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Acute Toxicity of Some Experimental Road Surfacing Compounds to *Daphnia pulex*

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The use of salt (NaCl and $CaCl_2$) for road deicing has resulted in physical and environmental damage. Salt damages highway structures, vehicles, utility lines and roadside vegetation, and its use has also caused the contamination of surface and groundwaters (HAYES et al. 1970). MURRAY and ERNST (1976) estimate that salt causes 2.6 billion dollars of damage per year in the United States. This economic and environmental cost has prompted a search for a salt substitute. Several chemical compounds are presently being evaluated for their effectiveness in preventing ice adhesion on road surfaces (AHLBORN and POEHLMANN 1976). These compounds are also potential contaminants of surface waters through runoff from prepared road surfaces. My objective was to assess the potential environmental hazard of these experimental surfacing compounds to aquatic organisms by determining the acute toxicity (96 h) of these compounds (as water leachates) to Daphnia pulex which is a common microscopic inhabitant of lakes and is a sensitive test organism for toxicity studies.

METHODS

Each of eight hydrophobic test compounds designated as compound B, C, F, I, J, K, or L contains a non-pigmented paint binder, a silicon rubber material, technical grade naphtha (petroleum ether), and 2-propanol (Table 1). Petroset AT, (Phillips Petroleum Co.) a water miscible material used for asphalt renovation, was also tested for toxicity. Compounds B through L are applied as a thin layer to the road surface and they dry rapidly (≃ ½ h). Petroset AT reacts chemically with the asphalt surface which reportedly results in an improved asphalt surface.

Weather and abrasion constantly erodes any coating of a road surface and runoff carries this material into surface waters. There is also a possibility of a storm during the application of these compounds. I wanted, therefore, to determine the toxicity of water (leachate) which was in contact with the dried surfacing compounds and the toxicity of water leachate from wet surfacing compounds.

The laboratory culture of D. pulex was cloned three times from a wild stock collected from Medical Lake, Washington. D. pulex was grown in aquaria at 20 ± 2 C under 16 h artificial daylight (100 foot candles) with an algae feed of Selenastrum capricornutum and Carteria quadrata. The algae were batch cultured with a medium of carbon filtered well water and additions of nitrogen (4.2 mg/ℓ), phosphorus (0.19 mg/ℓ) and manure extract (1 ml/ℓ).

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TABLE 1

Composition of Experimental Surfacing Compounds
Used to Control Ice Adhesion.

Quantity of component/liter of compound

Compound Code	LR8198[1] (ml)	LR8652[1] (ml)	Drisil 73[2] (ml)	DC732[3] (g)	naphtha (ml)	2-propanol (ml)
B	476			83	423	18
C	370			128	470	32
F		604		37	348	11
G		523		65	394	19
I			579	34	375	11
J			512	66	407	15
K			455	91	431	23
L			413	107	453	25

[1] Non-pigmented paint binder-Akron Paint and Varnish Company

[2] Non-pigmented paint binder-Texas Solvents and Chemicals Company

[3] Silicon rubber caulking-Dow Corning Company

The chemical characteristics of the carbon filtered well water used for the base of the algae media, for preparing leachates of the experimental compounds, and as dilution and control water were as follows: total hardness: 120 mg/ℓ $CaCO_3$, alkalinity: 169 mg/ℓ $CaCO_3$, Ca: 21.9 mg/ℓ, Mg: 15.7 mg/ℓ, specific conductance: 265 μmhos/cm, nitrate nitrogen: 0.005 mg/ℓ, nitrite nitrogen: 0.028 mg/ℓ, ammonia nitrogen: 0.18 mg/ℓ, pH: 8.3 - 8.5, and residual chlorine: <0.04 mg/ℓ . Chemical analyses were conducted by methods given in Standard Methods (1975).

The experimental compounds were initially dried in beakers for 24 h at room temperature. To prevent a surface film from developing, the beakers were placed on a shaker table at 200 rpm for the 24 h drying period. The beakers were then placed in a 100 C oven for 48 h. Compounds B through L formed a surface layer when dried, thus, the materials were frequently stirred while in the 100 C oven. Each of the dried materials (except Petroset AT) was placed in a blender with an equal weight of dilution water and were blended until finely ground. The slurry of water and ground material was placed in a stoppered flask and rotated at 300 rpm for 48 h at room temperature. The water was then separated from the ground materials with a #2 filter (Whatman) which had been previously rinsed with distilled water. This water leachate is referred to in later sections of this paper as 100% leachate of dried surfacing material or dry leachate.

Dried Petroset AT, which has a consistency of light tar, readily mixes with water when agitated. I added an equal weight of water to the dried Petroset AT and left it undisturbed for 48 h. The aqueous layer (leachate) was then collected by aspiration without filtration. Wet leachates of Petroset AT were prepared as water dilutions of the raw material. Fresh stock solutions of this material were prepared for each test run. Petroset AT is evaluated separately in the following results and discussion section.

Leachates of wet formulas B through L were prepared by adding a volume of water equal to the volume of the wet formula. The containers were placed on a shaker table and the speed was adjusted to move the surfacing material in the container slightly. I found that even though the surfacing compounds are hydrophobic, they do emulsify in water with strong agitation. After 48 h of agitation the aqueous layer (leachate) was aspirated and collected. This leachate is referred to as 100% leachate of wet materials or wet leachate. All leachates were stored at 4 C until used for testing and test dilutions were prepared 8 to 16 h before as assay was begun.

Assay vessels were 50-ml beakers with aluminum foil caps to retard evaporation. I used an eyedropper to place 10 or more young (estimated one or two days old) D. pulex in each test beaker which contained 20 or 40 ml of the test solution. The amount of culture water carried over to the test beakers was estimated to be 0.5 ml. Two control beakers which contained 20 and 40 ml dilution water and 10 or more D. pulex were used for each assay. The control mortality during the assays did not exceed 10%. The test and control animals were fed three drops of algae culture on the second day of the assay. The assays were conducted at 21 ± 2 C.

Mortality was ascertained during the assays by scanning the bottom of the test beakers with a 20 X dissecting microscope. Each D. pulex which had ceased all feeding and swimming motions and made no response to the eyedropper used to remove it was counted as dead. The assays were terminated at 96 h from the start and the pH of the test solution in each beaker was measured.

The dilution or concentration which caused 50% mortality (LC 50) was estimated by plotting the mortality on log probit paper and then visually fitting the line. The LC 50 was read from the fitted line.

RESULTS AND DISCUSSION

Dry Leachates: The LC 50 for Daphnia pulex ranged from 24% to greater than 100% of the dry leachate solution for formulas B through L (Table 2).

TABLE 2

Percentage Mortality of <u>Daphnia pulex</u> in Water Leachates of Dried Road Surfacing Compounds

Compound Code	100	75	67	56	50	42	32	18	10	Estimated LC 50
	% Solution of Dry Leachate in Dilution Water									
B	100	--	100	100	91	--	100	0	0	24
C	100	--	100	100	89	0	0	0	0	49
F	100	--	90	100	78	--	33	25	30	40
G	88	--	25	--	30	--	--	--	--	70
I	0	--	--	--	--	--	--	--	--	>100
J	11	--	--	--	0	--	--	--	--	>100
K	0	--	--	--	--	--	--	--	--	>100
L	100	85	90	0	10	--	0	0	--	60

Dry leachates of formulas I, J and K exhibited the least toxicity with zero to 11% mortality in 100% dry leachate solution. The dry leachate of formula B exerted the greatest toxicity with an estimated LC 50 of 24% of the leachate. The pH of the dry leachates (8.0 - 8.1) were similar to the pH of the dilution water (8.3 - 8.5).

The laboratory treatment of the dried surfacing compounds was much more rigorous than would be expected with rain falling on prepared road surfaces. In addition, rainwater runoff is diluted to some degree by runoff from other areas. When these factors are considered with the low toxicity found for the laboratory preparations, these dried surfacing compounds (B through L) are evaluated as practically non-toxic.

<u>Wet Leachates</u>: The toxicity of the wet leachates ranged from 3.4% of formula L to 14% of formula I (Table 3). The toxicity of formulas F and G corresponded with a sharp decrease in pH. The compound DC732, a component of all the mixtures releases acetic acid when it cures (drys) and the acidity appears to have exceeded the buffering capacity of the dilution water. The low pH may have been a cause of mortality for formulas F and G. Death of the test animals occurred quickly (<1 h) in solution of low pH which also indicates shock from the large pH change may have contributed to the mortality.

There is a high correlation for the wet leachates of formulas F through L between toxicity (1-LC 50) and the percentage of 2-propanol in each formula (r = 0.95), however, the percentage of DC732 and naphtha also correlate highly (r = 0.93 and r = 0.87 respectively) with toxicity. The toxicity of the wet leachates is apparently due to either the 2-propanol, the naphtha, the DC732 or a component of one of these.

The rapid drying time of the test compounds reduces the chance of forming a wet leachate in practical use and natural weathering would probably be less rigorous than the laboratory treatment. Thus, the toxicity of the wet leachates to Daphnia pulex and the probable environmental risk is minimal.

TABLE 3

Percentage Mortality of Daphnia pulex in Leachates of Wet Surfacing Materials.

Compound Code	% Solution of Wet Leachate in Dilution Water							Estimated LC 50
	18	14	10	7.5	5.6	3.2	1.8	
B	100 (7.9)[1]	60 (8.3)	70 (8.3)	40 (8.4)	22 (8.4)	0	--	8
C	100 (8.0)	100 (8.1)	30 (8.0)	20 (8.0)	--	--	--	9.4
F	100 (5.5)	5 (7.7)	0 (7.9)	14 (8.1)	0 (8.1)	--	--	13
G	--	--	100 (5.2)	40 (7.7)	30 (8.0)	10	0 (8.4)	5.8
I	100 (5.2)	40 (7.6)	0 (7.8)	0 (8.1)	--	--	--	14
J	--	--	100 (7.8)	0 (8.0)	0 (7.8)	0 (8.2)	0 (8.3)	8.6
K	--	--	100 (4.9)	100 (6.8)	0 (7.7)	0 (8.1)	0 (8.3)	6.4
L	--	--	100 (4.6)	--	100 (7.3)	15 (8.1)	0 (8.1)	3.4

[1] pH of test solution measured at the termination of each assay (96 h).

Petroset AT: In contrast to the relatively non-toxic formulas B through L, Petroset AT and the water leachate of dried Petroset AT are extremely toxic (Table 4).

Estimated LC 50's for water dilutions of Petroset AT and dilutions of dry leachate of Petroset AT were 0.11 µℓ/ℓ and 6.0 µℓ/ℓ respectively. This material is considered to present a considerable environmental risk because: 1) it is extremely toxic 2) it is slow drying and 3) it mixes readily with water. The use of Petroset AT should be carefully controlled.

Further confirmation of the toxicity of these materials should be carried out with runoff from road surfaces prepared with these experimental compounds.

TABLE 4

Percentage Mortality of _Daphnia pulex_ in Water Dilutions of of Petroset AT and Dry Leachate of Petroset AT.

Petroset AT dilution (μℓ Petroset AT/ dilution water)				Estimated LC 50
0.32	0.18	0.10	0.056	0.11 μℓ/ℓ
100	100	33	0	

Dried Petroset AT Leachate (μℓ leachate of dried Petroset At/ℓ dilution water)					Estimated LC 50
17.8	10	5.6	3.2	1.8	6.0 μℓ/ℓ
100	90	30	8	0	

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