



Exxon Valdez Oil Spill Trustee Council

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

Annual Project Reporting Form

Project Number: 23220202

Project Title: Continuation and expansion of ocean acidification monitoring in the *Exxon Valdez* Oil Spill area

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

Reporting Period: February 1, 2023 – January 31, 2024

Submission Date: March 1, 2024

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.**
 - Personnel changes.**
-

1. Summary of Work Performed:

With funding from the *Exxon Valdez* Oil Spill Trustee Council (EVOSTC), our team collected water samples for total alkalinity, dissolved inorganic carbon, and pH during the spring (256 samples), summer (259 samples), and fall (181 samples) 2023 Gulf Watch Alaska and Northern Gulf of Alaska Long-Term Ecological Research cruises along the Seward and Kodiak lines and in Prince William Sound. We finalized the laboratory analysis of all samples and the spring and summer data have been post-processed. We are currently working on the final QC. Data from the 2022 cruises and preliminary data from the spring and summer 2023 cruises were incorporated in the National Oceanic and Atmospheric Administration (NOAA) Gulf of Alaska (GOA) Ecosystem Status Report (ESR, Hauri et al. 2023), which included an ocean acidification contribution for the first time.

Necessary consumables for sample collection and lab analyses have been compiled and will be ordered this spring, and all sampling bottles were cleaned and prepped to be ready for the upcoming 2024 field season, which will consist of a spring and fall cruise.



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Communications have been underway with undergraduate analytical chemistry students to join our team as sample collectors and lab analysts.

Below we illustrate the data collected in 2022 and two cruises in 2023 (Fig. 1), summarize findings we published as part of the NOAA GOA ESR, and show how we can apply our new climate indices that we defined through model analysis (Hauri et al. 2021, Hauri et al. 2024) on this projects' in situ data. This last analysis is still ongoing and will likely lead to an additional paper on how the climate-ocean dynamics affect the GOA ecosystem.

Data from 2022 and 2023

The 2022 and 2023 data illustrated in Fig. 1 show the general pattern of high pH (lower dissolved inorganic carbon, DIC) in the surface layer in spring as a result of primary production. DIC and total alkalinity (TA) are also affected by freshwater, visible in the increasing on-offshore gradient. In summer, the freshwater influence on DIC and TA becomes stronger in the nearshore and further intensifies across the shelf in fall, which drives both DIC and TA to the seasonal low.



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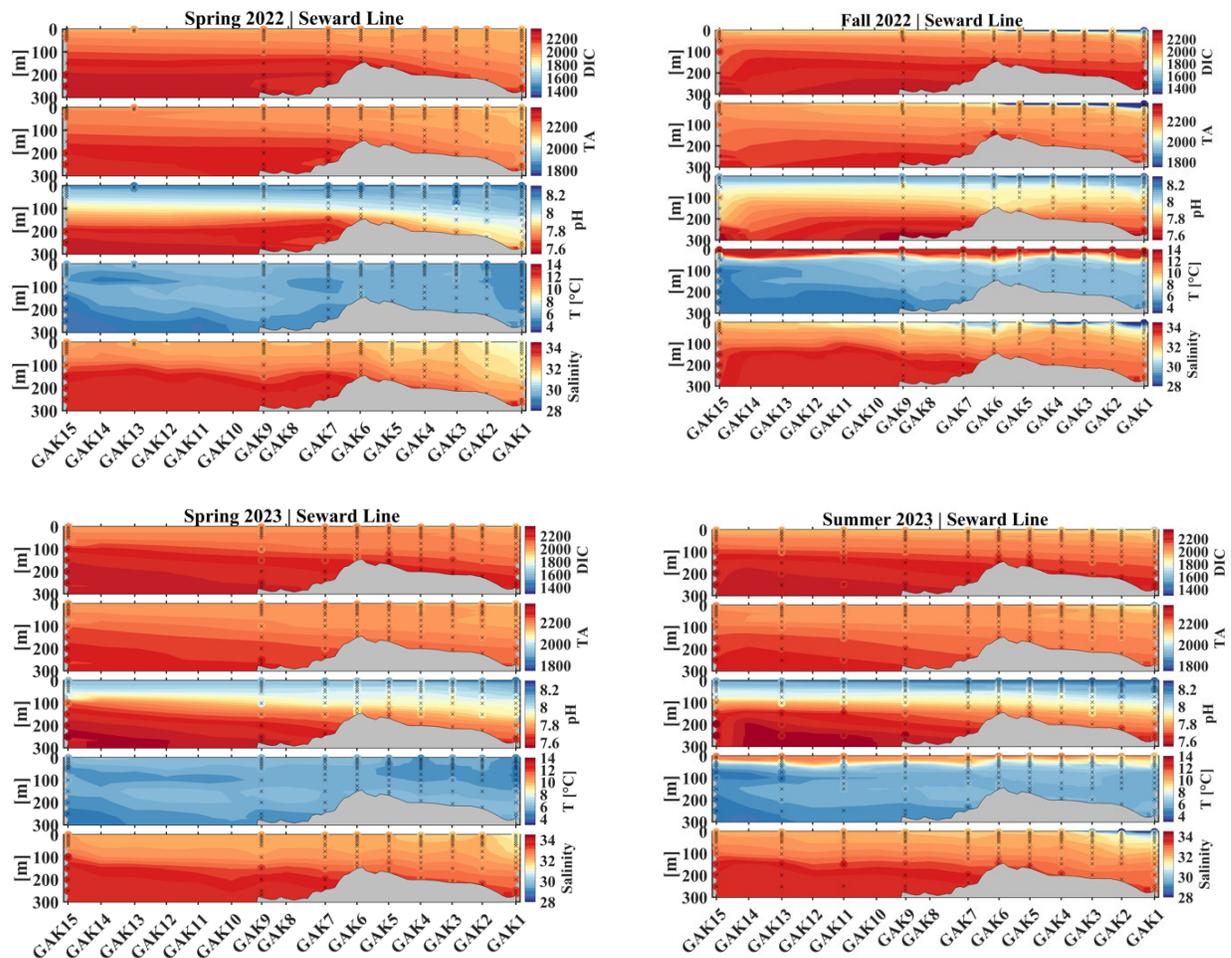


Figure 1. Seward Line transects from the Gulf Watch Alaska and Northern Gulf of Alaska Long Term Ecological Research 2022 (spring and fall) and 2023 (spring and summer) preliminary cruise data from GAK1 offshore to GAK15 shown in order, dissolved inorganic carbon (DIC), total alkalinity (TA), in situ pH, temperature, and salinity for each cruise. Black crosses show stations and depths where discrete samples were collected. In situ pH (bottom) is calculated using carbonate dissociation coefficients of Lueker et al. (2000). Temperature and salinity contours are from all conductivity and temperature at depth casts along the Seward Line and scatter points are from the bottle value at the position of inorganic carbonate measurements. Scatter circles are included to remind the reader that contoured transect plots do not represent actual data values.



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Effect of the natural climate variability on the Gulf of Alaska ecosystem

The GOA exhibits a strong natural climate variability that can be superimposed with other stressors such as ocean acidification (OA) and global warming, leading to extreme and compound extreme events. This combination of multiple environmental stressors can exacerbate the response of sensitive marine organisms and therefore disrupt marine life in the region (Hauri et al. 2024). Recent studies (Hauri et al. 2021, 2024) have shown that the GOA is affected by two major modes of natural climate variability.

The first mode, called the Northern Gulf of Alaska Oscillation index (NGAO, Fig. 2, top panel), describes the strength of the offshore upwelling and the extent of the subpolar gyre (Hauri et al. 2021). The NGAO corresponds to the primary mode of variability in sea surface height (SSH). A negative NGAO phase (Fig. 2, top panel in cyan) is characterized by a strong cyclonic circulation leading to strong offshore upwelling that brings cold, acidic, and de-oxygenated waters into the upper water column. A positive NGAO phase (Fig. 2, top panel in magenta) is characterized by a weak cyclonic circulation leading to weak offshore upwelling and therefore brings less cold, acidic, and de-oxygenated waters into the upper water column.

The second mode of variability, called the Gulf of Alaska Downwelling Index (GOADI, Fig. 2, middle panel) quantifies the intensity of the coastal SSH anomalies in the GOA, indicating the strength of coastal downwelling (Hauri et al. 2024). The GOADI corresponds to the second mode of variability in SSH. The GOADI serves as a proxy for the intrusion of deep water onto the bottom of the continental shelf. During a negative GOADI phase (Fig. 2, middle panel, blue), SSH anomalies are low in the shelf area, leading to weaker downwelling that permits intrusion of cold, salty, de-oxygenated, and acidic deep water onto the bottom of the shelf. In contrast, a positive GOADI phase (Fig. 2, middle panel, yellow) is characterized by high SSH anomalies and strong downwelling, making deep water intrusions less likely.

The effects of this natural climate variability are visible in DIC at GAK9 (Fig. 2, bottom panel). At the surface and sub-surface, the detrended DIC anomaly (DIC_{anom}) shows a clear anti-correlation with the NGAO index (-0.43 , $p < 0.05$). During a negative NGAO phase, the offshore upwelling strengthens and thereby increases DIC in the upper water column of the GOA. The signal at depth disappears at GAK9 because it is located on the edge of the offshore upwelling, allowing only the upper water column to be affected. Interestingly, the anti-correlation decreases when considering a time lag of one month, indicating a direct impact of the NGAO on the



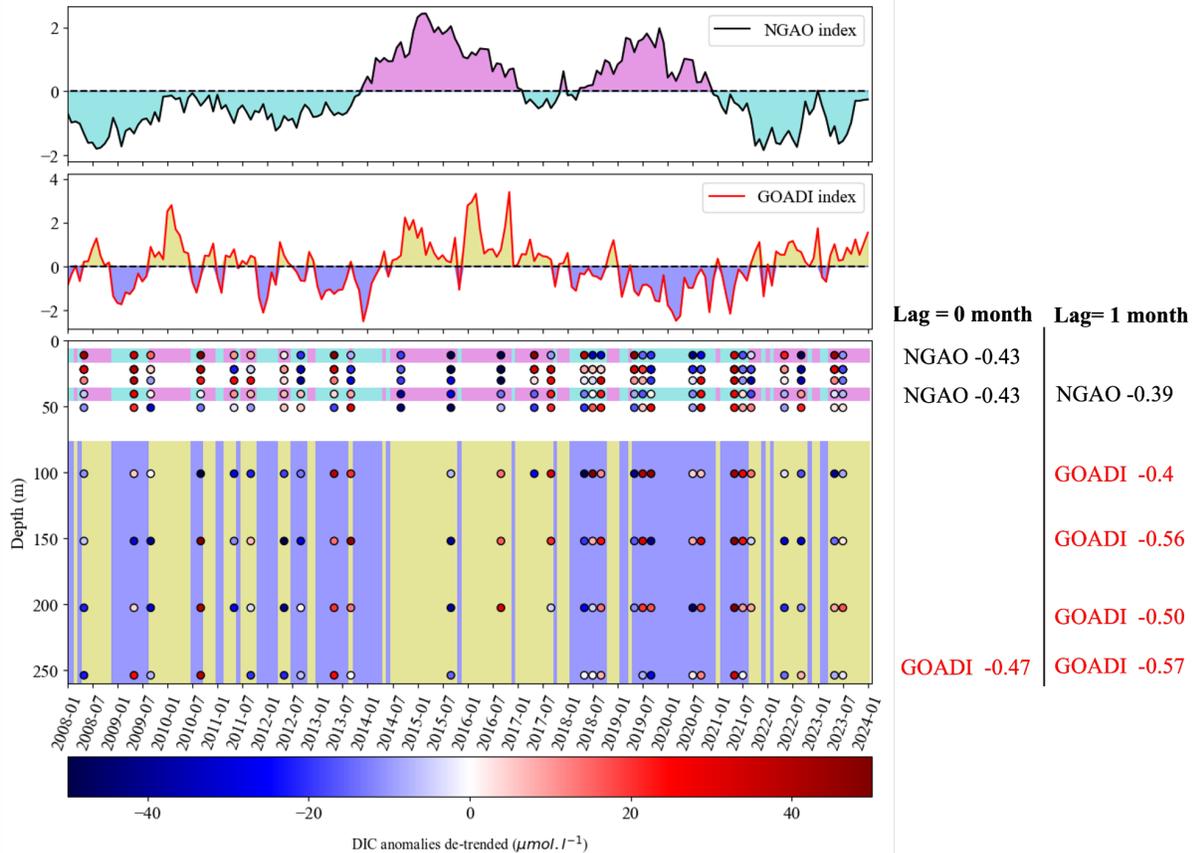
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surface DIC_{anom} . At the bottom (<250m), we observe an anti-correlation between DIC_{anom} and GOADI of ~ -0.47 ($p < 0.05$). During a negative GOADI phase, the weak coastal downwelling allows the intrusion of acidic deep water onto the continental shelf, increasing DIC (Hauri et al. 2024). The correlation between GOADI and the DIC_{anom} increases when considering one month lag, indicating that GOADI could be used as a predictor for bottom conditions.

The impact of the natural climate variability on the GOA has been shown in the past using model results (Hauri et al. 2021, 2024). However, this is the first time that such a correlation is shown based on in situ data. This is possible because of the duration of the time series. Despite the 15 year-long timeseries, disentangling the effect of OA from the effect of the natural climate variability remains a challenge. For example, in this case, only the deepest data points (<240 m) showed a statistically significant long-term trend. Shallower depths are most likely affected by other signals and thus more years of in situ data are still needed.





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Figure 2. Dissolved inorganic carbon (DIC) time-series at GAK9 and its correlation with the Northern Gulf of Alaska Oscillation index (NGAO) and the Gulf of Alaska Downwelling index (GOADI). The top panel shows the NGAO in the negative phase (cyan) and positive phase (magenta). The middle panel shows the GOADI in the negative phase (blue) and positive phase (yellow). Both indices are computed based on satellite sea surface height (Hauri et al. 2021, 2024). The bottom panel shows the detrended DIC anomaly (DIC - DIC average) at GAK9. The background colors on the bottom panel show the sign (positive or negative) of the NGAO (magenta or cyan, respectively) and GOADI (yellow or blue, respectively) index when a significant correlation ($p < 0.05$) exists between the data and the index. Finally, the correlation is given on the bottom right with no lag and one month lag in black for NGAO, and in red for GOADI. Data sources: 2008 - 2017 from Monacci et al. (2023), 2018 - 2021 from Hauri et al. (2021), and 2022 - 2023 preliminary data from this project.

NOAA Gulf of Alaska ecosystem status report

In the NOAA GOA ESR (Hauri et al. 2023), model and observation-based pH and Ω_{arag} data were used to give an overview of the state of ocean acidification in the GOA. Model output was derived from a high-resolution (4.5 km horizontal grid and 50 vertical levels) 3D coupled physics and biogeochemistry hindcast simulation of the Gulf of Alaska, known as the Regional Ocean Modeling System-Carbon, Ocean Biogeochemistry and Lower Trophic (ROMS-COBALT-GOA) marine ecosystem model that covered the period 1993 to the end of 2022 (Fig. 3). Observed bottom pH and Ω_{arag} at Seward Line stations GAK 5 and GAK 9 between 2018-2021 (Hauri et al. 2021) were also presented, along with preliminary data from the 2022 and 2023 Northern Gulf of Alaska Long Term Ecological Research (NGA LTER) cruises (Fig. 3C). In situ pH used in the ESR were calculated using CO2SYSv3 (Lewis and Wallace 1998) with dissociation constants for carbonic acid of Lueker et al. (2000), bisulfate of Dickson (1990), hydrofluoric acid of Perez and Fraga (1987), and the boron-to-chlorinity ratio of Lee et al. (2010), with nutrients assumed to be zero.

Ocean conditions at the seafloor were particularly acidic near the shelf slope in fall 2022 and on the middle of the shelf in spring 2023. Modeled time series at Seward Line stations GAK5 and GAK9 show statistically significant long-term decreasing trends of bottom water pH and Ω_{arag} , an indication for a steady degradation of the habitat of organisms sensitive to the effects of ocean acidification. Observed bottom pH at GAK 9 was particularly low (pH = 7.56, Fig. 3C). Data from Seward Line station GAK5, which is in the middle of the shelf, suggest that pH and Ω_{arag} were the lowest in spring 2023, compared to any other spring since 2019. A possible explanation could be that 2022 and 2023 were consecutive years of strong upwelling in the Alaska gyre



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(negative NGOA, Hauri et al 2021, Fig. 2), which generally leads to lower pH, Ω_{arag} , and oxygen concentration on the shelf.

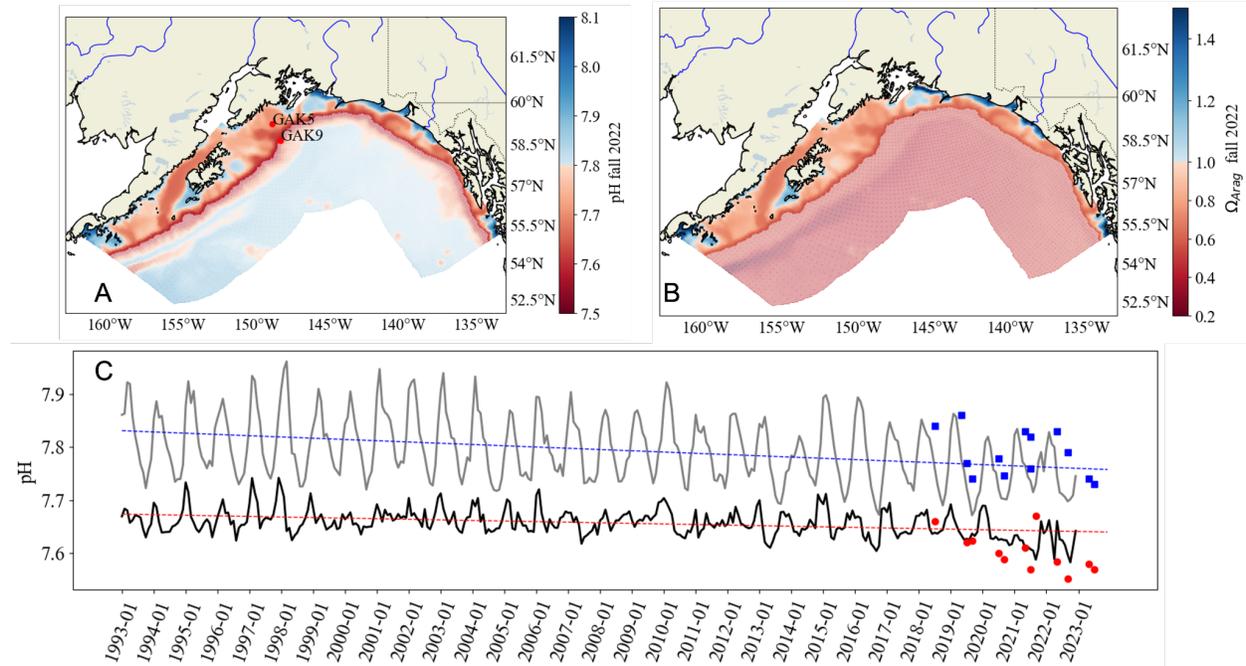


Figure 3. Fall 2022 bottom pH and Aragonite saturation state. Maps of fall 2022 (September, October, November) of bottom pH (A) and aragonite saturation state (Ω_{arag} , B). The faded area shows portions of the domain deeper than 500 m where the model vertical resolution decreases. The time series shows the modeled temporal evolution of pH (C) at the bottom of Seward Line stations GAK5 (gray line) and GAK9 (black line) between 1993 and 2022 (bottom depth of 170 m for GAK5 and 280 m for GAK9). The red circles show observations near the bottom of station GAK9 and the blue squares show in situ observations at station GAK5 between 2018 and 2023. The dotted line shows the linear regression for each time series (GAK5, -0.0023 /year, $R=-0.33$, $p < 0.01$ and GAK 9, -0.001 /year, $R=-0.37$, $p < 0.01$). Figure from Hauri et al. 2023.

Algorithm to estimate pH

Hydrographic inorganic carbon data were used to create an algorithm that estimates pH based on inputs of pCO_2 , temperature, and salinity. The algorithm can be applied to obtain estimates of pH from pCO_2 sensor measurements on glider and mooring platforms in the GOA, where pH sensor measurements are not available, following Hauri et al. (accepted). Here, the algorithm was



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validated using hydrographic data not included in the training dataset, showing agreement within 0.01 pH units (Fig. 4). Algorithm validation using pH and $p\text{CO}_2$ sensor data from the Gulf of Alaska Ecosystem Observatory (GEO) show agreement mostly within 0.05 pH units. The reduced accuracy of the algorithm applied to the GEO sensor measurements is likely due to interpolation of sensor measurements and inaccuracy of the pH sensor (Fig. 5). The algorithm will be published in a manuscript that is in preparation (led by Norgaard).

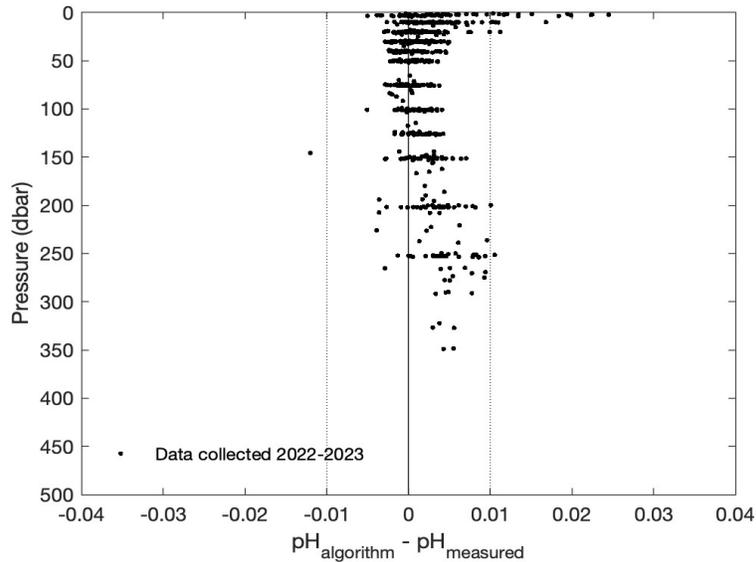


Figure 4. $p\text{CO}_2$ -based pH algorithm created and validated using hydrographic inorganic carbon data. Figure shows agreement mostly within 0.01.



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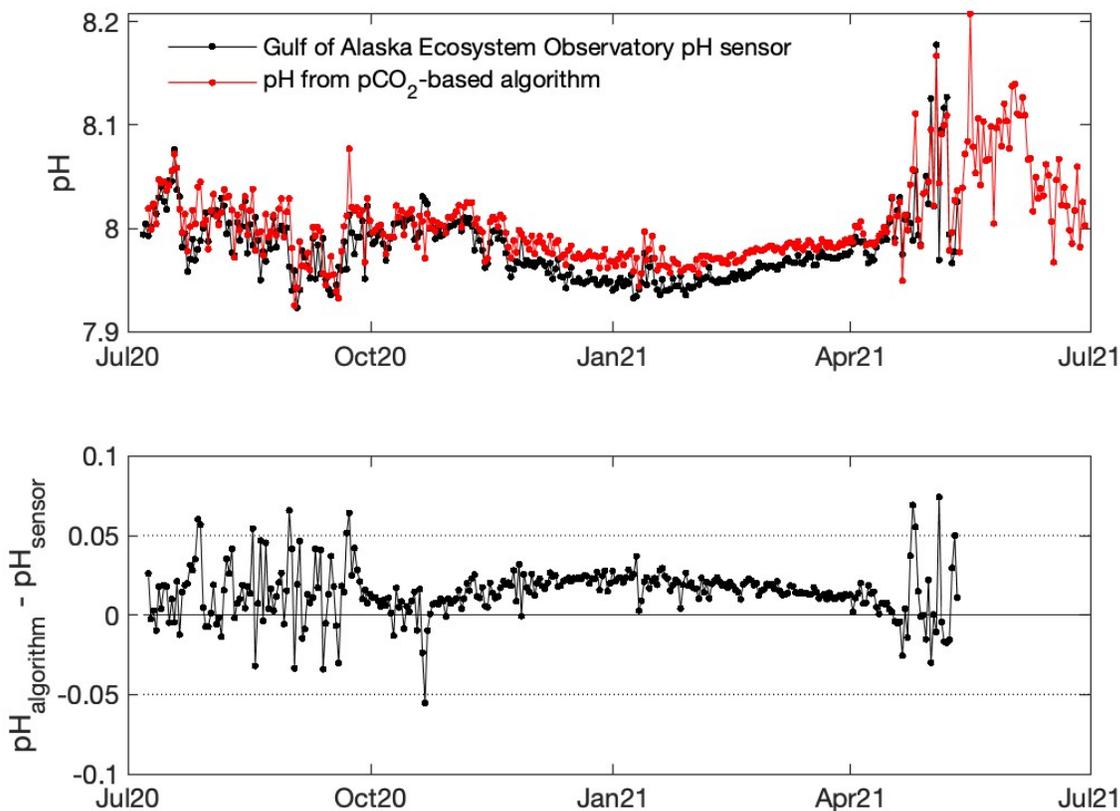


Figure 5. $p\text{CO}_2$ -based pH algorithm validated against pH sensor measurements made at the Gulf of Alaska Ecosystem Observatory. Algorithm estimates agree generally within 0.05.

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Dickson, A. G. 1990. Thermodynamics of the dissociation of boric acid in synthetic seawater from 273.15 to 318.15 K. Deep Sea Research Part A. Oceanographic Research Papers 37:755–766. [https://doi.org/10.1016/0198-0149\(90\)90004-F](https://doi.org/10.1016/0198-0149(90)90004-F).

Dickson, A. G., C. L. Sabine, and J. R. Christian, editors. 2007. Guide to best practices for ocean CO₂ measurement. Sidney, British Columbia, North Pacific Marine Science



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Monacci, N. M., J. N. Cross, S. L. Danielson, W. Evans, R. R. Hopcroft, J. T. Mathis, C. Mordy, D. Naber, K. L. Shake, K. Trahanovsky, H. Wang, T. L. Weingartner, and T. E. Whitley. 2023. Marine carbonate system discrete profile data from the Gulf of Alaska (GAK) Seward Line cruises between 2008 and 2017 (NCEI Accession 0277034). NOAA National Centers for Environmental Information. Dataset. <https://doi.org/10.25921/x9sg-9b08>. Accessed February 5, 2024.

Perez, F. F., and F. Fraga. 1987. Association constant of fluoride and hydrogen ions in seawater, *Marine Chemistry* 21:161–168. [https://doi.org/10.1016/0304-4203\(87\)90036-3](https://doi.org/10.1016/0304-4203(87)90036-3).

Sharp, J. D., D. Pierrot, M. P. Humphreys, J.-M. Epitalon, J. C. Orr, E. R. Lewis, and D. W. R. Wallace. 2023. CO2SYSv3 for MATLAB. <https://doi.org/10.5281/zenodo.7552554>.

Sulpis, O., E. Jeansson, A. Dinauer, S. K. Lauvset, and J. J. Middelburg. 2021. Calcium carbonate dissolution patterns in the ocean, *Nature Geoscience* 14:423–428. <https://doi.org/10.1038/s41561-021-00743-y>.

2. Products:

Peer-reviewed publications:

No new contributions for this reporting period.

Reports:

Hauri, C., T. Hurst, B. Irving, C. Long, and R. Pagès. 2023. Ocean Acidification in the Gulf of Alaska. Pages 62-67 in B. E. Ferriss, editor. *Ecosystem Status Report 2023: Gulf of Alaska, Stock Assessment and Fishery Evaluation Report*. North Pacific Fishery Management Council, Anchorage, Alaska. <https://apps-afsc.fisheries.noaa.gov/REFM/docs/2023/GOAecosys.pdf>.

Popular articles:

Norgaard, A., and C. Hauri. 2023. New support for ship-based ocean acidification monitoring in the Gulf of Alaska. *Delta Sound Connections*, 2023-2024. <https://pwssc.org/wp-content/uploads/2023/05/DSC-2023-FINAL-LR.pdf>



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Conferences and workshops:

No new contributions for this reporting period.

Public presentations:

Hauri C. 2023. Ocean acidification and ocean chemistry. Chugach Regional Resource Commission webinar on ocean acidification and ocean chemistry. November.

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](https://doi.org/10.24431/rw1k45g), version: 10.24431_rw1k45g_20230203T202101Z.

The 2022 data will be available on the GOA Data Portal by mid-March. We are currently working on restructuring our way of publishing the data, which took a little longer than expected.

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 PI coordinates with PWSSC on invoicing, reporting, and meeting attendance.



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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 (23120114-L; Russ Hopcroft) and GAK1 project (23120114-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

We engaged with the EVOSTC education and outreach projects with this group at the GWA-LTRM PI meetings in November 2022, January 2023, and November 2023 and we are looking forward to working with them to expand our capacity for bringing our science to new audiences.

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

We contributed ocean acidification information and narrative to NOAA's annual ecosystem status report for the GOA for the first time in 2023.

Native and Local Communities

PI Hauri serves as University of Alaska Fairbanks's accountability partner within the First Alaskan Institute's accountability partnership program and is a Tamamta affiliate faculty. She has participated in First Alaskan Institute led training sessions to attend the "Way of life" and "Boarding schools" Tribunals and has also participated in a Racial Equity Dialogue. The Hauri Lab is also closely working with the Alutiiq Pride Marine Institute on new co-produced proposals.



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Specific to the spill-affected area, project graduate student Addie Norgaard presented OA findings to Chugach Regional Resources Commission sponsored events, including their March gathering and a webinar on ocean acidification and ocean chemistry.

4. Response to EVOSTC Review, Recommendations and Comments:

As addressed in the proposal comments and recommendations by reviewers, and in our continuing efforts to ensure the highest quality data products, we planned to perform two dye experiments. The experiments were 1) a double dye experiment to generate a dye perturbation correction based on Li et al. (2020), and 2) an experiment using purified meta-Cresol Purple (mCP) indicator dye to address and correct any bias introduced by indicator impurities in samples from across the EVOS area previously analyzed in our lab.

The dye experiment, using purified mCP indicator dye (purchased from Dr. Byrne's lab at the University of South Florida), was carried out during the analysis of samples collected on the fall 2022 cruise. In brief, five consecutive spectrophotometric pH measurements using unpurified mCP indicator dye (-4-H JENA Engineering GmbH, S0045 from TCI lot number PKFSM-DQ) were carried out, and immediately before (or after) five measurements with purified mCP indicator dye were taken of the same seawater sample. This was repeated for 10 seawater samples, with a mean difference of 0.04 ± 0.014 . However, due to complications switching between pure mCP and unpurified mCP with the HydroFIA pH, results are inconclusive (Fig. 6). The experiment will be repeated using the lessons learned during our first attempt. For example, a dedicated experimental window using certified reference materials (CRMs) from different batches rather than running the experiment during the standard analysis of cruise samples, transferring samples/CRMs to gas-tight bags to remove possible biases due to gas exchange as samples are open longer, and carefully setting up the purified and unpurified mCP with a Luer stopcock adapter.



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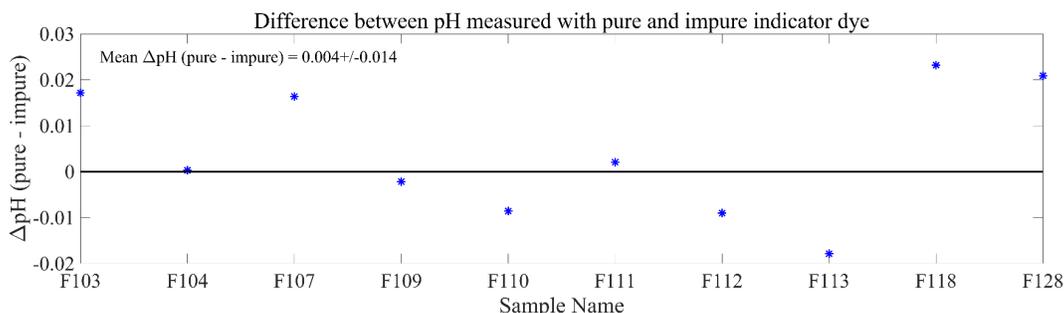


Figure 6. Inconclusive dye purity experiment results. The difference between the average pH (5 measurements) taken with purified and unpurified mCP for each seawater sample used in the experiment.

Progress was made on the planning and preparation for the double dye experiment during this reporting period. Due to the design of the HydroFIA pH instrument as a flow-through system, the ideal experimental setup of adding additional dye to the same sample volume and collecting further measurements was determined to be impossible. However, working with the HydroFIA pH manufacturers, -4-H JENA Engineering GmbH, we were able to come up with a procedure to change the injected dye volume between successive measurements. With this procedure, and the use of gas-tight bags and a dedicated experimental window, we have a plan to perform the double dye experiment over the next reporting period.

Following the recommendation to investigate the preparation of sodium carbonate solutions in our lab (Dickson et al. 2007) and storing the standard solutions and/or CRMs in gas-tight bags due to the shortage of CRMs available for purchase, we determined it was not feasible for our lab to take on the preparation of sub-standards, or sodium carbonate solutions. Fortunately, so far, we have been able to purchase all the necessary CRMs to analyze our samples.

An internal consistency study of the seawater inorganic carbonate system is planned for the next reporting period. We will use our data collected in the spill-affected region that has been analyzed for three inorganic carbonate parameters (pH, DIC, and TA) to perform this investigation looking into different thermodynamic dissociation constants available within CO2SYS (Sharp et al. 2023). We are keen to investigate this as the recent paper by Sulpis et al. (2020) found that the carbonic acid dissociation constants of Lueker et al. (2000), widely used including our previously published data (Hauri et al. 2021) may underestimate $p\text{CO}_2$ in cold regions (below $\sim 8^\circ\text{C}$) and, therefore, overestimate pH.



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5. Budget:

**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	\$73,945
Travel		\$0	\$331	\$0	\$365	\$0	\$696	\$1,085
Contractual		\$0	\$0	\$0	\$0	\$0	\$0	\$8,159
Commodities		\$43,875	\$30,750	\$30,750	\$30,750	\$31,750	\$167,875	\$32,586
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%	\$28,808	\$25,462	\$22,171	\$22,625	\$23,155	\$122,221	\$28,944
(non-equipment)								
SUBTOTAL		\$144,042	\$127,311	\$110,856	\$113,123	\$115,774	\$611,107	\$144,719
General Administration (9% of subtotal)		\$12,964	\$11,458	\$9,977	\$10,181	\$10,420	\$55,000	N/A
PROJECT TOTAL		\$157,000	\$138,800	\$120,900	\$123,400	\$126,200	\$666,400	
Other Resources (In-Kind Funds)		\$0	\$0	\$0	\$0	\$0	\$0	

We continue to be behind in spending because of the delay in issuance of the NOAA grant. Some purchases are still pending and not reflected in FY23 cumulative spending. We will see greater expenses in the upcoming years. Our graduate student, Addie Norgaard, will be graduating this summer. We will need to hire a part-time technician for cruise participation and laboratory work, which will cost more money. Norgaard also was partially funded through the Roger Markle endowment.