

Article

Phytoremediation Potential of the Coastal Plain Willow *Salix caroliniana* for Heavy Metals with Emphasis on Mercury

Ryan Greenplate¹, Serge Thomas², Ashley Danley-Thomson¹ and Thomas M. Missimer^{1,*} 

¹ U. A. Whitaker College of Engineering, Florida Gulf Coast University, 10561 FGCU Boulevard South, Fort Myers, FL 33965-6565, USA; rggreenplate0805@eagle.fgcu.edu (R.G.); athomson@fgcu.edu (A.D.-T.)

² Department of Ecology and Environmental Studies, Florida Gulf Coast University, 10561 FGCU Boulevard South, Fort Myers, FL 3956-6565, USA; sthomas@fgcu.edu

* Correspondence: tmissimer@fgcu.edu

Abstract: Remediation of heavy metals is a complex, difficult, and expensive exercise and commonly involves relocation of the problem from one place to another (e.g., a contaminated site to a hazardous waste landfill). Alternatively, bioremediation can be used so that metals can be sequestered into the woody portion of the plant, where they are fixed into the organic matter and remain undisturbed for extended periods (e.g., wetland area soils). A species of willow (*Salix caroliniana*) was investigated to ascertain its potential for use in the bioremediation of mercury. It was found that the plant did bioaccumulate mercury and did so especially in the wood compared to its leaves (8.8 to 1 ratio in the mercury activity; activity of 12,071 to 1164). While there is moderate potential for use in bioremediation, the measured concentration in the wood was quite low (average of 11.91 ppb). The low concentration was caused by the location of the sampled trees in environments that were either pristine or had low soil concentrations of mercury. Furthermore, 90% of the mercury accumulated in the leaves appeared to be adsorbed via atmospheric deposition in southwest Florida where there are minimal sources of anthropogenic mercury, but the region is impacted by Saharan dust, which does contain mercury.

Keywords: phytoremediation; willow tree (*Salix caroliniana*); heavy metals contamination; mercury



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1. Introduction

Soil and groundwater contamination represents a complex and important global issue because many different contaminants can damage ecosystems and pose a risk to human and animal health [1,2]. Arsenic, lead, mercury, and cadmium are common heavy metals that cycle through the environment and originate from both natural and anthropogenic sources [3]. Mercury (Hg) is a heavy metal that is regarded as one of the most prominent and dangerous contaminants in the terrestrial environment because of its mobility and its propensity to bioaccumulate [4,5]. The detrimental effects of mercury on human health and the environment led in 2013 to the establishment of an international agreement, the Minamata Convention, to protect both of those entities [6,7].

The primary sources of mercury found in the environment are natural emissions associated with volcanic eruptions [8,9], atmospheric dust [10,11], and biomass burning [12]. Anthropogenic mercury sources include the burning of coal for generating electrical power, incineration of waste materials, and industrial waste leachate discharge [13].

Mercury is also released into the environment by volatilization from the surface of the ocean, weathering of geologic areas, and deposits of the element itself. However, cataclysmic volcanic eruptions are the highest naturally occurring sources of volatile mercury [8]. Gaseous elemental mercury (GEM) is discharged into the troposphere, where it is transported long distances around the earth as either GEM or combines with sulfur as a sulfide in atmospheric dust [14,15]. GEM occurs in dust entrained in Africa and travels to

southern Europe and across the Atlantic Ocean to the west depending on seasonal wind directions [16].

As mercury pervades into the environment, it is converted by anaerobic bacteria into methylmercury, a lipophilic byproduct resulting from bacterial respiration [4]. These bacteria are generally found in the soil or associated with bacterial or periphytic mats [17]. Methylmercury (CH_3Hg) is one of the most common mercury cations found in the environment and is an organometal ($\text{H}_3\text{C-Hg}^+\text{X}^-$) toxicant compound that bioaccumulates [4,18]. Contrarily to organic pollutants, heavy metals are not biodegradable, hence their ability to accumulate in various organisms and in organic sediments containing plant debris like peat, where the metals are commonly chelated or lightly adsorbed with the organic carbon [19].

Conventional methods of remediation of soils contaminated with heavy metals can involve onsite management and direct treatment of the soil before it is transported to a hazardous waste landfill site [20]. The fact that these toxic metals are relatively costly and labor-intensive to safely remediate poses a significant challenge [21]. Sometimes, the remediation methods merely shift the problem with the hazards of transporting the contaminated soil or the contaminants leaking from the original site to adjacent environments [22]. Soil washing in order to cleanse contaminants from the soil is an alternative option as opposed to excavation and disposal [20]. Unfortunately, this method can be quite costly and sometimes produces residues and precipitants rich in various heavy metals, which usually require further treatments to be completely removed [23]. In the worst situations, sites are simply isolated (e.g., slurry walls) and quarantined to prevent the contaminants from spreading, such as in Brownfields sites. The remediation of heavy metals is very site-specific and based on risk assessments and the potential for movement of the contaminants into the environment or drinking water supplies [20].

Phytoremediation is a growing, environmentally friendly, and inexpensive solution being used to assist in the remediation of some common contaminants [14]. By isolating contaminants such as harmful metals and radionuclides, willow plants are known to uptake mercury and have been used in other parts of the world in the remediation of urban soils [24]. Hyperaccumulators are plants that specialize in extracting soil and groundwater contaminants through their root system, or xylem, in order to accumulate them in such a way as to render them harmless within the structure of the living plant [25]. Differences in how aquatic, vascular plants uptake chemicals are usually dependent on factors such as species, seasonal growth rates during the year, and the type of ion [26]. In some parts of the world, some species of *Salix* have been found to be useful in the phytoremediation of land contaminated with metals [23,27,28].

There are approximately 330–500 *Salix* species (willow) scattered throughout the world [29–32]. They are primarily located in temperate and arctic zones, but they also occur in tropical zones [30]. Most native flora in temperate regions of the world include some types of *Salix* species [32]. *Salix* species have been undergoing investigation as a phytoextractor and phytoremediator in order to see which genotypes have high accumulation rates and metal absorption [22,33,34]. Genetic engineering experiments on willow are currently being conducted to increase the uptake, translocation, accumulation, and volatilization abilities of mercury by altering the *merA* and *merB* genes [35]. *Salix* has especially been investigated for its use in the remediation of urban soils [23,36–41].

Salix caroliniana (the coastal plain willow or swamp willow) is a species of plant that grows in southwest Florida as well as in most tropical climates adjacent to freshwater bodies [42,43]. It can be considered a metals hyperaccumulator and potentially could be used to aid in the remediation of mercury rather than more intense, expensive treatment methods for contaminated soil and groundwater. If it stores mercury primarily in woody material, then it can potentially be used as a safer, cost-effective method to remove mercury from the environment by utilizing it as a trap until it can be properly remediated [44]. Mercury has been found to accumulate inside of the roots of willow trees, but it is possible for mercury to translocate towards the leaves and aerial tissue [45,46].

One purpose of this research is to examine how well *S. caroliniana* can absorb and adsorb mercury and other heavy metals. This study involves analyzing heavy metals that accumulate in the woody parts and in and on the leaves. While three other heavy metals concentrated were analyzed, the specific emphasis of this paper is on the mercury concentration. If the metals are translocated into the leaves, they will most likely fall off from the deciduous tree and will be incorporated into the ground from the litter to the soil, thus necessitating the need to assess where mercury is most concentrated. The other purpose is to ascertain if mercury is on the surface of the leaves of *S. caroliniana* or inside of the aerial tissue. If mercury is located inside of the aerial tissue, then it most likely is a result of mercury being translocated from the roots. If not, then mercury on the surface of the leaves is probably the consequence of atmospheric deposition [16] and is thus potentially an ephemeral accumulation of mercury. This investigation is not a comprehensive assessment of the biology of mercury uptake and must be considered to be a detailed screening analysis. A key question to be assessed is the relative percentage of mercury in the trunk wood compared to the percentage in the leaves.

2. Materials and Methods

2.1. Tree Sampling

In order to quantify the effectiveness of *S. caroliniana* as a phytoremediator of mercury and other heavy metals, trunk and leaf samples of *S. caroliniana* trees were collected in two different locations in southwest Florida: a freshwater location in the interior and one near the coast (Figure 1). To retrieve the trunk samples, an increment borer was used to drill into multiple *S. caroliniana* trees to retrieve their interior wood (core). Typically, trunk cores were collected at average chest height for a person or approximately one meter from the ground for consistency. However, trunk cores taken from *S. caroliniana* were taken at the base of the tree because of the structure of this species, which involves multiple, small branches that spread out in an irregular, crown-like manner. Furthermore, the base of the tree trunk was thick enough to properly use the increment borer to extract core samples. These trunk samples were placed in a dark, dry storage area at room temperature (22 °C) and inside appropriately labeled containers for a week before analysis. This was to prevent the mercury from volatilizing off the samples. Leaf samples were also snipped off the branches of the trees, collected, and stored in the same conditions as the trunk samples. After the cores were collected, the spectracide pruning seal was sprayed on the spot where the trunk cores were removed in order to prevent various wood-boring insects or other pests from damaging the tree. The GPS coordinates of the location of each individual tree from which samples were extracted were recorded in order to distinguish the collection sites and specific sampled trees. The sampling sites were chosen with one being on a barrier island away from intensive development and the other on the FGCU campus, which is intensely developed.

2.2. Sample Preparation Methods

After the samples were collected and stored, they were prepared for analysis using a NexION Model 2000C Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Perkin-Elmer™) to determine metal concentrations. With solid samples, digestion with strong acids at high temperatures is the usual protocol to use for sample preparation [47]. Unfortunately, the trunk and leaf samples could not be heated during any part of this analysis due to the volatility of mercury, which eliminated the possibility of drying the samples in an oven to make them brittle and using a thermal plate to heat them while being digested by acid. To prevent mercury from volatilizing out of the samples, every part of the procedure was conducted at room temperature (approximately 22 °C).

First, the trunk samples were sliced into 0.5 mm × 0.5 mm pieces with a razor blade. The tree core samples were then ground with a mortar and pestle for approximately five minutes each to increase their surface area. After grinding into a homogenous mixture, the samples were weighed on a scale in a glass dish (about 5 mg of dry weight). Leaf samples

were treated using two separate methods. A portion of the leaf samples was ground in the mortar and pestle for five minutes. Other leaf samples were vertically sliced along the stem into two separate halves with a razorblade after having the petiole snipped off. One-half was ground as described above to act as a control group. The other halves of the leaves were washed for 10 s on both sides with deionized water (pH = 5.0) with a 500 mL wash bottle before being ground to increase the surface area of the sample for the next step. The deionized water used was a type 1 analytical grade with a resistivity of 18.2 Megohm-cm. For every step, each tool was cleaned with methanol (HPLC from Fisher) in order to prevent cross-contamination between samples. The weight of the samples was then recorded, and they were placed into plastic 50 mL beakers.

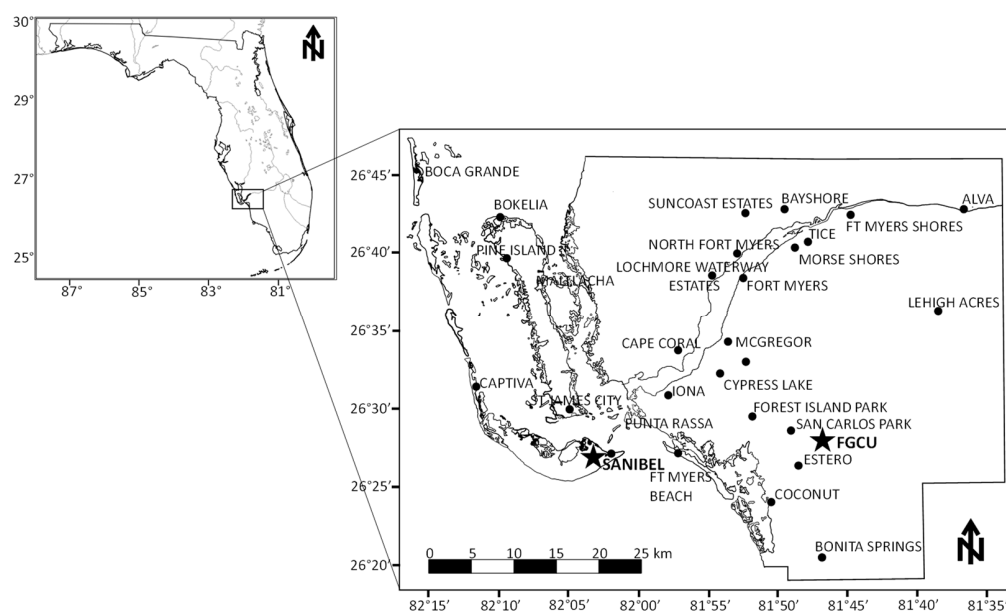


Figure 1. Map showing the locations of where *Salix* samples were collected. Note that site 1 (star in west) is in a nature reserve area on Sanibel Island, and site 2 is located on the campus of Florida Gulf Coast University (FGCU). Both occur in areas with very low mercury contamination potential.

Next, 5 mL of trace-metal-grade nitric acid (HNO_3) was added to each beaker and sealed with a cap. The nitric acid was analytical grade provided by Fisher. The nitric acid had an assay/analysis of 67–70% to help ensure that the samples would be readily dissolved without the addition of intense heat. Once the 5 mL of nitric acid was added, the samples were then digested inside the fume hood for a week at a temperature of about 22 °C.

After a week, the samples were then mixed with approximately 45 mL of deionized water. Nitric acid was added, and the mixture was then centrifuged at 3200 rpm for one hour in a Sorvall ST 8 Centrifuge (Thermo Scientific), thereby separating the supernatant from the leftover organic pellet. A series of 10 mL volumes of the diluted sample were then extracted and filtered through a disposable, cellulite 0.45 μm syringe filter. The samples were put into plastic 15 mL beakers before finally being analyzed in the NexION 2000 ICP-MS (from PerkinElmer).

2.3. Analysis Using the ICP-MS

A semi-quantitative scan was initially performed for some samples and one blank with the ICP-MS. This technique enables the determination of the concentrations of elements without the need for calibration standards. This method is commonly used for the scanning of metal concentrations and to determine the relative ratios of metals. First, the syringe tip used in the sample introduction system was washed with 1% nitric acid for 90 s to prevent cross-contamination between samples. Then, the tip of the syringe was mechanically

guided and dropped into the samples by the ICP-MS. For 90 s a peristaltic pump was utilized to flush out any fluid left in the tubes. Next, the sample was introduced to an ESI PFA nebulizer inside of a spray chamber to produce a fine aerosol for the following step. The aerosol particles were decompressed and dissociated before being atomized and finally ionized by the heated plasma in the ICP section of the ICP-MS. The ionized particles were then directed inside of a vacuum of the ICP-MS to finally be analyzed by the mass spectrometer. While inside of the vacuum, the ionized particles were subjected to the quad ion deflector to separate the ions from the uncharged particles. This is so that only charged particles would be able to enter the mass spectrometer. Next, the charged particles were guided down into the universal cell, which was used to correct for polyatomic ions. Then, ionized particles were put through a quadrupole mass to filter out undesirable ions. Finally, the discrete dynode detector quantified the ions exiting the quadrupole, and the results were subsequently recorded. This process was duplicated for each individual sample.

For the quantitative analysis, a mercury standard of 100 ppm Hg from Ricca was used to help calibrate the ICP-MS for detecting mercury for the same samples used in the semi-quantitative analysis. In addition, for the quantitative analyses, standards were created for concentrations of 2, 4, 6, 8, 10, and 20 ppb. The instrument was calibrated by measuring the intensity of mercury with the calibration standards that represent a range of concentrations likely to be encountered in the samples. The program Syngistix was used to develop the calibration curve of the measured intensity versus concentration. Once the calibration data were acquired, the unknown samples were analyzed by plotting the intensity of the elements, in this case, mercury, against the calibration curve. The software then automatically calculated the concentrations for the desired element in the unknown samples. After the calibration, the samples were put through the exact same procedure as the semi-quantitative analysis in the ICP-MS. For future analytical work, the calibration curve will be expanded by adding lower concentrations between 0.5 and 1 ppb to improve the error range in the lowest concentrations. Based on the standards and the calibration curve, the error of the mercury measurements is believed to be about 1 ppb according to the equipment manual.

The amount of organic solute obtained from the willow tree samples remained constant, which allowed the concentration of heavy metals in the original solution to be calculated before being diluted with water. First, a blank was designated from a diluted sample with the smallest amounts of mercury, lead, arsenic, and cadmium to establish the limit of detection, the lowest quantity of a substance, in order to distinguish it from system noise. The elemental concentrations of the blank were subtracted from the initial concentrations of the heavy metal concentrations for all other samples that were given by the ICP-MS to ensure that the diluted nitric acid was not directly adding to the concentrations of heavy metal contaminants. Then, the concentrations of the elements were converted from units of micrograms per liter to molarity. This was in order to calculate the concentration of the original solution, 5 mL of HNO₃, by multiplying the concentrations obtained from ICP-MS and the 50 mL volume of the diluted samples. This concentration, after being converted back to units of micrograms per liter, was then divided by the weight of the tree and leaf samples to deduct the concentrations of elements of the organic samples (µg/kg). This was carried out because not all of the masses of the organic samples were consistent when being dissolved in acid. This method was also used in regard to finding the intensity of mercury inside the undiluted samples digested by nitric acid. In samples with relatively low concentrations of mercury, the ICP-MS results can be reported as activities rather than parts per billion. This was carried out in this paper.

A statistical analysis was applied to the mercury data. A Wilcoxon two-tailed test was used to compare related sample data while a simple two-tailed *t*-test was best to see if the differences between mercury values in the trunk and leaves were significant.

3. Results

There were 14 samples of core material and leaf matter analyzed. The GPS coordinates of the various sampled *S. caroliniana*, their altitude, and the mass of the core and leaf samples before being digested in nitric acid are shown in Supplemental Data Table S1. The measured dry weight quantities of each sample before digestion are given in Supplemental Data Table S2.

3.1. Trunk Heavy Metals Data

The semi-quantitative concentrations of mercury, lead, arsenic, and cadmium were measured in trunk material (Table 1) and in the leaves (Table 2). Note that the three additional metals were analyzed strictly for comparison to the mercury data. The data for mercury show that the range of values in the wood were from 0.12 to 1.40 ppb and in the leaves were from 0.84 to 2.14 ppb. The means were 0.49 and 1.28 ppb, respectively. The mercury analyses reported are from the unwashed leaves. The comparative mean concentrations were 17.64 and 6.66 ppb, respectively. The scatter in the data for mercury is reflected by the standard deviations reported in Tables 3 and 4. The wood core material had a much larger range of standard deviation in all of the metals compared to the leaves.

3.2. Quantitative Comparison of the Mercury Concentrations in the Wood and Leaves

The mercury concentrations reported are from the unwashed leaves (Table 4). The range in the wood is from 1.69 to 47.09 ppb. In the leaves, the range in concentration is 3.97 to 20.18 ppb. The mean values for mercury concentrations in the wood compared to the leaves are 11.91 and 13.51 ppb with corresponding standard deviations of 11.30 and 4.26 ppb, respectively.

Table 1. Semi-quantitative trunk heavy metal concentrations.

Trunk Sample Number	Mercury Concentration (ppb)	Lead Concentration (ppb)	Arsenic Concentration (ppb)	Cadmium Concentration (ppb)
1	0.18	23.06	2.51	22.02
2	0.15	90.06	BDL	55.69
3	0.32	478	7.05	10.05
4	0.63	14.22	2.48	25.92
5	0.30	1095	13.38	15.16
6	0.50	251.5	5.29	18.61
7	1.40	173.4	6.01	31.19
8	0.37	844.2	2.28	6.55
9	0.35	54.49	3.49	3.12
10	0.30	29.49	4.22	2.45
11	0.76	91.22	21.68	2.11
12	0.74	400.5	7.45	44.16
13	0.12	184.9	2.62	1.96
14	0.79	33.87	6.77	7.96
Mean	0.49	268.9	6.09	17.64
Standard Deviation	0.33	320.7	5.34	16.11
Variance	0.11	102,825	28.55	259.4

Table 2. Semi-quantitative leaf heavy metal concentrations.

Tree Leaf Sample Number	Mercury Concentration (ppb)	Lead Concentration (ppb)	Arsenic Concentration (ppb)	Cadmium Concentration (ppb)
1	1.25	3.88	14.28	15.85
2	0.19	4.68	6.22	9.74
3	1.36	4.10	4.62	2.52
4	0.84	1.12	1.82	18.83
5	2.14	0.34	5.66	8.95
6	0.69	0.09	2.59	4.47
7	1.46	2.27	3.56	11.37
8	1.36	1.91	6.68	2.40
9	1.78	7.14	8.52	2.70
10	1.40	2.25	6.97	2.17
11	0.96	2.13	12.74	3.44
12	1.81	0.81	6.45	6.28
13	1.53	7.19	5.71	0.37
14	1.24	1.58	3.69	4.18
Mean	1.28	2.80	6.34	6.66
Standard Deviation	0.48	2.20	3.41	5.36
Variance	0.23	4.86	11.26	28.69

Table 3. Quantitative trunk and leaf mercury concentrations.

Sample Number	Trunk Mercury Concentration (ppb)	Leaf Mercury Concentration (ppb)
1	47.09	20.18
2	17.85	3.97
3	5.91	15.25
4	4.95	11.25
5	1.69	8.86
6	9.75	14.91
7	17.76	10.03
8	14.60	12.70
9	4.37	16.93
10	17.97	14.03
11	5.58	17.63
12	8.92	11.79
13	19.02	19.75
14	7.23	1.86
Mean	11.91	13.51
Standard Deviation	11.30	4.26
Variance	127.80	18.11

Table 4. Unwashed and washed leaf mercury intensity.

Leaf Sample Number	Unwashed Mercury Intensity	Washed Leaf Mercury Intensity
1	41,011	2676
2	30,059	2447
3	17,994	1389
4	1664	1544
5	10,676	1594
6	13,025	1358
7	9302	1606
8	6673	351
9	3248	723
10	2762	935
11	4956	568
12	6006	975
13	3416	51
14	3230	78
Mean	12,071	1164
Standard Deviation	10,895	768
Variance	118,694,129	590,157

3.3. Difference in Measured Mercury between Unwashed and Washed Leaf Material

It is important to evaluate whether the mercury concentrations measured in the leaves occur within the organic matter or are deposited on the surface of the leaves. Using the mercury intensity for comparison, the leaf material showed that the mean activity values for the 14 samples for the unwashed and washed leaves were 12,071 and 1164, respectively, with corresponding standard deviations of 10,895 and 768.2 (Table 4). Based on the ratio of the intensities, it showed that about 90% of the measured mercury occurred as a surface deposit on the leaves.

3.4. Statistical Analyses for Comparison of the Data

During the semi-quantitative analysis of elemental concentration, the results showed that there was a numerical difference between the trunk samples and the leaf samples. The differences were 0.7, 266, 0.26, and 10.98 ppb for mercury, lead, arsenic, and cadmium, respectively. The differences were the result of several two-tailed paired *t*-tests conducted using Microsoft Excel for statistical analysis calculations, comparing elemental concentration data between the core and leaf samples to show differences calculated with an alpha value of 0.05. The results showed a significant difference in concentration data for mercury, lead, and cadmium but not for arsenic between the *S. caroliniana* trunk and leaves.

The box plot of the trunk and the bulk leaf analyses showed that mercury concentrations had a mean concentration difference of 0.48 (Figure 2). This difference was not significant (Student's independent two-tail *t*-test with unequal variances, $p = 0.89$). The intensity of mercury data for the leaf samples, unwashed and washed with deionized water, showed an approximately 90.36% decrease in the intensity of mercury detected after samples were washed with deionized water (Figure 3). This difference was significant (paired samples Wilcoxon two-tail test, $p = 0.001$).

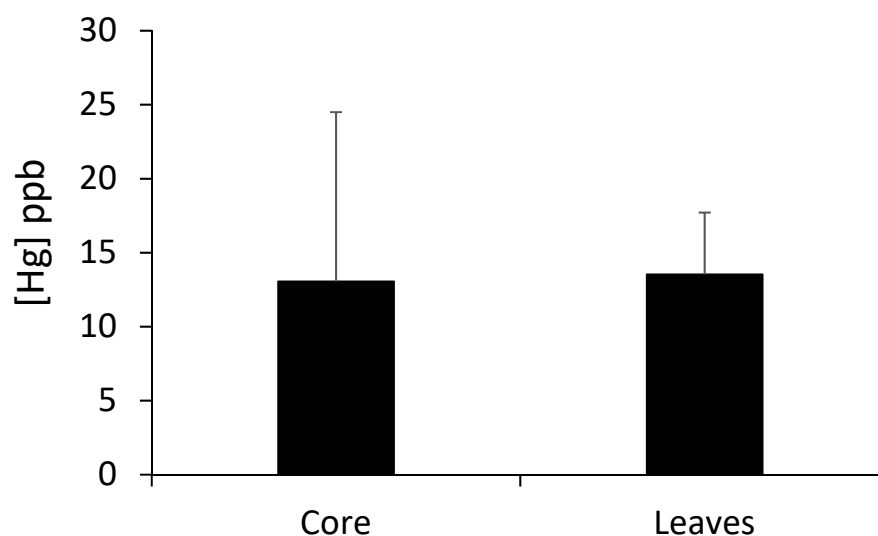


Figure 2. Average mercury concentrations in *S. caroliniana* trunk and leaves.

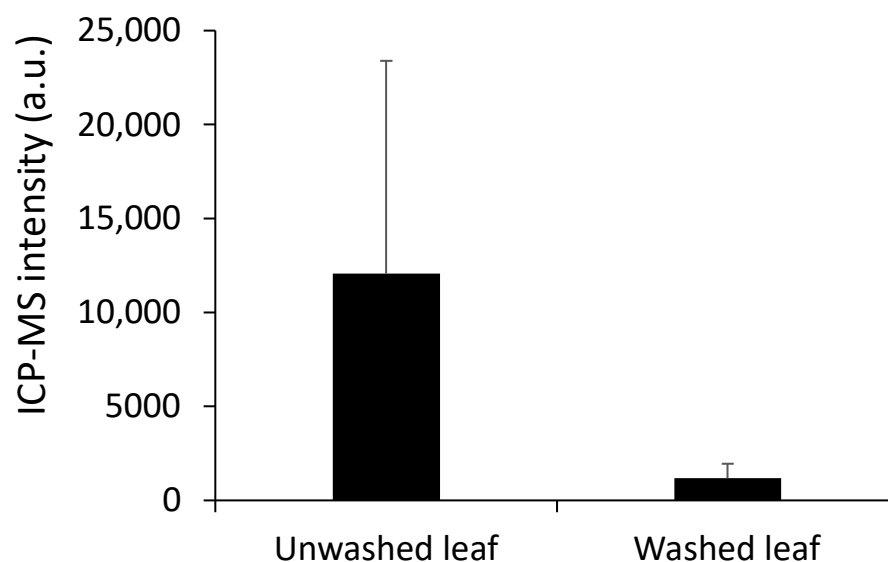


Figure 3. Average intensities as determined with the ICP-MS in washed and unwashed leaves.

4. Discussion

4.1. Possible Mercury Transfer within *S. caroliniana* from the Soil and Groundwater

The transfer of heavy metals from soils to any plant is reliant on three primary factors: the total quantity of the element potentially available, the ionic ratios of the elements in the soils, and the rate of element translocation from various phases of matter that the elements are contained within [48]. The dynamic between the quantity of mercury that exists in the soil and its absorption by plants is not necessarily linear [6]. High concentrations of mercury in soils do not necessarily equate to high rates of uptake via the root system into the wood. Methyl-Hg in very contaminated soils in the Rhône Valley of Switzerland accounted for <0.8% of the total mercury in the trees [49]. In mercury-mining areas, the highest concentrations were found in the roots with lower ones in the leaves [50]. There are usually several other variables that affect mercury uptake via the roots, including soil pH, soil aeration, cation-exchange capacity, and plant species. Still, the general concentration of mercury in plants often reflects the environment in which the plants grow. It has been clearly demonstrated that terrestrial plants play a significant role in the geochemical cycling of mercury [51–53].

Some plants accumulate mercury in the shoots because of direct translocation or direct absorption of the metal in its vapor form through the leaves [6]. With lower levels of mercury pollution, the relative amount of flora with high levels of mercury naturally drops [26]. *S. caroliniana* from which the samples were collected were not located in mercury-rich environments. As a result, very little mercury was found in both the trunks and the leaves overall. The concentration data in the semi-qualitative analysis explicitly express that more than double the amount of mercury was found in the leaves compared to the cores. Mercuric cations have a high affinity for sulfur. The fact that all proteins in willow trees contain the accumulation and translocation of mercury is likely caused by the sulfhydryl groups and disulfide bridges. Analyses generally show that sequestered toxic ions are locked in the cytoplasm in order to defend against phytotoxicity because of sulfur [54].

For the transportation of mercury from the roots to the rest of plants, the xylem-uploading process is crucial. A majority of mercury accumulation in plants remains in the roots, and only a small location is translocated to the wood and leaves. Mercury is thus primarily trapped in the roots of plants, and approximately 80% of it is bound to cell walls [18]. This is possibly because the mercury ion easily interacts with anionic compounds such as carbonate, phosphate, and sulfate. When mercury interacts with these anionic compounds, insoluble precipitates form and drastically limit the mobility of mercury. Mercury ions bound to the root cell walls have increased cationic exchange [13]. The data in Table 1 appear to contradict this assertion, as there seems to be significantly more mercury located in the leaves of the coastal plain willow rather than the interior core, with means of 11.90 and 13.51 ppb, respectively. However, the data in Table 2 support this sentiment, as the amounts of mercury in the trunk are higher than in the leaves. However, the discovery that 90% of the mercury occurring in the leaves is the result of surface deposition (Figure 3) shows that the ratio of mercury in the wood is 8.8 times greater than in the surface of the leaves. Based on the data, willow trees do seem to have the ability to uptake heavy metals trapped in sediment and sequester them in the wood. The mercury in the leaves is another issue of importance.

4.2. Mercury in the Leaves of *S. caroliniana*

The aerial part of plants, the leaves, serves as another important place for mercury and other heavy metals to accumulate. Mercury exchange between aerial tissue and the air is a dynamic process. The net deposition rates of mercury on leaves are directly correlated with increased atmospheric mercury concentrations. Studies of mercury in leaves suggest that the primary source of mercury in leaves originates from air pollution (atmospheric aerosols and gaseous elemental mercury) and not from contaminated soils [55–57].

Industrial emission of mercury into the air and microorganism-related emissions from the earth (soils in particular) could be related in a way that there are more heavy metals in the air than in the water [13]. The exact mechanism of how mercury enters the aerial part of the plants is still under debate. Some studies suggest that the leaves are thought to be responsible for the intake of atmospheric mercury through gas exchange [58], while others suggest it is related to the stomatal diffusion of mercury to cuticle surfaces [59]. There are other studies indicating that mercury tends to accumulate more in the leaves than the trunk of willow trees [47].

The evidence produced herein strongly suggests that the majority of the mercury on the leaves seems to have accumulated on the surface of the leaves instead of being located inside of the aerial tissues, as indicated in Figure 3. With a slightly greater than 90% decrease in the amount of mercury detected after a light washing with deionized water, the mercury is deposited on the surface of the leaves through atmospheric deposition. An enigma is that intense rainfall in southwest Florida does not wash the mercury from the leaf surface, while deionized water does accomplish this feat. This issue could be related to the specific leaf area, age of the leaves (increased indentation for trapping) [60], or the pH of the rainfall being 6 to 6.5 while the deionized water has a pH near 5. Rainfall in the

area of study averages over 137 cm per year. Another proposed possibility is the issue of sap occurring on the leaf surface, which may reject rainfall removal but may be subject to deionized water removal. Further research will be required to resolve this dilemma.

The intensity of mercury was used as a measurement for determining the amount of mercury on the leaves, washed and unwashed, rather than the concentration, which is related to the low concentrations used in the standard calibration curve. The concentrations of mercury for some samples, especially after being washed, were transcribed as negative based on the calibration curve created by the mercury standards since the amounts were too insignificant to be detected in parts per billion.

4.3. Possible Sources of Mercury for Leaf Surface Deposition

Atmospheric concentrations of mercury in southern Florida are rather low compared to other more industrialized areas. Coal-fired power plants have not been operated in the region for decades. However, high concentrations of mercury are found in the Everglades, particularly in the sediments [61–63]. During muck fires, the mercury may be volatilized and become part of local atmospheric aerosols. These fires occur during the dry season and periodically move from the southeast over the sites where the samples were collected. A single waste-to-energy incinerator does occur in Lee County but is located more than 20 km east of the sampled plants on Sanibel Island.

Another source of mercury in southwest Florida is African dust that occurs particularly in the summer months. Atmospheric deposition of mercury from various sources has been studied in Florida [64–66]. However, some researchers suggest that mercury can be emitted by plant leaves in the form of Hg^0 [56,67,68]. This mechanism and required conditions are not well understood, nor has it been documented in willow species in the past.

4.4. Usefulness of Willow (*Salix*) for Mercury Contamination Phytoremediation

The willow tree may be suitable for phytostabilization and phytoremediation by trapping the bioavailable mercury in the soil (via litter accumulation) to assist in controlling the leakage of mercury from contaminated areas with the mercury being stored in the woody part of the plant. However, many investigations have found that the effective uptake of mercury from the roots of other trees is small compared to atmospheric uptake [4]. While the usefulness of willow for bioremediation is open to question, further investigations would be necessary to reveal the true potential of the coastal plain willow in its uses of helping control mercury pollution. Preferably, this would mean gathering data on willow trees in somewhat mercury-contaminated soil for comparison to “clean” soils.

5. Conclusions

Mercury concentrations found in the trunk of the tree of the willow (*Salix*) were lower than those in the unwashed leaf material. However, when the unwashed versus washed leaves were analyzed, it was found that 90% of the mercury was adsorbed onto the leaf surfaces, likely from atmospheric deposition. When the mercury concentration of the wood was compared to the washed leaf matter, it had a concentration 8.8 times lower. This has significant implications for the usefulness of willow in phytoremediation.

Successful phytoremediation is dependent to a degree on the location of the mercury within the plant structure. If it occurs within the leaves, it will be likely re-dispersed into the environment unless the litter remains trapped within wetland soils and becomes fixed. Since only 10% of the mercury lies mostly within the wood, willow has dubious usefulness for bioremediation purposes. However, considerably more data need to be collected from natural low-concentration sites, moderately concentrated sites (e.g., highway swales), and highly concentrated sites to assess the potential use for bioremediation (e.g., old coal-fired power-plant sites or organic soils containing high mercury concentrations).

The finding that the mercury had accumulated mostly on the leaf surfaces also has important ramifications. Since southwestern Florida does not have modern large-scale anthropogenic sources of mercury (e.g., coal-fired power plants), the mercury must be

coming from another source. Only three other sources of mercury appear to be viable: African dust deposition, possibly aerosolized mercury from the Everglades and/or other wetland areas that have high soil concentrations of mercury and are subject to fire (muck fires being the worst), and a single waste-to-energy incinerator used for disposal of domestic solid waste in Lee County.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/w15203628/s1>, Table S1: Coastal plain *S. caroliniana* ground up core and leaf data.; Table S2: Coastal plain *S. caroliniana* washed and unwashed leaf data.

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