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Uptake and Release Kinetics of Sulfolane by Cattail Plants

Tiffany Leo
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UPTAKE AND RELEASE KINETICS OF SULFOLANE BY CATTAIl PLANTS

by

Tiffany Leo

A thesis submitted in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

In

Civil and Environmental Engineering

Approved:

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Dr. William Doucette          Dr. Bruce Bugbee
Major Professor               Committee Member

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Dr. Ryan Dupont              Dr. Byron Burnham
Committee Member             Dean of Graduate Studies

UTAH STATE UNIVERSITY
Logan, Utah
2008
ABSTRACT

Uptake and Release Kinetics of Sulfolane by Cattail Plants

by

Tiffany Leo, Master of Science
Utah State University, 2008

Major Professor: Dr. William Doucette
Department: Civil and Environmental Engineering

Sulfolane (tetrahydrothiophene 1,1-dioxide, C₄H₈O₂S) is a highly water-soluble, non-ionizable, organic compound used along with diisopropanolamine in the Sulfino™ process to remove hydrogen sulfide from natural gas. Sulfolane has been identified in wetland vegetation near a sour gas processing facility in Alberta, Canada, and extensive uptake of sulfolane by cattails has also been demonstrated in a laboratory environment. Consequently, it has been suggested that plants could play an important role in the natural attenuation of sulfolane in contaminated wetlands. This assumes that the sulfolane is metabolized and/or sequestered in the plant and not released back into the environment during winter dieback. To address the potential release issue, individual cattails (Typha latifolia) were grown hydroponically in 500-mL glass containers containing one of three initial sulfolane concentrations (8, 40, or 200 mg/L) for a specified duration (7 to 28 days). Half the cattails were used to quantify uptake as a function of
time and exposure concentration and the other half were used to evaluate the potential release of sulfolane into the hydroponic solution. Non-exposed cattails and non-planted systems containing sulfolane served as controls. The cattails used to evaluate the potential release of sulfolane were frozen directly in their individual containers at the end of the appropriate exposure period. After being frozen for a minimum of 72 hours, the containers were thawed and the amount of sulfolane released was monitored. At the end of the 28-day uptake period, sulfolane leaf tip tissue concentrations as high as 3600, 1050, and 165 mg/kg dry weight were found for the cattails initially exposed to 200, 40, and 8 mg/L sulfolane, respectively. The percentage of sulfolane subsequently released by the cattails after the freeze-thaw treatment declined as a function of the duration exposed. The percentages of sulfolane released measured in the water after 72 hours in addition to the plant tissue extractions were 71%, 54%, 27%, and 12% for the 40 mg/L concentration at 7-, 14-, 21-, and 28-day exposure periods, respectively. Other concentrations showed the same decreasing trend for increasing exposure periods. The declining release as a function of time suggests metabolism and/or sequestration of the sulfolane within the plant. The significant uptake and limited release of sulfolane from mature plants indicate that wetland plants could play an important role in its natural attenuation.

(42 pages)
ACKNOWLEDGMENTS

First, a gracious thank you to Dr. William Doucette for his continued support and guidance throughout this project. I would have never been able to accomplish what I have in the time I had. Also, extended thanks to the other members of my committee for their expertise and insight.

Thank you to Dr. John Headley and all the members of the National Water Research Institute of Saskatoon, Saskatchewan, Canada, for their financial support. The Utah Water Research Laboratory and its staff also deserve the acknowledgment for their expertise and support.

Lastly, thank you to my friends and family members who have encouraged me along the way. I would not have been able to maintain the confidence and patience to complete this. I would especially like to thank my parents, Don and Fong, for teaching and showing me how I could be the best I could be.

Tiffany Leo
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<td></td>
<td>and thawed not adjusted for extraction efficiency</td>
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</table>
BACKGROUND

Sulfolane is used in combination with diisopropanolamine (DIPA) during the Sulfinol™ process to remove sour gases, such as hydrogen sulfide and carbonyl sulfide, from natural gas. Sulfolane is highly water-soluble and has been identified in soil, groundwater, and surface water near sour gas processing plants (e.g., Green et al., 1998; Luther et al., 1998) as the result of accidental releases.

Sulfolane is also widely used as a solvent in the petrochemical, polymer, and photographic chemical industries (Moore et al., 2002). Additional commercial uses include: textile finishing, as a curing agent for epoxy resins, as a selective solvent for liquid-vapor and aromatic hydrocarbon extractions, plasticizers, and in the fractionation of wood tars, tall oil and other fatty acids. Medicinal applications include its use as a solvent for an injectable form of the drug heparin and as an encapsulated material for oral administration (Chevron Phillips Chemical Company LP, 2004).

Sulfolane is highly mobile in the aquatic phase of the environment and its limited sorption to solids is more closely correlated to cation exchange capacity than organic carbon (Luther et al., 1998). Sulfolane has been shown to undergo aerobic biodegradation but may not biodegrade or is slow to degrade in anaerobic environments (e.g., Gieg et al., 1999; Green et al., 1998). Experimental Biological Activated Carbon (BAC) systems have yielded significant aerobic sulfolane degradation (Headley et al., 2002).
Previous Hydroponics Study

Doucette et al. (2005) investigated the uptake of sulfolane by cattails grown hydroponically under anaerobic conditions. Using a total of 12 reactors in which cattails were exposed to either 40 or 200 mg/L of sulfolane, it was found that sulfolane was taken up passively and concentrated in the upper foliar region of the cattails. Aqueous phase concentrations of sulfolane decreased over the study time for the planted reactors but were statistically unchanged in the unplanted reactors.

Project Objectives

The overall objective of this study was to determine the mass distribution of sulfolane in a hydroponic system planted with a cattail plant in an attempt to better understand the ultimate fate of sulfolane in a wetland environment containing cattails. In order to accomplish the overall objective, the first specific project task was to determine the kinetics of uptake and potential release of sulfolane. This was accomplished by measuring sulfolane uptake into the plants after various exposure times (7 days, 14 days, 21 days, and 28 days) and following the sulfolane released from the plants after they were frozen to induce dormancy. As part of this task, sufficient tissue and water samples were collected to determine a sulfolane mass balance for the system. Phytovolatilization of sulfolane was also measured as part of the overall mass distribution determination. The second specific task was to determine the potential impact of
exposure concentration (15, 75, and 200 mg/L) on the plant uptake of sulfolane. The final specific task was use the uptake and release data to predict the impact of plants on the natural attenuation of sulfolane in the contaminated wetland.
LITERATURE REVIEW

In the environment, sulfolane is mobile with its limited sorption more closely correlated to cation exchange capacity than organic carbon (Luther et al., 1998). Sulfolane has been shown to undergo aerobic biodegradation (Headley et al., 2002) but is slow or resistant to degradation in anaerobic environments (e.g., Gieg et al., 1999; Green et al., 1998). A summary of environmentally relevant physical-chemical properties for sulfolane is provided in Table 1.

Sulfolane has also been found in vegetation located in contaminated wetlands (Headley et al., 1999a, b) with the highest plant tissue concentrations generally found in the foliar sections of the plants. However, significant variability among plant tissue replicates and a poor correlation between groundwater and plant tissue concentrations made definitive conclusions regarding the uptake data tenuous (Headley et al., 2002).

Table 1. Physical chemical properties of sulfolane.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value (25°C)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aqueous solubility (mg/L)</td>
<td>1.00E+06</td>
<td>Riddick et al, 1986</td>
</tr>
<tr>
<td>Vapor pressure (Pa)</td>
<td>0.827</td>
<td>Daubert and Danner, 1989</td>
</tr>
<tr>
<td>log Kow</td>
<td>-0.77</td>
<td>Hansch and Hoefman, 1995</td>
</tr>
<tr>
<td>log H (dimensionless)</td>
<td>-3.67</td>
<td>Meylan and Howard, 1991</td>
</tr>
</tbody>
</table>
For most xenobiotic organic compounds, plant uptake is believed to be a passive process related, at least in part, to the lipophilicity of the contaminant. Passive uptake occurs when a chemical is taken up directly with the water used by the plant (McFarlane, 1995). The transpiration stream concentration factor (TSCF) has been extensively used in modeling plant uptake and translocation and is defined as the dimensionless ratio of the concentration in the xylem sap to the bulk concentration in the root-zone solution (Russell and Shorrocks, 1959). Because xylem sap concentrations are difficult to measure directly for intact plants, TSCFs are often determined from measured shoot concentrations that are normalized to the amount of water transpired during exposure to the chemical.

With the possible exception of some hormone-like chemicals (e.g. 2,4-D), there is no evidence of active uptake (TSCF >1) of xenobiotic organic chemicals (McFarlane, 1995). A chemical is said to be excluded (TSCF <1) when uptake is not directly proportional to water uptake (TSCF=1), although the mechanism of uptake is still thought to be a passive process. However, factors such as membrane permeability and xylem sap solubility of the contaminant may limit the extent or kinetics of passive uptake (Hsu et al., 1990). Sorption and rapid metabolism of contaminants within the plant may also reduce xylem concentrations and keep measured TSCF values from reaching 1.

For organic chemicals, several empirical relationships between TSCF and the logarithm of the octanol/water partition coefficient (log Kow) have been
reported (e.g., Briggs et al., 1982; Burken and Schnoor, 1998; Hsu et al., 1990; Sicbaldi et al., 1997). The characteristic bell-shaped curves used to relate TSCF to the log Kow suggest an optimal lipophilicity for uptake and translocation and infer that compounds that are either highly polar (log Kow < 0.5) or are highly lipophilic (log Kow > 4.5) will not be significantly taken up by plants. However, laboratory experiments with 1,4 dioxane (Aitchison et al., 2000) and MTBE (Rubin and Ramaswami, 2001) along with the recent field (Headley et al., 1999a) and laboratory data for sulfolane (Doucette et al., 2005) suggest that the uptake of highly water-soluble organics may be significant and that the bell-shaped curves may not be applicable to highly water soluble, neutral organic compounds.

In a hydroponic uptake study by Doucette et al. (2005), the uptake and translocation of sulfolane and DIPA by cattails were found to be a function of exposure concentration and water transpired. However, while similar in log Kow values, the neutral sulfolane was translocated into the foliar portion of the cattails to a significantly greater extent than the protonated DIPA. Sulfolane concentrations were consistently greatest in the leaf tips with concentrations as high as 33,000 mg/kg dry weight for the 200 mg/L exposure. DIPA leaf concentrations were more uniform but much lower than sulfolane. The highest DIPA concentration observed was 1014 mg/kg dry weight for the 100 mg/L exposure. The average leaf to root tissue concentration ratio for sulfolane was 53 (152 for leaf tips), while for DIPA the ratio was 0.6. Normalizing the leaf
concentration in each system to the amount of water transpired during exposure and dividing it by the average exposure concentration yielded approximate transpiration stream concentration factors (TSCF) that ranged from 0.1 (entire leaf) to 0.9 (leaf tip) for sulfolane and 0.01 to 0.02 for DIPA. Overall, the laboratory uptake trends matched those observed in the limited field sampling and suggest that the uptake of non-ionizable, highly water-soluble organics such as sulfolane may not be well-predicted using existing relationships between TSCF and log Kow. In addition, the relatively high concentrations observed in the foliar tissue suggest that wetland plants could play an important role in the natural attenuation of sulfolane, provided the sulfolane is not released by the plants during winter dormancy. However, the uptake kinetics and potential release of sulfolane during plant dormancy were not adequately evaluated. The potential impact of plant age and sulfolane concentration were also not evaluated.
UPTAKE AND RELEASE OF SULFOLANE BY CATTAIL PLANTS

Sulfolane is used in combination with diisopropanolamine (DIPA) during the Sulfinol™ process to remove sour gases, such as hydrogen sulfide and carbonyl sulfide, from natural gas. Sulfolane is highly water-soluble and has been identified in soil, groundwater, and surface water near sour gas processing plants (e.g., Green et al., 1998; Luther et al., 1998) as the result of accidental releases.

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In order to better interpret the limited field data and to improve the understanding of the uptake of water-soluble organics by plants, a series of hydroponic studies was conducted to determine the kinetics of sulfolane uptake.
and release as a function of exposure concentration, exposure time, and water transpired. The overall mass balance of sulfolane was determined in order to indirectly evaluate potential loss mechanisms such as biodegradation within the plant.

Common cattails (Typha latifolia) were selected as the test wetland plant species because of their ubiquitous nature in North American wetlands and because sulfolane had been previously found in cattails near a sour gas facility. The cattails were grown in a hydroponic environment to minimize the exposure variability to the roots and to eliminate the potential influence of soil desorption kinetics in observed results.
**Previous Study**

The materials and methods used in a previous sulfolane uptake investigation (Guerrero, 2004) were adapted for use in this study. In the previous study, air was bubbled into all the reactors, therefore not creating an anaerobic environment typical of the wetland area. There were also 7-100 mg/L doses of sulfolane made over the course of the experiment. This method created difficulty in fully determining the rate of which sulfolane was taken up. Having a single dose of sulfolane introduced will provide the rate at which it is taken up by the plant and can be accounted for in a mass balance equation.
MATERIALS AND METHODS

Cattails, obtained as bare-root plants from Aquatic and Wetland Company (Fort Lupton, CO), were grown hydroponically in a greenhouse for several days, selected for uniformity, and then transplanted into aluminum foil wrapped (to exclude light) glass containers (500 mL) containing nutrient solution (Boyd and Hess, 1970). The cattails were then allowed to grow in their new containers for 3 days prior to the initial exposure to sulfolane. Each glass container included one plant held in place with a support constructed of both open-cell and closed-cell foam and an aeration tube to deliver compressed air or nitrogen to the root zone. One day prior to the initial dosing, the aeration gas for the containers was switched from atmospheric air to nitrogen in order to simulate the 1 to 3 mg/L dissolved oxygen typically observed at the contaminated wetland field site.
EXPERIMENTAL DESIGN

The experimental design consisted of two groups of planted reactors (uptake and release), three initial exposure concentrations (8, 40, and 200 mg/L sulfolane) and four exposure durations (7, 14, 21 and 28 days) all run in triplicate for a total of 72. In addition, eight non-dosed planted reactors, one for each group and exposure duration, served as controls for monitoring potential impacts of sulfolane exposure to plant transpiration. An additional set of 36 non-planted, dosed reactors, run separately after the planted reactors to minimize the amount of greenhouse space occupied, were used to evaluate potential loses of sulfolane not associated with the presence of plants. Non-control plants were dosed initially to yield the nominal concentrations (Fig. 1). Nutrient solution was added to each reactor as needed to maintain the initial volume. The amount of nutrient solution added was used to determine the volume of water each plant transpired (minus that lost from sampling and evaporation from non-planted controls). Triplicate reactors for each group (uptake and release) and exposure concentration were removed on days 7, 14, 21, and 28. The plants and solutions from the uptake group were immediately analyzed as described below, while the reactors for the release group were placed immediately in a freezer at -15 °C.
Sampling Protocol

Water samples (10mL) were collected from each container in duplicate every 7 days using a 30 mL syringe. Samples were placed in 40 mL glass vials at 4°C until extraction and analysis (<14 days). Plants were divided into three sections, roots, upper leaves and lower leaves. Samples were collected from each section and the fresh weight of each sample, sample section and the whole plant was recorded for each sampling event. The tissue samples were stored in glass jars in a 4°C refrigerator until they were analyzed (<14 days).

Sulfolane Extraction and Analysis

Aqueous samples (10 mL) were extracted three times with 2-mL aliquots of methylene chloride (Fisher Chemical) for 15 minutes using an Eberbach Model 6010 reciprocal shaker (Ann Arbor, MI) directly in the glass vials that the samples were collected in. Solvent and water were separated by centrifugation at 2500 rpm for 25 minutes. An aliquot of the combined methylene chloride extract was analyzed for sulfolane using a Shimadzu Model GC-14A equipped with a DB-5 (30 M x 0.45 mm, 0.25 µm film thickness) column (J&W Scientific, Folsom, CA), flame ionization detector, AOC-1400 autosampler, and Agilent GC Chemstation Rev A.08.03 [847] data acquisition and analysis software. Sulfolane eluted at 3.8 min using the following temperature program: 80°C (2 min hold) to 160 °C at 10 °C/min, then 40 °C/min to 220 °C (2 min hold). Nitrogen (10 mL/min) was used as the carrier gas.
Fig. 1. Experimental design used for the 80-planted reactors.

External standards were prepared in methylene chloride (minimum of five different concentrations) to quantify the amount of sulfolane in the extracts. Spike recoveries for the aqueous extracts ranged from 60-70% and duplicates varied within 5-10%.

Plant tissue samples were cut into small pieces with a stainless steel scissors then ground into a powder-like consistency with a hand-powered food processor. Sub-samples (1 g fresh weight) of the homogenized tissue were placed in a 30-mL Teflon centrifuge tube and agitated with 20 mL of distilled water for 1 hour at 180 oscillation/min using an Eberbach Model 6010 reciprocal shaker (Ann Arbor, MI). The tissue was separated from the water by centrifugation and the water was extracted and analyzed for sulfolane as previously described for the aqueous samples. Recoveries for the plant tissue spikes ranged from 50-60% and duplicate samples varied between 5-10%.
The water content of the leaves and roots was determined gravimetrically by weighing samples before and after drying. The percent dry weight of cattail roots and leaves were 15% and 22%, respectively.
RESULTS AND DISCUSSION

Cattail Water Use

Water transpired was determined from the volume of hydroponic solution needed to replenish the planted reactors each day minus that required by the unplanted reactors. The average amount of water transpired by the cattails during the course of the study is summarized in Table 2. Evaporation from the reactors was small relative to the planted reactors as illustrated by the data for the unplanted bioreactors (Table 2). The amount of water transpired was used to assess the relative health of each plant and to calculate approximate TSCF values for sulfolane. With increased exposure time and concentration, the health of the plants began to diminish including drying leaf tips. Less water was transpired through the plants with the declining health of the plants.

Aqueous Phase Sulfolane Concentrations

Sulfolane was readily removed from the aqueous phase of the planted reactors as shown in Fig. 2 that compares the decrease in sulfolane concentration in the planted and unplanted reactors as a function of time. Each point in Fig. 2 represents the average sulfolane water concentration for the triplicate uptake and release reactors.

For the highest initial exposure concentration, it took 28 days to reduce the sulfolane aqueous concentration to levels below the method detection limit (while it only took 14 days for the lowest exposure. For the 40 mg/L
Table 2. Average transpiration of water for 28-day exposure.

<table>
<thead>
<tr>
<th>Concentration (mg/L)</th>
<th>Volume of water transpired (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unplanted, dosed at 8, 40, and 200</td>
<td>333 +/-38</td>
</tr>
<tr>
<td>Undosed, planted</td>
<td>4212 +/-258</td>
</tr>
<tr>
<td>8</td>
<td>3600 +/-773</td>
</tr>
<tr>
<td>40</td>
<td>3944 +/-980</td>
</tr>
<tr>
<td>200</td>
<td>2838 +/-1409</td>
</tr>
</tbody>
</table>

Fig. 2. Mass of sulfolane in water in mg of sulfolane for 8, 40, and 200 mg/L concentrations at 7 days (a), 14 days (b), 21 days (c), and 28 days (d). The numbers on the X-axis represent the concentration with “P” representing planted and “U” representing unplanted reactors.

Concentration, there may have been contamination in the sample to generate the peak of sulfolane for the 14-day sampling. In other sample periods, there was not a peak for the 14-day sampling.
Fig. 2. Continued
Plant Tissue Sulfolane Concentrations

As shown in Table 3 for the 40 mg/L exposure, the concentration of sulfolane in the upper leaves attained levels in excess of 1000 mg/kg within 7 days. At 14 days, the leaf concentrations reached their maximum levels then declined. The decline was most likely due to growth dilution since only a single dose of sulfolane was added each reactor. The sulfolane concentrations from the triplicate plants were averaged to produce the data in Table 3. This same trend was observed for the other exposure concentrations.
Release of Sulfolane from Cattails

To evaluate the potential release of sulfolane from the cattails after winter die back, half of the plants from each exposure time and concentration were frozen directly in the container they were grown in. The plants were then thawed after 72 hours and water samples were collected to determine if sulfolane was released. The results of this portion of the study are shown in Fig. 3. It should be noted that these plants went immediately from a growth stage to freezing. The plants were green and actively growing when frozen. Several plants, mostly at the higher concentrations, also showed leaf tips that were brown and dry potentially indicating a toxic response to the sulfolane exposure. There were no incremental temperature changes.

Release of Sulfolane from Frozen/Thawed Plants

After freezing for 72 hours in their original containers, the plants used to evaluate the potential release of sulfolane during winter dormancy, were thawed and water samples were collected and analyzed over time to evaluate the release of sulfolane from the dead tissue (Fig. 3).

Table 3. Averaged tissue concentrations and distributions for 8, 40 and 200 mg/L initial sulfolane concentration for 7, 14, 21, and 28 day.

<table>
<thead>
<tr>
<th>Days/Tissue</th>
<th>Roots</th>
<th>Lower Leaf</th>
<th>Upper Leaf</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>exposure</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 days</td>
<td>0</td>
<td>0</td>
<td>117.239 +/-121.83</td>
</tr>
<tr>
<td>14 days</td>
<td>0</td>
<td>0</td>
<td>165.011 +/-133.55</td>
</tr>
<tr>
<td>21 days</td>
<td>0</td>
<td>0</td>
<td>111.034 +/-33.53</td>
</tr>
<tr>
<td>28 days</td>
<td>0</td>
<td>0</td>
<td>14.79 +/-13.816</td>
</tr>
<tr>
<td></td>
<td>40 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 days</td>
<td>15.149 +/-2.383</td>
<td>7.702 +/-12.590</td>
<td>1003.50 +/-358.25</td>
</tr>
<tr>
<td>14 days</td>
<td>20.765 +/-35.966</td>
<td>0.396 +/-0.561</td>
<td>1052.60 +/-102.53</td>
</tr>
<tr>
<td>21 days</td>
<td>1.733 +/-3.071</td>
<td>0</td>
<td>719.491 +/-81.70</td>
</tr>
<tr>
<td>28 days</td>
<td>0</td>
<td>0</td>
<td>139.219 +/-93.729</td>
</tr>
<tr>
<td></td>
<td>200 mg/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 days</td>
<td>246.792 +/-35.164</td>
<td>189.609 +/-75.213</td>
<td>3615.0 +/-2327.35</td>
</tr>
<tr>
<td>14 days</td>
<td>177.136 +/-20.430</td>
<td>144.489 +/-62.589</td>
<td>1337.207 +/-153.6</td>
</tr>
<tr>
<td>21 days</td>
<td>58.318 +/-32.598</td>
<td>51.721 +/-24.907</td>
<td>1516.73 +/-137.81</td>
</tr>
<tr>
<td>28 days</td>
<td>0</td>
<td>6.465 +/-11.198</td>
<td>1044.797 +/-32.16</td>
</tr>
</tbody>
</table>

Fig. 3. The percent recovery of sulfolane in the water and tissue for plants that were frozen and thawed.
**Sulfolane Recoveries**

The mass recovery of sulfolane was determined for each container by determining the difference between the mass of sulfolane introduced initially and the mass recovered at the end of the study in the plants (concentration in tissues times the weight of tissues) and water (concentration in water times the volume of water) substracting any removed during intermediate sampling events (Figs. 4 and 5).

Fig. 4 shows the distribution of sulfolane recovery for plants that were exposed for 30 days during the uptake phase of the study, and then immediately harvested for sulfolane concentration. As Fig. 4 shows, the longer the uptake time, the less sulfolane that was released from the tissue. There is an overall decrease in the amount of sulfolane that remains in the plants and water the greater the exposure time.

Unplanted dosed reactors were also evaluated. The unplanted dosed reactors were used to determine if the sulfolane concentration decreased outside of the normal dilution from sampling. There was no significant decrease in sulfolane concentration over time. If there had been significant losses, other processes would need to be tested to determine where the sulfolane was going and would also rule out the hypothesis that cattail plants were an effective resource for metabolizing sulfolane.

The decreasing percentage of recovery shows evidence that sulfolane is perhaps metabolized within the plant. The percentage of recovery was based on
the combination of sulfolane in the water and tissue. Therefore, with all things considered, including the concentrations being normalized to the plant size, it results that with increased exposure time, the amount of sulfolane recovered decreases. It can be seen in the figure that there was a consistent decrease in percent recovery with each passing week with the unplanted reactor having a consistent concentration adjusted for sampling dilution.

Over the 28-day time period, there was a 50% correction made for sulfolane in all the concentrations for the dilution from sampling and refilling of the reactors. The percent distributions for both the plants that were analyzed immediately after harvesting is shown in Fig. 4, while Fig. 5 shows the releasing of sulfolane from the plant tissue as it began to thaw from its frozen state. As soon as the reactors began to thaw, water samples were taken to determine if sulfolane was released from the tissue. After 72 hours, the concentration of sulfolane in the water became constant.

To possibly account for the loss of sulfolane over time, phytovolatization samples were collected using the method described by Doucette et al. (2005). The results from those samples did not show any detectable amounts of sulfolane. None of the recoveries were adjusted for extraction efficiency.
Fig. 4. The percentage of sulfolane recovered for 8, 40, and 200 mg/L concentrations and over 7, 14, 21, and 28 days for harvested plants not adjusted for extraction efficiency. The % recovery is based on mass. Percent recovery is the combined amount of sulfolane in water and tissue.
Fig. 5. The mass of sulfolane recovered for 8, 40, and 200 mg/L concentrations and over 7 days (a), 14 days (b), 21 days (c), and 28 days (d) for plants frozen and thawed not adjusted for extraction efficiency. The recovery is based on mass in the water.
Fig. 5 Continued
ENGINEERING SIGNIFICANCE

Environmental engineering entails the analysis and design of systems that will ensure an environment whether it is air, water, soil, habitat, etc. is restored or maintained to the best quality possible. As this study was expedited, it provides vital information that will create a better environment through the use of natural processes. This phytoremediation experiment has been designed to be a continuing process that will restore and maintain a contaminated area to the best quality possible. If this remediation technique proves to be successful in the field, it may be used for the cleanup of other compounds with properties similar to sulfolane.

The contamination of surface and ground water with sulfolane may create an environment where the wildlife may incur harm through ingestion of the plants or immersion in the water. Therefore, the cattail plants would need to be maintained so that the sulfolane is not re-released into the water and the concentrated sulfolane in the upper leaves are removed. Also, since sulfolane is a highly water-soluble compound, it is likely to move into other areas aside from the contaminated areas.

Harvesting could occur in as little as 21 days where the plants are stable enough to sustain harvesting. However, if metabolic processes are taking place and the growing season coincides with a longer time frame, harvesting may only need to take place once. Further studies should be conducted to determine the efficiency of uptake with multiple harvests throughout a season.
CONCLUSIONS

The objectives of this study were to show how readily sulfolane is taken up into cattail plants for exposure concentrations of 8, 40, and 200 mg/L and exposure times of 7, 14, 21, and 28 days, determine if and where the sulfolane is contained, determine whether or not the sulfolane is released after senescence and how readily, generate a mass balance, and determine if other processes such as phytovolatization or metabolism occur.

Cattail plants are an effective mean for removing sulfolane from a contaminated wetland area. Sulfolane is passively taken up by the plants and over an extended amount of time, approximately 28 days, a sulfolane concentration of 200 mg/L would become undetectable in the water.

The sulfolane is contained in the upper portion of the leaves. However, since the results of the release study show that a portion of the sulfolane contained in the plant can be released back into the water after senescence, harvesting should occur before the winter season approaches.

The mass balance also shows that there is a great portion of sulfolane that is not accounted for, especially after 28 days. This suggests that other processes are happening within the plant. Harvesting could occur in as little as 21 days where the plants are stable enough to sustain harvesting. However, if metabolic processes are taking place and the growing season coincides with a longer time frame, harvesting may only need to take place once. Further studies
should be conducted to determine the efficiency of uptake with multiple harvests throughout a season.

Phytovolatization samples show that sulfolane does not volatilize. Therefore, metabolism is another process that may be taking place. Further studies need to be conducted to determine if metabolism occurs and what compounds are being produced.
REFERENCES


