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Research and Development



# Treatability Studies of Pesticide Manufacturing Wastewaters: Carbaryl



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April 1980

# **Treatability Studies of Pesticide Manufacturing Wastewaters: Carbaryl**

by

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## ABSTRACT

In February 1979 Research Triangle Institute (RTI) was requested by the Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP) of the U. S. Environmental Protection Agency (EPA) to conduct laboratory and pilot studies of the treatability of pesticides manufacturing wastewaters. The project is designed to investigate the suitability of individual pesticide manufacturing wastewaters for discharge to biological treatment systems, whether publicly owned treatment works (POTW) or on-site systems.

The approach taken with each pesticide manufacturing wastewater is prioritized that is, less costly, more available methods of treatment are investigated first. The preferred method of treatment is assumed to be biological treatment. If the pesticide is judged suitable to biological treatment, a judgement based on chemical and toxicological evaluation of the waste before and after treatment, additional options were not investigated.

Based on the results of the bench scale experimental work involved in this study, both carbaryl manufacturing wastewater, when mixed one part in nine parts municipal wastewater, and carbaryl itself, when spiked at 10 mg/L in municipal wastewater, appear suitable for biological treatment by acclimated systems if additional provision is made for removing ammonia in the effluents from these biological treatment systems. Other parameters investigated in this study including carbaryl,  $\alpha$ -naphthol, and toluene concentrations and the chemical oxygen demand (COD) all showed large reductions (90% or greater). The mechanisms of reduction of these parameters include combined hydrolysis and biodegradation of carbaryl and  $\alpha$ -naphthol, volatilization of toluene and biodegradation of species contributing to COD.

A large increase in ammonia concentration was noted in the effluent from the biological units treating carbaryl manufacturing wastewater.

This ammonia concentration made the toxicological evaluation of the effectiveness of treatment problematic by rendering the effluent more toxic than the influent. Ammonia stripping lessened this toxicity. Because the technology of nitrogen control has been extensively developed, these treatment options were not pursued further.

This report was submitted in partial fulfillment of Contract No. 68-02-3688 by the Research Triangle Institute under the sponsorship of the U. S. Environmental Protection Agency. This report covers the period February 20, 1979 to May 1, 1979 and work was completed as of May 31, 1979.

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## SECTION I

### INTRODUCTION

In February 1979 Research Triangle Institute (RTI) was requested by the Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP) of the U.S. Environmental Protection Agency (EPA) to conduct laboratory and pilot studies of the treatability of pesticides manufacturing wastewaters. The project is designed to investigate the suitability of individual pesticide manufacturing wastewaters for discharge to biological treatment systems, whether publicly owned treatment works (POTW) or on-site systems.

The approach taken with each pesticide manufacturing wastewater is prioritized, that is, less costly, more available methods of treatment are investigated first. The preferred method of treatment is assumed to be biological treatment. If the pesticide is judged suitable to biological treatment, a judgment based on chemical and toxicological evaluation of the waste before and after treatment, additional options are not investigated.

If pesticide manufacturing wastewater disrupts biological treatment systems, the possibility of pretreating the waste prior to biological treatment is investigated. Pretreatment options may include pH adjustments, filtration, flocculation, oxidation and others depending on the nature of the waste and its chemical composition.

If pretreatment does not make the waste compatible with activated sludge systems, adsorption techniques may be investigated. These may include both carbon and resin systems. The necessity for physical-chemical treatment of wastewaters will again be evaluated as with the biological treatment system.

This report details a study of the treatability of a wastestream resulting from the manufacture of carbaryl, a product of the Union Carbide Corporation manufactured at their Institute, West Virginia plant.

## SECTION 2

### CONCLUSION AND RECOMMENDATIONS

Based on the results of the bench scale experimental work involved in this study, both carbaryl manufacturing wastewater, when mixed one part in nine parts municipal wastewater, and carbaryl itself, when spiked at 10 mg/L in municipal wastewater, appear suitable for biological treatment by acclimated systems if additional provision is made for removing ammonia in the effluents from these biological treatment systems. Other parameters investigated in this study including carbaryl,  $\alpha$ -naphthol, and toluene concentrations and the chemical oxygen demand (COD) all showed large reductions (90% or greater). The mechanisms of reduction of these parameters include combined hydrolysis and biodegradation of carbaryl and  $\alpha$ -naphthol, volatilization of toluene and biodegradation of species contributing to COD.

A large increase in ammonia concentration was noted in the effluent from the biological treatment units relative to their influent. This ammonia concentration made the toxicological evaluation of the effectiveness of treatment problematic by rendering the effluent more toxic than the influent. Ammonia stripping lessened this toxicity. Because the technology of nitrogen control has been extensively developed, these treatment options were not pursued further.

The carbaryl manufacturing wastestream investigated in this study is presently mixed with other manufacturing wastestreams and treated in a manufacturer-operated aerated lagoon with approximately a 3-day retention time. Based on the study detailed below, this treatment process should provide an adequate treatment of the carbaryl manufacturing wastestream provided there is no interference from the components of other wastestreams and provided nitrification of ammonia occurs.

### SECTION 3

#### CARBARYL

##### CHEMICAL INFORMATION

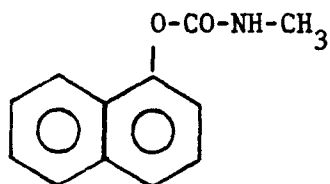
Chemical Names: Carbamic acid, methyl-1-naphthyl ester;  
N-methyl- $\alpha$ -naphthyluretha; 1 naphthol N-methylcarbamate

CAS No.: 63-25-2

Category: carbamate

Synonyms: Arylam, Atoxan, Caprolin, Carbaryl (DOT), Carbattox, Carbattox-60, Carbattox-75, Capolin, Compound 7744, Crag sevin, Denapon, Dicarbam, ENT 23, 969, Gamonil, Germain's, Hexavin, Karbaryl, Karbattox, Karbosep, Septene, Sevidol, SOK, Tricarnam, and others. (Fairchild, 1977).

Structure:



Properties:

M.W. 201.24

Solubility in water: 130 ppm at 25°C as determined in this study. Carbaryl chemically hydrolyzes to  $\alpha$ -naphthol at a rate which is pH dependent. Hydrolysis is accelerated at pH above neutral as shown below (Aly and El-Dib, 1971).

pH	Carbaryl half-life
7.0	10.5 days
8.0	1.8 days
9.0	2.5 hours
10.0	15 min.



## Application:

Wide spectrum insecticide for control of insects on cotton, vegetables, fruits, rice, sugarcane and ornamentals; used in agriculture, homes, animals, forests. Registered, 1959.

## MANUFACTURE

Figure 1 presents a generalized production and waste schematic for carbaryl manufacture.

## CURRENT WASTE DISPOSAL PRACTICE

Carbaryl manufacturing wastewater is presently combined with the effluent of other manufacturing processes at the Institute, West Virginia plant and treated in a system of aerated lagoons. This system consists of 3 aerated treatment basins run in parallel. Retention time of the entire system is reported to be approximately three days (plant engineer, personal communication).

The major carbaryl-containing wastestream is a continuous decantation stream generated during a solvent recovery step in the carbaryl production unit. This stream was sampled for this study. Other carbaryl inputs to the waste treatment systems include wash down from packing and cleaning procedures which is intermittent in nature and was not sampled.

Carbaryl has apparently been detected in a sample of the effluent from Union Carbide's waste treatment units at the Institute plant. Carbaryl concentration in a sample taken on 4/11/78 was found to be 260  $\mu\text{g/L}$  (Hathaway, 1979).

A possible interference in some methods of analysis for carbaryl should be noted. Routine in-plant analyses by Union Carbide personnel of production wastestreams known to be free of carbaryl have shown a compound which elutes at a similar retention time as carbaryl under the conditions for carbaryl analysis. This compound has not been identified, though it resists hydrolysis at high pH which is not characteristic of carbaryl. The method of analysis for carbaryl used by Union Carbide and the method used by Hathaway (1979) are described in Appendices F and G.

## ECOLOGICAL EFFECTS

Table 1 summarizes the published ecological effects data for carbaryl.

TABLE 1. ECOLOGICAL EFFECTS TESTING OF CARBARYL

Species	Duration	Result (LC <sub>50</sub> <sup>a</sup> )	Reference
<u>Stonefly,</u> <u>Pteronarcys</u> <u>californica</u>	48 hr	1.3 mg/L	Bond and Straub, 1973
<u>Daphnia pulex</u>	48 hr	6.4 mg/L	Bond and Straub, 1973
Brown trout	48 hr	1500 mg/L	Bond and Straub, 1973
<u>Gammarus lacustris</u>	48 hr	22 mg/L	Bond and Straub, 1973
Fathead minnow	96 hr	12 mg/L	Surber and Taft, 1962
Bluegill	96 hr	5.3 mg/L	Surber and Taft, 1962
<u>Daphnia magna</u>	48 hr	0.1 mg/L	Iliescu and Stefanescu, 1974
<u>Gobio gobio</u>	96 hr	1.0 mg/L	Iliescu and Stefanescu, 1974
Red crawfish	48 hr	3.0 mg/L	Muncy and Oliver, 1963
Fathead minnow	96 hr	9.0 mg/L	Carlson, 1971
Fathead minnow	Life cycle	0.21 to 0.68 mg/L	Carlson, 1971

<sup>a</sup>LC<sub>50</sub>--Concentration to kill 50% of a test population in the specified time.

#### ENVIRONMENTAL FATE

Half life of carbaryl in soil is dependent on numerous variables. Bollag and Lui (1972) state that a generally accepted half life of carbaryl in the soil is one week though others have shown stability in soil from 25 to 60 days before appreciable decay (Caro, Freeman and Turner, 1974). Bollag and Lui isolated fungi which were able to alter carbaryl by sidechain and ring hydroxylation.  $\alpha$ -Naphthol was shown to be more readily degraded by

the marine fungi and bacteria studied than carbaryl (Sikka, Miyazaki and Lynch, 1975).

It is difficult to separate the relative contribution of chemical and biological hydrolysis to the degradation of carbaryl. Paris et al. (1975), report that bacterial removal of carbaryl was dependent upon the rate of chemical hydrolysis of carbaryl. These authors also report that no sorption of carbaryl to microorganisms was found in their studies, though others have reported rapid sorption to saline sediments (Karinen et al., 1967).

#### HEALTH EFFECTS

An extensive review of the toxicological literature on carbaryl is contained in the volume: Drinking Water and Health (NRC, 1977). The NRC report classified the toxicity of carbaryl as moderate ( $LD_{50}$  for male rats 500 mg/kg; no effect for man at 0.13 mg/kg for 6 weeks). Carbaryl was not found to be either mutagenic, teratogenic, or carcinogenic after extensive testing. The Mark Commission (NRC, 1977) concluded that carbaryl was one of but three pesticides judged "not positive for carcinogenicity by appropriate tests in more than one species of test animals". The NRC report also concludes, "In general, metabolism of carbaryl and the appearance of metabolites in water systems would create no significant hazard in addition to that of carbaryl itself".

## SECTION 4

### TREATABILITY STUDIES

#### CHARACTERIZATION OF WASTEWATER FROM CARBARYL MANUFACTURE

Two grab samples of decantation wastewater were taken on two consecutive days during a normal winter operation period. Flow rate varied on the two days of sampling. Plant personnel estimated the flow during day 1 sampling to be approximately 6-7 gpm and flow rate on day 2 to be approximately 3-4 gpm. Pesticide content did not vary significantly between the two samples as analyzed according to the method given in Appendix A. Sample 1 contained 3.9 mg/L carbaryl and <0.15 mg/L  $\alpha$ -naphthol. Sample 2 contained 4.5 mg/L carbaryl and 0.25 mg/L  $\alpha$ -naphthol. These values are in close agreement with the analyses of split samples by plant personnel and represent typical values according to plant personnel.

Samples 1 and 2 were composited in approximate proportion to their flow rates (66% Sample 1 and 33% Sample 2). All tests and characterizations were run on this composited sample.

Table 2 summarizes the chemical parameters for this composited sample as analyzed according to the methods listed in Appendix B. The data indicate that the inorganic constituents should not provide difficulty in biological treatment.

One unusual result was noted in the determination of total dissolved solids (TDS). The method for the determination of TDS requires vacuum filtration of the sample through a 0.45  $\mu$  filter (Millipore HA). After filtration of the carbaryl waste and subsequent drying at 105° an oily residue was noted in the filtered sample that resisted further dessication. This residue was not noted during the dessication of the whole unfiltered sample. This artifact may arise from an interaction between components in the wastestream and the filter itself. The implication of these results on the conduct of the algal assay will be discussed below.



TABLE 2. WASTEWATER CHARACTERIZATION OF THE COMPOSITED CARBARYL SAMPLE

Parameter (units)	Value
pH	8.2
Cl <sup>-</sup> (mg/L)	120
Alkalinity (mg/L as CaCO <sub>3</sub> to pH 4.5)	385
Total kjeldhal nitrogen (mg/L as N)	1100
NH <sub>4</sub> -N (mg/L as N)	158
NO <sub>2</sub> + NO <sub>3</sub> (mg/L as N)	5.2
COD (mg/L)	4100
Total solids (mg/L)	100
Total dissolved solids, (mg/L)	75
Settleable solids (mg/L)	Trace
Carbaryl (mg/L)	4.3
Toluene (mg/L)	160

## BIOLOGICAL TREATABILITY STUDIES

The carbaryl composite sample was diluted 10% (v/v) with municipal wastewater which had been allowed to settle for 2 hours to simulate primary sedimentation. This mixture was then fed to bench-scale activated sludge (AS) units (test units) as described in Appendix C. Two AS units fed undiluted settled municipal wastewater were run as controls. Retention time on the AS units was 8 hours. Dissolved oxygen in the aerator section of the units was maintained at a minimum of 2 mg/L with an exception noted below. Mixed liquor volatile suspended solids (MLVSS) was initially determined to be 1800-2000 mg/L for the control units and the test units. Food to microorganism (F/M) ratio based on influent chemical oxygen demand (COD) values was initially approximately 0.94 day<sup>-1</sup> for the test units which is a relatively high level. F/M ratios in the control units averaged 0.30 day<sup>-1</sup>. MLVSS quantity in the test units was allowed to increase until it reached a value of 3100 mg/L on day 14. F/M ratios at that point were approximately 0.6 day<sup>-1</sup> based on influent COD values.

Figures 2 and 3 give the influent and effluent COD values for test and control units. A large drop in effluent COD values was noted after day 13

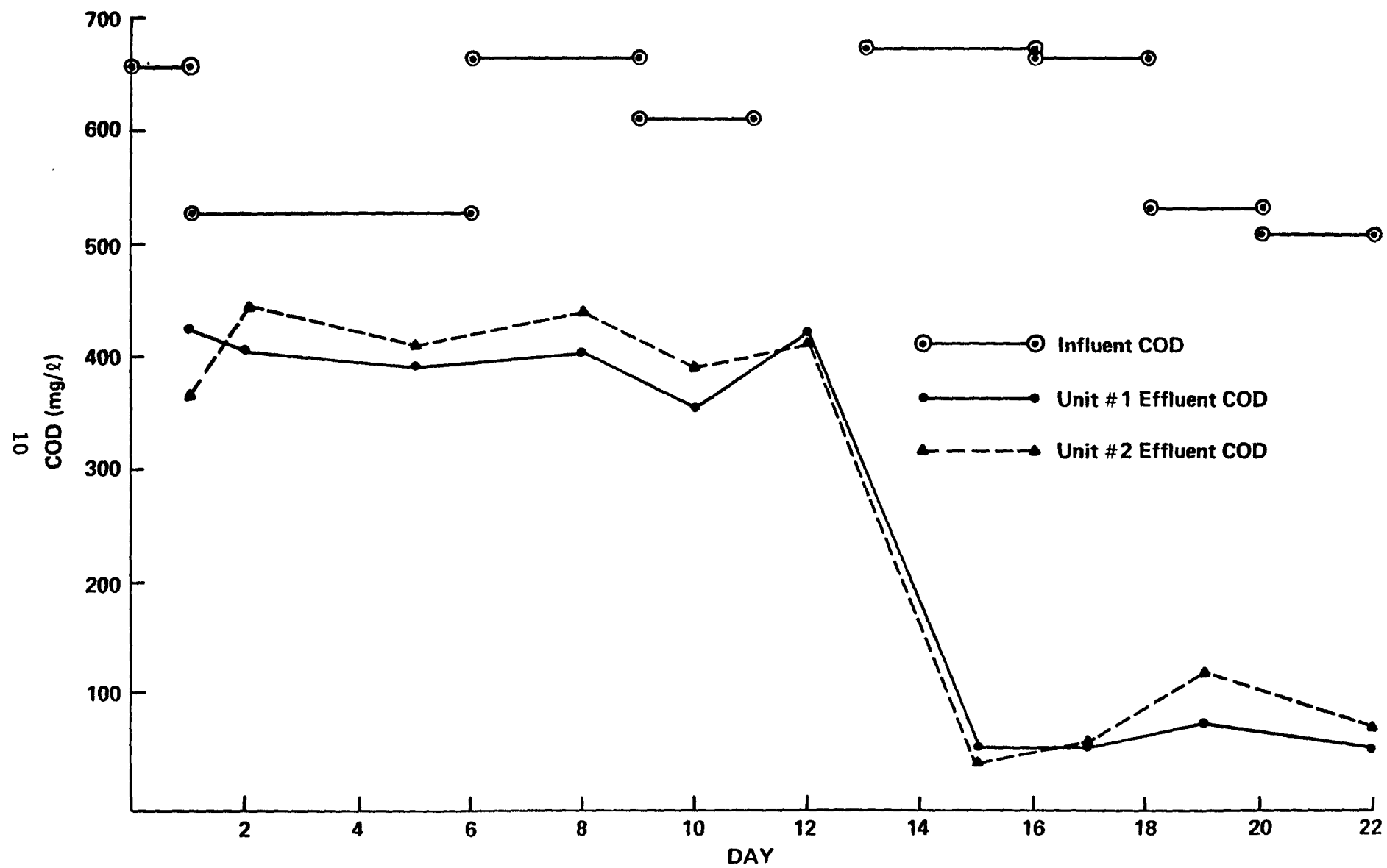


Figure 2. Influent and Effluent COD Values for Test Activated Sludge System

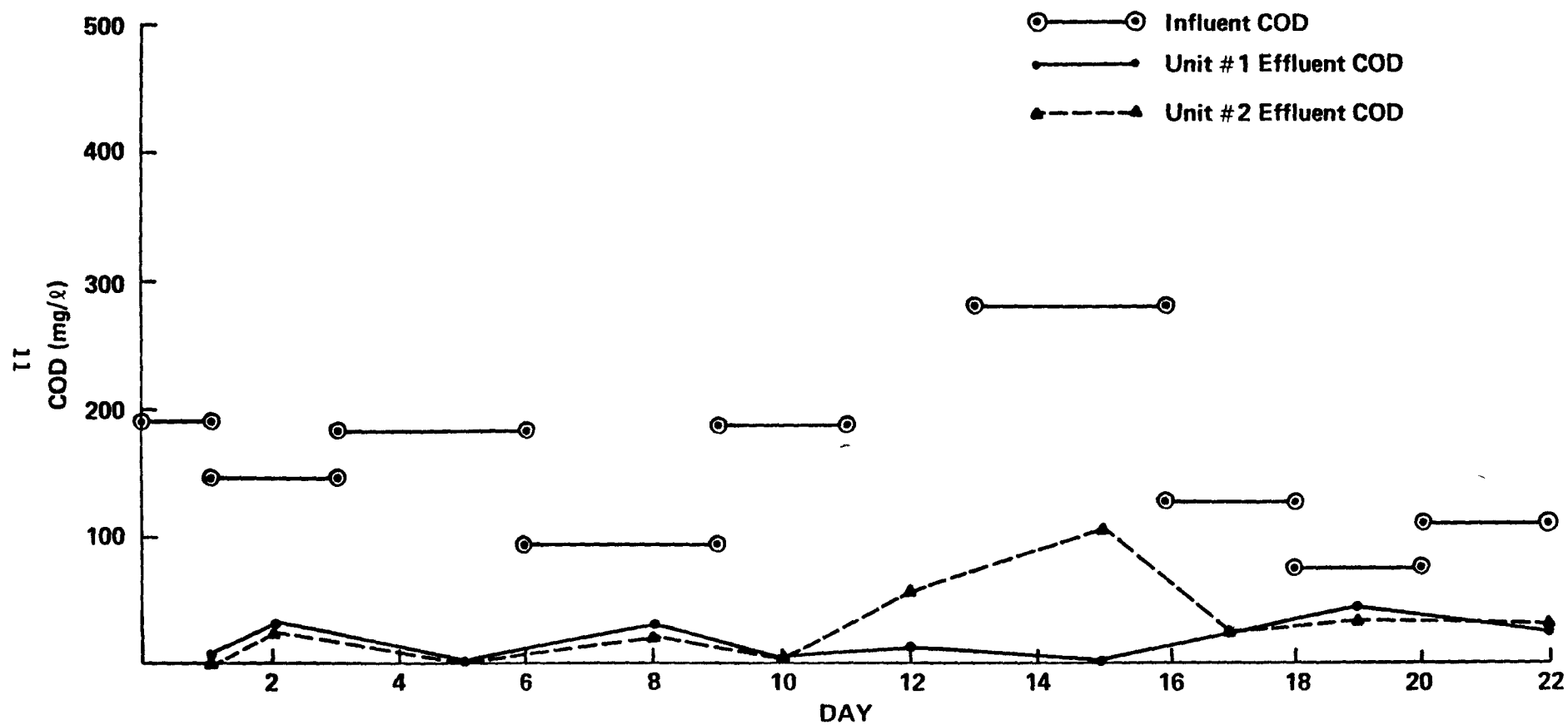


Figure 3. Influent and Effluent COD Values for Control Activated Sludge Units.

in the test units. On day 12 it had been noted that dissolved oxygen levels in both test unit reactors had dropped below 1 mg/L. Air flow to the test units was doubled on day 12 from 200 to 400 mL per minute. The increase in air flow, coupled with the gradual increase in MLVSS, resulted in a dramatic increase in COD removal. From day 15 on COD reduction averaged 89%, with influent averaging 595 mg/L and effluent averaging 66 mg/L.

Analysis for carbaryl and  $\alpha$ -naphthol revealed that carbaryl levels in the carbaryl manufacturing wastewater composite sample had dropped to 1.0 mg/L during the second week of biological testing period, presumably through the mechanism of chemical hydrolysis. The corresponding  $\alpha$ -naphthol levels were determined to be 0.3 mg/L. Carbaryl level in the influent to the test units was determined to be 0.06 mg/L instead of the expected 0.10 mg/L. Sorption of carbaryl to particles in the influent municipal wastewater could account for the losses.

Straight injection of aqueous effluent samples by the method presented in Appendix 1 revealed no carbaryl or  $\alpha$ -naphthol in the effluent of either A.S. unit (detection limit of 50  $\mu$ g/L). Extraction of samples with methylene chloride and concentration of the extract likewise revealed no carbaryl or  $\alpha$ -naphthol in effluent of units (detection limit 0.5  $\mu$ g/L). Recovery of carbaryl spiked in samples of wastewater and extracted and concentrated as above was 91%.

To examine the possible role of sorption of carbaryl onto bacterial cells, sludge samples from the test units and control units were extracted with methylene chloride and analyzed for carbaryl and  $\alpha$ -naphthol. Emulsion problems were encountered with all sludge samples during the extraction step. Filtration through glass wool followed by filtration through phase-separating filter paper alleviated some of these problems. However, recovery of carbaryl spiked at levels of 2 mg/L in municipal sludge was only 31%.

Because of incomplete resolution of other compounds in sludge with similar elution times as carbaryl in the high pressure liquid chromatographic (HPLC) system used, an absolute determination of carbaryl levels was not possible. Carbaryl concentration was no greater than 0.01 mg/L in sludge in the test units. Given the influent and effluent levels of carbaryl, this concentration in the sludges would not represent any sorptive accumulation.  $\alpha$ -Naphthol was not detected in any of the samples.

To test the possible role of air stripping in the removal of volatile organics an air stripping control (ASC) unit was run. Composite carbaryl wastewater was mixed 10% in deionized water (DIW) and pumped through an activated sludge unit which contained only DIW. An eight hour retention time and an air flow of 400 ml/min was maintained in the ASC unit. COD measurements were taken of the influent and effluent to the ASC units over a two day period. No difference was measured in the influent or effluent values (420 mg/L for both influent and effluent). This value corresponds to that expected of a 10% dilution of the composite carbaryl waste.

Toluene analyses were performed on both the influent and effluent of the biological treatment units and air stripping controls by the purge and trap method (Bellar and Lichtenberg, 1974; Bellar, Lichtenberg and Eichelberger, 1976). Analysis of data provided in Table 3 shows that only minimal handling of carbaryl waste will cause a substantial reduction in toluene concentration. The routine handling required to dilute samples and the subsequent exposure of samples to the open air during the pumping of influent over a 24 hour period is sufficient to reduce toluene concentration by 85 to 95 percent. Additional reduction in toluene concentration occurred after passage through a Swisher unit. It will be noted that this reduction in toluene concentration does not effect the COD determination. The dichromate digestion involved in COD measurement provides only minimal oxidation of aromatic compounds.

To more adequately test the biodegradation of carbaryl, a series of tests were run on municipal wastewater spiked at a concentration of 10 mg/L with technical grade carbaryl. Three activated sludge units (test units) were fed settled municipal wastewater diluted with carbaryl saturated deionized water to give a final calculated carbaryl concentration of 10.0 mg/L compared with a carbaryl concentration of 4.3 mg/L in the composited carbaryl wastewater sample. Three activated sludge units (control units) were fed with municipal wastewater diluted with a corresponding amount of unspiked DIW. New influent was mixed every 48 hours.

Immediately upon mixing of test unit influent an aliquot was withdrawn for carbaryl analysis. Aliquots were filtered through a 0.45 $\mu$  Millipore HA filter. Analyses of influent over the period of the study showed that carbaryl levels averaged 7.3 mg/L. Analyses of influent after its 48 hour

TABLE 3. TOLUENE CONCENTRATIONS IN VARIOUS FRACTIONS  
OF CARBARYL WASTEWATER

Sample	Toluene concentration (mg/L)
Carbaryl waste undiluted	160
Biological treatment units (10% carbaryl waste in municipal waste)	
Influent	2.5
Effluent	0.001
Air stripping control units (10% carbaryl waste in deionized water)	
Influent	0.9
Effluent	0.1

"shelf life" showed that carbaryl levels averaged 7.0 mg/L. The difference between the 10 mg/L spiked levels and the 7.3 mg/L analyzed levels probably represents sorbtion of carbaryl to influent solids and its loss during the filtration of samples prior to analysis by HPLC.

MLVSS levels were maintained between 1740 and 2300 mg/L. 0.85g/L of  $\text{NaHCO}_3$  was added to influent samples to maintain the pH in the units from 7.3 to 7.65. Residence time in the units was 8 hours. Dissolved oxygen was maintained between 2.0 and 5.5 mg/L. Temperature in the units varied from 20.7 to 25.2°C.

Figure 4 presents data on percentage reduction in carbaryl concentration over time in the test units. From day 7 on reduction was complete except for a period around day 15 when aeration difficulties were experienced in one unit. During the same period the COD reduction in the test units averaged 83%, with the influent averaging 227 mg/L and the effluent averaging 39 mg/L (range 24 to 60). The COD reduction in test units was 84% with the influent averaging 230 and the effluent averaging 37 (range 28 to 48).

As these data indicate, carbaryl is readily degraded in activated sludge systems after a short acclimation period.

#### EFFECT OF BIOLOGICALLY TREATED CARBARYL WASTEWATER ON ALGAE, FISH AND DAPHNIA

Algal assays were conducted in accord with the procedures outlined in

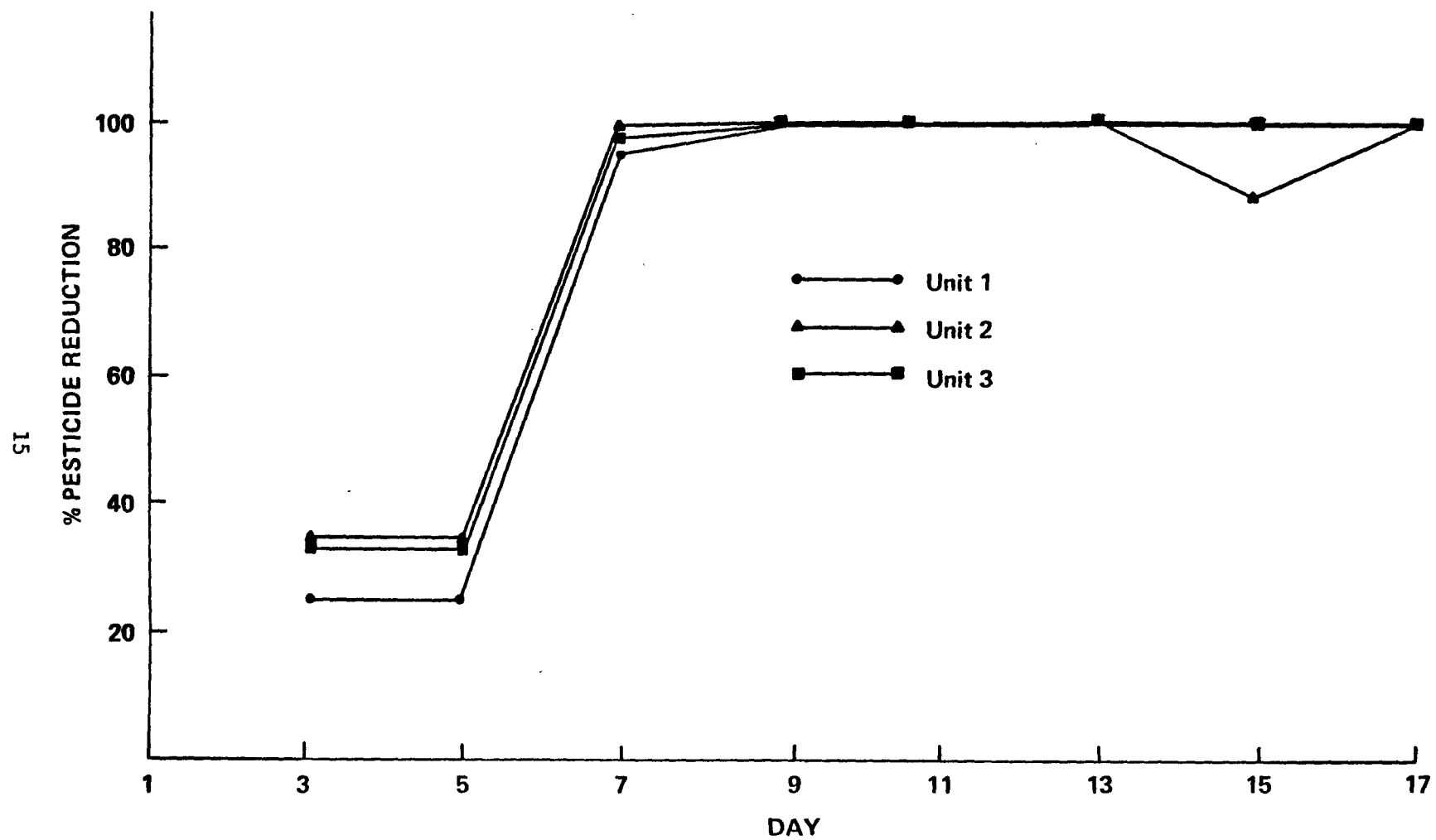


Figure 4. Pesticide Reduction in Activated Sludge Units Fed Municipal Sewage Spiked to 10 mg/l with Carbaryl

EPA manual: The Selenastrum Capricornutum Printz Algal Assay Bottle Test and described in Appendix D. Samples were vacuum-filter sterilized through a 0.45  $\mu$  filter.

Table 4 presents the results of an algal assay on the untreated carbaryl manufacturing wastewater. The data on algal growth in test flasks are presented in terms of percent of the growth in the control flasks on day 14 of the test. As can be seen in Table 4 the algal  $EC_{50}$  (concentration effective in reducing growth to 50% of controls) for carbaryl wastewater lies between 0.01 and 0.1 mL per liter.

When mixed 10% with municipal wastewater, the toxicity to algae decreased remarkably. As shown in Table 5 the  $EC_{50}$  for influent to the AS units was approximately 1000 mL/L. On the other hand the effluent from the AS units showed an increased toxicity over the influent. As shown in Table 6, the  $EC_{50}$  for the effluent samples was between 100 and 320 mL/L.

A similar pattern was exhibited by the fish bioassay using fathead minnows. The bioassay procedure is described in Appendix E. As shown in Table 7, the  $LC_{50}$  (concentration lethal to 50% of the test population) of carbaryl wastewater was approximately 100 mL/L. Table 8 shows the  $LC_{50}$  of the influent to the test units was between 320 and 1000 mL/L. The  $LC_{50}$  of the effluent from the AS units as shown in Table 9 was between 100 and 320 mL/L (Table 9).

It was hypothesized that the conversion of organic nitrogen to ammonia by biologically mediated processes in the treatment units caused an increase in the toxicity of the effluent from the AS unit. The ammonia levels increased from 30 mg/L in the influent to 110 mg/L in the effluent.

To test the biological significance of this ammonia concentration an additional bioassay was conducted comparing ammonia stripped samples with unmanipulated samples. To strip the test unit effluent of ammonia, the sample pH was raised from 7.2 to 14. Samples were aerated for 2 hours and pH readjusted to 7. Due to sample volume limitations this bioassay was conducted with Daphnia pulex. The results of this bioassay are presented in Table 10. As can be seen, the toxicity of the ammonia stripped effluent was less than that of the unmanipulated sample effluent or the influent. It could, of course, be argued that the stripping process may have removed some other volatile, toxic component of the effluent. However, these samples



TABLE 4. EFFECT ON ALGAL GROWTH OF CARBARYL MANUFACTURING WASTEWATER

Carbaryl wastewater (mL/L)	0.001	0.01	0.1	1.0
Growth (% of control on day 14)	137%	84%	0.8%	0.24%

TABLE 5. EFFECT ON ALGAL GROWTH OF CARBARYL MANUFACTURING WASTEWATER MIXED 10% WITH MUNICIPAL WASTEWATER

Carbaryl wastewater (mL/L)	100	320	1000
Growth (% of control on day 14)	107%	120%	64%

TABLE 6. EFFECT ON ALGAL GROWTH OF CARBARYL MANUFACTURING WASTEWATER MIXED 10% WITH MUNICIPAL WASTEWATER AND BIOLOGICALLY TREATED

Carbaryl wastewater (mL/L)	100	320	1000
Growth (% of control on day 14)	98%	25%	0.2%

TABLE 7. EFFECT ON FISH SURVIVAL OF CARBARYL MANUFACTURING WASTEWATER<sup>a</sup>

Carbaryl wastewater (mL/L)	0.0	10	18	32	56	100
Fish surviving 96 hr (%)	100%	100%	100%	100%	80%	40%

TABLE 8. EFFECT ON FISH SURVIVAL OF CARBARYL MANUFACTURING WASTEWATER MIXED 10% WITH MUNICIPAL WASTEWATER<sup>a</sup>

Carbaryl wastewater, mL/L	0.0	100	320	1000
Fish surviving 96 hr (%)	100%	100%	100%	0%

TABLE 9. EFFECT ON FISH SURVIVAL OF CARBARYL MANUFACTURING WASTEWATER MIXED 10% WITH MUNICIPAL WASTEWATER AND BIOLOGICALLY TREATED<sup>a</sup>

Carbaryl wastewater, mL/L	0.0	100	320	1000
Fish surviving 96 hr (%)	100%	100%	0%	0%

<sup>a</sup>Test population, 10 fish per concentration.

TABLE 10. EFFECT ON DAPHNIA SURVIVAL OF AMMONIA STRIPPING OF EFFLUENT SAMPLES FROM CARBARYL TEST UNITS<sup>a</sup>

Diluted (m/L)	Effluent ammonia stripped		Effluent unmanipulated		Influent unmanipulated	
	320	1000	320	1000	320	1000
Survival of Daphnia at 24 hrs (%)	60%	0%	0%	0%	0%	0%

<sup>a</sup>Test population, 10 organisms per concentration.

had previously been subjected to 8 hours of air stripping under neutral pH conditions during passage through an AS unit. This aeration would eliminate those volatile compounds which do not show a volatility-pH relationship characteristic of ammonia.

#### CONCLUSIONS

Based on the initial examination involved in this study, carbaryl manufacturing wastewater and carbaryl appear suitable for biological treatment by acclimated systems if additional provision is made for ammonia reduction. The production of ammonia in the digestion of this waste could provide toxicity problems if some form of ammonia removal is not employed or if the effluent is not diluted substantially. Because this technology is well established, extensive study in this area was not undertaken. The reader is directed to the EPA Technology Transfer Manual: Process Design Manual for Nitrogen Control for further information on these systems.

The execution and interpretation of various bioassays conducted on multi-component wastestreams, particularly those containing volatile compounds should recognize certain sources of uncertainty. A primary concern is the maintenance of sample integrity through the manipulations which are a part of many bioassay procedures.

The filter sterilization step required by algal assays can be a particularly important, especially if done under a vacuum. The loss of volatile components in the sample during vacuum filtration is an obvious result. In addition, the filter itself might provide active sites for the chemical formation of compounds not found in the unfiltered sample. This possibility

was noted in conjunction with the discussion of the determination of dissolved solids in carbaryl wastewater.

The sorption of toxic components to particulate portions of samples and their subsequent removal in the filtration step also provides a source of interference. This process could account for the reduction in toxicity to algae of carbaryl wastewater mixed 10% in municipal wastewater. This reduction in toxicity is greater than that expected by a simple 1:9 dilution.

While the fish or daphnia bioassays require much less sample manipulation than the algal assay, the maintenance of sample integrity can still be a problem. The loss of volatile compounds over the 96 hour test period will occur as the samples are exposed to open air. It might be argued that this loss represents an environmental reality; the volatile components of a waste will become less available over time. However, as with many of the factors involved in biological testing, the problem remains one of adequate laboratory accounting of environmental processes.

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## APPENDIX A

### ANALYTICAL PROCEDURE FOR DETERMINATION OF CARBARYL AND $\alpha$ -NAPHTHOL

The procedure for the analysis of carbaryl and  $\alpha$ -naphthol was adapted from Sparacino and Hines (1976) and involves the separation and quantitation of compounds by high-performance liquid chromatography (HPLC) with a reverse phase column and an ultraviolet absorption detection system.

A modular liquid chromatographic system was used for analyses. The basic system consisted of the following components: 2 M6000 pumps with an M660 solvent programmer and a U6K injector (Waters Assoc.); Model SF 770 variable wavelength detector (Schoeffel Inst.). A reverse phase column, packed in our laboratory, was employed. The column was packed with Partisil 10 bonded with octadecyl trichlorosilane in the conventional manner. The mobile phase consisted of acetonitrile mixed 40% in distilled water. A wavelength of 222 nm was used for the detection of both carbaryl and  $\alpha$ -naphthol. Flow rate of mobile phase was 2 mL/min. Sample injection size was either 10  $\mu$ L or 100  $\mu$ L. Samples were directly analyzed by HPLC. Separate calibration curves were run for each injection size. Detection limit of the system at these conditions was 0.5 nanograms carbaryl and 1.0 nanograms of  $\alpha$ -naphthol. Standard deviation of carbaryl determination at 0.25 mg/L was 5.6% and at 1.0 mg/L was 7.5%.

All samples were filtered through a 0.45  $\mu$  Millipore HA filter prior to analysis.

## APPENDIX B

### ANALYTICAL PROCEDURES FOR ROUTINE WASTEWATER CHARACTERIZATION

Routine wastewater analyses were conducted according to Standard Methods for the Examination of Water and Wastewater, 14th Edition, (APHA, AWWA, WPCF, 1976).

#### pH--

pH was determined electrometrically by Method 424.

#### Chloride--

Chloride was measured by the mercuric nitrate method (Method 408 B)

#### Acidity--

Acidity, as  $\text{CaCO}_3$ , was determined by Method 402.

#### Alkalinity--

Alkalinity, as  $\text{CaCO}_3$ , was determined by Method 403.

#### Nitrogen Forms--

Total Kjeldahl nitrogen was determined after digestion, according to Method 421. Ammonia ( $\text{NH}_3\text{-N}$ ) was determined by an acidimetric method as described in Sections 418 A and 418 D. Nitrite and nitrate nitrogen ( $\text{NO}_2\text{-N}$ ,  $\text{NO}_3\text{-N}$ ) were determined by the Devarda's alloy method (419 F).

#### COD--

Chemical oxygen demand (COD) was determined by Method 508.

#### Residues--

Suspended solids (SS) were determined by Method 208 D. Total solids (TS) were determined by Method 208 A. Total dissolved solids (TDS) were determined by Method 208 A. Settleable solids were determined by Method 208 F.

## APPENDIX C

### PROCEDURES FOR CONDUCTING ACTIVATED SLUDGE TREATABILITY TESTS

For biological treatability studies the bench scale, complete-mix, continuous-feed, activated sludge unit designed by Swisher (1970) was employed (Figure C-1). This unit has an aerator capacity of 0.3 L and a settler capacity of 0.075 L. The unit is made entirely of glass, avoiding the possibility of contamination by organics leaching from the container. Continuous feed to the units was supplied through Teflon tubing by a peristaltic pump to give the nominal retention time of 8 hours.

The units were started with activated sludge from the Hope Valley Treatment Plant, Durham, NC, which treats municipal wastewater. The units were then fed from a reservoir of primary wastewater from the Chapel Hill Treatment Plant. When a steady-state condition was reached, as indicated by consistent effluent quality in terms of COD and mixed liquid suspended solids levels, the feed to the test units was spiked with pesticide wastewater. Control units were fed only primary wastewater.

The pesticide spiked wastewaters were prepared by adding pesticide wastewater to the primary municipal wastewater which had been allowed to settle for a 120 min to simulate primary settling. Routine determinations were made of dissolved oxygen, pH, mixed liquor volatile suspended solids in the aerator and COD, and pesticides. Dissolved oxygen was determined with an oxygen probe (Yellow Springs Instrument Co.).



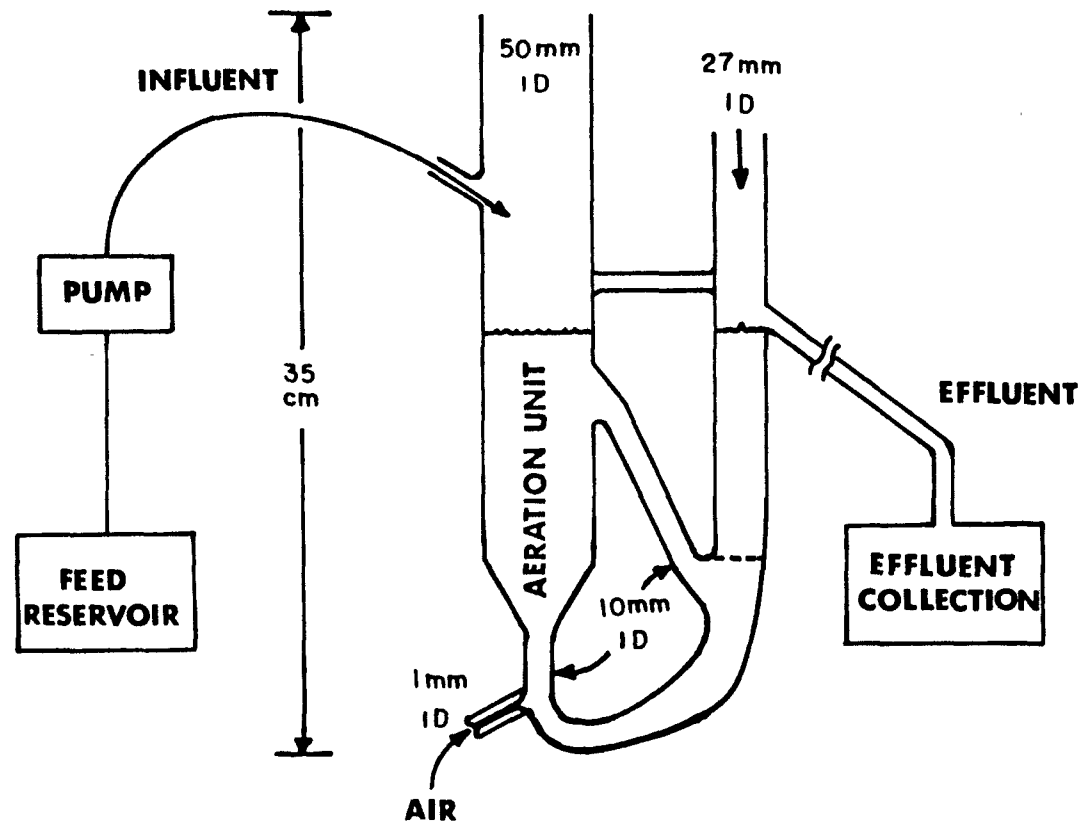


Figure C-1. Diagram of activated sludge pilot unit.

APPENDIX D  
PROCEDURES FOR ALGAL ASSAY TESTS

Algal bioassays were conducted according to the freshwater algal assay procedure described in the report The Selenastrum Capricornutum Printz Algal Assay Bottle Test (Miller, Greene, and Shiroyama, 1978). The test alga was Selenastrum capricornutum Printz, obtained from the National Eutrophication Research Program, EPA, Corvallis, Oregon. This test was designed to measure algal response to changes in nutrient concentrations and to determine toxicity or inhibition.

Wastewaters to be tested were filter sterilized through a sterile prewashed membrane filter (Millipore Filter, 0.45  $\mu$ m pore size). Serial dilutions were then made in sterile algal media to give the appropriate final concentration. Sufficient inoculum was added to produce an initial cell concentration of  $10^4$  cells/mL.

In each set of experiments, algal growth in the presence of a series of concentrations of the wastewater added to the nutrient medium was compared to algal growth in the nutrient medium alone. Growth was determined by direct counts of the algae during the 10-14 day incubation period. Effect of the wastewater on algal growth was determined in terms of the effect on the cell yield. Direct cell counts were performed by an automated procedure utilizing a Fisher Scientific Model FO 16 particle counter.

The tests were conducted in water bath shakers at  $24 \pm 2^\circ$  C and at approximately 80 oscillations per minute with constant white fluorescent lighting at 4300 lux. Test containers were 250 mL Erlenmeyer Pyrex flasks containing 60 mL of test medium and covered with an inverted Pyrex beaker.

The method of expressing inhibitory or stimulatory effects was that recommended by Miller et al. (1978), i.e., as the percent growth inhibition (I) or stimulation (S), as compared to growth in a control culture without the test materials. These authors suggest that, in general practice, the results be based on the growth at 14 days, i.e., as %  $I_{14}$  or %  $S_{14}$  at a given concentration of the effluent being tested.

Decreased growth, compared to the control, is evidence of an inhibitory effect. The manner in which the test is conducted does not allow determination of whether this inhibition is temporary (algistatic) or permanent (algicidal). Such a determination would require further testing by subculturing into fresh medium free of the test material.

## APPENDIX E

### PROCEDURE FOR FISH BIOASSAY TESTS

The fish bioassay procedure chosen was the standard 96-hour static bioassay (APHA, et al., 1976; Duke et al., 1977). The static method has been criticized as being rather simplistic, and more complex alternate methods have been suggested. However, the relative simplicity and economy of the static method make it the method of choice in initial screening. The test fish was the fathead minnow, Pimephales promelas, selected from a list of recommended species prepared by D. I. Mount of the National Water Quality Laboratory (as reported in Cairns, 1969). This species has been widely used in fish bioassay studies and is adaptable to laboratory conditions. Test fish were obtained from Kurtz's Fish Hatchery, Elverson, PA. New shipments of fish were routinely exposed on arrival to the broad-spectrum antibiotic tetracycline HCl at a dose of about 13 mg per gallon of water for 24-48 hr. This treatment helps prevent introduction into the stock tank of diseases from fishery stock or from fish damaged in shipment. On evidence of disease in the stock tanks, the tetracycline treatment was repeated. Fish were maintained in 30-gal. glass aquaria equipped with aeration devices and recirculating filtration. The water was Durham tapwater which was passed through a combined selective ion exchange and activated carbon system which removes 99+% of the organics and ionics present in the water. The water was then reconstituted by the addition of 48 mg/L  $\text{NaHCO}_3$ , 30 mg/L  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , 30 mg/L  $\text{MgSO}_4$ , and 2 mg/L KCl. The tanks were kept in a room maintained at  $24 \pm 2^\circ \text{C}$ , with a light cycle of 8-hr dark and 16-hr light.

Small-scale laboratory bioassays were conducted to determine the range of concentration to be tested in full-scale tests. For these screening tests solutions were prepared as decimal dilutions of the wastewater (such as 0.01, 0.1, 1.0 percent). A test volume of 3 liters and 3 fish per container was used.

Based on results of the screening assays, a full-scale test range was chosen, with the concentrations falling between the highest concentration at which all fish or most of the fish died. In these tests, the  $LC_{50}$  was determined by testing a series of concentrations based on progressive bisection of intervals of the logarithmic scale, such as 1.0, 1.8, 3.2, 5.6, and 10.0 percent, multiplied as necessary by any power of 10. These values are evenly spaced when plotted on a logarithmic scale.

In each test series, control tests were conducted concurrently with the experimental dilution water. In the large scale tests, results were considered invalid if more than 10% mortality occurred among the control fish. In the large scale tests, test containers were 10-gallon glass aquaria containing 15 liters of test solution. To test each experimental concentration, 10 fish were used. Fish were not fed for 48 hr prior to testing nor during the tests.

Use of 10 or more test fish per toxicant concentration has been the "usual practice" for short-term static tests according to Standard Methods (APHA et al., 1976). As noted in this document, "a number of factors govern the precision of the results of a bioassay and the arbitrary setting of the number of test organisms will not assure a certain precision for the results." An example is cited of tests with sewage effluent indicating that with 10 fish per toxicant concentration, the 95% confidence interval was within  $\pm 20\%$  of the means while when 20 fish were exposed it was within  $\pm 14\%$  of the mean value.

$LC_{50}$  values were estimated by interpolation after plotting the data on semilogarithmic coordinate paper with concentrations plotted on the logarithmic and percentage dead plotted on the arithmetic scale, as described in Section 801F.1 (APHA et al., 1976). This method of interpretation has been shown to give values within the precision of the test.

## APPENDIX F

### METHOD FOR CARBARYL ANALYSIS AS REPORTED BY HATHAWAY (1979)

#### Methodology: Carbaryl Analysis

A liter of the sample was extracted serially with three 50 mL portions of methylene chloride. The extracts were combined and passed through  $\text{Na}_2\text{SO}_4$  into a 250 mL round bottom flask. 50 mL of ethyl acetate was added to the flask and the solvents were concentrated to 10 mL in a rotary evaporator at 45° C. The extract was passed through a cleanup column of 3 cm Florisil topped with 1 cm of  $\text{Na}_2\text{SO}_4$ . The Carbaryl was eluted with 20 mL of ethyl acetate. The 30 mL of ethyl acetate was concentrated to 10 mL on a hot plate under a gentle stream of carbon filtered air.

The extract was analyzed on a Waters 204 Liquid Chromatograph with a M Bondapak  $\text{C}_{18}$  column. A methanol-1% acetic acid gradient was used over 25 minutes at a flow rate of 2.0 mL/min. The gradient was run from 0 to 80% methanol. The dual channel UV detector was operated at wave lengths of 254 nm and 280 nm.

Quality Control: A blank and a spike were analyzed along with the samples. The blank did not contain any interferences at the retention time of Carbaryl. The spike was at a concentration of 250  $\mu\text{g/L}$  of Carbaryl and the recovery was 117%.

The presence of Carbaryl in the samples was established by the coincidence of retention time and confirmed by the ratio of the 254 to 280 response.

## APPENDIX G

### METHOD FOR THE ANALYSIS OF CARBARYL AS DEVELOPED BY UNION CARBIDE

Samples were extracted serially with methylene chloride which was then dried with  $\text{Na}_2\text{SO}_4$ . The extract was analyzed on a Varian 825 Liquid Chromatograph with a Micropak CN-10 column. The mobile phase consisted of N-propanol 10% in iso-octane. A single UV detector was operated at a wavelength of 254 nm.

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16. ABSTRACT The report gives results of a bench-scale, experimental treatability study of wastewaters from the manufacture of the pesticide carbaryl. Results indicate that both carbaryl manufacturing wastewater (mixed one part in nine parts municipal wastewater) and carbaryl itself (spiked at 10 mg/L in municipal wastewater) appear suitable for biological treatment by acclimated systems if additional provision is made for removing ammonia in the effluents from these biological treatment systems. Other parameters investigated in this study--including carbaryl, alpha-naphthol, and toluene concentrations and the chemical oxygen demand (COD)--all showed large reductions (90% or greater). The mechanisms of reduction of these parameters include combined hydrolysis and biodegradation of carbaryl and alpha-naphthol, volatilization of toluene, and biodegradation of species contributing to COD. A large increase in ammonia concentration was noted in the effluent from the biological units treating carbaryl manufacturing wastewater. This ammonia concentration made the toxicological evaluation of the effectiveness of treatment problematic by rendering the effluent more toxic than the influent. Ammonia stripping lessened this toxicity. Because the technology of nitrogen control has been extensively developed, these treatment options were not pursued further.			
17. KEY WORDS AND DOCUMENT ANALYSIS			
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Industrial Processes		Carbaryl	13H
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