Relationships among Walleye Mercury, Selenium, Stable Isotopes, Size and Age

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RELATIONSHIPS AMONG WALLEYE MERCURY, SELENIUM, STABLE ISOTOPES, SIZE AND AGE— Bioaccumulation of mercury is well-documented in aquatic ecosystems and occurs as mercury is accumulated and passed up food chains (Kidd et al. 1995, Atwell et al. 1998, Downs et al. 1998). Trophic level correlations have been widely reported for mercury (Snodgrass et al. 2000) and other metals (Barron 1995). Generally, within a system, carnivores have the highest mercury loadings, omnivores intermediate and herbivores the lowest (Phillips et al. 1980). However, little research has focused on the differences in mercury bioaccumulation for a single species that ranges across multiple trophic levels (Burger et al. 2001).

Stable isotope analysis has expanded the understanding of pathways and mechanisms that promote bioaccumulation through food webs (Peterson and Fry 1987). For example, nitrogen enrichment at each trophic transfer can describe an individual's trophic position and often is correlated to contaminant concentrations (Sunda and Huntsman 1998) and bioaccumulation rates (Atwell et al. 1998). Further, distinct carbon signatures can describe energy inputs to a system or an individual (e.g., benthic vs. littoral energy base; Hecky and Hesslein 1995) and can provide information on how different contaminants are introduced into a water.

Selenium can function as a binding agent and subsequently reduce mercury distribution in animal tissues (Fang 1977, Mauk and Brown 2001). Selenium can have a mitigating effect on mercury accumulation in fish in freshwater (Cappon and Smith 1981, Chen et al. 2001) and marine systems (Lyle 1986, Barghigiani et al. 1991). Significant antagonistic effects of selenium on mercury accumulation have only been documented in a few instances (Paulsson and Lundberg 1991, Chen et al. 2001), whereas, mixed results have been found for far more species and systems (Heisinger et al. 1979, Turner and Rudd 1983). The antagonistic interaction of selenium and mercury are of special consideration when examining frequently consumed fish species from systems having high mercury loads. In some instances, selenium additions have been recommended to reduce negative impacts of mercury accumulation and toxicity (Rudd and Turner 1983, Turner and Rudd 1983).

The objective of our study was to determine mercury concentrations in walleye (*Sander vitreus*) muscle tissue in Lake Oahe, South Dakota and identify relationships between mercury concentrations to age, length, mass, selenium concentrations, and stable isotope values. We hypothesized that mercury levels would increase with walleye age and size (length and mass) and, as a result of the antagonistic properties of selenium, an inverse relationship between selenium and mercury loadings will be observed. Finally, we predict that mercury loading will be positively related to trophic position, further supporting the metal bioaccumulation concept.

Lake Oahe extends from Bismarck, North Dakota to Pierre, South Dakota. The South Dakota portion of Lake Oahe has a surface area of approximately 145,000 ha, with a mean depth of approximately 19 m and a maximum depth of

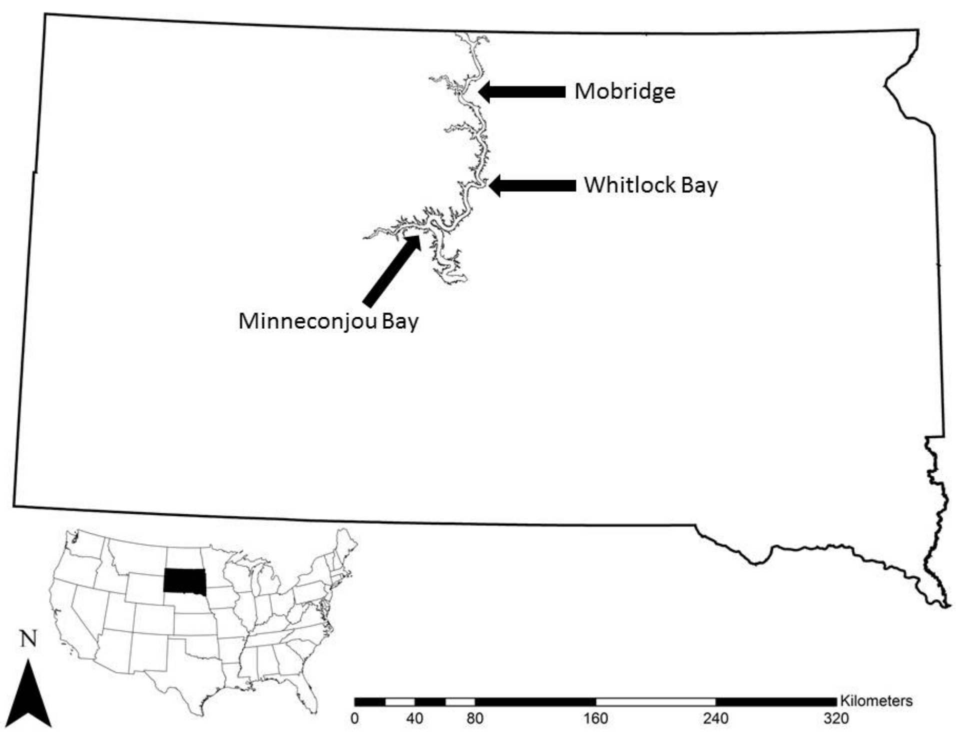

Figure 1. Lake Oahe study area in central South Dakota, USA, and the locations of walleye sampling sites, 2010.

67 m (Michaletz et al. 1986). We selected three sites within Lake Oahe based on proximity to a boat ramp and equidistant from each other, to collect adult walleye. These sites included Mobridge, Whitlock Bay, and Minneconjou Bay (Fig.1).

We collected walleye 13–15 May 2010 from Mobridge (n = 13), Whitlock Bay (n = 15), and Minneconjou Bay (n = 15) with standard multifilament nylon gill nets (91.4 m long × 1.8 m deep), with 15.2-m panels of the following mesh sizes: 12.7, 19.1, 25.4, 31.8, and 38.1 mm. We deployed three experimental mesh gill nets at sunrise and checked them within 2 hrs of their initial deployment. Upon retrieval, we measured walleye total length (TL; mm) and weight (g), and extracted sagittal otoliths for age determination. We used two experienced readers to estimate age of each fish. If a discrepancy in age existed between the two readers, we used a third reader to confirm a consensual age estimate. We placed walleye on ice for later tissue extraction. We removed a 2-g sample of white muscle tissue anterior to the dorsal fin from each walleye; all muscle samples were dried at 70° C for 72 hrs, pulverized, and placed in 4 × 6 mm tin capsules for isotopic analysis. We determined stable carbon (δ^{13}C) and nitrogen (δ^{15}N) isotope values using mass spectrometry. We reported isotope values in Δ notation, as per mille (‰) deviations from a standard material (Pee Dee Belemnite carbon or atmospheric nitrogen). We did not perform lipid extraction on tissue samples prior to analysis because the carbon-to-nitrogen (C:N) ratio was <4, which is indicative of non-fatty tissue (Sanderson et al. 2009). Because walleye isotope signatures were not compared across multiple systems, no baseline corrections were needed.

We analyzed the remaining dorsal muscle for total mercury and selenium concentrations following standard operating procedures outlined in the South Dakota Department of Natural Resources Fish Sampling Protocol, 2/2011; *Whole Fish Collection.* We removed approximately 200 mg of walleye muscle tissue anterior to the dorsal fin and above the lateral line. We analyzed muscle tissue for mercury concentration using EPA method 7473. We determined selenium concentration by ICP-MS for EPA method 200.8 by digesting approximately 0.25 g of tissue.

We compared age, total length, weight, selenium concentration and mercury concentration between sites using analysis of variance (ANOVA). If significant differences were found, we used a Tukey pairwise comparison to identify site specific differences. Current tagging studies suggest walleye in Lake Oahe can move up to 300 km in less than two months (E. Felts, South Dakota State University, personal communication), thus, specimens were pooled across sites for further analyses. We used linear regression to examine relationships between mercury concentration and walleye total length, weight, age and selenium content. We also used linear regression to examine relationships between element concentrations (e.g., mercury and selenium) and isotopic signatures.

Walleye ranged from 360 to 580 mm TL, weighed 381 to 2,109 g and were 2 to 14 yr-of-age (Table 1). There were no differences in mean TL ($F_{2,40}$ = 2.267, P = 0.12) or weight ($F_{2,40}$ = 3.046, P = 0.06) between sites. However, mean ages were different between sites ($F_{2,40}$ = 5.188, P = 0.01) with Mobridge walleye being older than those collected at Minneconjou Bay. Mercury concentrations ranged from 0.24 to 0.70 ppm and selenium concentrations from 0.34 to 1.02 ppm. Because metal concentrations were previously found to vary between sites on Lake Oahe (Mauk and Brown 2001), we tested walleye concentrations across sites. Mercury concentrations ($F_{2,40}$ = 8.569, P < 0.01) and selenium concentrations ($F_{2,40}$ = 18.31, P < 0.01) were different between samples locations with the Mobridge walleye exhibiting 0.08 and 0.21 ppm higher mercury and selenium concentrations, respectively, than walleye collected at more downstream locations.

We found significant positive relationships between mercury concentration and TL, mass and age of Lake Oahe walleye (P < 0.05; Fig. 2), which is frequently observed in other species. Other than age (r^2 = 0.61), relationships with TL or mass were weakly positive (r^2 = 0.23–0.31). The weak relationships between mercury concentration and TL or mass in Lake Oahe walleye are contrary to other findings. Wiener et al. (1990) used stepwise regression to determine predictors for muscle mercury concentration in walleye and identified muscle mercury as being maximally correlated to TL. Munn and Short (1997) found similar strength in models using age or TL to predict walleye mercury concentrations. Thus, the poor predictive ability of Lake Oahe walleye TL to forecast walleye mercury concentration during this study was unexpected.

Stronger correlations between mercury concentration and age, as opposed to length, are rare, but one explana-

Table 1. Mean walleye age, total length, weight, mercury, selenium, and nitrogen and carbon signatures (standard error in parentheses) from three sites on Lake Oahe, South Dakota, USA, 2010.

Site	n	Age (yr)	Total length (mm)	Weight (g)	Mercury (ppm)	Selenium (ppm)	δ^{15}N (‰)	δ^{13}C (‰)
Mobridge	13	8 (1.08)	513 (16.73)	1,406 (114.29)	0.42 (0.03)	0.66 (0.05)	17.6 (0.22)	–26.5 (0.19)
Minneconjou	15	4 (0.31)	473 (13.95)	1,071 (99.13)	0.31 (0.01)	0.47 (0.02)	17.1 (0.13)	–26.5 (0.19)
Whitlock	15	6 (0.70)	502 (10.31)	1,349 (97.67)	0.34 (0.01)	0.42 (0.01)	17.6 (0.19)	–26.5 (0.10)

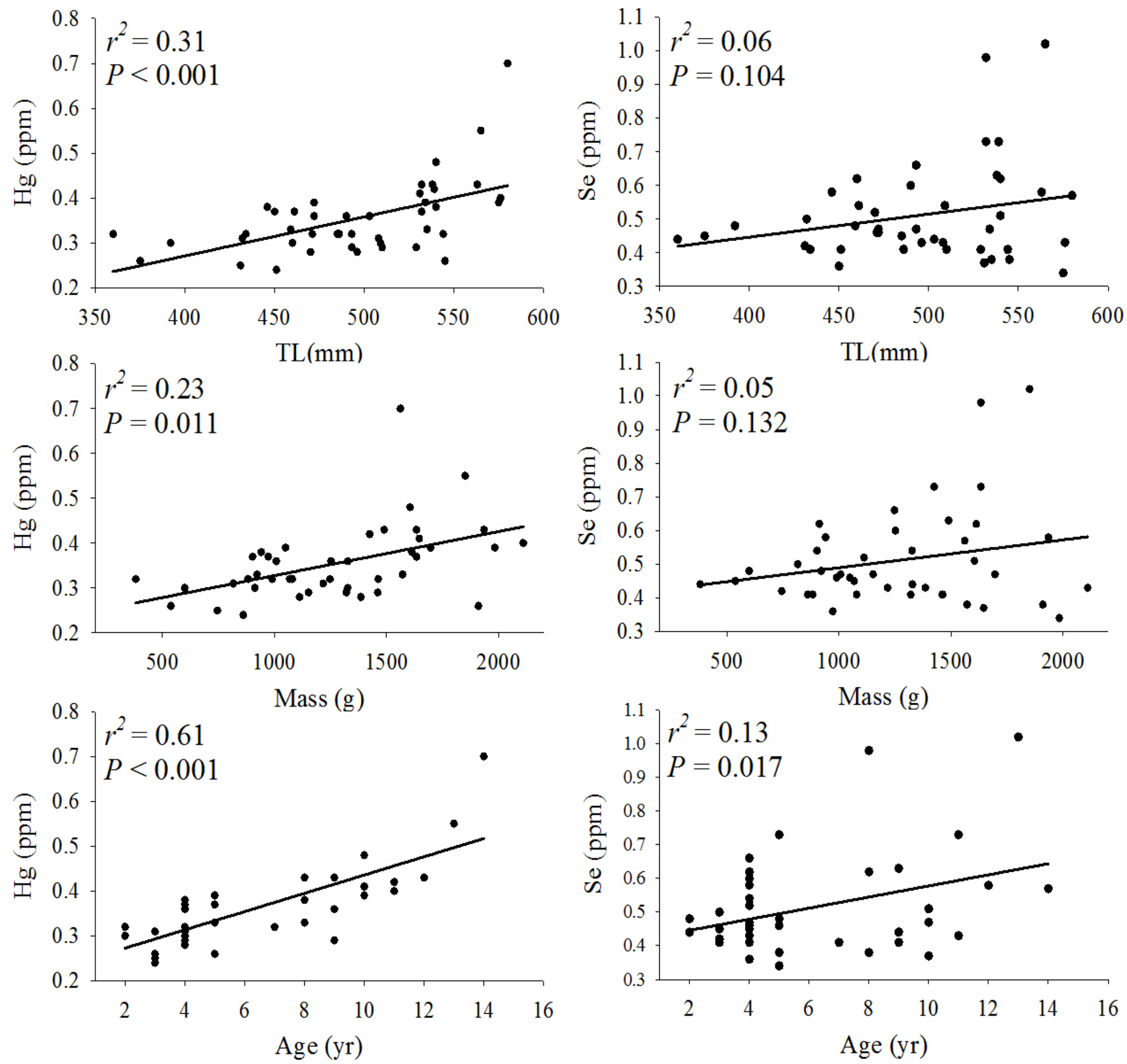

Figure 2. Relationship between total mercury (Hg; left panel) and total selenium (Se; right panel) concentrations (ppm) and total length (mm), weight (g) and age (yrs) of walleye collected from Lake Oahe, South Dakota, USA, 2010.

tion to this phenomenon is that mercury accumulates even when food becomes limited and fish growth slows (Downs et al. 1998). Thus, an age-predictor of mercury concentration better explains muscle tissue mercury when compared to length or mass. As fishery managers, this becomes increasingly problematic when determining fish consumption advisories. Guidelines are most often implemented based on a size category such as length or mass. However, age based implementation may be cumbersome, as size-at-age for Lake Oahe walleye can vary substantially. Age also was positively related to selenium concentrations ($r^2 = 0.13$, $P = 0.02$; Fig. 2) and a positive relationship was present between mercury and selenium concentrations in Lake Oahe walleye ($r^2 = 0.23$, $P < 0.01$; Fig. 3). The expected inverse relationship between selenium and mercury concentrations was not found in Lake Oahe walleye suggesting, in this case, increased selenium concentrations did not reduce mercury concentration in fish tissues.

The positive relationship between selenium and mercury in Lake Oahe walleye was noteworthy. Selenium has been shown to reduce the toxic effects of chronic methylmercury exposure in mammals (Ralston et al. 2008). At high concentrations, selenium exhibits protective properties on mercury toxicity in salmonid eggs (approximately 100 mg/l; Klaverkamp et al. 1983*b*), and selenium may decrease mercury metabolism in some systems (selenium concentrations from 1 to 10 µg/l; Fimreite 1979, Klaverkamp et al. 1983*a*). Although it does not appear that selenium is acting to reduce mercury concentrations in Lake Oahe walleye, the potential for selenium to reduce the toxic effect of mercury exposure is present.

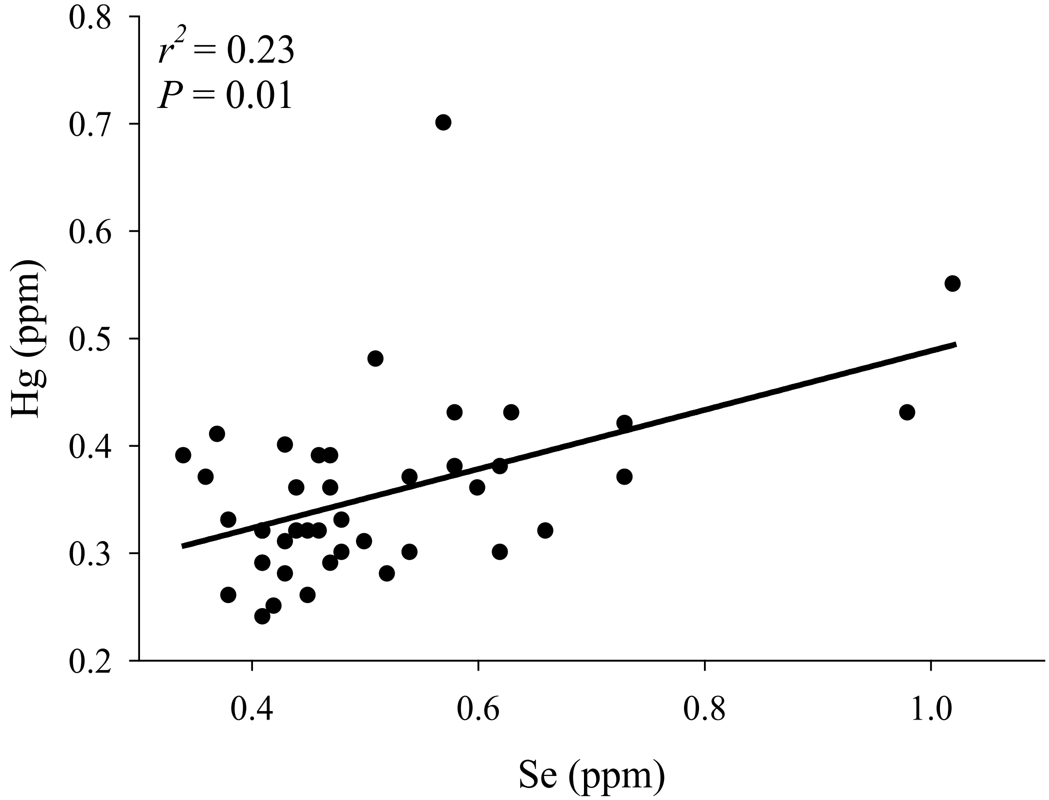

Figure 3. Relationship between total mercury (Hg) concentrations (ppm) and selenium (Se) concentrations (ppm) of walleye collected from Lake Oahe, South Dakota, USA, 2010.

Walleye $\delta^{15}N$ isotope signatures ranged from 15.99 to 18.83 which represented approximately one full trophic level using the 3.4‰ fractionation benchmark commonly used (Table 1; Minagawa and Wada 1984). Walleye $\delta^{13}C$ isotope signatures ranged from –28.35 to –25.47. No relationships were observed between mercury concentrations and $\delta^{15}N$ (r^2 = 0.00, P = 0.90), or $\delta^{13}C$ (r^2 = 0.05, P = 0.14) in muscle tissue. Additionally, no relationships were observed between selenium concentration and $\delta^{15}N$ (r^2 = 0.02, P = 0.35) or between selenium concentrations and $\delta^{13}C$ (r^2 = 0.01, P = 0.52). The lack of a relationship between mercury and selenium with stable isotope ratios is unusual because of the wide range of both $\delta^{15}N$ and $\delta^{13}C$ observed in our samples. Incidental sediment ingestion may increase chances of mercury accumulation and has been observed in species that spend considerable time near the water-sediment interface (Campbell 1994). Walleye, being a relatively benthic species, may ingest different rates of sediment mercury, adding variability to current models and potentially explain poor agreement with isotope signatures or growth metrics observed.

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LITERATURE CITED

Atwell, L., K. A. Hobson, and H. E. Welch. 1998. Biomagnification and bioaccumulation of mercury in an arctic marine food web: insights from stable nitrogen isotope analysis. Canadian Journal of Fisheries and Aquatic Sciences 55:1114–1121.

Barghigiani, G., D. Pellegrini, A. D'Ulivo, and S. DeRenieri. 1991. Mercury assessment and its relation to selenium levels in edible species of Northern Tyrrhenian Sea. Marine Pollution Bulletin 22:406–409.

Barron, M. G. 1995. Bioaccumulation and bioconcentration in aquatic organisms. Pages 625–666 *in* D. J. Hoffman, B. A. Rattner, G. A. Burton, Jr., and J. Cairns, Jr., editors. Handbook of ecotoxicology. Lewis Publishers, Boca Raton, Florida, USA.

Burger, J., K. F. Gaines, C. S. Boring, W. L. Stephens Jr., J. Snodgrass, and M. Gochfeld. 2001. Mercury and selenium in fish from the Savannah River: species, trophy level and locational differences. Environmental Research Section 87:108–118.

Campbell, K. R. 1994. Concentrations of heavy metals associated with urban runoff in fish living in stormwater treatment ponds. Archives of Environmental Contamination and Toxicology 27:352–356.

Cappon, C. J., and J. C. Smith. 1981. Mercury and selenium content and chemical form in fish muscle. Archives of Environmental Contamination and Toxicology 10:305–319.

Chen, Y., N. Belzile, and J. M. Gunn. 2001. Effect of selenium on mercury assimilation by fish populations near sudbery metal smelters. Limnology and Oceanography 46:1814–1818.

Downs, S. G., C. L. Macleod, and J. N. Lester. 1998. Mercury precipitation and its relation to bioaccumulation in fish: a literature review. Water, Air and Soil Pollution 108:149–187.

Fang, S. C. 1977. Interaction of selenium and mercury in the rate. Chemico-Biological Interactions 17:25–40.

Fimreite, N. 1979. Accumulation and effects of mercury in birds. Pages 601–627 *in* J. O. Nriagu, editor. The biogeochemistry of mercury in the environment. Elsevier/North-Holland Biomedical Press, Amsterdam, Netherlands.

Hecky, R. E., and R. H. Hesslein. 1995. Contributions of benthic algae to lake food webs as revealed by stable isotope analysis. Journal of the North American Benthological Society 14:631–653.

Heisinger, J. F., C. D. Hansen, and J. H. Kim. 1979. Effect of selenium dioxide on the accumulation and acute toxicity of mercuric chloride in goldfish. Archives of Environmental Contamination and Toxicology 8:279–283.

Kidd, K. A., D. W. Schindler, R. H. Hesslein, and D. C. G. Muir. 1995. Correlation between stable nitrogen isotope ratios and concentrations of organochlorines in biota from a freshwater food web. Science of the Total Environment 160:381–390.

Klaverkamp, J. F., D. A. Hodgins, and A. Lutz. 1983*a*. Selenite toxicity and mercury-selenium interactions in juvenile fish. Archives of Environmental Contamination and Toxicology 12:405–413.

Klaverkamp, J. F., W. A. Macdonald, W. R. Lillie, and A. Lutz. 1983*b*. Joint toxicity of mercury and selenium in salmonid eggs. Archives of Environmental Contamination and Toxicology 12:415–419.

Lyle, J. M. 1986. Mercury and selenium concentrations in sharks from Northern Australian waters. Australian Journal of Marine and Freshwater Research 37:309–321.

Mauk, R. J., and M. L. Brown. 2001. Selenium and mercury concentrations in brood-stock walleye collected from three sites on Lake Oahe. Archives of Environmental Contamination and Toxicology 40:257–263.

Michaletz, P. B., B. Johnson, J. Riis, C. Stone, D. Unkenholz, and D. Warnick. 1986. Annual fisheries surveys on the Missouri River reservoirs, 1981–1985. South Dakota Department of Game, Fish and Parks, Wildlife Division Progress Report 86-11, Pierre.

Minagawa, M., and E. Wada. 1984. Stepwise enrichment of 15N along food chains: further evidence and the relation between δ15N and age. Geochimica et Cosmochimica Acta 48:1135–1140.

Munn, M. D., and T. M. Short. 1997. Spatial heterogeneity of mercury bioaccumulation by walleye on Franklin D. Roosevelt Lake and the upper Columbia River, Washington. Transactions of the American Fisheries Society 126:477–487.

Paulsson, K., and K. Lundberg. 1991. Treatment of mercury contaminated fish by selenium addition. Water, Air, and Soil Pollution 56:833–841.

Peterson, B. J., and B. Fry. 1987. Stable isotopes in ecosystem studies. Annual Review of Ecology, Evolution, and Systematics 18:293–320

Phillips, G. R., T. E. Lenhart, and R. W. Gregory. 1980. Relationships between trophic position and mercury accumulation among fishes from the Tongue River Reservoir, Montana. Environmental Research 22:73–80.

Ralston, N. V., C. R. Ralston, J. L. Blackwell, and L. J. Raymond. 2008. Dietary and tissue selenium in relation to methylmercury toxicity. Neurotoxicology 29:802–811.

Rudd, J. W. M., and M. A. Turner. 1983. The English-Wabigoon River System: V. Mercury and selenium bioaccumulation as a function of aquatic primary productivity. Canadian Journal of Fisheries and Aquatic Sciences 40:2251–2259.

Sanderson, B.L., C. D. Tran, H. J. Coe, V. Pelekis, E. A. Steel, and W. L. Reichert. 2009. Nonlethal sampling of fish caudal fins yields valuable stable isotope data for threatened and endangered fishes. Transactions of the American Fisheries Society 138:1166–1177.

Snodgrass, J. W., C. H. Jagoe, A. L. Bryan, and J. Burger. 2000. Effects of trophic status, and wetland morphology, hydroperiod and water chemistry on mercury concentrations in fish. Canadian Journal of Fisheries and Aquatic Sciences 57:171–180.

Sunda, W. G., and S. A. Huntsman. 1998. Processes regulating cellular metal accumulation and physiological effects: Phytoplankton as model systems. Science of the Total Environment 219:165–181.

Turner, M. A., and J. W. M. Rudd. 1983. The English-Wabigoon River System: III. Selenium in lake enclosures: Its geochemistry, bioaccumulation, and ability to reduce mercury bioaccumulation. Canadian Journal of Fisheries and Aquatic Sciences 40:2228–2240.

Wiener, J. G., R. E. Martini, T. B. Sheffy, and G. E. Glass. 1990. Factors influencing mercury concentrations in walleyes in Northern Wisconsin lakes. Transactions of the American Fisheries Society 119:862–870.

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