgeted under Commodities as per of the cost per sample. There is no change in the scope of work for this project.

This project continues to be behind in spending because of the delay in issuance of the NOAA grant in FY22 and the long delay in NOAA's release of funds for FY24 until January 2025.

EXXON VALDEZ OIL SPILL TRUSTEE COUNCIL
PROJECT BUDGET PROPOSAL AND REPORTING FORM

Budget Category:	Proposed FY 22	Proposed FY 23	Proposed FY 24	Proposed FY 25	Proposed FY 26	5- YR TOTAL PROPOSED	ACTUAL CUMULATIVE
Personnel	$71,359	$70,768	$57,935	$59,384	$60,869	$320,315	$131,992
Travel	$1,085	$331	$0	$365	$0	$1,781	$1,085
Contractual	$9,620	$0	$0	$0	$0	$9,620	$10,698
Commodities	$33,170	$30,750	$30,750	$30,750	$31,750	$157,170	$62,699
Direct Costs Exempt from F&A	$0	$0	$0	$0	$0	$0	$0
Equipment	$0	$0	$0	$0	$0	$0	$0
Indirect Costs Rate = 25% **(non-equipment)**	$28,808	$25,462	$22,171	$22,625	$23,155	$122,221	$51,618
SUBTOTAL	$144,042	$127,311	$110,856	$113,123	$115,774	$611,107	$258,092
General Administration (9% of subtotal)	$12,964	$11,458	$9,977	$10,181	$10,420	$55,000	N/A
PROJECT TOTAL	$157,006	$138,769	$120,833	$123,304	$126,194	$666,107	
Other Resources (In-Kind Funds)	$0	$0	$0	$0	$0	$0	

COMMENTS:
We continue to be behind in spending because of the delay in issuance of the NOAA grant in FY22 and delay in funding the grant in FY24.

The late funding in FY22 resulted in rebudgeting, such as additional travel costs to deliver sampling bottles to Seward Line in time for a scheduled cruise, shipment and contractual services to ship the alkalinity instrument for repairs and receive a loaner to keep analyzing samples. The grant included instrument refurbishment funds but was budgeted under commodities as part of cost per sample. We will see greater expenses in the upcoming years.

FY22-26	Project Number: 24220202 Project Title: Ocean Acidification Monitoring Primary Investigator: Claudine Hauri (UAF)	NON-TRUSTEE AGENCY SUMMARY PAGE