Diurnal cycles of dissolved inorganic carbon and dissolved metals at Lambert Run, Harrison County, WV

Dr. Jill L. Riddell, Chatham University, Pittsburgh, PA

Dr. Dorothy J. Vesper, West Virginia University, Morgantown, WV

chatham
UNIVERSITY

Acknowledgements

NETL-RUA RES contract DE-FE0001000

West Virginia University Department of Geology and Geography

J.F. Allen Muzzleloader Club and John Ellyette and Guardians of the West Fork

Dr. Hank Edenborn, Dr. John Martin, Dr. Louis McDonald, Dr. Marie Kurz

Special posthumous acknowledgment to Dr. Helen Lang

Friends and field assistants Lindsey Bowman Miles, Beth Donovan, Catherine Patterson McElroy, Habib Bravo-Ruiz, Travis Wilson, Chris Nicholson, Michael Van Horn, and Corey O'Malley

Matthew Bell (photos and pictures)

Overview

- Big picture framework
- Objectives of the study
- Site information
- Methods and analyses
- Results and discussion
- Summary and conclusions

Big Picture Framework

- Concentrations of metals and ions can vary over a 24-hour period and with season in aqueous settings.
  - Water quality data must be collected in a variety of seasons and times of day for accuracy.
  - Understanding in-stream processes of metals and DIC requires intensive data collection and analysis.

- This study: diurnal data of metals and dissolved inorganic carbon has been collected in a number of studies but few studies have collected metal and DIC data concurrently or compared across seasons or vegetative settings.

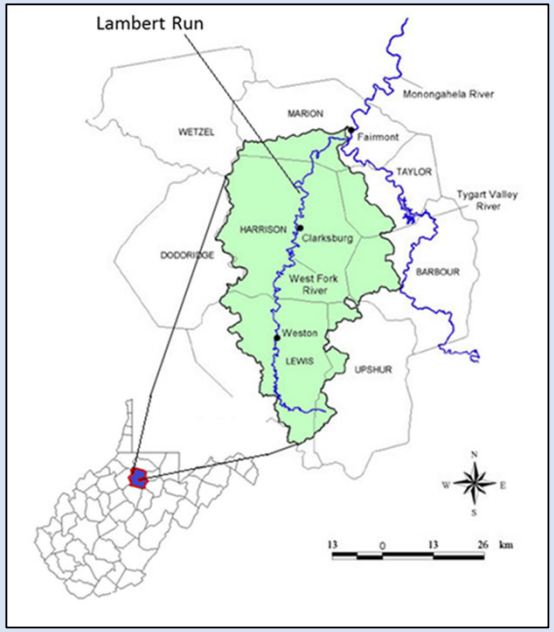
Objectives of this Study

1. Measure diurnal cycles of DIC and metals at 2 locations in the same CMD drainage with different initial CO_2 concentrations and vegetation – does vegetation effect this cycles?

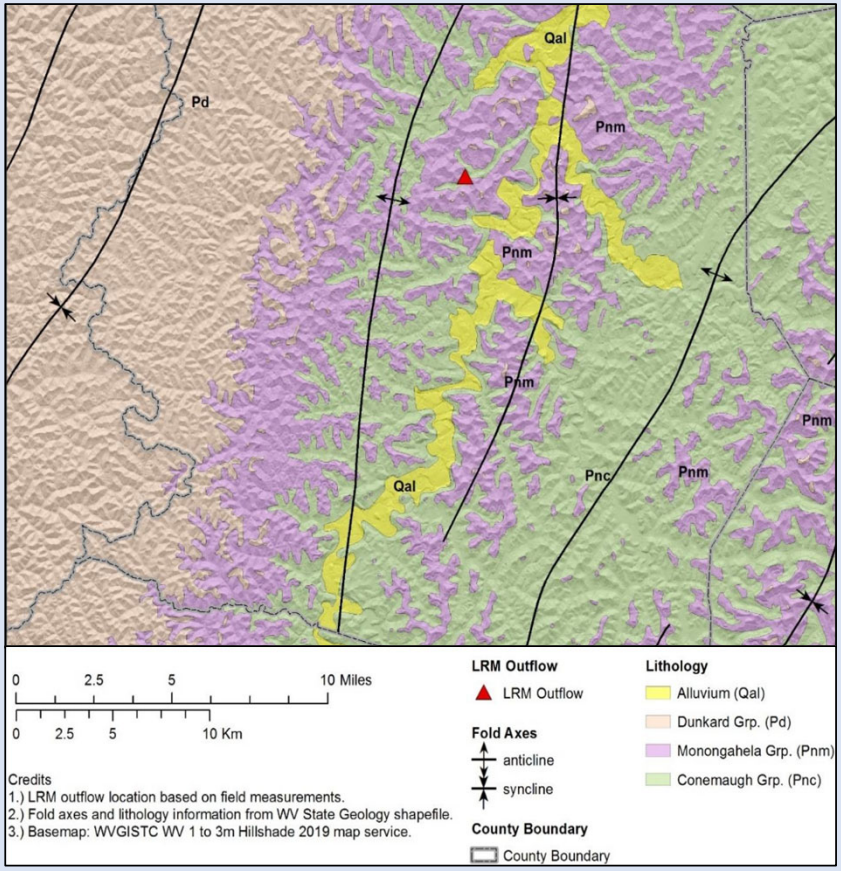
   What is diurnal? – 24-cycles

2. How do changing seasons affect the diurnal cycles of DIC and metals in this system?

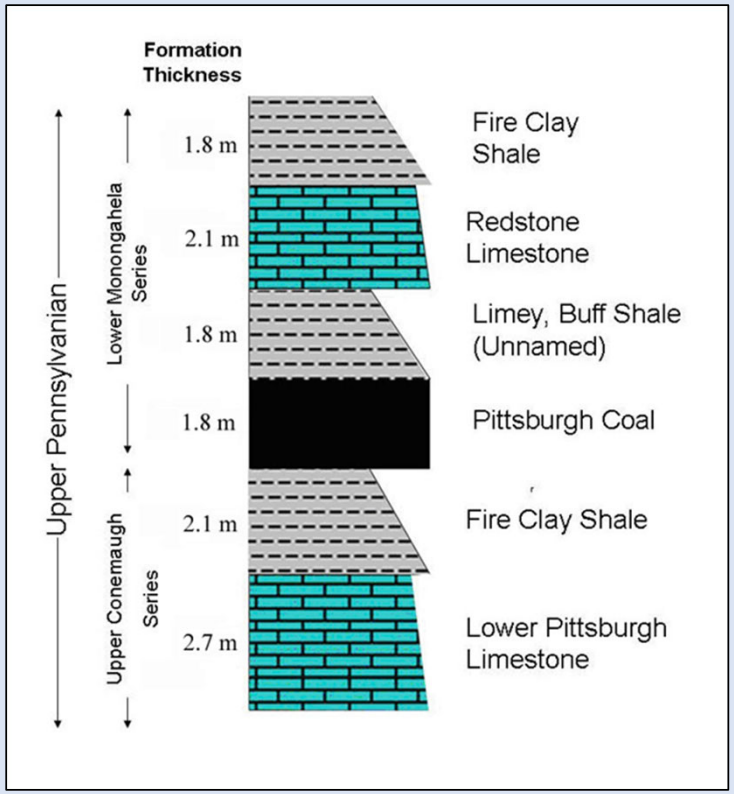
Site Information – Lambert Run - Location and Geology



Riddell, 2015

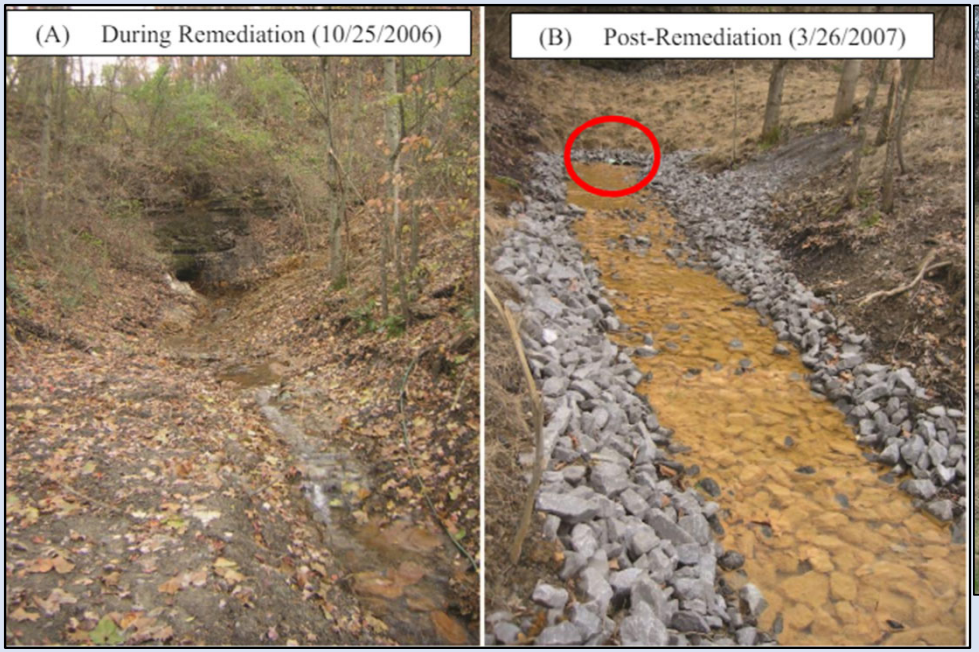


Modified from Bell, 2020



Riddell, 2015

Site Information – Lambert Run - Remediation History



Modified from Bell, 2020

LRM000: portal outflow
Modified with limestone rip-rap

Riddell, 2015

LRM138 – altered natural wetland

Site Information – Lambert Run - Sampling Locations

- Previous study – cycles of trace Spatial study: LRM000 – LRM172
- Diurnal study: LRM050 and LRM 138

LRM050

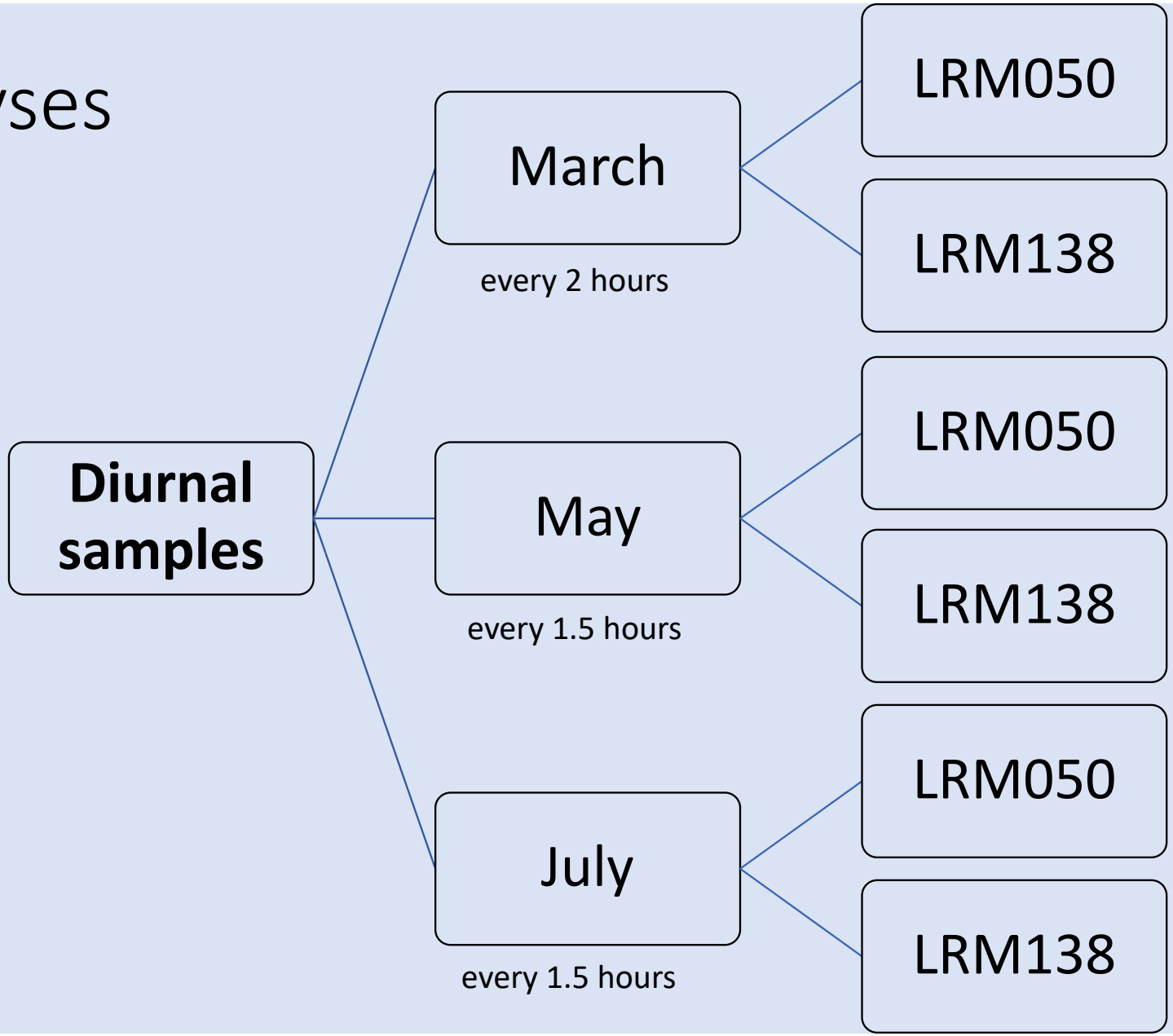
- little emergent vegetation, moderate tree cover
- higher CO_2
- substrate- limestone rip-rap
- water depth ~9-12 in

LRM138

- abundant emergent vegetation
- lower CO_2
- substrate- soft sediment
- water depth ~2-6 inches

Methods and analyses

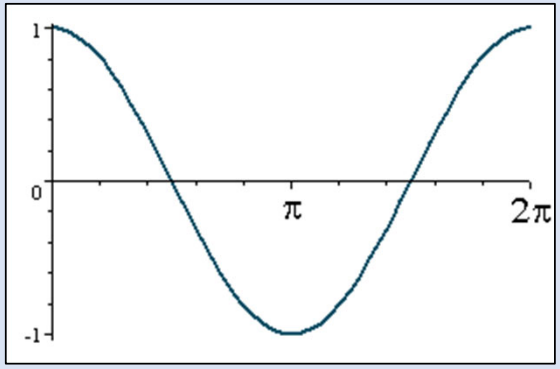
- Field data: CO_2, DIC, Fe(II), and Fe_{TOT}
- Lab data: cations, anions, $\delta^{13}C_{DIC}$
- Metered data: pH, temperature, ODO (optical dissolved oxygen)- logged every 15 min
- ~ total data points = 2,524
  - March ~ 708
  - May ~ 908
  - July ~ 908



Methods and analyses

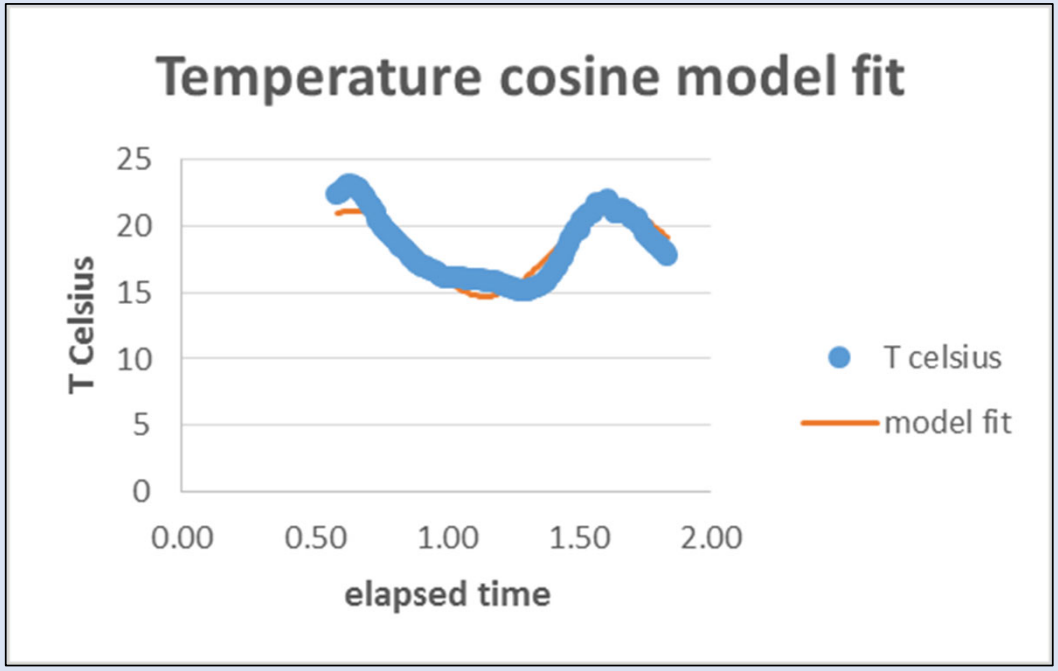
Diel data can be expected to follow the basic shape of a cosine curve

$y = cos\theta$



$$C_t = M + Acos(Bt - H)$$

F-test: data and model
$p \leq 0.01$



Methods and analyses

- Twenty of the collected parameters chosen for statistical analysis
- Parameters with a cosine model fit f-statistic of ≤ 0.01 were graphed on a polar plot and used for discussion.

DIC and carbonate related parameters:

- **DIC**
- **CO_2**
- **$\delta^{13}C_{DIC}$**
- **pH**
- **temperature**
- **ODO**
- **Ca**
- **Mg**

Mine drainage parameters:

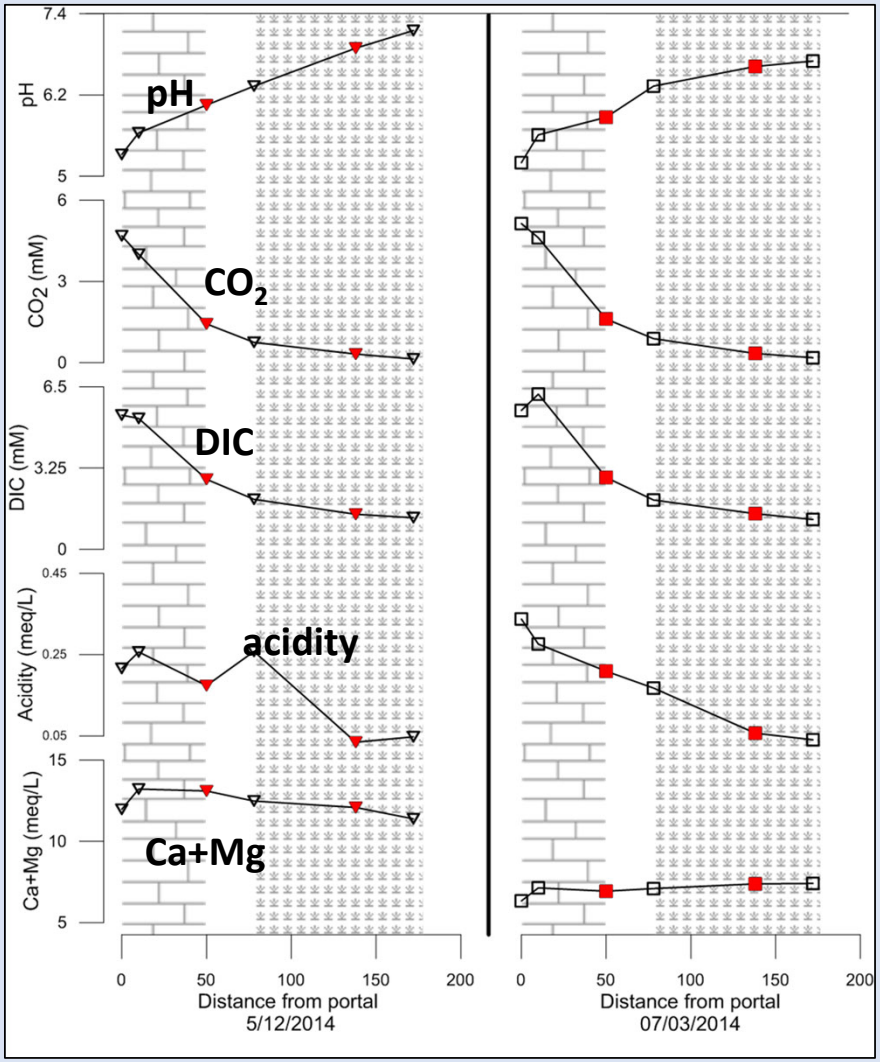
- **Fe(II)**
- **Fe_{TOT}**
- **Mn**
- **SO_4**
- **Al**

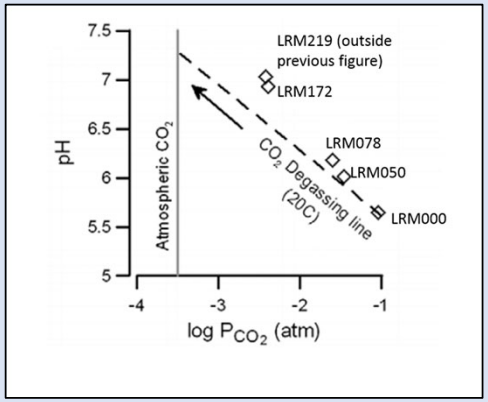
Other selected metals and ions:

- **SiO_2**
- **K**
- **Y**
- **Ce**
- **Ni**
- **Zn**
- **As**

Results – spatial study

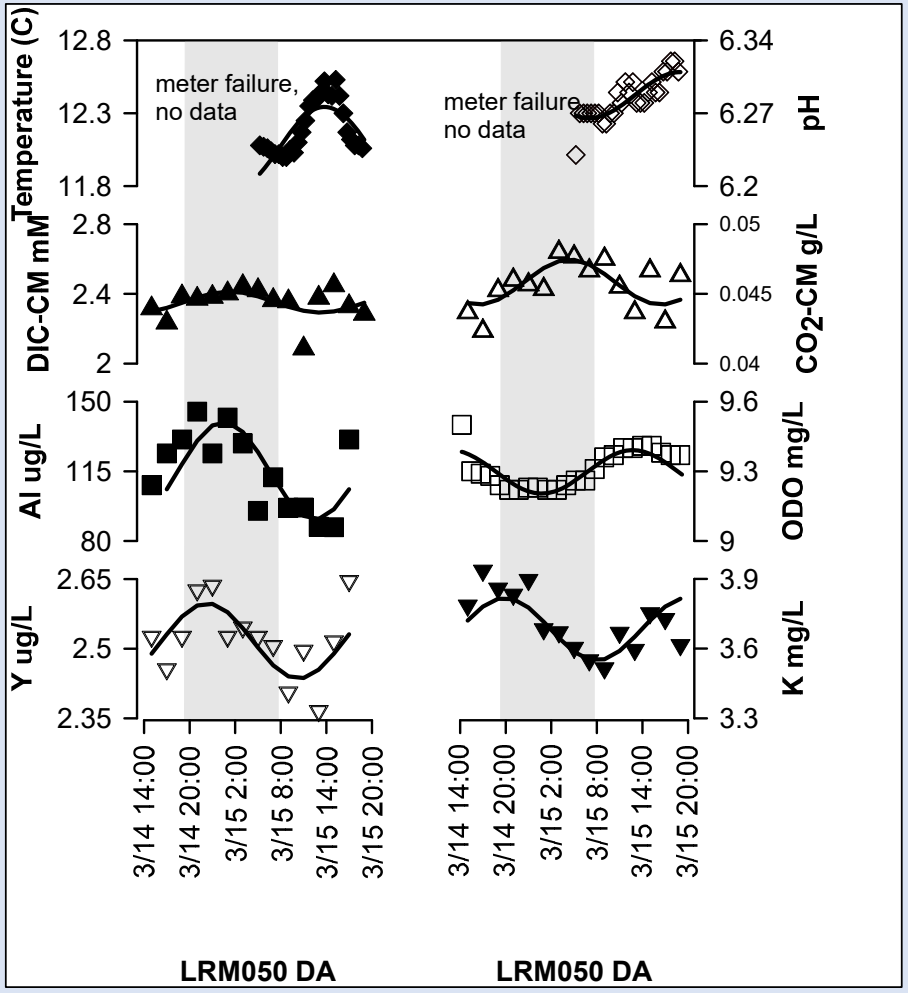
- DIC ranges from ~0-6mM and decreases steadily downstream
- pH increases in response
- acidity also decreases



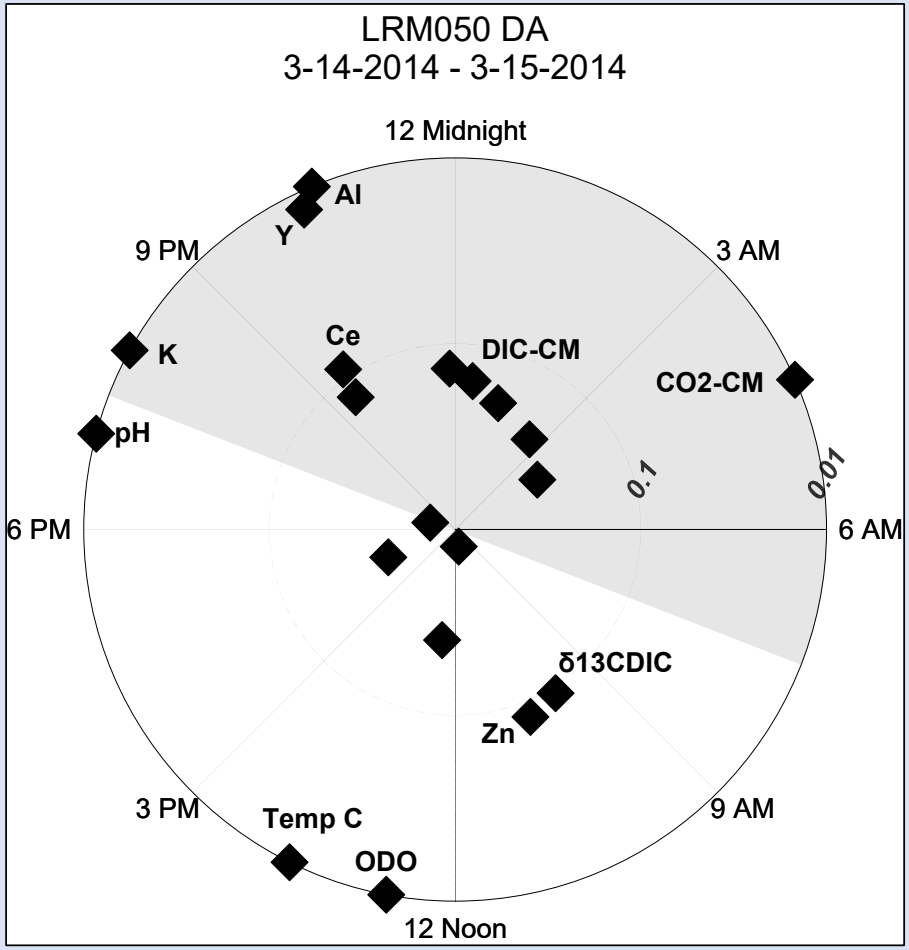


(Vesper and Smilley, 2010)

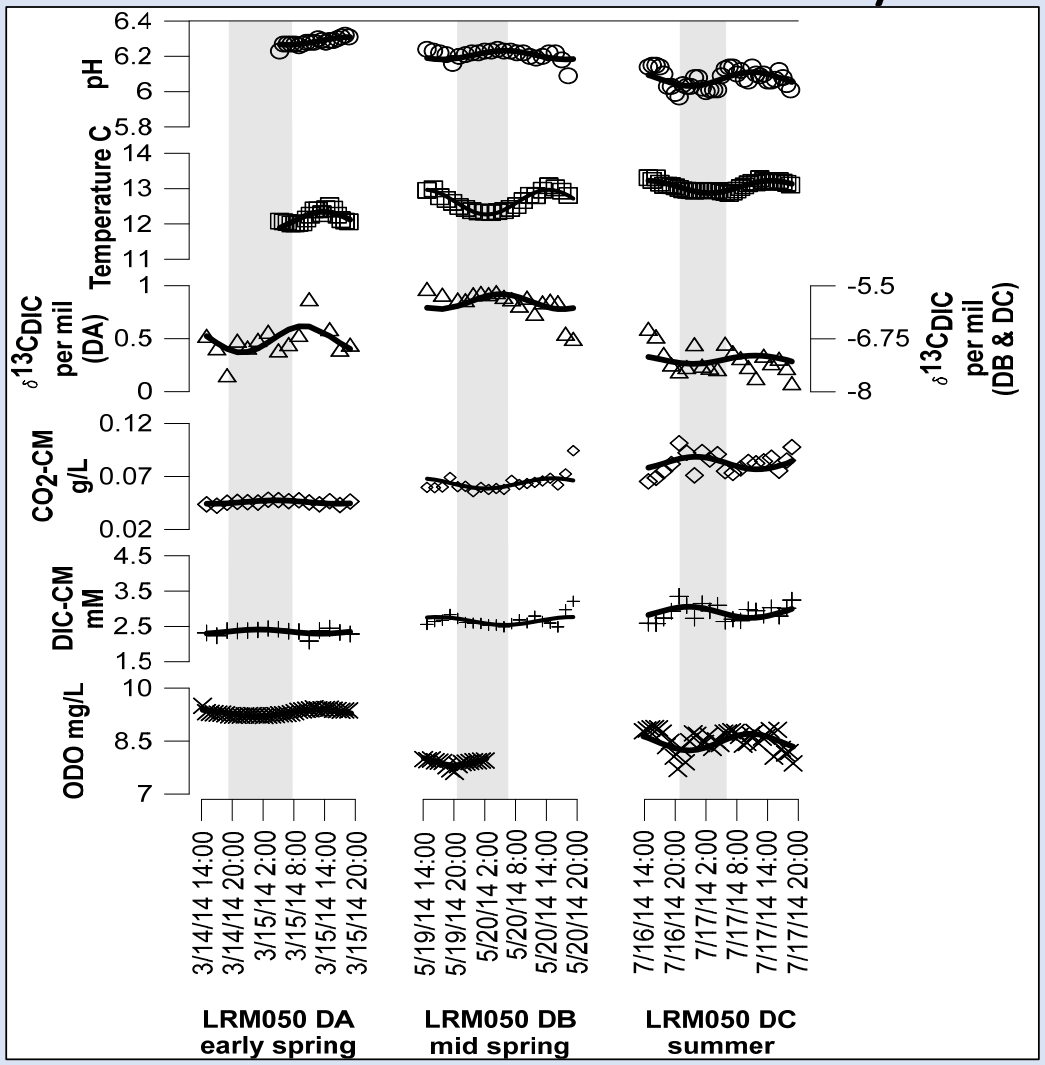
Results – Diurnal Study – LRM050

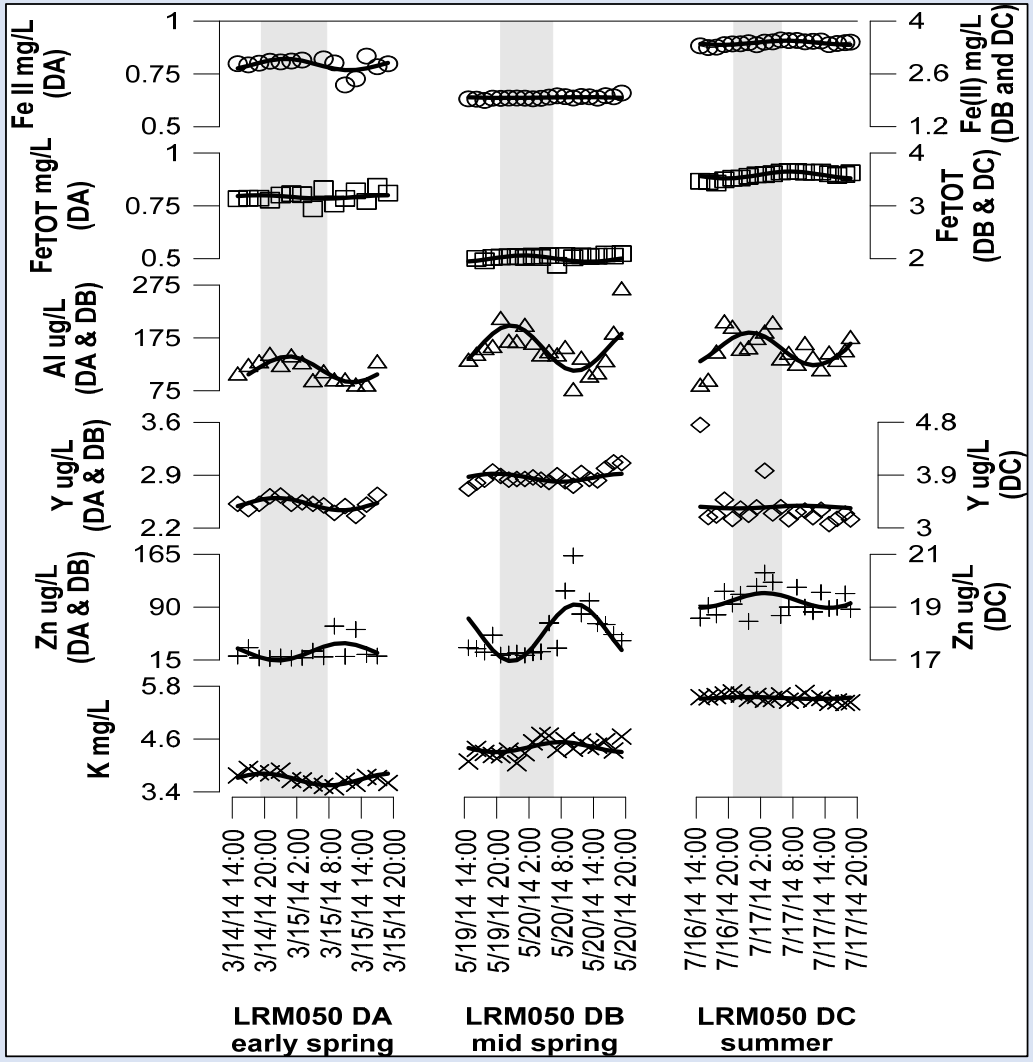


Parameters with $p \leq 0.01$: pH, temperature, ODO, CO_2, Al, K, and Y

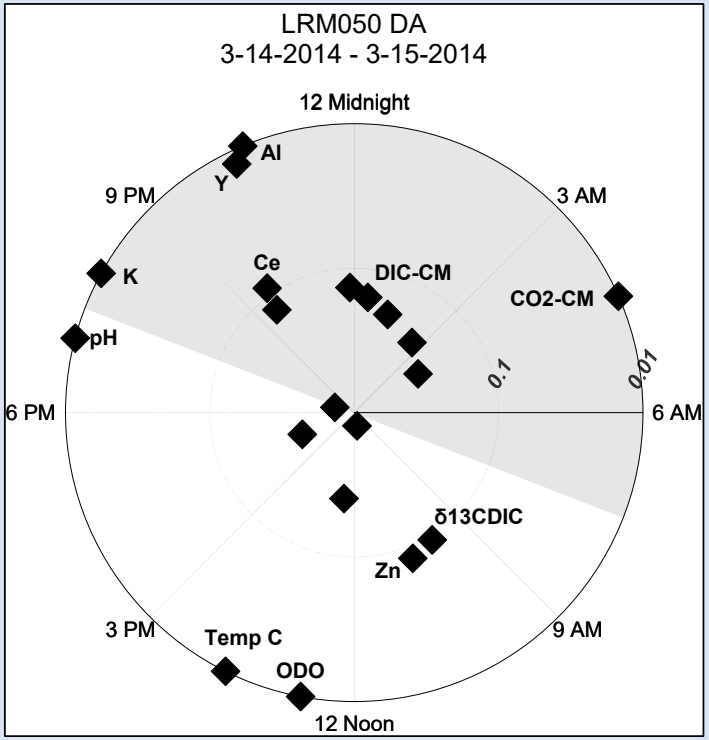


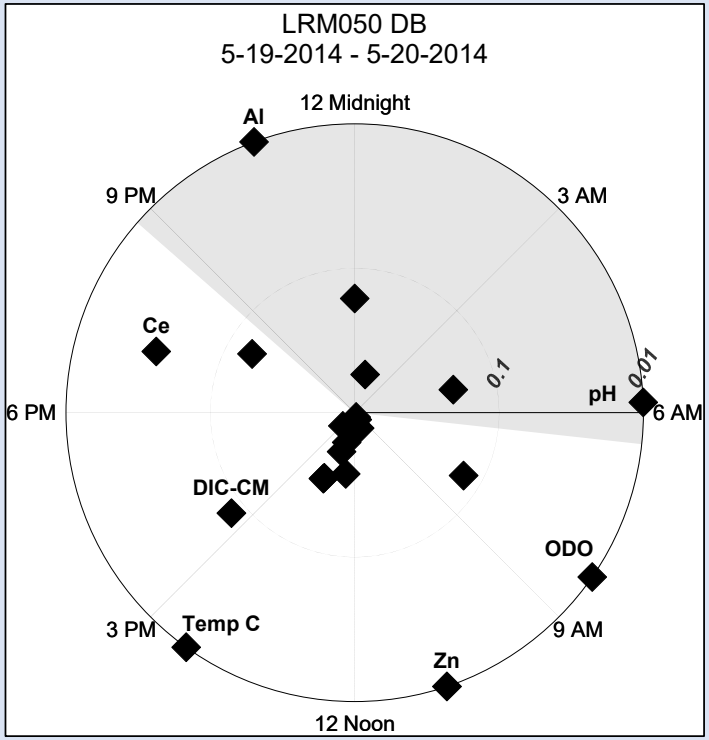
Results – Diurnal Study – LRM050

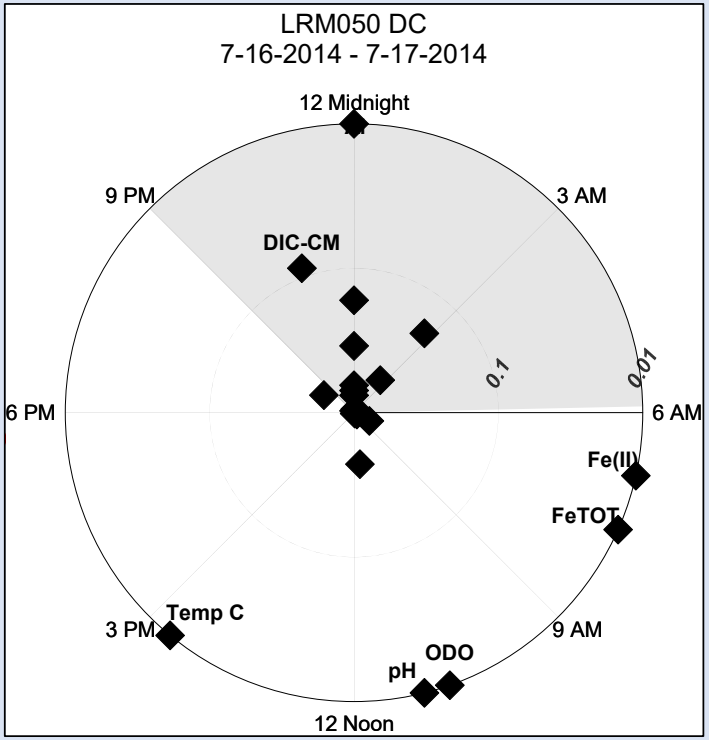




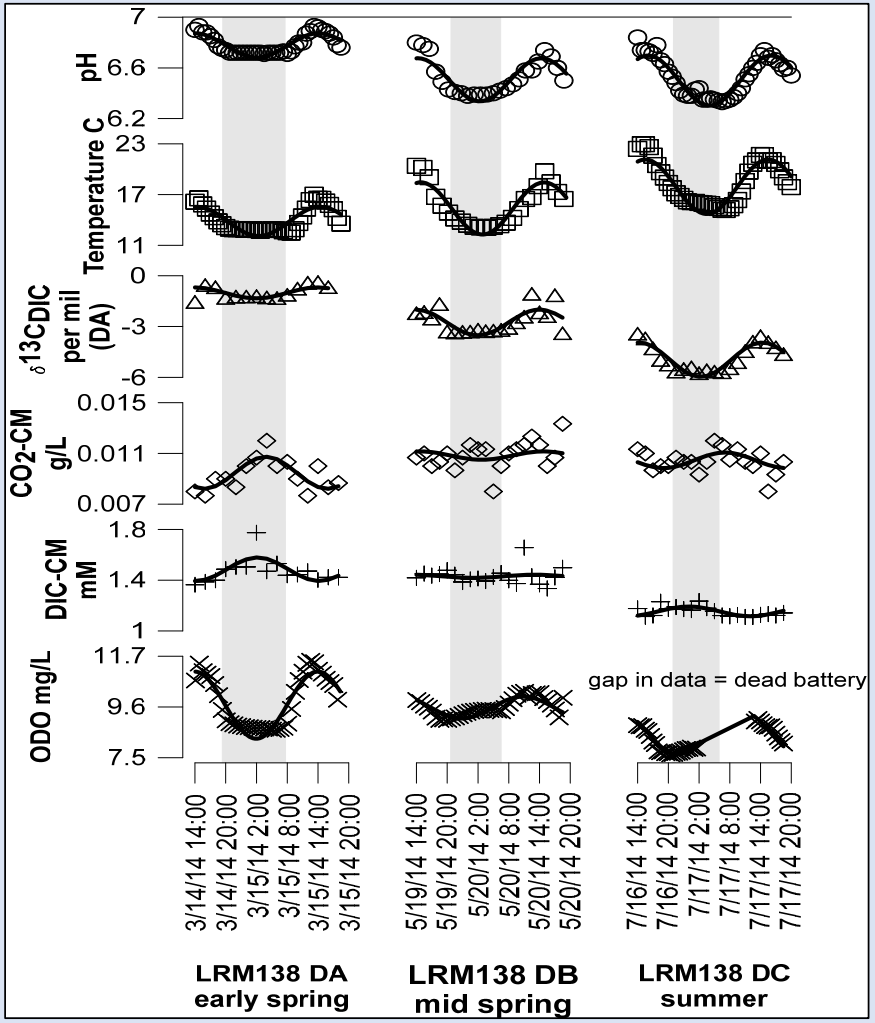
Results – Diurnal Study – LRM050

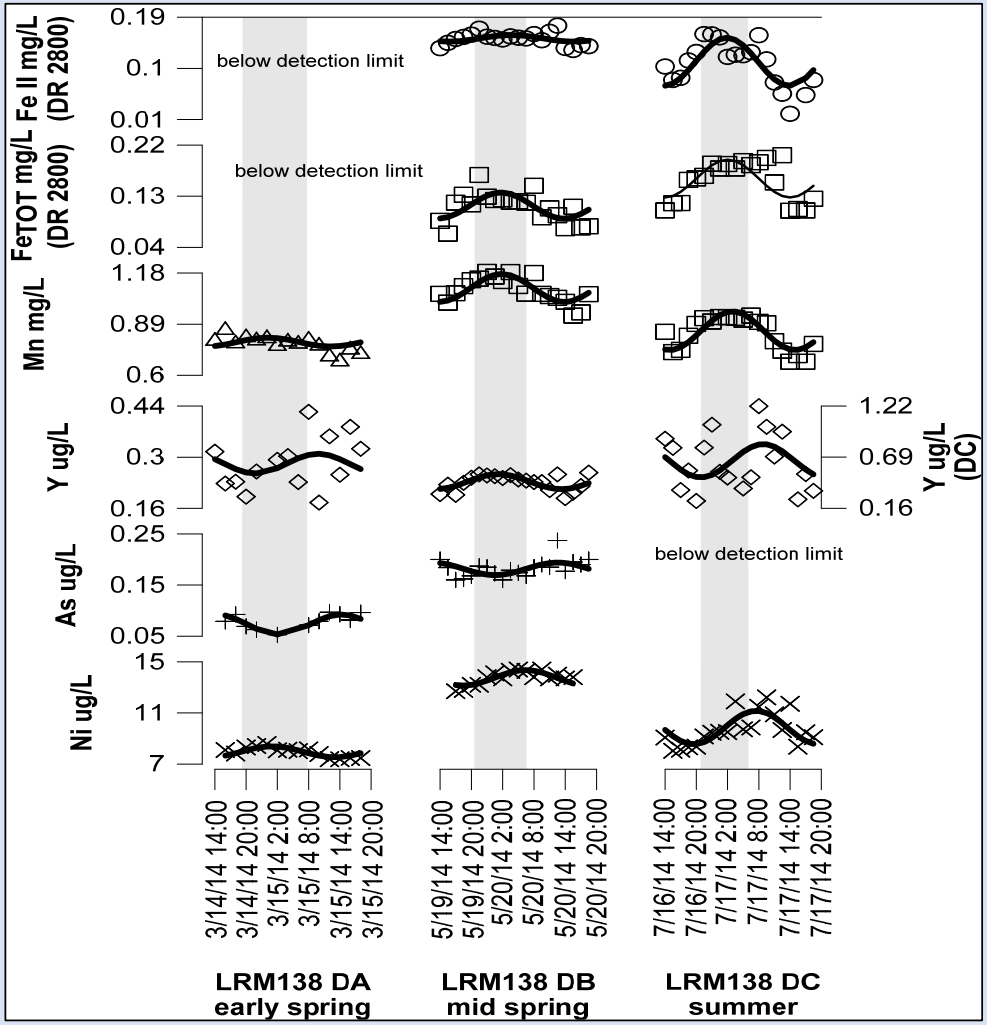




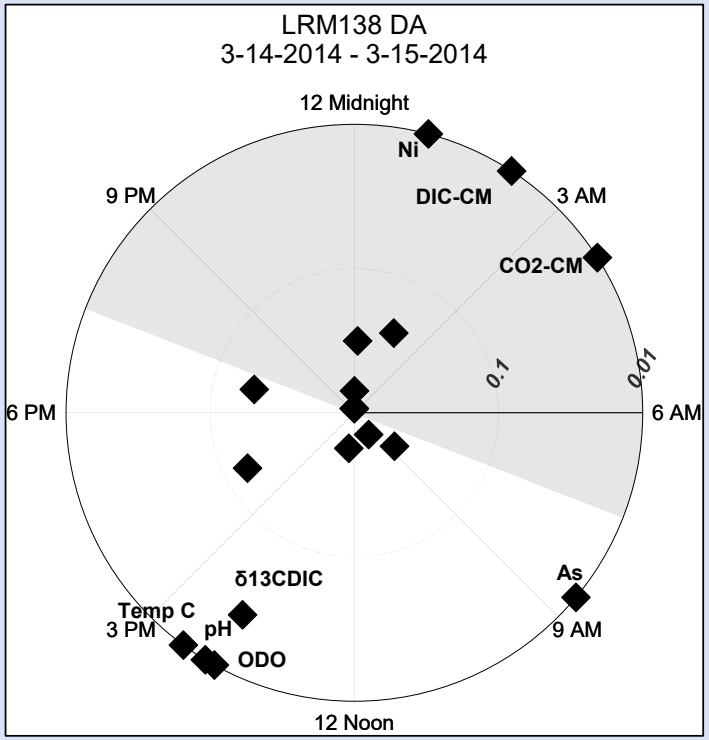


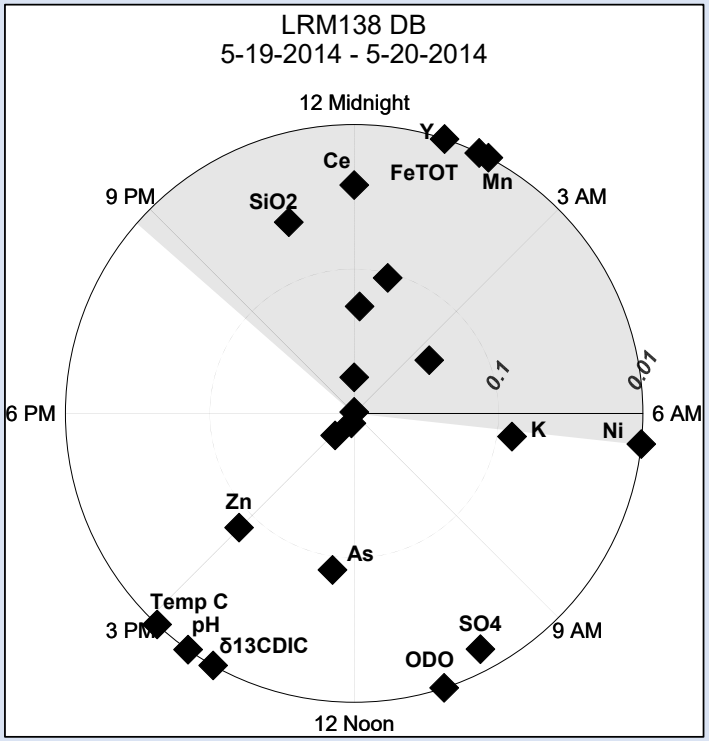
Results – Diurnal Study – LRM138

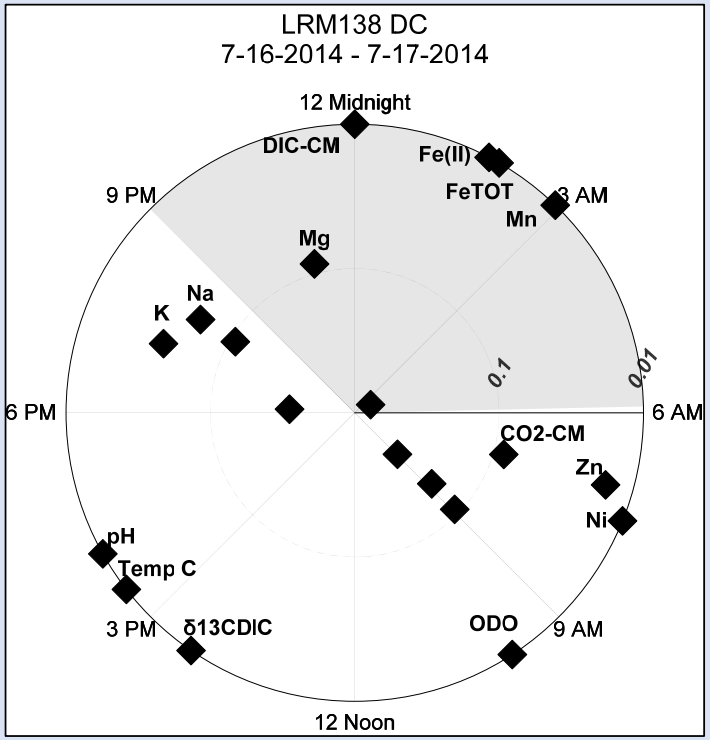




Results – Diurnal Study – LRM138



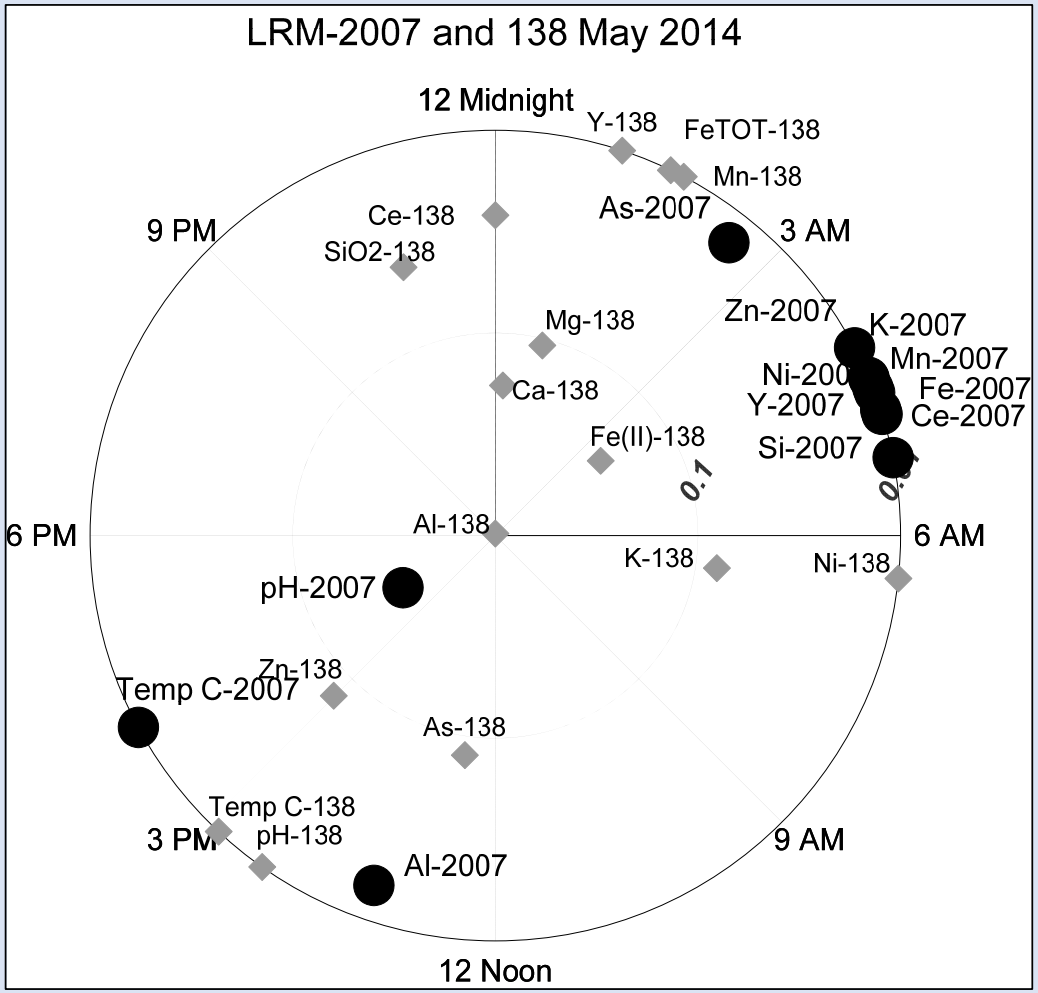




Discussion – Previous LRM Study

LRM-2007 wetland and LRM138 average parameter concentrations from cosine model

Parameter	Mean (2007)	Mean DB	% change
pH	6.96	6.51	-1.84
temperature	19.9	15.4	-29.2
Fe mg/L	0.439	0.153(FeTOT) 0.114 (Fe(II))	-184 -285
Mn mg/L	3.08	1.08	-185
Y ug/L	0.713	0.233	-206
Ce ug/L	0.430	4.99E-2	-761
Al ug/L	15.4	264	+16.1
Ni ug/L	32.3	13.7	-135
As ug/L	0.246	0.182	-35.2
Zn ug/L	38.8	16.2	-139
K ug/L	3.70	3.99	+7.27



Discussion – Mechanisms Driving Diurnal Behavior

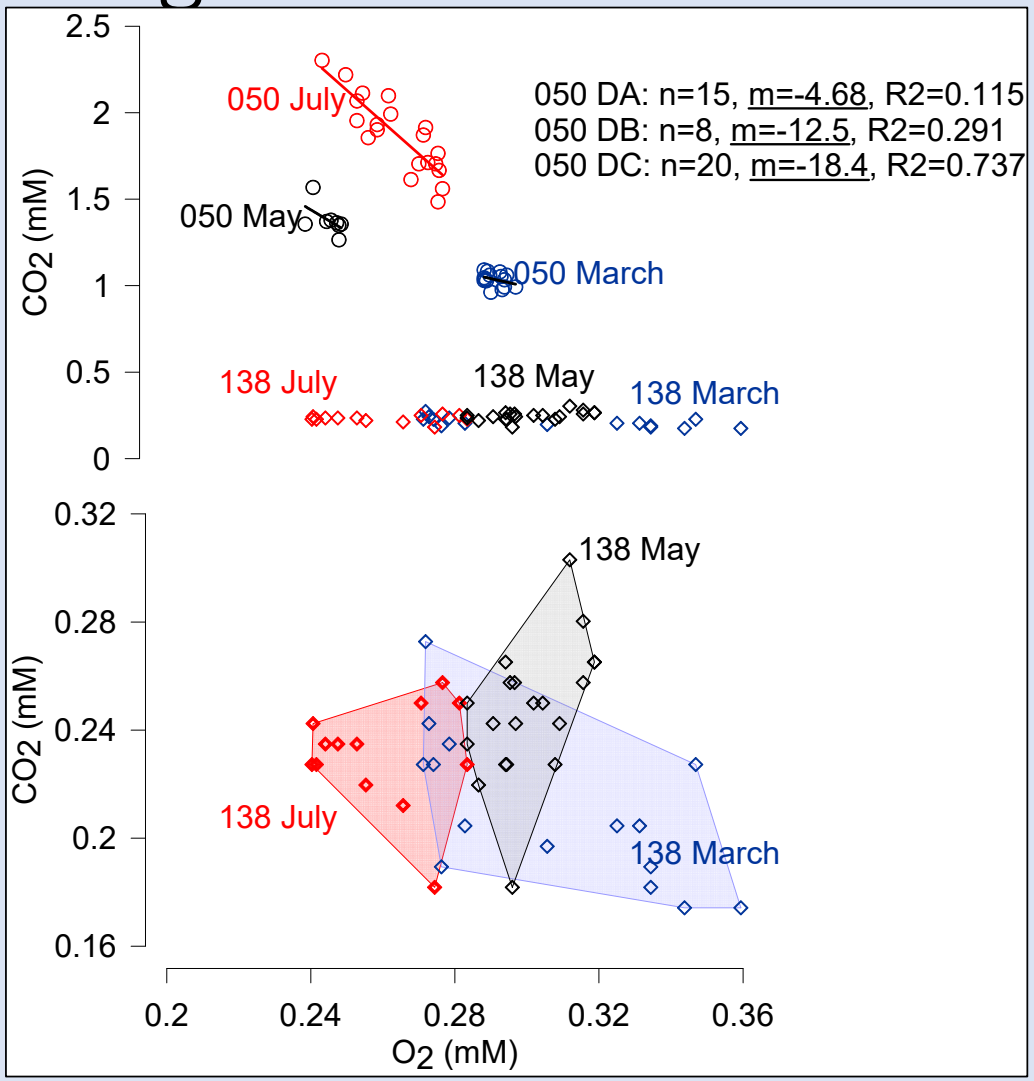
- **sorption (pH-temperature driven) – trace metals**
- photoreduction - iron
- **photosynthesis/respiration-CO_2, pH, DIC, $\delta 1^3C_{DIC}$**
- CO_2 degassing- **CO_2, pH, DIC, $\delta^{13}C_{DIC}$**
- carbonate dissolution- **CO_2, pH, DIC, $\delta^{13}C_{DIC}$**
- decay of organic matter?- **CO_2, pH, DIC, $\delta^{13}C_{DIC}$**

Discussion – Mechanisms Driving Diurnal Behavior

- Molar ratio of O_2/CO_2 not 1 to 1
- Other mechanisms are likely contributing to cycling of CO_2 and DIC.

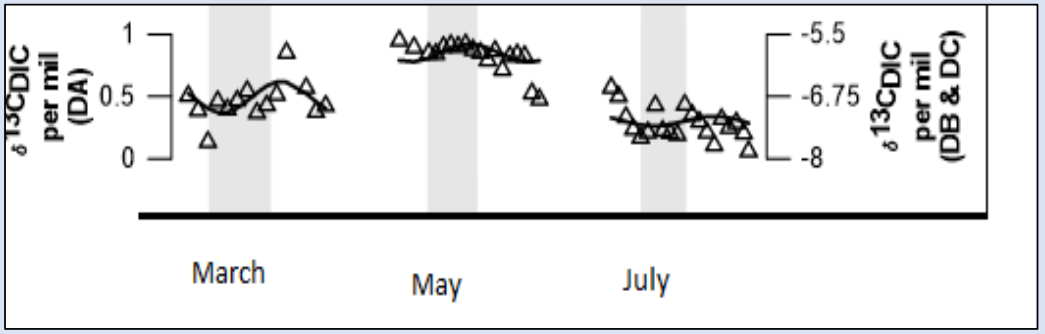
$$6CO_2 + 6H_2O + light \rightarrow C_6H_{12}O_6 + 6O_2$$

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

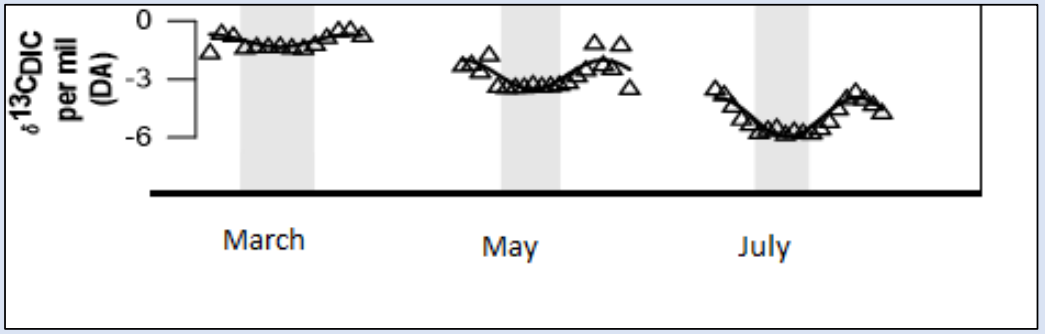


Discussion – Mechanisms Driving Diurnal Behavior

- $\delta^{13}C_{DIC}$ generally shows an increase during the day at LRM138 and LRM050 (except May)
- Lighter ^{12}C taken up during daytime hours
- Water becomes more enriched



LMR050



LRM138

Discussion – Interconnected Processes Drive Diurnal Cycles

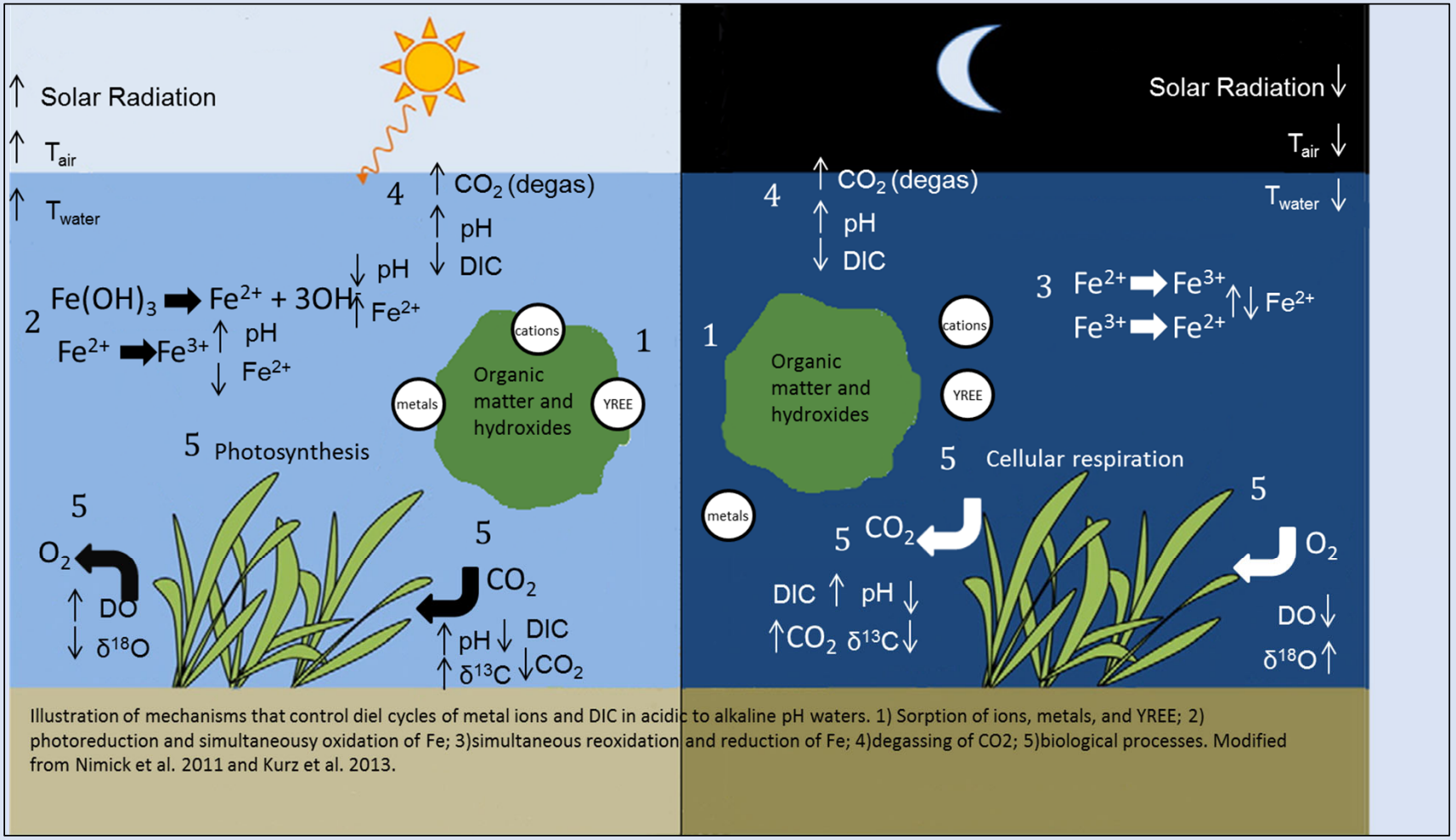


Illustration of mechanisms that control diel cycles of metal ions and DIC in acidic to alkaline pH waters. 1) Sorption of ions, metals, and YREE; 2) photoreduction and simultaneousy oxidation of Fe; 3)simultaneous reoxidation and reduction of Fe; 4)degassing of CO2; 5)biological processes. Modified from Nimick et al. 2011 and Kurz et al. 2013.

Summary and Conclusions

1. Measure diurnal cycles of DIC and metals at 2 locations in the same CMD drainage with different initial CO_2 concentrations and vegetation – does vegetation effect this cycles?

   A) Likely yes, different patterns seen between sites

1. How do changing seasons affect the diurnal cycles of DIC and metals in this system?

   A) Yes, more so in the wetland

Summary and Conclusions

- Diurnal behavior of metals and DIC is not consistent between seasons or between locations in the same site under different vegetative settings.
- Diurnal behavior of parameters can be modeled using a cosine model but the statistical significance of the model fit between different parameters is variable.
- The lower concentrations of metals present in 2014 vs. 2007 suggest the wetland may be effectively reducing metal load.
- The differences in metal concentrations between the two sites and over the 24-hour periods suggest that intensive sampling is necessary to truly assess overall water quality.

References

Bell, M.L. (2020). “Relating recharge mechanisms to chemical changes in an updip Appalachian coal mine discharge: A case study from Lambert Run, West Virginia”. Graduate Theses, Dissertations, and Problem Reports. 7772. pp. 1330

de Montety, V., J. B. Martin, M. J. Cohen, C. Foster and M. J. Kurz (2011). "Influence of diel biogeochemical cycles on carbonate equilibrium in a karst river." Chemical Geology **283**(1-2): 14

Drysdale, R., S. Lucas and K. Carthew (2003). "The influence of diurnal temperatures on the hydrochemistry of a tufa-depositing stream." Hydrological Processes **17**(17): 23.

Dzombak, D. A. and F. M. M. Morel (1990). Surface Complexation and Modeling. Hoboken, N.J., John Wiley.

Gammons, C. H., T. E. Duaime, S. R. Parker, S. R. Poulson and P. Kennelly (2010). "Geochemistry and stable isotope investigation of acid mine drainage associated with abandoned coal mines in central Montana, USA." Chemical Geology **269**(1-2): 13

Hennen, R. V. (1912). Doddridge and Harrison counties, Wheeling news Litho. Co.

Kurz, M. J., V. de Montety, J. B. Martin, M. J. Cohen and C. R. Foster (2013). "Controls on diel metal cycles in a biologically productive carbonate-dominated river." Chemical Geology **358**: 61-74.

Nimick, D. A., T. E. Cleasby and R. B. McCleskey (2005). "Seasonality of diel cycles of dissolved trace-metal concentrations in a Rocky Mountain stream." Environmental Geology **47**(5): 12.

Nimick, D. A., C. H. Gammons, T. E. Cleasby, J. P. Madison, D. Skaar and C. M. Brick (2003). "Diel cycles in dissolved metal concentrations in streams: Occurrence and possible causes." Water Resources Research **39**(9): 17.

Parker, S. R., C. H. Gammons, S. R. Poulson, M. D. DeGrandpre, C. L. Weyer, M. G. Smith, J. N. Babcock and Y. Oba (2010). "Diel behavior of stable isotopes of dissolved oxygen and dissolved inorganic carbon in rivers over a range of trophic conditions, and in a mesocosm experiment." Chemical Geology **269**(1-2): 22-32.

Plummer, L. N., Busenberg, E. (1982). "The solubilities of calcite, aragonite, and vaterite in CO_2-H_2O solutions between 0-90C, and an evaluation of the aqueosu model for teh system $CaCO_3$-CO_2-H_2O." Geochimica et Cosmochimicia Acta **46**(6): 40.

Poulson, S. R. and A. B. Sullivan (2010). "Assessment of diel chemical and isotopic techniques to investigate biogeochemical cycles in the upper Klamath River, Oregon, USA." Chemical Geology **269**(1-2): 9.

Smilley, M. J. (2007). Determination of diel chemical cycle presence within abandoned coal mine drainage streams in Harrison County, WV. Geology and Geography. West Virginia University Libraries, West Virginia University. M.S. Geology: 119.

Riddell, J.L. (2015). “Comparing diel cycles of dissolved inorganic carbon to diel cycles of Fe and Mn at a coal mine drainage site in Harrison Co., WV”. Graduate Theses, Dissertations, and Problem Reports. 6502. pp. 138.

Sullivan, A. B., J. I. Drever and D. M. McKnight (1998). "Diel variation in element concentrations, Peru Creek, Summit County, Colorado." Journal of Geochemical Exploration **64**(1): 5.

Vesper, D. J. and H. M. Edenborn (2012). "Determination of free CO2 in emergent groundwaters using a commercial beverage carbonation meter." Journal of Hydrology **438-439**: 7.

Vesper, D. J., H. M. Edenborn, A. A. Billings and J. E. Moore (2015). " A field-based method for determination of dissolved inorganic carbon in water based on CO_2 and carbonate equilibria." Water, Air, and Soil Pollution **226**(28): 12.