CONNECTICUT SEA GRANT PROJECT REPORT

Please complete this progress or final report form and return by the date indicated in the emailed progress report request from the Connecticut Sea Grant College Program. Fill in the requested information using your word processor (i.e., Microsoft Word), and e-mail the completed form to Syma Ebbin syma.ebbin@uconn.edu, Research Coordinator, Connecticut Sea Grant College Program. Do NOT mail or fax hard copies. Please try to address the specific sections below. If applicable, you can attach files of electronic publications when you return the form. If you have questions, please call Nancy Balcom at (860) 405-9107.

Please fill out all of the following that apply to your specific research or development project. Pay particular attention to goals, accomplishments, benefits, impacts and publications, where applicable.

Name of Submitter: **Craig Tobias**

Date of Report submission: **10/31/24**

Project #: **(R/CMC-20-CTNY), RFA#21077, EPA Award # LI-00A00284**
Check one: [ ] Progress Report [**X**] Final report

Duration (dates) of entire project, including extensions: From **[03/01/2021] to [08/31/2024]**.

Project Title or Topic: **Constraining models of metabolism and ventilation of bottom water in Long Island Sound using oxygen isotopes**

Principal Investigator(s) and Affiliation(s):

1. **Craig Tobias / University of Connecticut (PI)**
2. **James O'Donnell / University of Connecticut**
3. **Mark Altabet / U. Mass Dartmouth**

A. COLLABORATORS AND PARTNERS: None to date

B. PROJECT GOALS AND OBJECTIVES:

1. Quantify vertical and horizontal O_2 fluxes associated with mixing in western Long Island Sound (W-LIS).

2. Quantify the fractional contributions of benthic vs water column respiration in W-LIS.

3. Construct, parameterize, validate a coupled hydrodynamic biogeochemical simulation model of O_2 and its $^{18}O_2$ isotopic composition in the surface and bottom waters of W-LIS.

C. LISS CCMP IMPLEMENTATION ACTIONS: (*List the top 3 primary CCMP Implementation Actions that this project addresses. LISS CCMP Implementation Actions can be found at https://longislandsoundstudy.net/2021/01/ccmp-implementation-actions-supplemental-documents/*

1. **WW-8**: Conduct studies and research to better understand the ecosystem's response to nitrogen reductions to support an evaluation of the 2000 Dissolved Oxygen TMDL.

2. **WW-28**: Maintain and enhance the management utility of water quality monitoring of watershed nutrient loads and ecosystem responses to Long Island Sound and its embayments..

3. **SM-1**: Regularly update and refine the high-priority science needs relating to the understanding and attainment of management objectives and ecosystem targets.

D. PROGRESS:

Field and Laboratory Activities:
Field measurements quantified water column respiration and spatial gradients in oxygen, and oxygen isotopes in western Long Island Sound. Field work was executed through a series of deployments of the automated respiration chambers (ARCS), diel cruises, and synoptic sampling in partnership with CT DEEP. ARCS were deployed at the bottom and in the mixed layer from June till October in each year of the project at LISICOS stations WLIS and EXCR. A total of seven diel cruises were conducted in western Sound that captured pre hypoxia (two cruises), hypoxic conditions (three cruises), and post hypoxia mixing (two cruises). Vertically resolved diel sampling was conducted at two-hourly intervals at a station mid-way between the EXCR and WLIS LISICOS monitoring stations. The following parameters were measured: salinity; temperature, dissolved O_2 and ^{18}O. Vertical current profiles were measured using an upward looking ADCP mounted on benthic frames. Temperature profiles were monitored continuously using thermistor arrays extending through the water column. Vertically resolved synoptic measurements of the same parameters were made across the western sound to characterize the horizontal spatial gradient. As part of the CT DEEP sampling program, biweekly depth for dissolved O_2, $^{18}O_2$, were collected throughout the water column at multiple stations in the western Sound in 2022. Diel cruises occurred in 2021, 2023, and 2024.

Laboratory activities consisted of water and sediment core incubations to determine the water column and benthic respiration isotope fractionation factors used in the modeling. Enrichment factors for respiration associated with the water column and with the benthos were measured via a series of laboratory incubations using a variety of methods historically used to measure these factors. For water column respiration, surface and bottom water was collected from WLIS and EXCR on every cruise and incubated for up to one week at field temperature in the dark. Changes in O_2 and $\delta^{18}O_2$ were used to calculate the water column respiration enrichment factor. For benthic respiration, eight sediment cores and bottom water were collected from a station midway between WLIS and EXCR on three of the cruises. Overlying water in cores was replaced with filter-sterilized bottom water and incubated at in situ temperature until 70% of the starting dissolved oxygen had been consumed. Changes in O_2 and $\delta^{18}O_2$ were used to calculate the water column respiration enrichment factor. The O_2 and $\delta^{18}O_2$ analysis for the diel cruises and synoptic multi-station sampling was conducted in co-PI Altabet's lab at U. Mass. Dartmouth. The O_2 and $\delta^{18}O_2$ analysis for the fractionation factor incubations was conducted by Tobias at UConn.

Modeling: CoPI O'Donnell developed a one-dimensional model of the variability in the structure of $\delta^{18}O_2$ that included the effects of gas exchange, photosynthesis, respiration the water column and benthos, and vertical mixing. The effects of fractionation by gas exchange, production and respiration were also included and the fractionation factors were estimated from laboratory work and recent literature. Choices for the respiration rate parameters were guided by the measurements of the ARCs and laboratory incubations. The gas exchange parameters were obtained from the literature. Production rates were prescribed to vary with the time of day and day of year, and vertically with an exponential (light extinction) decay scale. Since the direct measurement of the vertical fluxes of heat, salt and O_2 for a season is both difficult and expensive, we used the one-dimensional model GOTM (Umlauf and Burchard, 2005) to make estimates using more readily obtained measurements. The GOTM-based model was developed by graduate student M. Abbasian. The near-surface wind was measured at the LISICOS buoys, the vertical structure of the currents using bottom-mounted ADCPs, and a the along-estuary (east-west) gradients in salinity and temperature were obtained from our ship surveys and those of CTDEEP. GOTM simulations were evaluated by comparing predictions of the structure and variability of the temperature and salinity profiles to observations, and the derived vertical eddy diffusivity (or mixing) coefficients used in the $\delta^{18}O_2$ model.

SUMMARY OF FINDINGS TO DATE:

The relationship between dissolved oxygen concentration and its $\delta^{18}O$ value was the core metric used to evaluate the relative importance of different components of the oxygen mass balance, including the contributions of water column vs benthic respiration contributing to declining oxygen concentrations. Each component of the oxygen budget has a unique O_2 vs $\delta^{18}O$-O_2 trajectory that serves as a diagnostic for the relative importance of a specific pathway (Fig. 1). In particular, water column respiration removes O_2 and results in a large enrichment in $\delta^{18}O$ of the residual O_2, while benthic respiration decreases O_2 without changing the $\delta^{18}O$. Photosynthesis adds O_2 using water as the source of oxygen which has a uniquely low, or depleted $\delta^{18}O$. Gas transfer pushes both the O_2 and the $\delta^{18}O$-O_2 towards air saturated equilibrium values (intersecting dashed lines; Fig. 1). Mixing flattens, or compresses, the trajectories in O_2 vs $\delta^{18}O$-O_2 space to weighted averages of the water masses being mixed.

Continuous in-situ measurements and laboratory derived fractionation factors

The ARCS-based respiration measurements provided a continuous record of water column respiration (Fig. 2). Water column respiration varied systematically across a 5-fold range. Measured rates were higher in shallow water vs deep (Fig. 3). Mean water column respiration rates in the shallow, mid, and bottom waters were 60, 50, and 40 mmol O_2 $m^{-3}d^{-1}$. ARCs rates were higher than those measured previously using synoptic bottle incubations which largely missed periods of high rates that were captured by the ARCS (Fig. 3). ARCs rates were used to calibrate the oxygen/isotope model. Benthic respiration in the model was calibrated using rates from summertime core incubations previously measured (Tobias 2018 and Mazur et al. 2020;

Fig. 4A). Summertime benthic respiration rates in western LIS ranged from 0.4 – 0.9 mmol O_2 m^{-2} hr^{-1}. Benthic respiration followed first-order kinetics and was parameterized in the model as such (Fig. 4B). Laboratory-derived isotope enrichment factors (ε) for water column respiration yielded a well-constrained value of -20 ‰ ± 1‰ from n=12 incubations. Laboratory derived enrichment factors for benthic respiration ranged from 0 to -4 ‰ from n=6 incubations.

Physical mixing was characterized using multiple time series records. The first record was temperature and salinity in surface and bottom waters, at LISICOS stations WLIS and EXCR (also known as EXRX; Fig. 5). These records revealed the onset of seasonal stratification coincident with hypoxia formation, several mixing events that punctuated the summer and temporarily relaxed hypoxia, and the subsequent breakdown of stratification in the fall with full ventilation of the water column. The second record was from high vertical resolution thermistor arrays (Fig. 6). These data provided similar temperature information as the LISICOS buoys but with better vertical structure needed to evaluate the vertical eddy diffusivity coefficients estimated by the GOTM model. The third record was derived from CTD casts on each of diel cruises (Fig. 7). These data were used primarily for calculating the air-saturated equilibrium O_2 concentrations that accompanied the $\delta^{18}O$-O_2 measurements. They also indicate that the O_2 and $\delta^{18}O$-O_2 measured at a single fixed station over a diel cycle reflect the combined effects of the photosynthetic cycle as well as tidal excursion effects that transport different water parcels of different composition past the Eulerian sampling framework.

Oxygen and oxygen isotope patterns

The O_2 and $\delta^{18}O_2$ distribution measured synoptically throughout western LIS, and at a fixed over a diel period revealed the general, and expected, pattern of decreasing O_2 concentration with increasing depth accompanied by enrichment of the $\delta^{18}O_2$ - O_2 consistent with the fractionation effects of water column respiration (Figs. 8-11). The in situ effective enrichment factors measured at all synoptic stations however were all less than the laboratory derived enrichment factor of -20 ‰ (Figs 9 and 10). Further, the enrichment factors got smaller at all stations in western LIS during the onset of hypoxia (Fig. 10). Previously, in situ enrichment factors below -20 ‰ were interpreted as reflecting a contribution of benthic respiration (Altabet, 2018). This explanation would require that benthic respiration becomes proportionally more important during hypoxia. However benthic respiration rates decline at lower oxygen concentrations (Fig. 4B), and there should be a sharp leveling in $\delta^{18}O_2$ - O_2 with declining O_2 concentrations below the pycnocline during hypoxia onset which was not observed during hypoxia. Only the May 2024 diel showed the flattening of the $\delta^{18}O_2$ - O_2 with declining O_2 concentration in deeper water that would be characteristic of more benthic respiration. This pattern occurred at a time when O_2 concentrations were still relatively high, thus relaxing kinetic constraints on benthic respiration, and in close proximity to a spring bloom period of 'fresh' organic matter sinking to the benthos. It is possible that benthic respiration is an important contributor to oxygen demand just preceding summertime conditions, and is the focus of current work.

Aside from May 2024, all other data shows that the lowering of the in situ enrichment factor from May through August resulted from changes that occurred throughout the water column. An alternate explanation for the decreasing effective enrichment factor that would result from changes throughout the water column would be an increase in the photosynthetic contribution of isotopically light O_2 that is mixed downward in the water column. The isotopically light O_2

derived from photosynthesis effectively offsets some of the fractionation from water column respiration and yield an in situ enrichment factor less than -20 ‰. The intercepts of the Rayleigh plots (Fig. 10) reflect decreasing $\delta^{18}O_2$ - O_2 values during hypoxia onset indicative of increasing contributions of O_2 from photosynthesis. This pathway is the only source of O_2 that can provide O_2 that is isotopically lighter than the atmosphere (24 ‰). All intercepts for the synoptic sampling are below 24 ‰ (Fig 10). All the diel measurements similarly show photosynthetically derived light O_2 in shallow waters, and during all periods, except for Oct 2021 when there was strong gas transfer, the isotopically light photosynthetic signal is mixed downward into deeper water (Fig 11). That signal is strong enough to be retained as a $\delta^{18}O_2$ - O_2 value lighter than air saturated water even at O_2 concentrations that are as low as half air saturation concentrations. These data are reflected in the lower left quadrant of each panel in Figure 11 and clearly support the proposed mechanism that water column respiration of photosynthetically derived isotopically light O_2 is the cause of the effective enrichment factors falling below the expected -20 ‰ value expected for water column respiration, and that more benthic respiration is unlikely to be the cause. The role of water column vs benthic respiration was tested using the oxygen/isotope model.

The physical mixing in the oxygen isotope model was derived from output of the GOTM model that used time series temperature and salinity records to estimate the vertical eddy diffusivity coefficient (Figs. 12,13). The oxygen/isotope model simulated the distributions of O_2 and $\delta^{18}O_2$ - O_2 (Fig. 14) and used the GOTM results. Model results simulated the diel O_2 and $\delta^{18}O_2$ - O_2 during hypoxia (August) with good skill with or without temperature functionality for respiration using nominal eddy coefficients from the range provided from GOTM (Fig. 15). Good model fits could only be obtained with water column respiration accounted for over 90% of the total system respiration. The small contribution of benthic respiration equated with rates that were consistent with measurements (Fig 4A). During hypoxia the contribution from benthic respiration in the model was limited by the oxygen concentration at the sediment surface which was in turn limited by the vertical mixing. The relative importance of benthic respiration could be increased in simulations that increased vertical mixing but yielded output that could not reproduce the observed O_2 and $\delta^{18}O_2$ - O_2 relationship (Fig. 16). The use of the $\delta^{18}O_2$ - O_2 ensured that both the split of water column and benthic respiration, and vertical mixing were accurately represented in the model.

Conclusions

The addition of $\delta^{18}O_2$ - O_2 measurements to O_2 measurements, and their inclusion into modeling revealed that water column respiration is a much larger oxygen sink than benthic respiration during hypoxia in LIS. The balance between these two respiratory pathways in the spring, perhaps setting the stage for summertime hypoxia, remains undetermined however. It is the focus of on-gong work. The isotope tracer also revealed the large and persistent signature of photosynthetically derived O_2 propagated through the water column in all seasons, but particularly in summer. Given this additional source of O_2, it is likely that both water column respiration and mixing are larger than previously thought during hypoxia in order to yield the same net O_2 concentrations that are measured in western LIS. The incorporation of $\delta^{18}O_2$ - O_2

into models provides an important constraint to ensure that models are mechanistically correct, and thus enhanced in their predictive capabilities.

E. PROJECT PUBLICATIONS, PRODUCTS, PRESENTATIONS AND PATENTS: *(Include published materials with complete references, as well as those which have been submitted but not yet published and those in press. Please attach electronic versions of any journal articles, reports, and abstracts not previously provided.)*

Journal Articles (List URLs): **none to date**

Conference Papers: **none to date**

Proceedings or book chapters: **none to date**

Web sites, Software, etc.:

Oxygen/isotope model

Technical Reports/Other Publications: **none to date**

Other Products (including popular articles): **none to date**

Publications planned / in progress:

One publication including observational and experimental data will be prepared. At least two modeling papers will result from the work. One PhD dissertation will result from this project.

Patents: *(List those awarded or pending as a result of this project.)* **none to date**

Presentations and Posters:

Abbasian, M., O'Donnell, J., Tobias, C. 2022. Modeling eddy diffusivity and oxygen isotopes to characterize hypoxia in Long Island Sound. Feng Symposium 2022, Groton CT. Poster.

Altabet, M. Tobias, C. O'Donnell, J. 2023. Stable isotope constraints on the oxygen budget of eutrophic Long Island Sound. ASLO, Majorca.

O'Donnell, J., Tobias, C., Altabet, M., Abbasian, M., 2023. A Model for the Vertical Structure of the Oxygen Isotope Ratio in a Hypoxic Estuary: Long Island Sound. Gordon Research Conference. Poster.

Abbasian, M., O'Donnell, J., Tobias, C. 2024. The Structure and Variability of Vertical Transport by Turbulence in Western Long Island Sound. Long Island Sound Research Conference, Port Jefferson, NY. Poster

Tobias, C., Altabet, M., O'Donnell, J. 2024. Using oxygen stable isotopes to assess respiration – the conspiracy of mixing and other things. Long Island Sound Research Conference, Port Jefferson, NY

F. **FUNDS LEVERAGED**: *(If this Sea Grant funding facilitated the leveraging of additional funding for this or a related project, note the amount and source below.)*
None

G. **STUDENTS**: ***(****Document the number and type of students supported by this project.)*
*Note: **"Supported"** means supported by Sea Grant through financial or other means, such as Sea Grant federal, match, state and other leveraged funds. "**New"** students are those who **have not** worked on this project previously. "**Continuing"** students are those who **have** worked on this project previously. If a student volunteered time on this project, please use section G, below.*

Total number of **new*** K-12 students who worked with you:
Total number of **new** undergraduates who worked with you:
Total number of **new** Masters degree candidates who worked with you:
Total number of **new** Ph.D. candidates who worked with you:

Total number of **continuing**** K-12 students who worked with you:
Total number of **continuing** undergraduates who worked with you:
Total number of **continuing** Masters degree candidates who worked with you:
Total number of **continuing** Ph.D. candidates who worked with you:

Total number of volunteer hours: **Zero**

*(Note: ***New** students are those who have not worked on this project previously. ****Continuing** students are those who have worked on this project previously.)*

In the case of graduate students, please list student names, degree pursued, and thesis or dissertation titles related to this project.

*Student Name: Merhnoosh Abbasian.
Degree Sought: PhD Oceanography
Thesis or Dissertation Title: **OXYGEN ISOTOPE CONSTRAINTS ON HYPOXIA MODELING**
Date of thesis completion: **05/14/26**
Expected date of graduation: **05/14/26**

H. **VOLUNTEER HOURS:**
(List the number of hours provided to the project by volunteers, i.e., individuals who were not compensated in any way or for whom involvement is not part of their paid occupation. This could be students or citizens. What was their contribution?)
None

I. PICTORIAL: Please provide high resolution images/photos of personnel at work, in the field or laboratory, equipment being used, field sites, organism(s) of study. Attach images as separate files (do not embed). Include links to websites associated with the research project. Please include proper photo credits and a caption with date, location, names of people, and activity. These images are useful to document your project in future CTSG publications, websites and presentations.

Attached at end of document after figures.

J. HONORS AND AWARDS: *(List any honors or awards received during the reporting period, for anyone working on the project. This can be for best paper or poster, university awards, etc.*) Specify: **None to date**.

a) Name of person or group receiving recognition:
b) Name of award or honor:
c) Group or individual bestowing the award or honor:
d) What it was for:
e) Date:

K. DATA MANAGEMENT PLANS: Proposals funded in 2014-2016 and later cycles are required to have a data management plan in place. All environmental data and information collected and/or created must be made visible, accessible, and independently understandable to general users, free of charge or at minimal cost, in a timely manner (typically no later than two years after the data are collected or created). This is a reminder that your CTSG funded research data needs to be archived and accessible as outlined in the data management plan you submitted with your proposal. If there have been any modifications, adjustments or new information available regarding the location, timing, type, formatting and metadata standards, content, sharing, stewardship, archiving, accessibility, publication or security of the data produced please elaborate here.

FOR FINAL DEVELOPMENT AND RESEARCH GRANT REPORTS, PLEASE COMPLETE THIS SECTION:

L. PROJECT OUTCOMES AND IMPACTS

RELEVANCE OF PROJECT: *(Describe briefly the issue/problem / identified need(s) that led to this work.)*

Hypoxia models are built to simulate time series changes in dissolved oxygen concentration. This metric is a net measurement and the models can achieve good skill either by correctly representing processes and rates, or by incorrectly representing processes that cancel each other out. It is the problem of ‘getting the right answer for the wrong reasons’. Those models have poor predictive capacity.

RESPONSE: *(Describe briefly what key elements were undertaken to address the issue, problem or need, and who is/are the target audience(s) for the work.)*

This project added an additional constraint in the form of $^{18}O – O_2$. The ^{18}O-O_2 abundance responds uniquely to different components of the oxygen mass balance. Thus it provided an excellent constraint in that the model must now properly simulate both the oxygen concentration and its $\delta^{18}O$-O_2 composition.

RESULTS: *(Summarize findings and significant achievements in terms of the research and any related education or outreach component; cite benefits, applications, and uses stemming from this project, including those expected in the future. Include qualitative and quantitative results.)*

See summary of findings in Section D - Progress.

Consider the following as they apply to your research and any related outreach/education.

- What new tools, technologies, methods or information services were developed from this work? Have any been adopted / implemented for use and by whom?

  The new tool is the addition of the ^{18}O-O_2 isotopic constraint into models that simulate hypoxia.

- What are the environmental benefits of this work? Have policies been changed? How has conservation (of ecosystems, habitats or species) been improved?

  Better hypoxia models that are mechanistically correct and therefore more robust predictors of future change.

- What are the social payoffs of this work? Who has benefited from this work? Have attitudes / behaviors of target audience changed? Elaborate. Have policies been changed?

  Better predictions of hypoxia responses to management actions and climate drivers inform management strategies and appropriately calibrate expectations of extant changes in hypoxia duration and/or extant.

- What are the economic implications / impacts of this work? (Where possible, please quantify.) Have new businesses been created /or existing businesses retained as a result of this research? Have new jobs been created or retained? Are new businesses or jobs anticipated?

  The management actions noted above equate to nutrient reduction implementation. To date, those expenditures total in the billions of dollars and should be informed by the best possible models.

J. Stakeholder Summary (This is an abstract of your research and findings written for a lay audience)

Western Long Island Sound (LIS) suffers from seasonally low dissolved oxygen in deep waters. Oxygen levels can fall so low that they threaten the health of marine organisms that live in the water and on the bottom. These low oxygen periods are referred to as 'hypoxia'. Much effort has been spent to build mathematical models to predict the severity and duration of hypoxia. These models have to consider multiple sources and losses of oxygen in water and bottom sediments. Different processes can mask each other, making it difficult to make models that accurately each of the processes. Getting the processes ‘right’ however is the key to a model that is a good predictor. Luckily the dissolved oxygen molecule contains chemical information locked in it that reveals the history of the different processes that might have added or removed oxygen. This project used that chemical information and incorporated it into a hypoxia model to make sure that the model predictions were correct, and correct for the right reasons. The project results showed: 1) that oxygen consumption by microorganisms in the water is much more important for creating low oxygen conditions when compared to oxygen consumption of the sediments on the bottom of LIS; 2) photosynthesis in shallow water that is mixed downward is an important pathway for replenishing oxygen all year, but especially in the summer when hypoxia starts to form in deeper water; 3) all of the processes that are producing and consuming oxygen in LIS are probably occurring at rates faster than previously thought. Collectively the results, and the improved model from this project will help to inform smart decisions about nutrient management designed to reduce extent and severity of hypoxia in LIS.

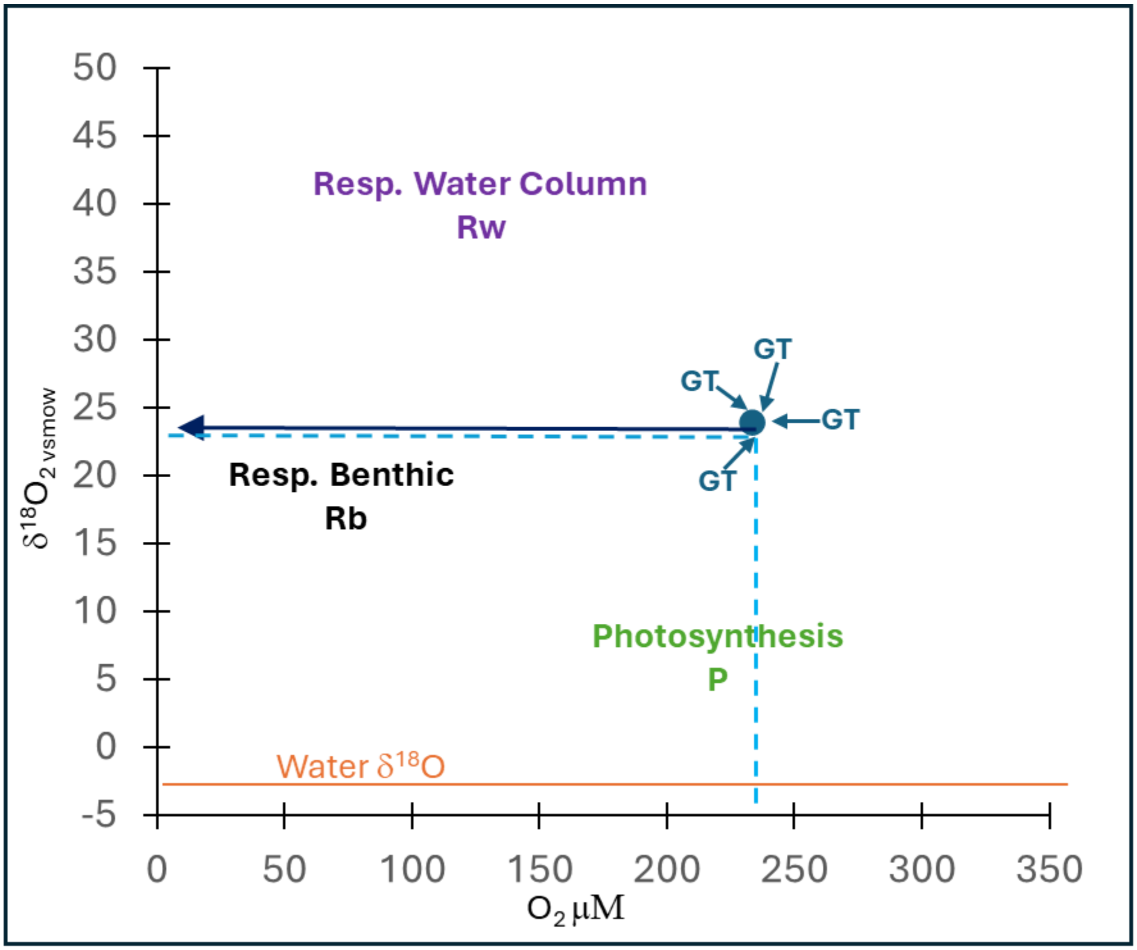

Figure 1. Idealized $\delta^{18}O$-O_2 and O_2 changes of a water parcel starting at air saturated equilibrium (blue dot) resulting from individual components of the dissolved oxygen mass balance. GT is gas transfer. Water $\delta^{18}O$ is the isotopic composition (-2 per mil) of oxygen produced from photosynthesis.

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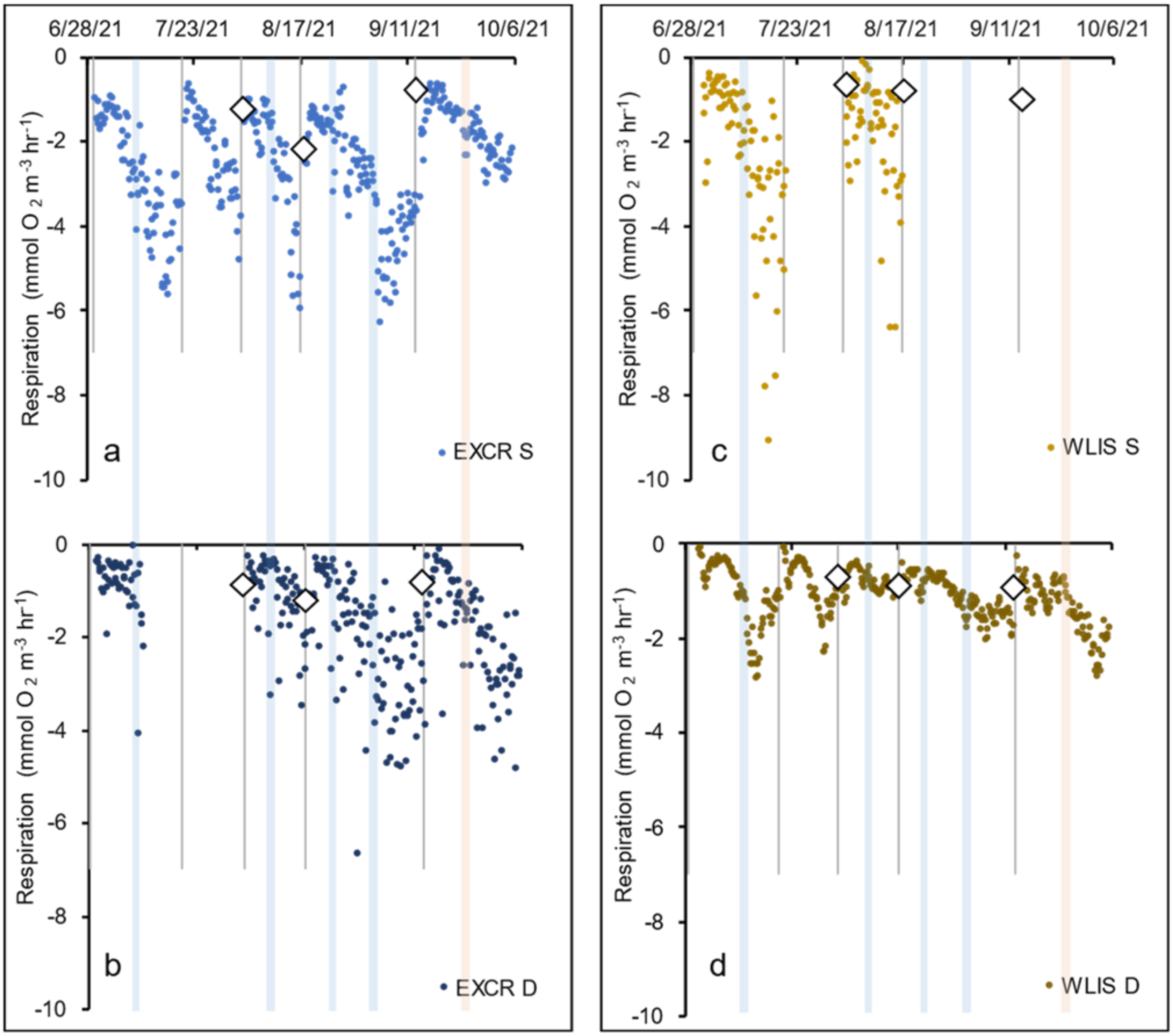

Figure 2. In situ respiration rates measured in surface and bottom waters at EXCR (a, b), and WLIS (c, d) in 2021. Each data point represents a three-point running average of continuous rates measured from six-hour incubations. Diamond symbols represent average rates from laboratory incubations corresponding to initial rates for each deployment. ARC deployment intervals are bounded by vertical gray lines. Blue vertical lines represent storm and rain events, and the red vertical bar represents seasonal overturning of the water column. Rates determined in situ with ARCS. 2022 data shown, but similar data was collected in all project years.

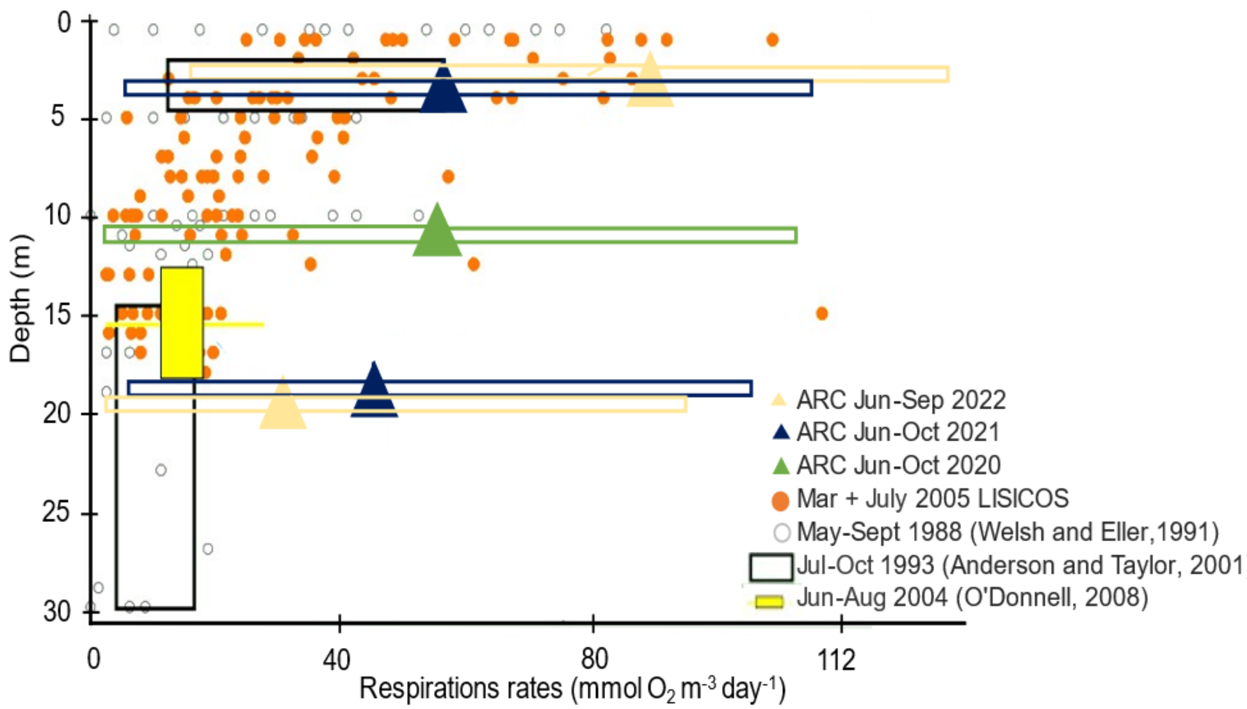

Figure 3. Vertical distribution of respiration rates in Western LIS from previous studies with ARC-derived rates measured in this study (yellow, blue and green triangles). Yellow, blue and green horizontal lines represent the range of average daily ARCS rates measured at each depth by the ARCs; the height of the triangles represent the range of water depths seen by the ARCS. ARCS rates were used to calibrate water column respiration in the oxygen / isotope model.

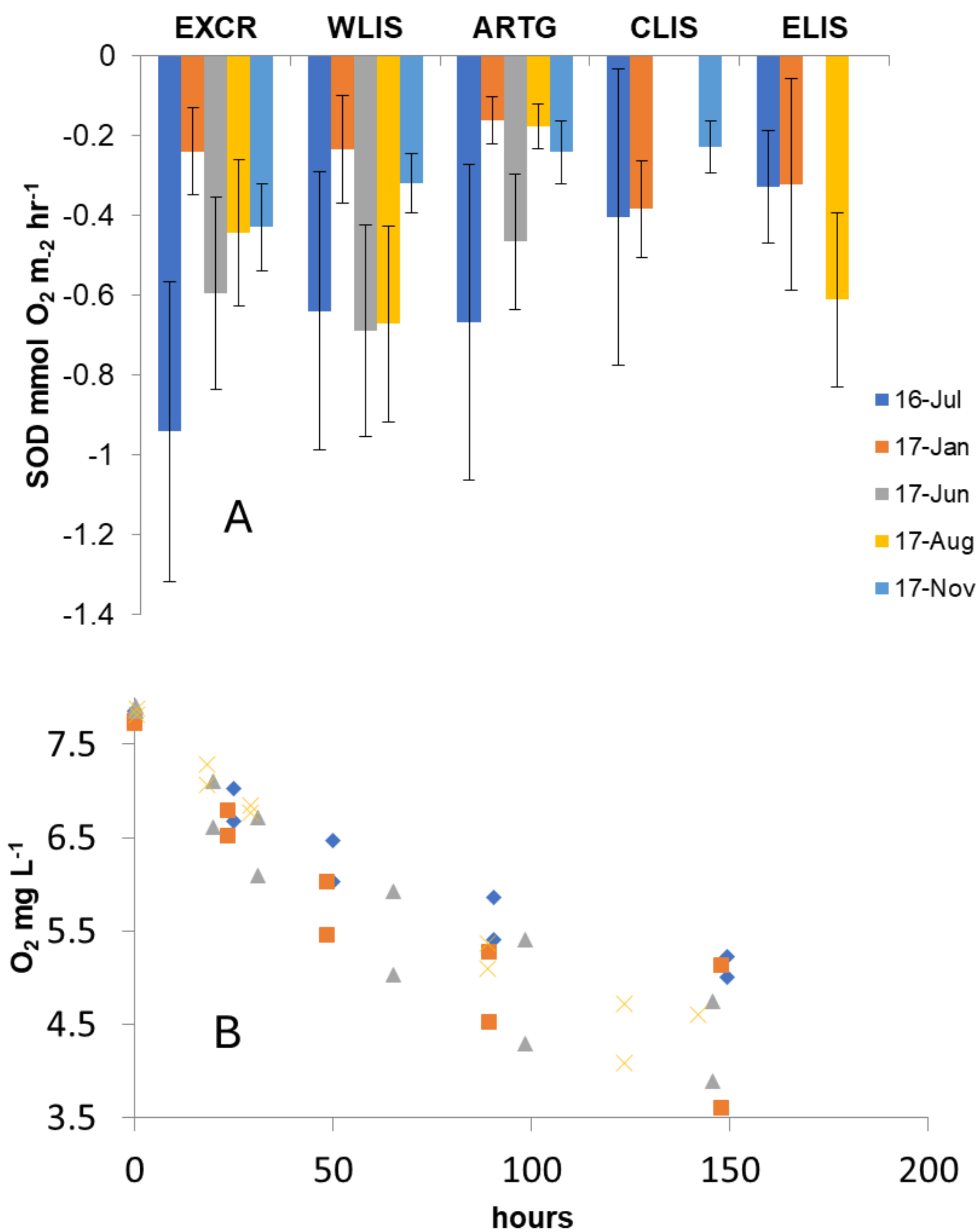

Figure 4. Sediment oxygen demand (SOD) – panel A. Time series dissolved O_2 concentrations measured during sediment-water core incubations –panel B. Rates are from Tobias, 2018. Rates and kinetics were used to parameterize and calibrate benthic respiration in the oxygen/isotope model.

Figure 5. Salinity, temperature, and dissolved oxygen measured in bottom waters at WLIS and EXRX LISICOS stations. Data was used to calibrate the GOTM model.

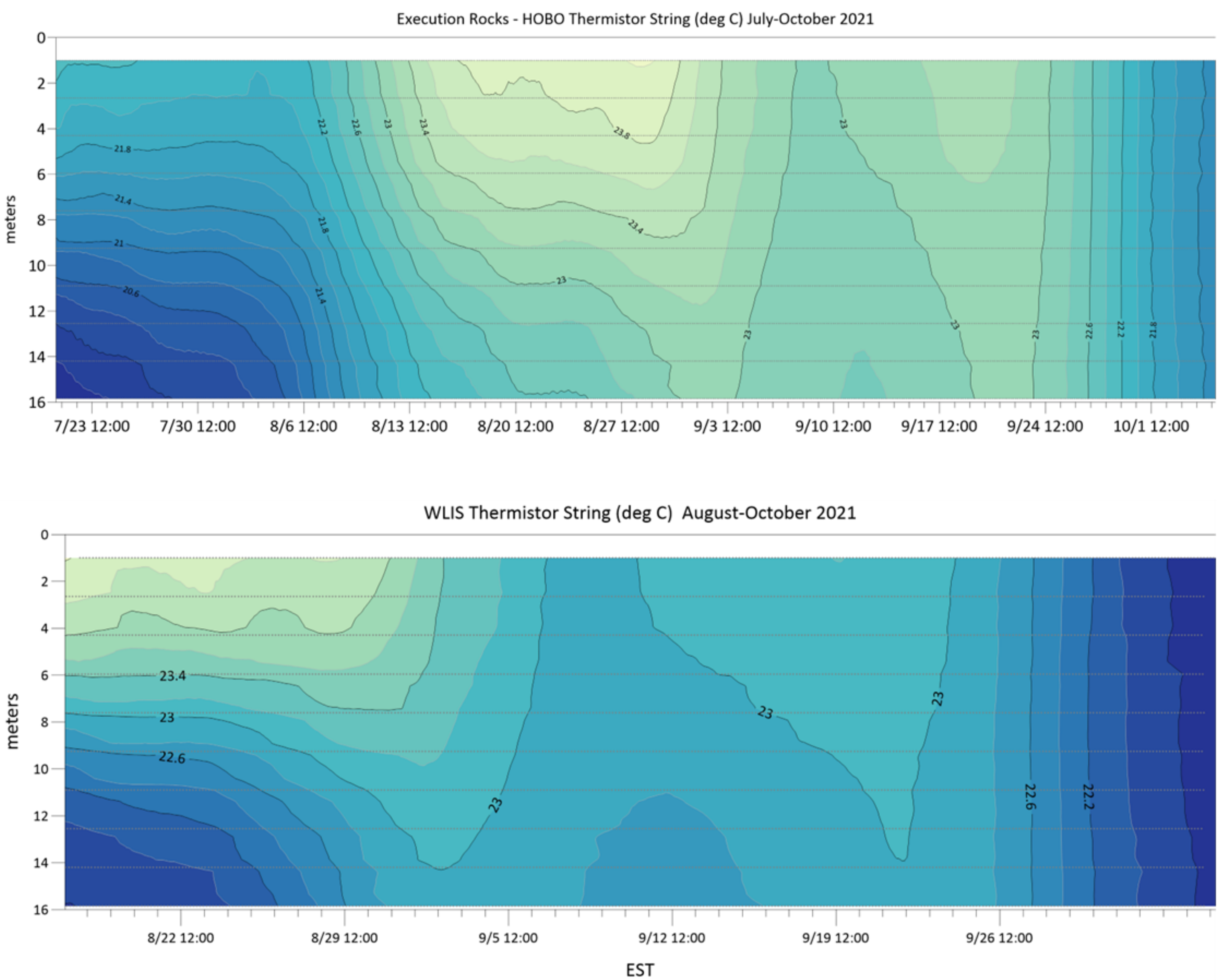

Figure 6. Thermistor string records from LISICOS stations WLIS and EXRX used to derive vertical eddy diffusivity coefficients in the GOTM model. Coefficients were then assimilated into the oxygen/isotope model to parameterize vertical mixing.

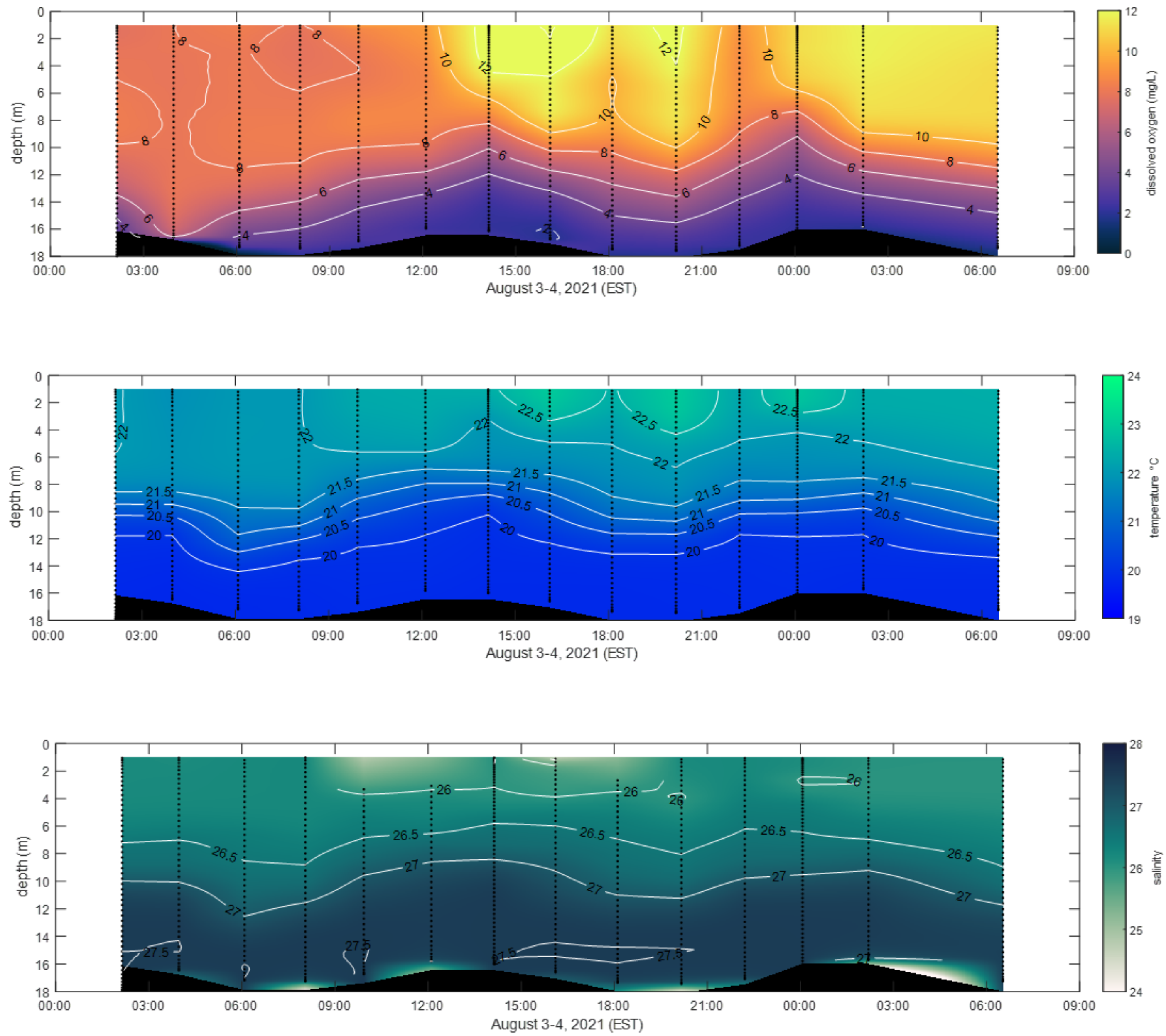

Figure 7. Example CTD profiles collected during each diel cruise. Temperature and salinity was used to calculate equilibrium dissolved oxygen concentrations. CTD oxygen data, combined with $\delta^{18}O$-O_2, provided the validation data set for the oxygen/isotope model.

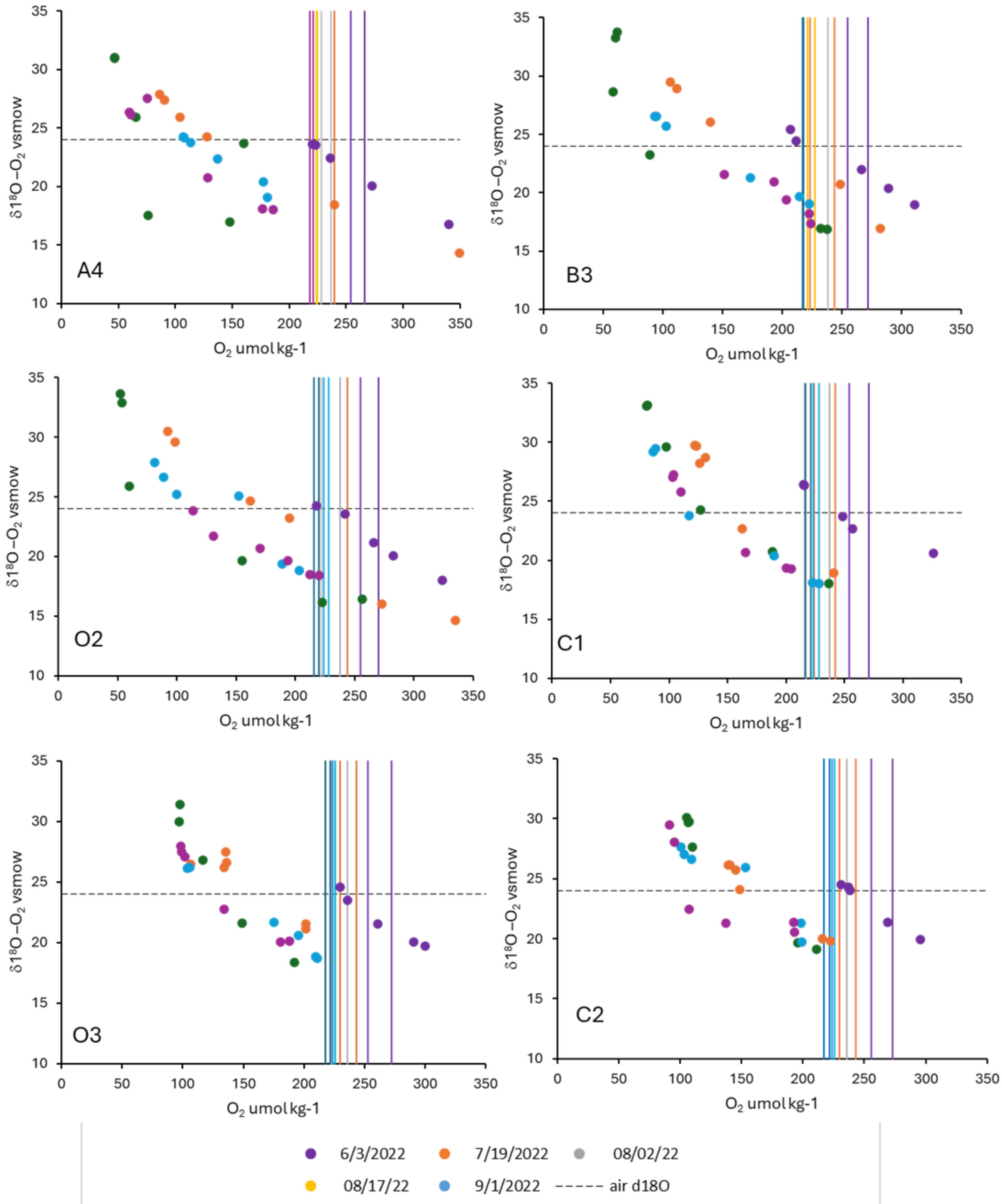

Figure 8. Vertically resolved synoptic distribution of O_2 and $\delta^{18}O\text{-}O_2$ from six stations in western LIS. Station locations from west to east are: A4 → B3 → O2 → C1 → O3 → C2 . Vertical lines denote air saturated equilibrium O_2 concentrations. Dashed horizontal line is the $\delta^{18}O\text{-}O_2$ value for air saturated water absent production and/or respiration.

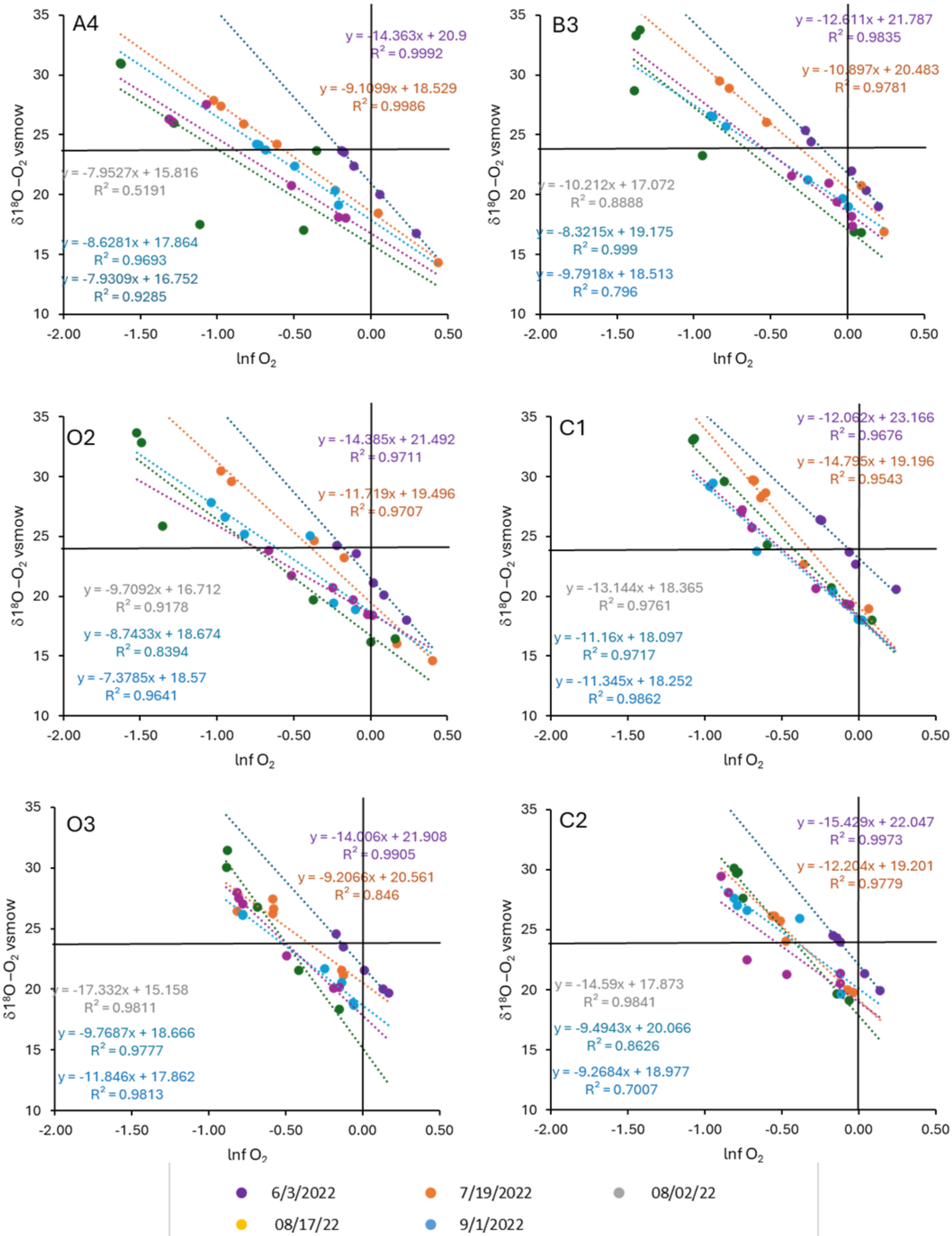

Figure 9. Synoptic Rayleigh fractionation plots from six stations in western LIS. The regression slope denotes the effective enrichment factor exhibited in situ that is the net of fractionations of all processes affecting the O_2 concentration and mixing. The intercept is the $\delta^{18}O$-O_2 value at a concentration that is equivalent to the air saturated equilibrium dissolved O_2 concentration.

	A4			B3			O2		
	A4 ε slope	A4 int	r^2	B3 ε slope	B3 int	r^2	O2 ε slope	O2 int	r^2
3-Jun	-14.3	20.9	0.99	-12.6	21.8	0.98	-14.4	21.5	0.97
19-Jul	-9.1	18.5	0.99	-10.9	20.5	0.98	-11.7	19.2	0.97
2-Aug	-7.9	15.8	0.52	-10.2	17.1	0.89	-9.7	16.7	0.92
17-Aug	-8.6	17.8	0.97	-8.3	19.2	0.99	-8.7	18.7	0.83
1-Sep	-7.9	16.7	0.93	-9.8	18.5	0.8	-7.4	18.5	0.96

	C1			O3			C2		
	C1 ε slope	C1 int	r^2	O3 ε slope	O3 int	r^2	C2 ε slope	C2 int	r^2
3-Jun	-12.1	23.2	0.97	-14.0	21.9	0.99	-15.4	22	0.99
19-Jul	-14.8	19.2	0.95	-9.2	20.6	0.85	-12.2	19.2	0.98
2-Aug	-13.1	18.4	0.97	-17.3	15.2	0.98	-14.6	17.9	0.98
17-Aug	-11.2	18.1	0.97	-9.8	18.7	0.98	-9.5	20.1	0.86
1-Sep	-11.3	18.3	0.98	-11.3	17.9	0.98	-9.3	19	0.7

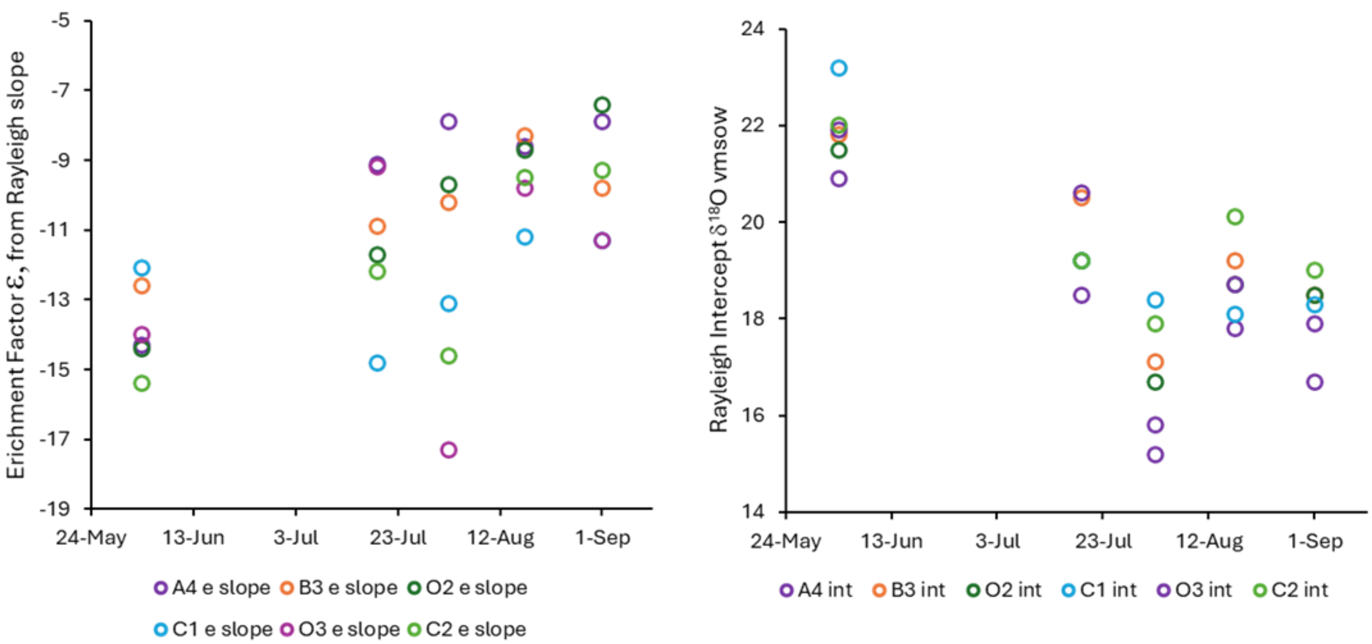

Figure 10. Rayleigh plot summary of effective enrichment factors and intercepts from six stations in western LIS.

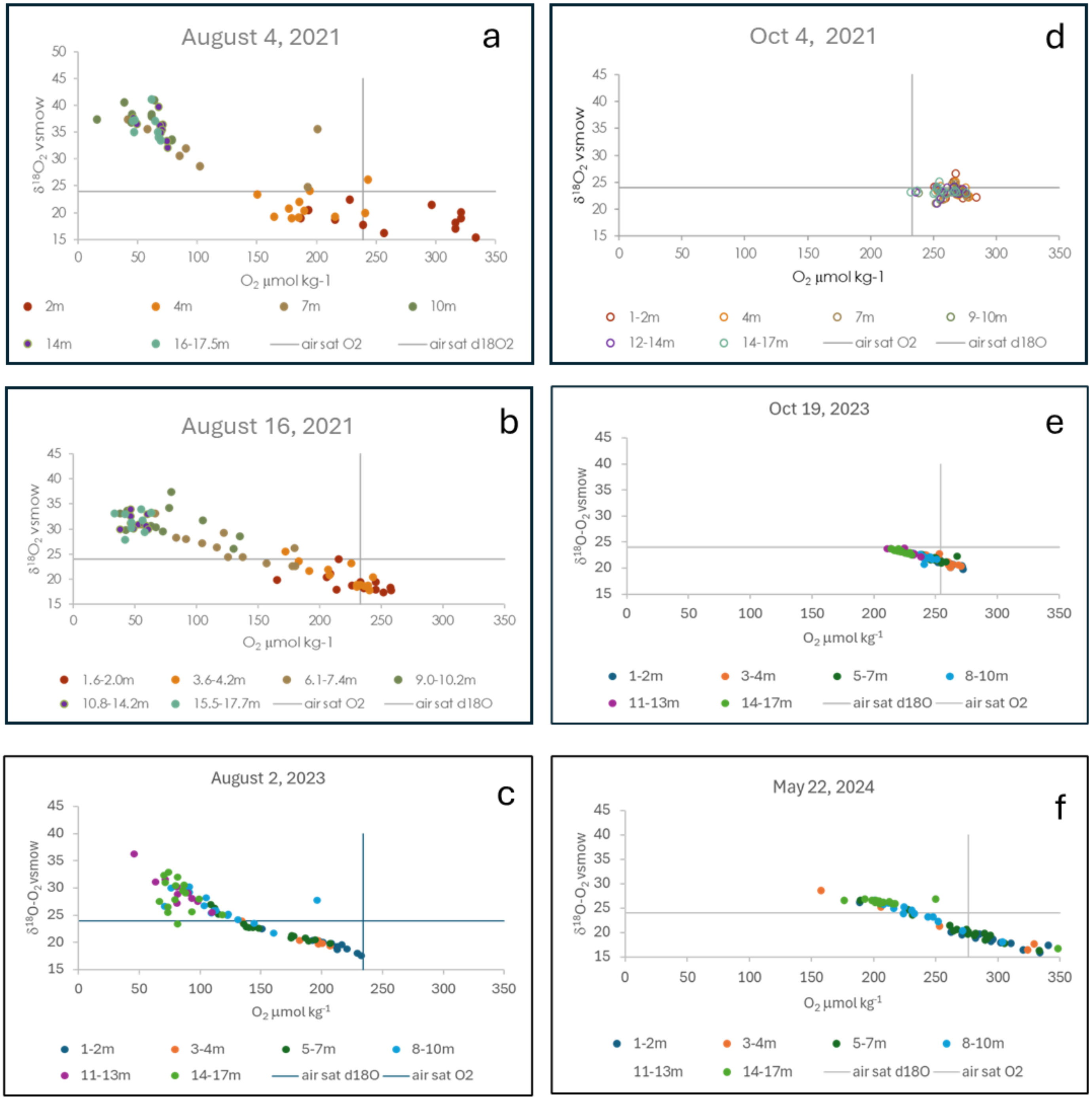

Figure 11. Dissolved O_2 and $\delta^{18}O$-O_2 in western LIS at station Mid-4 over a diel cycle. August (a,b,c), October (d,e), and May (f) are periods of hypoxia, post-hypoxic mixing, and pre-hypoxia, respectively.

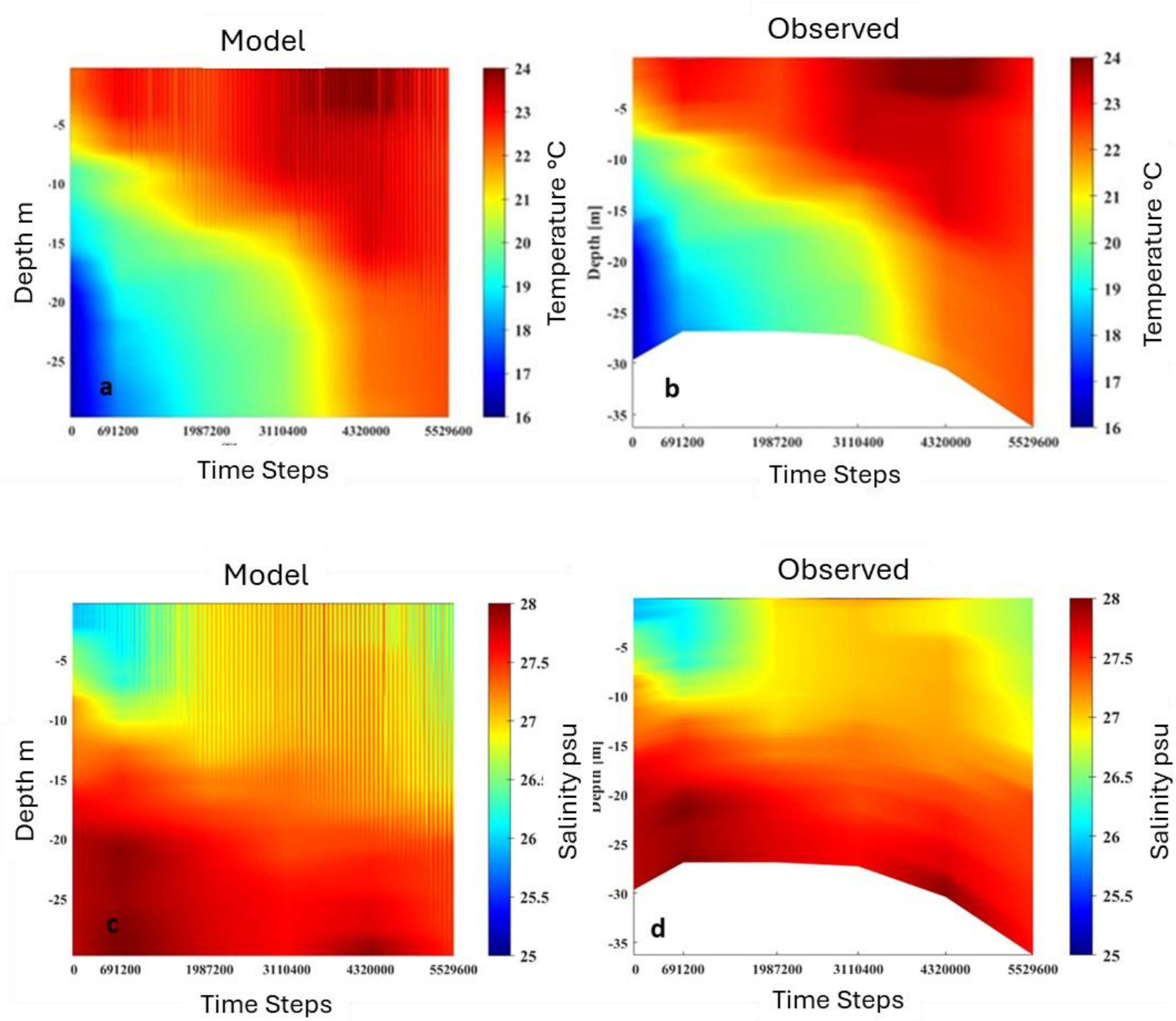

Figure 12. Observed and GOTM simulated temperature (a.b) and salinity distribution (c.d) for western LIS in 2021.

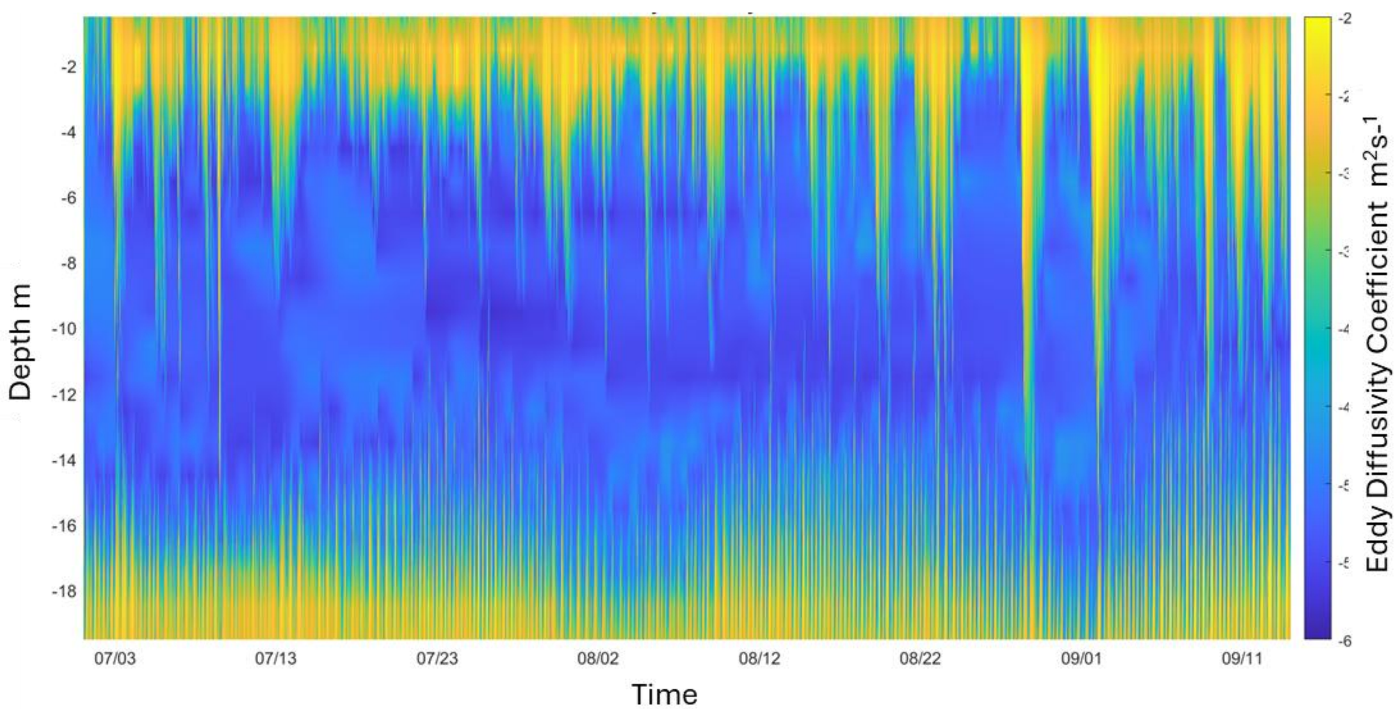

Figure 13. Vertical eddy diffusivity coefficients (mixing) modeled (GOTM) to reproduce observed temperature and salinity profiles in western LIS in 2021.

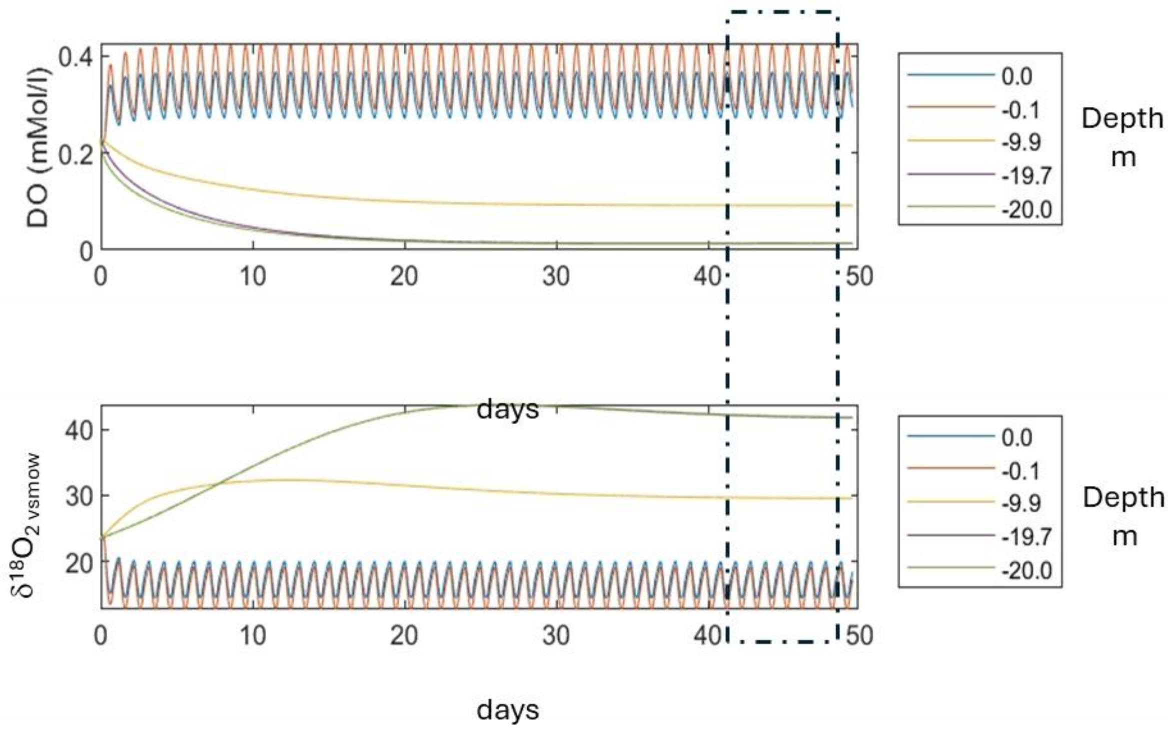

Figure 14. Oxygen isotope model simulation of vertical distribution of O_2 and $\delta^{18}O$-O_2. The model resolves ^{18}O and ^{16}O independently at each time step and is parameterized with ARCS water column respiration data, measured fractionation factors, and vertical mixing from GOTM (Figure 8), and LIS literature values for gross primary production and benthic respiration. Model spin up and stabilization period to reach steady state distributions of O_2 and $\delta^{18}O$-O_2 (dashed box). Model was run to simulate hypoxic periods and parameters were adjusted to best-fit the observed diel O_2 and $\delta^{18}O_2$ distributions during August.

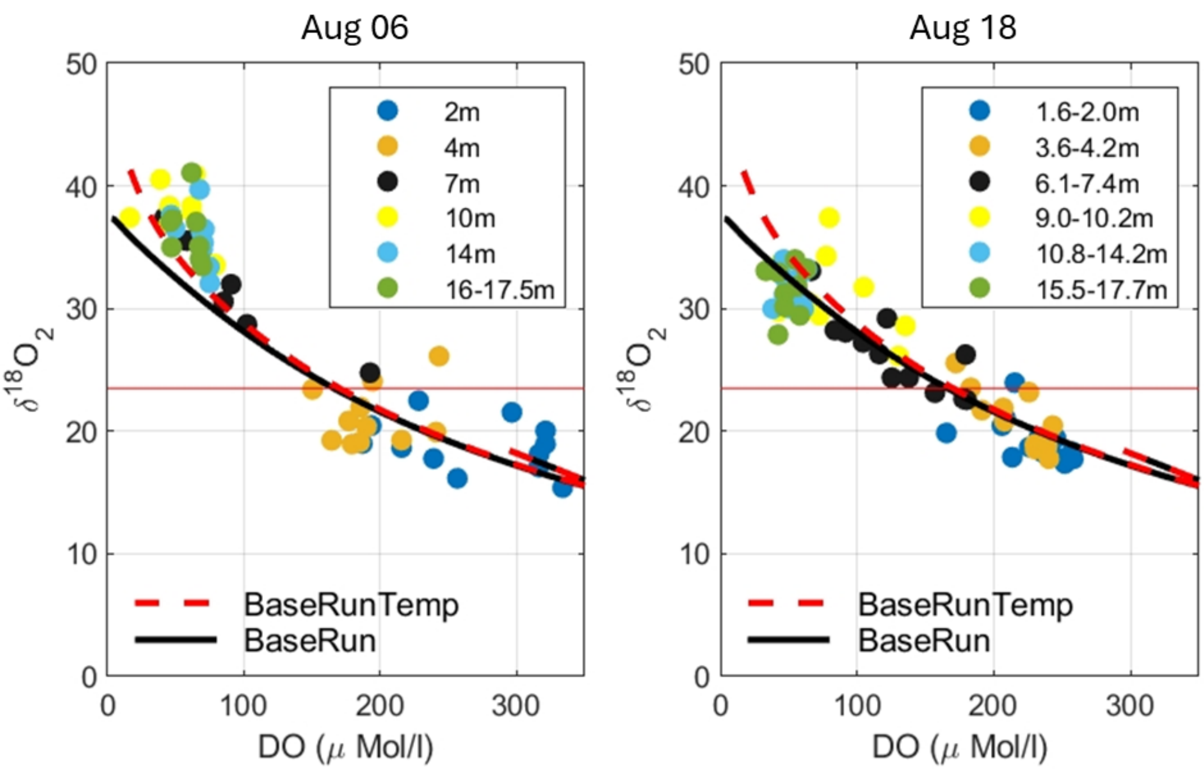

Figure 15. Steady state model simulations (solid lines) of the measured vertical distribution of O_2 and $\delta^{18}O$-O_2 (symbols) in August 2021. Red and black lines indicate model runs with and without temperature functionality for respiration. All model runs required that water column respiration (Rw) be 10-20 times larger than benthic respiration (Rb) in the summer. Variance in measured values are attributable to diel and tidal excursion effects.

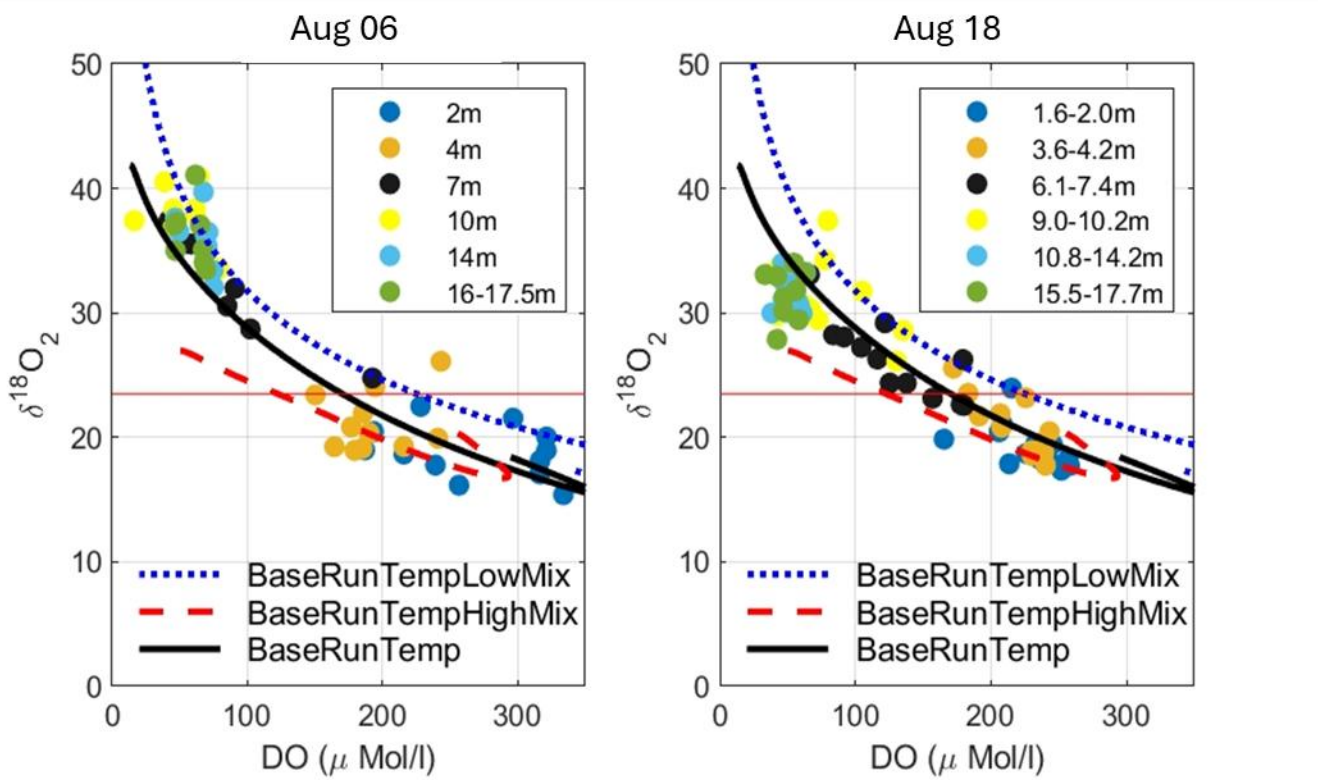

Figure 16. Steady state model simulations (solid lines) of the measured vertical distribution of O_2 and $\delta^{18}O\text{-}O_2$ (symbols) in August 2021 – sensitivity of mixing. All model runs include temperature functionality for respiration. Black, red-dashed, and blue-dashed lines denote nominal mixing using GOTM-derived eddy diffusivity, 2 times nominal mixing, and ½ nominal mixing respectively. High mixing flattens the O_2 and $\delta^{18}O\text{-}O_2$ trajectory as expected. Benthic respiration is more important in the high mixing scenario but causes the simulation to deviate considerably from the measured O_2 and $\delta^{18}O\text{-}O_2$.

Field activities. From upper left clockwise: Alex Frenzel in the filtering nest; ARCS deployment; Rosette sampling on the RV Connecticut.