MERCURY IN ATLANTIC WHITE CEDAR (*CHAMAECYPARIS THYOIDES*) TREE RINGS FROM GREAT DISMAL SWAMP NATIONAL WILDLIFE REFUGE: ANALYSIS OF CONCENTRATIONS THROUGH TIME

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Abstract: Peatlands such as the Great Dismal Swamp (GDS) can sequester large quantities of mercury (Hg) from global, regional, or local sources. While no local point sources are known for GDS, recent studies of GDS and other peatlands in the Mid-Atlantic Coastal Plain have reported elevated mercury concentrations. Little is known about woody material as a sink for Hg in peatlands, which may be remobilized via peat oxidation and fire. The purpose of this study is to determine mercury concentration within *Chamaecyparis thyoides* (cedar) tree boles. Cross-sectional segments of 80-year-old cedar trees blown down during Hurricane Isabel (2003) were collected from the Great Dismal Swamp National Wildlife Refuge. Nineteen of these cedar cross-sections were analyzed for mercury within 10-year increments corresponding to 1934-1944, 1964-1974, and 1992-2002 year rings of each tree. Concentrations of mercury [Hg] within each 10-year increment ranged from 0.003 to 0.017 mg Hg/kg dry weight (DW) and averaged 0.0088 mg Hg/kg DW (n = 57). Median [Hg] of the 1992-2002 increment were significantly lower than 1964-1974 increment. The 1964-1974 increments had the highest median [Hg] and 1992-2002 had the lowest [Hg]. Based on the median of all samples [Hg], we estimate that a single living cedar stem would contain 1.574 mg Hg and a 1-ha stand would contain 1.583 g Hg. Based on these estimates, salvage-logging of cedar following the blowdown in 2003 may have prevented remobilization of 3.944 kg (8.70 lbs) of Hg from the swamp. Speciation of mercury in trees and peat would allow determination of best management strategies to reduce the risk of remobilization by decomposition and fire; however, strategies that maintain saturated peat are likely optimal.

Key Words: Mercury, Atlantic White Cedar, peatlands, Great Dismal Swamp, dendrochemistry, remobilization

INTRODUCTION

Mercury and Wetlands

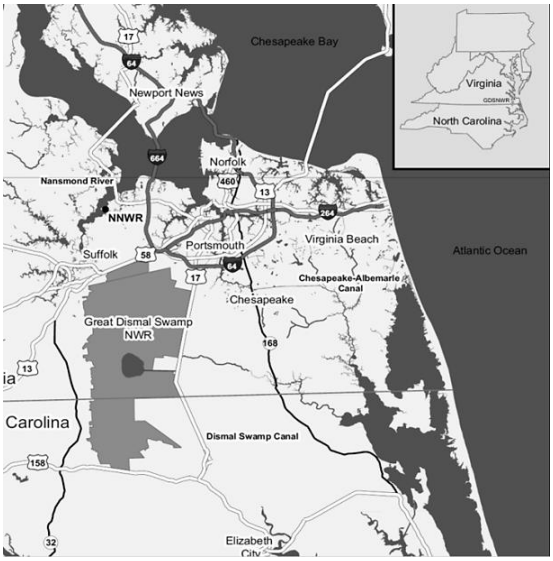


Figure 1. Map of GDSNWR as located at the border of Virginia and North Carolina. The star denotes generallized cedar tree sample location (shown in grey).

Mercury (Hg) is a naturally occurring metal that exhibits low toxicity in either elemental or inorganic form, but is highly toxic when found as methylmercury, the organic form. Methylmercury is lipid soluble and can therefore accumulate in living tissues (Weiner et al. 2002). When biomagnified to high concentrations, methylmercury acts as a neurotoxin that damages the brain and other parts of the nervous system.

The atmosphere contains a pool of inorganic Hg from various natural and anthropogenic sources (Beauchamp et al. 2002, Friedli et al. 2009, Streets et al. 2009), that after deposition, can be converted into methylmercury in anaerobic soils (Weiner 1987) where sulfate-reducing bacteria methylate Hg (Compeau and Bartha 1985, Morel et al. 1998). Mercury contamination is a wide spread concern for waterways across the United States, e.g. Evers et al. (2007). Mercury in wetlands is of particular interest because of the high rates of mercury methylation there and the movement of methylmercury into wetland food chains, which may impact wildlife and humans.

Mercury in the Great Dismal Swamp

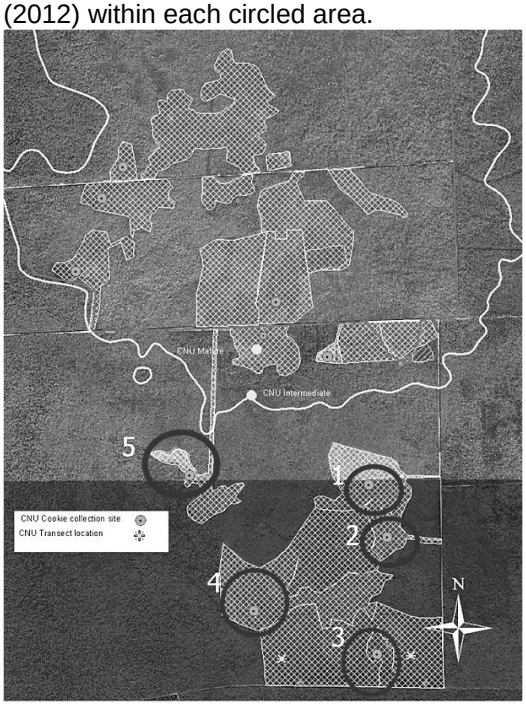
The Great Dismal Swamp National Wildlife Refuge (GDSNWR) encompasses 453 km^2 (120,000 acres) of the GDS and recent studies led by the US Fish and Wildlife Service have found elevated concentrations of methylmercury in both sediments and wildlife of GDSNWR. Concentrations range from 0.03 mg Hg/kg to 2.63 mg Hg/kg DW in GDSNWR ditch sediments; and wildlife, including many species of fish, some frogs, as well as the feathers and blood of several bird species, contained Hg concentrations above 0.3 ppm (Ligenfelser 2010). There is no known point source of Hg to the swamp or its watershed, and there is no history of activities such as mining (GDSWNR 2006); therefore atmospheric deposition is the most likely source of inorganic Hg to the swamp. Mercury that enters or accumulates on the surface of leaves (Ericksen et al. 2003, Witt et al. 2009) can fall to peat, and atmospheric Hg can be deposited directly onto substrates by wet (rain through fall) or dry deposition (Benoit et al. 2002). During the long term accumulation of organic matter in peat formation, Hg also accumulates (Selvendrian et al. 2008, Friedli et al. 2007, Poulter et al. 2006).

Mercury in Trees from Contaminated Sites

Plants in a highly contaminated site in Spain demonstrated uptake of Hg from the soil into both roots and aboveground parts (Molina et al. 2006). Greenhouse and laboratory studies show limited soil uptake but implicate fallen foliage as a source of Hg in organic soil (Grigal 2003). Air surface exchange and stomatal intake of mercury has also been suggested as the source of heavy metals in tree rings in studies by Beauchamp et al. (2002) and Zhang et al. (1995).

Tree rings are capable of recording heavy metal concentrations in vivo, display trends of environmental contamination, and consequently, are used to identify sources of local contamination (Abreu et al. 2008, DeWalle et al. 1995, White and Letard 2002). Radial patterns of chemicals are found within tree cores as well (Dewalle et al. 1995), suggesting that environmental conditions could be characterized based on a pattern of chemical concentrations in space and time as delineated by tree rings. Uptake rates for chemicals of interest differ among plant species (Butkus and Baltrenaite 2007) and organs (Molina et al. 2006), and no studies have examined tree rings in bole wood of standing live cedar from the GDSNWR. The purpose of this study is to determine Hg concentration in cedar rings from tree bole segments during three time periods to aid our understanding of mercury distribution in peatlands.

Figure 2. Map of the cedar salvage-logging units (hatched pattern) and extent of fire (white line) provided by GDSNWR. Highlighted by numbered circles (1-5) are 80-year class cedar salvage logging units within GDSNWR that were investigated by Patterson (2012) within each circled area.



METHODS

Site Description and Sample Collection

Samples were collected from cedar swamps within the GDSNWR in southeast Virginia and northeast North Carolina (figure 1). The Refuge was formed with the Dismal Swamp Act of 1974 which mandated that the US Fish and Wildlife Service manage the area for the primary purpose of protecting and preserving a unique and outstanding ecosystem, including protection and restoration of cedar.

Cross-sectional bole wood segments (cookies) from GDSNWR were used in this study (figure 2). All cookies were obtained from a dendrochronology investigation

by Patterson (2012) in which cedar cookies were collected from 60 and 80-year old stands in coordination with a post-hurricane Isabel salvage-logging operation between 2003 and 2007. We randomly selected four cookies from each of four cedar stands and three cookies from a fifth stand, which yielded a total of 19 cookies from 19 trees.

Figure 3. Example of bolewood segment with year class approximate locations highlighed and labeled.

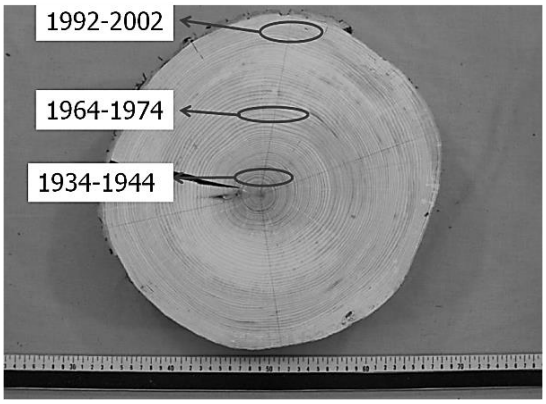


Figure 4. Chisel and hammer tools from Colonial Williamsburg Master Craftman, Name, used to collect 10-year increments of selected bolewood cookies. De-ionozed water rinses and food grade wax paper barriers were used to ensure clean surfaces.

Sample Preparation

The yearly growth rings were marked and dated for each cookie by Patterson (2012). The first year growth rings were dated to as early as 1923 and all trees died simultaneously in 2003 as a result of Hurricane Isabel. Three 10-year increments were obtained from each cookie and included near the center of the heart wood (1934 to 1944), the outer edge of the heart wood (1964-1974), and the sapwood (1992-2002) (figure 3). Wood extraction techniques were developed in collaboration with a Colonial Williamsburg Master Craftsman and were performed using a chisel and hammer (figure 4). All samples were cut to match the size of the DMA-80 sample trays (1 cm x 0.4 cm x 0.4 cm) and then frozen overnight and freeze dried for 48 hours such that concentrations are based on dry weight (DW) of samples.

Analysis

Freeze dried samples were weighed and then measured in the DMA-80 atomic absorption spectrophotometer to yield the concentration of mercury in mg/kg DW. Analysis was performed in triplicate according to the EPA Method 7473 (February 2007) modified by eliminating the spike percent recovery. The analysis of reference materials was applied and blanks (n = 61) were included once every three samples and the amount of mercury found in these blanks was used to establish limit of detection (LOD) and limit of quantitation (LOQ) (table 1).

Two separate standard reference materials (SRMs) were used in this study. Curvilinear calibration curves were generated using SRM 1575a, a solid standard from

dried ground pine needles purchased from the National Institute of Standards and Technology (NIST) with a documented mercury concentration of 0.0399 $\pm$ 0.007 mg Hg/kg DW. For percent recovery and quality control (QC) verification, DORM-3, National Research Council Canada (NRCC) certified reference material was used. This solid powder standard is derived from dogfish muscle and was purchased from NRCC (0.382 $\pm$ 0.060 mg Hg/kg DW). Experiments were deemed in control if the DORM-3 QC sample remained within 15% of the NRCC certified [Hg].

Grubbs Outliers test (Grubbs 1969) at alpha = 0.05 was used to eliminate any suspect concentrations that were also statistical outliers of all samples and replicates, which resulted in the loss of 6 of 171 sample replicates. Data were analyzed in Sigma Plot 12.3 (Systat Software Inc. 2011) and plotted in Excel (Microsoft 2010). The potential effect of 10-year increment on median mercury concentration within each bole segment was tested using ANOVA. The effect of the five stand locations on mean mercury concentration within the tree ring samples was also tested using ANOVA.

Total mercury per stem was calculated based on stem density (1006 cedar stems/ha) reported for GDSNWR by DeBerry et al. (2003). The [Hg]/ha in standing cedar was calculated by multiplying aboveground biomass estimates from DeBerry et al. (2003) (179,886 kg/ha) by the median mercury concentration of all samples (0.0088 Hg/kg DW).

Table 1. Detection and quantitation limits determined for Direct Mercury Analyzer 80 atomic absorption instrument.

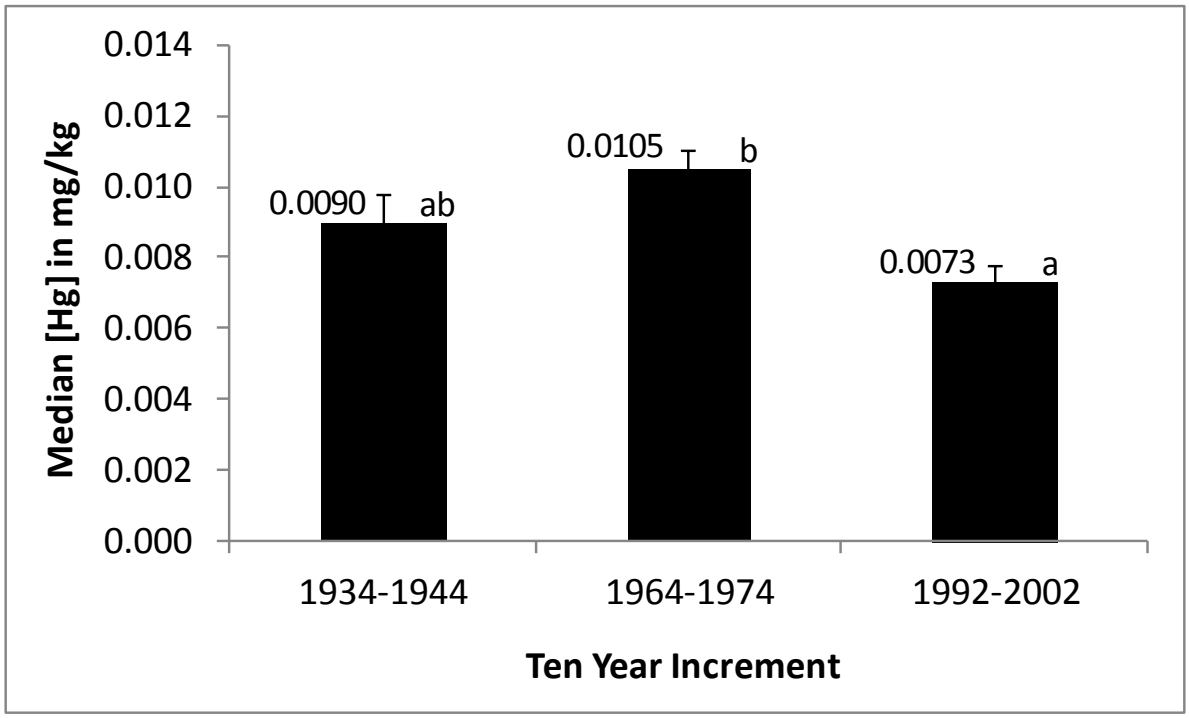
	Peak Height (ng)
Mean blank reading (n=61)	0.0023 +/- 0.0013 (SD)
LOD (mean + 3*SD)	0.0062
LOQ (mean + 10*SD)	0.0154

*0.0062 ng is rounded to <0.1 ng Hg

RESULTS

Concentrations of mercury within all samples (n = 57) ranged from 0.0027 to 0.0170 mg Hg/kg (median = 0.0088 mg Hg/kg). Mercury concentration among the five salvage-logging unit locations did not differ significantly ($p = 0.154$)(n = 12). With the salvage-logging units combined, median mercury concentration in the 1992-2002 increment contained less mercury per kg DW than the 1964-1974 year class ($p < 0.05$)(n = 19)(figure 5).

Figure 5. Median mercury concentration (mg Hg/kg dry weight) in 10-year increments of cedar from GDSNWR (Error bars represent +1 SE, n = 19). Medians with the same letter are not significantly different ($p > 0.05$).



Based on concentrations found within the 10-year increments, a single 60-year old cedar stem contained 1.574 mg Hg and the concentration of mercury in standing cedar was calculated to total 1.583 g Hg/ha.

DISCUSSION

Average cedar concentrations among the three 10-year increments ranged from 0.007-0.011 mg Hg/kg dry weight, which is slightly below the range (0.013-0.037 mg Hg/kg) reported by Zhang et al. (1995) for rings of another conifer, Black Spruce (*Picea mariana*), which was studied in contaminated sites in Canada. Our estimate of mercury in cedar is slightly higher than most findings for deciduous species compiled

in a frequency distribution (n = 95) by Nader (2003) which accessed other studies that used live-wood samples (figure 6).

The median concentration of mercury appeared to increase from the 1934-1944 to 1964-1974 increments, and then decreased significantly in the 1992-2002 increment. While translocation of mercury from outer to inner rings could account for some of these differences (sensu Nabais et al. 1999), it is unknown for cedar and two other explanations may be considered. First, cumulative industrial emissions and fossil fuel combustion coincide with increased mercury concentrations (Streets et al. 2009) as found in our rings, which then decreased and coincided with passage of the federal Clean Air Act in1970, reauthorized in 1990. The Clean Air Act sought to establish "maximum achievable control technology standards" to limit particles and specific chemicals (CWA Section 112). Other studies suggest that US emissions of mercury peaked in the 1970s and have since declined (Pirrone et al. 1998) which corresponds with the trends observed in our cedar tree rings.

A second factor that may have influenced decadal mercury concentrations in this study is hydrologic management in GDSNWR, the significant decrease in wood tissue mercury in cedar observed between 1964-1974 and 1992-2002 increments may be related to hydrologic conditions in the swamp. The GDSNWR was created in 1974 and water levels were soon raised as an early restoration strategy (Great Dismal Swamp National Wildlife Refuge 2006). Saturated conditions would have reduced peat decomposition rates and allow retention of sequestered mercury, limiting tree uptake from the soil. Higher water tables would have also promoted wetland soil conditions that were more favorable for methylation and accumulation of mercury (Woodruff and Cannon 2010), which coincides with the highest concentrations found among our three 10-year intervals.

Stand-Level Analysis and Management Recommendations

We contend that salvage logging reduced the risk of bole wood oxidation via fire and therefore reduced the risk of mercury remobilization from GDSNWR to surrounding ecosystems. Based on the mean [Hg] in cedar of the current study, and assuming that all of the stands that burned were composed of trees similar to those we sampled, the 2,491-ha (6,156-acre) fire would have released 3.944 kg (8.70 lbs) of Hg from aboveground trees. That total is equivalent to 13.4% of annual emissions from the average of three local coal-fired power plants (65 lbs per year). If water levels were raised still higher, as is becoming possible with hydrologic management infrastructure currently being developed in GDSNWR, peat oxidation by both fires and decomposition would be reduced and would further limit volatilization of mercury.

CONCLUSION

Cedar tree rings may be a reliable indicator of historical pollution but further investigation is still necessary. Previous research reports mixed results on the ability of tree rings to track historical pollution, but the significant difference in mercury

concentration of cedar tree rings over time indicates there is a realistic possibility to use dendrochronology to track historical mercury content in the environment.

The GDSNWR lies within two watersheds (Chesapeake Bay and Albemarle Sound) and both serve as popular recreational and commercial fisheries. While speciation of Hg in wood and peat would improve our recommendations, our current understanding suggests that maintaining saturated soil conditions would reduce the risk of Hg remobilization and protect local watersheds.

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