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MERCURY IN ALTERNATIVE FUELS

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Rationale

As many fossil fuel supplies are being exhausted, various biomass sources have been suggested for use as cocombustion fuels with coal. Yet, various aspects must be investigated to determine if these fuels are appropriate.

Project Description

High mercury (Hg) content in the environment has been determined to be a hazard. Both natural and anthropogenic sources contribute to the surface concentration, making it necessary to find methods of remediating areas that may produce dangerous levels in the food chain. One method for remediation of bodies of water involves using dense growths of plants to remove the Hg from the water and the bed through normal growth processes, then harvesting the plants and removing them from the site. In this project, cattails (genus *Typha*) which can be used as gasification or combustion feedstock were studied to determine whether they could be used to remove Hg from an area while providing an alternative energy source. Two areas known to have high Hg content were chosen for the study. One area was surrounded by virgin prairie, and the second area was near agricultural cropland and less than a mile from a small municipality.

Plants were gathered from three locations at each of two study areas early in the growing season and again later in the growing season when the plants had flowered. Slough water, other flowering plants, and soil were also gathered along with the cattails. All parts were air-dried, ground, and analyzed. The leaf (stem) and rhizome more often contained more Hg than the soil from which it was growing. Those harvested late typically contained a higher Hg concentration than those harvested earlier, indicating an accumulation of Hg during the growing season. Although the flowers contained Hg, the concentration was generally less than that of the leaf (stem) or rhizome.

Goals

The goal of this study was to evaluate cattails (genus *Typha*) as a potential vehicle for removal of mercury from water and wetland beds. The objectives included determining and comparing the uptake of

mercury by the flower, leaves, and rhizome of the plants and to determine whether a variation in Hg concentration occurs in different locations within well-established wetlands.

Approach

Ponds, lakes, and streams and their beds are likely to accumulate mercury (Hg) forms from natural sources as well as anthropogenic contributions. These bodies of water host many plant and animal species. When the Hg in either the elemental or oxidized form reaches an elevated concentration, physiological damage occurs to the biota and fauna living in that environment. Subsequently the Hg moves up the food chain, eventually resulting in a potential threat to humans. To prevent this from happening, either the Hg contributions to the water bodies must be stopped, which is not practical based on ongoing contributions from natural as well as anthropogenic sources, even with reductions from the latter, or it must be removed as it is deposited. The alternative is to introduce a means of removing Hg from the environment of interest by practical means.

It has been known for sometime that *Typha* tissues can store relatively high concentrations of some metals. *Typha* appears to have an internal copper and nickel tolerance mechanism. It is not likely that there is an evolutionary selection for heavy-metal tolerance, but rather the tolerance toward heavy metals is inherent in the species (1). One method for remediation of bodies of water involves using dense growths of plants to remove the Hg from the water and the bed through normal growth processes, then harvesting the plants and removing them from the site. The question is, what do you do with all of this harvested plant material (biomass)? The answer lies in finding a profitable use for the biomass. It cannot be used for animal feed, since that simply exacerbates the problem of Hg moving up the food chain. Using it as a combustion fuel would be acceptable if a good technology were available for removing Hg from flue gas. Currently, a better use would be as feedstock for a gasification process. In that application, the product including volatilized Hg is controlled and can be prevented from escape to return to the environment. Cattails as gasification feedstock has been studied and shown to provide a rich synthesis gas stream (2).

The choice of biota to accomplish the Hg removal is based on the conditions of rapid growth, adaptability to wet environments, rapid reproduction to produce dense stands, and yield of biomass. Cattail plants (genus *Typha*) are well known, to the point of being a nuisance, as plants that meet these growth criteria. Yield of *Typha* has been extensively studied, and data on yield expectations is in the literature (3). This study was designed to determine the ability of *Typha x glauca*, the predominant cattail in the study areas, a hybrid of *Typha augustifolia* and *Typha latifolia*, to act as a mercury remediation device on and around bodies of water. *Typha* is prolific, growing rapidly from runners (rhizomes) and reportedly producing 6 to 20 metric tons per hectare annually (4). Harvesting equipment is adapted from common agricultural equipment, adaptations depending on season of harvest. In states where winter results in frozen ponds or lakes, common haying equipment used to harvest tall grasses, e.g., rotary scythes, impeller-mower-conditioner, swather, hay chopper, or ensilage cutter, has been evaluated on heavy stands of tall grasses (5). Similar equipment has been adapted with flotation tires or pontoons for use in climates where hard freeze is not part of the winter season.

Methods

Selection of Sample Sites

Sites in North Dakota and Minnesota were considered as sources of Typha samples for this study. Potential for concentrations of Hg and ability to obtain permission for access to the study area were considerations in selecting sites. Discussions with state and federal government personnel as well as private interested parties regarding recommendations for areas suspected of having measurable mercury concentrations in the soil resulted in selection of two U.S. Bureau of Fisheries and Wildlife areas near Detroit Lakes, Minnesota. One area was surrounded by virgin prairie, and the second area was near agricultural cropland and less than a mile from a small municipality. The first visit to the sites to collect samples occurred in June 2004 prior to flowering, and a follow-up visit occurred to the same sites in August 2004. Three locations at each site were sampled on the first visit, and two of the original three at each site were sampled on the second visit. The locations at each site were separated by 75–100 yards and were about 10 yards from the nearest dry land.

Collection and Preparation of Samples

A minimum of three entire intact plants, complete with rhizome, leaf (stem), and flower (on the second visit), were collected at each location at the two sites. On the first visit, soil surrounding the plant, water from the base of the plant, and plants of other species were collected from the same locations for Hg analysis. Each sample was labeled as to location and site. They were spread out in a laboratory to air dry. Following drying for two weeks, the cattails were divided into flower (second visit only), leaf (stem), and rhizome, and all samples were ground and sealed in plastic jars. The soil and second plant specie served as references to available Hg and selectivity to Hg, respectively. Except for the slough water, the samples were analyzed on an air-dry (nominally 10 wt% moisture) basis.

Methods of Analysis for Hg

Acid digestion of the ground samples was used to extract and solubilize the mercury from the plant material. Mixed acid digestion was used to remove and solubilize the mercury from the soil. Cold vapor atomic absorption spectrophotometry (CVAA) was used to measure the Hg concentration.

Quality Assurance/Quality Control

Mercury analyses were performed in the EERC Analytical Research Laboratory. Moisture analyses of air-dried samples were conducted in the EERC Process Chemistry and Development Laboratory.

Quality Objectives

The objective of this project was to determine the mercury content of cattails grown in an environment containing mercury levels above those considered compatible to healthy living, the concern of which is to determine whether mercury remediation is inherent to cattail growth and harvest in this environment. The data collected represented two or more sites on two established wetland to take advantage of established growths of cattails and naturally occurring Hg.

The data generated by this study is a measure of the Hg content of sections of the cattail plant and the soil and water surrounding the plants. The uptake of Hg by the plant was deduced by comparing the Hg content of the samples as they relate to the maturing of the plant.

Measurement/Data Acquisition

A minimum of three entire intact plants complete with rhizome, leaf (stem), and flower (on the second visit) were collected at each location at the two sites. On the first visit, soil surrounding the plant, water from the base of the plant, and plants of other species were collected from the same locations for Hg analysis. Each sample was labeled as to location and site. They were spread out in a laboratory to air dry. Following drying for 2 weeks, the cattails were divided into flower (second visit only), leaf (stem), and rhizome, and all samples were ground and sealed in plastic jars. The soil and second plant species served as references to available Hg and selectivity to Hg, respectively.

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Assessment and Validation

Data obtained in this study are generated by an approved laboratory that has as one of its specialties analysis of samples for Hg content. This laboratory analyzes hundreds of samples for Hg each year following protocol accepted by EPA with instruments sensitive to parts per billion Hg. Samples reporting less than 2 ppb were taken as a zero value. Routine calibration of equipment precedes analyses. The samples analyzed in this study were composite ground samples of each part of the cattail plant and its immediate environment.

Accomplishments/Results

The two study areas contained relatively high Hg content in the soil. The Hg content in the water when analyzed neat was below the detection limits of the CVAA method used. Figure 1 shows the Hg concentration of the water and the soil in the immediate vicinity of the cattail samples. The Hg content of the slough water was below detection limits; therefore, the bar representing that concentration is buried in the baseline of Figure 1.

Early in the growing season, cattails incorporate significant Hg into their leaves (stems) and rhizomes. With the maturing of the plant and development of the flower, additional Hg is incorporated into the flower. Figure 2 shows the Hg concentration in the parts of the cattail plants from the same areas during early and late growing season. Also shown is the Hg content in dead 1-year-old cattail leaf at two different sites. Cattails, although capable of significant Hg uptake in the live plants, and rhizomes, appear to lose the Hg with the death of the plant as shown by the results in Figure 2. Note that the Hg content is significantly less in the old plants as compared with the live plants indicating that long-term storage of Hg by cattails probably is not a useful step in remediation. However, this is not an issue if the plants are to be harvested for carbon sources for gasification or combustion fuel. Transporting the cattails to the site of use results in removal of Hg from the slough area.

Figure 3 shows the Hg concentration in the rhizomes of the cattail plants from the same areas during early and late growing season for two of the three sample sites at each area. The Hg content in the rhizome has decreased in three of the four areas tested both early and late. The Halleckson 2 site, however,

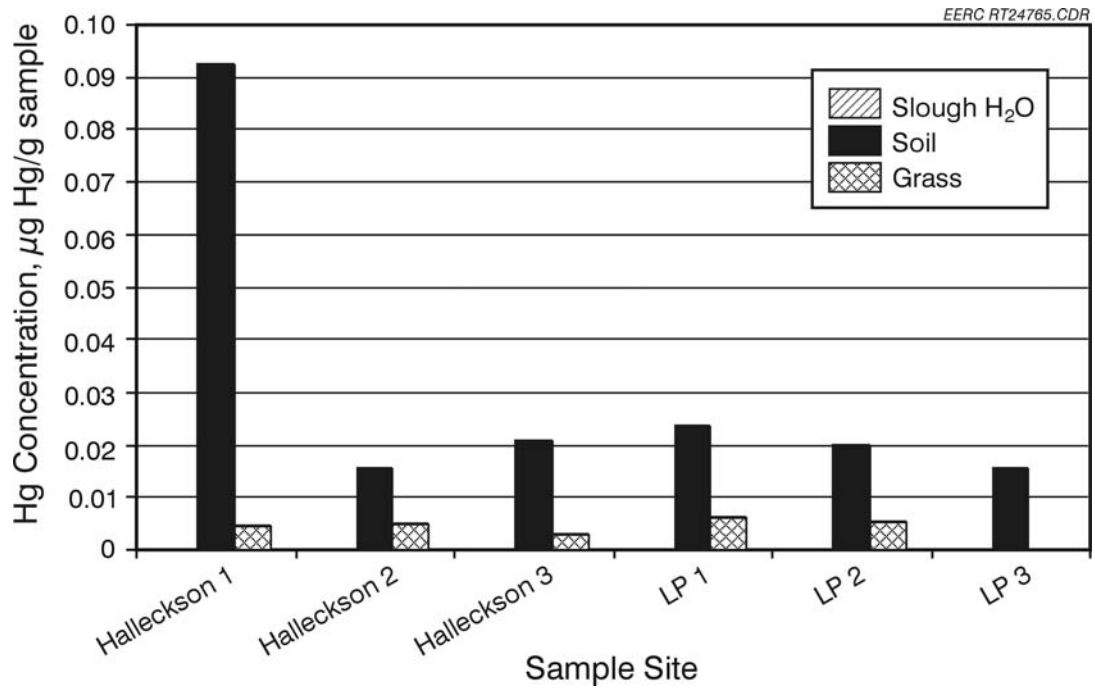


Figure 1. Mercury levels in samples taken at various sites.

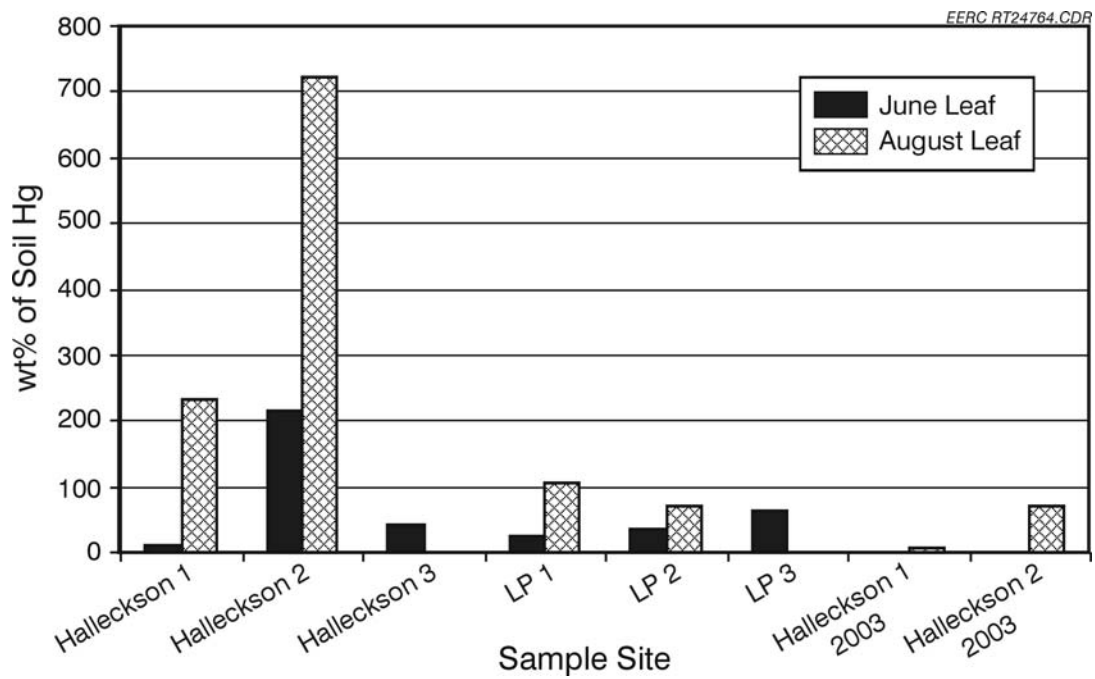


Figure 2. Hg concentration in the parts of the cattail plants from the same areas by growing season.

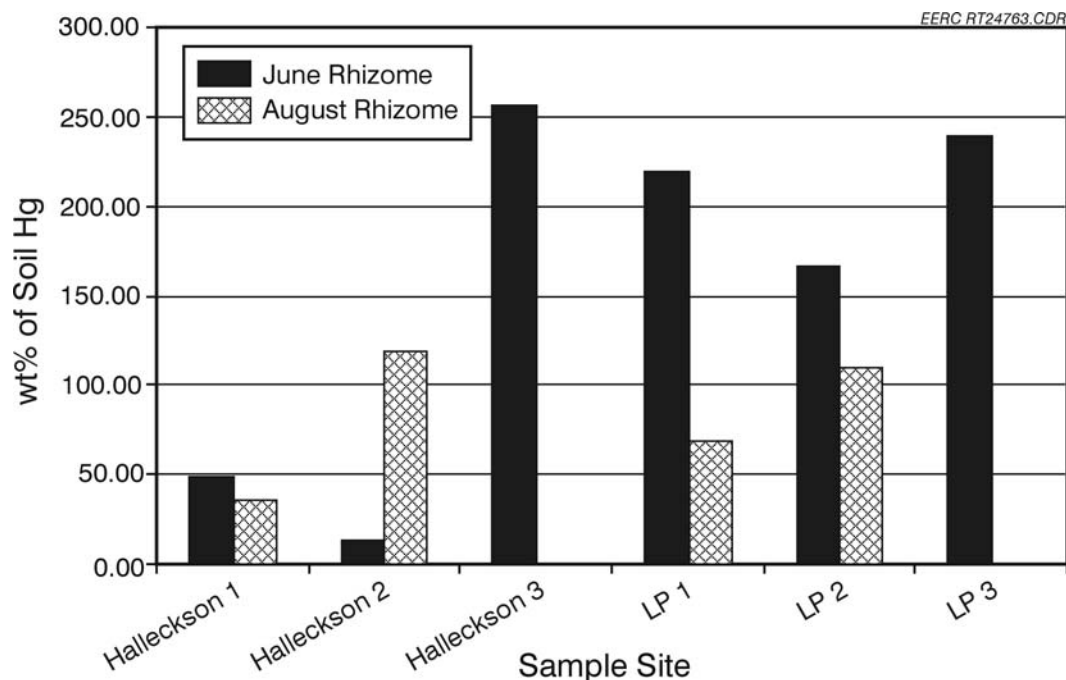


Figure 3. Hg concentration in the rhizomes of the cattail plants by growing season.

which showed the greatest Hg uptake by the plants increased the Hg content in the rhizome during the period of maturation. Promoters of cattails for energy use encourage the use of rhizomes as part of the fuel, again resulting in Hg removal from the slough area.

Cattail flowers, although capable of significant Hg uptake, generally contained a lower Hg concentration than the stem or rhizome at this stage in their growth, as shown by the results in Figure 4. Since the flower was still growing, it is expected that if sampled later, the Hg concentration would be higher.

Although the cattail and its parts are edible, the presence of the Hg prevents them from being used as either animal or human food.

Future Research Needs

Since remediation is essential in areas of heavy-metal contamination in general and of mercury in specific because of the deleterious effects on the food chain, an inexpensive, effective method is important. Cattail growth is easily established in wet soil and produces prolific stands of carbonaceous material which has been shown to be a productive gasification feedstock and an ethanol source, and for which harvesting and handling equipment is available. This study which indicates the uptake and concentration of Hg in the biomass should be expanded to determine the extent of remediation that can be accomplished. Parallel studies involving gasification and ethanol production utilizing the leaf (stem) and rhizome should be carried out to acquire data to support an economic study, evaluating the worth of this concept as a remediation process.

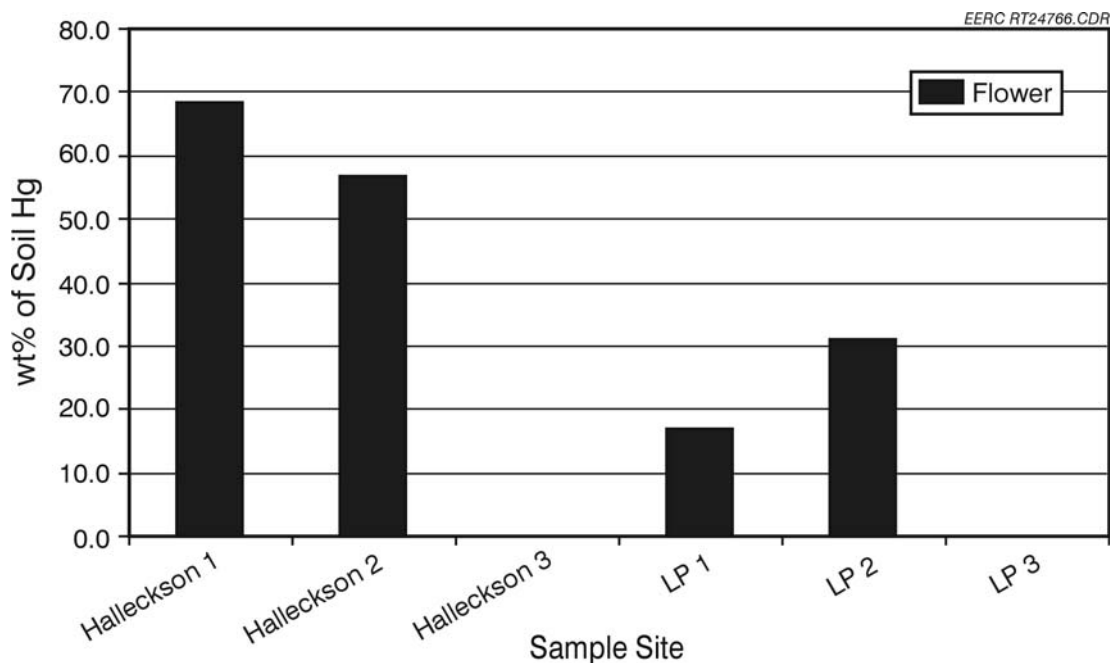


Figure 4. Mercury concentration in the flower of cattail.

Status

All research on this project has been completed. Research done previously investigated the mercury content of wheat, sunflowers, soybeans, corn, hybrid poplar, switchgrass, hybrid willow, sugar beet pulp, flax straw, bromgrass, and rice hulls. Research conducted for this year focused on a determination of mercury in cattails as a function of plant portion and growing season.

Potential Users/Technology Transfer

Alternative fuels have the potential to be significant sources of mercury emissions because of the low energy density associated with them. Although most are expected to be significantly lower than fossil fuels on a mass basis, when compared as a function of Btu, the levels are more comparable. As various biomass sources are considered as supplements to the current fossil fuel supply, the mercury levels must be considered on this basis.

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