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Identification of Tire Leachate Toxicants and a Risk Assessment of Water Quality Effects Using Tire Reefs in Canals

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Cover is an important component of aquatic habitat and fisheries management. Fisheries biologists often try to improve habitats through the addition of natural and artificial material to improve cover diversity and complexity. Habitat-improvement programs range from submerging used Christmas trees to more complex programs using sophisticated artificial habitat modules. Used automobile tires have been employed in the large scale construction of reefs and fish attractors in marine environments (D'Itri 1985) and to a lesser extent in freshwater (Johnson and Stein 1979) and have been recognized as a durable, inexpensive and long-lasting material which benefits fishery communities.

Recent studies by the U.S. Bureau of Reclamation (Mueller and Liston 1991) have quantified the importance of tire reefs to enhancing freshwater canal fisheries in the southwestern United States. These studies have demonstrated that fishes and aquatic macroinvertebrates are attracted to these structures, increasing species diversity, densities and biomass where reefs are placed in canals. Potential benefits to fishermen are great in the form of recreational fishing. However, the use of tire reefs in aquatic environments which have relatively small volumes compared to marine or reservoir environments has raised water quality concerns. Effects of tires on water quality have not typically been studied in the past because of the obvious presence of fishes and other aquatic organisms that make use of tire reefs; the implication being that tires are inert and non-toxic.

Little information on effects of tires on water quality is contained in the literature. Stone et al. (1975) demonstrated that tire exposure had no detrimental effects on two species of marine fish while results of Kellough's (1991) freshwater tests were inconclusive, but suggested that some factor in tire leachate was toxic to rainbow trout (*Oncorhynchus mykiss*). Nozaka et al. (1973) found no harmful substances leached from tire material soaked in fresh water.

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Because there are few data on toxicity associated with tires, this became the focus of our study. Toxicity Identification Evaluation (TIE) procedures developed by the EPA (1991) were used to evaluate water quality impacted by tires.

MATERIALS AND METHODS

Three series of tests using plugs cut from tires and whole tires were conducted. Tire leachate was collected from tire plugs and used for toxicity testing and a separate set of plug leachate was tested for potential bioconcentrated organic contaminants. Whole tires were used in depuration studies.

Tire leachate for toxicity testing was prepared by soaking 29 tire plugs (10.25 cm diameter) in 16 L of Lake Mead, Nevada water for a period of 31 days. This water source was selected as being representative of irrigation canal water in the southwestern United States. Tire plugs were soaked in water contained in glass aquaria in a darkened room; gentle aeration was provided. Control water for dilutions from the same source, minus the tire material, was also treated in this manner. Tire plugs ranged in weight from 72.5 to 120.0 grams (mean = $99.6 \pm SE 1.5$ grams) and were obtained from nonbias ply tires by drilling with a steel hole saw. This particular loading resulted in ca. 181 g tire material per liter of water. Water was collected in 20-L cubitainers from Lake Mead, Nevada and refrigerated until used.

To test for toxic and/or potentially bioconcentrated organic contaminants that might be present in tire leachate, ten 2.5 cm diameter plugs (mean weight = $5.3 \pm SE 0.1$ g) were cut from the tread pattern of 10 tires. Plugs were placed in a clean glass flask with 1 L of deionized water. Another cleaned flask was prepared and 1 L of deionized water was added to the flask to serve as a blank. Gas chromatography/mass spectroscopy methods were then used to identify possible organic contaminants after 40 days.

Additional leachate tests were performed to examine leaching of materials from whole tires and to determine whether depuration of toxicants from tires occurred. Three glass aquaria containing 28 L of Lake Mead, Nevada water in which 1/2 of a whole tire was exposed were maintained with aeration for 30 days. Loading for the three aquaria ranged from 123 to 136 g of tire material per liter. After 30 days the tanks were drained, and fresh water was returned to the tanks. Water samples were collected and analyzed at 30 and 60 days to determine whether depuration of materials occurred. A control tank with water only was also maintained for comparison.

Acute 24-hr toxicity tests (EPA 1991) were conducted using both Ceriodaphnia dubia (< 24 hr old) and fathead minnows (Pimephales promelas) (24-48 hr old). Toxicity characterization consisted of a baseline toxicity test of tire leachate diluted with Lake Mead water, along with aeration, filtration, C_{18} solid phase extraction

(SPE) tests, and pH-adjusted samples to test for volatiles, particulate-bound toxicants, non-polar organic compounds, and changes in metal bioavailability, respectively. Samples were also treated with sodium thiosulfate or ethylenediaminetetraacetate (EDTA) to assess metals toxicity. Methods generally followed those presented in EPA (1991), with blanks and controls utilized for all tests.

Lethal concentrations to 50% of the organisms (LC_{50}) were calculated, where appropriate, using the Trimmed Spearman-Kärber Test (Hamilton et al. 1977). Acute toxic units (TU_a) were also calculated to compare leachate toxicity to measured concentrations of suspect toxicants. Leachate TU_a 's were calculated by dividing 100% by the LC_{50} , and TU_a for individual toxicants were calculated by dividing the measured concentration ($\mu\text{g/L}$) by the acute toxicant LC_{50} ($\mu\text{g/L}$).

Measured physical and chemical characteristics of toxicity test waters included dissolved oxygen, pH, conductivity, alkalinity, and hardness. Additional samples from toxicity tests were collected in polyethylene bottles for analyses of major ions and total recoverable metals. Water samples from whole-tire leachate tests were also analyzed for total recoverable metals. Total recoverable metal samples were preserved by adjusting them to $\text{pH} \leq 2$ with concentrated HNO_3 and analyzed using inductively coupled plasma/emission spectroscopy.

RESULTS AND DISCUSSION

Physico-chemical characteristics of toxicity test water are presented in Table 1 and TIE results are presented in Table 2. The leachate was acutely toxic to *C. dubia* (24-hr LC_{50} 20.3%) but not to fathead minnows. All blanks and controls exhibited 100% organism survival. Sample toxicity reduction associated with water manipulation tests, along with differences in species susceptibility, indicated the presence of metals. Toxicity was partially removed in the 100% leachate concentration by sodium thiosulfate and totally removed by EDTA, indicating cationic metal toxicity and a mixture of metals (EPA 1991). Toxicity was also partially removed by SPE but this toxicity was not eluted from SPE using methanol. This is also indicative of metals being the toxin. Chemistry results from toxicity tests (Table 3) indicated that zinc was present in concentrations that could be toxic and that cadmium, copper, and lead were above background in 100% concentrations. Copper may be highly toxic at the relatively high pH (Howarth and Sprague 1978; Miller and MacKay 1980; Meador 1991) observed in these tests (Table 1). At the 100% concentration, EDTA would remove both zinc and copper, while sodium thiosulfate would remove copper, but not zinc (EPA, 1991). It is likely, however, that copper would be of most importance in the 100% leachate concentration as it would be more dilute at lower concentrations. Nominal toxicant concentrations at the dilution equal to the LC_{50} would suggest that zinc is the main toxicant.

Table 1. Physico-chemical parameters of toxicity test waters.

Parameter	Tire leachate	Lake Mead dilution water
Dissolved oxygen (mg/L)	6.1	6.1
pH	8.36	8.60
Conductivity (μ S/cm)	1128	1070
Total alkalinity (mg/L)	110	108
Total hardness (mg/L)	328	309

Table 2. Results of TIE tests.

Manipulation	24-hr LC ₅₀ (%) and 95% confidence limits	
	<u>C. dubia</u>	Fathead Minnow
Baseline toxicity test (this test repeated twice for <u>C. dubia</u>)	21.0 (15.9-27.7)	> 100
	20.3 (17.0-24.2)	
pH 3 Adjustment	30.8 (24.0-39.4)	> 100
pH 11 Adjustment	35.4 (24.9-50.2)	> 100
Aeration	17.7 (confidence limits not reliable)	--
Filtration	23.3 (17.2-31.6)	> 100
SPE	61.6 (48.0-78.9)	> 100
Eluted SPE	> 100	> 100
Other Tests	Results (% survival in 100% concentration)	
EDTA	100	--
sodium thiosulfate	20	--

Confirmation that zinc was the primary toxicant was obtained by adding zinc to control water through the addition of zinc chloride and then performing an additional toxicity test using C. dubia. The nominal value of 750 μ g/L zinc in the 100% concentration was confirmed through chemistry analysis that indicated zinc was present in duplicate samples at 88 and 91% of the nominal value.

Table 3. Chemistry results from TIE tests.

Parameter	Type of water			
	Lake Mead dilution water	Deionized water blank	Tire leachate- duplicate 1	Tire leachate- duplicate 2
Zn ($\mu\text{g/L}$)	8.7	<4.0	751	755
Cd ($\mu\text{g/L}$)	0.2	<0.1	0.6	0.6
Cu ($\mu\text{g/L}$)	<5.0	<5.0	6.7	5.7
Pb ($\mu\text{g/L}$)	<1.0	<1.0	6.7	6.7
Ni ($\mu\text{g/L}$)	<10.0	<10.0	<10.0	<10.0
Ca (mg/L)	71.2	--	74.7	--
Mg (mg/L)	31.2	--	31.6	--
Na (mg/L)	98.3	--	102	--
K (mg/L)	5.35	--	5.93	--
CO ₃ (mg/L)	<0.00	--	<0.00	--
HCO ₃ (mg/L)	136	--	143	--
SO ₄ (mg/L)	266	--	277	--
Cl (mg/L)	113	--	115	--

The 24-hr LC₅₀ calculated from this test was 147.1 $\mu\text{g/L}$ zinc (95% C.I. 131.7-164.3 $\mu\text{g/L}$ zinc). It is of interest to note that our 24-hr LC₅₀ value is lower than the 48-hr LC₅₀ (255 $\mu\text{g/L}$ zinc) reported by Carlson et al. (1986) for *C. dubia* exposed to zinc in softer water (hardness of 90 mg/L). EPA (1987) presents hardness as being most important in determining zinc toxicity and according to this scenario our LC₅₀, at a hardness of 300 mg/L, should be much higher. It is possible, however, that pH may be as important as hardness in determining toxicity, with increased pH leading to increased zinc toxicity. This has been demonstrated with fishes (Mount 1966, Everall et al. 1989) and our data is at least suggestive that this may be the case with *C. dubia*. In addition, our low alkalinity relative to hardness differs from many stream waters (3:1 ratio hardness:alkalinity vs. the average 1.3:1 ratio observed in river waters of North America (Livingstone 1963)) and it is possible that this may cause increased toxicity. With the use of *C. dubia* as a standard toxicity test organism, it is unfortunate that the relationship of hardness, alkalinity, and pH on zinc toxicity to *C. dubia* has not been described.

The TU_a calculated for the original leachate test was 4.9 and our zinc bioassay indicated that zinc could be held accountable for 5.1 TU_a of the leachate. The closeness of these values suggests that most of the leachate toxicity is from zinc.

Laboratory analyses for organic compounds did not detect any analytical differences between tire leachate and deionized control waters. Benzothiazole was found in both samples (1-2 mg/L), suggesting an origin other than the tire material. Other analytes (Table 4) were below detection limits of 1.0 $\mu\text{g/L}$.

Depuration tests with whole tires were analyzed for zinc, because of its demonstrated toxicity in leachate, and mercury because it had not been analyzed for earlier. The amount of zinc declined over time (222.6 \pm SE 47.3 $\mu\text{g/L}$ zinc at 30 days vs 131.0 \pm SE 15.5 $\mu\text{g/L}$ zinc at 60 days) indicating that concentrations of toxicants in tire reefs would also decrease with continuous leaching by water. Zinc concentrations in control water were at background concentrations (3-7 $\mu\text{g/L}$). The amount of zinc leached per gram of whole tire (1.7 $\mu\text{g Zn/g tire}$) was lower than that leached from tire plugs (4.2 $\mu\text{g Zn/g tire}$). The differences in loading rates likely accounted for most of this disparity in numbers; however, freshly cut tire plug surfaces may have allowed for some additional leaching of zinc. Mercury was not detected (<0.1 $\mu\text{g/L}$) in any samples.

While toxicity caused by zinc was observed in laboratory tests, it is unlikely that the zinc concentrations leached from the tires used in artificial reefs would ever cause acute or even chronic toxicity. At a suggested rate (Mueller and Liston 1991) of 20 tire reefs containing 900 tires per 1 kilometer of canal and a weight of 8 kg/tire this would result in 7,200 kg of tire material per kilometer of canal. If the cross sectional area of the canal is 33.5 m^2 , approximately 33,500,000 L of water would be contained in this 1 kilometer section of canal. Our tire leachate studies indicated that 755 μg of zinc could be leached from 0.181 kg of tire plug material. Using this value, the amount of zinc that would be leached into this 1 kilometer section of canal, under a conservative no flow scenario, would result in the presence of 0.896 $\mu\text{g/L}$ of zinc. This would likely be the maximum ever encountered because in most cases lotic conditions prevail in canals and because our tests with whole tires showed that zinc concentrations declined over time. Chemistry tests for organic compounds (Table 4) also indicate that these materials would not be a problem.

There may be other situations such as landfills, disposal sites, or road beds (Minnesota Pollution Control Agency 1990) where zinc leached from whole or shredded tires could result in water quality problems. We believe, however, that the use of tires in artificial reefs in water similar to that which we tested would not result in deleterious changes in water quality.

Table 4. List of organic compounds tested for in tire leachate water. None of these compounds were detected at a detection limit of 1.0 µg/L.

Acenaphthene	4,4'-DDT	Isophorene
Acenaphthylene	Dibenz(a,j)acridine	Methoxychlor
Acetophenone	Dibenz(a,h)anthracene	3-Methylcholanthrene
Aldrin	Dibenzofuran	Methyl methanesulfonate
Aniline	Di-n-butylphthalate	2-Methylnaphthalene
Anthracene	1,3-Dichlorobenzene	2-Methylphenol (o-cresol)
4-Aminobiphenyl	1,4-Dichlorobenzene	4-Methylphenol (p-cresol)
Aroclor-1016	1,2-Dichlorobenzene	Naphthalene
Aroclor-1221	3,3-Dichlorobenzidine	1-Naphthylamine
Aroclor-1232	2,4-Dichlorophenol	2-Naphthylamine
Aroclor-1242	2,6-Dichlorophenol	2-Nitroaniline
Aroclor-1248	Dieldrin	3-Nitroaniline
Aroclor-1254	Diethylphthalate	4-Nitroaniline
Aroclor-1260	p-Dimethylaminoazobenzene	Nitrobenzene
Benizidine	7,12-Dimethylbenz(a)anthracene	2-Nitrophenol
Benzoic Acid	α,α-Dimethylphenethylamine	4-Nitrophenol
Benzo(a)anthracene	2,4-Dimethylphenol	N-Nitroso-di-n-butylamine
Benzo(b)fluoranthene	Dimethylphthalate	N-Nitrosodimethylamine
Benzo(k)fluoranthene	4,6-Dinitro-1-methylphenol	N-Nitrosodiphenylamine
Benzo(g,h,i)perylene	2,4-Dinitrophenol	N-Nitrosodipropylamine
Benzo(a)pyrene	2,4-Dinitrotoluene	N-Nitrosopiperidine
Benzyl alcohol	2,6-Dinitrotoluene	Pentachlorobenzene
α-BHC	Diphenylamine	Pentachloronitrobenzene
β-BHC	1,2-Diphenylhydrazidine	Pentachlorophenol
σ-BHC	Di-n-octylphthalate	Phenacetin
BHC (Lindane)	Endosulfan I	Phenanthrene
Bis(2-chloroethoxy)methane	Endosulfan II	Phenol
Bis(2-chloroethyl)ether	Endosulfan Sulfate	2-Picoline
Bis(2-ethylhexyl)phthalate	Endrin	Pronamide
4-Bromophenyl phenyl ether	Endrin aldehyde	Pyrene
Butyl benzyl phthalate	Endrin ketone	1,2,4,5-tetrachlorobenzene
Chlorodane	Ethyl methanesulfonate	2,3,4,6-Tetrachlorophenol
4-Chloroaniline	Fluoranthene	1,2,4-Trichlorobenzene
1-Chloronaphthalene	Fluorene	2,3,5-Trichlorophenol
2-Chloronaphthalene	Heptachlor	2,4,6-Trichlorophenol
4-Chloro-3-methylphenol	Heptachlor epoxide	Toxaphene
2-Chlorophenol	Hexachlorobenzene	
4-Chlorophenyl phenyl ether	Hexachlorobutadiene	
Chrysene	Hexachlorocyclopentadiene	
4,4'-DDD	Hexachloroethane	
4,4'-DDE	Indeno (1,2,3-cd)pyrene	

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