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Selenium Ecotoxicology in Freshwater Lakes Receiving Coal Combustion Residual Effluents: A North Carolina Example

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Abstract

Anthropogenic activities resulting in releases of selenium-laden waste streams threaten freshwater ecosystems. Lake ecosystems demand special consideration because they are characterized by prolonged retention of selenium and continuous cycling of the element through the food chain, through which it becomes available to toxicologically susceptible egg-laying vertebrates. This study documents the current selenium burden of lakes in North Carolina (NC) with historic selenium inputs from nearby coal-fired power plants. We measured selenium concentrations in surface waters, sediment pore waters, and resident fish species from coal combustion residual (CCR)-impacted lakes and paired reference lakes. The data are related to levels of recent selenium inputs and analyzed in the context of recently updated federal criteria for the protection of aquatic life. We show that the Se content of fish from lakes with the highest selenium inputs regularly exceed these criteria and are comparable to those measured during historic fish extirpation events in the United States. Large legacy depositions of CCRs within reservoir sediments are likely to sustain Se toxicity for many years despite recent laws to limit CCR discharge into surface waters in NC. Importantly, the widespread use of high-selenium coals for electricity generation extends the potential risk for aquatic ecosystem impacts beyond U.S. borders.

Graphical Abstract

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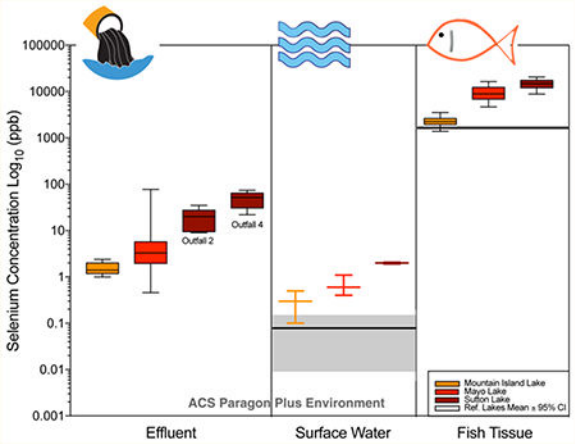
ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b05353.

Lake water quality measurements, selenium loading and concentration data, tissue percent moisture content, and supplementary figures and graphs (PDF)



INTRODUCTION

Selenium (Se) is a naturally occurring trace element that is both an essential nutrient for aquatic plants and animals at relatively low concentrations and a toxin at concentrations only slightly elevated above those considered nutritionally optimal. Extractive processes including coal mining and combustion, uranium milling, and seleniferous soil irrigation mobilize selenium, thereby enhancing its release to freshwaters.[1,2] Selenium is characterized by a uniquely complex biogeochemistry that is the subject of numerous reviews.[3−6] Briefly, selenium is primarily released into aquatic environments as the inorganic species, selenate and selenite. From abiotic compartments (i.e., the water column and sediment surface), selenium undergoes bioaccumulative enrichment and biotransformation by microorganisms and primary producers at the base of the food web. Subsequently, bioavailable organoselenium is transferred to higher trophic levels by dietary uptake.[5,7,8]

Oviparous vertebrates, including fish and aquatic birds, are especially sensitive to elevated selenium concentrations in their diet. The associated effects of selenium exposure is typically greatest during early windows of organismal development when maternally deposited selenium is resorbed from the yolk. Overexposure at this stage commonly manifests as a suite of characteristic deformities that include exopthamus (i.e., protruding eye due to fluid buildup), spinal curvatures, and abnormal fin, head, and mouth development.[9,10] The mechanisms underlying these toxicological responses remain incompletely understood, with prevailing hypotheses implicating either oxidative stress resulting from the metabolism of selenium-compounds or improper functioning of proteins in which selenium has been substituted for sulfur as the most likely modes of action.[7,11−13]

Selenium ecotoxicology has been an active area of environmental research since the 1970s when drastic changes in fish population structures were first observed in lakes constructed as cooling reservoirs for coal-fired power plants. At Belews Lake, North Carolina (NC), decreased juvenile recruitment to the adult fish population altered the fish community within three years of initial power plant operation in 1974. By 1978, the populations of 16 fish species had been extirpated and incidence of teratogenesis in surviving fish (10−70%) was significantly elevated above baseline. To the northeast, a similar scenario was unfolding at

Hyco Lake, NC where assessments revealed substantial reductions in adult and larval fish populations after the power plant began operating in 1973. At roughly the same time, the power plant at Martin Reservoir in Texas became operative (1977) and unauthorized discharges between 1978 and 1979 were linked to a 90% reduction in planktivorous fish biomass and 50% reduction in red-winged blackbird egg hatchability. These effects were attributed to contamination from selenium-laden coal combustion residual (CCR) effluents to the cooling reservoirs after selenium was determined to be the only trace element elevated in both water column and fish tissue samples.[14]

In 1987, the U.S. Environmental Protection Agency (USEPA) established a freshwater aquatic life criterion of 5.0 μg Se L^{-1} and a whole body fish tissue limit of 7.91 mg Se kg^{-1} dry weight (dw) was proposed in 2004.[15,16] In the intervening years, ecological assessments of selenium in a variety of contamination contexts around the world have reached similar conclusions that traditional methods for predicting selenium impacts via dissolved concentrations are inadequate. In June 2016, the USEPA finalized a revision of the freshwater aquatic life criteria, lowering the chronic criterion in freshwater lakes to 1.5 μg Se L^{-1} and introducing tissue-specific criteria of 11.3 mg Se kg^{-1} for muscle tissue and 15.1 mg Se kg^{-1} dw for egg-ovary tissue.[17] While these more restrictive guidelines are more consistent with research findings, these numeric standards do not take into account variation in the efficiency of selenium incorporation into and transfer through biota. Because the biogeochemical cycling of Se is primarily controlled by nonpassive carrier-mediated uptake across biological membranes, site-specific studies of indigenous biota are needed to improve risk characterization and management.[18]

In the present study, we surveyed the current selenium burden in three NC lakes with a history of selenium-laden CCR effluent loading from associated coal-fired power plants. Recent catastrophic releases of coal ash to the Emory and Clinch Rivers, TN (December 22, 2008) and the Dan River, NC (February 2, 2014) have spurred federal efforts to modernize CCR disposal practices at active and inactive surface impoundments.[19] In NC, Duke Energy Progress has responded by implementing coal ash excavation plans at four facilities, prompting questions about contaminant persistence and legacy impacts in CCR-receiving ecosystems following input termination. Here we report selenium concentrations in surface and sediment pore waters and in tissues of four resident fish species that represent recreational and subsistence fisheries supported by these lakes. Surface water and tissue concentrations are commonly reported in field studies of elevated selenium in aquatic environments and are the media for which the USEPA has established protective criteria.[17] The inclusion of sediment pore water selenium data in this study serves to complement maternal ovary/egg tissue concentrations; together, these two data sets represent the sources of early life exposure for embryos laid in shallow sediment nests, encapsulated in a protective chorion until hatch (between 0 and 120 h post fertilization for species in this study). We relate these abiotic and biotic concentrations to the selenium input estimates provided by Duke Energy, the utility operating the coal-fired power plant, in order to substantially increase our understanding of the current contaminant status and of the potential for legacy impacts throughout the state and in similar CCR-impacted aquatic systems globally.

MATERIALS AND METHODS

Site Selection.

Six lakes across NC were selected for this study−three with historic selenium loading from CCR effluent inputs (hereafter “CCR-impacted lakes”) and three reference lakes individually paired with the CCR-impacted lakes on the bases of geographical proximity and productivity classification as determined by the North Carolina Trophic State Index (Figure 1) (personal communication with Debra Owen, NC Lake Monitoring Program, NC Department of Environmental Quality (DEQ), Raleigh, NC).[20] Mountain Island Lake is an oligotrophic lake in the Mountains region. It was constructed in 1924 and received CCR effluent from the Riverbend Steam Station ash basins which were constructed in 1957 and 1979. The Riverbend Steam Station was retired in April 2013.[21] Lake Adger is the reference lake for Mountain Island Lake. Mayo Lake is a mesotrophic lake in the Piedmont region. It was impounded and filled in 1983 and continues to receive effluent discharges from the active Mayo Plant. Lake Tillery is its reference lake. Sutton Lake is a eutrophic lake in the Coastal Plain region. It was constructed as a cooling reservoir for the L.V. Sutton Steam Plant in 1971 and the Plant was operated from 1972 until November 2013 when the coal-fired units were retired.[22] Lake Waccamaw is the reference lake for Sutton Lake. Background information for these lakes is provided in Table 1.

Selenium Loading and Effluent Concentrations.

Estimated selenium loading and effluent selenium concentrations were analyzed from facility-specific final effluent reports provided to the National Pollutant Discharge Elimination System (NPDES). Selenium loading data points were calculated for each individual date between 2010−2015 for which both concentration and flow data were available. The frequency and type of data reported by coal-fired power plants reflect the conditions of their individual permits and there is considerable variability in characteristics measured and measurement frequency between facilities. The permits relevant to this study are NC0004961 (Riverbend Steam Station), NC0038377 (Mayo Plant), and NC001422 (L.V. Sutton Steam Plant).

Water, Sediment, and Fish Sampling.

Lake sampling took place between March-May 2015. Water quality measurements are presented in Supporting Information (SI) Table 1. Surface water and sediment samples were collected from three interlake locations (Figure 1). Surface water samples were collected from the top 30 cm by grab sampling. Subsamples intended for dissolved trace element analysis by inductively coupled plasma mass spectrometry (ICP-MS) were immediately filtered (0.45 μm, mixed cellulose esters membrane) and packed on ice for transport to Duke University. Sediment samples up to 25 cm deep were collected using a Wildco box core and stored in 2 gallon buckets for transport back to the University where they were stored at 4 °C. Within 48 h of collection, sediment samples were homogenized and packed into metal-free sterile polypropylene centrifuge tubes. Supernatant pore waters were extracted from sediments by centrifuge at 3000g for 25 min and subsequently vacuum filtered (0.45 μm, poly(ether sulfone) membrane). Filtered surface and pore water samples were stored at 4 °C in acid-washed bottles until analysis.

Fish collection was conducted in accordance with Duke University IACUC protocol #A139–16-06 and NC Collection Permit #15-SFC00163. Targeted species of the Centrarchidae family included largemouth bass (*Micropterus salmoides*), bluegill sunfish (*Lepomis macrochirus*), redear sunfish (*Lepomis microlophus*), and redbreast sunfish (*Lepomis auritus*). Fish were collected by electroshocking from a sampling boat and subsequently retrieved by net, maintained in an oxygenated live well for sorting, euthanized, tagged, and transported on ice to the University. Fish were stored on ice at 4 °C overnight and dissected for liver, muscle, and gonad tissues within 24 h of collection. Tissues were stored at −20 °C for future processing prior to analysis.

Sample Preparation and Chemical Analysis.

Dissolved trace elements in surface and pore waters samples were measured by ICP-MS using a VG PlasmaQuad-3 (Thermo Fisher Scientific Inc.) calibrated to National Institute of Standards and Technology (NIST) 1643e. Prior to analysis, internal standards of In, Th, and Bi were spiked into all samples. The limit of detection (LOD) for selenium in water samples was 0.22 μg/L. This value was substituted in statistical analyses and data figures for samples with selenium concentrations measured below the detection limit. This approach generates conservative estimates of the difference between reference and CCR-impacted reservoirs.

Fish tissue samples were microwave digested (CEM Discover SP-D Closed Vessel Microwave Digester) in omnitrace nitric acid (HNO_3, EMD Millipore, CAS 7697−37−2) at a ratio of 1g tissue wet weight to 10 mL acid. Tissues were subsequently analyzed with two ICP-MS instruments at Duke University. Samples analyzed by the VG PlasmaQuad-3 ICP-MS (instrument and method described above) were diluted in 2% HNO_3. For those run on an Agilent 7700x equipped with an Octopole Reaction System (Agilent Technologies), digested tissue samples were subsequently diluted in a 2% HNO_3/ 0.5% HCL matrix. A certified reference material of trace metals in drinking water (CRM-TMDW-A, High Purity Standards, Charleston, SC) was used as an external standard and internal standards of Sc, Rh, and Bi were used for instrument calibration. Limits of detection (LOD) were calculated by dividing three times the standard deviation of repeated blank measurements by the external standard slope. Inter-ICP-MS instrument agreement for tissue selenium concentrations was assessed by analyzing a small subset of samples on both instruments (relative mean difference = 3.7%). Accuracy of both instruments was assessed using certified reference material (CRM) DORM-4 (National Research Council Canada, fish protein CRM for trace metals); recovery of the CRM was >94% (n = 27). Species-specific percent tissue moisture was determined by drying whole tissue samples (or muscle tissue subsamples) in a drying oven at 100 °C for 48 h (n = 7−11/tissue/species) (SI Table 2, Figure 1). Moisture content was calculated as $(W_w - W_d/W_w) \times 100$ where W_w is sample wet weight and W_d is sample dry weight.

Statistical Analysis.

All statistical analyses were performed in Prism 7 (GraphPad Software, Inc., La Jolla, CA). Differences in dissolved surface water and pore water selenium concentrations were analyzed by one-way ANOVA with Tukey's posthoc test. Differences in fish tissue-specific selenium concentrations between CCR-impacted and reference lakes were assessed by

unpaired *t* test with Welch's correction. An alpha-level of 0.05 was set for all statistical analyses.

RESULTS

Selenium Loading and Effluent Concentration Data.

Estimated selenium loading to the CCR-impacted lakes and effluent selenium concentrations included in this study are presented in SI Figure 2. Despite the significantly limited data available from the Riverbend Steam Station between 2010 and 2013, Mountain Island Lake appears to have the smallest selenium burden with loading peaking at 0.05 kg Se/day in July 2011 and decreasing by 2 orders of magnitude by the time the plant retired in April 2014. The active Mayo Plant continues to discharge effluent to Mayo Lake. The more robust data set indicates that average daily loading between 2010 and 2015 was 0.27 kg Se/day. Over time, however, average daily loading has decreased by an order of magnitude from 0.35 kg Se/day between 2010 and 2013 to 0.035 kg Se/day between 2014 and 2015. The L.V. Sutton Steam Plant was retired as a coal-fired power plant in November 2013. Available data from 2010 to 2013 indicate that Sutton Lake had the greatest selenium burden of the three CCR-impacted lakes studied herein with an average daily loading rate of 0.85 kg Se/day from Outfall 4 and an additional average loading of 0.085 kg Se/day from Outfall 2 between February 2010 and January 2011.

Surface and Pore Water Selenium Concentrations.

Dissolved selenium concentrations in surface water and sediment pore waters in CCR-impacted and paired reference lakes are presented in Figure 2A. Significant differences in dissolved selenium concentrations between CCR-impacted and paired reference lakes were measured in two instances; pore water concentrations in Mayo Lake were significantly elevated relative to those in Lake Tillery ($p = 0.04$) and Sutton Lake surface water concentrations were significantly elevated relative to those at Lake Waccamaw ($p < 0.0001$). While Sutton Lake pore water selenium concentrations also appear to be elevated above those in Lake Waccamaw, we had insufficient sample size to make statistical comparisons. In Sutton Lake, dissolved Se concentrations were significantly higher in surface waters than in pore water ($p < 0.0001$), with most samples exceeding the US EPA's Aquatic Life Criteria level of 1.5 μg Se L^{-1}. The only other exceedance was measured in sediment pore water collected from one location in Mayo Lake, near the effluent outfall from the Mayo Plant.

Fish Tissue Selenium Burden.

Aggregate fish species selenium concentration by tissue type and lake pair are presented in Figure 2B. In each case, liver, muscle, ovary, and testes selenium concentrations in fish collected from CCR-impacted lakes were significantly elevated relative to those in fish collected from the respective reference lake ($p < 0.05$). Overall, selenium concentrations in fish collected from Mountain Island Lake were the lowest and those from Sutton Lake were the highest. From Sutton Lake, 85% of fish were found to have muscle selenium concentrations exceeding the USEPA's tissue-specific criterion of 11.3 mg Se kg^{-1} dw (average ± SEM muscle [Se] = 14.96 ± 0.67, $n = 26$), while 31% had ovary/egg selenium concentrations exceeding the criterion of 15.1 mg Se kg^{-1} dw (average ± SEM ovary/egg

[Se] = 14.24 ± 1.73, n = 13). Of the fish collected from Mayo Lake, 27% had muscle concentrations exceeding the criterion (average ± SEM muscle [Se] = 9.61 ± 0.57, n = 30) while no ovary/egg samples were elevated above the established threshold (average ± SEM ovary/egg [Se] = 7.82 ± 0.79, n = 12). None of the fish sampled from Mountain Island Lake had muscle or ovary/egg tissue concentrations exceeding these criteria. In aggregate, male fish from the three impacted lakes had significantly higher testes selenium concentrations than fish from the paired reference lakes. Although a USEPA tissue-specific criteria for freshwater fish testes does not currently exist, gonadal selenium concentrations measured in male and female fish collected from the individual impacted lakes were not statistically different from one another when analyzed in aggregate or by species.

Species-specific selenium concentrations by tissue type and lake pair are presented in Figure 3. By species, muscle tissue selenium concentrations were significantly elevated in fish from CCR-impacted lakes relative to those from the corresponding reference lake. This is also true for ovary/egg selenium concentrations except for two cases when the number of female fish collected from the study lake was insufficient to establish a statistical difference at the 5% level (i.e., n = 2 female bluegill sunfish collected from Mayo Lake and Sutton Lake). A subset of muscle and ovary/egg samples from all species of fish collected at Sutton Lake exceeded the USEPA criteria of 11.3 and 15.1 mg Se kg^{-1} dw, respectively. From Mayo Lake, only a subset of largemouth bass and redear sunfish muscle tissues were found to exceed the tissue-specific threshold. None of the species-specific tissues sampled from Mountain Island Lake had concentrations of selenium in excess of the USEPA criteria. Summary data for tissue-specific and species-specific selenium concentrations by lake are provided in SI Table 3.

DISCUSSION

In the present study, we show that three lakes with a history of CCR-inputs from coal-fired power plants are burdened with significantly elevated selenium concentrations in all biological tissues relative to those from paired, reference lakes. These differences were observed regardless of lake trophic status, surface water concentrations, and despite more than an order of magnitude difference in mean selenium loading via the associated coal-fired power plant effluent discharge. Selenium loading appears to be the primary driver of tissue concentration differences among CCR-impacted lakes, but lake size, trophic status, and hydrological connectivity are important factors as well.

The USEPA publishes ambient water quality criteria for the protection of aquatic organisms from consequences of pollutant exposure based on available scientific data. In 2016, they published updated freshwater selenium criteria that, for the first time, prioritize tissue-specific over dissolved concentrations to reflect that aquatic organism toxicity primarily occurs via dietary exposure.[17] Exceedances of the muscle, ovary/egg, and water selenium criteria were measured in two of the lakes included in this study; at Sutton Lake, 100% of surface water, 83% of fish muscle, and 31% of ovary/egg samples exceed respective criteria levels. At Mayo Lake, 27% of fish muscle samples also exceeded the protective threshold level even though dissolved surface water concentrations did not; this finding supports the

prioritization of tissue-specific selenium concentrations over those in other environmental media in field assessments and protective criteria implementation.

In this study, we also report significantly elevated selenium concentrations in the testes of fish collected from impacted lakes relative to those from paired reference lakes. The significance of this finding remains incompletely understood; selenium concentrations in fish testes are uncommonly reported in field studies and a recent analysis of such studies found that reported testes/milt concentrations are given little consideration relative to those of female fish muscle and ovary/egg tissue concentrations.[23] This issue likely reflects the prevailing theory that environmentally relevant selenium toxicity in early life stage fish occurs primarily due to selenium transfer from the maternal fish during vitellogenesis and embryonic exposure to this selenium during yolk resorption.[1] However, a recent study investigating the influence of parental selenium exposure on the occurrence of phenotypic abnormalities in F1 generation Japanese medaka (*Oryzias latipes*) reported paternal influence over some deformity categories (e.g., craniofacial) and that the highest rate of phenotypic alterations were found in the exposure group in which both maternal and paternal fish were dietarily exposed to seleno-Lmethionine.[23] This evidence coupled with the large gap in understanding surrounding the significance of paternal selenium contributions to early life toxicity indicate the need for further study.

Relative to species-specific muscle tissue concentrations measured during the height of the Belews Lake extirpation period 40 year ago,[9] concentrations in Sutton Lake redear, bluegill, and largemouth bass from this study were only 2.6, 3.4, and 4.4-fold lower, respectively (SI Table 4). This suggests that selenium-imposed ecosystem stress could be impacting fish population health.

The sampling methodology chosen for this study was restricted to shallow spawning areas to ensure adequate adult fish sample sizes and in order for sampling to coincide with when maternal egg/ovary selenium concentrations would most closely reflect doses administered to developing fish embryos via yolk resorption. While serving those purposes well, this methodology was inadequate for understanding population level impacts from a given stressor or combination of stressors. The potential for Se toxicity to have population level impacts is realized in developing larval and juvenile subpopulations where morphological deformities can influence fish recruitment to the adult population by hindering respiration, feeding, and the ability to evade predation.[24] A recent assessment of Lepomis spp. in Sutton Lake reported 28.9% incidence of juvenile phenotypical abnormalities with 7.2% teratogenic mortality indicated by the teratogenic deformity index, relative to 0.5% abnormality incidence in a reference population.[25] While annual assessments of Sutton Lake adult sportfish also indicate recent periods of substantial population decline, populations are substantially subsidized by regular stocking to support recreational activities, confounding the accuracy of such assessments.[26,27]

Though the three CCR-impacted sites included in this study are each classified as lakes, their hydrological connectivity to adjacent rivers differs dramatically; Mountain Island Lake has a residence time of only 12 days and behaves most similarly to a lotic system while Sutton Lake is nearly a closed system as it only receives freshwater inputs from an intake

pump operated by the energy company and evaporation is the primary form of water export.[28] It follows that the selenium burden in Mountain Island Lake surface water and fish tissues are much lower than those in Sutton Lake, but this discrepancy is further influenced by lesser selenium loading to Mountain Island Lake and its trophic status. Modern selenium loading to and the trophic status of Mayo Lake are more similar to Sutton Lake. Mayo Lake has an approximately 3 year residence time. Even so, mean surface water and fish tissue concentrations were significantly lower than those in Sutton Lake (0.7 vs 1.9 μg L^{-1} surface water, 9.61 vs 14.96 mg Se kg^{-1} dw muscle). The variation across these three lakes with very different residence time generally supports and extends the widely accepted premise that elevated selenium poses a greater potential risk in lentic ecosystems than in lotic ecosystems.[3,29] The higher biological exposure in lakes with longer residence times also raises important questions about how reservoir morphology and management alter the timeline of recovery for Se pollution once CCR impacts slow or cease.

Belews Lake is one of the best-studied recoveries of selenium impacts in a freshwater lake ecosystem. In 1986, following the extirpation events of the late 1970s, changes to ash disposal practices prevented further releases of selenium-laden wastewater to the lake. Ecosystem surveys continuing into the 1990s concluded that a moderate hazard level persisted after more than a decade-long recovery period due to sufficiently elevated concentrations in the sediment, at the base of the sediment-detrital pathway.[24] The potential for ecosystem recovery at Sutton Lake is conceivably restrained by the minimal exchange between this lake and other surface waters. Moreover, there is an immense repository of selenium in the Lake's sediments that seems to be increasing with time; location-specific concentrations ranged from 21 to 28 mg Se kg^{-1} dw in 2011[30] and increased substantially to 26−43 mg Se kg^{-1} dw in 2012,[28] strongly suggesting that the biogeochemical cycling and environmental persistence of selenium will continue long after loading to these reservoirs ceases.

Redox state influences selenium mobility such that selenite and selenate may be released into pore waters if adsorbed selenides or elemental selenium are oxidized.[31,32] Under such conditions, pore water could become an important exposure route, especially to benthic organisms and embryonic fishes laid in shallow sediment nests where they remain until hatch. During this period, the embryos are enveloped in a protective chorion which is a known barrier to particulates.[33] For these reasons, we also measured dissolved selenium in sediment pore waters. With the exception of one sediment pore water collected near the effluent outfall at Mayo Lake, all pore water selenium concentrations were measured below the surface water threshold value. Our data do not allow us to distinguish whether these small pore water Se concentrations are an indication of low rates of Se oxidation or high rates of biological assimilation.

Importantly, selenium inputs to the systems studied here need to be permanently terminated before recovery processes can begin. Under the North Carolina Coal Ash Management Act of 2014, Duke Energy Progress is moving forward with excavation plans to remove coal ash from basins at four of its facilities, including those located at Mountain Island Lake and Sutton Lake.[34] Under the terms of these excavation plans[21,22] and associated facility NPDES permits,[35,36] initial activities involve ash basin dewatering (i.e., releasing ash pond

water to reduce water level) by which CCR-effluents will be released to receiving freshwaters via existing outfalls. These plans indicate that inputs will continue through 2016 (Sutton Lake) and until 2020 (Mountain Island Lake). It will be important for monitoring of abiotic and biotic compartments to continue during and after this dewatering process so that peak concentrations can be established with which to assess recovery; the results of this study can serve as preinput-termination benchmarks in support of that assessment effort.

Elevated selenium impairment of aquatic ecosystems is an international issue most commonly resulting from anthropogenic activities that cause increased mobility of the element from concentrated mineral deposits and metal-sulfide ores. Ongoing case studies emphasizing impacts on aquatic biota implicate uranium ore milling and processing,[4] mountain top removal coal mining,[37,38] and coal combustion for electricity generation.[39] Across these studies, researchers are regularly measuring fish tissue concentrations in the parts per million (ppm) range, 3 orders of magnitude enrichment above surface water selenium concentrations which are typically in the low parts per billion (ppb) range.

The elemental composition of these mineral resources underlies their ultimate contamination potential. Selenium enrichment in coal is particularly well established; concentrations are 82 times greater than those in Earth's crust and coals in the United States contain 5−300 times more selenium as other rock formations.[40] Notwithstanding selenium's huge enrichment in coal, concentrations vary considerably among geographically dispersed coal deposits. North Carolina gets the majority of its coal (41.5% or 7.13 million tons in 2014) from West Virginia[41] where the Appalachian coal region is characterized by medium- and high-volatile bituminous deposits with average selenium concentrations of 3.9 ppm, among the highest of surveyed coal regions in the US.[40] This high selenium coal is distributed throughout the United States and internationally; Appalachia supplied 22% of domestic coal demand and contributed 67% of US coal exports to foreign markets in 2014. Individually, West Virginia sent its coal to 26 states (~8% of domestic demand) and supplied 35% of total U.S. coal exports in the same year.[41] Such widespread coal distribution indicates that there is a risk of aquatic ecosystem impairment wherever CCR wastes from high-selenium coals are discharged to freshwaters subsequent to similar treatment processes as those employed in North Carolina.

While the focus of this study, selenium is only a single component of CCR mixtures. A recent study of receiving waters in North Carolina profiled CCR effluents documented elevated concentrations of many additional elements including manganese, vanadium, and arsenic.[42] The lakes in this study actively encourage recreational activities such as sport fishing and facilitate their public access.[25,27,28] What is more, these lakes serve as subsistence fisheries for local people. It is essential that these public resources be maintained with both ecosystem and human health in mind.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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ABBREVIATIONS

ANOVA	analysis of variance
BG	bluegill
Bi	bismuth
CCR	coal combustion residuals
CRM	certified reference material
dw	dry weight
HCL	hydrochloric acid
HNO_3	nitric acid
IACUC	institutional Animal Care and Use Committee
ICP-MS	iInductively coupled plasma mass spectrometry
In	indium
LMB	largemouth bass
LOD	limit of detection
MW	megawatts
NC	North Carolina
NC DEQ	North Carolina Department of Environmental Quality
NIST	National Institute of Standards and Technology
NPDES	National Pollutant Discharge Elimination System
ppb	parts per billion
ppm	parts per million
RD	redear sunfish
RB	redbreast sunfish

Rh	rhodium
Sc	scandium
Se	selenium
SEM	standard error of the mean
Th	thorium
US EPA	U.S. Environmental Protection Agency
US	United States

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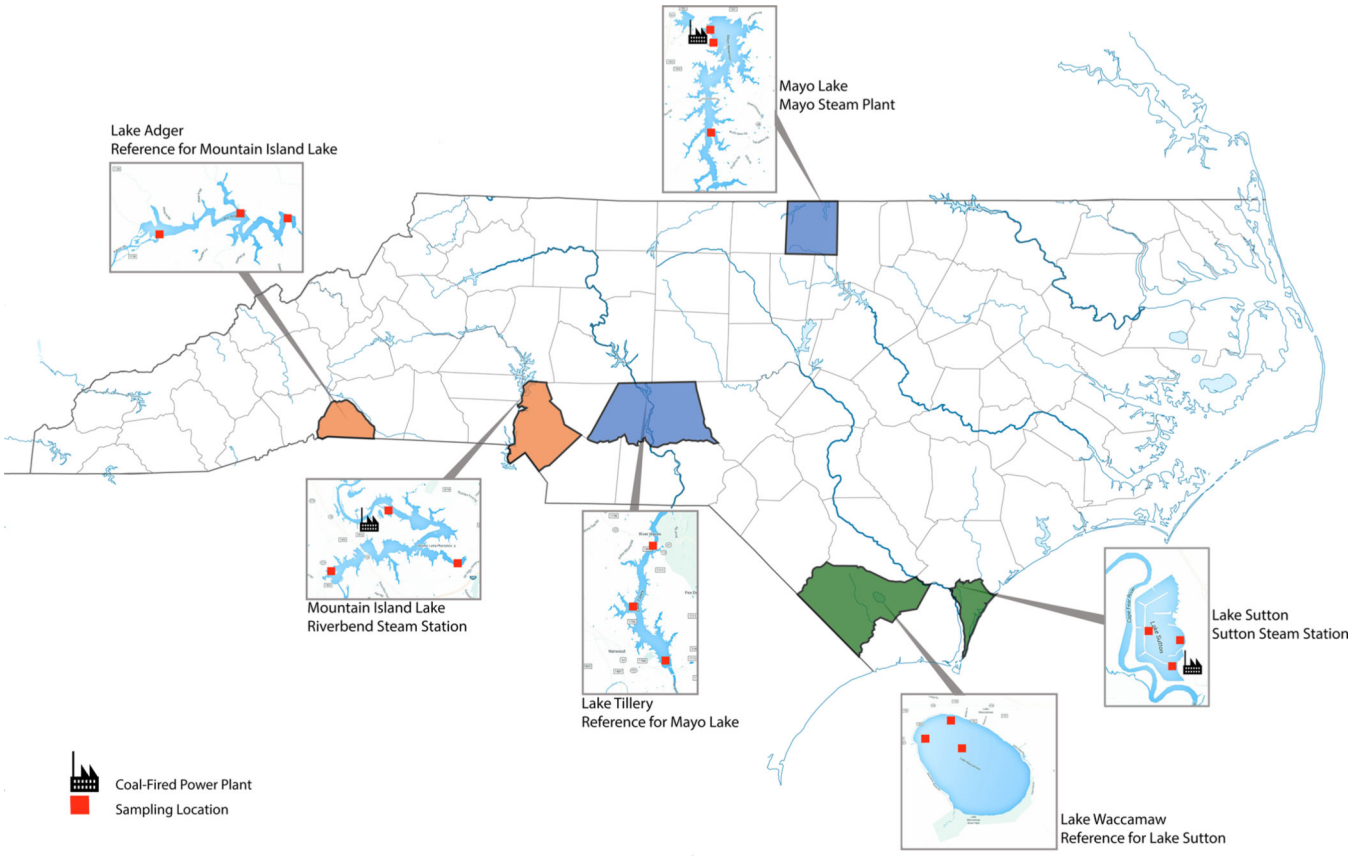

Figure 1.

Map of North Carolina highlighting the lakes included in this study. Colors indicate lake pairs; orange counties contain oligotrophic lakes in the Mountain Region, blue counties contain mesotrophic lakes in the Piedmont, and green counties contain eutrophic lakes in the Coastal Plain. Red squares indicate approximate locations within lakes from which surface and sediment samples were collected and black icons indicate approximate locations of coal-fired power plants at CCR-impacted lakes.

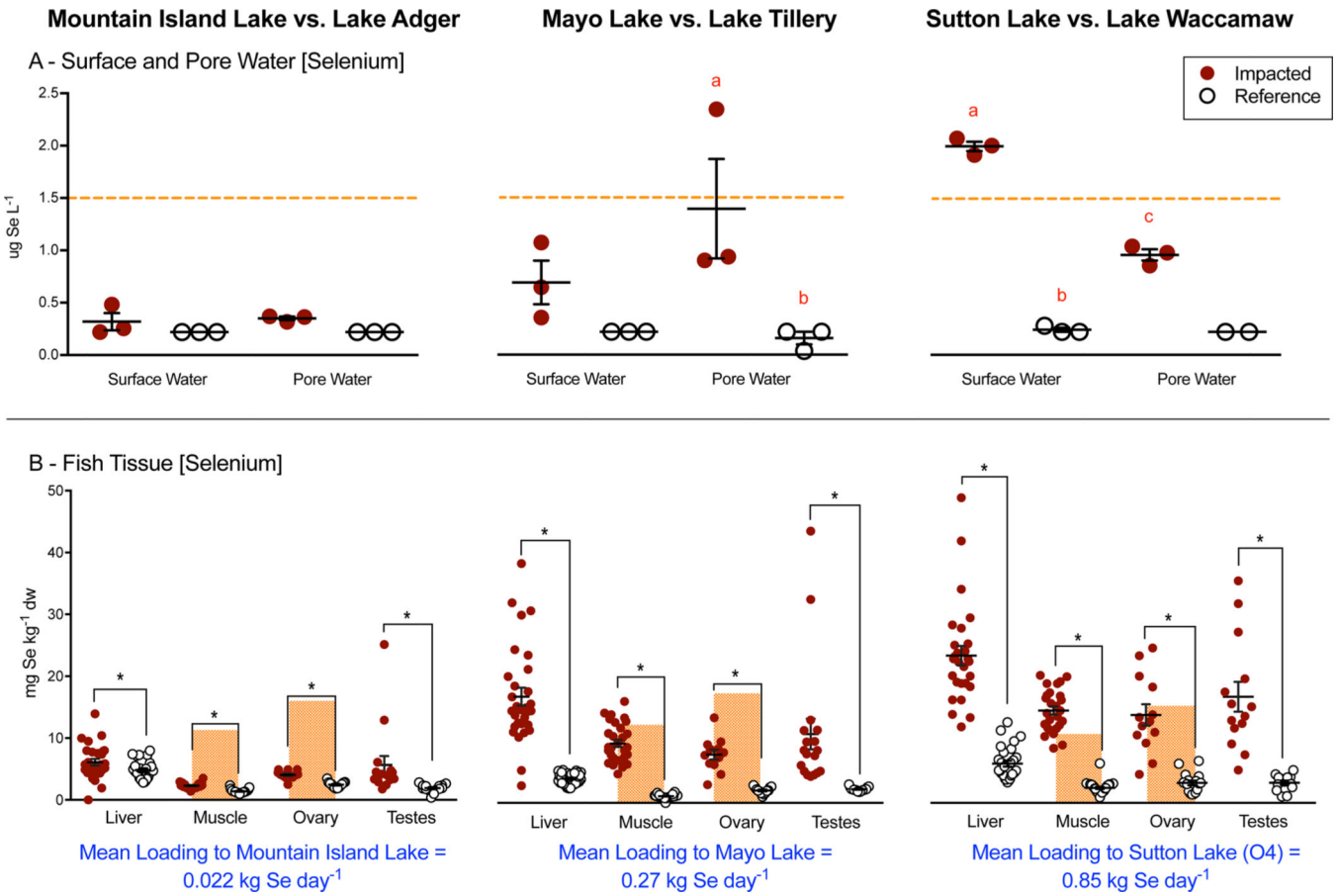

Figure 2.

Water and fish tissue selenium concentrations. Data points are represented individually with summary data shown by the bars (mean ± standard error of the mean). Red circles represent individual samples collected from CCR-impacted lakes and white circles represent samples collected from non-CCR impacted reference lakes. Panel A: Surface water and sediment pore water dissolved selenium concentrations. Significant differences between water sample groups are marked with unique letters such that groups designated with the same letter are not statistically different from one another. Panel B: Fish tissue selenium concentrations by tissue type by lake pair. Significant differences between fish tissues collected from paired lakes are marked with "*" ($p < 0.05$). Orange dashed lines and bars represent the USEPA's Aquatic Life Ambient Criteria for dissolved selenium in surface water (1.5 μg Se L^{-1}) fish muscle (11.3 mg Se kg^{-1} dw) and ovary/egg tissues (15.1 mg Se kg^{-1} dw).

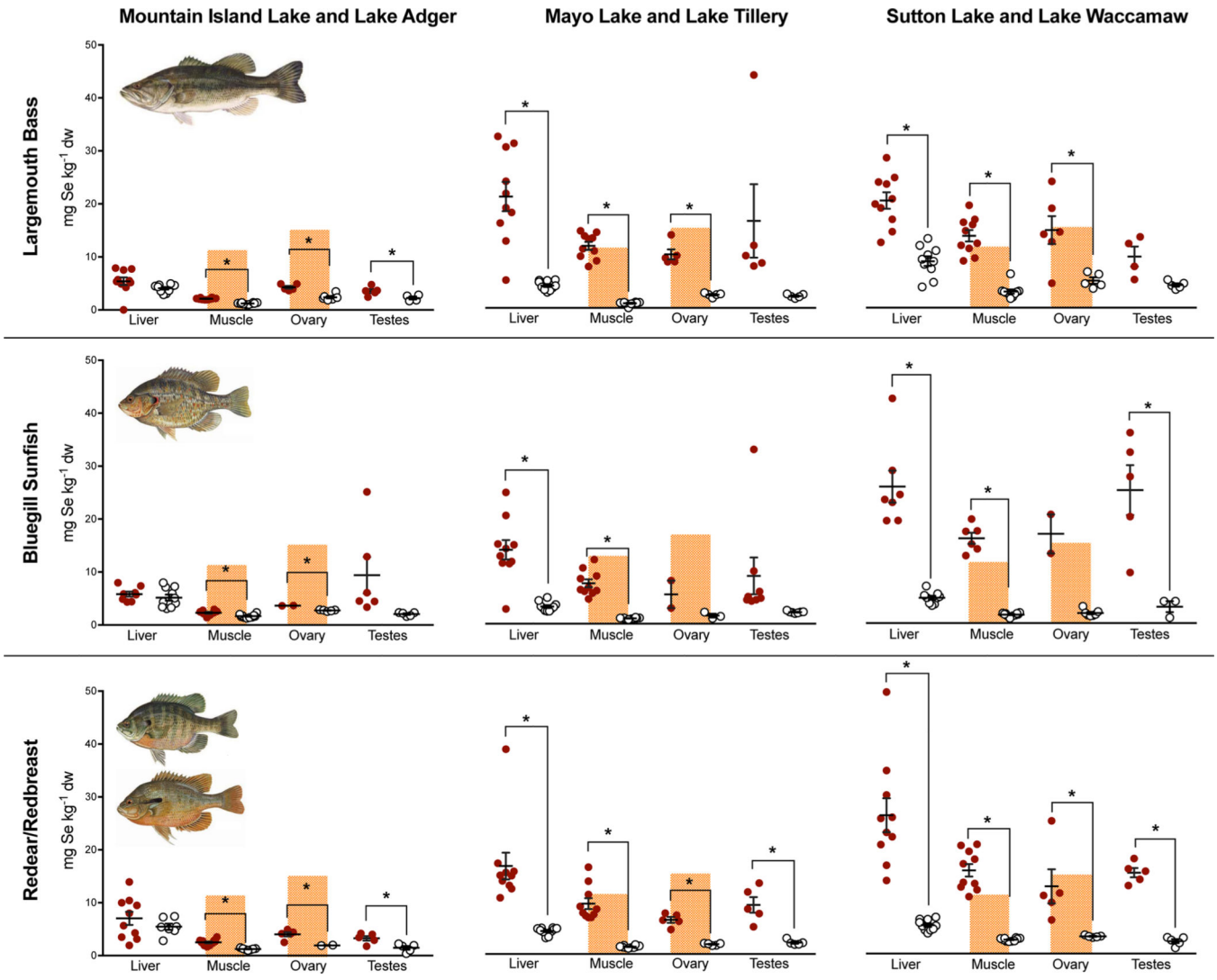

Figure 3.

Fish tissue selenium concentrations by tissue type arranged by species (left to right) and lake pair (top to bottom). Significant differences between corresponding tissues in fish collected from impacted lakes and reference lakes are marked with "*" ($p < 0.05$). Orange bars represent the USEPA's Aquatic Life Ambient Criteria for selenium in fish muscle and ovary/egg tissues, 11.3 and 15.1 mg Se kg^{-1} dw. Fish images from ncwildlife.org, © Duane Raver.

Table 1.

Background Information for Lakes Included in This Study[a]

lake	river basin	surface area (acres)	mean depth (ft.)	retention time (days)	associated coal-fired power plant	capacity (MW)	power plant status
Mountain Island Lake	Catawba	3235	17.7	12[b,43]	Riverbend Steam Station	454	retired, 4/2014
Lake Adger	Broad River	440	26.2	21[44]	na	na	na
Mayo Lake	Roanoke	2800	30	1095[43]	Mayo Plant	727	active
Lake Tillery	Yadkin	5000	33.6	7[b,43]	na	na	na
Sutton Lake	Cape Fear	1100	5	variable water inputs[c,43]	Sutton Plant	575	retired, 11/2013
Lake Waccamaw	Lumber River	8940	7	242[45]	na	na	na

[a] n.a., not applicable.

[b] Retention times provided for Mountain Island Lake and Lake Tillery are theoretical estimates and depend on releases from upstream hydroelectric plants.

[c] Water pumped into lake from Cape Fear River at variable rate to account for evaporation and other factors.