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Acute Toxicity of an *in situ* Shale Oil Process Wastewater and Its Major Components to *Daphnia magna*

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New energy technologies are being developed in this country to reduce our dependence on rapidly disappearing petroleum reserves. This is seen in increased utilization of coal and in the expansion of the oil shale industry in Colorado, Wyoming and Utah. For in situ technologies such as in situ retorting of oil shale and underground coal gasification, the potential contamination of groundwater remains the most serious aquatic ecosystem and water use problem (BERGMAN et al. 1978, DEGRAEVE et al. 1980).

There is considerable variation between the chemical components of aqueous effluents from these technologies (PARKHURST et al. 1981, ANDERSON et al. 1980). Even effluents from a single process may vary substantially, depending on operating conditions and the type of coal or shale being processed. Because of this variability it is advantageous to develop rapid biological and chemical tests for identifying and evaluating the components of effluents which are acutely toxic to aquatic biota (PARKHURST et al. 1979).

Our objective was to assess the potential environmental hazard of an in situ shale oil process wastewater to aquatic organisms by determining the acute toxicity (48 h) of this effluent to Daphnia magna, a microcrustacean commonly found in lakes in northern and western North America and a sensitive test organism for many toxicity studies (PENNAK 1978). The effluent under study, designated Omega-9 water, was obtained from the Laramie Energy Technology Center's experimental true in situ shale oil site near Rock Springs, Wyoming (FARRIER et al. 1977). Though the water was collected in 1976, it has undergone little apparent deterioration because of stringent storage procedures such as maintenance at $4^{o}C$.

METHODS

Procedures for the cultivation and performance of acute bioassays using Daphnia magna were developed by the Environmental Protection Agency (1981) and used successfully in this study. The chemical characteristics of the culture medium used for rearing and as control and dilution water in the acute bioassays were as follows: total hardness: 170 mg/L $CaCO_3$, alkalinity: 115 mg/L $CaCO_3$, specific conductance: 734 μmhos/cm, ammonia nitrogen:

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0.41 mg/L, pH: 8.3-8.5. Standard Methods (1975) were used for all chemical analyses.

A synthetic effluent was prepared by mixing together, using reagent grade chemicals, each of the major inorganic components identified in the Omega-9 water and at the concentrations found (ANDERSON et al. 1980). The acute toxicity of the synthetic mixture was compared with that of the Omega-9 water. If they were not found to be significantly different, it was assumed that the chemicals and their respective concentrations tested in the synthetic effluent were the only chemicals present in the original effluent at acutely toxic concentrations. If, instead, the acute toxicity of the synthetic effluent was significantly lower than the acute toxicity of the Omega-9 water, it was assumed that the original effluent contained as yet unidentified components at acutely toxic concentrations (PARKHURST et al. 1979). A computer program based on the probit methods of FINNEY (1971) was used to calculate EC_{50}s and standard errors.

RESULTS AND DISCUSSION

Results of the acute bioassays for the Omega-9 water and the synthetic mixture are presented in Table 1. The difference between the acute toxicities for the two test waters is significant ($p<.05$). The relative toxicity was 1.49; thus the Omega-9 water was approximately 1.5 times as toxic as the synthetic mixture.

TABLE 1

Acute toxicities of Omega-9 water and the synthetic effluent to *Daphnia magna*

Water type	48 h EC_{50} (% Dilution)	95% Confidence limits	
		Lower	Upper
Omega-9	0.71	0.68	0.75
Synthetic	1.06	1.00	1.13

Figure 1 is a plot of percent mortality versus concentration. The sigmoidal pattern typical of dose-response relationships was evident for both the original and synthetic waters. A probit plot is given in Figure 2. Linearity was exhibited between log concentration and mortality for both the Omega-9 water and the synthetic mixture. The regression lines were parallel, indicating

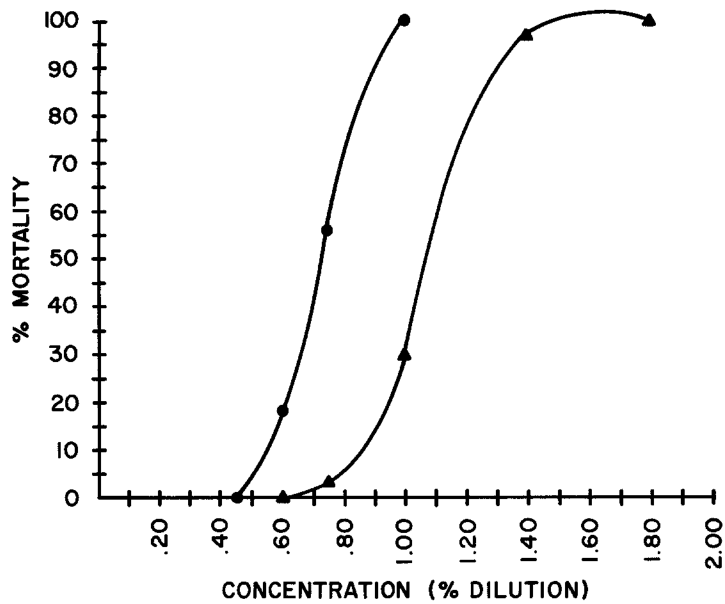

Figure 1. Plot showing the percent mortality of D. magna versus concentration. Circles, Omega-9 water; triangles, synthetic mixture.

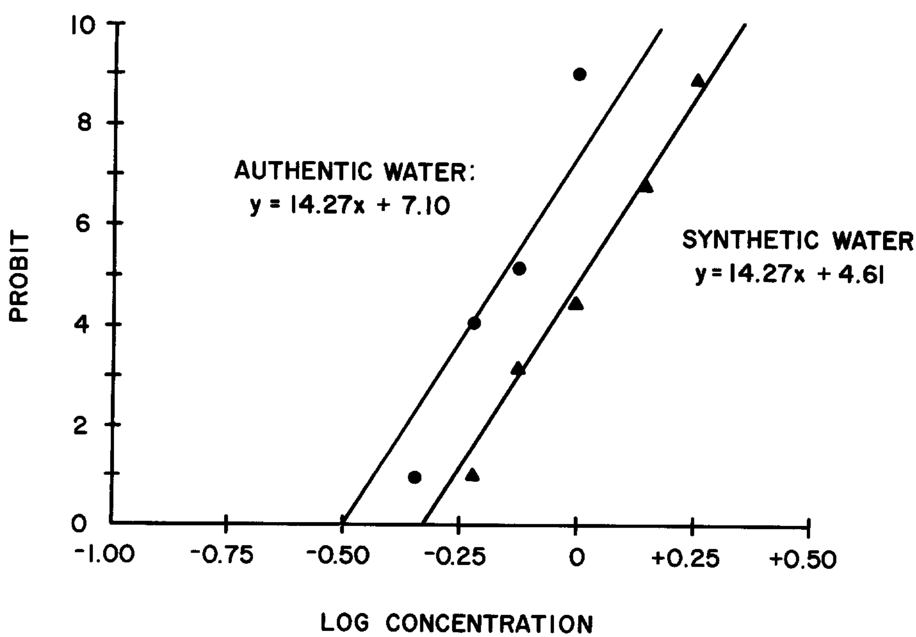

Figure 2. Probit plot showing the percent mortality of D. magna versus log concentration. Circles, Omega-9 water; triangles, synthetic mixture.

similar modes of toxicity. In fact, the synthetic mixture appeared to exert toxic effect as if it were a dilution of the original effluent. Table 2 lists the relative concentrations of the original and synthetic waters required to achieve selected percent mortalities, and the standard errors.

TABLE 2

Relative concentrations of Omega-9 water and the synthetic effluent required to achieve selected percent mortalities

Percent Mortality	Omega-9 water		Synthetic	
	% Dilution	s.e.†	% Dilution	s.e.†
1	0.49	0.06	0.74	0.11
5	0.55	0.04	0.82	0.08
10	0.58	*	0.87	*
50	0.71	0.17	1.06	0.03
90	0.87	*	1.31	*
95	0.93	0.04	1.39	0.08
99	1.03	0.06	1.55	0.11

*Not calculated. †s.e. is standard error.

Calculated concentrations of un-ionized ammonia (NH_3), the toxic species in total ammonia (NH_3 + NH_4^+), at the 48 h EC_{50} dilutions and at the highest dilution at which no kill was observed are given in Table 3 for both test waters. The former values compared favorably with PARKHURST's (1981) calculated 48 h LC_{50} value of 2.08 mg/L (T25°C, pH 8.2) un-ionized ammonia for D. magna.

Despite similar toxicity values for un-ionized ammonia, the 48 h EC_{50} values for the Omega-9 water and the synthetic mixture differ significantly. While the results indicate an important role for inorganics, particularly un-ionized ammonia, in the toxicity of the Omega-9 water, they cannot as yet be thought to be primarily responsible for acute toxicity to D. magna. It appears that not all the chemicals present in the original effluent at acutely toxic concentrations have been identified.

TABLE 3

Calculated concentrations of un-ionized ammonia in Omega-9 water and the synthetic effluent in *D. magna* acute bioassays

Bioassay	Effect	Dilution (%)	Test pH	Test temperature (^{o}C)	Calculated un-ionized ammonia[a]
Omega-9					
48 h					
dilution	EC_{50}	0.71	8.4	19.0	2.28[b]
	none	0.45	8.4	18.6	1.10[c]
Synthetic					
48 h					
dilution	EC_{50}	1.06	8.2	19.5	2.11[b]
	none	0.60	8.2	19.3	0.87[c]

[a]Expressed in mg/L as NH_3. Method for calculation of percent un-ionized ammonia taken from TRUSSELL (1972).

[b]Based on total ammonia concentration of 3.80 g/L (NH_3 + NH_4^+) for Omega-9 water and 3.48 g/L for the artificial mixture (ANDERSON et al. 1980).

[c]Based on mean values of 13.4 mg/L total ammonia for 0.45% Omega-9 water and 15.4 mg/L total ammonia for 0.60% synthetic mixture.

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