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Leaching from Stone Crab Traps Dipped in Fungitrol: Diesel Fuel Preservative

J. S. Barre, E. S. Van Vleet

Department of Marine Science, University of South Florida, 140 Seventh Avenue South, St. Petersburg, Florida 33701, USA

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The stone crab fishery is one of the most important commercial fishing industries in Florida (Adams and Prochaska, 1992). Since stone crabs are generally caught and harvested by trapping, trap construction and longevity are crucial elements to the success of the industry. For years, stone crab fishermen have been fishing with wooden traps. Over time, traps become infested with wood-boring animals such as shipworms (*Bankia* and *Teredo*) and isopods (*Sphaeroma* and *Limnoria*) thus leading to the destruction of the trap. Various wood treatments have been applied to keep wood-borers from infesting the traps (Dealteris et al., 1988) in an attempt to increase their longevity and reduce fishing costs.

For the past several years, stone crab fishermen have been using a copper-based substance called Fungitrol[R] with diesel fuel as a carrier to inhibit wood-borers. Fungitrol (Huls America) is a Cu-naphthenate fungicide containing 8% Cu and is normally used to protect fibrous substrates. Initially, most fishermen dip the wood for their traps in a Fungitrol:diesel fuel mixture (1:10) for anywhere from a few minutes up to 10 days. The traps are then constructed from the treated wood and are allowed to sit outside for up to 5 months before using them for crabbing. In subsequent seasons, the traps are dipped for only 1-3 minutes, then are allowed to sit outside until the opening of the season.

The concern with using diesel fuel as a carrier in the dipping process is that this refined petroleum product has been found to be more toxic to marine animals than many crude oils (Anderson et al., 1974). Hydrocarbons found in other petroleum products (including fuel oils and crude oils) have been shown to have both lethal and sublethal effects on crustaceans (Anderson et al., 1974; Edwards, 1978; Laughlin et al., 1978).

Various studies have been conducted on wood preservatives and the changes that occur in treated wood with prolonged exposure to water (Miller, 1977; Ingram et al., 1982; Lebow and Morrell, 1988). This study investigates many of the same characteristics of a leachate from marine woods as do the others; however, this particular leachate, diesel fuel, has not been studied until now.

Correspondence to: E. S. Van Vleet

MATERIALS AND METHODS

All wood used for the following study was either pressure-treated pine or cypress slats identical to the wood used for trap construction. Initially, the wood was analyzed for background levels of hydrocarbons or other potentially interfering lipids in order to correct the absorption and loss data. In addition, the preservative mixture (1:10 Fungitrol:diesel fuel) was characterized, as were diesel fuels from three petroleum companies (Amoco, Texaco, and Mobil) to determine chemical similarities and differences to the diesel fuel used to prepare the dip. Procedural details are described below.

Once the initial characterization of undipped woods and dip components was completed, effects of dipping the wood were determined as follows. Slats of pine and cypress were dipped in the 1:10 Fungitrol:diesel fuel mixture for periods of both 10 days and 3 minutes. Gravimetric analysis of wood before and after dipping and gas chromatography (GC) (described below) were used to determine how much dip the different types of wood absorbed during the dipping process. After dipping, the slats were drip-dried and were then allowed to weather (i.e. were exposed to natural elements) both in the open air as well as in the salt water environment (Bayboro Harbor, Tampa Bay, Florida) for periods of up to 8 weeks in order to examine the losses of hydrocarbons during pre-use weathering and during actual use. Weathering and submergence studies were carried out both during the warm summer months as well as during the cooler temperatures of winter. Periodically throughout the study (days 1, 3, 7, 10, 14, 21, 28, 42, 56), hydrocarbons were extracted from various sections of the slats and were analyzed using GC and combined gas chromatography/mass spectrometry (GCMS) as described below.

Hydrocarbons were extracted overnight by submerging wood sections in approximately 200 ml of dichloromethane (EPA, 1986; Axiak et al., 1988). Extracts were filtered and, after rotary-evaporation to reduced volume, were analyzed using a Shimadzu GC-14A gas chromatograph equipped with a flame ionization detector and a 15 m x 0.25 mm i.d. DB5 fused silica column with hydrogen as a carrier gas. The oven temperature was programmed from 80°C to 280°C at 4°C per minute. Hydrocarbon concentrations were calculated relative to an ortho-terphenyl internal standard.

Peak identification and confirmations were made using a Finnigan MAT INCOS-50 GCMS system. GCMS conditions were identical to those of the GC except helium was used as the carrier gas. Electron impact spectra were obtained by scanning from 50-500 amu in 0.1 sec at an ionization potential of 70 eV.

RESULTS AND DISCUSSION

Samples of different brands of diesel fuel (i.e. Mobil, Amoco, and Texaco) all had similar alkane distributions. Diesel fuel mixed with Fungitrol in a 10:1 mixture (dip) did not show any chromatographic differences from the pure diesel fuels. Fungitrol alone produced no interfering peaks when analyzed by GC or GC/MS. The amounts of diesel fuel absorbed by pine and cypress were generally 16-30 times greater than the background levels of hydrocarbons found in the undipped wood.

Experimentation was conducted on individual slats of wood but henceforth diesel concentrations will be extrapolated to trap values based on wood surface area of a standard trap (pine = 18,474 cm^2, cypress = 18,439 cm^2; conversion of diesel fuel weights to volumes was based upon a measured density of 0.85 g diesel/ml). Gas chromatographic data commonly underestimates the total amount of petroleum components due to the presence of non-volatile polar compounds that do not pass through the GC column. Thus all gas chromatographic values have been normalized to the gravimetric data for comparison. The percent relative standard deviations between dipped slats (n=6) were taken into account in interpreting subsequent data (pine: ±35%; cypress: ±43%).

After soaking in dip for 10 days, pine slats absorbed the equivalent of 1.56 l diesel fuel/trap (SD = ±0.34, n=6). Cypress slats absorbed the equivalent of 2.04 l diesel fuel/trap (SD = ±0.30, n=6). After slats of pine and cypress were dipped for 10 days, they were allowed to weather for various periods of time up to 8 weeks. Diesel concentrations in the wood decreased with increasing exposure to outside weathering (Table 1). Concentrations in the wood were measured over time and the values were then used to generate a regression curve from which the percent diesel remaining in the trap at any given time could be predicted (Table 1, Fig. 1). Over the 8-week weathering period, there was approximately an 84% decrease in the diesel concentration in the pine. The diesel fuel concentration in the cypress decreased by even more, approximately 92%. Thus, after weathering 8 weeks, pine traps would retain an average of 250 ml diesel fuel/trap. Cypress would retain an average of 160 ml diesel fuel/trap. Stone crab fishermen generally dip, build, and weather their traps from May to October, up to 5 months before being used in the water to catch crabs during the season (16 October - 14 May). Thus the stone crab traps used by the fishermen may be weathered for up to 2.5 times longer than the longest period of time wood was weathered in our study. Even though cypress traps tend to absorb greater initial concentrations of diesel fuel, they also have a greater and more rapid loss of diesel fuel during weathering than pine. The decrease in diesel fuel concentration is most likely due to evaporation, but photooxidation may also play a possible role.

Wood dipped for 10 days and weathered various periods of time was then submerged. Results from these studies were used to generate regression curves for the amount of diesel fuel lost from the wood after submergence in seawater (Fig. 2). With increased weathering time, there is a decrease in the amount of diesel fuel retained by the wood, and therefore leached into seawater. Similar results have been reported for the weathering of creosote treated wood (Ingram et al., 1982). Most of the diesel fuel retained in the wood after

Table 1. Diesel concentrations estimated for wooden traps (based upon extrapolation of data from slats) dipped for 10 days and weathered with time.

Days on roof	l diesel trap[1]	predicted % diesel remaining[2]	predicted l diesel trap[3]
A. Pine			
0	1.56	100.0	1.56
1	2.24	96.9	1.51
3	0.67	90.8	1.42
7	1.14	79.8	1.24
10	0.42	72.4	1.13
14	0.86	63.3	0.99
21	0.37	51.0	0.80
28	0.25	40.8	0.64
42	0.38	25.5	0.40
56	0.17	16.3	0.25
B. Cypress			
0	2.04	100.0	2.04
1	--	94.9	1.94
3	1.65	86.7	1.77
7	1.69	71.9	1.47
10	0.61	63.3	1.29
14	2.19	52.0	1.06
21	1.04	37.8	0.77
28	0.70	27.0	0.55
42	0.04	14.3	0.29
56	0.47	7.7	0.16

[1]Concentrations are based on GC data normalized to values determined gravimetrically.
[2]Percent remaining predicted from regression curve for GC/gravimetric data. [A. $Y = 1163*10^{-0.016X}$, $r=-0.832$, $p< 0.01$; B. $Y = 2236*10^{-0.021X}$, $r = -0.693$, $p< 0.05$].
[3]Volume predicted from regression curve for GC/gravimetric data.
--Value missing due to extraction problems or wood loss.

weathering is released into seawater within the first few weeks after being placed in the water. By the end of the first 3 weeks of water exposure, less than 5% of the diesel fuel remained in either the pine or cypress that had been weathered 8 weeks. Essentially all of the diesel fuel remaining in the wood after weathering appears to be leached into seawater if it is submerged long enough. After dipping for 10 days, weathering for 8 weeks then submerging for 8 weeks, a piece of pine was re-dipped for 3 minutes (to simulate dipping in subsequent years) and was found to absorb the equivalent of 167 ml diesel fuel/trap. A highly biodeteriorated piece of wood from an old trap (used the previous season), was also

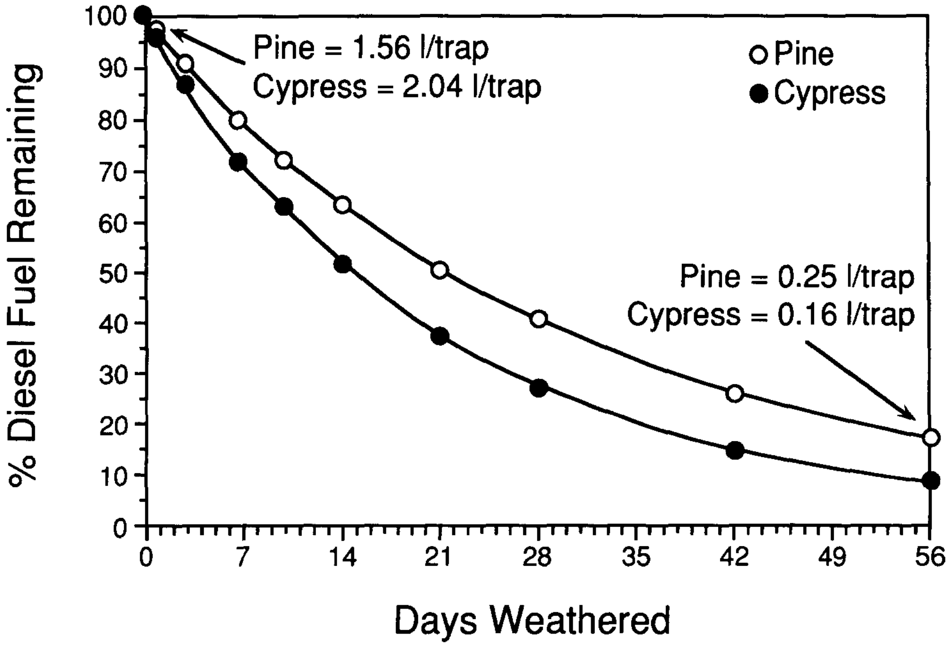

Figure 1. Diesel fuel remaining in weathered pine and cypress dipped for 10 days but not exposed to seawater. Values were obtained from a regression curve plotted through raw data points and converted into percent diesel remaining (Table 1). Initial concentrations (top left) are measured averages. Final concentrations (lower right) are predicted from regression curves.

re-dipped for 3 minutes, and was found to absorb the equivalent of 1.2 l diesel fuel/trap. If traps in good condition are dipped for 3 minutes, they only absorb about 10% of the amount absorbed if they were dipped for 10 days. The highly degraded piece of wood absorbed much more diesel fuel in 3 minutes than the well-preserved wood. This was believed to be due to the increased surface area created in the older piece of wood by worm burrows. In addition, the dip could have become trapped in the worm burrows, thus increasing its apparent absorption. After 8 weeks of weathering, diesel fuel concentrations in this wood decreased from an estimated 167 ml to 6 ml diesel fuel/trap, or a 96% decrease. Wood from the old, previously used, pine trap showed a 90% decrease in diesel over 8 weeks of weathering. These results suggest that similar percentages of diesel fuel may be released from traps during weathering regardless of dipping time.

In addition to the above studies which were all carried out during the summer months, dipped pine and cypress were also weathered in the winter (November to February) and submerged in seawater with temperatures of approximately 18°C compared to summer temperatures of approximately 30°C. Weathering during the winter was found to be less effective than weathering during the summer. After 5 weeks weathering in the winter, approximately 45% of the diesel fuel was

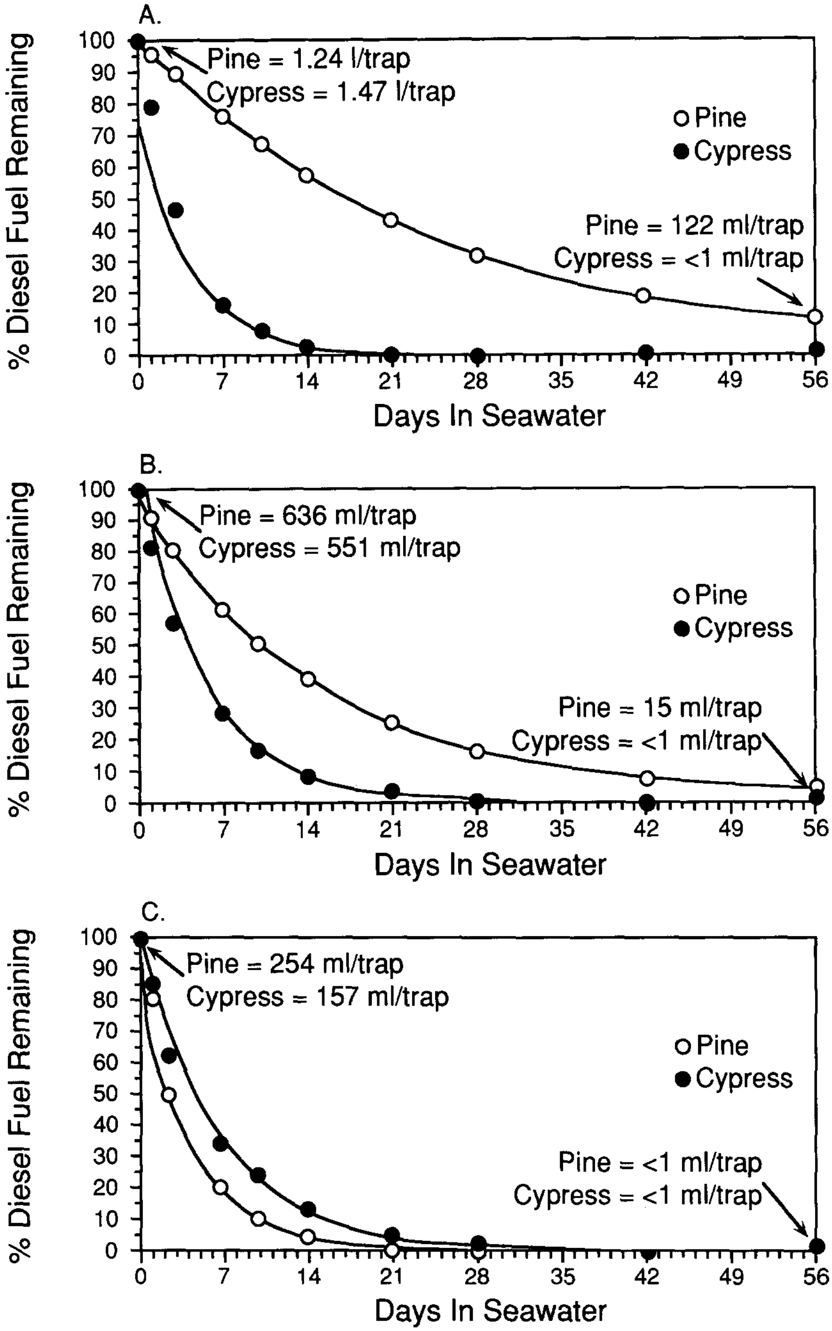

Figure 2. Diesel fuel remaining in pine and cypress weathered various period of time then placed in seawater. Values were obtained from regression curves plotted through raw data points and converted into percent diesel remaining. Initial (top left) and final (lower right) concentrations are predicted from regression curves. A. Weathered 1 week. B. Weathered 4 weeks. C. Weathered 8 weeks.

lost from the pine and 18% was lost from the cypress, while approximately 80% was lost from both types of wood when they were weathered during the summer months. Diesel fuel losses to seawater during the winter were similar to those in the summer, with decreases of up to 97% in pine and 87% in cypress. Since stone crab traps are generally built, dipped, and weathered during the summer, but are submerged and used during the winter, it appears that the dipping method currently used by stone crab fishermen would minimize the losses of diesel fuel to the environment if the pre-use weathering periods were rigidly adhered to.

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