

Transfer of Legacy Mercury from Aquatic Habitats to the Terrestrial Food Web Surrounding the St. Louis River

Sarah E. Janssen¹, David M. Walters², Joel C. Hoffman³, Gale B. Beaubien⁴, Mark A. Mills⁴, Collin Eagles-Smith⁵, David P. Krabbenhoft¹, Greg Peterson³, and Mark Pearson³

Contact: sjanssen@usgs.gov or mercury@usgs.gov



INTRODUCTION

Elevated mercury (Hg) concentrations have been documented in the St. Louis River (SLR) Area of Concern (AOC) due to point source contamination (legacy and current) and atmospheric deposition. Legacy contamination has been shown contribute to Hg levels in benthic insects, prey and game fish feeding within SLR. However, there is growing recognition that aquatic contaminants, like Hg, can be transported from aquatic to terrestrial food webs via emerging adult aquatic insects, and riparian predators, such as spiders, are increasingly used as bioindicators of aquatic contamination levels. In order to assess the Hg sources being transferred to the terrestrial food web, we measured Hg stable isotopes in long-jawed spiders (*Tetragnathidae*), benthic invertebrates (e.g., odonates, hexagenia), and prey fish (e.g., cyprinids) within SLR spanning from upstream reservoirs to the lower estuary near Duluth, MN and reference locations in Boulder Reservoir, MN and the Bad River, WI.

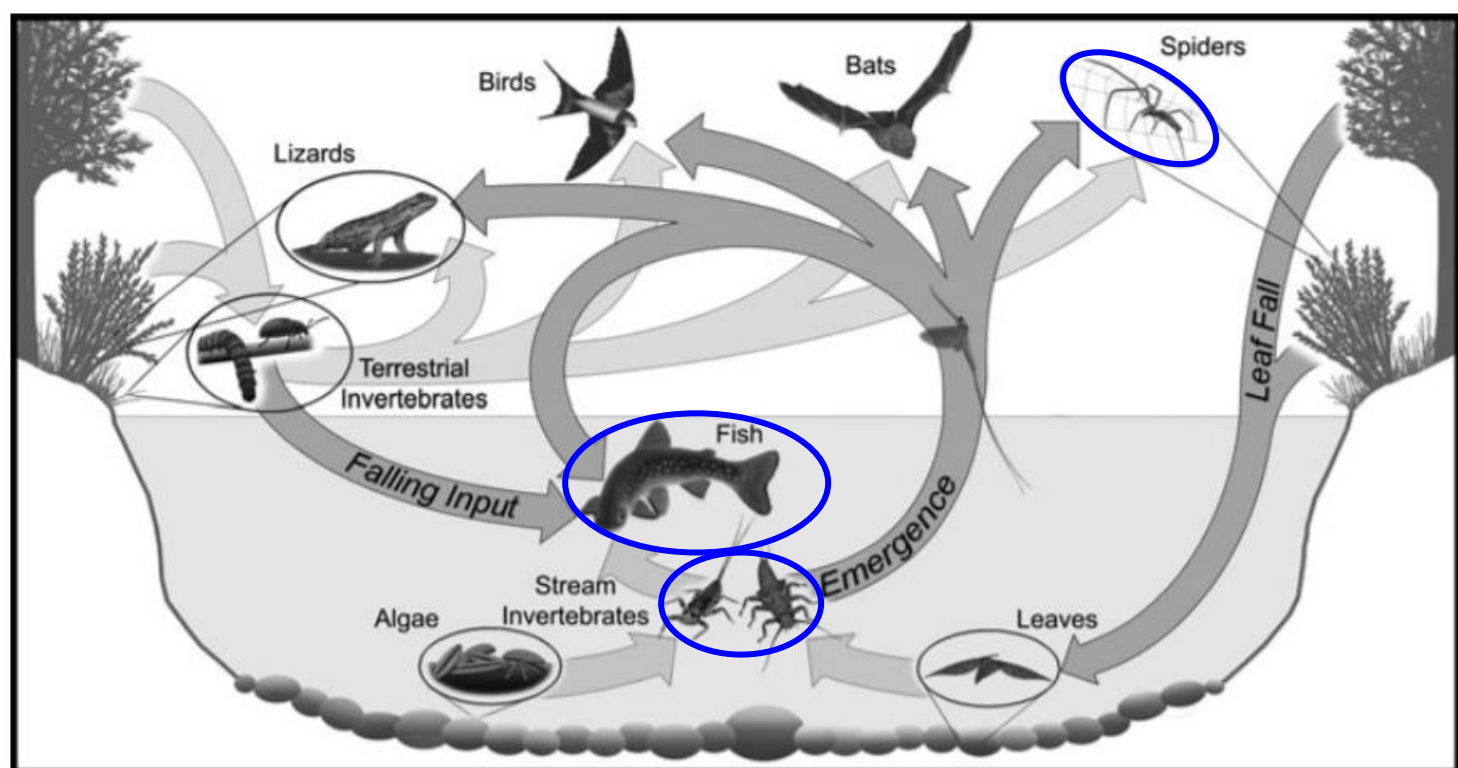


Figure 1: Aquatic-terrestrial food web interactions in rivers. Stream insects spend their life as aquatic larvae then undergo metamorphosis into winged adults and become an important food for many terrestrial predators. Blue circles represent organisms studied in the SLR AOC. Figure from Baxter et al. 2005 (doi:10.1111/j.1365-2427.2004.01328.x)

OBJECTIVES

- Assess if sediment Hg sources are conserved in both the aquatic and terrestrial food webs of SLR
- Determine if Hg isotopic values are conserved through physiological changes in emergent insects (e.g., metamorphosis)

RESULTS – Hg Concentration

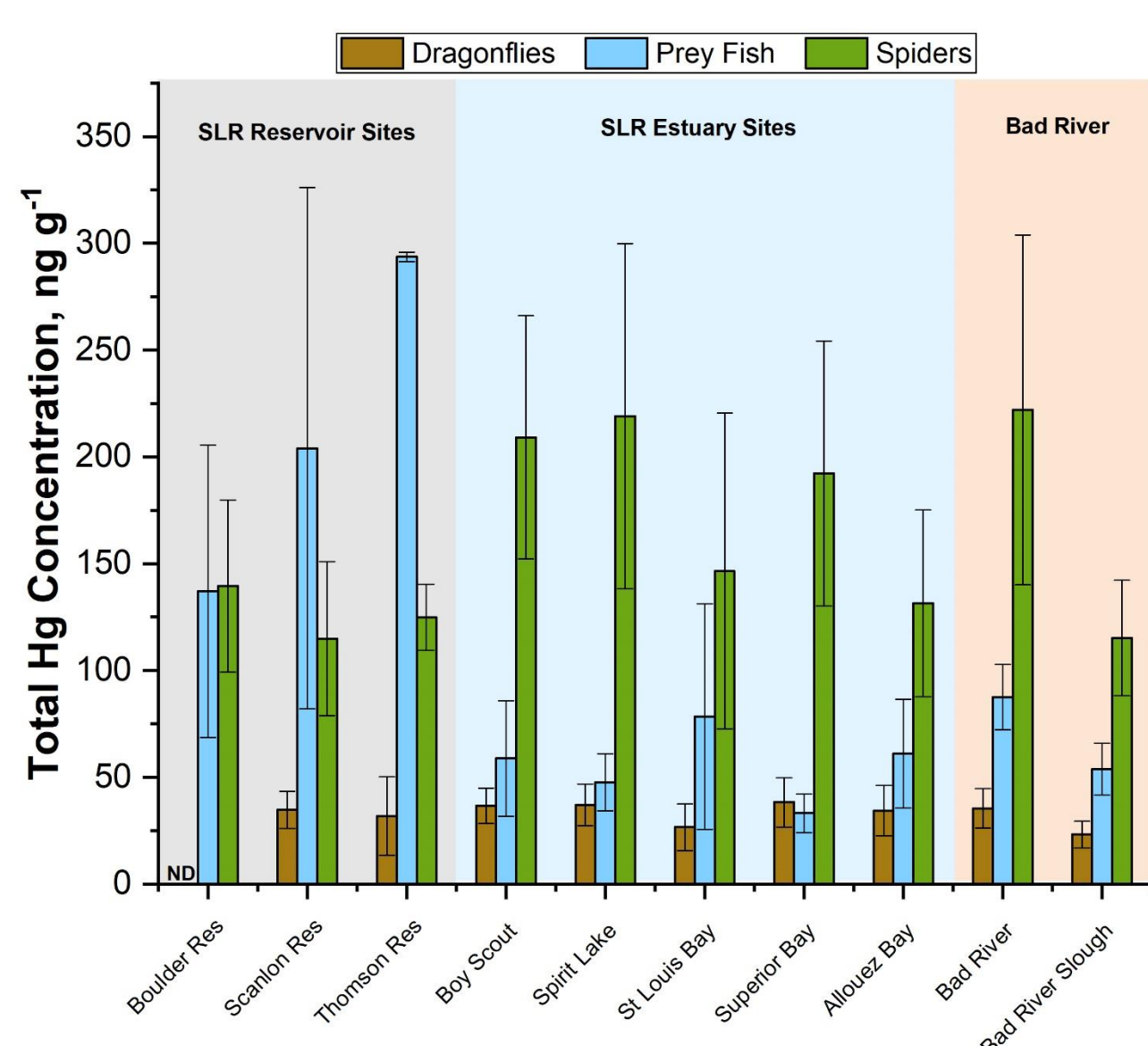


Figure 2: Hg concentrations across taxa. Spiders (green) show consistently higher concentrations than prey fish (blue) and dragonflies (brown) in the SLR estuary and Bad River, but lower concentrations in comparison to fish in the reservoirs. Both prey fish and spiders are believed to target benthic invertebrates as prey, but differences in bioaccumulation of Hg could result from foraging differences, Hg source exposure, or physiological changes.

RESULTS – Hg Isotopes

I. Sediment Hg Sources to the Aquatic Food Web

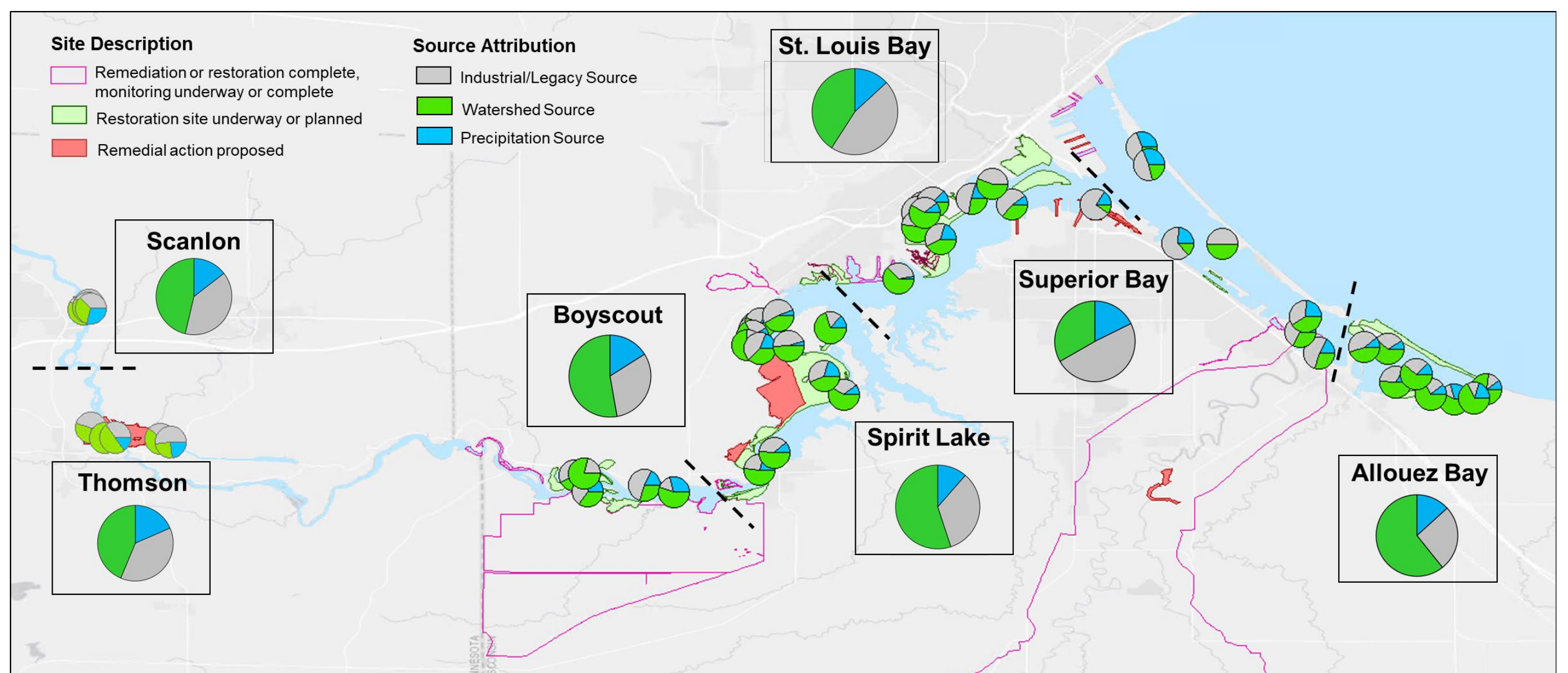


Figure 3: Source apportionment in sediments of the SLR AOC using Hg isotopes: Large inset pie charts represent the average source contribution at each site. The SLR reservoir and estuary sites show large proportions of industrial legacy Hg within sediments, a potential exposure route to the food web. The Bad River and Boulder Reservoir (not shown) were predominantly watershed Hg sources (> 70%). Average source model error is ± 14%.

II. Variation in Spider Hg Isotope Values

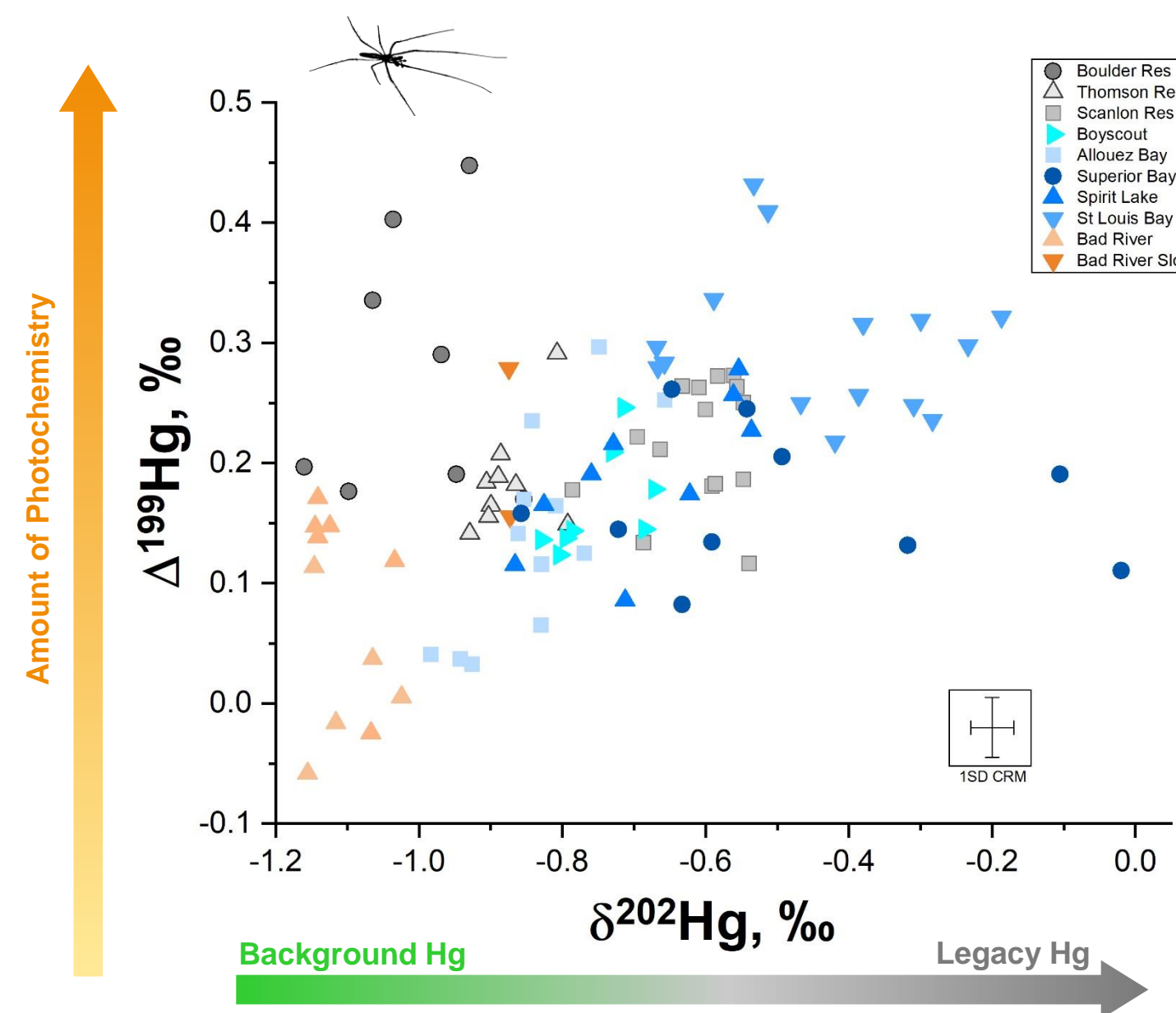


Figure 4: Hg isotope biplot for spiders collected within SLR and reference locations. Spiders show a wide range of Hg isotope values associated with Hg sources (denoted by $\delta^{202}\text{Hg}$) and photochemical demethylation in the water column (denoted by $\Delta^{199}\text{Hg}$). Reservoir and estuarine sites show positive $\Delta^{199}\text{Hg}$ indicating the incorporation of Hg that has been photochemically cycled in the water column.

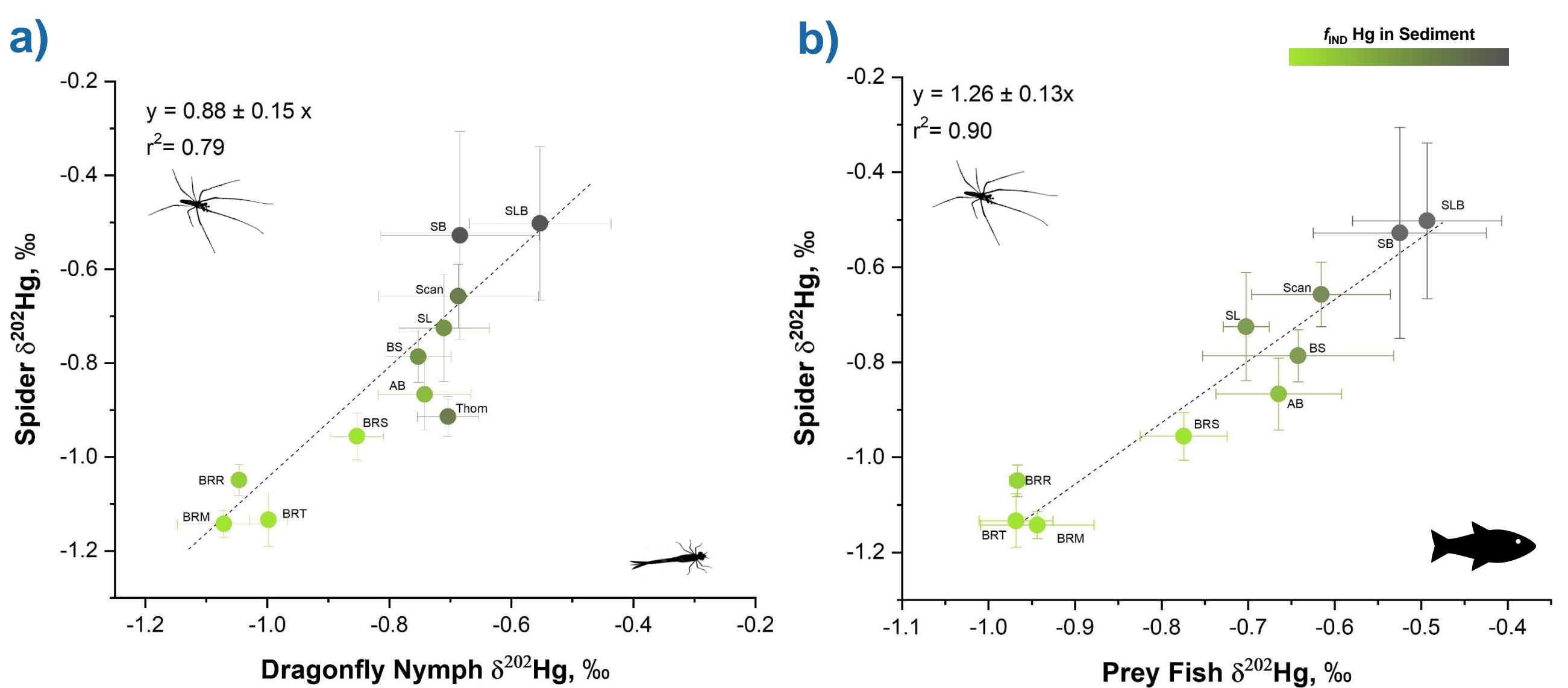


Figure 5: Comparison of spider isotope values to a) dragonflies and b) prey fish. Spider Hg isotope values are strongly correlated to benthic insects and prey fish indicating the transfer of aquatic Hg sources. The slopes of these relationships are not 1:1 indicating that there may be physiological or foraging differences between the species. Organisms also follow the same source gradient observed in sediments with more positive $\delta^{202}\text{Hg}$ values indicating a higher fraction of industrial Hg (f_{IND}).

CONCLUSION: Mercury isotope tracers indicate that industrial Hg is widespread within the SLR system and accumulates within the aquatic and terrestrial food web. Isotope values are well conserved between spiders and aquatic species, allowing spiders to serve as sentinels for legacy Hg transfer to the terrestrial food web.

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Affiliations: ¹ U.S. Geological Survey Upper Midwest Water Science Center, Middleton, WI; ² U.S. Geological Survey Columbia Environmental Research Center Columbia, MO, 65201; ³ U.S. Environmental Protection Agency Office of Research and Development, Center for Computational Toxicology and Exposure, Great Lakes Toxicology and Ecology Division, Duluth, MN, 55804; ⁴ U.S. Environmental Protection Agency Office of Research and Development, Center for Environmental Solutions and Emergency Response, Cincinnati, OH 45220, USA; ⁵ U.S. Geological Survey, Forest and Rangeland Ecosystem Science Center, Corvallis, OR 97331, USA

