FINAL REPORT

*Project Title*

# Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones

DOE Award Number DE-SC0019422

Principal Investigator: Jeffrey G. Catalano (Washington University)
Team Member: Daniel E. Giammar (Washington University)

## EXECUTIVE SUMMARY

Biogeochemical cycling in subsurface aquatic systems is driven by anaerobic microbial processes that employ metalloenzymes. Pure culture studies reveal that low availability of trace metals may inhibit methanogenesis, mercury methylation, and reduction of $N_2O$ to $N_2$ during denitrification. However, whether such limitations occur in natural subsurface aquatic systems is currently unclear. This project sought to establish mechanistic links between trace metal availability and biogeochemical transformations in subsurface systems. Integrated field and laboratory studies of trace metal availability and biogeochemical processes were conducted in riparian wetlands in the Tims Branch watershed at the Savannah River Site, marsh wetlands at Argonne National Laboratory, and the streambed of East Fork Poplar Creek at Oak Ridge National Laboratory, with supplemental work with wetland soils from sites in Missouri and Florida. The speciation of trace metals in wetland soils and stream sediments shows surprising consistency across the field sites. Dissolved metals also show consistent uptake behavior by the soils and sediments but form distinct species at each site. Geochemical controls on trace metal availability may thus be site-specific despite similar native solid-phase speciation and binding affinities. Maximum bioavailable concentrations of ~10 nM for Cu and ~40 nM for Ni and Co occur in the porewater of stream sediments, below optimal for biogeochemical processes. The addition of Cu stimulates $N_2O$ reduction in stream sediments and riparian wetland soils but not in marsh wetland soils. The formation of nickel-bisulfide complexes induced nickel limitations on methane production in a sulfidic wetland in Missouri, with nickel addition stimulating a factor of 10 increase in methane production. No such limitations were observed in a non-sulfidic wetland in Florida despite the soil sustaining lower dissolved nickel concentrations. The impact of bisulfide complexation was further explored in two additional wetland soils. Production of $CH_4$ in riparian wetland soils increases by 75% following addition of Ni but marsh wetland soils generate indistinguishable amounts of $CH_4$ after similar amendment. Metal limitations on methane production in wetland soils are thus likely muted in the absence of sulfidic conditions. Redox fluctuations in wetland soils and stream sediments promote Co and Zn availability and inhibit Cu availability under anoxic conditions. Oxic conditions in stream sediments and anoxic conditions in riparian wetland soils increase Ni availability. Repeated cycling of redox conditions enhances Zn and Cu bioavailability but decrease Ni and Co bioavailability. Metal limitations on biogeochemical processes may thus differ between consistently anoxic systems and those that redox cycle. Finally, addition of cobalt to incubations of stream sediments did not produce a significant effect on the rate of mercury methylation.

## COMPARISON OF ACCOMPLISHMENTS TO OBJECTIVES:

Listed below are the three primary objectives as originally proposed followed by a summary of the corresponding research accomplishments.

***1. Determine the seasonal and spatial dynamics of trace metal micronutrient availability in wetland soils and stream hyporheic zones.***

This project demonstrated that metal species in wetland soils and stream sediments are largely similar across sites spanning a 1000 km transect. However, the labile metal pool is likely unique at each site, as indicated by distinct mechanisms of uptake by soils and sediments displayed by marsh wetland soils, riparian wetland soils, and stream sediments. The project was not able to address the seasonality of trace metal availability because field activities were curtailed by the COVID-19 pandemic.

***2. Assess how addition of trace metals to wetland soils and hyporheic zone sediments alters important biogeochemical processes that involve metalloenzymes.***

This project demonstrated that nitrous oxide accumulates in wetland soils and stream sediments because of low copper availability, which is inhibited by complexation with natural organic matter. The inability to produce nitrous oxide reductase because of low copper availability may enhance N2O emissions from wetlands. Nickel limitations on methane produce in freshwater wetlands are more limited in extent, constrained to sulfidic systems. The project results were inconclusive regarding whether low cobalt availability may inhibit mercury methylation in aquatic systems.

***3. Identify how fluctuating redox conditions affect trace metal availability in wetland soils and hyporheic zone sediments.***

This project demonstrated that trace metals display element-specific availability patterns during redox fluctuations in wetland soils and stream sediments.

## PROJECT ACTIVITIES:

Below are brief summaries of the activities conducted under this award, including their major findings.

### *Effect of copper on nitrous oxide accumulation in wetland soils and stream sediments*

Denitrification is microbially mediated through enzymes containing metal cofactors. Laboratory studies of pure cultures have highlighted that the availability of Cu, which is required for the multicopper enzyme nitrous oxide reductase, can limit $N_2O$ reduction. However, in natural aquatic systems, such as wetlands and hyporheic zones in stream beds, the role of Cu in controlling denitrification had been incompletely understood. In this study, we collected soils and sediments from three natural environments - riparian wetlands, marsh wetlands, and a stream - to investigate transformation of nitrogen species at background Cu levels and different supplemented Cu loadings. All of the systems contained solid-phase Cu below or around geological background levels (40 - 280 nmol $g^{-1}$) and exhibited low dissolved Cu (3-50 nM), which made them appropriate sites for evaluating the effect of limited Cu availability on denitrification. In laboratory incubation experiments, high concentrations of $N_2O$ accumulated in all microcosms lacking Cu amendment except for one stream sediment sample. With Cu added to provide dissolved concentrations at trace levels (10-300 nM), the reduction rate of $N_2O$ to $N_2$ in the wetland soils and stream sediments was enhanced. This study demonstrated that natural aquatic systems containing Cu at concentrations less than or equal to crustal abundances may display incomplete reduction of $N_2O$ to $N_2$ that would cause $N_2O$ accumulation and release to the atmosphere.

### *Consistent controls on trace metal micronutrient speciation in wetland soils and stream sediments*

Trace metal are essential for microbially-mediated biogeochemical processes occurring in anoxic wetland soils and stream bed sediments, but low availability of these elements may inhibit anaerobic element cycling and transformations. Solid-phase speciation is likely a critical control on trace metal availability but has seen limited study in anoxic systems having concentrations similar to geological background levels, where metal limitations may be most prevalent. We have investigated trace metal concentrations and solid-phase speciation in three freshwater subsurface aquatic systems: marsh wetland soils, riparian wetland soils, and the sediments of a streambed. These systems displayed low solid-phase trace metal concentrations, generally at or below geological background levels, which generally followed the trend Zn > Cu ≈ Ni > Co and showed no correlation with major element compositions. All soils and sediments were dominated by quartz but varied in clay mineralogy as well as the organic matter, total sulfur, and total iron contents. X-ray absorption near-edge structure (XANES) spectroscopy shows that sulfur speciation in both wetlands is dominated by organic sulfur. Elemental sulfur and iron sulfides together made up <25% of the sulfur in the wetland soils, but the distribution between inorganic and organic forms was reversed in the stream sediments. Ferrous and ferric iron in clay minerals were common species identified by both XANES and extended X-ray absorption fine structure (EXAFS) spectroscopies at all sites. Iron(III) oxides were substantial components in all but the marsh wetland soils. Quantitative analysis of copper, nickel, and zinc XANES spectra revealed similar metal speciation across all sites. Copper speciation was dominated by sulfides, adsorbed species, and minor amounts of copper bound to organic matter; no metallic copper was detected. Nickel speciation also varied little and was dominated by nickel in clay mineral octahedral sheets and nickel sulfide, with adsorbed species also present. Zinc speciation was slightly more varied, with the marsh wetland soils and stream bed sediments containing adsorbed species, zinc associated with clay mineral structures, and zinc bound to reduced sulfur groups on organic matter, whereas the riparian wetland soils lacked clay-associated zinc but contained zinc sulfide. Trace metals bound to reduced sulfur occurred at every site, with a greater sulfur-bound fraction for copper. The fractional abundance of sulfur-bound species showed no relationship with soil or sediment total sulfur content, which varied by two orders of magnitude. More broadly, the observations in this study suggest that trace metal speciation in freshwater wetland soils and stream sediments is consistently dominated by a small set of recurring components which are distinct for each metal. This may represent a general geochemical phenomenon in anoxic soils and sediments containing trace metals at background concentrations (as low as 3 $\mu g\ g^{-1}$) that was not predicted from systems that are contaminated with or naturally-enriched in copper, nickel, or zinc.

### *Effect of redox fluctuations on the bioaccessibility of trace metals in natural aquatic systems*

Natural aquatic systems undergo fluctuating redox conditions due to microbial activity, varying water saturation levels, and nutrients dynamics. With fluctuating redox conditions, trace metals can be mobilized or sequestered in response to changes in iron and sulfur speciation and the concentrations and lability of organic carbon. Our study examined the effect of redox fluctuations on trace metal mobility in samples collected from two different natural aquatic systems: riparian wetlands and a stream. We incubated water-saturated soils and sediments under three cycles of anoxic-oxic conditions ($\tau_{anoxic}$:$\tau_{oxic}$ = 3) spanning 24 days and monitored the change in dissolved and bioavailable metal concentrations. For both natural systems, reduction of iron oxides under anoxic conditions caused Co and Zn release. In contrast, oxidation of sulfides mobilized Cu under oxic conditions with materials from both sites. In wetland soils, dissolution of Fe (hydr)oxides increased Ni solubility; however, in stream sediments, Ni release occurred when sulfides or organic matter were oxidized. For stream sediments, each subsequent redox cycle increased the bioavailability of trace metals. Redox fluctuations in wetland soils increased bioavailable Zn and Cu and decreased bioavailable Ni and Co. This study illustrates that different trace metals display distinct bioavailability patterns during redox fluctuations in natural environments.

### *Uptake and speciation of trace metal micronutrients in wetland soils and stream sediments*

Metal solid phase speciation plays a crucial role in determining bioavailability of metals for biogeochemical processes in aquatic ecosystems. Our study combined metal uptake experiments and synchrotron-based spectroscopy to determine the factors controlling copper, nickel, and zinc availability in soils and sediments from three different natural aquatic systems. While soils and sediments from all sites could strongly bind added trace metals, there were substantial differences in trace metal uptake trends between different sites, especially for Cu. There was no distinct correlation between trace metal uptake and the total organic matter, iron, and sulfur content present in the samples. X-ray absorption spectroscopy indicated that the speciation of the freshly added metals taken up by the solids differs substantially from the speciation of the metals originally present in unamended samples. Cu sulfides dominated speciation at low loadings (1 µmol/g), whereas complexation to thiol groups and formation of metallic Cu governed speciation at high loadings (10 µmol/g). For Ni and Zn, adsorption to mineral surfaces and organic matter governed their speciation in materials from most sites. This study suggests that the background speciation of metals in natural aquatic systems is a poor predictor of the speciation and lability of metals introduced to terrestrial aquatic systems from anthropogenic or natural processes. Our findings imply that geochemical processes controlling trace metal speciation may vary considerably with metal loading in different natural systems.

### *Nickel limitations on methane production in freshwater wetlands induced by sulfide complexation*

Wetlands are the largest natural sources of methane to the atmosphere, with emissions controlled by methanogen metabolism modulated by environmental factors. Low trace metal availability inhibits methanogenesis in pure culture and anaerobic bioreactors, but the prevalence of such limitations in freshwater wetlands is ambiguous. If present, these would lower methane emissions, an effect not currently accounted for in Earth system models. The impact of nickel availability on soil methane production from two freshwater wetlands, one in Missouri and one in Florida. Both sites display dissolved trace metal concentrations that pure culture studies predict induce metal limitations on methanogenesis. Amending soil incubations with nickel causes an order of magnitude increase in methane production for one wetland, but soil from the second site shows no response to the addition of nickel, despite having lower metal levels overall. Iron sulfides occur in soils from the first wetland and play a dominant role in binding nickel at the site. In contrast, soils lack iron sulfides at the second site that displays no metal limitations on methane production, with nickel binding primarily to organic matter. The origin of this contrast in nickel-limited methanogenesis between the two sites is not related to sulfide-induced solubility constraints because the wetland soil containing iron sulfides produced greater total dissolved nickel concentrations. Instead, nickel limitations were caused by the formation of nickel-bisulfide aqueous complexes. Prior studies with anaerobic digestors indicate that such complexes are not accessible to methanogens and similar effects are likely the cause of nickel limitations in freshwater wetlands experiencing sulfidic conditions. Review of the pure culture studies indicating optimal nickel concentrations for methanogenesis occur near 1 µM show that $H_2S$ was present in gas headspaces and that much of the dissolved nickel in those experiment also occur as aqueous nickel-bisulfide complexes. Optimal dissolved nickel levels in the absence of such complexation appear to be below 100 nM and are likely provided by soils in non-sulfidic wetlands. Nickel limitations in freshwater wetlands will be restricted to those receiving sulfur inputs capable for inducing sulfidic conditions. The substantial decrease in sulfur deposition over recent decades may lessen the occurrence of such limitations, potentially enhancing rates of methane emissions.

### *Evaluating sulfur impacts on methane production in marsh and riparian wetland soils*

Initial studies conducted for this project revealed that nickel limitations were displayed by a sulfidic freshwater wetland but absent from a non-sulfidic wetland. The lack of nickel limitations in non-sulfidic wetland was further investigate in soils from a marsh wetland and a riparian wetland, both non-sulfidic. Microcosm incubation studies were carried out using soils from both sites to further explore the effect of dissolved Ni concentrations on methane production. Dissolved Ni concentrations were substantially lower than the optimal range for methanogenesis identified in pure culture studies but both wetland soils continuously produced methane over a 7 to 10 weeks incubation period. Methane production by the marsh wetland soil did not change when dissolved Ni concentrations were increased to 0.5 to 4 µM through amendment to parallel incubations, indicating a lack of Ni limitation. In contrast, amending the riparian wetland soil to increase dissolved Ni concentrations to 0.4 to 1.3 µM stimulated up to a ~75% increase in methane production from 3 to 10 weeks of incubation time. The water at the marsh wetland contained substantially greater dissolved sulfate concentration than for the riparian wetland (576 µM versus 8 µM), which may have impacted apparent methane production through substrate competition or promotion of anaerobic methane oxidation. Incubations of marsh wetland soils in sulfate-free water also displayed no evidence for Ni limitations. The subtle evidence of nickel limitations on methane production displayed by the riparian wetland soil may reflect the low nickel content in this system, limiting its ability to sustain adequate nickel availability. However, neither soil displayed the order of magnitude increase in methane production displayed previously by a sulfidic freshwater wetland soil when nickel was added. This demonstrates that substantial impacts on methane production by low nickel availability are limited to sulfidic wetlands.

### *Estimating labile trace metal concentrations in freshwater sediments using diffusion-based sampling devices*

Microbial enzymes essential for carrying out the biogeochemical processes, such as methanogenesis, denitrification, and aerobic methanotrophy, contain trace metals (Ni, Co, Cu, and Zn) in cofactors. Low bioavailability of trace metals can inhibit the microbial processes and affect carbon and nitrogen cycling in natural systems. We conducted an extensive study to determine the bioavailability of trace metals using the diffusive gradients in thin films (DGT) technique in freshwater sediments and streams located at East fork Poplar Creek (EFPC), Tennessee. DGT sediment probes were deployed at four different locations to obtain high-resolution depth profiles of trace metals (Cu, Co, Ni, and Zn). The technique provided estimates of the labile metal concentrations in the pore water ($M_{DGT}$). The depth profiles of trace metals varied substantially across different metals and locations and followed the trend $Zn_{DGT} > Co_{DGT} > Cu_{DGT} \approx Ni_{DGT}$. $Co_{DGT}$ and $Mn_{DGT}$ exhibited closely corresponding profiles, whereas $Cu_{DGT}$ and $Ni_{DGT}$ were positively correlated with $Fe_{DGT}$. The variability in dissolved organic carbon concentrations at the locations studied substantially affected the labile trace metal concentrations. We observed that extended deployment times (> 24 h) underestimated the DGT-estimated labile trace metal concentrations. Our study indicated that the trace metals are strongly associated with solid-phases at the studied locations and are not mobilized due to a local sink induced by DGT samplers.

### ***Trace metal uptake and mercury methylation by stream sediments***

The formation and transport of methylmercury (MeHg), a neurotoxin, in aquatic environments is a global concern for human health as MeHg can bioaccumulate and biomagnify to high concentrations in aquatic food webs. MeHg is formed by conversion from inorganic mercury through microbial mediated methylation. Sulfate-reducing bacteria have been identified as the primary organisms responsible for MeHg production. Pure-culture studies suggest that low availability of cobalt and copper may inhibit mercury methylation, but whether such limitations occur in the environment is unclear. To explore this possible interaction, sediments from the East Fork Poplar Creek in Oak Ridge, Tennessee were incubated in the presence and absence of added dissolved cobalt and copper. This section of the creek contains elevated mercury concentrations in the sediments due to industrial contamination and the rates and controls on methylation have been studied extensively. Part one of this study examined mercury methylation in sediments with two levels of dissolved cobalt additions within the range suggested to be ideal for MeHg production in pure culture studies. These concentrations were estimated from preliminary measurements of cobalt binding by the sediments. Sulfide was generated over the 72-hour incubation period indicating that sulfate-reducing bacteria were active. MeHg concentrations increased over the time period studied with no noticeable enhancement of methylation resulting from the addition of cobalt. Methylation and demethylation rates both decreased with increasing cobalt concentrations. Overall, cobalt appeared to either inhibit or have no effect on mercury methylation in the sediments. The second part of the study explored the effects of added cobalt and copper to the sediments. Again, concentrations within targeted range suggested by pure culture studies were estimated from cobalt and copper uptake to the sediments. The cobalt or copper, sediments, and artificial site water were allowed to interact for 4 weeks or 8 weeks, respectively, with samples taken periodically. Dissolved sulfate concentrations decreased after 10 days in the presence and absence of the metals and sulfide was generated which suggested sulfate-reducing bacteria were active. Dissolved phosphate increased over time in both the cobalt and copper systems. The addition of cobalt and copper had no effect on the dissolved concentrations of other trace metals (Zn, Ni, Cu, Co). The systems with added copper had increased concentration of dissolved Fe compared to the no copper added. Overall, the addition of cobalt or copper at the concentrations studied seem to have little or no impact on behavior of other ions in the sediments suggesting that they may not influence mercury methylation at the conditions studied.

**PRODUCTS:**
The following products were supported wholly or in part by this DOE award.

***Peer-reviewed Journal Articles:***

1. Sharma N., Wang Z., Catalano J.G., Giammar D.E. (2022) Dynamic response of trace metal bioaccessibility to fluctuating redox conditions in wetland soils and stream sediments. *ACS Earth and Space Chemistry* **6**, 1331-1344.
2. Sharma N., Flynn E.D., Catalano J.G., Giammar D.E. (2022) Copper availability governs nitrous oxide accumulation in wetland soils and stream sediments. *Geochimica et Cosmochimica Acta* **327**, 96-115.
3. Yan J., Frierdich A.J., Catalano J.G. (2022) Impact of Zn substitution on Fe(II)-induced ferrihydrite transformation pathways. *Geochimica et Cosmochimica Acta* **320**, 143-160.
4. Chatterjee A., Zhang K., Rao Y., Sharma N., Giammar D.E., Parker K.M. (2022) Metal-catalyzed hydrolysis of RNA in aqueous environments. *Environmental Science & Technology* **56**, 3564-3574.
5. Yan J., Sharma N., Flynn E.D., Giammar D.E., Schwartz G.E., Brooks S.C., Weisenhorn P., Kemner K.M., O’Loughlin E.J., Kaplan D.I., Catalano J.G. (2022) Consistent controls on trace metal micronutrient speciation in wetland soils and stream sediments. *Geochimica et Cosmochimica Acta* **317**, 234-254.

***Manuscripts under Review:***

1. Sharma N., Yan J., Flynn E.D., Catalano J.G., Giammar D.E. (2023) Uptake and speciation of trace metal inputs to soils and sediments from terrestrial aquatic systems. Submitted to *ACS Earth and Space Chemistry*, November 2022.

***Manuscripts in Preparation:***

1. Sharma N., Brooks S.C., Catalano J.G., Giammar G.E. (2023) Applicability of diffusion-based sampling devices to quantifying labile trace metal concentrations in freshwater sediments.
2. Crompton N.M., Hasenmueller E.A., Chambers L.G., Bradley A.S., Flynn E.D., Giammar D.E., Catalano J.G. (2023) Indirect sulfidic inducement of nickel limitations on methane production in freshwater wetland soils.
3. Flynn E.D., Schwartz G.E., Brooks S.C., Catalano J.G. (2023) Trace metal uptake and mercury methylation by sediments from a stream in Tennessee, USA.
4. Yan J., Flynn E.D., Weisenhorn P., Kemner K.M., O’Loughlin E.J., Kaplan D.I., Catalano J.G. (2023) Evaluation of potential nickel limitations on methane production from marsh and riparian wetland soils.

***Ph.D. Dissertations:***

1. Jinshu Yan, “Trace Metal Speciation and Impacts on Iron Oxide Transformations and Biogeochemical Cycling” Ph.D. dissertation, April 2022, Washington University.
2. Neha Sharma, “Fate of metals in presence of minerals and mineral-organic assemblages” Ph.D. dissertation, December 2022, Washington University.

***Datasets:***

1. Flynn E.D., Schwartz G.E., Brooks S.C., Catalano J.G. (2023) Trace Metal Uptake and Mercury Methylation by Sediments from a Stream in Tennessee. Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. Dataset. ess-dive-6c50ca378f11d11-20230112T145204296.
2. Sharma N., Brooks S.C., Catalano J.G., Giammar D.E. (2023): Trace metal bioaccessibility in freshwater sediments using diffusion-based sampling devices. Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. Dataset. ess-dive-6fa24b63642ff22-20230105T001851908.
3. Yan J., Flynn E.D., Catalano J.G. (2023) Wetland Soil Characterization and Methane Production Impacted by Nickel Addition, Argonne and Tims Branch Wetlands, September and October 2020. Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. Dataset. doi: 10.15485/1908426.
4. Sharma N., Yan J., Flynn E.D., Catalano J.G., Giammar D.E. (2022): Uptake and speciation of trace metal inputs to Wetland Soils from Illinois and South Carolina and Stream Sediments from Tennessee. Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. Dataset. doi: 10.15485/1888044.
5. Sharma N., Flynn E.D., Catalano J.G., Giammar D.E. (2022) Role of copper in nitrous oxide accumulation in wetland soils from Illinois and South Carolina and stream sediments from Tennessee. Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. Dataset. doi: 10.15485/1871342
6. Sharma N., Wang Z., Catalano J.G., Giammar D.E. (2022) Effect of fluctuating redox conditions on trace metal release from wetland soils from South Carolina and stream sediments from Tennessee. Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. doi:10.15485/1871343
7. Yan J., Sharma N., Flynn E.D., Giammar D.E., Schwartz G.E., Brooks S.C., Weisenhorn P., Kemner K.M., O'Loughlin E.J., Kaplan D.I., Catalano J.G. (2021) Soil and Water Chemistry and Trace Metal Extractability and Speciation in Wetland Soils from Illinois and South Carolina and Stream Sediments from Tennessee. Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. doi:10.15485/1773008.
8. Catalano J.G., Cromptom N.M., Hasenmueller E.A., Chambers L.G., Bradley A.S., Flynn E.D., Giammar D. E. (2020) Trace Metal Content and Speciation, Water and Soil Chemistry, and Methane Production for a Wetland in Missouri (September 2015) and in Florida (January 2016). Trace Metal Dynamics and Limitations on Biogeochemical Cycling in Wetland Soils and Hyporheic Zones, ESS-DIVE repository. doi:10.15485/1630815.

***Conference Presentations:***

Note: This list does not include presentations at principal investigator meetings because those were required and are thus implicit.

1. Sharma N., Brooks S.C., Catalano J.G., Giammar D.E. (2022) Quantifying labile trace metal concentrations and desorption kinetics in freshwater sediments using diffusion-based sampling devices. Oral presentation at the *ACS Spring 2022 National Meeting*, April 2022.
2. Sharma N., Wang Z., Catalano J.G., Giammar D.E. (2022) Impacts of oscillating redox conditions on trace metal mobilization in natural aquatic systems. Oral presentation at the *ACS Spring 2022 National Meeting*, April 2022.
3. Yan J., Sharma N., Flynn E.D., Giammar D.E., Catalano J.G., Schwartz G.E., Brooks S.C., Weisenhorn P., Kemner K.M., O'Loughlin E.J., Kaplan D.I. (2020) Speciation and availability of trace metals essential for microbial element cycling in wetland soils and stream sediments. Virtual oral presentation at the *Goldschmidt Conference 2021*, July 2021.
4. Sharma N., Yan J., Flynn E.D., Catalano J.G., Giammar D.E. (2021) Role of copper availability on denitrification in natural systems. Virtual oral presentation at the *ACS Spring 2021 National Meeting*, April 2021.
5. Catalano J.G., Yan J., Flynn E.D., Sharma N., Giammar D.E., Schwartz G.E., Brooks S.C., Weisenhorn P.B., Kemner K.M., O'Loughlin E.J., Kaplan D.I. (2020) Consistent Controls on Trace Metal Micronutrient Speciation in Wetlands Soils and Stream Sediments. Virtual keynote presentation at the *2020 Virtual Goldschmidt Conference*, June 2020.
6. Yan J., Sharma N., Flynn E.D., Giammar D.E., Catalano J.G., Schwartz G.E., Brooks S.C., Weisenhorn P., Kemner K.M., O'Loughlin E.J., Kaplan D.I. (2020) Speciation and availability of trace metals essential for microbial element cycling in wetland soils and stream sediments. Oral presentation at the *ACS Spring 2020 National Meeting & Expo*, March 2020 (cancelled by COVID-19 pandemic).
7. Flynn E.D., Schwartz G.E., Brooks S.C., Giammar D.E., Catalano J.G. (2020) Impact of cobalt on mercury methylation in East Fork Poplar Creek, Oak Ridge, Tennessee. Oral presentation at the *ACS Spring 2020 National Meeting & Expo*, March 2020 (cancelled by COVID-19 pandemic).
8. Catalano J.G., Crompton N.M., Bradley A.S., Flynn E.D., Yan J., Sharma N., Giammar D.E., Hasenmueller E.A., Chambers L.G. (2019) Connection between Heavy Metals and Greenhouse Gas Emissions from Wetlands. Invited oral presentation at the *Society of Wetland Scientists 2019 Central Chapter Annual Meeting*, October 2019.
9. Yan J., Sharma N., Flynn E.D., Giammar D.E., Catalano J.G. (2019) Controls on Trace Metal Speciation and Availability in Wetland Soils. Poster presentation at *Midwest Geobiology 2019*, September 2019.
10. Yan J., Catalano J.G., Chen H., Wang K. (2020) Zinc Release and Reimmobilization during Fe(II)-induced Ferrihydrite Transformation. Oral presentation at the *Goldschmidt Conference 2019*, August 2019.
11. Catalano J.G. (2019) Hidden Iron Cycling at Redox Interfaces: Impact on Contaminant Fate and Micronutrient Availability. Invited presentation at *Peking University*, May 2019.
12. Catalano J.G. (2019) Hidden Iron Cycling at Redox Interfaces: Impact on Contaminant Fate

and Micronutrient Availability. Invited presentation at *China University of Geosciences*, May 2019.

13. Catalano J.G. (2019) Trace Metal Limitations on Methane Production in Freshwater Wetlands. Invited presentation at *China University of Geosciences*, May 2019.
14. Catalano J.G., Crompton N.M., Bradley A.S., Giammar D.E., Hasenmueller E.A., Chambers L.G. (2019) Link between Metal Speciation and Biogeochemical Processes in Wetland Soils. Keynote presentation at *ICOBTE 2019*, May 2019.
15. Catalano J.G. (2019) Hidden Iron Cycling at Redox Interfaces: Impact on Contaminant Fate and Micronutrient Availability. Invited presentation at *Nanjing University*, May 2019.