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A Reevaluation of the Toxicity of Coal Conversion Process Waters

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The acute toxicity to Daphnia magna of both untreated and treated process waters from a hydrocarbonization (HCZ) coal conversion process was evaluated recently by PARKHURST et al. (1979). Phenol, ammonia, and the three cresol isomers displayed additive toxicity in the untreated HCZ effluent. However, the treated HCZ effluent, in which concentrations of ammonia, phenol, and the cresols were reduced by biological oxidation, was much less toxic than might have been predicted from the concentrations of the individual components. At the LC_{50} dilution for the treated HCZ effluent, the concentration of total ammonia present was more than three times the LC_{50} value for D. magna. This indicated a less-than-additive ammonia toxicity and/or antagonistic interactions among ammonia and the other constituents. The less-than-additive ammonia toxicity was calculated from total ammonia concentrations and was attributed by PARKHURST et al. to a lower pH in the treated HCZ effluent than in a separate ammonia toxicity bioassay.

But total ammonia includes both un-ionized ammonia (NH_3) and ionized ammonia (NH_4^+) in a pH- and temperature-dependent equilibrium. Un-ionized NH_3 is toxic to many aquatic organisms while NH_4^+ is relatively nontoxic (MCKEE and WOLF 1963). Therefore, if D. magna are indeed more sensitive to NH_3 than to NH_4^+, PARKHURST et al. incorrectly calculated the contribution of ammonia to the HCZ effluent toxicities by using total ammonia rather than un-ionized ammonia concentrations. Their interpretations of the importance of ammonia in these HCZ effluents may, therefore, be misleading and are reevaluated in the present report.

The purposes of this paper are (1) to clarify the role of ammonia in the toxicity of complex coal conversion wastewaters, (2) to reevaluate the toxic contribution of ammonia in the treated HCZ effluent, and (3) to compare these results with literature reports for other coal conversion effluents (DEGRAEVE et al. 1980, HERBERT 1962). For the U.S. Department of Energy's Hanna-3 underground coal gasification (UCG) condenser water, DEGRAEVE et al. evaluated the interaction of phenol and ammonia in the toxicity of this process water to aquatic biota. Similarly, HERBERT determined the toxic contributions of phenol and ammonia in spent coal distillation process liquors to rainbow trout.

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MATERIALS AND METHODS

We estimated the percentage of un-ionized ammonia in the HCZ coal conversion effluents and in the ammonia toxicity bioassays from the following equations of Emerson et al. (1975):

$$pK_a = 0.09018 + 2729.92/T, \text{ and} \quad (1)$$

$$f = 1/(10^{pK_a - pH} + 1), \quad (2)$$

where "T" is the Kelvin temperature, "pK_a" denotes the NH_4^+ - NH_3 dissociation constant, and "f" is the fraction of NH_3 present in the solution. The concentration of un-ionized NH_3 is thus the product of total ammonia concentration and the fraction of un-ionized ammonia present at that pH and temperature.

The contribution of each major component in each effluent was recalculated by the method of PARKHURST et al. (1979), replacing total ammonia with the calculated values for un-ionized ammonia. From these combined toxicities, we recomputed additivity indexes for the components in each effluent by the method of MARKING and DAWSON (1975), where:

$$S = \sum_i \frac{C_i}{LC_{50_i}}; \text{ and} \quad (3)$$

$$\text{additivity index (when } S \geq 1) = 1.0 - S; \text{ or} \quad (4)$$

$$\text{additivity index (when } S \leq 1) = \frac{1}{S} - 1.0. \quad (5)$$

Here "C_i" is the concentration of component "i" at the LC_{50} dilution of the effluent, "LC_{50_i}" is the toxicity (median lethal concentration) of the individual component i, and "S" represents the sum of the biological activity of all the effluent components. The 95% confidence interval for the index was calculated using the method of MARKING and DAWSON (1975). An index value of 0.0 indicates additive toxicity; index values greater than and less than 0.0 indicate, respectively, greater-than- and less-than-additive toxicity of the effluent components. In addition, we also calculated additivity indexes for the ammonia plus phenol toxicity bioassays reported by DEGRAEVE et al. (1980) and HERBERT (1962).

RESULTS

PARKHURST et al. (1979) reported toxicities from ammonia and effluent bioassays conducted at 25 C and at either pH 7.3 or pH 8.2. From the equations of EMERSON et al. (1975), we calculated a pK_a of 9.246 for the NH_4^+ - NH_3 equilibrium at 25 C. We also computed that at 25 C the pH 7.3 and pH 8.2 ammonia solutions contained 1.12% and 8.25% un-ionized ammonia, respectively. Thus, for the 25.4 mg/L total ammonia LC_{50} at pH 8.2, the un-ionized ammonia LC_{50} to D. magna was 2.08 mg NH_3/L (Table 1). And, as also shown in Table 1, for the untreated effluent we calculated that 0.17 mg NH_3/L was present at the LC_{50} dilution, while the treated effluent contained 0.94 mg NH_3/L at its LC_{50} dilution.

Because the pH of both the ammonia bioassay and the untreated HCZ effluent bioassay was the same (8.2), the fraction

TABLE 1. Contributions of un-ionized ammonia (NH_3) to Daphnia magna acute toxicity for ammonia and for treated and untreated HCZ coal conversion effluents[a]

Parameter	Ammonia solution	Untreated HCZ effluent	Treated HCZ effluent
pH	8.2	8.2	7.3
Temperature (°C)	25	25	25
$f = \frac{[NH_3]}{[NH_3 + NH_4^+]}$	0.0825	0.0825	0.0112
$[NH_3 + NH_4^+]$ at 48-h LC_{50} (mg/L)	25.4	2.1	85.9
Calculated NH_3 at 48-h LC_{50} (mg/L)	2.08	0.17	0.94
$\frac{[NH_3]\text{effluent}}{[NH_3]\ 48\text{-h } LC_{50}}$	-	0.08	0.45

[a]From PARKHURST et al. (1979).

of un-ionized ammonia was identical in the two solutions. Hence, the component toxicities and additivity index of the untreated effluent are correct as they appear in PARKHURST et al. However, the calculations for the treated HCZ effluent are incorrect because both the pH (7.3) and the fraction of un-ionized ammonia were lower than in the ammonia toxicity bioassay. Calculated from un-ionized ammonia rather than total ammonia concentrations, the revised contributions of each major component to the toxicity of the treated HCZ effluent appear in Table 2. And based on these calculations, the corrected additivity index for this effluent is +0.69 with a 95% confidence interval of -0.21 to 2.55, instead of -2.52 as reported by PARKHURST et al.

To evaluate the toxicity of the Hanna-3 UCG condenser water, DEGRAEVE et al. (1980) exposed fish and Daphnia pulex to ammonia, phenol, the UCG condenser water, and an ammonia plus phenol mixture at the same concentrations as found in the condenser water (Table 3). They reported LC_{50} dilutions of 0.11%, 0.21%, and 0.26%, respectively, for rainbow trout (Salmo gairdneri), fathead minnows (Pimephales promelas), and D. pulex exposed to the reconstituted ammonia-phenol mixture. From the corresponding ammonia and phenol toxicities, we calculated additivity indexes of +0.11, +0.67, and -0.07, respectively, at these dilutions (Table 4).

HERBERT (1962; Figure 12) plotted rainbow trout mean survival time vs. coal processing liquor dilution for both untreated and biologically treated effluents. From the curves for observed and predicted toxicities, we computed additivity indexes varying between +1.0 for 2-h mean survival and -0.2 for 10-h mean survival in the untreated effluent (Table 4). The treated effluent exhibited a +0.1 index value throughout the range of mean survivals.

DISCUSSION

PARKHURST et al. (1979) concluded that the toxicity of ammonia in the treated HCZ effluent was less than additive. But this conclusion was based on total ammonia concentrations rather than un-ionized ammonia (NH_3), which is the form of ammonia toxic to many aquatic organisms. Although the total ammonia concentration was 3.38 times higher in the LC_{50} dilution of the treated effluent than the LC_{50} concentration for total ammonia, a lower pH in the treated effluent decreased the proportion of un-ionized ammonia from 8.25% to 1.12%. Thus, the treated effluent contained, at its LC_{50} dilution, only 45% of the un-ionized ammonia LC_{50} concentration. The additivity index changed from -2.52 to +0.69 and now indicates an approximately additive or slightly greater-than-additive combined toxicity for the treated HCZ effluent components since the 95% confidence interval of the index overlaps zero. This new conclusion contradicts the previous interpretation of PARKHURST et al.

TABLE 2. Concentrations, acute toxicities to Daphnia magna, and contribution to the effluent toxicity of the major chemical components of the treated HCZ effluent[a]

Chemical component, i	Concentration in the treated HCZ effluent, C_i (mg/L)	48-h LC_{50_i} (mg/L)	$C_i\ (LC_{50_i})^{-1}$ for component	Contribution to the effluent's toxicity (%)[b]
Phenol	0.5	30.1	0.017	2.9
o-Cresol	0	5.0	0	0
p-Cresol	0	1.4	0	0
m-Cresol	0	18.8	0	0
Un-ionized ammonia(NH_3)	0.94	2.08	0.452	76.5
Sulfate	60.9	2233.0	0.027	4.6
Total nitrate	1.8	2008.0	0.001	0.2
Total phosphate	167.4	2399.0	0.070	11.8
Thiocyanate	1.4	57.4	0.024	4.1

[a]See PARKHURST et al. (1979) for original data.

[b]Contribution to the effluent's toxicity of component i =

$$\frac{C_i\ (LC_{50_i})^{-1}}{\sum_{i=1}^{n} C_i\ (LC_{50_i})^{-1}} \times 100$$

TABLE 3. Concentrations of ammonia and several phenolic compounds in coal processing effluents

Compound	Concentration (mg/L)			
	HCZ untreated effluent[a]	HCZ treated effluent[a]	UCG condenser water[b]	Spent still liquors[c]
Total ammonia (as NH_3)	1,970	770	20,000	4,500
Phenol	4,780	4	2,300	910
o-Cresol	990	< 1	d	160
m-Cresol	600	< 1	d	260
p-Cresol	500	< 1	d	220

[a]PARKHURST et al. 1979.

[b]DEGRAEVE et al. 1980.

[c]Calculated from HERBERT 1962.

[d]No measurements made.

TABLE 4. Additivity indexes for acute toxicity of actual and reconstituted coal processing effluents[a]

Test organism	Additivity index				
	HCZ untreated effluent[b]	HCZ treated effluent[c]	UCG condenser water[d]	Untreated Spent still liquors[e]	Treated spent still liquors[e]
Daphnia magna	+0.07	+0.69	-	-	-
Daphnia pulex	-	-	-0.07	-	-
Rainbow trout	-	-	+0.11	+1.0 to -0.2	+0.1
Fathead minnows	-	-	+0.67	-	-

[a]In reconstituted process waters, concentrations of ammonia and phenolic compounds duplicated original process water concentrations.

[b]PARKHURST et al. 1979; index values identical for actual and reconstituted effluent.

[c]Recalculated from PARKHURST et al. 1979; index values identical for actual and reconstituted effluent.

[d]Calculated from DEGRAEVE et al. 1980; index values for reconstituted ammonia plus phenol mixtures only.

[e]Calculated from HERBERT 1962, Figure 12; index values for actual effluents.

and emphasizes the importance of assessing ammonia toxicity from un-ionized, rather than total ammonia concentrations.

In all of the coal conversion effluents discussed here, phenol and un-ionized ammonia were the dominant toxic components. Although the relative abundance of these compounds varied among the process waters, the additivity of their toxicities was similar for the fish and Daphnia species tested. Additive to slightly-less-than-additive interactions occurred in all but the 2-h mean survival bioassay conducted by HERBERT (1962), in which the component toxicities were much greater than additive (+1.0 index value).

We suggest from the limited data available that coal conversion effluents may be expected to contain high concentrations of ammonia and phenol (Table 3). The LC_{50} dilutions of these process waters can be predicted from the individual LC_{50} concentrations of the major toxic components, the concentrations of these components in the effluents, and from the pH and buffering capacities of dilution waters.

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