THE EFFECTS OF ORGANIC TOXIC COMPOUNDS ON THE PERFORMANCE OF A BATCH-OPERATED ACTIVATED

SLUDGE PROCESS

By

GYE DAE WHANG " Bachelor of Engineering

Yonsei University

Seoul, Korea

1972

Submitted to the Faculty of the Graduate College of the Oklahoma State University in partial fulfillment of the requirements for the Degree of MASTER OF SCIENCE July, 1979

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Thesis Approved:

Thesis Adviser m

Dean of the Graduate College

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to my major adviser, Dr. A. F. Gaudy, Jr., for his valuable assistance, guidance, advice, and friendship throughout the course of this investigation and my graduate studies. I would also like to thank Dr. D. F. Kincannon, Dr. Marcia H. Bates, and Dr. R. N. DeVries for their valuable instruction and for serving as committee members. I wish especially to thank Dr. Manickam for his help and encouragement during this study and to all of my fellow students in Bioenvironmental Engineering for their continued support, advice, encouragement, and friendship. Special thanks are extended to Mrs. Grayce Wynd for her excellent typing, and Eldon Hardy for his professional drafting.

Finally, I would like to give my special recognition to my parents, Young Ha and Kyung Sek Whang, my wife, Myung Hee, and my parents-in-law, Jeng Ho and Jeng Bo Song, for their continued love, encouragement, and support throughout these studies.

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CHAPTER I

INTRODUCTION

Rapid industrialization and increasing demand for products by modern society has been the cause of introduction of new chemicals into the environment at an ever increasing rate. In the past, the immediate benefits to society through the use of new chemical products has far outweighed considerations of the possible environmental deterioration they might cause. However, at the present time, society has become well aware of adverse environmental effects and has expressed its concern through the organization of new governmental agencies to regulate and control water pollution.

Fortunately, some of the industrial compounds are degraded in the biosphere, and there is growing investigative effort to determine which compounds are biodegradable and which may not be easily biodegradable. Some compounds may persist in the aqueous environment for some period of time before microorganisms with the genetic capability to metabolize them can acclimate to the compounds.

An important practical problem which arises because of the fairly recent passage of Public Law 92-500 is the effect of rather small concentrations of potentially toxic compounds on the metabolic efficiency of biological wastewater treatment processes. It is recalled that Public Law 92-500 provides for 75 percent or more of the financing of publicly owned treatment works (POTWs). Many of the newly designed and

constructed municipal sewage works employ biological treatment, and in particular, the activated sludge process. From a practical standpoint, the nation cannot afford to spend billions of dollars on the installation of activated sludge processes without concern over the effect that various chemicals in certain industrial wastes may have on the effectiveness of the treatment facility if these industrial wastes are sewered to the municipal sewerage system. There are some very important scientific questions which need to be answered for the purpose of establishing sound regulatory policies in regard to discharge of certain of these chemicals to municipal sewers. For example, which compounds should be removed prior to discharge, and which type of compounds can be discharged without causing harm? Also, are there limitations on the amounts and concentrations of these compounds which can be handled adequately by the municipal sewage treatment plant?

The work reported in this thesis forms a part of an overall effort being made in the bioenvironmental engineering laboratories to investigate this problem under the sponsorship of a research project from the Environmental Protection Agency (#805242). This report deals with the biological response to varying concentrations of the following priority (toxic) pollutants: benzene, hexachlorobenzene, anthracene, o-nitrophenol, chloroform, trichloroethylene.

CHAPTER II

LITERATURE REVIEW

The widespread use of synthetic chemicals has caused many pollution problems. Some of these compounds are readily degraded by microorganisms, but others are resistant to biological decomposition and tend to accumulate in the environment, resulting in a potential hazard to public health and general degradation of environmental quality (1). It is very important to evaluate bacterial toxicity before potentially toxic chemicals are discharged to the receiving stream or to municipal wastewater facilities. In addition to toxicity to animal and humans, certain compounds can inhibit the self-purification capabilities of receiving streams or can have damaging effects on the treatment process, particularly on activated sludge processes.

Pitter (2) classified organic substances into four groups based on biodegradability and toxicity: 1) biodegradable and nontoxic; 2) nonbiodegradable and toxic; 3) biodegradable and toxic; and 4) nonbiodegradable and toxic. He also listed four stages of degradation: primary, partial, acceptable, and total.

Alexander (1) reported that several conditions must be fulfilled in order that a particular substance can be degraded. First, microorganisms must be present in the environment. These organisms must have the ability to degrade the compound, and the compounds must be in proper molecular configuration to be degraded by the microorganisms;

that is, the structure of the compound could be modified by the environment in such a way as to hamper its attack by an organism which had the ability to metabolize the compound in its native form. Furthermore, there should be no substance present which would prevent induction of enzymes needed to initiate the metabolism of the compound. Also, there should be an environment generally favorable for microbial proliferation and enzyme production. He also reported 15 mechanisms of "recalcitrance." Much research has been done to find relationships between chemical structure of compounds and their biodegradability; such work has been accomplished using both pure culture and heterogeneous populations of microorganism (3)(4)(5)(6)(7)(8)(9). However, there has been no uniformity in the method of assessing the biodegradability of various compounds in the many studies which have been performed. It has been found that slight changes in the chemical structure of many molecules change their biodegradability (3)(4)(7), and the position of the functional groups on compounds also change the metabolic availability (5)(6)(8)(9). The ability of an activated sludge to degrade certain compounds has been tested by adapting the cells to analogs or parent compounds or related compounds (10)(11)(12). It has been found that the general mechanisms of response are that activated sludge may change predominant species or undergo induction of specific enzymes in the species already predominating so as to acclimate to the new chemical compounds. Acclimation may be needed even though the population may have been preadapted to other similar compounds. However, judicious selection of preadapting compounds can shorten the time required for acclimation or adaptation to new compounds in a wastewater; that is, if one wishes to develop an activated sludge on a specific

industrial waste containing one or more toxic pollutants, the sludge can be developed faster if is first acclimated to a compound (or to compounds) similar to those known to be in the industrial waste.

Eckenfelder et al. (13) found that influent wastewater strength, temperature, biodegradation rate, and total dissolved solids would influence the performance of biological treatment plants treating various organic chemical industry wastes. Some of the factors affecting biodegradability are (2): physical-chemical factors, temperature, solubility and degree of mixing of the compound in the medium, dissolved oxygen, and pH.

Biological factors include the source and condition of the microorganisms, adaptabilities, and resistance to toxic substances and specific metabolic control mechanisms which make the cells responsive to other substrates in the environment.

Chemical factors include the size of the molecule and the number, location, and the kinds of substituents as well as the general stereochemistry of the molecules.

Various methods have been used to measure the inhibition of microbial activity in the presence of toxic compounds or to measure the metabolic availability of a compounds as substrate for growth. Batch studies are ideal for the measurement of growth, and they can be used to test the substrate removal rate. Ludzack (14) discussed various methods for measuring biodegradability of organic pollutants in wastewaters. He discussed the advantages and limitations of bench scale tests as design guides. Although he concluded that bench scale studies will give a basis for predicting later behavior in the treatment plant, factors which effect the microbial responses and performance should also be studied after the plant has been placed in full scale operation. Patterson (15) held that the BOD and COD tests were not adequate as standards for measurement of bio-mass and activity parameters of activated sludge undergoing toxic stress, since toxicity of the compounds may vary according to the nutrient supply and the physiological condition of the microorganisms. He recommended the use of such analyses as total dehydrogenase activity, oxygen uptake, and cellular ATP for assessment of toxic effects. However, it cannot be denied that substrate removal tests using the COD test for assessing the removal rate have advantages over other measurements because they are relatively quick and the results are rather reliable.

It is important to note that many organic chemicals found in wastewaters are of rather low solubility and some are subject to stripping during the biological treatment process (16). Gaudy (17)(18) found that stripping kinetics were dependent upon airflow rate, tank geometry, and temperature. He also found that independently determined stripping and biological kinetic coefficients could be used to predict the removal of volatile compounds by the dual process of biological metabolism and physical stripping. Bunch (19) determined the biodegradability of several compunds by analyzing the reaction liquor after seven days of incubation at room temperature under static aerobic conditions. He employed settled sewage as inoculum to BOD dilution water containing small amounts of yeast extract and known concentrations of test compounds. His results indicated that the degree of biodegradability of compounds during the test period provides an indication of the time required for adaption and is valuable for predicting the behavior of a compound in a wastewater treatment plant and in surface

water to some extent because this test shows biodegradation only under given conditions.

McKinney (10) studied the oxidation of several aromatic compounds using adapted activated sludges. He concluded that activated sludge can oxidize phenolic and related compounds. Ludzack (4) attempted to clarify relationships between chemical structure and microbial acclimation. He showed that activated sludge could be adapted to a wide variety of compounds. His methods of study included oxygen uptake and BOD. However, he found that the number of functional groups in a molecule, the size and solubility of the molecule, isomerism, etc. made it extremely difficult to outline very simple rules describing the metabolic availability of a material as a function of its structure. Chambers (11) studied 104 compounds, using phenol-acclimated sludge. His findings indicated that the position and type of groups in the aromatic ring, the number and type of substituents, and size and complexity of the substituents would effect the relationship between molecular structure and biodegradability.

Heidman et al. (20) studied the effect of sodium pentachlorophenol on activated sludge. It was found that this compound did not affect the treatment efficiency in concentrations up to 250 mg/l, but it was the cause of poor settling and brought about a change in predominating microorganisms. Also, it was noted that shock loading of rather small concentrations affected the treatment efficiency. Camisa (21) developed rapid and reproducible methods for analysis of tri-chloroethylenebearing wastes. He found that considerable amounts of trichloroethylene are absorbed by activated sludge solids and the fact that TCE is strippable contributed to the efficiency of removal. Haller

(12) studied chloro,nitro substituted aromatic compounds to determine whether they could be degraded by soil and wastewater microorganisms and by organisms pre-adapted to the compounds. He found that the positions of the functional groups affected the biodegradability. Strackle and Baumann (22) studied problems associated with biological treatment of municipal wastewaters subjected to various industrial wastes including those containing substituted benzene ring compounds and phenol. They operated a trickling filter pilot plant and an activated sludge plant and observed that a fairly long period of time was required to adapt the microflora to these organic pollutants. The conclusion was that the activated sludge process was the best method to use for treatment because biomass concentration as well as the contact time with the organic material could be more readily controlled.

At the time of writing this thesis, the list of priority pollutants includes 129 toxic components, most of which are organic compounds. The six chosen for study here represent a broad spectrum of characteristics. Some pertinent facts about these compounds are given in Table I. The values listed for COD recovery are the percentage of the theoretical (calculated) COD which are recorded upon subjecting the compounds to the COD test.

TABLE I

SOME GENERAL CHARACTERISTICS OF PRIORITY POLLUTANTS STUDIED DURING THIS INVESTIGATION

	BENZENE	HEXACHLOROBENZENE	ANTHRACENE	0-NITROPHENOL	CHLOROFORM	TRICHLOROETHYLENE
Formula	с ₆ н ₆	°6°16	$C_{6}H_{4} = (CH)_{2} = C_{6}H_{4}$	NO2 ^{C6H40H}	снс1 3	C2HC13
Physical State (23)	colorless liquid	white needles solid	white solid	light yellow needles solid	colorless liquid	colorless liquid
Molecular Wt. (23)	78.11	284.80	178.22	139.11	119.38	131.5
Density (23)	0.8786	2.044	1.24	1657	1.489	1.46
Solubility (24)	1780 mg/1	nonsoluble	0.075 mg/1	2100 mg/1	8.000 mg/1	1.1 mg/1
Method of Production	fractional distillation of light oil	ultimate production from chlorinating benzene in the presence of ferric chloride	heat the crude benzole and tar	react nitrobenzene with sodium hydrox- ide, hydrolysis of 0-nitrochloro- benzene, nitration of phenol	chlorinate the methane	chlorination of acetylene
Uses (24)	organic chemicals, pesticide plastics and resins, synthetic rubber, dye, pharmaceuti- cals, flavors and perfumes, paints and coatings, etc.	wood preservatives, fungicide, produc- tion of aromatic fluorocarbons	dye intermediate	synthesis of o-amino phenol, o-nitroanisole, and certain other dyestuff intermediates	intermediate in the manufac- ture of chloro- fluoromethane, solvent, fire extinguisher	metal degreas- ing, solvent extraction, refrigerant and heat exchange liquid, organic synthesis
COD Recovery	95.3 percent	NO	85.4 percent	99.4 percent	15.7 percent	47.7 percent
Biodegradability	biodegradable (25) difficult to degrade	refractory (25)	biodegradable (26)	biodegradable (2)	refractory (25)	very difficult to degrade (25)

CHAPTER III

MATERIALS AND METHODS

Bench scale batch reactors were employed to study the effects of toxic organic compounds on activated sludges. Three 3.75-inch diameter batch reactors made of Pyrex glass were used, and each had a total volume of 3.5 liters (3.0 liter aeration liquor volume). The experimental apparatus used in these studies is shown in Figure 1.

To keep the units completely mixed and to provide sufficient oxygen to meet the respiration requirement of the microorganisms, diffused air was supplied through a carborundum diffuser; the airflow rate was two liters per hour. Dissolved oxygen concentration in the reactor was measured from time to time to ensure that the system was maintained under highly aerobic conditions. The temperature in the reactor was not controlled; thus, it varied somewhat during the study. The temperature variation was not severe, and was closely monitored.

Biomass was developed in a batch reactor using effluent from the primary settling tank of the Stillwater municipal sewage treatment plant as seed. After developing a sufficient concentration of biomass in the batch reactor, the biomass was divided into three equal portions. These portions of the sludge were used to start two units which were to receive normal wastes plus varying concentrations of the test compounds; a first unit was retained as a control unit. After studying the effects of two priority pollutants for an extended period

Figure 1. Schematic Diagram of Laboratory Scale Batch Reactors



of time, the units were rested by feeding the standard or normal waste material for several weeks and thereafter the units were used to study the effects of another pair of priority pollutants. The unit used as the control in the first set of experiments was also used as the control (undosed with toxicant) in studying succeeding pairs of priority pollutants.

Feed Preparation and Dosing Schedule

Sewage from the primary effluent of the Stillwater municipal sewage treatment plant was used as the normal feedstock. Stillwater is a rather small campus town, and the strength of the sewage is subject to periodic variation; it is extremely weak during periods between semesters. Average total COD during this study was 137 mg/l; average soluble COD was 74 mg/l, and average total BOD was 39 mg/l. Soluble BOD averaged 21 mg/l. In order to maintain adequate feeding strength, the municipal sewage was supplemented with 200 mg/l glucose and 75 mg/l ammonium sulfate. In general, the COD-to-nitrogen ratio was approximately 20:l. No other mineral salts or buffer were added since it was expected that the primary effluent would possess all of the trace nutrients required.

A total of six high priority pollutants were studied. Prior to dosing, the batch reactors were operated for a sufficient time to be sure that they had come to a relatively steady condition with regard to residual COD and biological solids production; that is, they were undosed until all three units were producing approximately the same residual COD and biological solids prior to the daily feeding.

Daily Feeding Procedure

The three reactors were fed once daily. The general feeding procedure was as follows: first, the sidewalls of the reactor above the liquid level were scraped down and mixed thoroughly in the reactor. One liter of mixed liquor was wasted from each unit; then the air diffusers were removed and the remaining two liters were allowed to settle for one hour. After one hour of settling, a second liter (supernatant) was wasted from each unit. Glucose and ammonium sulfate were added from stock solutions and the dosages of priority pollutants were added to the appropriate test reactors. All units were then returned to the 3-liter mark with primary effluent from the Stillwater municipal treatment plant. Occasionally, anti-foam spray was used to prevent foaming. The priority pollutants examined in this study were:

benzene

chloroform

trichloroethylene

o-nitrophenol

hexachlorobenzene

anthracene

During the study of any particular compound, dosage levels were increased as follows. There was a period in which the dosage was 5 mg/l. After examining the effect for a period of time, the dosage was increased to approximately 25 mg/l, and thereafter to approximately 50 mg/l. It is important to note that these dosage levels were based upon the two liters of daily feed material; thus, the initial concentration of these substances in the reaction liquor after bringing each unit to its 3-liter operational level was two-thirds of the feed dosage level. After obtaining information on the effects of repeated daily dosages at the same level, the dosage level was cycled to gain some idea of the system's ability to accommodate a fluctuating load with priority pollutants.

Sampling Procedure and Analyses

Samples were taken before each wasting and feeding period and immediately after feeding the reactors and bringing them to the 3-liter operating volume. In general, the samples were not taken daily, i.e., before and after every wasting and feeding. Usually, samples were taken on alternate days; however, during cyclic shocking of the units with toxic compounds, samples were taken daily.

Total suspended solids concentration was measured using the membrane filter technique (Millipore Filter Co., Bedford, Mass., H.A. 0.45 µm). Soluble substrate in the reaction liquor was measured as chemical oxygen demand according to procedures outlined in Standard Methods for the Examination of Water and Wastewater. pH was measured before and after each feeding; dissolved oxygen was measured periodically using a Weston-Stack dissolved oxygen analyzer, Model 330. Periodically, samples were taken for measurement of total COD, soluble TOC before feeding, total COD supernatant after one hour of settling, and total suspended solids of the supernatant after one hour of settling. Also, during each period at a specific toxic loading level, 1-liter samples of mixed liquor, supernatant, and feed were taken for analysis of the specific test compound, where such analyses were possible. These samples were taken to the chemistry department for analysis.

Auxiliary Studies

During the study of the effects of each compound it was advisable to gain information on the rate of purification during the 23-hour reaction time following each daily feeding. Also, since a significant number of priority pollutants are volatile, it was desirable to gain some idea of the strippability of each compound.

24-hour Batch Studies

Batch studies were usually conducted on the day the concentration of the priority pollutant was changed. Thus, after the feeding of the unit, soluble COD and suspended solids in the reactor were determined at frequent intervals during the ensuing 23-hour aeration period. Samples were taken frequently during the initial 2-hour period and thereafter the frequency of sampling was decreased.

Stripping Tests

Each of the six priority pollutants was tested for its batch stripping characteristics. Using similar batch reactors void of microbial cells, concentrations of 250, 500, and 1000 mg/l COD of test compound were aerated at the same airflow rate used in the batch aerator sludge units. These concentrations were made up in 2-liter volumes of tap water and placed in tightly sealed two 2-liter volumetric flasks. After ten minutes of mixing using a magnetic stirrer, this material was transferred to the batch reactor, bringing total volume to three liters, and the stripping tests were initiated. This procedure minimized error due to evaporative losses for highly strippable compounds.

CHAPTER IV

RESULTS AND DISCUSSION

Long-term Batch Studies

In Figures 2 through 7, the performance characteristics for control units and test units for the six high-priority pollutant compounds are presented. While these graphs are very helpful in showing comparative performance, the statistical analyses of these data during each period of operation provide a more quantitative numerical comparison. Values of the statistical parameters are given in Tables II, III, and IV; results of other analyses made periodically but not as often as those plotted in the figures are given in Table V. In Table VI, the results of analyses for specific compounds dosed to the units are listed. In the following discussion of effects of each compound, reference will be made to all three sets of information.

Benzene

Figure 2 shows little or no indication that benzene at 5, 20, or 50 mg/l feeding levels caused behavior any different than in the control system. Under cyclic loading (omitting the enormously high data point for soluble COD in the control), it would appear that benzene may cause a higher concentration of soluble COD, i.e., note the mean value of 33 vs. 45 mg/l. However, the short period of cyclic loading

Figure 2. Performance of Control Unit vs. Performance of Benzene Unit



Figure 3. Performance of Control Unit vs. Performance of Hexachlorbenzene Unit



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Figure 4. Performance of Control Unit vs. Performance of Anthracene Unit

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Figure 5. Performance of Control Unit vs. Performance of O-nitrophenol Unit



Figure 6. Performance of Control Unit vs. Performance of Chloroform Unit


Figure 7. Performance of Control Unit vs. Performance of Trichloroethylene Unit

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TABLE II

STATISTICAL ANALYSIS COMPARISON OF CONTROL AND TEST UNITS DOSED WITH BENZENE AND HEXACHLOROBENZENE

	CONTROL			BENZENE				HEXACHLOROBENZENE				Pomanica		
late	Parameter	Before	After	Before	After	Before	After	Before	After	Before	After	Before	After	Reildriks
9-13	N (Mean) G R C.V	6 36.7 6.5 28-46 17.7	5 257.4 67.2 194-369 26.1	6 391.3 45.6 354-464 11.6	6 304.3 34.6 254-340 11.4	6 38.0 6.2 26-44 16.3	5 242.0 55.9 206-341 23.1	6 386.3 51.6 334-458 13.4	6 289.3 31.8 234-320 11.0	6 38.0 7.8 26-50 20.5	5 258.4 103.4 193-442 40.0	6 374.0 84.4 280-486 22.6	6 281.7 40.0 230-326 14.2	No toxic
9-2 4 10- 8	N (Mean) G R C.V	7 45.9 9.5 36-60 20.7	7 199.4 43.5 136-274 21.8	7 376.9 44.4 324-448 11.8	7 286.1 44.7 256-384 15.6	7 33 7.5 24-44 22.6	7 184.7 41.2 112-233 22.3	7 362.3 21.4 326-394 5.9	7 305.4 44.8 246-362 14.7	7 33.9 8.7 24-44 25.5	6 195.7 46.1 148-262 23.5	7 382.6 46.6 330-456 12.2	7 315.1 55.6 226-396 17.6	5 mg/l toxic
10- 9 11-16	N (Mean) G R C.V	19 42.6 11.4 23-68 26.8	18 232.4 50.5 179-392 21.7	20 422.9 73.2 304-640 17.3	20 345.6 41.2 272-440 11.9	19 40.0 10.3 20-64 25.8	19 219.4 55.3 134-396 25.2	18 461.1 51.9 328-552 11.2	19 405.0 47.5 284-484 11.7	19 39.6 11.1 24-68 28.0	18 221.3 30.5 67-308 13.8	19 457.8 74.6 342-638 16.3	19 369.5 42.3 280-432 11.4	20 mg/l toxic
11- 7 12-12	Ν (Mean) σ R C.V	13 50.5 21.7 20-88 43.0	13 212.5 37.3 170-265 17.6	13 520.0 57.4 400-620 11.0	13 381.8 53.2 296-496 13.9	12 46.2 10.7 24-61 23.2	13 185.0 33.5 118-238 18.1	13 480.2 59.8 408-576 12.4	11 390.9 66.8 272-472 17.1	13 51.7 26.2 24-126 50.7	13 192.3 31.6 135-237 16.4	13 496.0 81.7 408-660 16.5	10 392.8 34.0 332-444 8.7	50 mg/l toxic
12-13 12-24	N (Mean) G R C.V	3 33 5.6 28-39 16.9	6 196.3 22.0 157-220 11.2	4 501 55.1 452.568 11.0	5 418.4 40.3 352-460 9.6	4 45.5 13.4 28-59 29.4	6 191.7 34.6 129-223 18.1	4 509 25.0 484-536 4.9	6 422.7 57.9 376-536 13.7	4 38.5 12.2 28-51 31.7	6 183 48 102-239 26.2	4 547 96 440-632 17.6	6 432 42.6 372-500 9.9	cyclic shock toxic
9-13 12 - 28	N (Mean) G R C.V	48 44.23 20.8 23-88 47.1	49 216 50.3 136-392 23.3	50 452.2 88.1 304-640 19.5	51 353.6 64.7 256-496 18.3	48 41.9 20.7 20-64 49.4	50 206.3 54.8 112-396 26.6	48 453.4 71.7 326-576 15.8	49 379.2 70.0 234-5 ³ 6 18.5	49 43.6 27.1 24-126 62.1	48 206.6 50.9 102-442 24.6	49 454.8 87.8 280-660 19.3	48 370.2 65.7 226-500 17.8	Total
	N													

TABLE III

Date	Paramotor		CONTROL			ANTHRACENE SOL TOS					0-NITROPHENOL			
1978	rarameter	Before	After	Before	After	Tiefore	After	Before	After	Before	After	Before	After	Remarks
1-10	N (Mean) o R C.V	7 56.3 40.7 26-145 72.3	7 275.3 131.7 154-543 47.8	7 544.0 65.0 456-632 12.0	7 394.3 98.9 204-524 25.1	7 55.7 37.1 26-134 66.6	7 282.3 145.0 173-571 51.4	7 543.4 80.0 412-684 14.7	7 413.7 76.5 260-472 18.5	7 -55.9 38.3 24-134 68.5	7 278.9 149.2 169-389 53.5	7 556.6 94.3 448-684 16.9	7 428.6 58.5 320-504 13.6	No toxic
1-23 2-20	N (Mean) o R C.V	15 54.5 20.8 30-104 38.2	15 292.6 93.4 238-560 31.9	15 542.9 156.7 456-964 28.9	15 368.0 71.3 268-508 19.4	15 60.1 35.0 26-138 58,2	15 300.8 100.8 180-546 33.5	15 545.3 112.8 412-796 20.7	15 384.0 59.6 296-516 15.5	15 59.0 25.0 30-124 42.4	15 293.4 101.4 214-576 34.6	15 608.3 129.2 456-964 21.2	15 402.9 91.7 284-604 22.6	5 mg/l toxic
2-21 3-31	N (Mean) o R C.V	19 62.1 34.8 24-187 56.0	19 245.5 28.1 203-318 11.5	20 543.2 109.6 392-848 20.2	19 459.2 138.7 324-936 30.2	18 58.3 41.8 35-215 71.7	19 231.0 28.8 173-278 12.5	20 606.6 165.4 420-1192 27.3	19 492.4 141.1 304-968 28.7	19 58.2 39.6 31-211 68.0	18 269.2 26.6 220-326 9.9	20 528.4 120.8 292-772 22.9	19 462.1 130.8 320-912 28.3	25 mg/l toxic
4-1 5-1	N (Mean) o R C.V	16 48.4 13.1 28-69 27.1	16 208.9 51.3 88-279 24.5	16 476.5 83.7 296-588 17.6	16 470.8 110.0 312-704 23.4	16 46.9 8.5 28-58 18.2	15 193.3 39.3 117-251 20.3	16 514.3 95.7 360-708 18.6	16 545.8 122.0 400-796 22.4	15 47.1 16.1 26-76 34.2	16 244.4 45.9 154-348 18,8	16 549.8 112.3 284-784 20.4	16 481.3 120.7 308-804 25.1	50 mg/] toxic
5- 2 5-12	Ν (Mean) σ R C.V	10 41.9 10.0 28-61 23.9	9 228.9 22.2 193-266 9.7	10 496.4 61.3 440-636 12.4	9 420.4 46.0 356-516 10.9	9 40.11 8.4 28-56 20.9	9 236.3 40.9 189-323 17.3	10 576 78.0 484-748 13.5	9 494.7 57.9 432-592 11.7	10 54 49.8 28-194 92.3	9 272 3 31.9 216-323 11.7	10 466.8 95.8 336-604 20.5	9 464 29.5 432-516 6.4	25 mg/1 - 50 mg/1
113 5-25	N (Mean) O R C.V	10 71.9 11.6 53-89 16.2	10 347.5 136.1 240-704 39.2	10 460 97.2 344-600 21.1	10 298.8 54.2 228-388 18.1	10 75.7 23.0 35-112 30.4	10 339.2 105.9 274-633 31.2	10 475 110.7 228-640 23.3	10 351.2 89.5 216-480 25.5	10 50.7 11.8 39-77 23.4	10 341.4 203.5 215-911 59.6	10 616 96.5 440-768 15.7	10 436.8 56.2 340-512 12.9	0 mg/1 - 25 mg/1
5~2C 6~ 3	N (Mean) o R C.V	9 42.4 9.0 36-60 21.2	9 250 24.3 218-297 9.72	9 486.2 62.6 396-608 12.9	9 352 42.7 300-436 12.1	9 42 10.8 32-60 25.8	9 254.7 27.5 214-305 10.8	9 483.6 82.5 388-608 17.1	9 345.8 32.3 304-392 9.3	9 40 11 28-60 27.4	9 239.4 41.1 178-329 17.2	9 491.1 79.9 412-612 16.3	9 395.6 34.3 360-448 8.7	0 mg/1, 0 mg/1, 25 mg/1
6- 4 6-16	N (Mean) d R C.V	13 38.2 7.6 21-52 20.0	12 237.3 14.5 221-265 6.1	13 503.4 92.4 320-636 18.4	12 329.7 37.7 268-400 11.4	13 33.8 7.8 21-40 22.9	12 245.3 12.7 221-269 5.2	13 570.8 90.5 352-684 15.8	12 378.3 51.2 312-512 13.5	13 34.5 7.3 17-44 21.0	12 237.3 19.8 209-269 8.3	13 527.7 95.9 348-692 18.2	12 365.7 52.6 284-484 14.4	0, 0, 0 mg/1, 25 mg/1
5- 2 6-16	N (Mean) a R C.V	42 48 16.4 21-89 34.3	40 265.8 83.0 193-704 31.2	42 487.6 80.2 320-636 16.4	40 347.4 61.9 228-516 17.8	41 47.2 21.0 21-112 44.5	40 268.9 69.7 189-633 25.9	42 530.5 100.0 288-748 18.9	40 390.4 83.1 216-592 21.3	42 44.2 26.1 17-194 59.1	40 271.7 109.9 178-911 40.4	42 526.4 105.3 336-768 20.0	40 412.3 58.6 284-516 14.2	cyclic shock toxic
1-10 6-16	N (Mean) Ø R C.V	99 52.3 23.6 21-187 45.1	97 257.5 80.2 88-704 31.2	100 509.2 103.1 296-964 20.2	97 396.2 106.0 204-936 26.8	97 51.9 28.4 21-215 54.7	16 255.5 79.9 117-633 31.3	100 546.3 118.2 288-1192 21.6	97 430.7 117.1 216-968 26.8	98 50.5 29 17-211 57.4	96 270.6 92.4 169-911 34.2	100 544.9 114.1 284-964 20.9	97 432.9 96.0 284-912 22.2	Total

STATISTICAL ANALYSIS COMPARISON OF CONTROL AND TEST UNITS DOSED WITH ANTHRACENE AND O-NITROPHENOL

TABLE IV

	CONTROL					CHE OPOEODM				TRICHI OROETHYLENE				
Date	Parameter	Referre	COD	SO	LIDS	CC Before	After	SOL	IDS	CC	D	SO	.IDS After	Remarks
7-24 8- 1	N (Mean) G K C.V	5 38.8 10.5 24-52 23.5	5 228.4 38.8 180-264 17.0	5 440.0 17.2 428-468 3.9	5 358.4 39.9 324-416 11.1	5 36.4 9.6 20- 44 26.4	5 226.0 52.1 156-268 23.1	5 472.8 30.8 440-520 6.5	5 384.4 64.8 328-460 16.9	5 39.6 7.2 24- 45 18.2	5 213.4 43.2 163-256 20.2	5 462.4 31.6 424~504 6.8	5 375.2 52.5 320-440 14.0	No toxic
8-2 9-3	N (Mean) R C.V	16 46.4 24.1 28-132 51.9	16 238.8 22.8 211-292 9.6	15 424.3 21.3 372-464 5.0	15 280.8 30.4 216-320 10.8	16 47.19 29.9 28-148 63.3	16 249.8 22.9 220-300 9.2	15 430.7 40.3 328-496 9.4	16 281.4 36.0 192-328 12.8	16 44 23 20-120 52.2	16 244.3 22.2 224-296 9.1	16 409.6 45.15 320-468 11.0	16 284 35.3 220-340 12.4	5 mg/l toxic
9- 4 10-12	N (Mean) Ø R C.V	20 42.4 9.1 28-68 21.5	20 248.8 34.6 195-336 13.9	20 482.5 64.9 375-625 13.4	20 360.1 65.7 270-410 18.2	19 38.7 11.2 24-64 28.9	20 244.2 33.3 176-304 13.6	20 475.2 59.4 355-580 12.5	20 378.6 64.8 296-485 17.1	19 45.7 9.9 28-70 21.7	20 249.5 33.1 160-309 13.3	20 453.4 62.9 328-600 13.9	20 338.2 44.9 260-400 13.3	25 mg/l toxic
10-13 11-13	N (Mean) G R C.V	16 37.6 7.1 26-56 18.9	16 240.5 18.6 206-280 7.7	16 527.8 107.51 365-790 20.4	15 377.7 58.3 300-475 15.4	16 38.9 7.2 31-56 18.5	16 245.8 17.5 217-276 7.1	16 520. 82.8 395-710 15.9	16 395 61.6 310-525 15.6	16 35.2 4.4 26-45 12.6	16 243.9 20.3 221-280 8.3	16 488.8 71.5 385-615 14.6	16 381.9 63.1 310-503 16.5	50 mg/l toxic
11-14 11-27	N (Mean) o R C.V	8 30 4.9 24-36 16.3	9 237.6 22.0 207-270 9.24	8 434.4 78.8 350-570 18.1	9 346.7 70.5 275-500 20.3	8 33 5.3 24-42 16.1	9 235.2 45.4 127-278 19.3	8 432.5 73.8 320-520 17.1	9 296.7 46.6 235-365 15.7	8 32.2 6.0 24-45 18.7	9 219.6 40.7 131-262 18.5	8 428.8 66.4 320-505 15.5	9 311.7 46.8 245-390 15.0	25 mg/1 - 50 mg/1
11-28 12-10	Ν (Mean) σ R C.V	6 46.2 9.7 30-57 21.0	6 260.2 17.3 240-269 6.7	6 419.2 67.2 370-535 16.0	6 312.5 50.4 245-390 16.1	6 46.3 4.2 41-53 9.0	6 252.3 23.1 209-273 9.2	6 465 58.9 390-565 12.7	6 354.2 56.9 280-415 16.1	6 40,5 5.5 30-45 13,5	6 237.8 32.4 184-272 13.6	6 461.7 76.7 365-545 16.6	6 373.3 73.7 265-470 19.8	0 mg/1 - 25 mg/1
i2-11 12-20	N (Mean) R C.V	6 68.3 20.3 36-96 29.7	5 298.4 14.6 276-316 4.9	6 454.2 98.3 335-590 21.6	5 312.0 24.1 285-350 7.7	6 65 15.6 40-80 24.0	5 296.8 17.8 276-320 6.0	6 489.2 65.5 420-585 13.4	5 43.9 325-425 12.3	6 56 11.0 44-72 19.7	5 285.6 11.2 276-304 19.9	6 480.8 87.6 395-615 18.2	5 363 62.7 305-460 17.3	0 mg/l. 0 mg/l - 25 mg/l
11-14 12-20	N (Mean) R C.V	20 46.4 20.2 24-96 43.5	20 259.6 30.9 207-316 11.9	20 435.8 78.8 335-590 18.1	20 327.8 56.5 245-500 17.2	20 46.6 16.2 24-80 34.8	20 255.8 41.5 127-320 16.2	20 459.2 68.1 320-585 14.8	20 328.5 55.3 236-425 16.8	20 41.9 12.6 24-72 30.2	20 241.6 15.9 131-304 6.6	20 454.3 75.5 320-615 16.6	20 343 63.6 245-470 18.5	cyclic shock toxic
7- 4 12-20	N (Mean) G R C.V	77 43.0 16.3 24-132 37.9	77 246.5 29.6 180-336 12.0	76 465.7 81.0 335-590 17.4	76 334.6 56.4 216-500 16.9	76 42.5 17.6 20-148 41.4	77 247.5 32.7 127-320 13.2	76 471.5 68.4 320-710 14.5	77 346.4 66.2 192-525 19.1	76 41.9 13.9 20-120 33.1	77 242.9 32.5 131-309 13.4	77 452.4 67.5 320-615 14.9	77 399.7 61.7 220-505 18.2	Total

STATISTICAL ANALYSIS COMPARISON OF CONTROL AND TEST UNITS DOSED WITH CHLOROFORM AND TRICHLOROETHYLENE

TABLE V

COMPARISON OF SETTLEABILITY AND TOC VALUES BE-TWEEN CONTROL UNIT AND TEST UNITS DOSED WITH BENZENE, HEXACHLOROBENZENE, ANTHRACENE, O-NITROPHENOL, CHLOROFORM, AND TRICHLOROETHYLENE

DATE (1977) 12- 2	ANALYSIS 1-hr Settled Susp. Sol.	CONTROL (mg/l) 60	BENZENE (mg/1) 56	HEXACHLORO- BENZENE (mg/l) 6	REMARKS 50 mg/l toxic dosage Day 81, Fig. 2-3
12-10		42	70	20	50 mg/l toxid dosage Day 89, Fig. 2-3
(1978) 2-20	TOC	18	ANTHRA- CENE 23	O-NITRO- PHENOL 25	25 mg/l toxid dosage Day 42, Fig. 4-5
	Mixed Liquid Total COD l-hr Settled	653	658	628	
	Susp. Sol.	8	18	8	
3-30	Mixed Liquid Total COD l-hr Settled	625	690	738	25 mg/l toxic dosage Dav 80, Fig. 4-5
	Susp. Sol.	40	44	56	
3-31	TOC	18	32	25	25 mg/l toxic dosage Day 81, Fig.
5- 1	тос	33	19	52	50 mg/l toxic dosage
	Mixed Liquor Total COD	620	596	612	Day 112, Fig. 4-5
	l-hr Settled Total COD	38	38	42	
5-2	TOC	56	30	46	50 mg/l toxic dosage
	Mixed Liquor Total COD	636	697	570	Day 113, Fig. 4-5
	1-hr Settled Total COD	53	66	66	
	Susp. Sol.	28	26	22	
5-17	TOC	38	56	38	0 toxic dosage
	Total COD	624	729	757	Day 128, F1g. 4-5
	Total COD	100	59	47	
	Susp. Sol.	62	20	20	
8- 1	тос	26	CHLORO- FORM 11	TRICHOLORO- ETHYLENE 14	No toxic dosage
	Total COD	516	576	516	Day 9, Fig. 6-7
	Total COD	44	44	48	
	Susp. Sol.	6	6	6	
8- 7	l-hr Settled Susp. Sol.	10	14	9	5 mg/l toxic dosage Day 15, Fig. 6-7
8-17	l-hr Settled Susp. Sol.	10	12	14	5 mg/l toxic dosage Day 25, Fig. 6-7
8-29	TOC	-	33	45	5 mg/l toxic dosage
	Susp. Sol.	19	7	47	Day 37, Fig. 6-7
9-3	l-hr Settled Susp. Sol	6	6	14	5 mg/l toxic dosage Day 42, Fig. 6-7
9- 4	l-hr Settled Susp. Sol.	5	9	14	25 mg/l toxic dosage Day 43, Fig. 6-7
9-12	l-hr Settled Susp. Sol.	26	37	28	25 mg/l toxic dosage Day 51, Fig. 6-7
9-20	l-hr Settled Susp. Sol.	14	28	15	25 mg/l toxic dosage Day 59, Fig. 6-7

DATE (1978)	ANALYSIS	CONTROL (mg/l)	CHLORO- FORM (mg/1)	TRICHOLORO- ETHYLENE (mg/1)	REMARKS
10- 2	l-hr Settled Susp. Sol.	19	22	12	25 mg/l toxic dosage Day 71, Fig. 6-7
10-12	TOC	43	10	10	25 mg/l toxic dosage
	Mixed Liquor Total COD	584	580	564	Day 81, Fig. 6-7
	Susp. Sol.	12	12	13	
10-13	1-hr Settled Susp. Sol.	26	22	25	50 mg/l toxic dosage Day 82, Fig. 6-7
10-22	TOC	9.2	8	9	50 mg/l toxic dosage
	Susp. Sol.	. 14	16	15	Day 91, Fig. 6-7
10-26	l-hr Settled Susp. Sol.	26	19	19	50 mg/l toxic dosage Day 95, Fig.
11- 9	TOC	-	10	7	50 mg/1 toxic dosage
	Susp. Sol.	13	17	15	Day 109, Fig. 6-7
11-14	TOC	5	3	9	50 mg/1 toxic dosage
	Mixed Liquor Total COD	582	598	537	Day 114, Fig. 6-/
	1-hr Settled Susp. Sol.	15	19	29	
11-15	TOC	11	12	12	25 mg/l toxic dosage
	Total COD	577	611	604	Day 115, Fig. 6-7
	I-hr Settled Susp. Sol.	22	18	20	
11-30	TOC	20	22	19	0 mg/l toxic dosage
	I-hr Settled Susp. Sol.	16	9	19	Day 130, Fig. 6-7
11-31	TOC	21	22	17	25 mg/l toxic dosage
	Mixed Liquor Total COD	575	565	575	Day 131, Fig. 6-7
	1-hr Settled Susp. Sol.	20	6	13	• * · · · · · ·
12-13	TOC	12	5	9	0 mg/l toxic dosage
	l-hr Settled Susp. Sol.	18	24	48	Day 143, Fig. 6-7

TABLE V (Continued)

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TABLE VI

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Date (1978)	Sample Name	Amount of Dosage (mg/l)	Quantitative Analysis of Compound in Sample (mg/l)
		Anthracene	· · · · · · · · · · · · · · · · · · ·
2-12	feed sample	5	1.9
2-13	mixed liquor	5	2.8
2-13	l-hr settled effluent	5	0.006
2-18	feed sample	5	2.0
2-19	mixed liquor	5	6.5
2-19	l-hr settled effluent	5	<0.003
3-29	feed sample	25	9.6
3-30	mixed liquor	25	10.8
3-30	l-hr settled effluent	25	<0.002
4-23	feed sample	50	26.0
4-24	mixed liquor	50	31.6
4-24	l-hr settled effluent	50	0.08
4-28	mixed liquor	50	47.0
4-28	l-hr settled effluent	50	0.17
6-15	feed sample	25	13.2
6-16	mixed liquor	25	22.0
		Nitrophenol	
2-12	feed sample	5	3.8
2-13	mixed liquor	5	<0.06
2-13	l-hr settled effluent	5	<0.06
2-18	feed sample	5	3.6
2-19	mixed liquor	5	<0.02
2-19	l-hr settled effluent	5	<0.02
3-29	feed sample	25	23.1
3-30	mixed liquor	25	<0.04
3-30	l-hr settled effluent	25	<0.06
4-23	feed sample	50	37.5
4-24	mixed liquor	50	<0.04
4-24	l-hr settled effluent	50	<0.06
4-28	mixed liquor	50	<0.06
4-28	l-hr settled effluent	50	<0.04
6-15	feed sample	25	20.9
6-16	mixed liquor	25	<0.06

QUANTITATIVE ANALYSIS FOR REMOVAL OF TEST COMPOUNDS, ANTHRACENE, O-NITROPHENOL, CHLOROFORM, AND TRICHLOROETHYLENE IN TEST UNITS

Date (1978)	Sample Name	Amount of Dosage (mg/1)	Quantitative Analysis of Compound in Sample (mg/l)
		Chloroform (CHCl ₃)	
8-25 8-26 8-26	feed sample mixed liquor l-hr settled efflue	5 5 9 5	<0.2 <0.2 <0.2
10-11 10-12 10-12	feed sample mixed liquor l-hr settled efflue	25 25 ent 25	14.2 <0.2 <0.2
10-21 10-22 10-22	feed sample mixed liquor l-hr settled efflue	50 50 ent 50	27.0 <0.15 4.2
11- 8 11- 9 11- 9	feed sample mixed liquor l-hr settled efflue	50 50 50	14.4 <0,15 <0.2
12- 1	l-hr settled efflue	ent 25	<0.2
12-13 12-14 12-14	feed sample mixed liquor l-hr settled efflue	25 25 ent 25	27.5 <0.2 <0.2
		Trichloroethylene (C ₂ HCl ₃)	
8-25 8-26 8-26	feed sample mixed liquor l-hr settled efflue	5 5 9 5	3.1 <0.01 <0.01
10-11 10-12 10-12	feed sample mixed liquor l-hr settled efflue	25 25 25 25	12.2 <0.01 <0.01
10-21 10-22 10-22	feed sample mixed liquor l-hr settled efflue	50 50 snt 50	50.0 <0.005 <0.005
11- 8 11- 9 11- 9	feed sample mixed liquor l-hr settled efflue	50 50 snt 50	7.0 <0.005 <0.01
12- 1	l-hr settled efflue	ent 25	<0.01
12-13 12-14 12-14	feed sample mixed liquor l-hr settled efflue	25 25 25 25	9.6 <0.01 <0.01

TABLE VI (Continued)

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and the small number of samples obtained during this period are not really adequate for statistical analysis. Two samples taken for analysis of suspended solids during operation at the 50 mg/l dosing level (see Table V) indicate little difference between supernatant suspended solids values on day 81, whereas for the sample taken on day 89 there was a very noticeable increased suspended solids concentration in the supernatant of the benzene unit.

Hexachlorobenzene

At the concentrations fed, hexachlorobenzene did not appear to cause any significant increase in soluble COD (Figure 3). When all data points on soluble COD were lumped to determine overall average, it can be seen (Table II) that the mean values for soluble COD in the control and in the hexachlorobenzene units were the same. However, the coefficient of variation for the hexachlorobenzene unit was noticeably higher than for the control (47.1 vs. 62.1). The supernatant suspended solids concentration was much lower in the hexachlorobenzene units than in the controls on days 81 and 89 (Table V).

Anthracene

The second study period included comparative assessment of the effects of anthracene and o-nitrophenol. During this study period, the municipal sewage occasionally exhibited a foamy character. At the beginning of the period, there were wide fluctuations in the concentration of municipal sewage, as can be seen in Figure 4, which shows the results for dosage with anthracene. Also, an abnormally high feed COD was manifested on day 129. The highly soluble COD before feeding

on day 74 corresponded with the occurrence of a large amount of foaming in the unit. The addition of 5 mg/l of anthracene did not appear to affect behavior of the unit adversely, except for a period of significantly higher leakage than in the control between days 25 and 30. This result did not greatly affect the mean COD values during this period (see 55 vs. 60 for control and anthracene system, Table III) but it did cause quite some change in the standard deviation and coefficient of variation. When the dosage was increased to 25 mg/l, there was little difference in the soluble COD in the control and anthracene units, but the unit receiving the toxic compound exhibited a somewhat higher biological solids concentration. Increasing the dosage to 50 mg/l did not seriously affect the effluent quality with respect to soluble COD. On the contrary, the average COD in the test unit was slightly lower than in the control. Fluctuating the loading between 25 and 50 mg/l from days 113 to 123 did not cause any difference in the soluble COD in the control and test units. Cycling the loading from O to 25 mg/l did not appear to cause any significant differences in the soluble COD. During this period, there was a considerable dropoff in the biological solids concentration in both the control and the anthracene units. Increasing the time of zero concentration beginning on day 137 did not lead to any change in behavior; that is, the control unit and the anthracene test unit exhibited essentially the same COD concentration. The results shown in Table VI provide some indication that anthracene was removed during the aeration period.

0-Nitrophenol

It is seen from Figure 5 that addition of 5 mg/l o-nitrophenol had

little effect on the behavior of the system. The statistical analyses shown in Table III for this period indicate a slightly higher mean soluble COD and higher coefficient of variation due to the dosage of 5 mg/l of o-nitrophenol. It is interesting to note that this dosage level of o-nitrophenol caused a soluble color of the reaction liquor; the reaction liquor turned slightly yellow. The color persisted until the second day of feeding. However, there was a slight reduction in its intensity by this time. This provided some indication that the onitrophenol was partially removed or partially converted to some other intermediate which did not exhibit any color. This condition prevailed for eight days. From day 8 on, even though there was a slight yellow color immediately after feeding, no color was observed by the time for the next day's feeding. This indicates that the biomass may have acclimated to the compound. It is also possible that this period may have been one of adaptation wherein a few species capable of using the o-nitrophenol increased in relative numbers in the sludge; that is, this may have been a period of adaptation rather than acclimation. When the dosage was increased to 25 mg/l on day 42, the yellow color increased after feeding. In response to this dosing level, there was a decrease in biomass concentration; however, the biomass level recovered after the first four days at this dosing level. The color due to the presence of o-nitrophenol was removed during the first day of dosage. When the dosage was increased to 50 mg/l, the yellow color of o-nitrophenol was not removed on the first day; however, after three days of such feeding, o-nitrophenol was removed during the daily feeding period, as evidenced by the absence of color when compared to the control. During the period of feeding 50 mg/l, the suspended solids

concentration in the unit receiving o-nitrophenol became higher than that in the control. The fact that the residual COD at the end of the feeding period was essentially the same as in the control whereas the higher COD due to the feeding of o-nitrophenol was evident in the sample taken immediately after feeding coupled with the fact that the biological solids concentration was somewhat higher during this feeding period can be taken as rather good evidence that the compound was metabolized by the sludge. When the loading was fluctuated between 25 and 50 mg/l between days 113 and 123, the biomass concentration in the o-nitrophenol unit fluctuated considerably and the coefficient of variation was twice as high as in the control. Also, the coefficient of variation for the residual soluble COD was considerably higher than for the control (92.3 for the o-nitrophenol system compared to 23.9 for the control, see Table III). When the cyclic loading was changed to 0-25-0 mg/l, the suspended solids concentration in the o-nitrophenol unit remained somewhat higher than in the control. The settling characteristics of the o-nitrophenol unit compared very favorably throughout the experimental period with those of the control. The results shown in Table VI indicate that o-nitrophenol was removed during the aeration period.

Chloroform

It is seen from Figure 6 and from Table IV that chloroform had little or no effect on the system under any of the loading conditions examined. Chloroform is only slightly soluble in water, and although it was partially emulsified by the agitation caused by the vigorous aeration supplied, there would appear to be no adverse effects.

Trichloroethylene

It can be seen from Figure 7 and from Tables IV and V that trichloroethylene which is only very slightly soluble had little or no adverse effect on the behavior of the batch activated sludge. It does seem significant to note, however, that a considerable number of samples were taken of supernatant suspended solids after the 1-hour settling period and when there were differences in the suspended solids concentration in the supernatant, the trichloroethylene unit exhibited a higher solids leakage than the control, i.e., settling effectiveness in the trichloroethylene unit was not as good as in the control. For example, see the 1-hour supernatant solids concentrations for days 37, 114, and 143 (Table V).

24-hour Batch Studies

All 24-hour batch studies conducted during this investigation to compare the effect of various concentrations of priority compounds on the rate of removal of soluble COD are shown in Figures 8 through 37. For the experiments conducted with benzene and with hexachlorobenzene, the biomass in the control unit was taken from units which had received and had been adapted to concentrations of 5 to 20 mg/l. However, in all other cases, anthracene, o-nitrophenol, chloroform, and trichloroethylene, the biomass in the control unit is that in the control unit for the main line of study; that is, these undosed control units were those which had at no time received any dosage of the test compounds.

It is seen from the results for benzene (Figures 8 and 9), that dosages of 20 mg/l and 50 mg/l did not have any effect on the removal Figure 8. Performance of Control Unit vs. Performance of Benzene Unit During 24-hour Batch Study. On Day 57, Unit was fed 20 mg/l Benzene



Figure 9. Performance of Control Unit vs. Performance of Benzene Unit During 24-hour Batch Study. On Day 86, Unit was fed 50 mg/l Benzene

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Figure 10. Performance of Control Unit vs. Performance of Hexachlorobenzene Unit During 24-hour Batch Study. On Day 57, Unit was fed 20 mg/l Hexachlorobenzene



Figure 11. Performance of Control Unit vs. Performance of Hexachlorobenzene Unit During 24-hour Batch Study. On Day 86, Unit was fed 50 mg/l Hexachlorobenzene



Figure 12. Performance of Control Unit vs. Performance of Anthracene Unit During 24-hour Batch Study. On Day 13, Unit was fed 5 mg/l Anthracene



Figure 13. Performance of Control Unit vs. Performance of Anthracene Unit During 24-hour Batch Study. On Day 42, Unit was fed 25 mg/l Anthracene



Figure 14. Performance of Control Unit vs. Performance of Anthracene Unit During 24-hour Batch Study. On Day 81, Unit was fed 50 mg/l Anthracene



Figure 15. Performance of Control Unit vs. Performance of Anthracene Unit During 24-hour Batch Study. On Day 114, at Beginning of Daily Switching of Anthracene Dosage From 50 mg/l to 25 mg/l, Unit was fed 50 mg/l Anthracene



Figure 16. Performance of Control Unit vs. Performance of Anthracene Unit During 24-hour Batch Study. On Day 122, at End of Daily Switching of Anthracene Dosage From 50 mg/l to 25 mg/l, Unit was fed 50 mg/l Anthracene



Figure 17. Performance of Control Unit vs. Performance of Anthracene Unit During 24-hour Batch Study. On Day 128, at Beginning of Daily Switching of Anthracene Dosage From 25 mg/l to 0 mg/l, Unit was fed 25 mg/l Anthracene



Figure 18.

Performance of Control Unit vs. Performance of Anthracene Unit During 24-hour Batch Study. On Day 136, at End of Daily Switching of Anthracene Dosage From 25 to 0 mg/1, Unit was fed 25 mg/l Anthracene


Figure 19. Performance of Control Unit vs. Performance of O-nitrophenol Unit During 24-hour Batch Study. On Day 13, Unit was fed 5 mg/l O-nitrophenol



Figure 20. Performance of Control Unit vs. Performance of O-nitrophenol Unit During 24-hour Batch Study. On Day 42, Unit was fed 25 mg/l O-nitrophenol



Figure 21. Performance of Control Unit vs. Performance of O-nitrophenol Unit During 24-hour Batch Study. On Day 81, Unit was fed 50 mg/l O-nitrophenol



Figure 22.

Performance of Control Unit vs. Performance of O-nitrophenol Unit During 24-hour Batch Study. On Day 114, at Beginning of Daily Switching of O-nitrophenol Dosage From 50 mg/l to 25 mg/l, Unit was fed 50 mg/l O-nitrophenol

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Figure 23. Performance of Control Unit vs. Performance of O-nitrophenol Unit During 24-hour Batch Study. On Day 122, at End of Daily Switching of O-nitrophenol Dosage From 50 mg/l to 25 mg/l, Unit was fed 50 mg/l O-nitrophenol

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Figure 24.

Performance of Control Unit vs. Performance of O-nitrophenol Unit During 24-hour Batch Study. On Day 128, at Beginning of Daily Switching of O-nitrophenol Dosage From 25 mg/l to 0 mg/l, Unit was fed 25 mg/l O-nitrophenol



Figure 25.

Performance of Control Unit vs. Performance of O-nitrophenol Unit During 24-hour Batch Study. On Day 136, at End of Daily Switching of O-nitrophenol Dosage From 25 mg/l to 0 mg/l, Unit was fed 25 mg/l O-nitrophenol



Figure 26. Performance of Control Unit vs. Performance of Chloroform Unit During 24-hour Batch Study. On Day 9, Unit was fed 5 mg/l Chloroform



Figure 27. Performance of Control Unit vs. Performance of Chloroform Unit During 24-hour Batch Study. On Day 42, Unit was fed 25 mg/l Chloroform



Figure 28. Performance of Control Unit vs. Performance of Chloroform Unit During 24-hour Batch Study. On Day 81, Unit was fed 50 mg/l Chloroform



Figure 29. Performance of Control Unit vs. Performance of Chloroform Unit During 24-hour Batch Study. On Day 115, at Beginning of Daily Switching of Chloroform Dosage From 50 mg/l to 25 mg/l, Unit was fed 50 mg/l Chloroform



Figure 30.

Performance of Control Unit vs. Performance of Chloroform Unit During 24-hour Batch Study. On Day 130, at Beginning of Daily Switching of Chloroform Dosage From 25 mg/l to 0 mg/l, Unit was fed 25 mg/l Chloroform



Figure 31. Performance of Control Unit vs. Performance of Chloroform Unit During 24-hour Batch Study on Day 143, at Beginning of Cyclic Shock Load, 0 mg/1, 48 hrs., 25 mg/1, 24 hrs.



Figure 32. Performance of Control Unit vs. Performance of Trichloroethylene Unit During 24-hour Batch Study. On Day 9, Unit was fed 5 mg/l Trichloroethylene



Figure 33. Performance of Control Unit vs. Performance of Trichloroethylene Unit During 24-hour Batch Study. On Day 42, Unit was fed 25 mg/l Trichloroethylene



Figure 34. Performance of Control Unit vs. Performance of Trichloroethylene Unit During 24-hour Batch Study. On Day 81, Unit was fed 50 mg/1 Trichloroethylene



Figure 35. Performance of Control Unit vs. Performance of Trichloroethylene Unit During 24-hour Batch Study. On Day 115, at Beginning of Daily Switching of Trichloroethylene Dosage From 50 mg/l to 25 mg/l, Unit was fed 50 mg/l Trichloroethylene



Figure 36.

Performance of Control Unit vs. Performance of Trichloroethylene Unit During 24-hour Batch Study. On Day 130, at Beginning of Daily Switching of Chloroform Dosage from 25 mg/l to 0 mg/l, Unit was fed 25 mg/l Trichloroethylene


Figure 37. Performance of Control Unit vs Performance of Trichloroethylene Unit During 24-hour Batch Study on Day 143, at Beginning of Cyclic Trichloroethylene Shock Load O mg/1, 48 hrs -25 mg/1, 24 hrs



rate. The same can be said for the two figures showing results of dosage of hexachlorobenzene at 20 mg/l and 50 mg/l. It should be understood that in Figures 10 and 11, each control unit, although undosed in these experiments, had previously received 5 mg/l and 20 mg/l, respectively, before running the shock experiments. Thus, the biomasses in the control and the test reactors for these two compounds (Figures 8-11) was the same except that in the four experiments shown, the controls received no dosage of priority compounds as the dosage was increased from 5 to 20 mg/l in one case and 20 to 50 mg/l in the other case for the test compounds. From the results shown in these four figures, it must be concluded that neither benzene nor hexachlorobenzene at the dosage levels applied had any effect on substrate removal rate. Beginning with the experiments on anthracene, the control sludge was one which had never been dosed with test compound. These later comparisons may provide a somewhat more conservative or cautious comparison in regard to assessment of the effect of priority pollutants on municipal activated sludge. All batch results using varying concentrations of anthracene (Figures 12 through 18) indicate that the substrate removal rate was unaffected by this compound. However, for 25 and 50 mg/l dosing levels, the net increase in biomass concentration was lower than in the control system.

Regarding o-nitrophenol, there was no apparent difference in the COD removal curves for control and dose systems for o-nitrophenol feeding levels of 5 and 25 mg/l (Figures 19 and 20). However, at a dosage of 50 mg/l (Figure 21), there was a noticeable retardation in COD removal. This retardation was also evident when the o-nitrophenol unit dosage was changed from 25 to 50 mg/l (Figures 22 and 23); however,

when the dosage was cycled from 0 to 25 mg/l o-nitrophenol did not appear to have any adverse effect on substrate removal rate (Figure 24). However, the growth and substrate removal response for the control in this experiment seems abnormally slow.

Chloroform did not affect the substrate removal rate, nor did trichloroethylene.

Stripping Tests

Figures 38 through 45 show the results of stripping tests run by the feeding levels of 250, 500, and 1000 mg/l theoretical (calculated) feed COD. These figures show that anthracene is not stripped, and that o-nitrophenol is stripped only slightly during the 24-hour reaction period. Benzene, chloroform, and trichloroethylene are stripped at very rapid rates.

Semilogarithmic plots of the results (Figures 43-45) indicated that benzene followed a first-order decreasing rate kinetic mode of removal, but that chloroform and trichloroethylene did not follow first-order removal kinetics. These experiments were repeated, and the results were essentially identical. It can be seen from these results that metabolism of such compounds as benzene, chloroform, and trichloroethylene would have to be very rapid in order for these compounds to be removed biologically at a municipal activated sludge treatment plant. In any event, the compounds would have to be taken up very rapidly by the cells before they would be stripped, unless the stripping characteristics were decidedly slowed down by the presence of the biomass suspended solids. None of the compounds studied is stripped so rapidly, Figure 38. Stripping Test of Benzene at Concentrations of 250, 500, and 1000 mg/1 COD



Figure 39. Stripping Test of Anthracene at Concentrations of 250, 500, and 1000 mg/1 COD



Figure 40. Stripping Test of O-nitrophenol at Concentrations of 250, 500, and 1000 mg/l COD



Figure 41. Stripping Test of Chloroform at Concentrations of 250, 500, and 1000 mg/l COD



Figure 42. Stripping Test of Trichloroethylene at Concentrations of 250, 500, and 1000 mg/l COD



Figure 43. Semilogarithmic Plot of Benzene Stripping Test at Concentrations of 250, 500, and 1000 mg/1 COD



Figure 44.

Semilogarithmic Plot of Chloroform Stripping Test at Concentrations of 250, 500, and 1000 mg/l COD



Figure 45. Semilogarithmic Plot of Trichloroethylene Stripping Test at Concentrations of 250, 500, and 1000 mg/l COD



however, that the effect of its presence in a municipal wastewater can be neglected because of its possible removal by stripping pior to contact with the microorganisms in the activated sludge.

CHAPTER V

CONCLUSIONS

In general, one may conclude from these batch studies that rather high concentrations of the test compounds (5 to 50 mg/l) will have little or no effect on the substrate removal characteristics of an activated sludge process treating municipal sewage. However, it is as yet unclear whether such batch studies can be readily used to make conclusions in regard to behavior of activated sludge. Although batch fed units are subjected to rather severe shock loading conditions at each daily feeding, the 23-hour aeration period allows time for recovery which would not normally be available for a continuous flow activated sludge process unless it was one which employed an extended aeration period. The separate batch studies revealed for o-nitrophenol at rather high dosages (Figures 21, 22, and 23) that there was a decided retardation in removal rate. Such a finding is not noticeable in the normal daily feeding log of results, because after 23 hours of aeration, the control and the dosed systems are essentially the same regarding soluble COD.

There was some evidence, as can be seen from Table V, that hexachlorobenzene and anthracene affected the settleability of the sludge. At the time of completing this thesis, it is not possible to include in the analyses of these data the general findings of other experiments going on concurrently using other compounds, and in some instances, the

study of the same compounds used here in continuous flow activated sludge pilot plants. However, from the results thus far available, it appears that batch studies (which are more easily facilitated than are continuous flow operations) can be used to gain an overall insight regarding gross effects but are not a particularly good indicator of the magnitude and type of problem which may be encountered in an activated sludge. However, in regard to the six compounds herein tested, the dosed concentrations were purposely made higher than those anticipated at a publicly owned treatment works and it seems safe to conclude that in concentrations of a few milligrams per liter these compounds would not adversely affect the operation of a treatment plant or its sludge treatment and disposal facility. Also, for the compounds which were subjected to specific quantitative analysis, it does not appear that significant concentrations would pass through the treatment works.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

A significant number of the priority pollutants are essentially not soluble in water. It may be a worthwhile expenditure of experimental effort to determine if changes in the chemical composition of the wastes could affect the solubility of some of these compounds.

Also, it would be well to extend the study to higher concentrations of some of the compounds; that is, it would be well to study biological pretreatment aspects with regard to certain of the priority pollutants.

In regard to pretreatment studies as well as to studies at low dosage concentrations to POTWs, the effect of addition of mixtures of compounds rather than single compounds would make an interesting subject for investigation.

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VITA

Gye Dae Whang

Candidate for the Degree of

Master of Science

Thesis: THE EFFECTS OF ORGANIC TOXIC COMPOUNDS ON THE PERFORMANCE OF A BATCH-OPERATED ACTIVATED SLUDGE PROCESS

Major Field: Bioenvironmental Engineering

Biographical:

- Personal Data: Born April 12, 1950, in Seoul, Korea, the son of Young Ha and Kyung Sek Whang.
- Education: Graduated from PoSung High School, Seoul, Korea, in February, 1968; received the Bachelor of Engineering degree from Yonsei University, Seoul, February, 1972; the Master of Science degree from Yonsei University, Seoul, in September, 1976; completed requirements for the Master of Science degree in Bioenvironmental Engineering at Oklahoma State University in July, 1979.
- Professional Experience: Graduate research assistant, Bioenvironmental Department, Oklahoma State University, 1977-1979; field technician, Environmental Engineering Consultants, Stillwater, Oklahoma, 1979.

Membership in Professional Societies: Water Pollution Control Federation; National Society of Professional Engineers.