Creosote movement from treated wood immersed in fresh water

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Abstract

Creosote has a long history of successful use as a wood preservative, but polycyclic aromatic hydrocarbons in this preservative have raised environmental concerns, particularly when creosote-treated wood is used in aquatic environments. A number of models have been developed to predict the risk of creosote use in aquatic environments, but one limitation of these models is a lack of data on the initial rates of creosote migration from treated wood. In this study, the effect of flow rates on creosote migration from freshly treated wood immersed in fresh water were examined. Seven of 16 polyaromatic hydrocarbons listed as hazardous pollutants were detectable with the analytical protocol developed. Creosote component levels declined from values in the tens of µg/cm² day to undetectable levels within 7 days, with the exception of phenanthrene, indicating that creosote migration decreased sharply after initial exposure. These data provide the experimental foundation for the development of mathematical models to predict emissions from creosote-treated wood into the aquatic environment.

Creosote has been widely used to protect railroad ties, utility poles, bridge timbers, and piling against fungal, insect, and marine borer attack since its introduction in the 1830s. Creosote is a distillate of coal tar, a byproduct of the carbonization of coal. Creosote is thus a complex mixture of hydrocarbon compounds, including nearly 80 percent by weight of polycyclic aromatic hydrocarbons (PAHs) (Environment Canada 1992). PAHs are nonionic, similarly structured organic compounds characterized by low water solubilities and high partition coefficients with organic matter (Swartz et al. 1995, Vilholth 1999).

Public concern has been raised because some PAHs contained in creosote have shown acute and chronic toxicity to marine animals (Ozretich et al. 2000, Brooks 2000). However, no increased cancer risk was found for workers handling and using creosote on a daily basis (Alscher and Lohnert 1985). Although creosote has relatively low toxicity, continuous release of PAHs into the environment might potentially create problems. While hydrocarbon pollution associated with transportation has been broadly investigated, there are relatively few data on the migration of PAHs into surrounding environments from creosote-treated wood exposed over or adjacent to surface water. Brooks (1996) pointed out that the release of creosote components from treated wood created the potential for biological impacts. He also detected elevated PAH levels in the sediments 1.8 to 3.0 m downstream from creosote-treated bridges. Brooks (1996) reported PAH contamination and significant biological impacts near newly installed piling. Swartz et al. (1995) developed a model to predict PAH toxicity in sediments, and Ozretich et al. (2000) tested PAH models at creosote-contaminated sites. Mathematical models associated with PAH releases from immersed creosote-treated wood were also developed to assess the environmental risks associated with use of these materials (Brooks 1996). Water flow rate, however, could not be included in the models, despite its potential importance, because of a lack of data. The absence of such data makes it difficult to build accurate predictive models for assessing environmental impacts of PAH contamination.

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The objective of this study was to establish the leaching behavior of creosote-treated wood submerged in flowing fresh water by monitoring the PAH concentrations over time under different flow rates. These data could be used to improve existing predictive models evaluating the risk of creosote use in aquatic environments.

Materials and methods

Douglas-fir (Pseudotsuga menziesii (Mirb.) Franco) lumber (50 mm by 150 mm by 2.4 m long) was treated with creosote (American Wood-Preservers’ Association [AWPA] standards P1/P13 [AWPA 2002]) in a commercial treatment facility located in Eugene, Oregon. The treatment was in accordance with the Best Management Practices specified by the Western Wood Preservers Institute (WWPI 1996). A modified empty cell process was used to achieve a target retention of 192 kg/m$^3$ in the 15-mm-deep assay zone as specified in AWPA Standard C16 for highway timbers and lumber (AWPA 2002). Eight leaching specimens (300 mm long) free of large knot sections were cut from each board and the remaining 50 mm of the board was discarded. The samples were end-sealed using marine-grade epoxy resin to minimize end effects and then randomly allocated to be exposed in one of three leaching tanks in a creosote leaching system (Fig. 1).

Municipal drinking water was passed through a carbon filter to remove chlorine and contaminants and stored in a 400-L storage tank. Then the filtered water was pumped at a constant pressure into the three aluminum sample boxes in the leaching system that were designed to submerge an entire wood sample (Fig. 2). A check valve was used to ensure complete immersion during the leaching process. Three water flow rates (0.47, 1.2, and 3.3 cm/sec) were used at a constant temperature (12° to 13°C). Water samples (1 L) were collected from each box immediately after the treated wood was installed and water began to flow through the system. Additional samples were collected 0.042, 0.125, 0.25, 0.5, 1, 2, 3, 4, 5, 6, 7, 11, and 14 days after immersion. Each water flow rate was replicated on three creosote-treated wood samples from different boards.

Organic solvent extraction and gas chromatographic mass spectrometry (GC/MS) analysis were performed on each water sample using a modification of U.S. Environmental Protection Agency (EPA) Methods 610 (EPA 1982) and 8100 (EPA 1986). The water sample was transferred from the sample bottle to a 1000 mL separatory funnel. Thirty mL of methylene chloride were added to the sample bottle, which was sealed and shaken for 30 seconds to rinse the inner surface. The solvent was transferred to the separatory funnel, and then PAHs were extracted from the water by shaking the funnel for 2 minutes with periodic venting to release excess pressure. The organic
layer (methylene chloride) was separated from the water phase, and then the methylene chloride extract was collected in a 100 mL round bottom flask. The extraction procedure was repeated two more times, and extracts were combined in the flask and concentrated to 1 mL using a rotary evaporator (Yamato RE-51) equipped with a hot water bath (62°C).

PAH concentrations in the extracts were determined by injecting 1 µL of extract into a Shimadzu high-resolution gas chromatograph with a low-resolution mass spectrometer detector. Separation was achieved using a XTI-5 capillary column (Restek) (0.25 mm ID by 30 m long) composed of fused silica with a 0.25-µm-thick film of 95 percent dimethyl, 6 diphenyl polysilarylene. The carrier gas was Grade 5 helium at flow and split rates of 0.6 and 5 mL/minute, respectively. Injector and detector temperatures were 265°C and 280°C, respectively. Column temperature was set at 35°C for 2 minutes, then ramped at 10°C/minute to 265°C, and held for 10 minutes. Levels of all 16 priority pollutant PAHs including naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzoanthracene, chrysene, benzo[b]fluoranthene, benzo[e]fluoranthene, benzo[a]pyrene, indenopyrene, benzo[e] perylene, and dibenzo[a,h]anthracene were quantified by comparison with known standards (EPA 1982). The data for the three replicates were averaged and expressed as µg of each compound leached per cm² of exposed wood surface area per day (µg/cm² day).

The limit of detection (LOD) for each PAH was estimated (Table 1) as defined according to Part 136, Appendix B, procedure (b) (EPA 1984), as three times the standard deviation of replicate analyses of the analyte.

### Results and discussion

Seven of 16 target PAHs were detected in the leachate water, representing seven of the eight low molecular weight (i.e., \( \approx 203 \) g/mol) PAHs. Although acenaphthylene is also a lower molecular weight PAH with a low boiling point, it was not detected at any flow rate.

Higher molecular weight PAHs, including benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, indenopyrene, benzo[e] perylene, and dibenzo[a,h]anthracene were not detected at any point in the test. The high molecular weight compounds have not only higher boiling points, but also higher partition coefficients in organic carbon, producing lower water solubilities (Swartz et al. 1995, Vilholth 1999). For example, pyrene is 14 times and 73 times more soluble in water than benzo[a]anthracene or chrysene, respectively (May 1980). Municipal water contains little organic matter, and the series of carbon filters at the inlet to the storage tank were intended to remove contaminants that might inadvertently enter the system. Conversely, dissolved organic matter in sediment and interstitial water in the sediment adjacent to treated wood would tend to adsorb the heavier PAHs (Brooks 2000; Ozretich et al. 2000, 2002). The absence of these PAHs in the test water does not appear to be due to any loss in the leaching tanks or collection system. PAH volatilization was also considered as a reason for lack of detection, but the low temperatures in the system (12° to 13°C) and the immersion conditions argue against this explanation. As a result, the absence of detectable high molecular weight PAHs appears to be due to a failure of these compounds to enter the water column at levels above our detection limits.

![Table 1](image)

<table>
<thead>
<tr>
<th>PAHs</th>
<th>LOD (ng/mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>0.53</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.56</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>0.52</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.57</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.60</td>
</tr>
<tr>
<td>Anthracene</td>
<td>0.38</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.28</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.34</td>
</tr>
<tr>
<td>Benzoanthracene</td>
<td>0.31</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.60</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>0.87</td>
</tr>
<tr>
<td>Benzo[e]fluoranthene</td>
<td>0.50</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>0.74</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>na</td>
</tr>
<tr>
<td>Benzo[e] perylene</td>
<td>na</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>na</td>
</tr>
</tbody>
</table>

*Not quantified, but detectable at ≥ 2 ng/mL.*

The concentrations of all detected PAHs increased immediately after immersion, then decreased sharply, and reached a steady state after one week (Fig. 3). High concentrations of naphthalene, phenanthrene, and anthracene were detected immediately after immersion (Fig. 3). These components are also present at higher concentrations in liquid creosote (Xiao et al. 2000, Ingram et al. 1982, Lebow and Morrell 1988). Phenanthrene was the only component measured whose leaching rates did not decline to LOD after about one week. The phenanthrene leaching rates remained in the range of 0.2 to 0.5 µg/cm² day for the duration of the test (Fig. 3). Phenanthrene is one of the more common PAHs, composing up to 30 percent of PAHs reported at creosote-contaminated sites. Anthracene, fluoranthene, and pyrene are also commonly found at levels exceeding 5 percent of total PAH concentrations at these sites (Ozretich et al. 2000).

As a rough estimation, the AWPA assay zone for creosote-treated lumber, 15 mm, was uniformly treated at 192 kg/m². The samples used in this study then contained approximately 304 g of creosote in the assay zone. Phenanthrene comprises approximately 11 percent of this total, or 33 g (Xiao et al. 2000). The observed steady state leaching rate of approximately 0.5 µg/cm² day of phenanthrene would result in a loss of 0.23 g from the sample per year, or 0.08 percent of the total amount present in the creosote. As creosote depletes from the wood surface over time, it would be expected that the leaching rate would further decrease. Furthermore, the relative mobility of creosote beneath the surface may be limited. As a result, it may have less potential to leach from the treated wood. Thus, the estimate of 0.08 percent loss per year is probably a worst case scenario since it assumes that all of the creosote in the assay zone is available for migration.

Naphthalene concentrations were initially at relatively high values, and then decreased dramatically. Naphthalene is a relatively volatile compound that is sometimes difficult to retain in
leachates. PAHs in aquatic environments experience evaporation, dispersion into the water column, and incorporation into bottom sediments or bio-concentration where they can be removed by oxidation and biodegradation. Turnover time for naphthalene in most environments is very short (days to weeks) in comparison with the long times required for turnover of the heavier PAHs (Brooks 2000). The relatively sharp drop in naphthalene levels appears to reflect the high volatility and short residence time in the environment.

Concentrations of the seven PAHs detected tended to increase with increasing flow rate (Fig. 3). The increases of PAH concentrations with flow rate were much more distinctive for heavier PAHs such as fluoranthene and pyrene. This may be due to the presence of turbulence in the sample boxes. Turbulence could both increase the diffusion of the PAHs by reducing the extent of the stationary laminar flow region and, if the turbulence is severe enough, could even lift small droplets of creosote from the surface. The higher surface area of the dislodged droplets would be expected to be conducive to greater diffusion and therefore higher water concentrations of the creosote components. The effect of turbulence on the leaching rates of creosote components is poorly understood and additional studies would be required for a thorough understanding of this phenomenon.

This study measured only the components which dissolved in water. Others (K. Brooks, private communication 2003) have suggested that the primary loss of creosote is not through solubilization, but through “bleeding,” i.e., the physical movement of the creosote out of the wood, or from abrasion, where small droplets of creosote detach from the wood surface and enter the environment as discrete particles. Thus the total picture of creosote leaching remains incompletely understood and more research will be required before a comprehensive evaluation of creosote’s impact on the environment is possible.

Conclusions

PAH migration from creosote-treated wood into a flowing water column decreased sharply from initial high values and reached a steady state within one week. While further studies will be necessary to explain leaching behavior at different water flow rates, temperatures, and amounts of dissolved organic matter, the results suggest that PAH concentrations from creosote-treated wood appear to decline rapidly to ng/mL levels after initial exposure to flowing water. The relative smoothness of the data trends should allow for the development of predictive models. Additional loss mechanisms (i.e., particulate loss) are possible, but not accounted for in this study.

**Literature cited**


