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An Evaluation of the Acute Toxicity to Aquatic Biota of a Coal Conversion Effluent and Its Major Components[1]

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The opportunity now exists for new energy technologies to be developed concomitant with consideration of their possible environmental impact. The cooperation and interaction of design engineers, waste control engineers, and ecologists has created the unique opportunity to identify and correct potential environmental problems before they occur. This is especially true for the synthetic fuels industry (GEHRS 1977). Increased utilization of coal is being promoted to reduce our dependence on rapidly disppearing petroleum reserves. However, coal is a "dirty" fuel. Its use has been considered to be both an environmental and health hazard since the 19th century, principally because of its complex chemical composition which includes a considerable quantity of impurities. The purpose of coal conversion technologies is to produce liquid, gaseous, or solid fuels from coal which are both more versatile and less environmentally hazardous (GEHRS 1977). A problem which exists with coal conversion is that, although it results in a cleaner fuel (lower sulfur and ash content), considerable quantities of solid and liquid wastes are produced and require disposal. These wastes are chemically very complex, reflecting both the complex chemical nature of coal and the coal conversion processes.

This paper describes a systematic evaluation of the potential acute toxicity to aquatic organisms of aqueous wastes from a coal conversion process. We discuss how the information gained can be used to anticipate environmental problems arising from this new technology before it is implemented on a large commercial scale.

MATERIALS AND METHODS

The approach used for the hazard evaluation involved both chemical analysis of the effluent and short-term toxicity tests

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of the effluent and the major components of the effluent identified in the analyses. The following procedures were used.

(1) The major chemical components of the effluent were analyzed using standard analytical techniques (APHA 1971). The components were selected for analysis based on their known presence as major constituents of some coal conversion effluents (SCOTT 1976, 1977, KLEIN and BARKER 1977).

(2) The toxicity of each of the components to Daphnia magna, measured as the 48-hr LC_{50}, was determined. The procedure used has been previously described (PARKHURST et al. 1977). Reagent grade chemicals were used.

(3) The toxicity (48-hr LC_{50}) of the original effluent was determined.

(4) A synthetic effluent was produced by mixing together, using reagent grade chemicals, each of the individual components identified in (1) above at the concentrations found in the effluent. The toxicity of the synthetic effluent was then determined.

(5) The contribution of each of the individual chemical components of the effluent to the toxicity of the total effluent was determined using the formula:

$$\text{toxic contribution of component A} = \frac{C_i(LC_{50_i})^{-1}}{\sum_{i=1}^{n} C_i(LC_{50_i})^{-1}}$$

where i is the component, LC_{50} is the toxicity (48-hr LC_{50}) of the individual component, and C is the component concentration at the 48-hr LC_{50} of the effluent. Additivity between the toxicants is assumed for this calculation and this assumption is tested in Step 6.

(6) The presence of interactions (more-than-, or less-than-additive) between the components of the effluent which may affect the toxicity of the whole effluent and could compromise the above calculation was determined, using the additivity index of MARKING and DAWSON (1975). If less-than-additive or more-than-additive interactions are indicated, the non-additive acting chemicals are identified by comparing the percentage concentration of the chemicals in the effluent to their calculated contributions to the toxicity of the effluent, as determined from the individual toxicities. If significant differences are found, the chemical(s) are exerting a non-additivity toxicity to the toxicity of the whole effluent.

(7) The toxicities of the original effluent and the synthetic effluent were compared. If the acute toxicities of the original and synthetic effluents 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. However, if the acute toxicity of the synthetic effluent was significantly lower than the acute toxicity of the original effluent, it was assumed that all the chemicals present in the original effluent at acutely toxic concentrations had not been identified. If the toxicity of the synthetic effluent was significantly higher than the original, it was assumed that some of the chemicals in the synthetic had been added at concentrations greater than were actually present in the original effluent. In either case, steps one through seven were then repeated.

If further testing is indicated, a different procedure is used to identify and evaluate the toxic contributions of the minor components of the effluent. This is necessitated by the large number of organic compounds present in the effluent which could be contributing to its acute toxicity. The procedure involves combining chemical fractionation of the effluent with acute toxicity tests using *D. magna* and has been described previously (PARKHURST et *al.* 1977).

The toxic components from two effluents from a hydrocarbonization (HCZ) coal conversion process development unit at Oak Ridge National Laboratory were identified and evaluated for acute toxicity, using the procedure outlined above for the major components of the effluent. The first effluent was an untreated effluent. The second effluent was an HCZ effluent that had been treated by biological oxidation in a fluidized-bed bio-reactor developed at Oak Ridge National Laboratory (MCNEESE 1978).

RESULTS

The chemical characteristics of the untreated and treated HCZ effluents are listed in Table 1. The untreated waste had much higher concentrations of phenol, cresols, ammonia, and total organic carbon, while the treated waste had higher concentrations of sulfate, nitrate, phosphate, and thiocyanate. The higher concentrations of nitrate and phosphate in the treated effluent resulted from their addition to the effluent as nutrients for the bacterial culture used in the waste treatment process. The toxicities (LC_{50}'s) of the major components of the effluents to *D. magna* are presented in Table 2. The most toxic components were the cresols followed by phenol, ammonia, and thiocyanate. Nitrate, phosphate, and sulfate were relatively nontoxic.

TABLE 1

Major chemical components of two hydrocarbonization effluents

Component	Concentration (mg/liter)	
	Untreated effluent	Treated effluent
Phenol	4780	4
O-cresol	990	< 1
P-cresol	600	< 1
M-cresol	500	< 1
Ammonia	1970	770
Sulfate	< 1	546
Total nitrate	0.4	17
Total phosphate	3	1500
Thiocyanate	< 5	13
Total organic carbon	8300	100

TABLE 2

Concentrations of effluent components at 48-hr LC_{50} dilutions and additivity indices of the untreated and treated hydrocarbonization effluents

Effluent component	Concentration of component at 48-hr LC_{50} concentration of effluent		48-hr LC_{50} (mg/liter)	Additivity index
	Untreated effluent	Treated effluent		
Phenol	5.1	0.5	30.1	
O-cresol	1.1	0	5.0	
P-cresol	0.6	0	1.4	
M-cresol	0.5	0	18.8	
Ammonia	2.1	85.9	25.4	
Sulfate	0	60.9	2233.0	
Total nitrate	< 0.1	1.8	2008.0	
Total phosphate	< 0.1	167.4	2399.0	
Thiocyanate	< 0.1	1.4	57.4	
Untreated effluent			1060(µl/liter)	+0.07
Treated effluent			116,000(µl/liter)	-2.52[b]

[a] Additivity index > 0 = more-than-additive toxicity.
Additivity index = 0 = simple additive toxicity.
Additivity index < 0 = less-than-additive toxicity.

[b] Significantly different from 0 at $p = 0.05$.

The 48-hr LC_{50} of the untreated HCZ effluent was determined to be at a dilution of 1.06 ml/liter (Table 3). The toxicity of the synthetic effluent was not significantly different (t-test, $p = 0.05$) from the toxicity of the original effluent. The calculated contributions of each of the major chemical components of the untreated effluent to the toxicity of the effluent are presented in Table 4. The concentration of phenolics in the untreated effluent contributed 91% of the

TABLE 3

Acute toxicities of untreated and treated hydrocarbonization effluents to *Daphnia magna*

	48-hr LC_{50}(μl/liter)[a]	95% confidence limits Lower	Upper
Untreated effluent			
Original	1,060	700	1,700
Synthetic	1,080	760	1,600
Treated effluent			
Original	116,000	82,000	164,000
Synthetic	96,700	77,000	128,000

[a] 48-hr LC_{50}(μl/liter) = dilution of effluent in well water which kills 50% of the *Daphnia magna* in 48-hr of exposure.

TABLE 4

The calculated contribution of each of the major components of the hydrocarbonization effluents to the toxicity of the effluents

	% of total effluent toxicity	
Component	Untreated effluent	Treated effluent
Phenol	18.0	0.4
O-cresol	22.5	0.0
P-cresol	47.8	0.0
M-cresol	3.0	0.0
Ammonia	8.8	80.1
Sulfate	0.0	0.7
Total nitrate	0.0	< 0.1
Total phosphate	0.0	1.7
Thiocyanate	0.0	0.6
Unidentified	0.0	16.5

toxicity of the effluent; ammonia contributed an additional 9%; and the remaining components of the effluent accounted for less than 1%. The additivity index calculated for the components of the untreated effluent was 0.07 (Table 2). This value was not significantly different from zero (simple additivity), indicating that the toxicities of the individual components of the effluent were additive.

The second effluent to be tested was the treated HCZ effluent. Its 48-hr LC_{50} was at a dilution of 111.60 ml/liter (Table 3), demonstrating that the treatment process reduced the acute toxicity of the untreated effluent by about 99%. The toxicity of the synthetic treated effluent (48-hr LC_{50} = 96.70 ml/liter was slightly greater than that of the original treated effluent (Table 3), although these differences were not statistically different (t-test, $p = 0.05$).

Ammonia was the predominant toxic component remaining in the effluent, contributing 80% of its toxicity (Table 4); phosphate contributed about 2%. The phenolics accounted for less than 0.5% of the treated effluent's toxicity as compared to 91% for the untreated effluent, and sulfate, nitrate, and thiocyanate each contributed less than 1%.

The additivity index calculated for the treated effluent is -2.52 (Table 2). This value is significantly less than zero and indicates that the toxicities of the individual components of the effluent were significantly less-than-additive in their combined toxicity.

DISCUSSION

Using the described procedure, the components of two coal conversion effluents present in acutely toxic concentrations were rapidly identified and quantified in respect to the contribution of each component to the toxicity of the effluent.

Phenols were found to be the major toxic components of an untreated HCZ effluent. The toxicity of the treated HCZ effluent was 1% of the toxicity of the untreated effluent, while the principal toxic component of the treated effluent was ammonia.

The acute toxicities of the components of the untreated effluent were simply additive. However, the toxicities of the components of the treated effluent were less-than-additive, i.e., the actual toxicity of the effluent was less than the predicted toxicity, based on its chemical composition and the toxicities of the individual components. One component of the treated effluent which is obviously exhibiting a less-than-additive toxicity is ammonia. The 48-hr LC_{50} of ammonia to *Daphnia magna* is 25 mg/liter, however ammonia was present at 86 mg/liter at the 48-hr LC_{50} dilution of the treated HCZ effluent (Table 2). At the 48-hr LC_{50} of the HCZ effluent, there was three times the concentration of ammonia necessary to kill 50% of the *Daphnia*. Obviously, some factor within the effluent is reducing the toxicity of the ammonia. Several explanations are possible.

Measurements of ammonia concentration taken during the course of the test indicated negligible losses, thus eliminating the loss of ammonia from the exposure beakers as a cause of the apparent lower toxicity of ammonia in the effluent.

The toxicity of ammonia to aquatic biota is greatly affected by the chemistry of the water in which it is dissolved. Although ammonia toxicity is influenced by alkalinity, temperature, free carbon dioxide, and dissolved oxygen (BROWN 1968), the factor of primary importance is pH (MCKEE and WOLF 1963), because it controls the dissociation of ammonia in solution. Ammonia is most toxic in its undissociated form (MCKEE and WOLF 1963). The higher the pH, the greater the proportion of ammonia in solution that will be undissociated. In the present study, the 48-hr LC_{50}

of ammonia was determined to be 25 mg/liter at a pH of 8.2; however, the pH of the effluent at the 48-hr LC_{50} concentration was 7.3, almost one whole pH unit less. At this lower pH, the ammonia present in the original effluent has a considerably lower toxicity than it would have at a pH of 8.2. For example, the toxicity of a given concentration of ammonia compounds toward fish was found to increase by 200% or more between pH 7.4 and 8.0 (MCKEE and WOLF 1963). The lower pH of the effluent would thus appear to explain the apparent lower toxicity of the ammonia present in the effluent as compared to ammonia tested by itself. This would, in turn, explain the apparent less-than-additive toxicities of the components of the effluent.

Several valuable uses can be made of the data obtained from this type of study:

(1) The effectiveness of treatment processes in reducing the acute toxicity of the effluent can be quickly assessed.

(2) The presence of chemical interactions between the components of an effluent can be quickly identified and evaluated. These interactions may affect the toxicity of the effluent and may, therefore, influence the way the effluent should be treated to reduce its toxicity. For example, the toxicity of the ammonia in the treated HCZ effluent appeared to be reduced due to the lower pH of the treated effluent. Any modifications of the treatment process which would change the pH of the effluent would be expected to influence the toxicity of the ammonia in it.

(3) The rapidily with which these data can be obtained should be of benefit to the designers and operators of waste treatment facilities at coal conversion plants for anticipating acute toxicity problems to aquatic organisms from releases of aqueous effluents.

The results obtained in these examples are not necessarily typical of all coal conversion effluents. Other compounds, besides phenols and ammonia, may be present in acutely toxic concentrations. Our analysis of a solvent-refined coal effluent identified both the organic base and the organic neutral fractions as contributing substantially to the acute toxicity of the effluent, while the inorganics were present in virtually nontoxic concentrations (PARKHURST et al. 1977).

There is considerable variation between the chemical compositions of aqueous effluents from different coal conversion processes. Even effluents from a single process may differ substantially, depending on operating conditions and the type of coal being processed. These factors point out the advantages of using rapid biological and chemical tests for identifying and evaluating the components of these effluents which are acutely toxic to aquatic biota.

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