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TOXICITY OF SHALE OIL TO FRESHWATER ALGAE: COMPARISONS WITH PETROLEUM AND COAL-DERIVED OILS[1]

MASTER

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DISCLAIMER

INTRODUCTION

Spills of liquid products from oil shale and coal liquefaction may be among the most significant environmental hazards of synthetic fuels production. Full-scale commercialization of coal liquefaction and shale oil production in this country will almost inevitably be accompanied by a certain amount of accidental release of synthetic oils during transportation, storage, and handling.[1] Because oils derived from coal and shale differ from petroleum products in important chemical and physical characteristics, the ecological effects of synfuels spills will be different from, and probably more serious than, the effects of petroleum spills. In recognition of this fact, the Advanced Fossil Energy Program in the Environmental Sciences Division at Oak Ridge National Laboratory is now conducting research on the potential problems of synthetic oil spills. The algal toxicity tests described below are part of this program.

ALGAL TOXICITY TEST

Algae are the dominant primary producers in most freshwater ecosystems. Because algae are at the base of most aquatic food webs, changes in the quantity, quality, or productivity of the algal community could have far-reaching consequences for the rest of the ecosystem. Our algal toxicity screening test is simple, rapid, and ecologically meaningful, and it has been used successfully with several dozen aromatic compounds and more than 20 conventional and synthetic oils.[2] The major objective of the test is rapid comparison of different materials with respect to their short-term effects on

freshwater algae. The test organisms are Selenastrum capricornutum, a unicellular green alga, and Microcystis aeruginosa, a non-nitrogen-fixing, blue-green alga. Photosynthetic inhibition is the criterion of toxicity. A second objective of the algal bioassay is determination of the range of toxic concentrations to guide further testing.

The test procedure has been described previously[2,3] and only a brief outline will be presented here. Cells from an actively growing culture are suspended in the test solution and incubated for 4 h. After 2 h, a ^{14}C-bicarbonate solution is added to each sample. The algae take up this inorganic ^{14}C and incorporate it into organic compounds during photosynthesis. At the end of the 4-h incubation, formaldehyde is added to kill the cells. Aliquots from each sample are acidified with HCl to convert all remaining inorganic carbon to CO_2, which is removed by bubbling with air. The remaining (organic) ^{14}C is then assayed by liquid scintillation spectrometry to determine the rate of photosynthesis. Results are expressed as percentages of controls.

MATERIALS TESTED

Coal liquefaction products have been the focus of our most intensive efforts to date.[4,5,6] However, when Dr. Griest informed us of the arrival of the Paraho/SOHIO shale oil suite in the Fossil Fuels Research Materials Facility,[7,8] we requested samples of several of the oils for toxicity screening tests, because of their inherent interest to our program as well as for comparison with petroleum- and

coal-derived oils. The oils tested (with their Fossil Fuels Research Materials Facility numbers in parentheses) were the following:

*Crude shale oil (No. 4601)

*Hydrotreated shale oil (No. 4602)

*Hydrotreated residue (No. 4607)

*JP-5 (jet fuel) (No. 4608)

*DFM (diesel fuel marine) (No. 4610).

We also tested three petroleum products for comparison:

*JP-5 (No. 4614)

*DFM (No. 4616)

*No. 6 residual fuel oil (No. 5401).

Crude petroleum was not tested because there is abundant evidence that petroleum crudes are generally less toxic to aquatic organisms than refined petroleum products.[9,10,11]

When oil is spilled on water, most of it either floats on the surface or sinks to the bottom, depending on its density and that of the water. The hazard to aquatic organisms stems more from exposure to components of the oil that dissolve into the water than from direct contact with the oil itself.[11,12] Moreover, the oil may be contained and ultimately recovered, while the water with which it comes in contact will affect a wider area and for a longer period of time. For these reasons and to avoid the experimental difficulties of working with immiscible materials, we tested the water-soluble fractions (WSFs) of the oils rather than the whole oils. Each WSF was prepared by adding oil to distilled water in a 1:8 (oil:water) ratio and stirring very gently for 16 h in the dark. The WSF was then separated from the

oil and filtered (Whatman No. 41) before testing. Algal growth nutrients were added, and dilutions were made into fresh algal growth medium.[13] Test solution concentrations were expressed as percentages of full-strength WSF.

RESULTS AND DISCUSSION

The effects of the five shale oil WSFs on photosynthesis by Selenastrum capricornutum are shown in Fig. 1. The crude shade oil WSF was the most toxic; a 10% solution of this material inhibited photosynthesis by nearly 80%. Hydrotreating significantly reduced the toxicity of this oil. The residue of the hydrotreated oil, however, was more toxic than the whole hydrotreated oil--in fact, the hydrotreated residue was nearly as toxic to S. capricornutum as crude shale oil. Neither of the refined shale oil products was toxic in these tests.

The effectiveness of hydrotreating in reducing the toxicity of crude shale oil was demonstrated with both test species (Fig. 2). We believe that this reduction in toxicity is due to removal of nitrogen and oxygen from the oil during hydrotreating.[14] The nitrogen- and oxygen-containing compounds, especially primary amines and phenols, are among the most toxic aromatic compounds to freshwater algae.[3] These compounds are also much more soluble in water than their hydrocarbon analogs, so their abundance in WSFs is greater, proportionally, than their abundance in oil. Preliminary analyses of the WSFs by UV spectroscopy have shown that the concentration of dissolved oil in the crude shale oil WSF is approximately five times that in the

hydrotreated shale oil WSF.[5] In studies with coal liquefaction products, we have found the ether-soluble bases to be the most toxic components of WSFs, with ether-soluble acids next in importance.[2,6] Similar investigations with shale oils have yet to be carried out, but we expect the same general trends to hold true.

The refined shale oil products, JP-5 and DFM, were not toxic to S. capricornutum. The petroleum-derived JP-5 was also nontoxic, but the petroleum DFM was completely inhibitory at 100% WSF (Fig. 3). The DFM was the most toxic petroleum product we have tested in our laboratory.[5,6]

The results with residual fuel oils (Fig. 4) do not present a clear pattern. The petroleum residual fuel oil had little effect on S. capricornutum, while the hydrotreated shale oil residue was toxic at 10% WSF. In the case of M. aeruginosa, however, the WSFs of the two oils were equally toxic. Subfractionation of these WSFs, followed by bioassays of individual subfractions, would be useful in explaining these results.

Figure 5 presents a comparison of the effects on S. capricornutum of the WSFs of petroleum DFM, crude shale oil, and a typical unrefined coal liquefaction product. The 12 coal-derived oils we have tested do not differ greatly in their toxicity to algae; all are considerably more toxic than crude shale oil.[5,6]

CONCLUSIONS

While these results do not constitute a complete evaluation of the relative ecological hazards of the oils tested, several tentative conclusions are suggested:

(1) The WSFs of some of the Paraho/SOHIO shale oils, particularly crude shale oil, are more toxic to algae than WSFs of petroleum products. Shale oil spills might, therefore, be expected to have greater ecological impact than petroleum spills.

(2) Unrefined coal liquefaction product WSFs are more toxic to algae than WSFs of shale oils in the Paraho/SOHIO suite.

(3) Refining reduces the toxicity of shale oil to algae.

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FIGURE CAPTIONS

Fig. 1. Relative photosynthesis (% of controls) of Selenastrum capricornutum exposed to water-soluble fractions (WSFs) of five shale oils. Fossil Fuels Research Materials Facility sample identification numbers are given in parentheses.

Fig. 2. Relative photosynthesis (% of controls) of Selenastrum capricornutum and Microcystis aeruginosa exposed to water-soluble fractions (WSFs) of crude and hydrotreated shale oils. Error bars indicate ± 1 S.D.

Fig. 3. Relative photosynthesis (% of controls) of Selenastrum capricornutum exposed to water-soluble fractions (WSFs) of shale oil DFM, petroleum DFM, shale oil JP-5, and petroleum JP-5. Error bars indicate ± 1 S.D.

Fig. 4. Relative photosynthesis (% of controls) of Selenastrum capricornutum and Microcystis aeruginosa exposed to water-soluble fractions (WSFs) of hydrotreated shale oil residue and a petroleum-derived residual fuel oil. Error bars indicate ± 1 S.D.

Fig. 5. Relative photosynthesis (% of controls) of Selenastrum capricornutum exposed to water-soluble fractions (WSFs) of petroleum DFM, crude shale oil, and unrefined coal-derived distillate oil. Error bars indicate ± 1 S.D.

FIG. 1

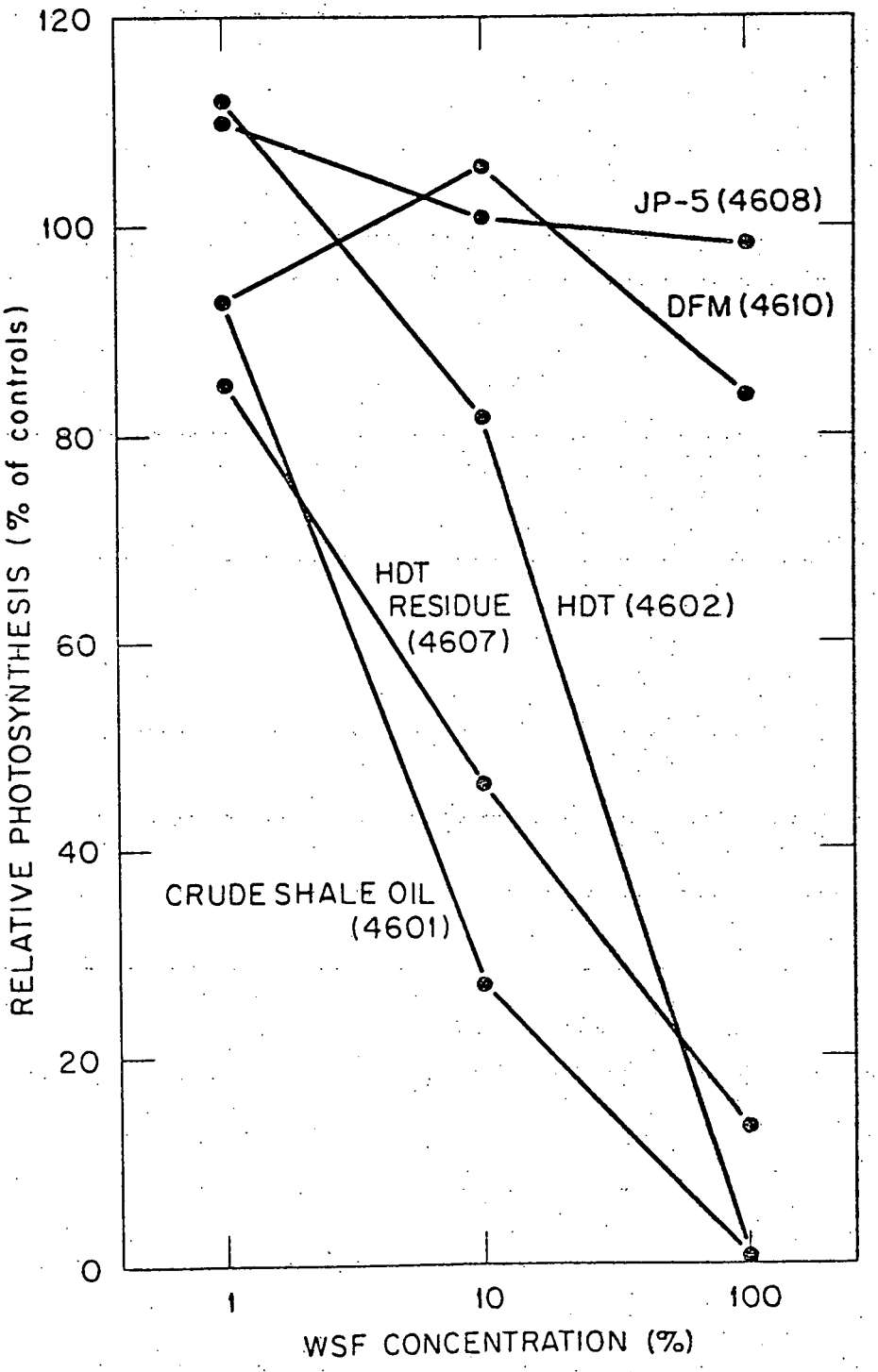

120
100
80
60
40
20
0
RELATIVE PHOTOSYNTHESIS (% of controls)
JP-5 (4608)
DFM (4610)
HDT (4602)
HDT RESIDUE (4607)
CRUDE SHALE OIL (4601)
1
10
100
WSF CONCENTRATION (%)

FIG. 2

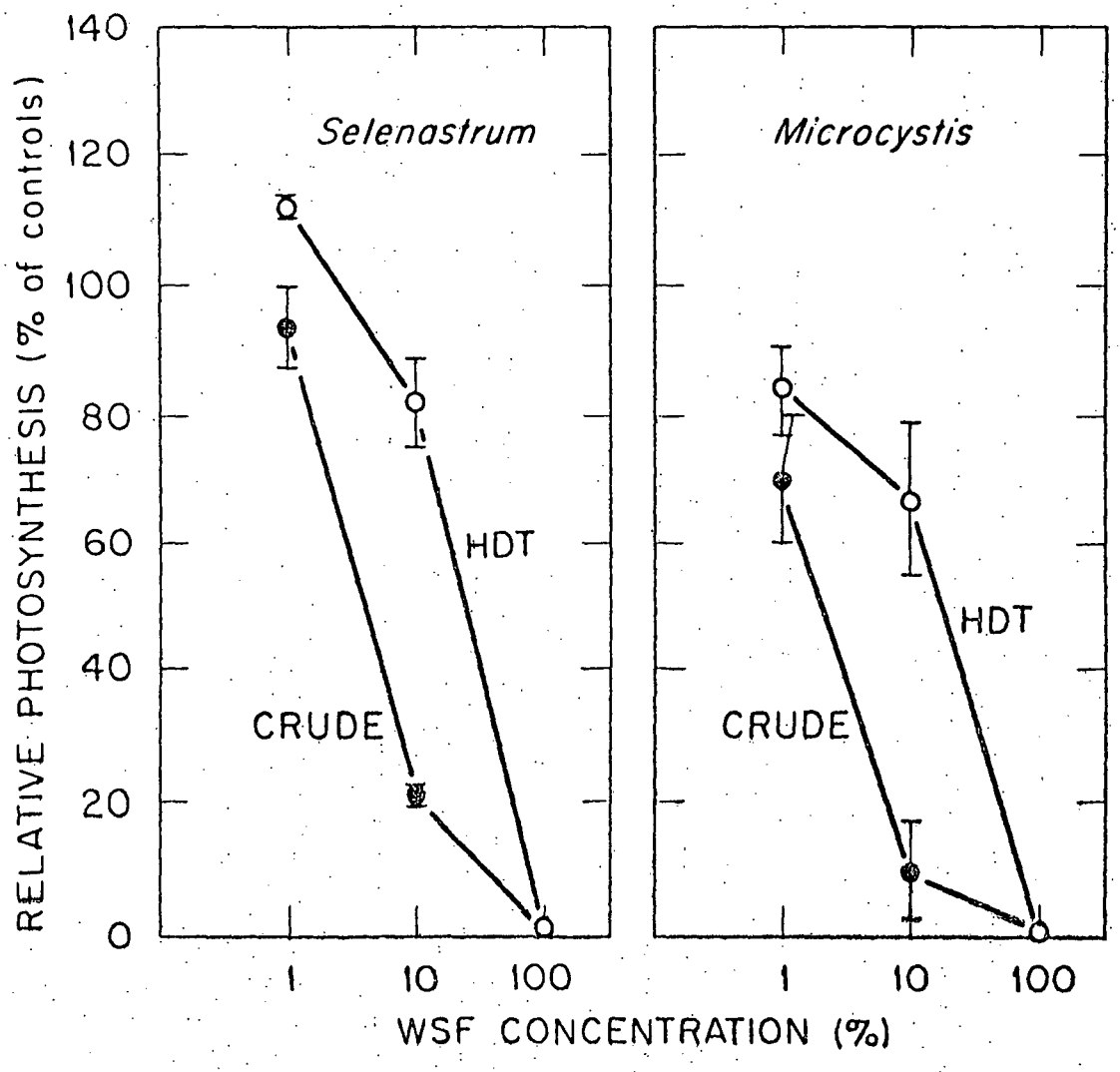

Selenastrum
Microcystis
HDT
CRUDE
HDT
CRUDE
RELATIVE PHOTOSYNTHESIS (% of controls)
140
120
100
80
60
40
20
0
1
10
100
1
10
100
WSF CONCENTRATION (%)

FIG. 3

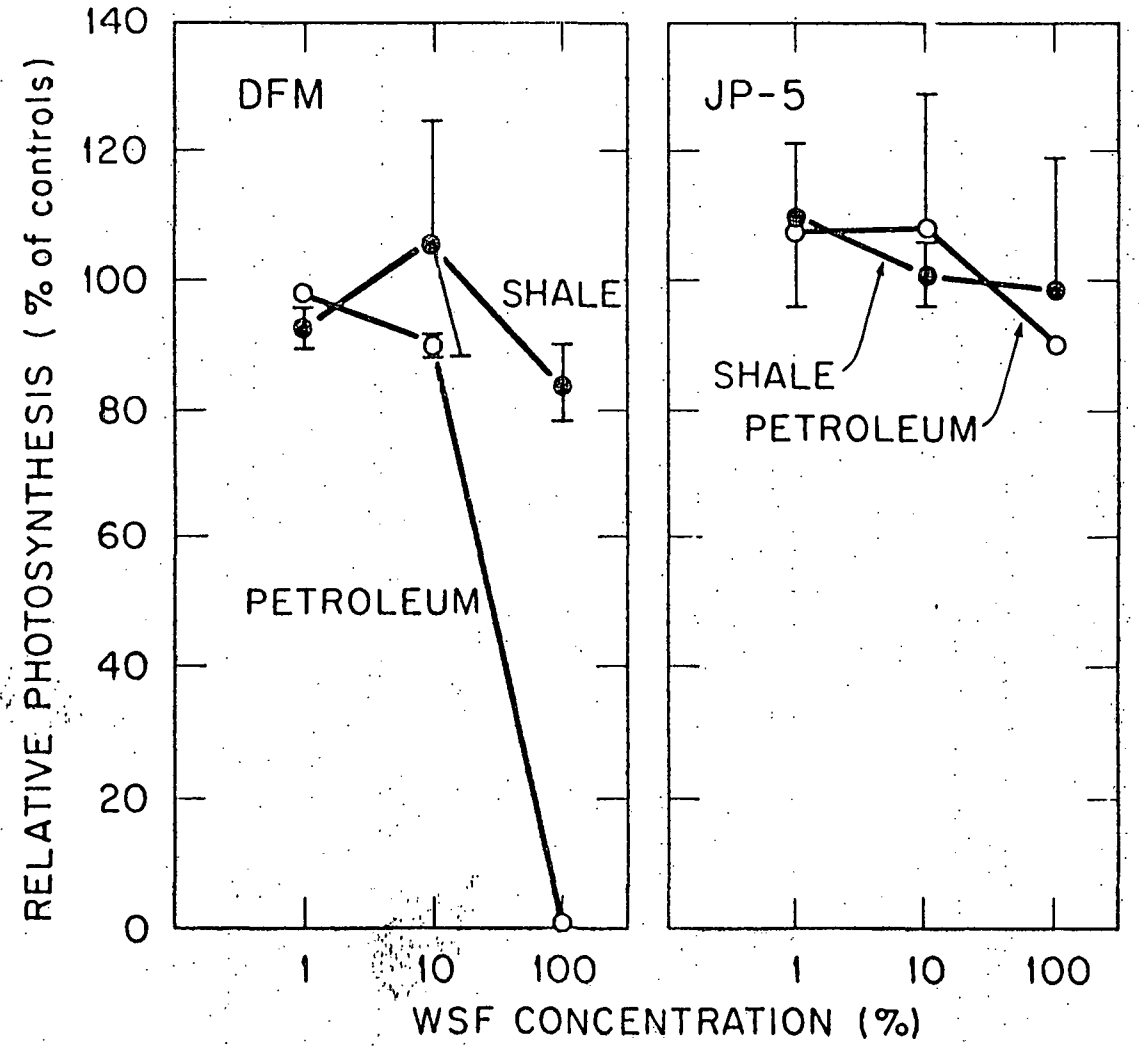

DFM
JP-5
SHALE
PETROLEUM
SHALE
PETROLEUM
RELATIVE PHOTOSYNTHESIS (% of controls)
140
120
100
80
60
40
20
0
1
10
100
1
10
100
WSF CONCENTRATION (%)

FIG. 4

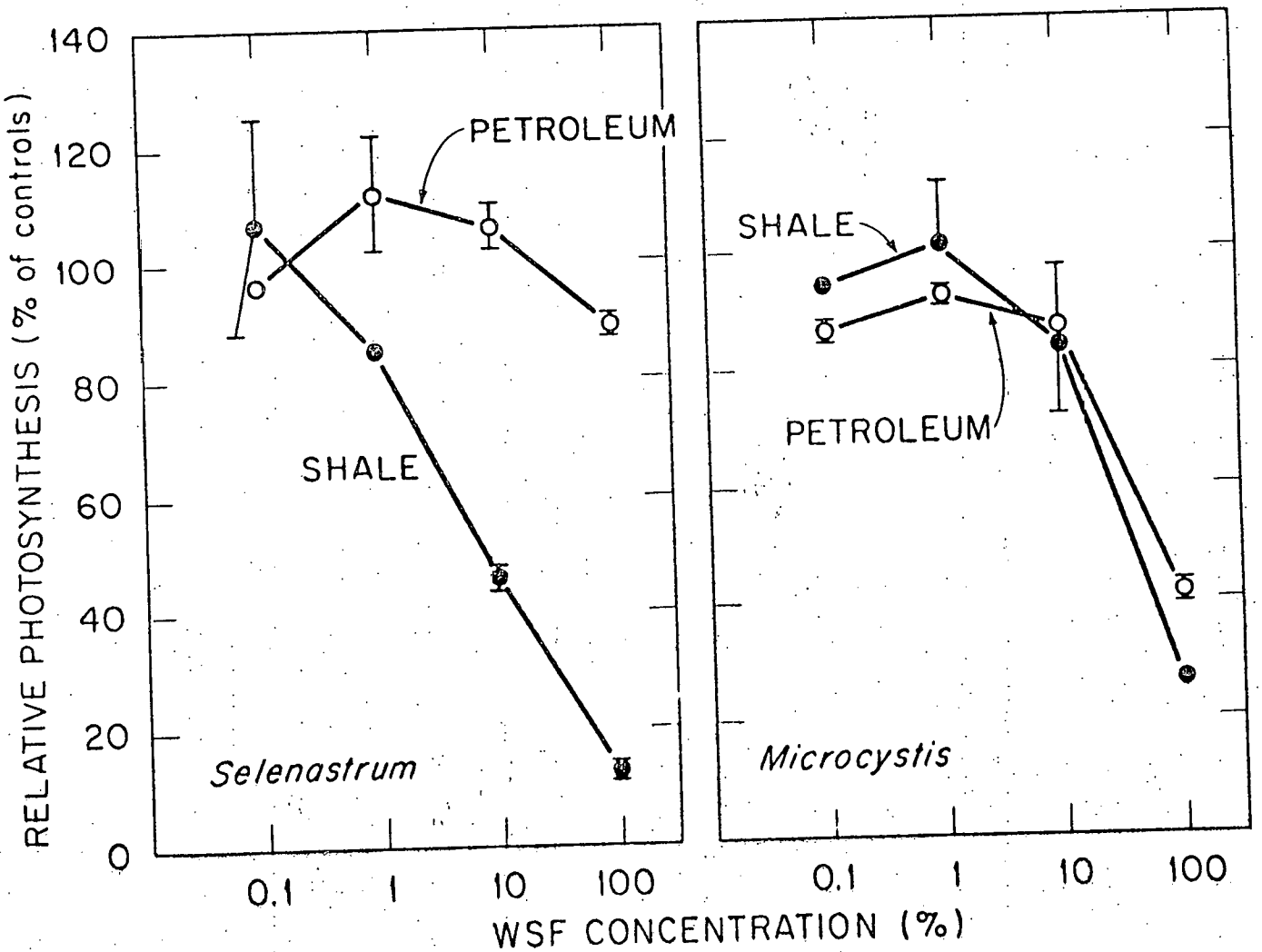
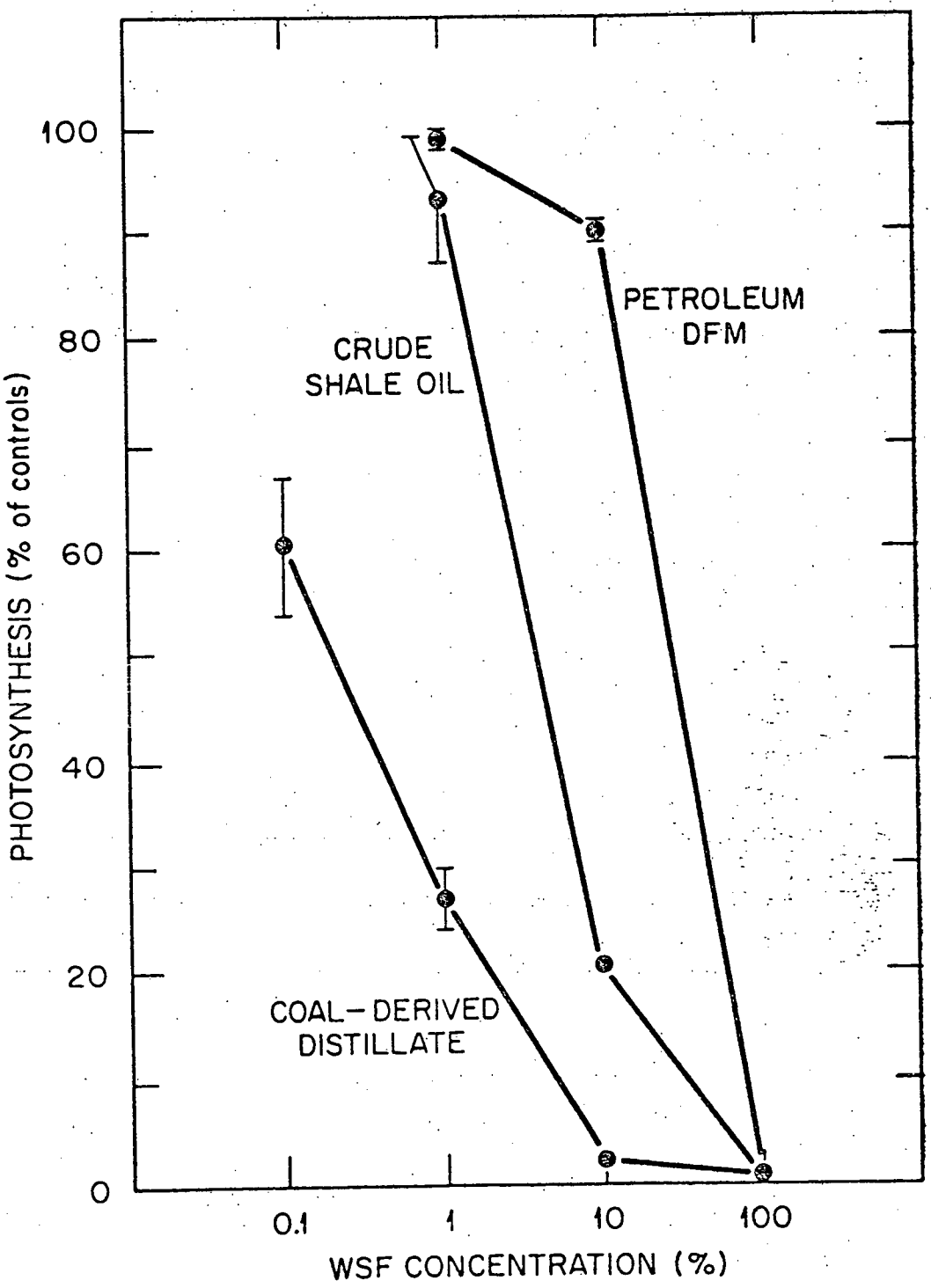

RELATIVE PHOTOSYNTHESIS (% of controls)
140
120
100
80
60
40
20
0
PETROLEUM
SHALE
Selenastrum
SHALE
PETROLEUM
Microcystis
0.1
1
10
100
0.1
1
10
100
WSF CONCENTRATION (%)

FIG. 5


100
80
60
40
20
0
PHOTOSYNTHESIS (% of controls)
CRUDE
SHALE OIL
PETROLEUM
DFM
COAL–DERIVED
DISTILLATE
0.1
1
10
100
WSF CONCENTRATION (%)