

Clumped isotope verification of $\delta^{18}\text{O}$ -based freshwater mussel shell growth chronology for a high-resolution climate and river discharge record

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Introduction

Stable isotopes in freshwater mussel shells can be used to reconstruct climate, river discharge, water source, and salinity. In the Brazos River, a large semi-arid sub-tropical river in Central Texas, water isotope values and temperature variation cause the oxygen isotope signal predicted for aragonite to be irregular and nonperiodic, complicating environmental reconstruction. Clumped isotope values from mussel shells provide temperature estimates that serve as anchor points to align high-resolution shell $\delta^{18}\text{O}$ values to the river data set and to other shell $\delta^{18}\text{O}$ series. Then shell isotope values can be used to reconstruct river discharge, water source, and salinity.

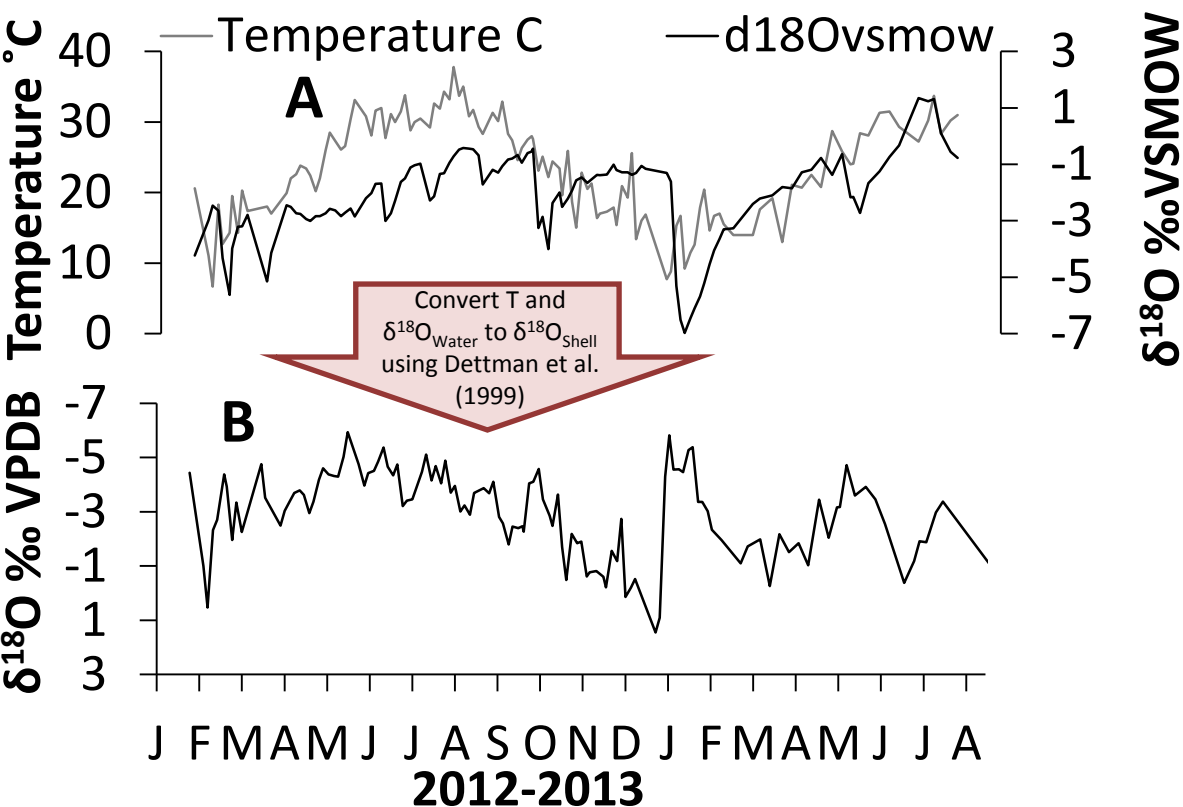


Figure 1. Brazos River oxygen isotope and temperature values from 2012-2013 in College Station, TX (A), and predicted aragonite $\delta^{18}\text{O}$ using Dettman et al. (1999) (B).

Location and Methods

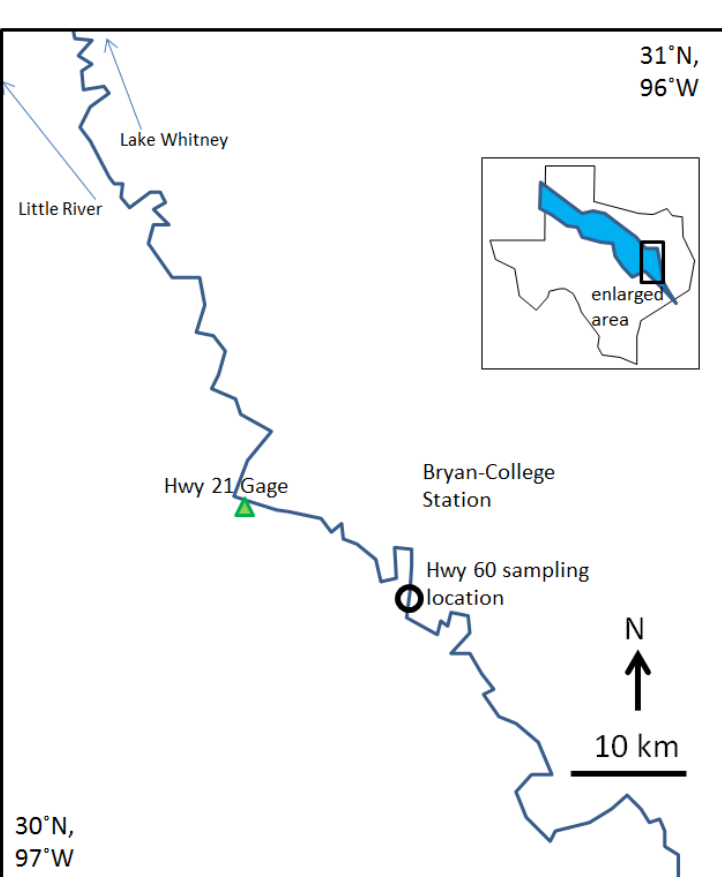
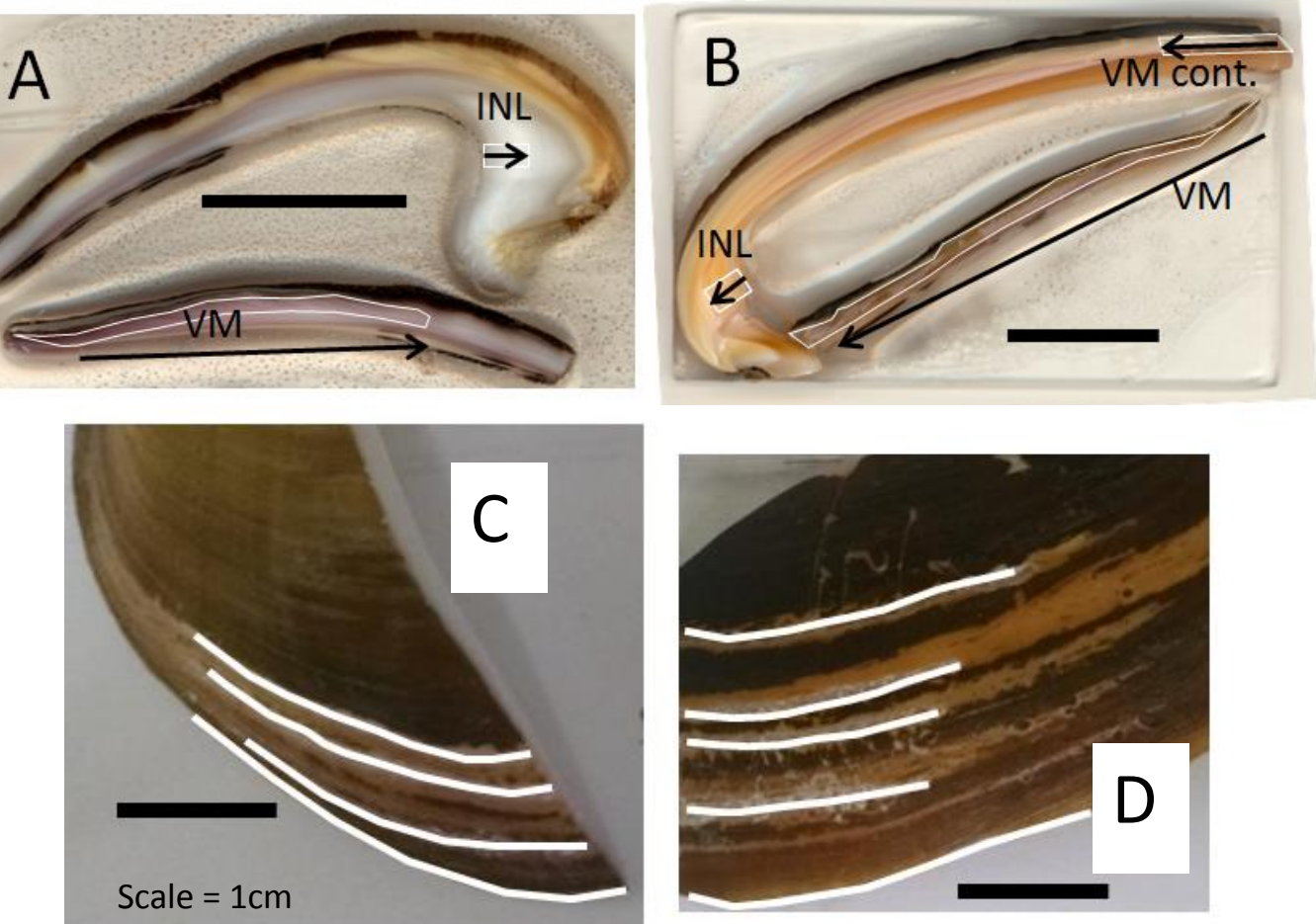
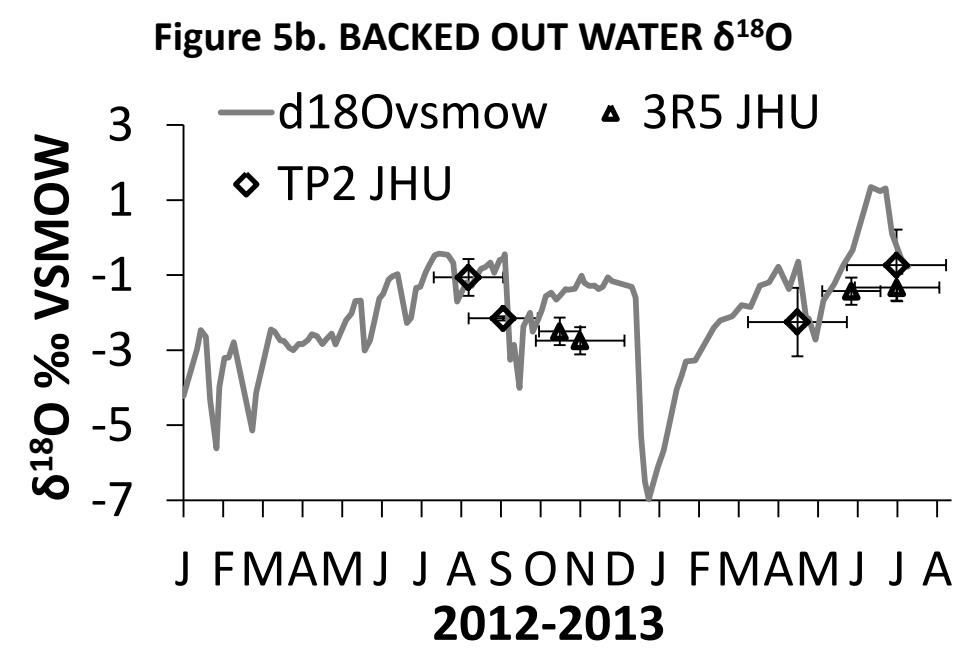
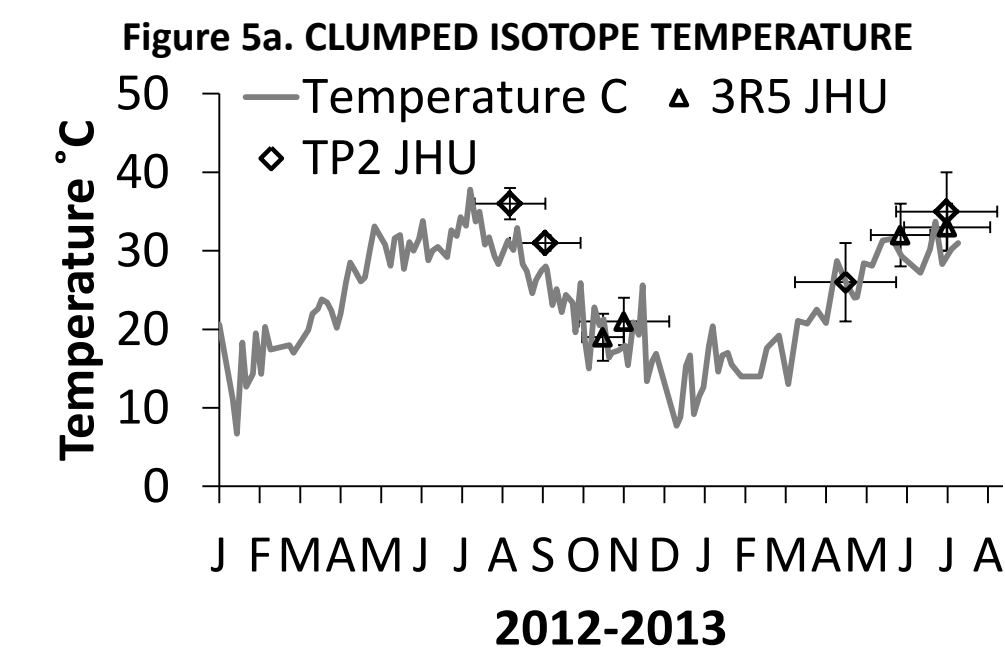
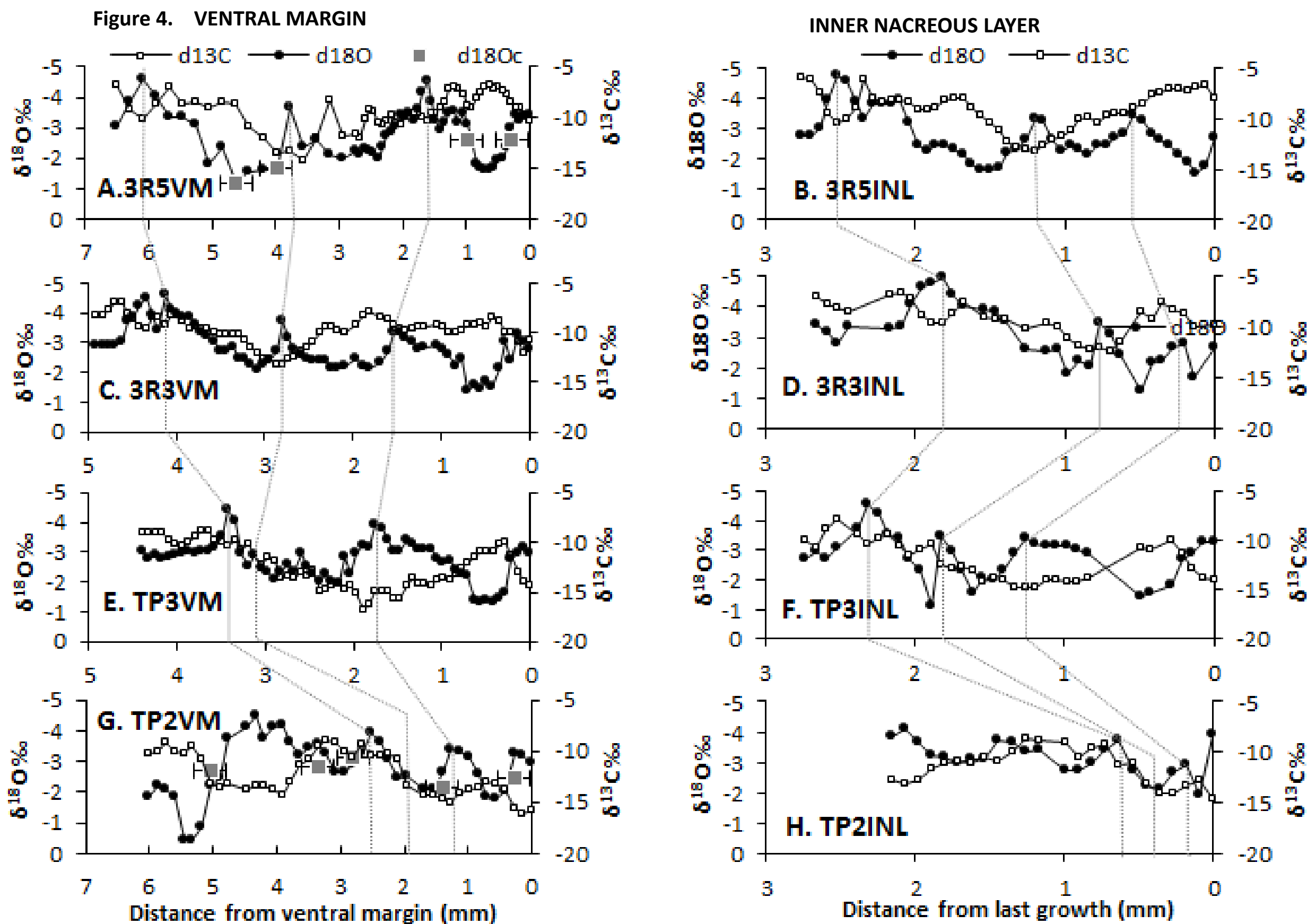


Figure 2. The middle to lower run of the Brazos River in Texas. Water and mussel sampling location is at the black circle near College Station and the USGS gage is a green triangle. The Brazos watershed is in inset. Lake Whitney is a major on-channel reservoir upstream, and is a high salinity water source.

Live *Amblema plicata* (Threeeridge) and *Cyrtoneias tampicoensis* (Tampico pearlymussel) mussel specimens were collected from the Brazos River near College Station in August 2013. Shells were micromilled at 60-120um intervals in the inner nacreous layers (INL) and ventral margins (VM) (Figures 3A and 3B) and samples were analyzed on a Kiel-MAT 253 IRMS for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. Arrows are sampling direction. Clumped isotope samples were drilled from light and dark bands following growth layers in the tops of the shells (Figures 3C and 3D), and analyzed at the Johns Hopkins University Stable Isotope Lab on a custom gas purification line and MAT 253 IRMS, and calibrated using the reference frame method from Dennis et al. (2011). Δ_{47} values were converted to temperature using the aragonite equation from Henkes et al. (2013).



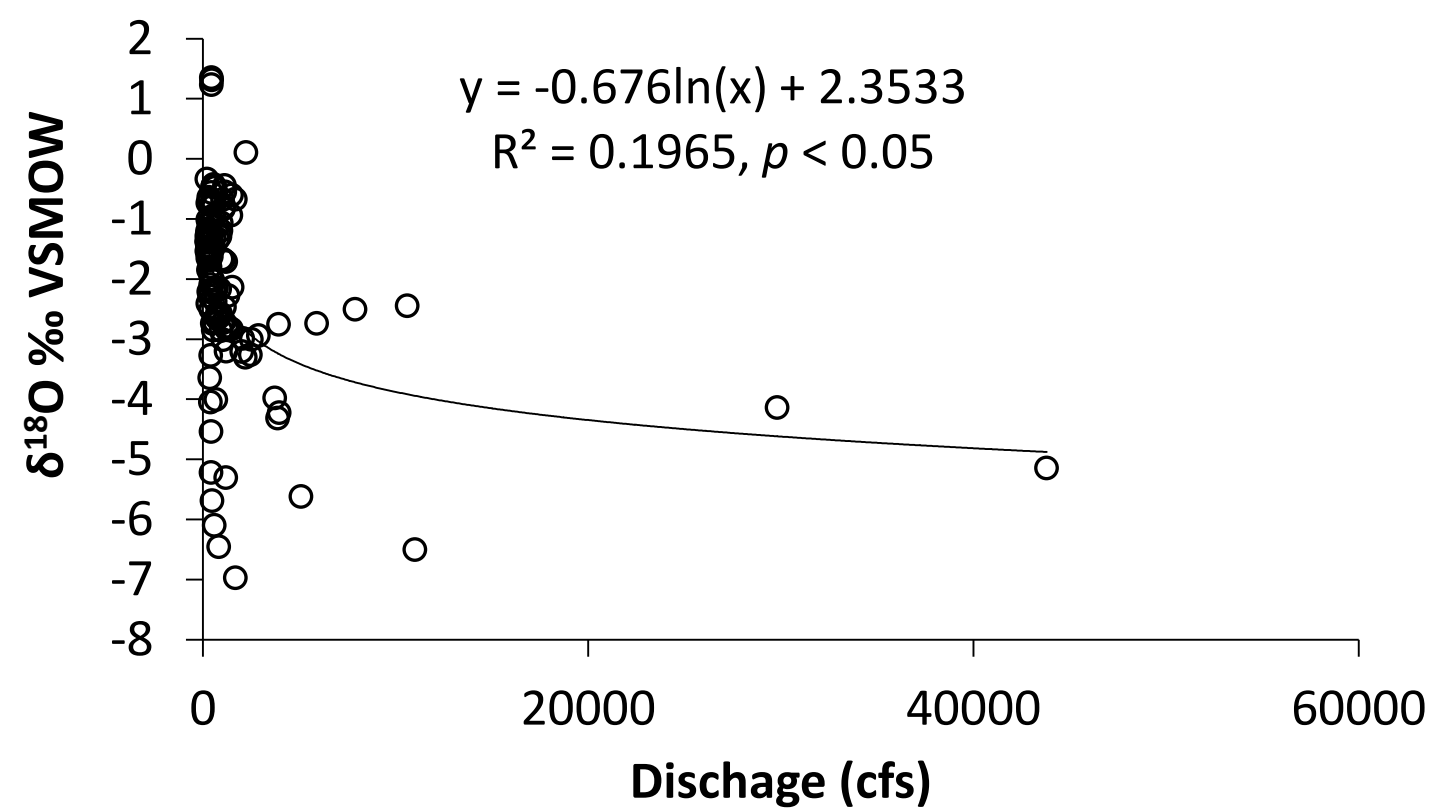
Results



Assigning chronologies

- First, identify isotope value cycles across transects as depicted with dashed vertical lines in Figure 4 (above).
- $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ trends are consistent between transects.
- INL and VM isotope values show similar trends both between and within shells.
- Specimens 3R5 (Threeeridge) and TP2 (Tampico) Δ_{47} temperatures (Figure 5) support chronologies based on $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ trends.
- The dates of the winter growth hiatuses (dashed lines in Figure 7) have an error of about ± 10 days.
- The shell extension rate implied by a proposed chronology must be realistic. If a chronology implies accelerating growth from one year to the next, (Haag and Rypel, 2011), then the chronology deserves extra scrutiny.

Figure 6. Brazos River discharge vs. water $\delta^{18}\text{O}$



Assume sinusoidal temperature and back out $\delta^{18}\text{O}$ from shell isotope chronology.

Discussion

Chronology

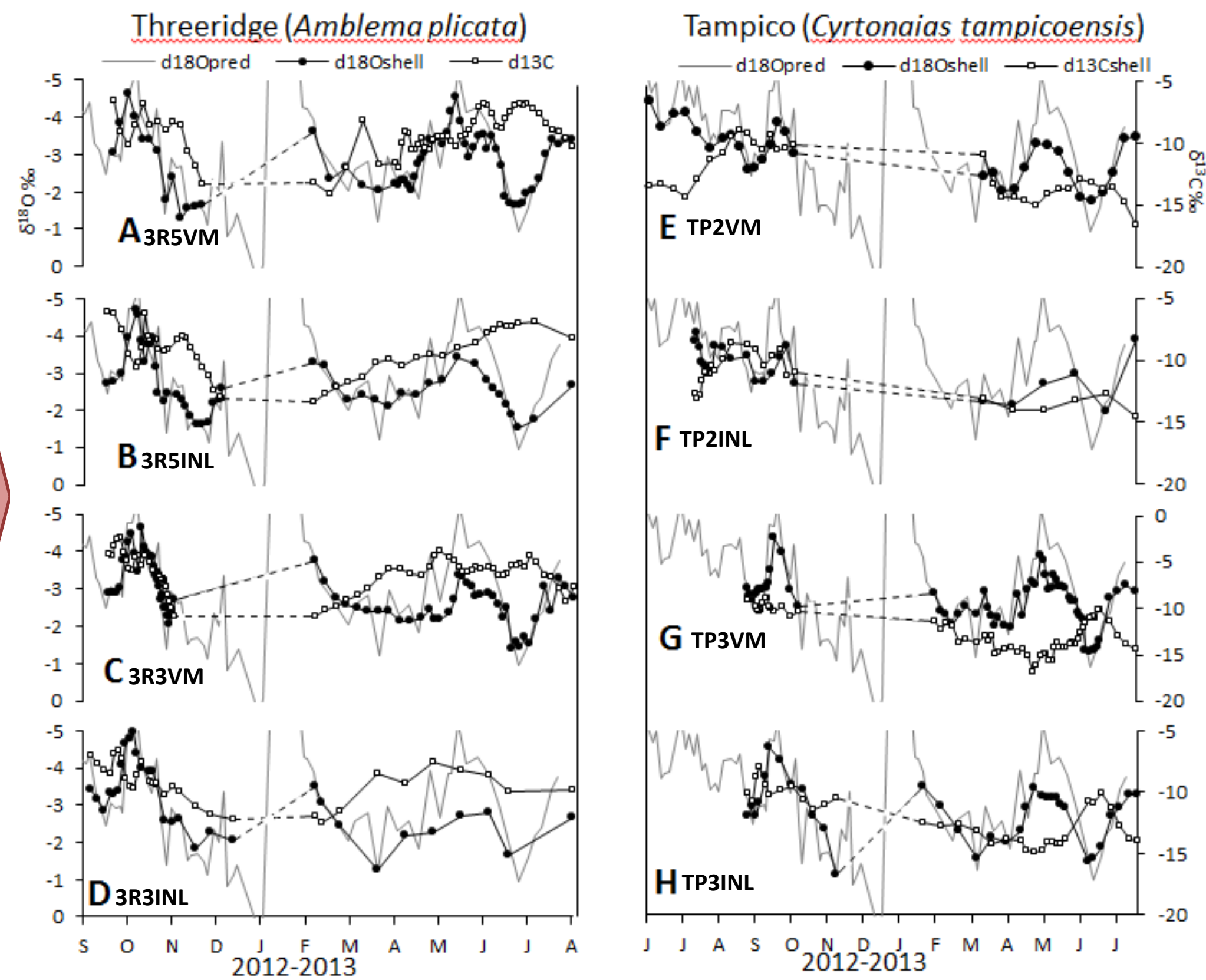


Figure 5. Assigned isotope chronologies for 3R5VM (A), 3R5INL (B), 3R3VM (C), 3R3INL (D), TP2VM (E), TP2INL (F), TP3VM (G), and TP3INL (H).

Reconstructing discharge, electrical conductivity, and water source

- Environmental conditions can be reconstructed from the shell oxygen and carbon isotope chronologies from Figure 7 (above) when using the regression equations for relationships between water isotope values and discharge, salinity, and water source (% Lake Whitney contribution). Backing out water $\delta^{18}\text{O}$ from high-resolution shell $\delta^{18}\text{O}$ values relies on assuming annual temperature variation is sinusoidal. Applying the regression equation from Figure 6 to the backed-out water $\delta^{18}\text{O}$ chronology reconstructs river discharge.
- Figure 8 shows the river discharge reconstructed from shell isotope values as a black solid line.
- Figure 9a compares observed and reconstructed river salinity as electrical conductivity (EC) based on the linear relation between river $\delta^{18}\text{O}$ and EC ($\text{EC} = 0.0043 \cdot \delta^{18}\text{O} - 5.56$, $R^2 = 0.58$, $p < 0.05$).
- Figure 9b compares observed and reconstructed river water source as percent of river flow from Lake Whitney (%LW) where $\%LW = 2.18 \cdot \delta^{18}\text{O} - 2.65$, $R^2 = 0.25$, $p < 0.05$).
- Dashed black lines in Figure 9 represent winter hiatuses in shell growth.
- Presented reconstructions significantly covary with actual river observations ($p < 0.05$).

Figure 8. Observed and reconstructed discharge in the Brazos River near Bryan-College Station for 2012-2013

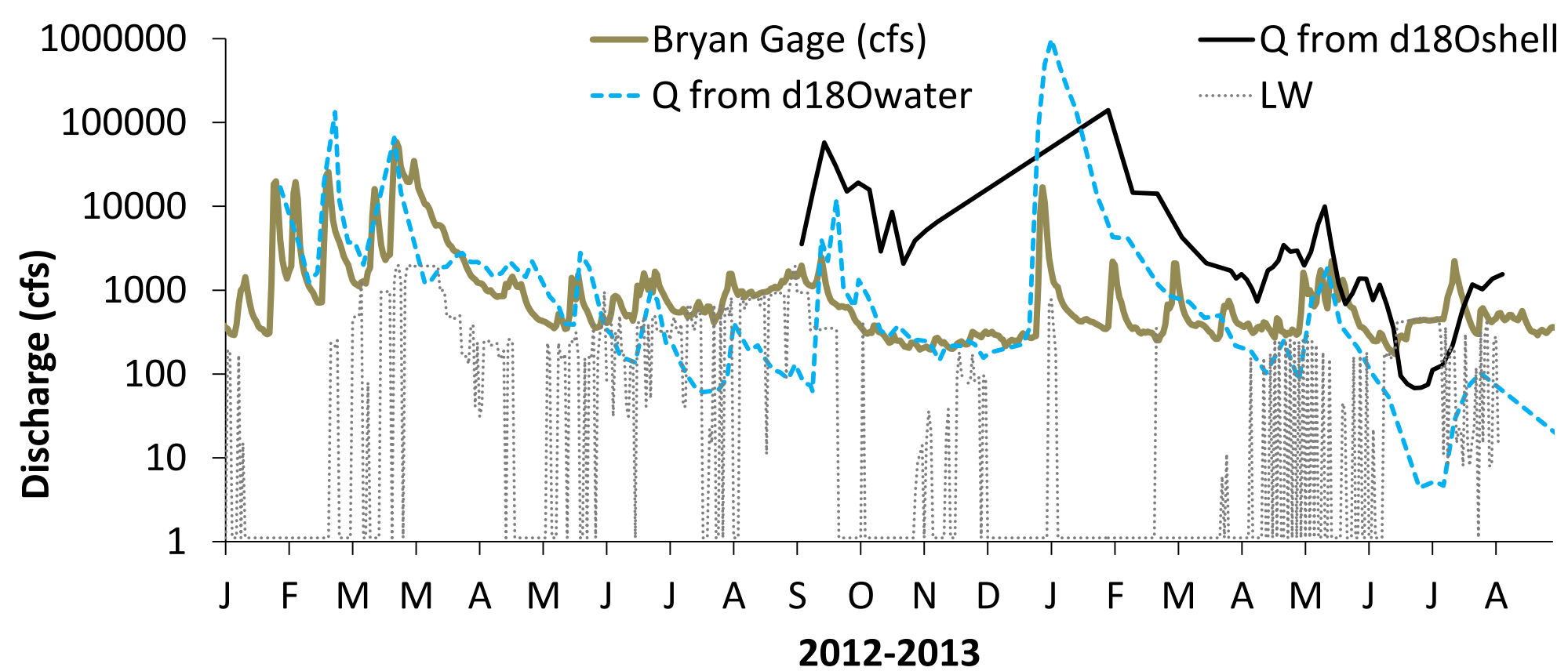


Figure 9a. Observed and reconstructed salinity (EC)

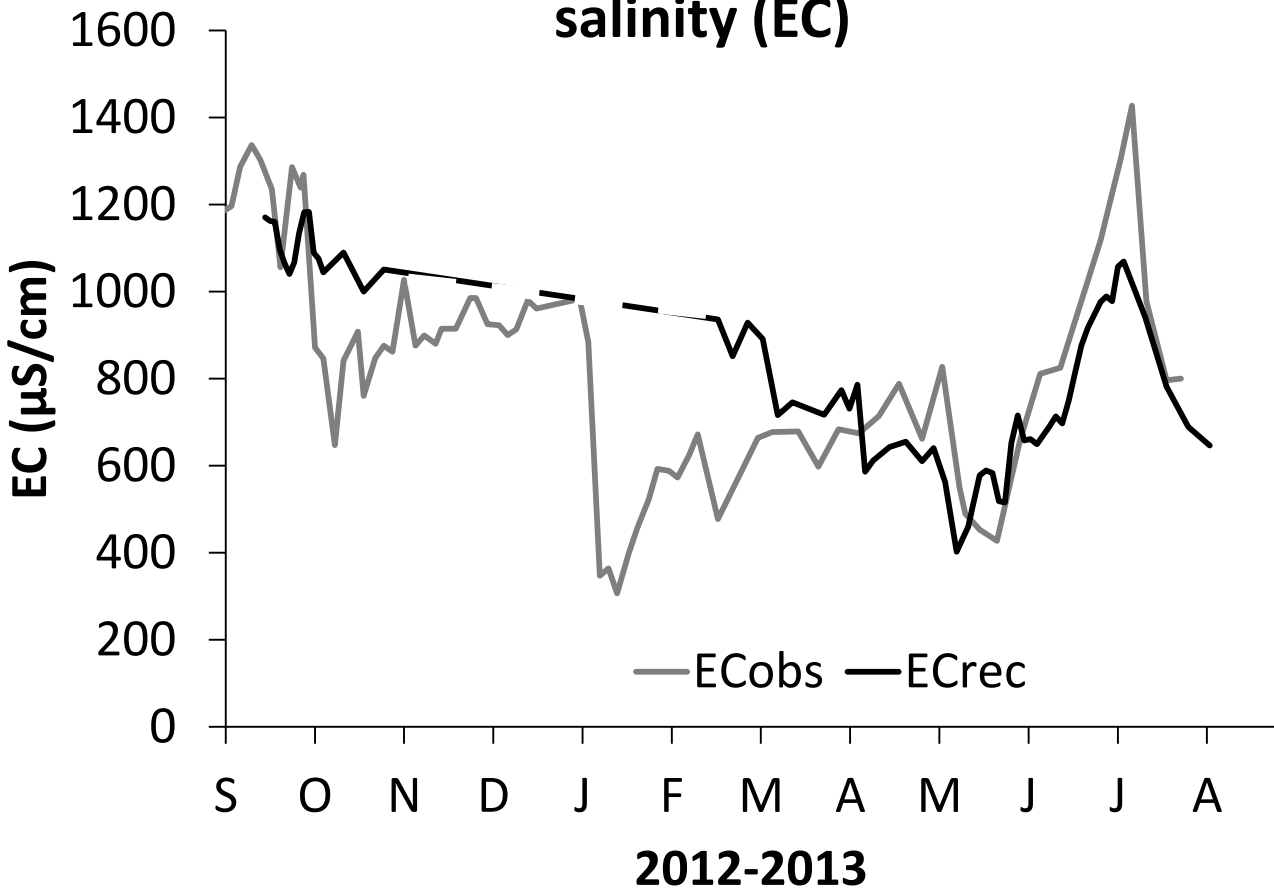
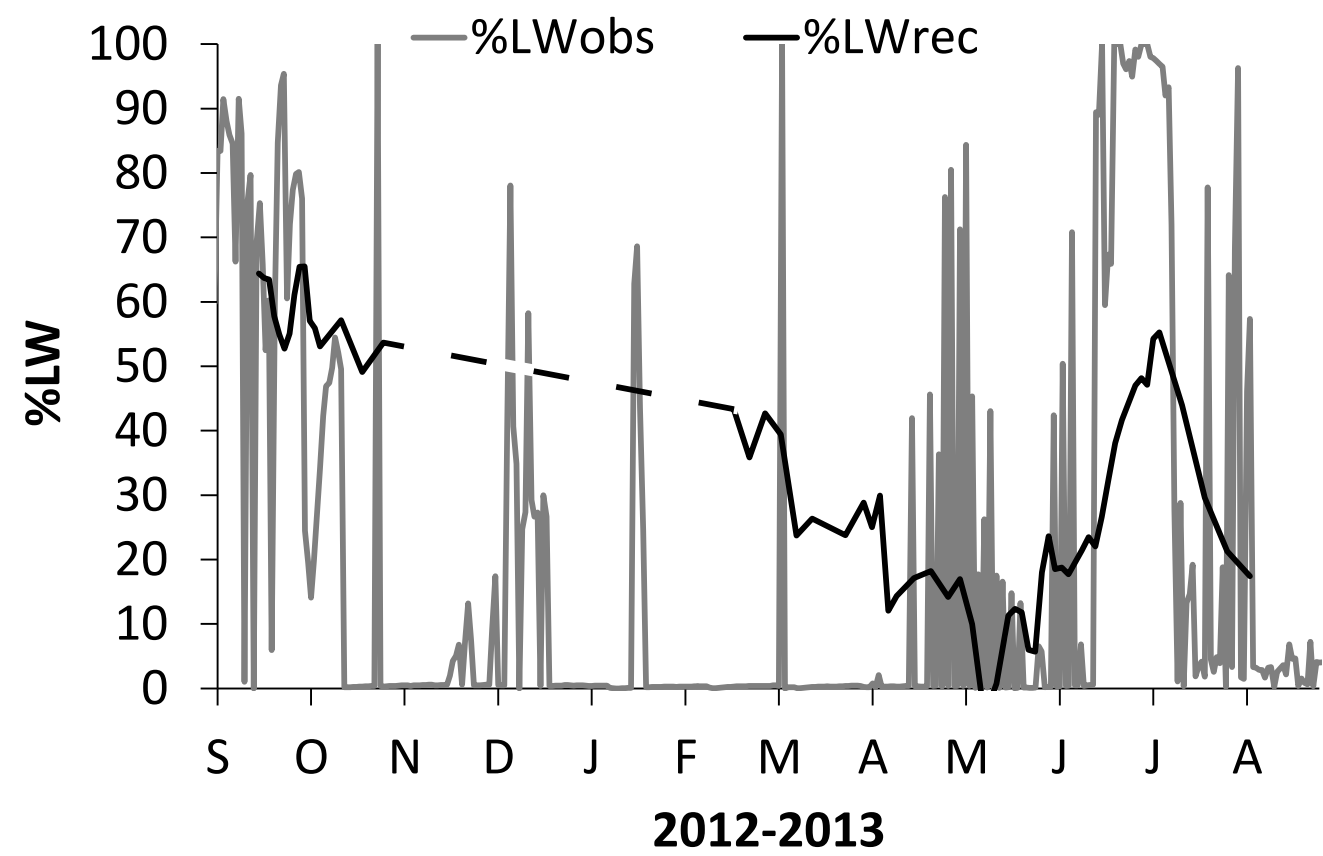


Figure 9b. Observed and reconstructed water source (%Lake Whitney flow)



Conclusions

Reconstructing mussel shell growth temperatures with clumped isotopes validates high-resolution shell isotope chronologies.

High-resolution shell oxygen and carbon isotope chronologies can be used to accurately reconstruct variation in river discharge, salinity, and water source.

References

- Dennis, K. J., Affek, H. P., Passey, B. H., Schrag, D. P., and Eiler, J. M., 2011, Defining an absolute reference frame for 'clumped' isotope studies of CO_2 : *Geochimica et Cosmochimica Acta*, v. 75, no. 22, p. 7117-7131.
- Dettman, D. L., Reische, A. K., and Lohmann, K. C., 1999, Controls on the stable isotope composition of seasonal growth bands in aragonitic fresh-water bivalves (Unionidae): *Geochimica et Cosmochimica Acta*, v. 63, no. 7, p. 1049-1057.
- Haag, W. R., and Rypel, A. L., 2011, Growth and longevity in freshwater mussels: evolutionary and conservation implications: *Biol Rev Camb Philos Soc*, v. 86, no. 1, p. 225-247.
- Henkes, G. A., Passey, B. H., Wanamaker, A. D., Grossman, E. L., Ambrose, W. G., and Carroll, M. L., 2013, Carbonate clumped isotope compositions of modern marine mollusk and brachiopod shells: *Geochimica et Cosmochimica Acta*, v. 106, p. 307-325.

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