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Toxicity of a Coal Liquefaction Product to Aquatic Organisms

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As coal liquefaction processes approach commercialization in the United States, there is a growing need for information on their potential environmental impacts. Effects of product spills on aquatic ecosystems are of particular concern, because occasional spills are likely to occur once full-scale liquefaction facilities begin operation. Past oil spill experiences will not be adequate for predicting the effects of coal-derived oils, because the latter are chemically quite different from petroleum products (GRIEST et al. in press). We took a comparative approach to the environmental assessment of synthetic oils, asking, "Are coal-derived oils more or less hazardous to the aquatic environment than the petroleum-derived oils they are intended to replace?" Using acute bioassay tests, we compared a representative coal liquefaction product with a petroleum-derived residual fuel oil and a diesel fuel, materials whose ecological effects have been documented following actual spills over the past 15 years (VAN GELDER-OTTWAY and KNIGHT 1976; AIBS 1978).

The tests were conducted on a heavy boiler fuel, equivalent to a No. 6 residual fuel oil, produced by a 50-ton-per-day coal liquefaction pilot plant. The test sample was considered by the producer to be representative of the average commercial product from this liquefaction technique. The oil was intended for direct use, without further refining (KAPER 1979). The synthetic oil and a conventional No. 6 oil were obtained from the EPA/DOE Fossil Fuels Research Materials Facility at Oak Ridge National Laboratory (Samples #171 and #6101, respectively). A No. 2 diesel fuel was purchased from a local distributor.

We determined the acute toxicity of water soluble fractions (WSFs) of the three oils to two freshwater algae and one freshwater crustacean. The WSFs were tested instead of the whole oils because (a) the water soluble components of an oil are responsible for most of its acute toxicity (EVANS and RICE 1974; MOORE and DWYER 1974; RICE et al. 1977); and (b) while spilled oil can be contained and often recovered, the water with which it comes in contact will affect a larger area and for a longer time. We prepared the WSFs by layering one part oil on eight parts water (algal growth medium (MILLER et al. 1978) in the algal bioassays, and well water in the experiments with Daphnia magna) in a closed glass vessel and stirring gently for

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16 hr. The WSFs were separated from the oils in separatory funnels and filtered (Whatman #41 filter paper) before use. All preparations were done under gold fluorescent lighting to prevent photooxidation of the oils or WSFs.

The species used in the algal bioassays were Selenastrum capricornutum (a green alga) and Microcystis aeruginosa (a blue-green alga). These species have been adopted by the U.S. Environmental Protection Agency (EPA) as standard test organisms for assessing the effects of nutrients and toxicants on freshwater algae (MILLER et al. 1978). We obtained our cultures from the EPA Environmental Research Laboratory at Corvallis, Oregon, and maintained them according to the EPA procedure (MILLER et al. 1978). For each bioassay, rapidly growing cultures were concentrated by centrifugation, resuspended in the test solutions [10^{11} cells/M^3 (10^5 cells/ml)], and incubated (24°C; 1.0 x 10^3 J/M^2/min photosynthetically active radiation) in 1.25 x 10^{-4} M^3 (125-ml) BOD bottles for 4 hr. Details of the bioassay procedure have been published elsewhere (GIDDINGS 1979). Photosynthesis was measured by the ^{14}C-bicarbonate method (SCHINDLER et al. 1979; THEODORSSON and BJARNASON 1975) during the final 2 hr of incubation, and expressed as percentage of controls. The WSFs were tested at 100, 10, 1, and 0.1% of full strength (diluted in algal growth medium), with two replicates per concentration.

Figure 1 shows the algal bioassay results. The No. 6 fuel oil caused no significant inhibition (Student's t-test, $P \leq 0.05$) of S. capricornutum, and it inhibited M. aeruginosa only at 100%. Both species were significantly stimulated by 0.1% WSF of this oil; low concentrations of No. 6 oil also stimulate photosynthesis by natural marine phytoplankton communities (GORDON and PROUSE 1973). The WSF of No. 2 diesel oil inhibited both species at 100%, but at 10% had no significant effect. In contrast with the two petroleum-derived oils, the WSF of the coal liquefaction product reduced algal photosynthesis significantly even at 1%.

We also determined the acute toxicities of the three WSFs to first-instar Daphnia magna in static 48-hr exposures. (See PARKHURST et al. (1979) for details of bioassay procedure.) The test concentrations ranged from 100 to 5.7%, 100 to 0.4%, and 0.5 to 0.002%, for the No. 6, No. 2, and coal-derived oils, respectively. The toxicity criterion was immobilization. Computerized PROBIT analysis (BARR et al. 1976) was used to estimate 48-hr EC_{50}'s (concentrations resulting in immobilization of 50% of test animals in 48 hr). The coal-derived oil WSF was highly toxic to D. magna, with a calculated EC_{50} of 0.31% (95% fiducial limits 0.23 - 0.43%). The No. 2 WSF was intermediate in toxicity, with an EC_{50} of 6.7% (4.8 - 9.8%). No immobilization occurred in 100% No. 6 WSF in 48 hr.

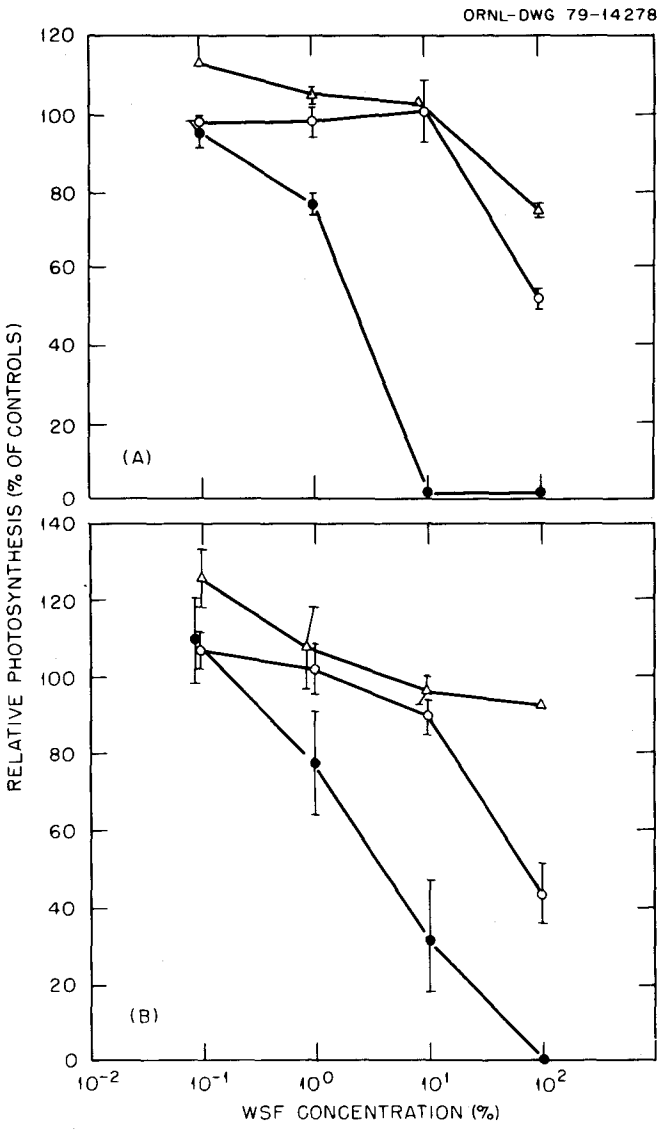

Fig. 1. Acute toxicity of WSFs of No. 6 fuel oil (triangles), No. 2 diesel fuel (open circles), and a coal liquefaction product (filled circles) to Microcystis aeruginosa (A) and Selenastrum capricornutum (B). Each point represents the mean of two replicates. Bars indicate standard deviation; bars have been omitted if they would not extend beyond the datum points. Photosynthesis is expressed as a percentage of the mean ^{14}C fixation of 3 controls (control data not shown).

The toxicity of the synthetic oil WSF at high dilutions suggests that highly soluble compounds such as benzenes or phenols may be present. We prepared WSFs of the three oils with distilled water and measured the phenolic content of each by the direct photometric method (APHA 1976). We also determined total organic carbon (TOC) with a Beckman TOC Analyzer. To avoid loss of volatile organics, the WSFs were not purged as usual for TOC analysis, but a distilled water blank was analyzed and subtracted from the WSF values. The TOC concentration in the synthetic oil WSF was 5 Kg/M^3 (5 g/l), with phenols predominating (Table 1).

TABLE 1

Total organic carbon (TOC) and phenols in the WSFs of three oils

WSF	TOC (10^{-3} kg/M^3)	Phenols (10^{-3} kg/M^3)
No. 6	19	22
No. 2	105	38
Synthetic oil	5000	3000

Phenols, unlike aromatic and aliphatic hydrocarbons, are rapidly and almost completely removed from oils by dissolution into water (GUARD et al. 1975; WINTERS et al. 1976). Even if the spilled oil were quickly recovered, the phenolic fraction would likely have already dissolved. Once in the water, phenols evaporate more slowly than other water soluble components such as benzene. For these reasons, phenolic compounds are more important components of WSFs than their abundance in oils would suggest (GUARD et al. 1975; WINTERS et al. 1976; FRANKENFELD 1973). The synthetic oil we tested contained 4% phenols (determined by acid/base fractionation) (GRIEST et al. in press), whereas the phenolic content of most petroleum products is below 1% (GRIEST et al. in press; FRANKENFELD 1973; LARSON et al. 1977). Since coal-derived oils are high in phenols regardless of the liquefaction process used (GRIEST et al. in press; BRAUNSTEIN 1977), the toxicity we observed with this particular product may be characteristic of unrefined coal liquefaction products in general.

We are currently screening other liquefaction products to evaluate this hypothesis. The results presented here indicate a need for further acute and chronic bioassays with other organisms, followed by studies of the effects of experimental synthetic oil spills on whole communities and ecosystems.

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REFERENCES

AMERICAN INSTITUTE OF BIOLOGICAL SCIENCES (AIBS): Proceedings of the conference on assessment of ecological impacts of oil spills, Keystone, Colorado (1978).

AMERICAN PUBLIC HEALTH ASSOCIATION (APHA): Standard methods for the examination of water and wastewater. 14 ed. Washington, D.C.: APHA 1976.

BARR, A. J., J. H. GOODNIGHT, J. P.SALL, and J. T. HELWIG: User's guide to SAS 76. Raleigh, N. C.: SAS Institute 1976.

BRAUNSTEIN, H. M., E. D. COPENHAVER, and H. A. PFUDERER, eds.: Environmental, health, and control aspects of coal conversion: an information overview. ORNL/EIS-94. Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1977.

EVANS, D. R., and S. D. RICE: Fish. Bull. 72, 625 (1974).

FRANKENFELD, J. W.: Conference on prevention and control of oil spills, 1973, Washington D.C. New York: American Petroleum Institute. p. 485 (1973).

GIDDINGS, J. M.: Bull. Environ. Contam. Toxicol 23, 360 (1979).

GORDON, D. C., and N. J. PROUSE: Mar. Biol. 22, 329 (1973).

GRIEST, W. H., M. R. GUERIN, B. R. CLARK, C. -h. HO, I. B. RUBIN, and A. R. JONES: Symposium on assessing the industrial hygiene monitoring needs for the coal conversion and shale oil industries, Nov. 1978. Uptown, N. Y.: Brookhaven National Laboratory (in press).

GUARD, H. E., L. HUNTER, and L. H. DISALVO: Bull. Environ. Contam. Toxicol. 14, 395 (1975).

KAPER, B.: Inside D.O.E., Feb. 12, 1979, Washington, D.C.: DOE 1979.

LARSON, R. A., L. L. HUNT, and D. W. BLANKENSHIP: Environ. Sci. Technol. 11, 492 (1977).

MILLER, W. E., J. C. GREENE, and T. SHIROYAMA: The Selenastrum capricornutum Printz algal assay bottle test. EPA-600/9-78-018. Washington, D.C.: U.S. Environmental Protection Agency, 1978.

MOORE, S. F., and R. L. DWYER: Water Res. 8, 819 (1974).

PARKHURST, B. R., C. W. GEHRS, and I. B. RUBIN: Aquatic Toxicology, eds. L. L. MARKING, and R. A. KIMERLE. American Society for Testing and Materials ASTM STP 667. p. 122 (1979).

RICE, S. D., J. W. SHORT, and J. F. KARINEN: Fate and effects of petroleum hydrocarbons in marine organisms and ecosystems, ed. D. A. WOLFE. New York: Pergammon. p. 78 (1977).

SCHINDLER, D. W., R. V. SCHMIDT, and R. A. REID: J. Fish. Res. Board Can. 29, 1627 (1972).

THEODORSSON, P., and J. O. BJARNASON: Limnol. Oceanogr. 20, 1018 (1975).

VAN GELDER-OTTWAY, S., and M. KNIGHT: Marine ecology and oil pollution, ed. J. M. BAKER. New York: John Wiley and Sons. p. 483 (1976).

WINTERS, K., R. O'DONNELL, J. C. BATTERTON, and C. VAN BAALEN: Mar. Biol. 36, 269 (1976).