

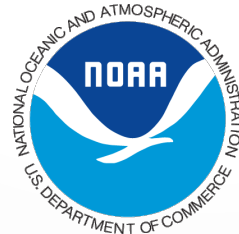
Use of stable oxygen isotope composition of water as a tracer in coastal waters of Northern Gulf of Mexico

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Mentor

Dr. Alan M. Shiller

- Trace elements in natural water
- Marine and estuarine chemistry
- Chemistry of rivers and weathering
- Oil spill effects on ocean chemistry
- Global carbon system
- Sedimentary fluxes.



Ph.D. Oceanography,
Scripps Institution of
Oceanography,
University of California,
1982

B.S. Chemistry, Caltech,
1975

Me

- Graduated from Mumbai University with a Bachelors degree in Zoology, 2008
- Graduated from Mumbai University with a Masters degree in Environmental Science, 2010
- Currently enrolled in the Masters program in Marine Science at the University of Southern Mississippi
- Research Interests:
 - Marine chemistry
 - Biogeochemistry
 - Biochemistry of toxins



Introduction

- 3 stable isotopes of oxygen: ^{16}O (99.63%), ^{17}O (0.0375%) and ^{18}O (0.1995)
- The ratios of stable isotopes of hydrogen-deuterium to hydrogen (D/H)-and of oxygen-18 to oxygen-16 ($^{18}\text{O}/^{16}\text{O}$) are useful as 'fingerprinting' tools for water
- The ratio between ^{18}O and ^{16}O is expressed as $\delta^{18}\text{O}$
- Fractionation due to phase change and kinetic equilibrium causes unique composition of ^{18}O and ^{16}O



Stable Isotopes of Oxygen and their uses

- A tracer of different fresh waters
- Understanding mixing and circulation of sea water in coastal and marginal seas
- Provides record of climate change and fluctuations



Stable isotopes in the Gulf of Mexico

- Water entering the Gulf of Mexico has different isotopic signature depending on the location of the rivers' drainage basin
- Stable isotope values for fresh water sources to the Gulf of Mexico need to be evaluated
- Open ocean end member oxygen isotope values need to be established from the Northern Gulf where there is large freshwater input and mixing.



Analysis: Picarro L2120-I Analyzer for Isotopic H₂O

- IRIS (Isotope ratio infrared spectroscopy): direct measurement of water vapor
- More resource efficient and cheaper than traditional IRMS (Isotope Ratio Mass Spectrometry)
- Susceptible to organic contamination



Issues

- Linearity
- Memory effect
- Drift
- Normalization



Data Processing

- In house standards of High isotope water, Low isotope water and Intermediate isotope water were calibrated to International standards of VSMOV (Vienna standard mean ocean water) and SLAP2 (Standard light Antarctic precipitation)

DIST (distilled)	Intermediate water for drift correction
ENR (Enriched)	High isotope water for normalization to VSMOV/SLAP scale
AK (Alaska)	Low isotope water for normalization to VSMOV/SLAP scale
Mix	Intermediate water for quality control (treated as a sample)

Sample Table			
Tray	Vial	Identifier 1	Identifier 2
1,	1,	Distilled,	standard
1,	2,	Enriched,	standard
1,	3,	Alaska,	standard
1,	4,	Distilled,	standard
1,	5,	Mix,	standard
1,	6,		sample
1,	7,		sample
1,	8,		sample
1,	9,		sample
1,	10,	Distilled,	standard
1,	11,		sample
1,	12,		sample
1,	13,		sample
1,	14,		sample
1,	15,		sample
1,	16,		sample
1,	17,		sample
1,	18,		sample
1,	19,	Distilled,	standard
1,	20,		sample
1,	21,		sample
1,	22,		sample
1,	23,		sample
1,	24,		sample
1,	25,		sample
1,	26,		sample
1,	27,		sample
1,	28,	Distilled,	standard

- Linearity is corrected by keeping sample injection size the same
- An optimized standard sequence is followed standards are arranged in a distinct carry over that is used for memory correction for every run.
- The DIST vials are interspersed within the samples in order to correct for drift
- All values are expressed in per mil as:

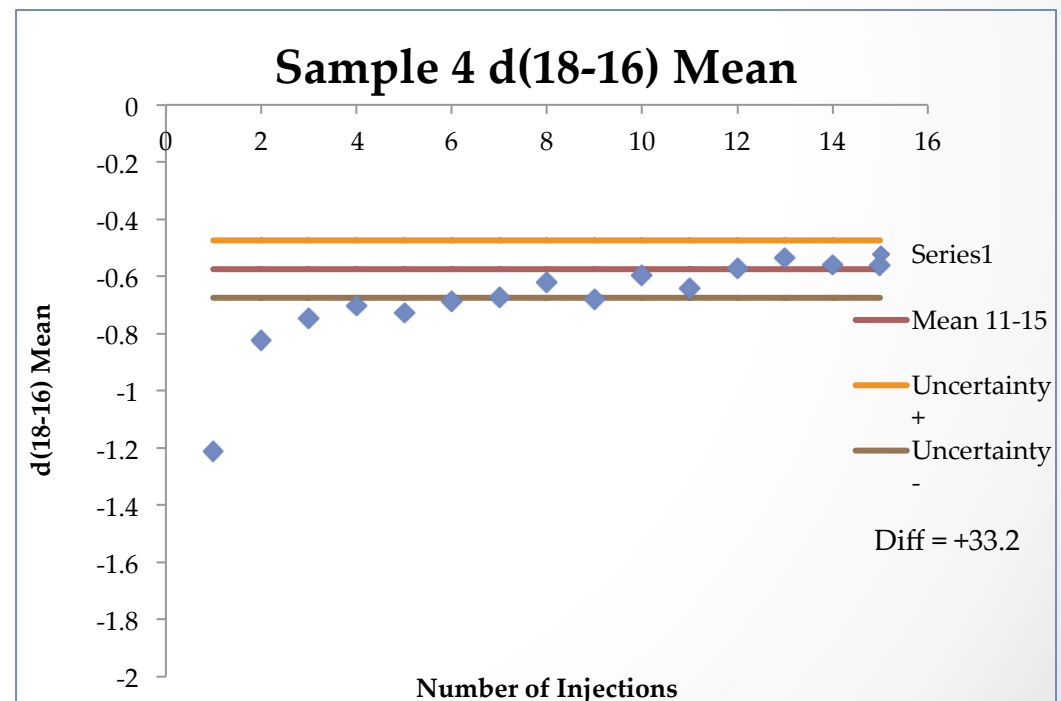
$$\delta = \left(\frac{R_{sample}}{R_{reference}} - 1 \right) \times 1000$$

Memory correction

- The first injection of subsequent vials is affected by the last injection of previous vials.

- A memory coefficient is calculated to correct the carry over of injections

$$m_i^n = \frac{\delta_t^{(n-1)} - \delta_i^n}{\delta_t^{(n-1)} - \delta_t^n}$$

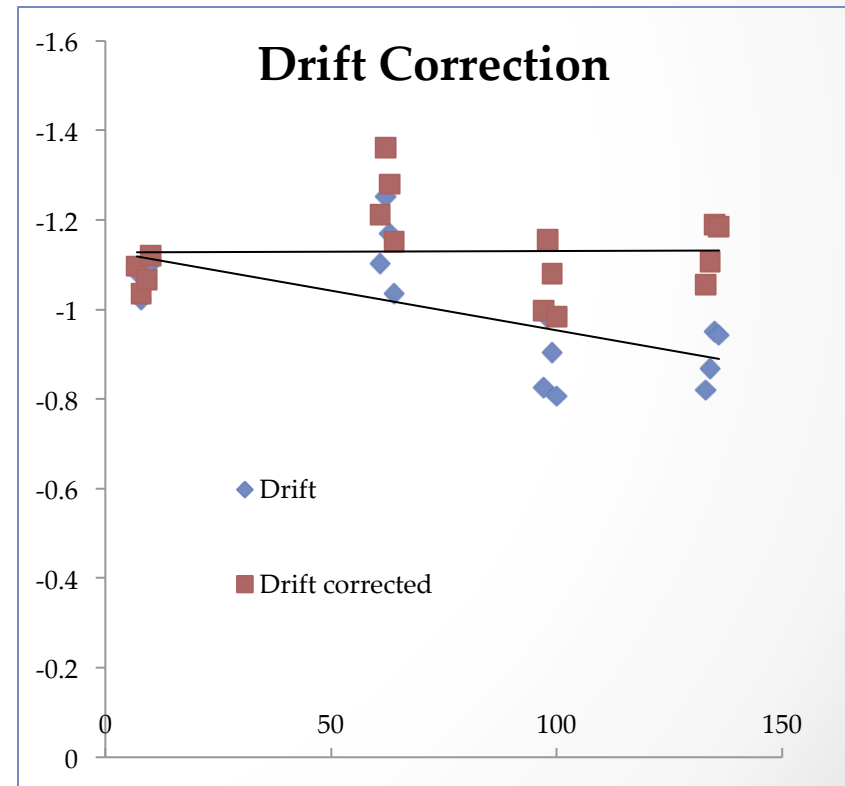
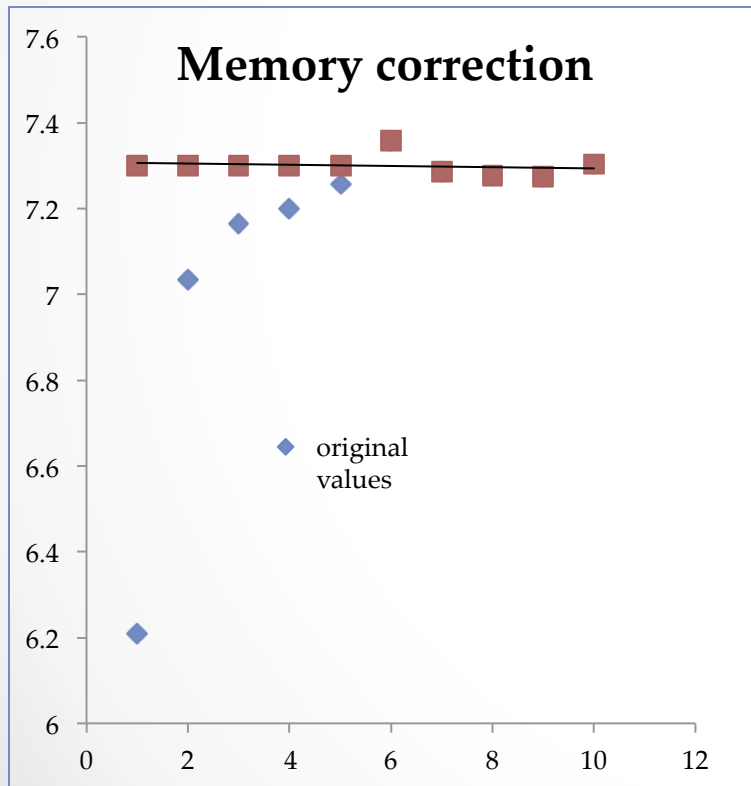


- Memory correction

$$\delta_{memory\ corrected} = \delta_{i(raw)}^n + (1 - m_i) \times (\delta_{i(raw)}^n - \delta_t^{(n-1)})$$

- Drift correction :

In house standard DIST is used for drift correction -absolute change in mean delta values over a 24 hour run

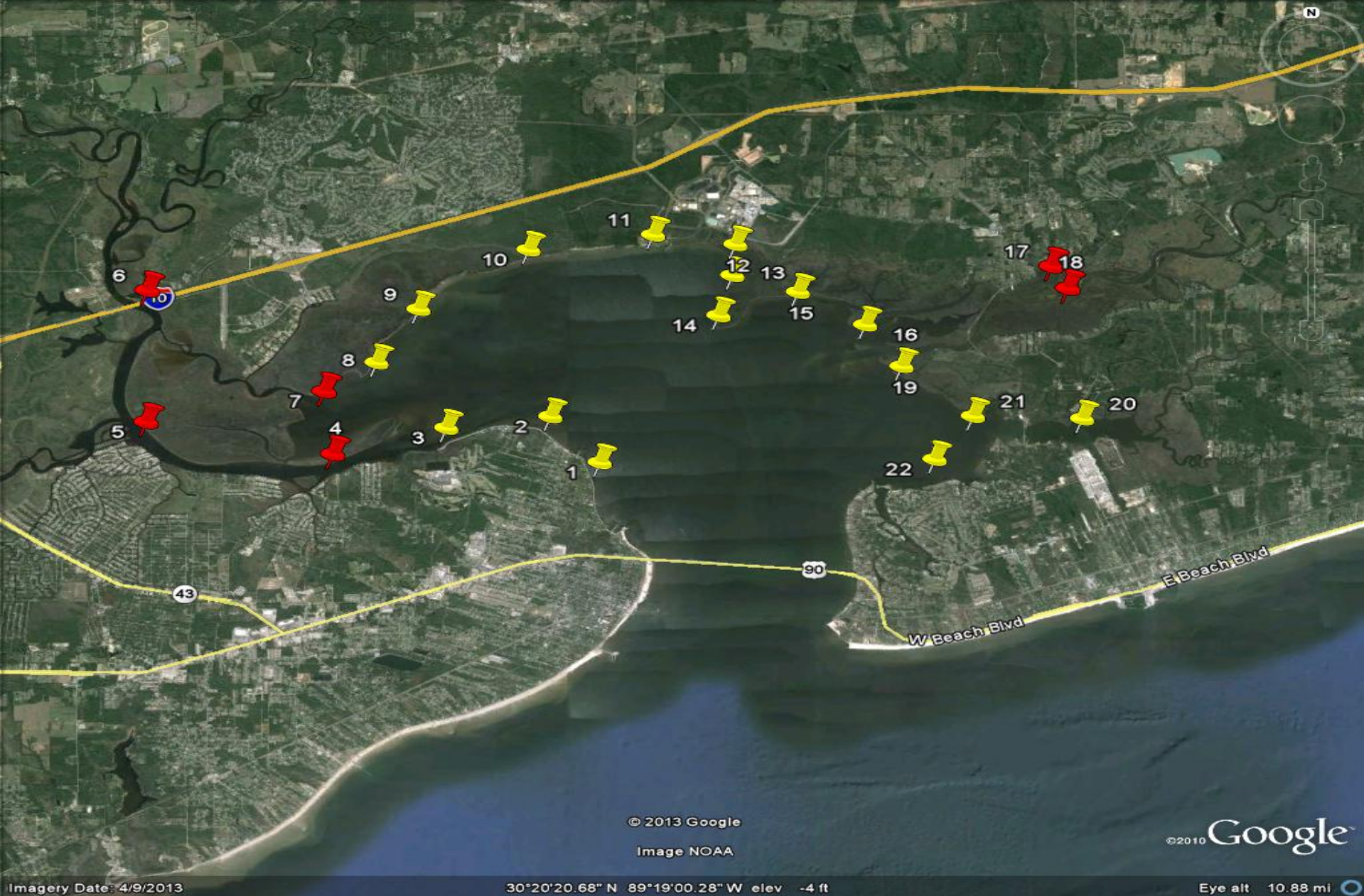


Sampling

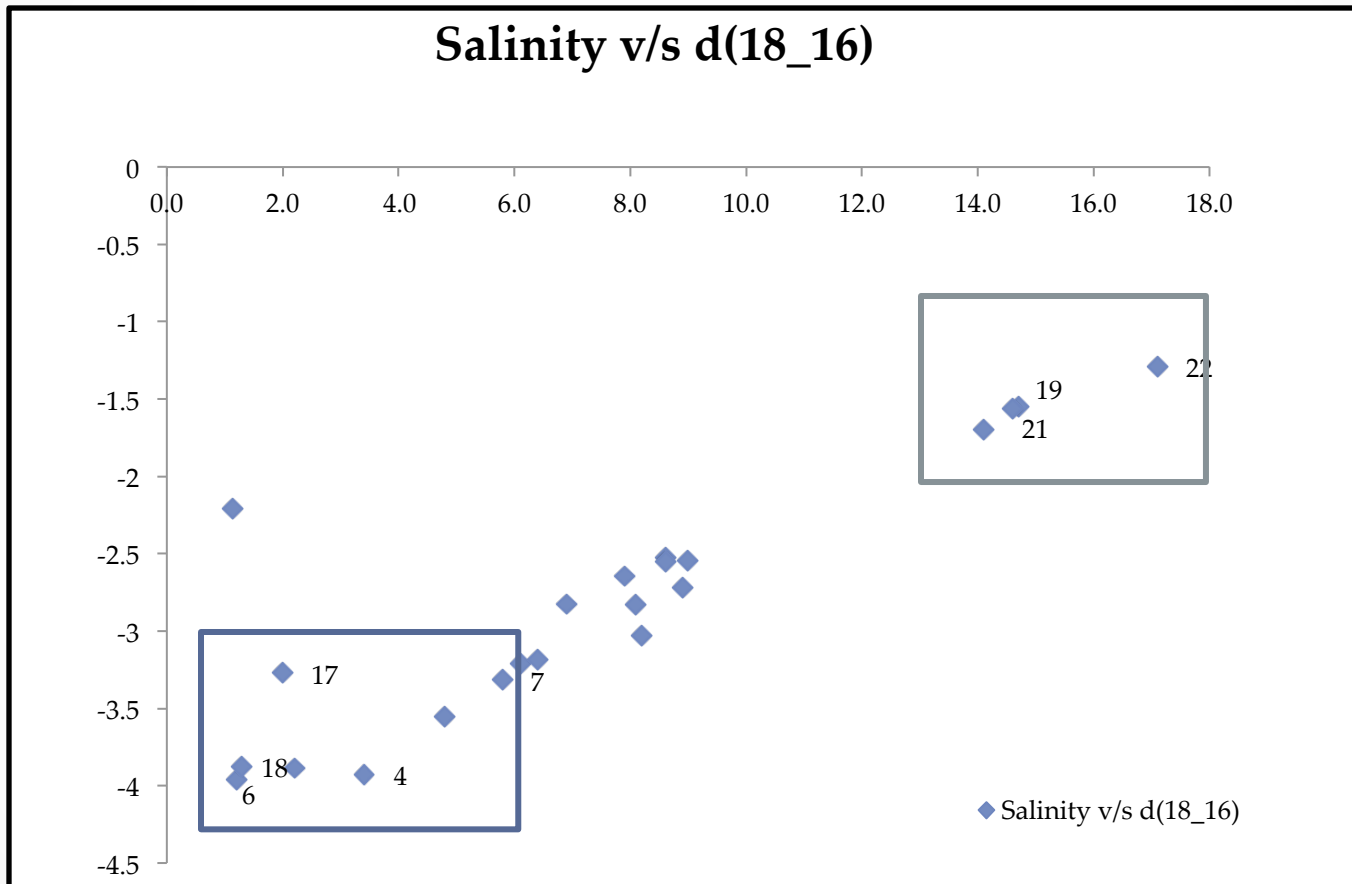
- Samples collected from St. Louis Bay
- Syringes were used to collect water
- Collection amber bottles were capped tightly and sealed with Parafilm and transported in coolers.

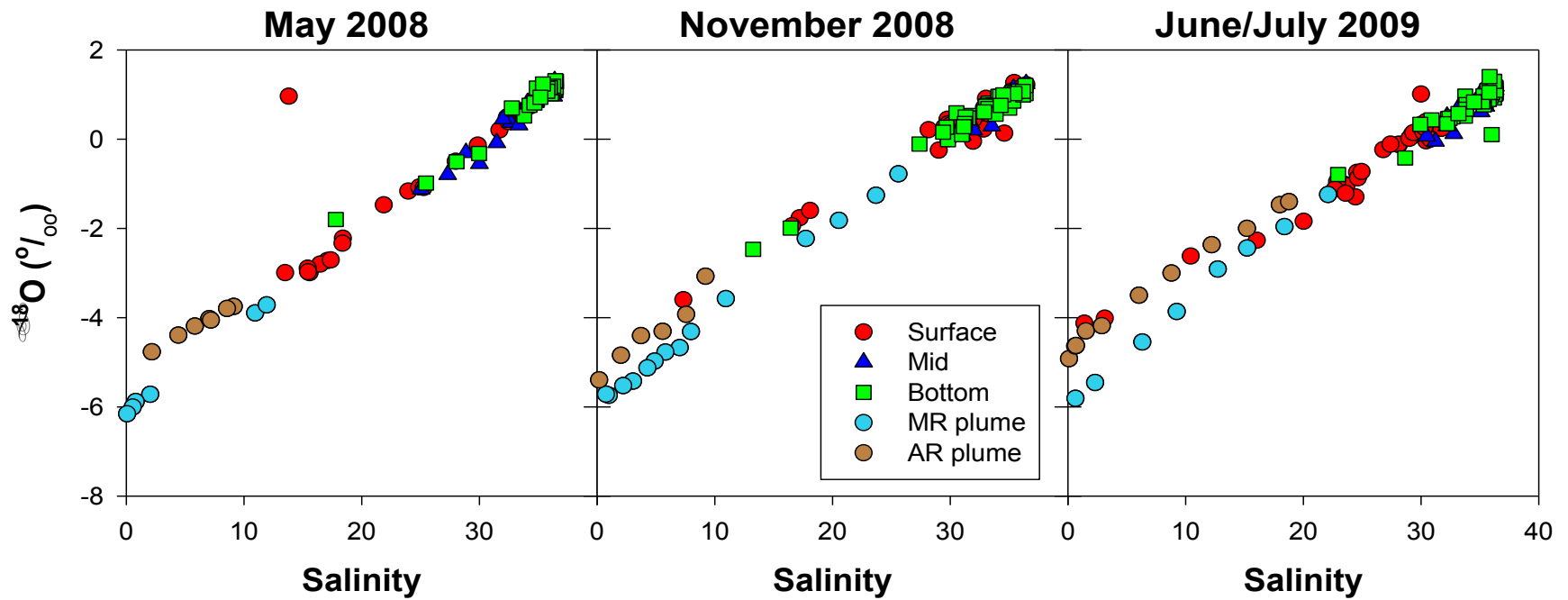


Sampling Area



Result





Previous record of stable isotopes in
Mississippi and Atchafalaya Rivers

Value of internship

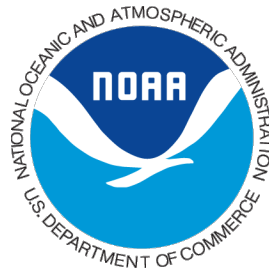
- Learned how to sample for O18, stable isotopes
- Gained proficiency in using Picarro L2120-I Analyzer for Isotopic H₂O
- Learned to analyze and draw conclusions from O18 measurements by IRMS
- Better understanding of the Northern Gulf of Mexico
- More appreciation of sampling and actually seeing the sun

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- JoAnn Moody
- Tina Miller-Way
- Dr. Alan M. Shiller
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Questions?

