DETERMINATION OF CELLSOLVE AND CHLOREX CONCENTRATIONS INHIBITORY TO INDUSTRIAL WASTE STABILIZATION POND TREATMENT EFFICIENCIES

E. M. Davis, E. C. Sullivan and T. D. Downs

The University of Texas, School of Public Health, P.O. Box 20186, Houston, Texas 77225, U.S.A.

BACKGROUND AND OBJECTIVES

A major chemicals and plastics industry treats its process wastewater in a series of three waste stabilization ponds which historically have produced an exceptionally high quality effluent. Detention times, for the primary, secondary and tertiary ponds, are 60, 50 and 40 days (150 total), respectively. Bis(2-chloroethyl)ether (Chlorex or CX) and 2-ethoxyethanol (Cellosolve or CS) are present in the manufacturing process. Although neither has ever been detected in the final (tertiary) effluent, the amount of each chemical resulting from an accidental spill which could adversely affect the performance of the wastewater treatment process has not been established. CX is one of the U.S. E.P.A.'s organic priority pollutants. CS is one of the hazardous chemicals listed as reportable if discharged at a level of 1 lb d⁻¹ (0.453 Kgd⁻¹) under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980. In considering these ponds at a 5.0 mgd (1.91x10⁴ m³d⁻¹) effluent discharge rate, the allowable CS concentration would be <0.024 mgL⁻¹. The purpose of this research was to identify the concentrations of CS and CX which would be inhibitory to the biodegradation function of each of the three ponds.

METHODS AND MATERIALS

Respirometric responses were measured with the Hach Model 2173 Manometric B.O.D. apparatus. Total Organic Carbon (T.O.C.) was analyzed with a Beckman Model 915 Carbonaceous Analyzer (Combustion Infrared Method). Quantification of CS was done using direct aqueous injection on a Perkin-Elmer Model 910 GC equipped with a polyethylene glycol, 0.53 mm x 30 m megabore capillary column and flame ionization detector. Chemical Oxygen Demand (C.O.D.) was analyzed using the Hach reactor digestion method. Dose-responses were calculated as ratios of the 5-day B.O.D. value of the different concentrations of CS or CX added to the wastewater samples to the control 5-day B.O.D. To take into account the activity of the CS or CX, the following relationship was used:

\[
\text{Calculated ThB.O.D. Removal} = \frac{\text{Observed dosed 5-day B.O.D.}}{\text{Control + Correction Factor}}
\]

The ThB.O.D. (Theoretical B.O.D.) is used here as the C.O.D. of the compound: Cellosolve = 1.93 mg C.O.D. mg⁻¹ compound and Chlorex = 1.08 mg C.O.D. mg⁻¹ compound. Therefore the "Correction Factor" alone was 1.93 x the amount in mgL⁻¹ dosed for CS or 1.08 x the amount dosed for CX. Wastewater samples for testing were obtained on a weekly basis from the influent points to all three waste stabilization ponds for the project duration (October 1986-June 1987). Testing was initiated within 24-hours after the samples were taken. All values for 5-day B.O.D. are the average of 3 or 4 manometric unit replicates per dose of the respective chemical.
RESULTS AND DISCUSSION

Initial testing for B.O.D. response of the influents of all three ponds showed very little, if any, oxygen uptake. Concurrent plate counting of the bacteria populations indicated that the populations present should have been high enough to show oxygen uptake at appreciable levels. Chemical analysis of the wastewaters then revealed that they were severely deficient in phosphorus. Additions of phosphorus were then made on all samples which were tested and reported here at levels which would approximate the anticipated average B.O.D. of the wastewaters. A B.O.D.:N:P of 100:20:1 was maintained, based on B.O.D. data obtained from the industry. This is significant in that the standard B.O.D. dilution bottle technique has nutrient and bacterial seed added. The larger volume (157 ml) samples of 100% wastewater tested in this project responded, more or less, as they would under actual on-site conditions.

Screening of CS dose-responses involved three sequences of dose concentrations. The "low series" was run in increments from 10 mg/l to ~70,000 mg/l. More resolution was needed between 10,000 mg/l and ~70,000 mg/l and the "high series" then was screened at between 13,000 mg/l and ~70,000 mg/l. The "combined series" was run between 10 mg/l and ~70,000 mg/l for the purpose of analyzing for T.O.C., C.O.D. and CS to quantify degradability.

Figures 1 and 2 and Table 1 summarize the dose-response data for the primary pond influent. The first notable observation in Figure 1 is the highly variable responses between sample dates. A decrease in oxygen uptake at a CS dose as low as 10 mg/l is shown for two test dates. Significant decreases in responses began occurring at 1,000-5,000 mg/l. Severe inhibition occurred above those levels. When the correction factor for CS was taken into account (Figure 2) a clearly distinguishable decrease in activity is shown at 1,000 mg/l. Taking this factor into account gives a more reliable result of what was occurring in the wastewater. Quantification of the three parameters (Table 1) shows a sharp drop in degradation of CS and amounts of T.O.C. and C.O.D. above the 1,000 mg/l concentration. Only very slight degradation in CS to none at all occurred above 5,000 mg/l. Note that the sample contained 120 mg/l CS on receipt, indicating even more so the high variability of the wastewater quality.

Figures 3 and 4 and Table 2 contain the data for the secondary waste stabilization pond influent. This series of wastewater samples appeared throughout the project to have been more uniform in quality than the primary pond sequence. The increase in dose-response (Figure 3) shown for the combined series appeared to have suggested a stimulatory effect up to 5,000 mg/l CS. Past that point, all tests showed inhibition. However, as before, the CS correction factor inclusion (Figure 4) clearly shows a remarkably similar inhibition response at 1,000 mg/l. This is also shown in Table 2. At 1,000 mg/l, 71% of the CS was degraded at 5 days whereas at the 5,000 mg/l level only 20% was degraded.

Figures 5 and 6 and Table 3 contain the data for the tertiary pond influent. Once the wastewater reaches this point, an even more stable quality occurs on-site. The dose-response ratios were all above 1.0, up to 10,000 mg/l CS concentration (Figure 5). This would suggest that the CS was stimulatory. Nevertheless, as in the first two pond series, almost complete inhibition of respirometric activity is shown in Figure 6 at the 1,000 mg/l level after taking into account the correction factor. The 10 mg/l data point is not included for the combined series because that replicate series of bottles had unreliable results: <10 mg/l compared to the control at ~60 mg/l. The data in Table 3 shown for the 10 mg/l CS appear to substantiate this contention. They also show the decrease in degradation of all three parameters at 1,000 mg/l. The tertiary influent appeared to have been more sensitive to a CS dose of 1,000 mg/l than the primary or secondary pond influents.

CX dose-responses were run at three concentrations on one set of samples. By agreement, this compound was of lesser concern as production would be phased out. Figures 7 and 8 summarize the oxygen uptake data for all three waste stabilization pond influents. The dose of 3,000 mg/l in the primary pond influent (Figure 7) appeared to have been stimulatory whereas 300 mg/l showed marked inhibition of activity in the tertiary influent. Inclusion of the correction factor (Figure 8) for the amounts of CX added shows that 300 mg/l CX was definitely inhibitory to the overall wastewater treatment activity in all three pond influents.

In summary, while measuring oxygen uptake is a recognized method for determining microbial activity in waste treatment processes, the use of larger sample sizes of wastewater in the treatment process, without nutrient dilution, appears to provide a more meaningful assessment of the actual field condition. In addition, taking into account the degradability of the test compounds, our results indicated that the wastewaters were not only deficient in phosphorus but also in other nutrients necessary for microbial activity.
Determination of CS and CX concentrations

compound itself adds more credibility to the respirometric results. The results of this research project showed that CS caused significant inhibition of overall degradation in the wastewaters at and above, 1,000 mg/L. CX was even more inhibitory. Decreases in biodegradation activity occurred in all wastewaters tested at, and above 300 mg/L. In many of the oxygen uptake dosing series, a lag period of up to two days was present before oxygen uptake occurred. That suggested that the microbial populations were responding to the chemical additions by acclimation before their normal respiration/degradation activity could proceed.

### TABLE 1

<table>
<thead>
<tr>
<th>CS Conc., mg/L</th>
<th>PRIMARY POND INFLUENT</th>
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<tbody>
<tr>
<td></td>
<td>Day 0, Day 5, Percent</td>
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<tr>
<td>Day 0, Day 5, mg/L</td>
<td>Change</td>
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</tbody>
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| 120*             | 992    | 716  | -27    | 2814 | 1880  | -33    | 50
| 130              | 1067   | 706  | -34    | 3068 | 1870  | -58    | 58
| 1120             | 1640   | 1433 | -13    | 4797 | 3712  | -25    | 885
| 5120             | 3970   | 3571 | -10    | 12745 | 10530 | -17    | 5000
| 10120            | 6859   | 6254 | -9     | 22376 | 19980 | -10    | 9520
| 13820            | 8999   | 8301 | -8     | 29509 | 26350 | -10    | 14100
| 41820            | 25222 | 123851 | -5    | 83587 | 75750 | -9.3   | 42700
| 69720            | 41378 | 39080 | -5    | 137438 | 123000 | -10    | 66300

*Sample contained 120 mg/L CS before dosing.

### TABLE 2

<table>
<thead>
<tr>
<th>CS Conc., mg/L</th>
<th>SECONDARY POND INFLUENT</th>
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<tbody>
<tr>
<td></td>
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<td>Day 0, Day 5, mg/L</td>
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| 10*              | 159    | 28   | -82    | 330  | 90    | -72    | 0.41
| 20               | 169    | 31   | -61    | 372  | 55    | -85    | 3
| 1010             | 745    | 427  | -37    | 2283 | 1319  | -42    | 287
| 5010             | 3075   | 2740 | -11    | 10949 | 8620  | -14    | 4010
| 10010            | 5964   | 5300 | -11    | 19680 | 17700 | -9.9   | 9290
| 13710            | 8104   | 7074 | -13    | 26813 | 27800 | +3.7   | 14700
| 27410            | 16043  | 13900 | -13.3  | 53277 | 49050 | -7.9   | 25900
| 69610            | 40483  | 34900 | -13.7  | 134742 | 123812 | -8    | 71100

*Sample contained 10 mg/L CS before dosing.

### TABLE 3

<table>
<thead>
<tr>
<th>CS Conc., mg/L</th>
<th>TERTIARY POND INFLUENT</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Day 0, Day 5, Percent</td>
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<tr>
<td>Day 0, Day 5, mg/L</td>
<td>Change</td>
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</table>
| 0                | 47     | 23   | -51    | 100  | 42    | -58    | 0
| 10               | 54     | 24   | -55    | 123  | 44    | -64    | 4.7
| 1000             | 627    | 477  | -24    | 2034 | 1409  | -30    | 564
| 5000             | 2957   | 2120 | -28    | 9800 | 8368  | -14    | 4176
| 10000            | 5846   | 5061 | -13    | 19431 | 17960 | -7     | 9183
| 13700            | 7986   | 7000 | -12    | 26564 | 24062 | -9     | 12550
| 27400            | 15925  | 13200 | -17   | 53028 | 51000 | -3.8   | 29870
| 69600            | 40365  | 37458 | -7    | 134493 | 120187 | -10    | 66360

*Sample contained 10 mg/L CS before dosing.
Fig. 1. Relative dose-responses of Cellosolve in primary pond influent. Low dose series 10/21, 12/8 and 12/30; high series 1/6 and 1/20; combined series 6/31.

Fig. 2. Primary pond influent dose-responses including correction factor for Cellosolve C.O.D. (Th.B.O.D.).

Fig. 3. Relative dose-responses of Cellosolve in secondary pond influent. Low dose series 2/3 and 2/10; high series 2/17 and 2/24; combined series 7/7.

Fig. 4. Secondary pond influent dose-responses including correction factor for Cellosolve C.O.D. (Th.B.O.D.).

Fig. 5. Relative dose-responses of Cellosolve in tertiary pond influent. Low dose series 3/10 and 3/24; high series 3/31 and 4/7; combined series 7/14.

Fig. 6. Tertiary pond influent dose-responses including correction factor for Cellosolve C.O.D. (Th.B.O.D.).

Fig. 7. Relative dose responses of Chlorex in primary, secondary and tertiary pond influents on 4/21/87.

Fig. 8. Chlorex dose-responses in primary, secondary and tertiary pond influents including correction factor for Chlorex C.O.D. (Th.B.O.D.).