

ornl

**OAK RIDGE
NATIONAL
LABORATORY**

MARTIN MARIETTA

Environmental Studies in Support of the Live Fire Training Facilities Project

T. D. Hylton
J. F. Walker

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
ORNL ROOM 375
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this
report, send to name with report and
the library will arrange a loan.

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

1

2

3

4

5

6

Chemical Technology Division

ENVIRONMENTAL STUDIES IN SUPPORT
OF THE LIVE FIRE TRAINING FACILITIES PROJECT

T. D. Hylton
J. F. Walker

Date Published: August 1989

Prepared for the
U.S. Air Force
under
Interagency Agreement DOE 1489-1489-A1
by
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400



CONTENTS

	<u>Page</u>
LIST OF FIGURES	v
LIST OF TABLES	vii
ABSTRACT	1
1. INTRODUCTION	2
1.1 SAMPLING CRITERIA	5
2. STUDIES AT TYNDALL AFB	6
2.1 BACKGROUND	6
2.2 SAMPLE RESULTS	7
3. DAVIS-MONTHAN STUDIES	12
3.1 BACKGROUND	12
3.2 SAMPLING PLAN DESCRIPTION	13
3.3 SAMPLING METHODS	15
3.4 RESULTS	15
3.4.1 In-Field Chemical Oxygen Demand Analyses	15
3.4.2 Total Organic Carbon	17
3.4.3 Chemical Oxygen Demand	17
3.4.4 Oil and Grease	20
3.4.5 Nonhalogenated Volatile Organics	22
3.4.6 Volatile Organic Components	24
3.4.7 Dissolved Oxygen	29
3.4.8 Biological Oxygen Demand	31
3.4.9 Butyl Carbitol®	31
3.4.10 Fluoride	33
3.4.11 Temperature and pH	33
3.4.12 Ignitability and EP-Toxicity Results from Burn Pit	36
3.4.13 Efficiency of Fuel/Water Separator	37
3.4.14 Total Suspended Solids in Holding Pond	37

CONTENTS (continued)

	<u>Page</u>
4. CONCLUSIONS AND RECOMMENDATIONS	39
APPENDIX A. GENERAL PROCEDURE FOR CONDUCTING A TRAINING EXERCISE	41
APPENDIX B. SAMPLE DESCRIPTIONS	42
APPENDIX C. SAMPLE RESULTS	47

LIST OF FIGURES

<u>Figure</u>		<u>Page</u>
1.1	Schematic of Fire Training Facility	3
2.1	TOC results from separator at Tyndall AFB	8
2.2	COD results from separator at Tyndall AFB	9
3.1	In-field analyses of chemical oxygen demand	16
3.2	Results of total organic carbon analyses	18
3.3	Results of chemical oxygen demand analyses	19
3.4	Results of oil & grease analyses	21
3.5	Results of nonhalogenated volatile organics	23
3.6	Results of benzene analyses	25
3.7	Results of toluene analyses	26
3.8	Results of xylene analyses	27
3.9	Results of ethylbenzene analyses	28
3.10	Results of dissolved oxygen analyses	30
3.11	Results of BOD analyses	32
3.12	Results of fluoride analyses	34
3.13	Results of pH analyses	35

LIST OF TABLES

<u>Table</u>	<u>Page</u>
2.1 Results from the sixth burn from fuel/water separator at Tyndall AFB	12
3.1 Results of ignitability tests from burn pit at Davis-Monthan	36
3.2 Results of EP-Toxicity metal analysis from burn pit at Davis-Monthan	38
3.3 Fuel/water Separator efficiency results	38
B.1 Sample plan for preliminary studies at Tyndall AFB	43
B.2 Analyses performed on holding pond during test program	44
B.3 Analyses performed on fuel/water separator during test program	45
B.4 Miscellaneous analyses performed during test program	46
C.1 TOC and COD results from fuel/water separator at Tyndall AFB	48
C.2 Results from fuel/water separator at Davis-Monthan AFB	49
C.3 Results from the holding pond at Davis-Monthan AFB	50

**ENVIRONMENTAL STUDIES IN SUPPORT
OF THE LIVE FIRE TRAINING FACILITIES PROJECT**

T. D. Hylton
J. F. Walker

ABSTRACT

The Engineering Division of the Oak Ridge National Laboratory of Martin Marietta Energy Systems, Inc., provided services, under an Interagency Agreement, to the U.S. Air Force to design, construct, and test environmentally acceptable fire training facilities at several Air Force bases for the purpose of providing live fire training capabilities without harming the environment.

The purpose of this effort was to evaluate the wastewater treatment systems of the training facilities. The study focused on taking a set of background samples at a facility and then allowing the Air Force to conduct a series of training exercises. A set of samples was taken immediately following the training exercises to determine the effect the exercises had on the wastewater in the fuel/water separator and the holding pond. The separator and pond were also allowed to set undisturbed, except for sampling and environmental influences, for ~60 d to determine if any stripping or biodegradation was occurring. Samples of the separator and pond were taken at 2, 4, 6, 8, 10, 11, 32, and 59 d following the training exercises. In addition, the burn pit was sampled immediately following the extinguishment of a fire and then again after the burn pit was flushed with water to determine if the materials remaining could be classified as hazardous under the Resource Conservation and Recovery Act (RCRA).

The major conclusions from this study are (1) that the volatilization/biodegradation occurring is insufficient, and (2) the burn pit would not be considered a RCRA hazardous waste site if the pit is properly flushed after the completion of a series of training exercises. It is recommended that (1) bench-scale studies be conducted in order to determine methods to stimulate biological activity, (2) the burn pit flushing procedure be modified, and (3) a proper amount of time should be allowed between training exercises to promote the separation of organics from the water.

1. INTRODUCTION

The Environmentally Acceptable Fire Training Facilities (EAFTFs) were designed and constructed by Martin Marietta Energy Systems, Inc. (Energy Systems), Engineering for the U.S. Air Force at (1) Tyndall Air Force Base (AFB), Florida, (2) Davis-Monthan AFB, Arizona, and (3) Grand Forks AFB, North Dakota. It is anticipated that another EAFTF will be constructed at Mountain Home AFB in Idaho. The specific goals of these EAFTFs are to: (1) eliminate contamination of area soil, groundwater, and surface water by the loss of JP-4 jet fuel and fire suppressants; (2) provide enhanced training and improved safety for fire-fighting personnel; and (3) minimize water pollution impact by treatment, recycling, and reuse of resultant effluent/wastewater and recovered fuel. The resulting design, which is shown schematically in Fig. 1.1, is a closed system which basically consists of three major components: (1) burn pit, (2) fuel/water separator, and (3) holding pond.

The circular burn pit consists of the following layers (bottom to top): (1) a double liner composed of two high-density polyethylene sheets with a plastic mesh sandwiched between the liners for leak detection; (2) a 6-in. layer of sand to protect the liners; (3) a geotextile filter fabric to separate the sand from the overlying coarse stone and prevent surface settling; and (4) a layer of graded, crushed stone to provide a nonslippery, stable surface for fire fighters to walk on during exercises. A vehicle maneuvering area encircles the burn pit.

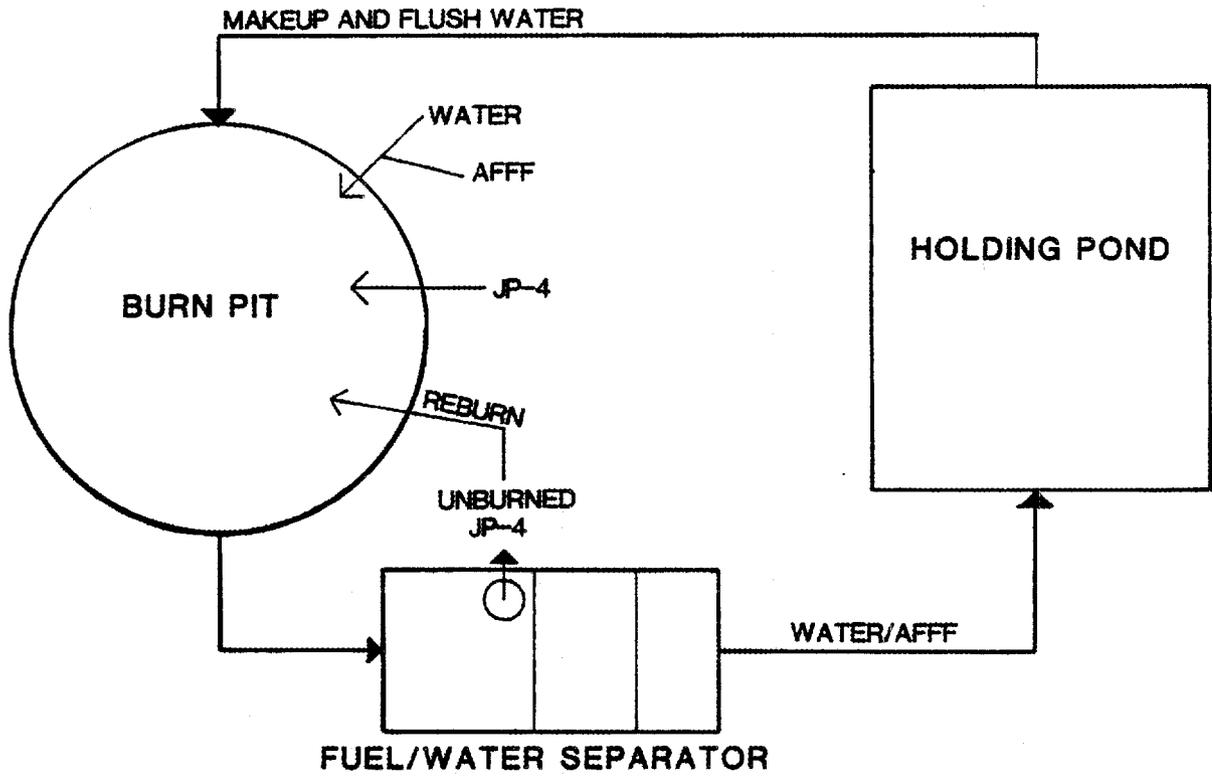


Fig. 1.1 Schematic of Fire Training Facility.

The fuel/water separator is a three-stage concrete unit which is designed to reduce the concentration of oils and greases (O & G) to 25 mg/L in the effluent. The separator is also designed to contain the water used in two fire training exercises. Additional waters from burn exercises can be discharged to the separator every 45 min. The fuel, which is skimmed off in the first stage of the separator, is pumped to a holding tank prior to being returned in the burn pit.

The holding pond is designed with a double liner of two high-density polyethylene sheets with a plastic mesh sandwiched between the liners. The purpose of the pond is to collect the discharge water from the fuel/water separator and to provide water to flush the burn pit after a training exercise.

The facilities are designed to be totally closed systems. The only additional volume added to the system during a series of training exercises is the volume of water and extinguishing agent used to extinguish the fire. The extinguishing agent used is a 3% solution of LIGHT WATER® Brand Aqueous Film Forming Foam (AFFF).

The Chemical Technology Division of the Oak Ridge National Laboratory (ORNL) was requested by the ORNL Engineering Technology Division to prepare a test plan to conduct a study of an EAFTF wastewater treatment system. Tasks to be addressed in the study included (1) identifying the contaminants added to the treatment system during a series of typical training exercises,

(2) determining the quantity of contaminants added to the treatment system during a series of typical training exercises, and (3) resolving the fate of the contaminants after the fire training exercises (e.g., Are the contaminants being removed from the treatment system by volatilization and/or biodegradation?)

The environmental studies were initially scheduled for Tyndall AFB in Florida; however, the Air Force decided to move the location to Davis-Monthan AFB in Tucson, Arizona, since the EAFTF at Davis-Monthan was more representative of the design used at the other training facilities. Some initial studies were conducted at Tyndall AFB to determine concentration estimates that could be expected when the detailed studies were conducted. This report discusses the results of the studies which were conducted at Tyndall and Davis-Monthan Air Force Bases.

1.1 SAMPLING CRITERIA

Samples taken to determine total organic carbon (TOC), chemical oxygen demand (COD), and O & G were acidified with sulfuric acid to a pH of <2 in order to stop any changes due to biodegradation. Acidification also converts inorganic carbon, such as carbonates, to carbon dioxide, which can be purged out of the sample before analyzing for TOC.

Samples were taken for EPA Methods 8015 and 8020 in amber VOA sample vials, with the vials being completely filled with sample solution so that no air bubbles were in the vials.

Samples taken to determine biological oxygen demand (BOD) were also completely filled to eliminate the contact between air and liquid. The BOD samples were sent to Copper State Laboratory in Tucson for analysis because it must be done within a short time period following sampling.

All samples taken were refrigerated as soon as possible. Except for those analyzed in the field, the samples were wrapped to prevent bottle breakage, packed under ice in an insulated container to maintain the integrity of the samples, and shipped to the Oak Ridge Gaseous Diffusion Plant (ORGDP) for analysis.

Duplicate samples were taken in some of the sampling periods to satisfy quality assurance requirements. The duplicate results, which are included in the results tables in Appendix C, showed good agreement among the data.

2. STUDIES AT TYNDALL AFB

2.1 BACKGROUND

Tyndall AFB was the first site at which an EAFTF was constructed. The Tyndall EAFTF includes the burn pit, fuel/water separator, and holding pond, as previously described in Sect. 1. In addition, the facility includes a smoke abatement system which was designed to reduce the air pollution associated with conventional fire training facilities. This study was not concerned with air pollutants, and the smoke abatement system was not utilized. The burn pit flush system at Tyndall was designed to flush from

one side of the pit to the drain weir on the opposite side of the pit. During the training exercises, it was visually apparent that the flush system was not working adequately. The wind would blow the AFFF foam to one side of the burn pit and prevent the AFFF and jet fuel from being flushed from the pit. The general procedure for conducting the training exercises is described in Appendix A.

A total of six training exercises were conducted September 21 and 22, 1988. Grab samples from the influent and effluent streams of the fuel/water separator were taken and composited during the period the burn pit was being drained and flushed. TOC and COD loading on the system by each burn was determined by analyzing composite samples. In addition, the fuel/water separator streams were sampled following the sixth burn for additional analyses to provide a more detailed characterization of the fuel/water separator influent and effluent streams. Table B.1 provides information about the analyses requested, sample locations, and information pertaining to particular samples (e.g., preservation).

2.2 SAMPLE RESULTS

The concentrations of TOC and COD in the influent and effluent streams of the fuel/water separator, as a function of the number of burns, are presented in Figs. 2.1 and 2.2, respectively. Actual data are compiled in Table C.1. Jet fuel is known to be partially soluble in water, and AFFF is water soluble. Both jet fuel and AFFF are carbon-based compounds that would be expected to contribute to both the TOC and COD concentrations.

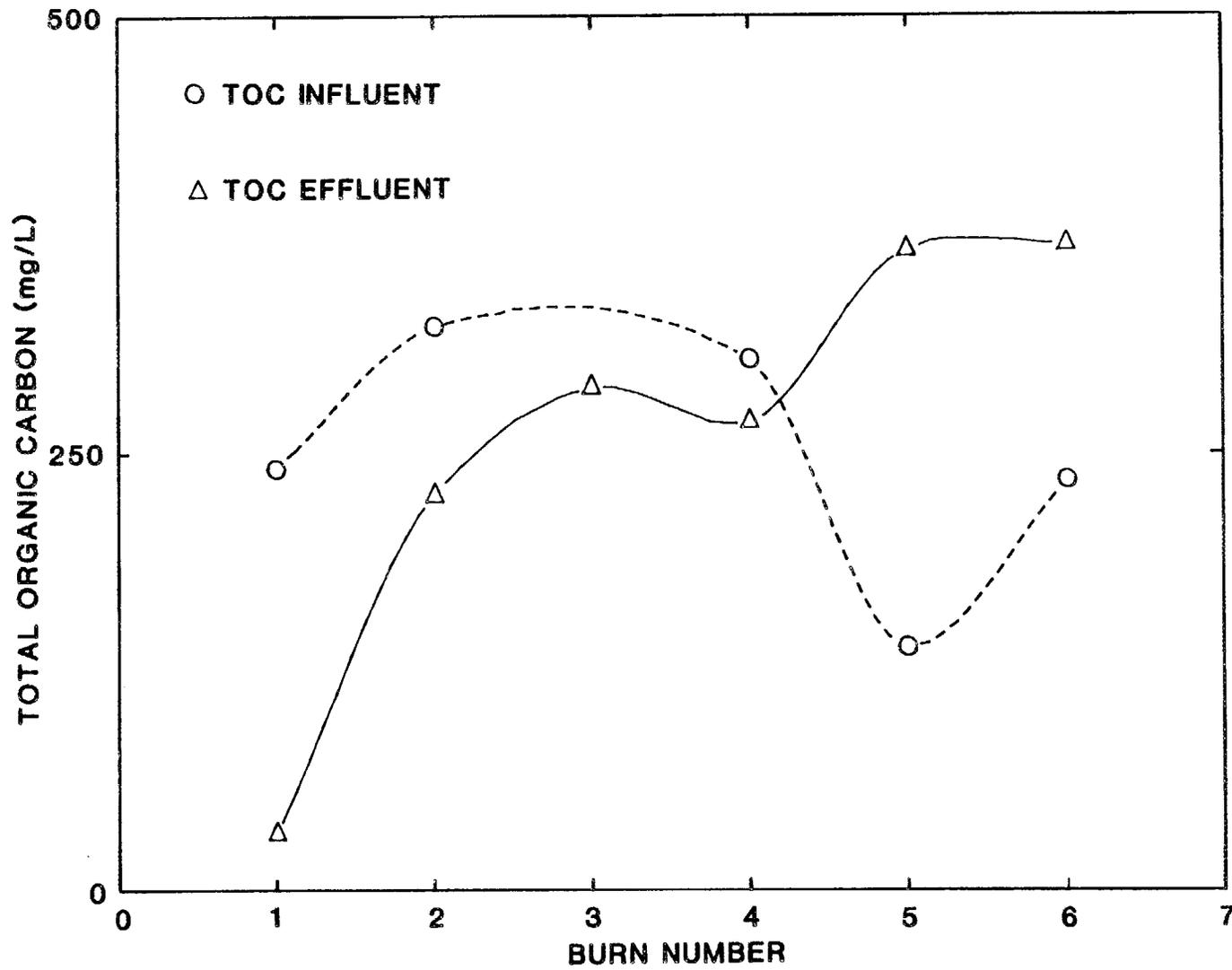


Fig. 2.1 TOC results from separator at Tyndall AFB.

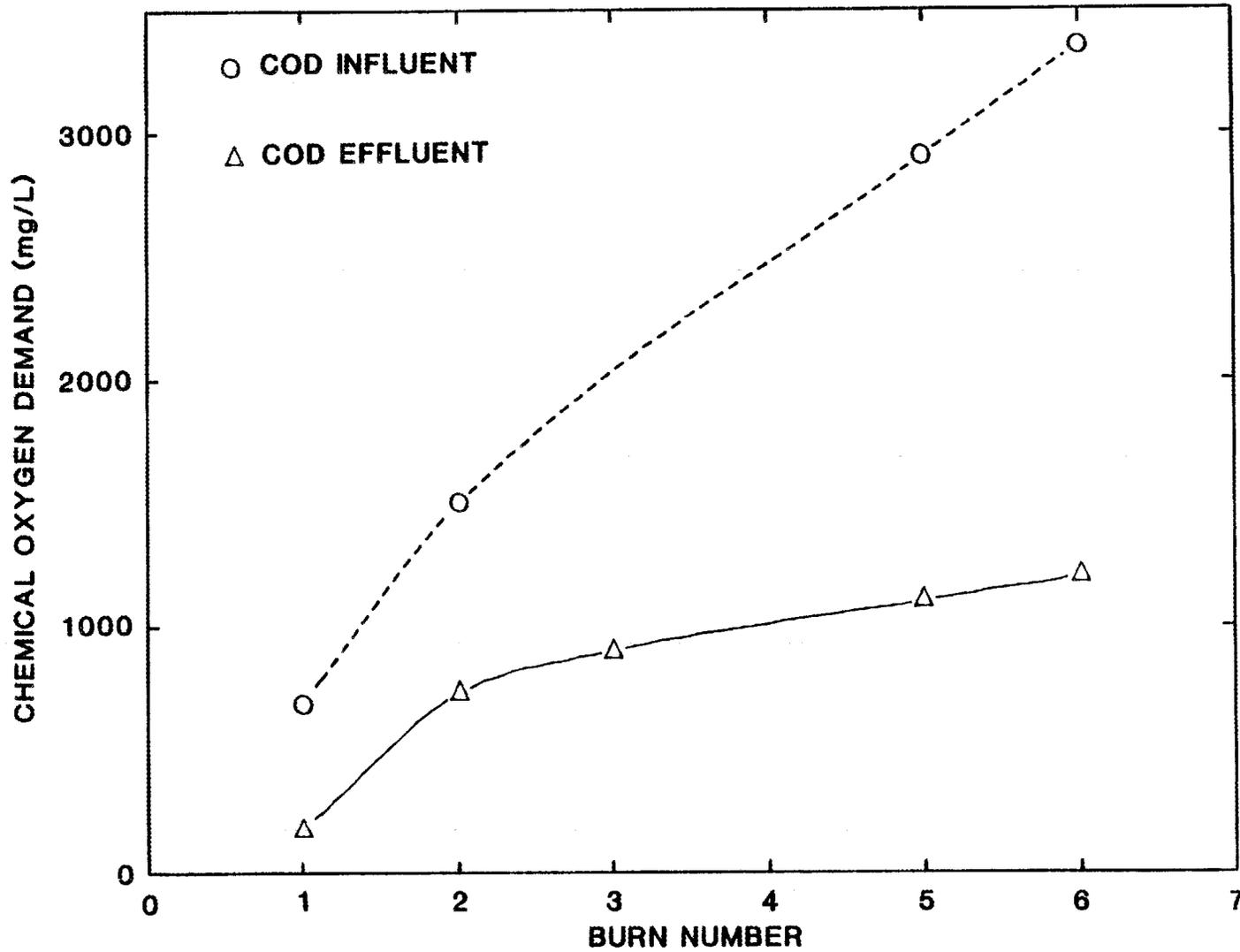


Fig. 2.2 COD results from separator at Tyndall AFB.

One would expect the TOC and COD concentrations to the fuel/water separator to be quite variable due to parameters which are not controlled. For instance, the time required to extinguish a fire and the quantity of AFFF used can vary greatly depending on the personnel involved in the exercise. Both of these parameters would affect the concentration of TOC and COD to the fuel/water separator. From Fig. 2.1, it is seen that the TOC to the separator varied from ~140 to 320 mg/L, which shows the expected variability. The separator influent COD, as shown in Fig. 2.2, seemed to climb steadily. Not enough burns were conducted to determine if the influent COD would eventually level out or would begin to show variability.

Because the treatment system at Tyndall had been used very little, one would expect the COD and TOC concentrations in the separator effluent to (1) initially be very low, (2) climb rapidly as the soluble organics reach the third stage of the separator, and (3) level out at some limiting value. In Fig. 2.2, the separator effluent COD behaves as expected; in Fig. 2.1, the separator effluent TOC initially behaves as expected and then seems to increase and level out at a higher value. It should also be noted that on burns 5 and 6, the effluent TOC concentrations are higher than the inlet TOC concentrations. This difference may possibly be due to the way the fuel/water separator operates. The separator has a capacity of ~8500 gal, and the flush from each pit burn is estimated to contain ~1500 gal. Therefore, depending on the level at which the separator is operated, the wastewater from several burns may be held in the separator.

Because the separator is designed to minimize mixing, the wastewater from one burn is actually pushing the wastewater from a previous, possibly more concentrated, burn out of the fuel/water separator. This assumes that the majority of the TOC entering the separator is soluble and that little TOC is actually removed in the separator.

Since the primary objective for conducting the test at Tyndall was to provide estimates for the concentrations to be expected at Davis-Monthan, there were not enough samples taken to properly evaluate what was happening with the COD and TOC concentrations through the fuel/water separator.

Analytical results from the composite samples taken from the fuel/water separator following the washout of the sixth burn are presented in Table 2.1. By comparing the O & G effluent concentration of 30 mg/L with the design average effluent concentration of 25 mg/L, it can be seen that the separator was removing >99% of the O & G. This removal efficiency indicates that the fuel/water separator was working close to the design limits. EPA Method 8015 and 8020 data indicate ~70% removal of the volatile fuel components. The fluoride results were not explainable, but it is expected that the fluoride effluent concentration is the result of a bad sample or analysis.

Table 2.1. Results from the sixth burn from fuel/water separator at Tyndall AFB

Component	Influent (mg/L)	Effluent (mg/L)
TOC ^a	234	369
COD ^b	3,350	1,200
Fluoride	2.9	10
O & G ^c	60,000	30
NHVO ^d	86	23
Benzene	3.0	0.77
Toluene	6.5	1.9
Xylene	5.7	1.8
Ethylbenzene	0.9	0.4

^aTotal organic carbon.

^bChemical oxygen demand.

^cOil and grease.

^dNonhalogenated volatile organics.

3. DAVIS-MONTHAN STUDIES

3.1 BACKGROUND

Major differences between the EAFTF at Davis-Monthan AFB and the EAFTF at Tyndall AFB were (1) the size of the facility components, (2) the design of the flush system in the burn pit, and (3) the absence of a smoke abatement system in the Davis-Monthan facility. The diameter of the Davis-Monthan burn pit is 75 ft, whereas that of the burn pit at Tyndall AFB is 100 ft. Also, the Davis-Monthan flush system is designed to flush from the center of the pit to its outer edge, where a trench carries the water and unburned jet fuel to the drain weir. This flushing system should minimize the effect caused by the wind blowing the AFFF foam.

Fire training exercises were scheduled to begin December 1, 1988; however, the training was rescheduled for December 3 and 4 due to high winds and mechanical problems. The submersible pump in the holding pond, which was used to flush the burn pit to the separator, was inoperable, and repair would have been possible only by draining the holding pond. The Air Force project officer decided to pipe into the flush system a portable gasoline-powered pump of lower capacity to prevent the environmental tests from being delayed. The portable pump had a lower pumping capacity than the normal operating pump; therefore, the flushing period was extended so that the amount of water used to flush the burn pit was approximately the same as would have been used with the normal pump. The Air Force completed eight training exercises on December 3 and three exercises on the morning of December 4.

3.2 SAMPLING PLAN DESCRIPTION

Samples that were taken during the Davis-Monthan studies are listed in Tables B.2 through B.4. A short description of the sampling procedure is given here.

A set of samples was taken from the fuel/water separator and the holding pond prior to the training exercises in order to obtain an initial characterization of the wastewater. Because it was important to obtain chemical oxygen demand (COD) concentrations in the separator and the holding pond that were high enough to detect whether stripping or biodegradation was occurring, the fuel/water separator and the holding pond were sampled and analyzed in the field after each training exercise until the COD climbed to >250 mg/L. This COD level occurred on the first day of training exercises.

The influent and effluent streams of the separator were sampled after the second jet fuel fire was extinguished on the second day to determine the effectiveness of the separator. Grab samples were taken from the burn pit drain weir during the burn pit flush out and composited to obtain the separator influent sample. The separator effluent sample was obtained by taking core samples from the third stage of the separator during the flushing out of the burn pit.

A set of samples was also taken from the burn pit immediately following extinguishment of a fire and again after the pit had been flushed to the fuel/water separator and analyzed for ignitability and EP-Toxicity. Another full set of samples was taken from the separator and the pond immediately following completion of the final training exercise to determine what effect the training exercises had on the wastewater characteristics.

Following the last training exercises, the training facility was left undisturbed for ~60 d, except for the influence of sampling efforts and natural environmental influences. The separator and pond were sampled on alternating days over a period of 10 d after the final training exercise to determine the short-term effect on TOC, COD, pH, dissolved oxygen (DO), and biological oxygen demand (BOD) in the separator and pond. Air Force personnel requested permission to take samples during the 10 d period following the training exercises. Permission was granted after demonstrating the sampling methods to the Air Force personnel and then observing them performing the sampling methods. Full sets of samples were also taken 11, 32, and 59 d following the final training exercise.

3.3 SAMPLING METHODS

Core composite samples were taken from the holding pond and the third stage of the fuel/water separator. Both the separator and the pond were sampled in a grid pattern in order to obtain representative samples. The grid pattern was easily accomplished in the separator; however, following the grid pattern in the pond was complicated by strong winds, which made it difficult to maneuver the row boat over the pond.

3.4 RESULTS

3.4.1 In-Field Chemical Oxygen Demand Analyses

Composite core samples from the third stage of the fuel/water separator and from the holding pond were taken after each training exercise and analyzed in the field for COD by the HACH method. This method of COD analysis provided the COD concentrations in a relatively short period of time (~2 h). The in-field samples for COD, taken the first day of training exercises, indicated that the separator COD concentration had climbed to >3000 mg/L and that the pond had attained a COD concentration of 1200 mg/L. This COD behavior is shown in Fig. 3.1. These COD concentrations were sufficiently high to allow monitoring of any change in COD with time. Training exercises were held on the second day to provide additional training for the fire fighters, but samples were not taken for in-field analysis for COD. As expected, the COD concentration in the separator increases at a higher rate than does that in the pond due to the pond's larger volume.

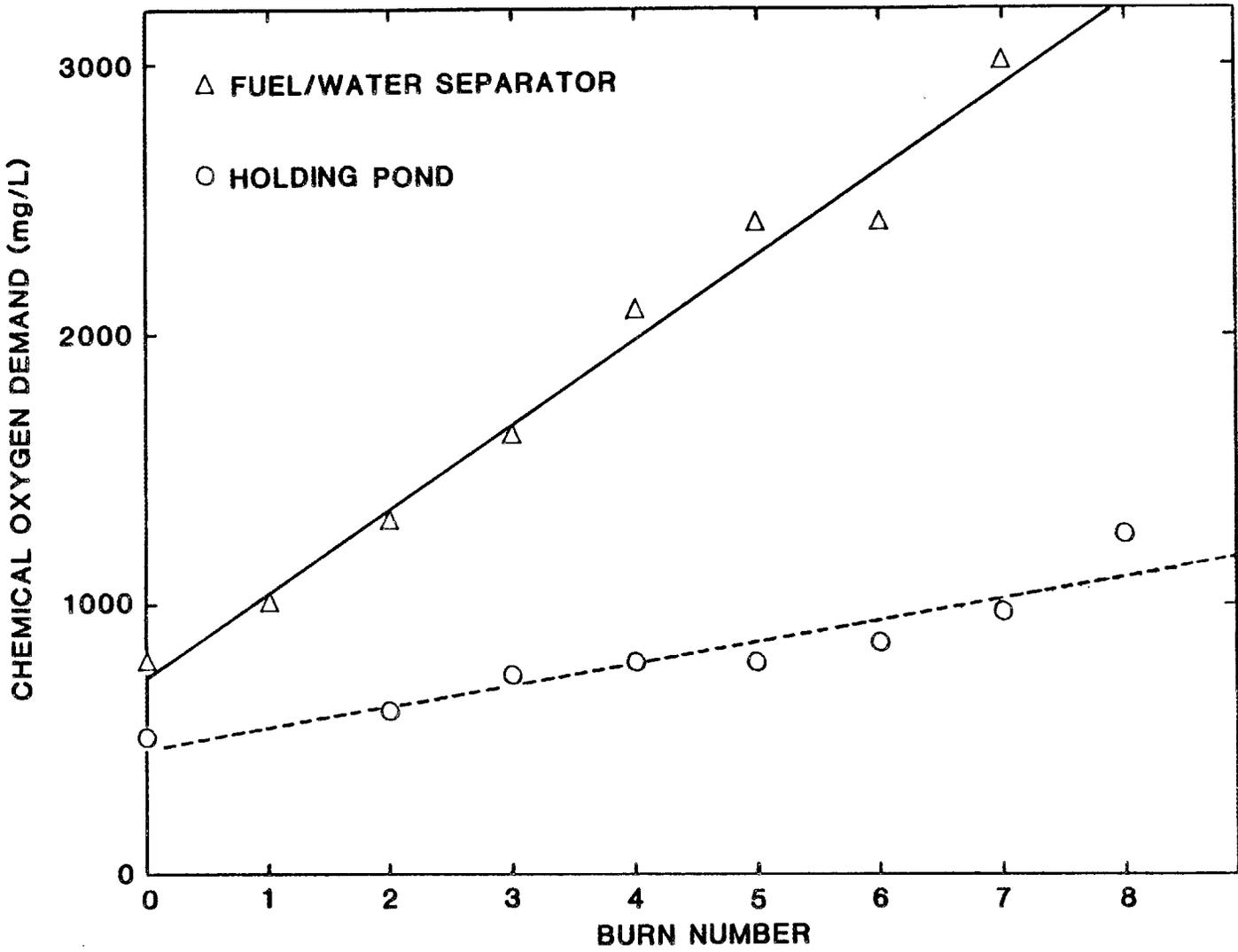


Fig. 3.1 In-field analyses of chemical oxygen demand.

3.4.2 Total Organic Carbon

Composite core samples were taken from the separator and pond over a period of ~60 d and analyzed for TOC by Method 415.1. The U.S. Environmental Protection Agency (EPA) quotes a precision of 10% and an accuracy of 5% using this method. A duplicate pond sample was taken with the 59-d samples. Results are presented in Fig. 3.2, and the data are compiled in Tables C.2 and C.3. TOC samples are purged to remove CO₂ before analysis. This purging will also remove the volatile organic compounds; therefore, the TOC is actually a measure of the nonpurgeable organic compounds. The series of fire training exercises increased the TOC level in the separator and the pond to ~1200 and 400 mg/L, respectively. Over the 59-d period following the exercises, essentially no decrease in the TOC concentration occurred in either the pond or the separator. This inactivity indicates that the nonpurgeable organics were not being biodegraded during this period.

3.4.3 Chemical Oxygen Demand

Core composite samples that were taken from the separator and the holding pond during the 59-d period were analyzed for COD by Method 410.4. The EPA cites a precision of 10% and an accuracy of 5% for samples analyzed by this method. A duplicate sample from the separator was submitted to the laboratory with the 59-d samples. Results of the analysis are presented in Fig. 3.3 and Tables C.2 and C.3. The series of fire training exercises increased the COD concentration in the pond and the separator to ~2000 and 6000 mg/L,

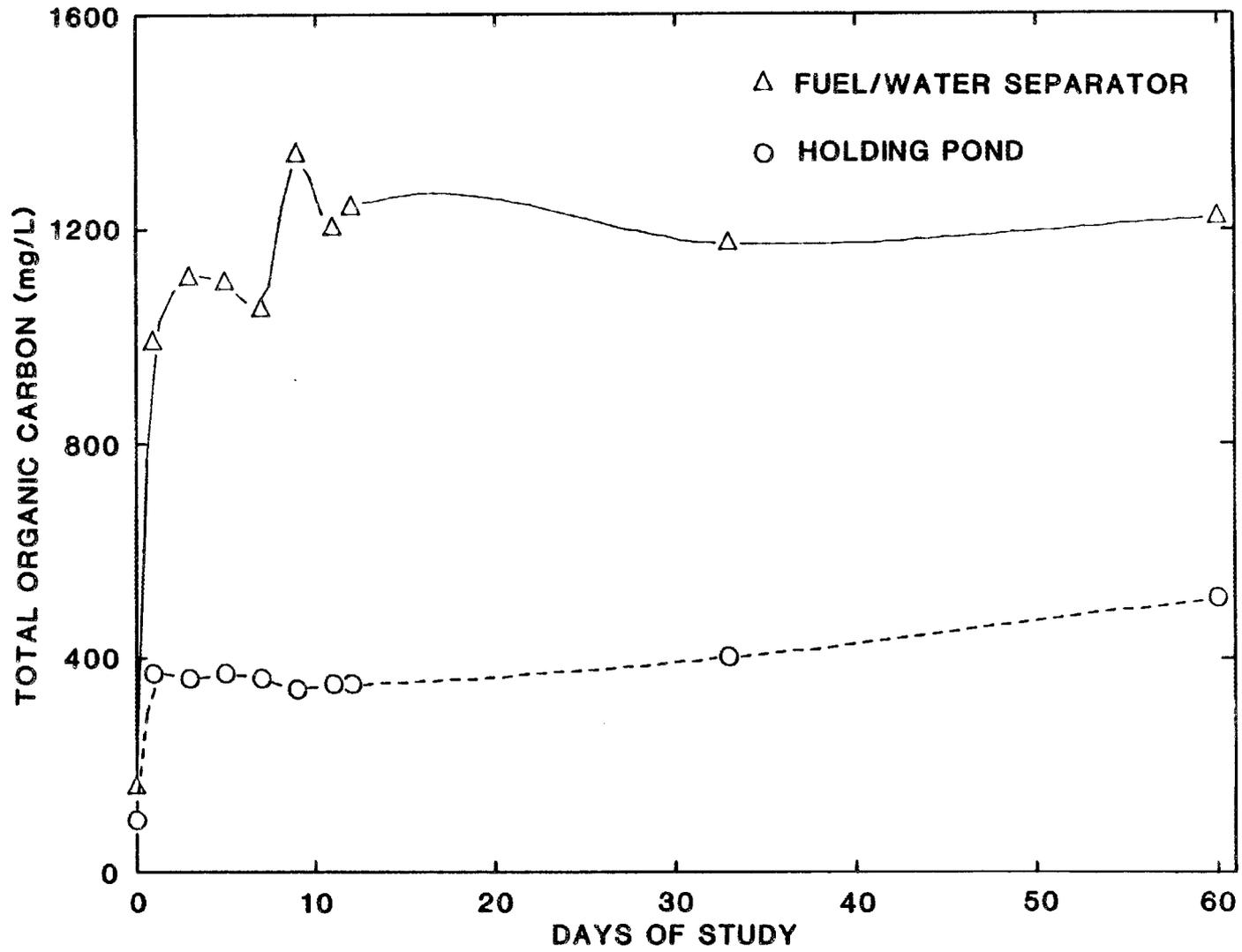


Fig. 3.2 Results of total organic carbon analyses.

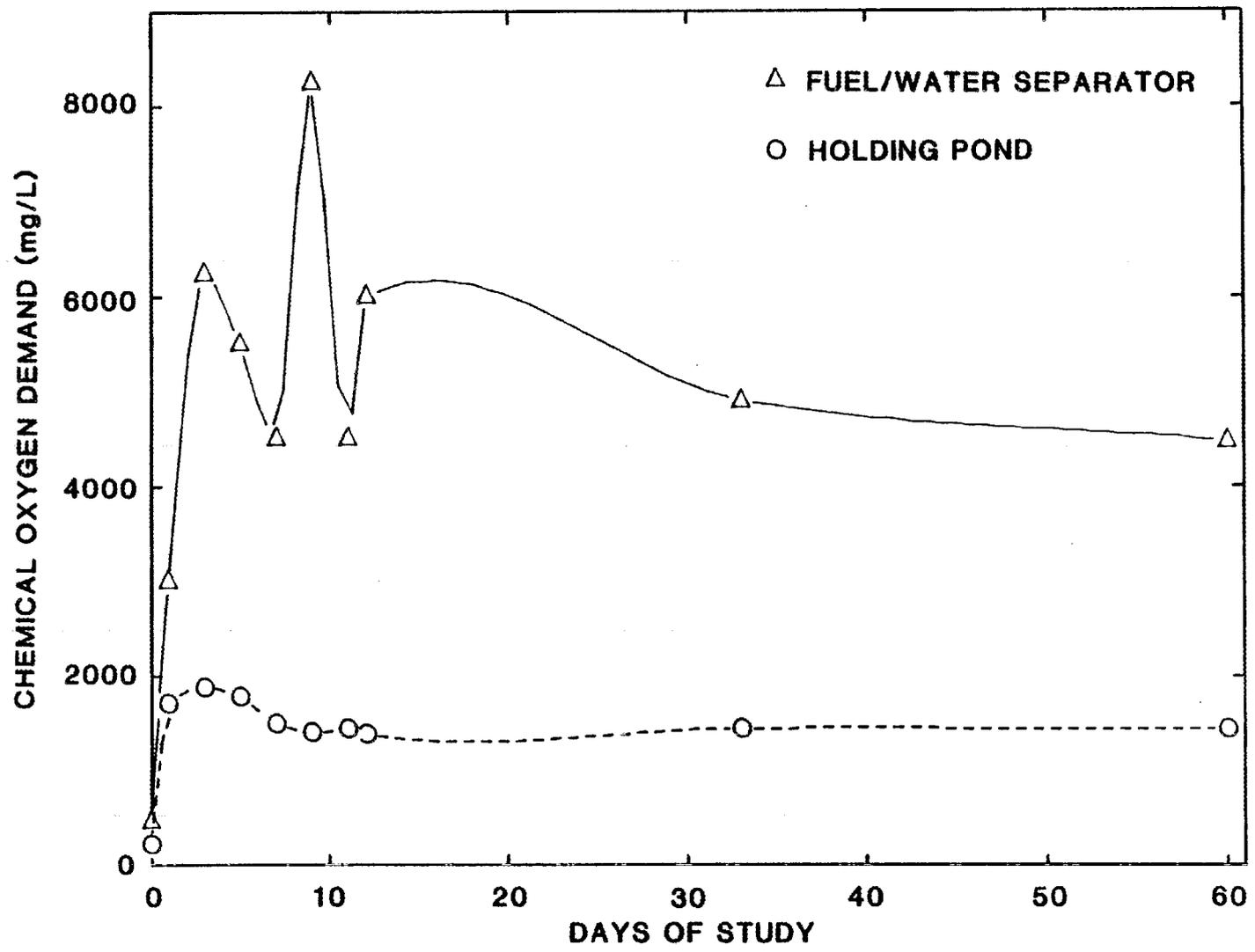


Fig. 3.3 Results of chemical oxygen demand analyses.

respectively. The sample data for the separator appear to be somewhat erratic during the 10-d, alternating-day samples. This variance could possibly be due to differences in sampling techniques by persons obtaining the samples. During the ~60-d period, there appears to be little, if any, decrease in COD concentration in either the pond or the separator, which is consistent with the TOC analyses.

3.4.4 Oil and Grease

The O & G core composite samples taken from the separator and the pond during the study were analyzed according to Method 413.1. O & G samples are usually used for a screening method, and there are no data concerning precision or accuracy for this method of analysis. A duplicate sample was taken from the holding pond and submitted to the laboratory with the 59-d samples. Sample results are presented in Fig. 3.4 and Tables C.2 and C.3. Analysis of the O & G samples indicates a concentration of heavy organics, but it could be influenced by semivolatiles, such as the Butyl Carbitol® in the AFFF. The O & G concentration in the third stage of the separator and in the holding pond reached ~170 and 30 mg/L, respectively, after the series of exercises. The concentration of O & G in both the separator and the holding pond seemed to decrease somewhat over the 60-d period following the exercises. This decrease was likely due to the further separation of the fuel/water phases as the wastewater sat in the pond and in the separator. This separation was visibly apparent by the increased number of oil globules that had collected on the sides and corners of the separator and pond, as observed by the project principal investigator who

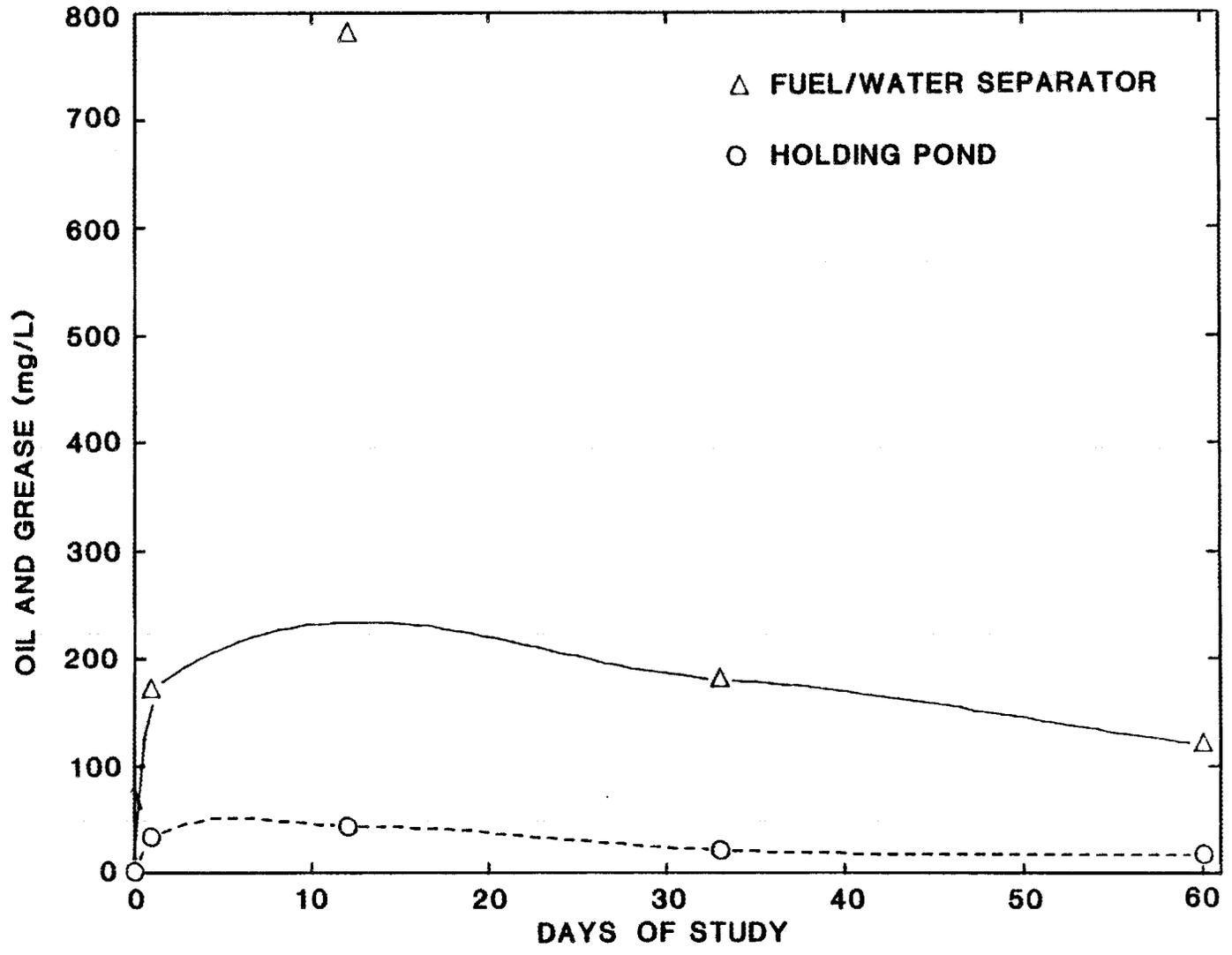


Fig. 3.4 Results of oil & grease analyses.

returned to take samples 11 d after the exercises had been completed. The oil globules that collected on the sides and corners of the pond and separator would not have been picked up while taking the composite core samples. The fact that the O & G concentration in the third stage of the separator reached 170 mg/L and the concentration in the pond exceeded 25 mg/L suggests that either the fuel/water separator was overworked by doing too many burns in a specified time period or the separator was not working as designed. The efficiency of the fuel/water separator could probably be increased by holding the wastewater in the first stage of the separator for as long as possible before pumping it to the pond. The datum point for the O & G from the fuel/water separator taken 11 d following the last burn is assumed to be from a bad sample or analysis, since it is completely out of the range of the other data points.

3.4.5 Nonhalogenated Volatile Organics

The samples submitted to determine the total concentration of non-halogenated hydrocarbons were analyzed by Method 8015. Data are not available concerning the precision or accuracy for this analytical method. Results are presented in Fig. 3.5 and compiled in Tables C.2 and C.3. The data indicate that there was an increase in nonhalogenated volatile organics during the training exercises; however, their concentration diminished over the 59-d period, even reaching nondetectable limits in the pond prior to the sample taken 32-d after the training exercises. Although it is not possible to positively identify the manner in which the concentration is decreasing, it is speculated that the decrease in concentration

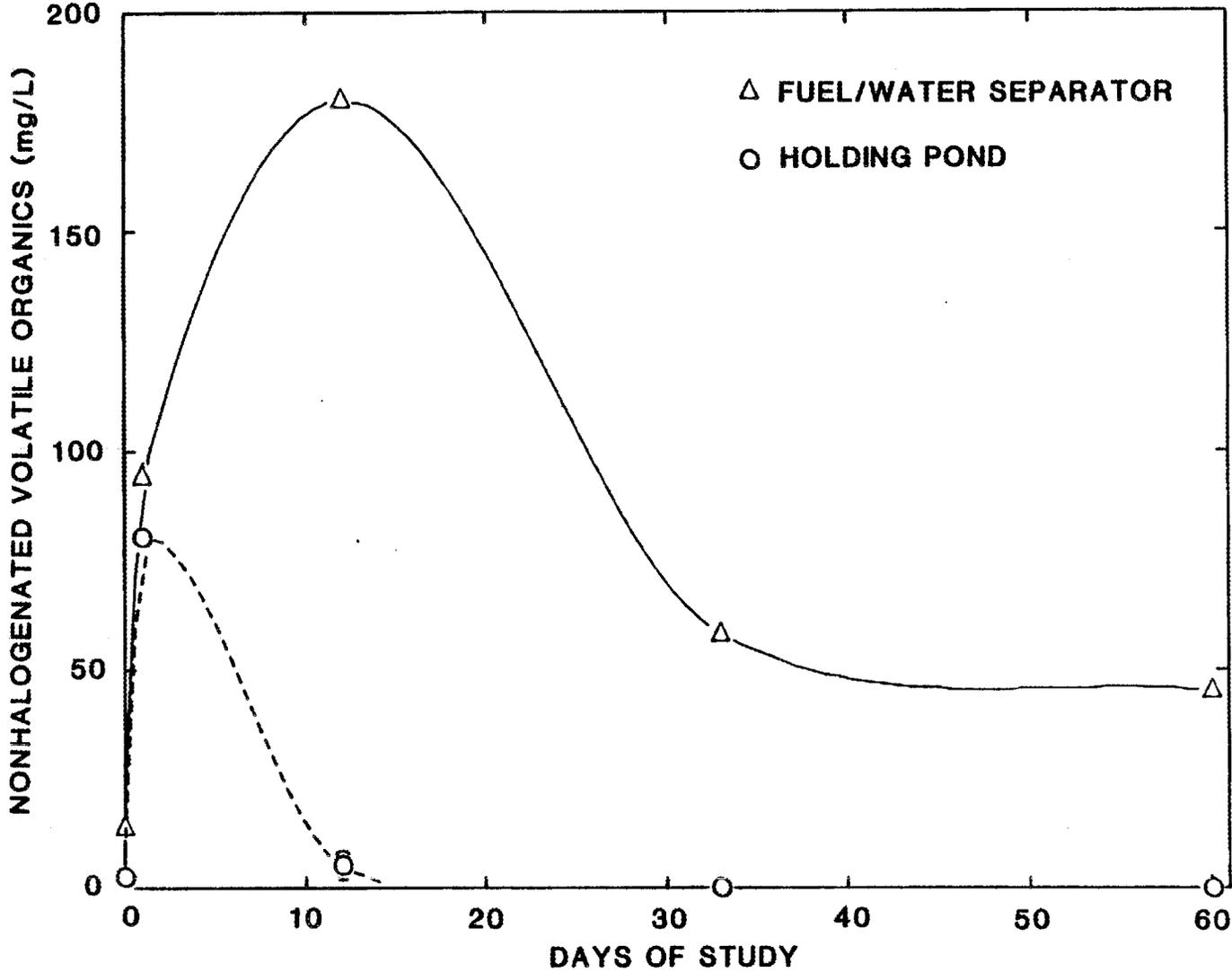


Fig. 3.5 Results of nonhalogenated volatile organics.

is due to volatilization, rather than biodegradation, since previous data have not shown any decrease in TOC or COD concentration. The datum point for the fuel/water separator following the last burn is assumed to be from a bad sample or analysis based on the behavior of the specific volatile components, which is to be discussed in Sect. 3.4.6. It is expected that the concentration of nonhalogenated organics should be much higher in the fuel/water separator following the final burn.

3.4.6 Volatile Organic Components

Samples submitted to determine the concentrations of benzene, toluene, xylene, and ethylbenzene were analyzed by Method 8020. The precision and accuracy of this method of analysis are dependent on several factors including (1) component of interest, (2) concentration of component, and (3) the position of the concentration of the component on the spectrum. The behavior results of benzene, toluene, xylene, and ethylbenzene are shown graphically in Figs. 3.6 through 3.9 and numerically in Tables C.2 and C.3. Matrix spike recovery analyses, in which a known amount of a component is added to the samples, were done on samples from the holding pond taken 32 and 59 d after the training exercises. These findings suggest that some kind of interference occurred in the analysis. These results indicate that the actual concentrations of benzene, toluene, xylene, and ethylbenzene may be a factor of 3 higher than what the results show for the 32-d samples and a factor of 2 higher for the 59-d samples. However, the trend can still be followed, as shown in the behavior curves. The four components

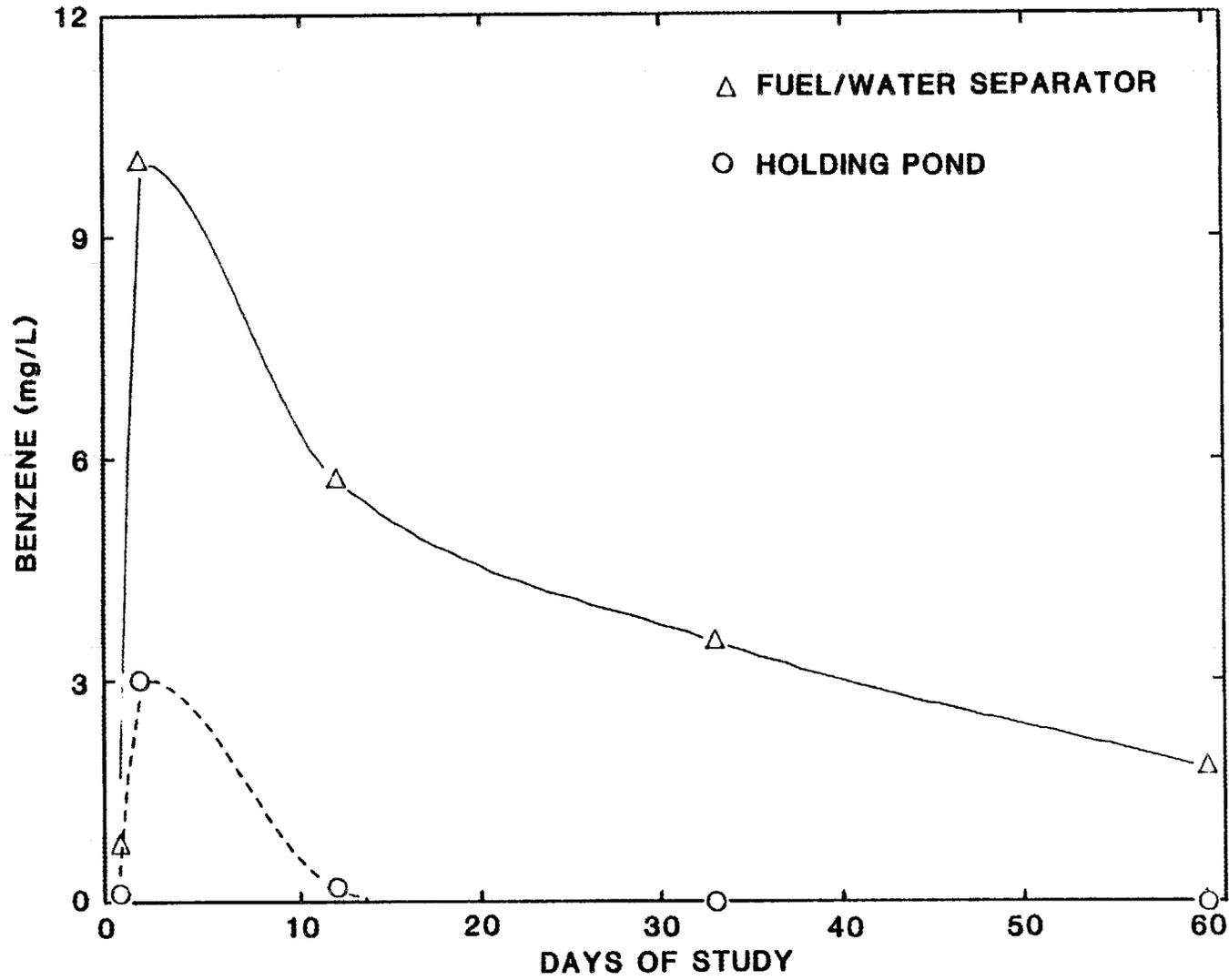


Fig. 3.6 Results of benzene analyses.

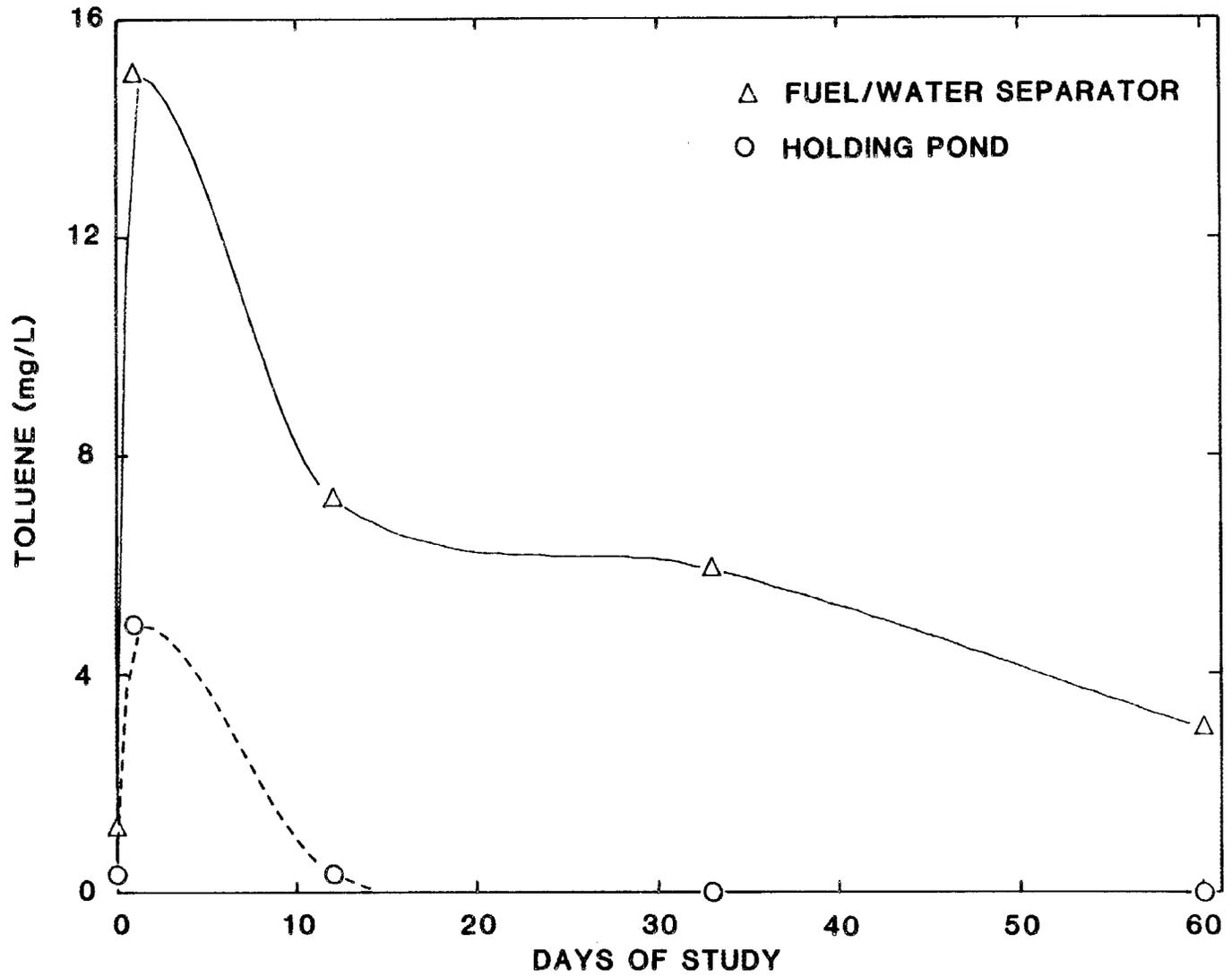


Fig. 3.7 Results of toluene analyses.

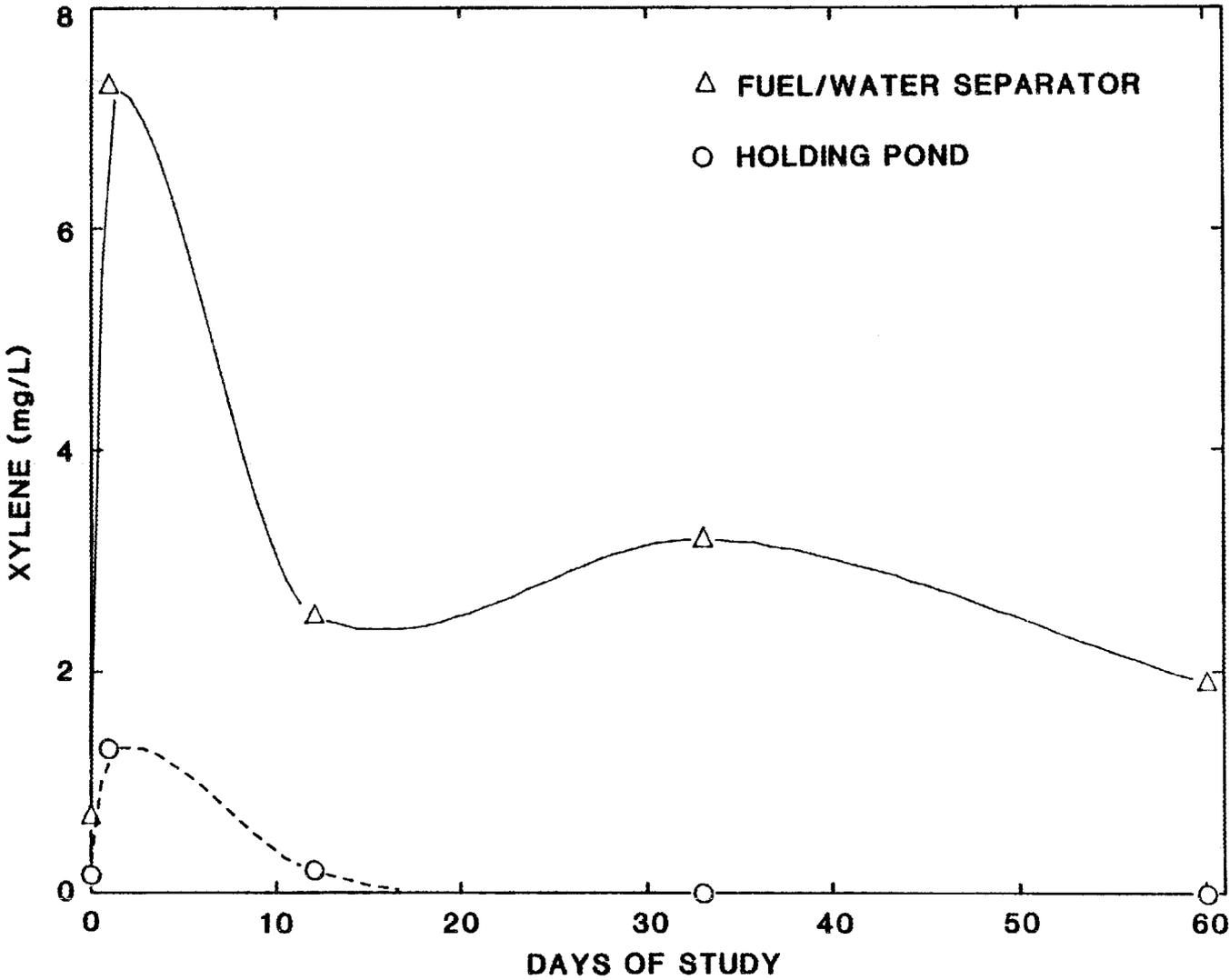


Fig. 3.8 Results of xylene analyses.

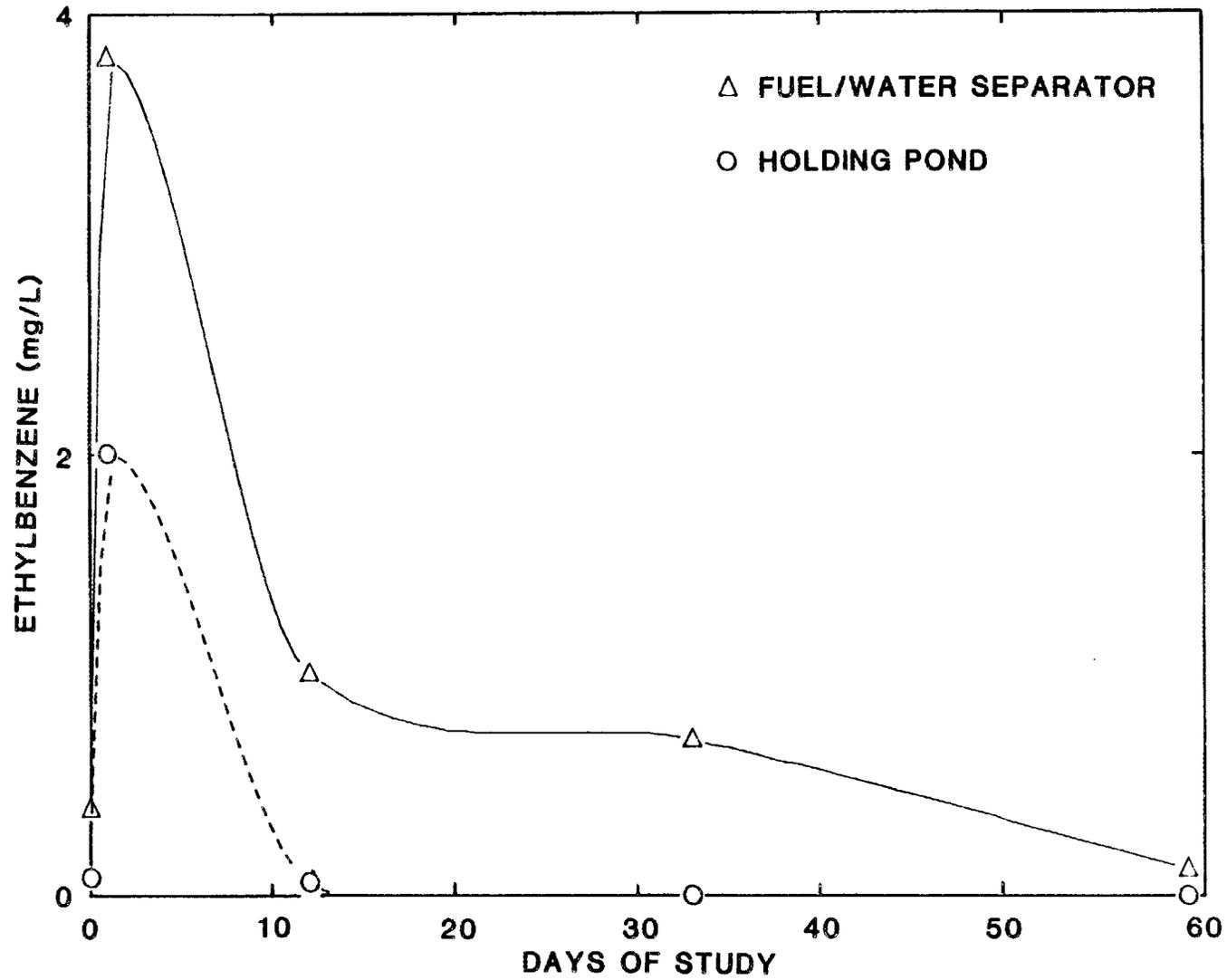


Fig. 3.9 Results of ethylbenzene analyses.

are diminishing over the long-term period in the fuel/water separator, and none of the four components are measurable in the holding pond after allowing 32 d for the components to biodegrade and/or volatilize. Although it cannot definitely be determined from the data, it is likely that the decrease in concentration during the 59 d is due to volatilization rather than to biodegradation, based on the previous results showing relatively no changes in TOC and COD concentrations. It should be noted that the decrease in volatile organics would not be expected to cause a similar decrease in the COD concentration because the volatile compounds make up <10% of the COD. These results correlate with the results of the EPA Method 8015 samples. One of the data points for xylene in the fuel/water separator (either 11-d or 32-d) is assumed to be due to expected variance within the sampling and analytical methods.

3.4.7 Dissolved Oxygen

The DO analysis was performed in the field with a YSI Model 57 DO meter and a YSI 5739 DO probe. The instruction manual supplied with the DO meter cites an accuracy of $\pm 1\%$ of full scale at calibration temperature, or 0.1 mg/L, whichever is larger. The data obtained from the DO analyses are presented in Fig. 3.10 and Tables C.2 and C.3. The results indicate that the oxygen concentration decreases during the training exercises; however, the oxygen concentration increases over the 60-d period of inactivity. The DO concentration can be expected to change some depending on the temperature, weather conditions, bioactivity, etc. The DO concentration has reestablished itself over the 59-d period of inactivity.

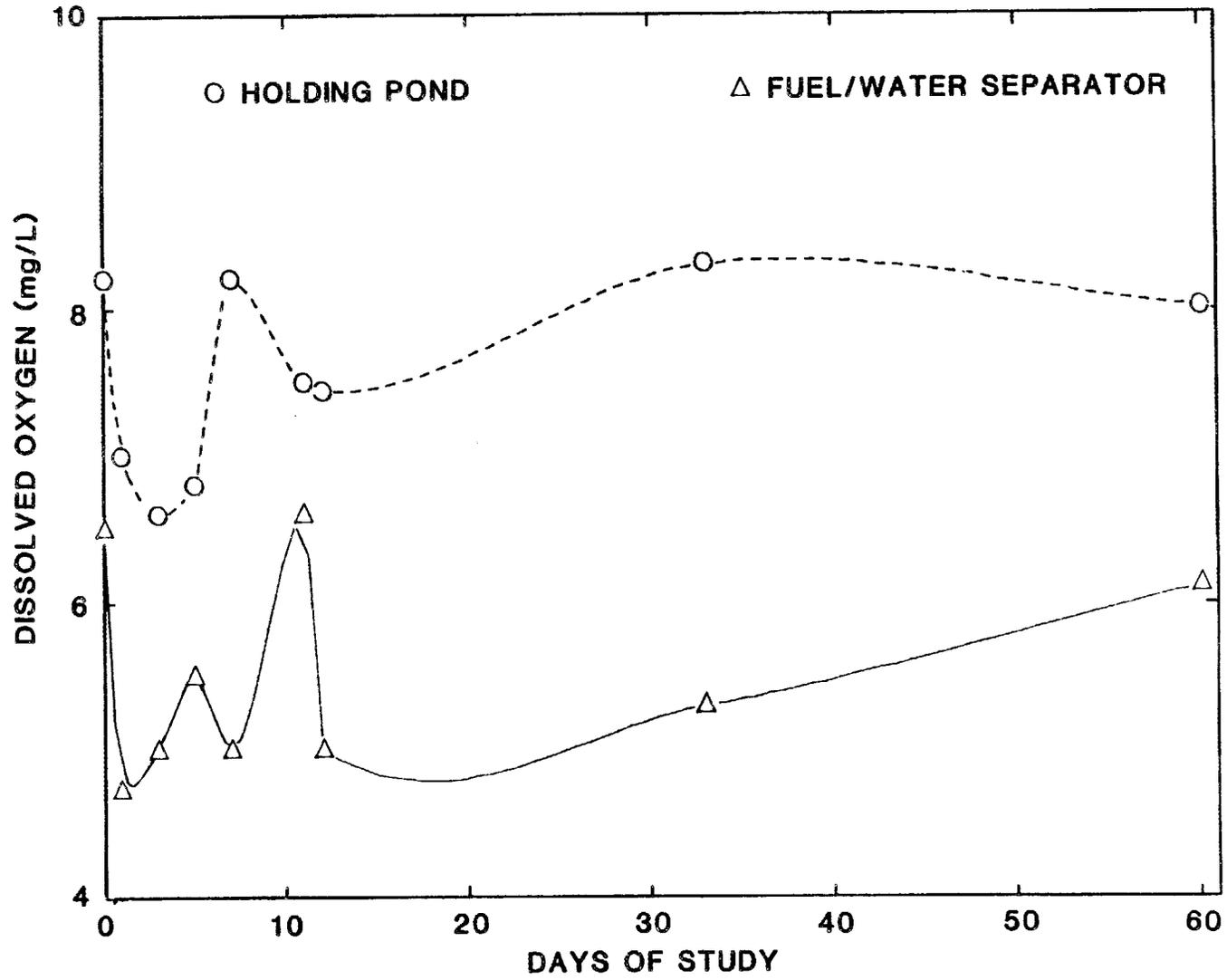


Fig. 3.10 Results of dissolved oxygen analyses.

3.4.8 Biological Oxygen Demand

The BOD samples were analyzed by Method 405.1, which is cited by the EPA as having a 20% precision. The BOD data are listed in Tables C.2 and C.3, and represented graphically in Fig. 3.11. The data basically show that little, if any, biodegradation is occurring since the BOD concentration at the end of 60 d is approximately the same as that at the completion of the burn exercises. Most of the scatter in this data is within the range of precision for experimental error cited by the EPA.

3.4.9 Butyl Carbitol®

The concentration of Butyl Carbitol® was determined by Method 8270 for bases, neutrals, and acids. Butyl Carbitol® is the registered name for diethylene glycol monobutyl ether, and it is the chief chemical component in the extinguishing agent AFFF. The behavior of Butyl Carbitol® during the 59-d period is indicated in Tables C.2 and C.3. However, the confidence of these results is not very high because of the erratic results and because of the poor recovery of matrix spikes added to the samples. It is suspected that some kind of interference occurred which prevented the accurate measurement of Butyl Carbitol®.

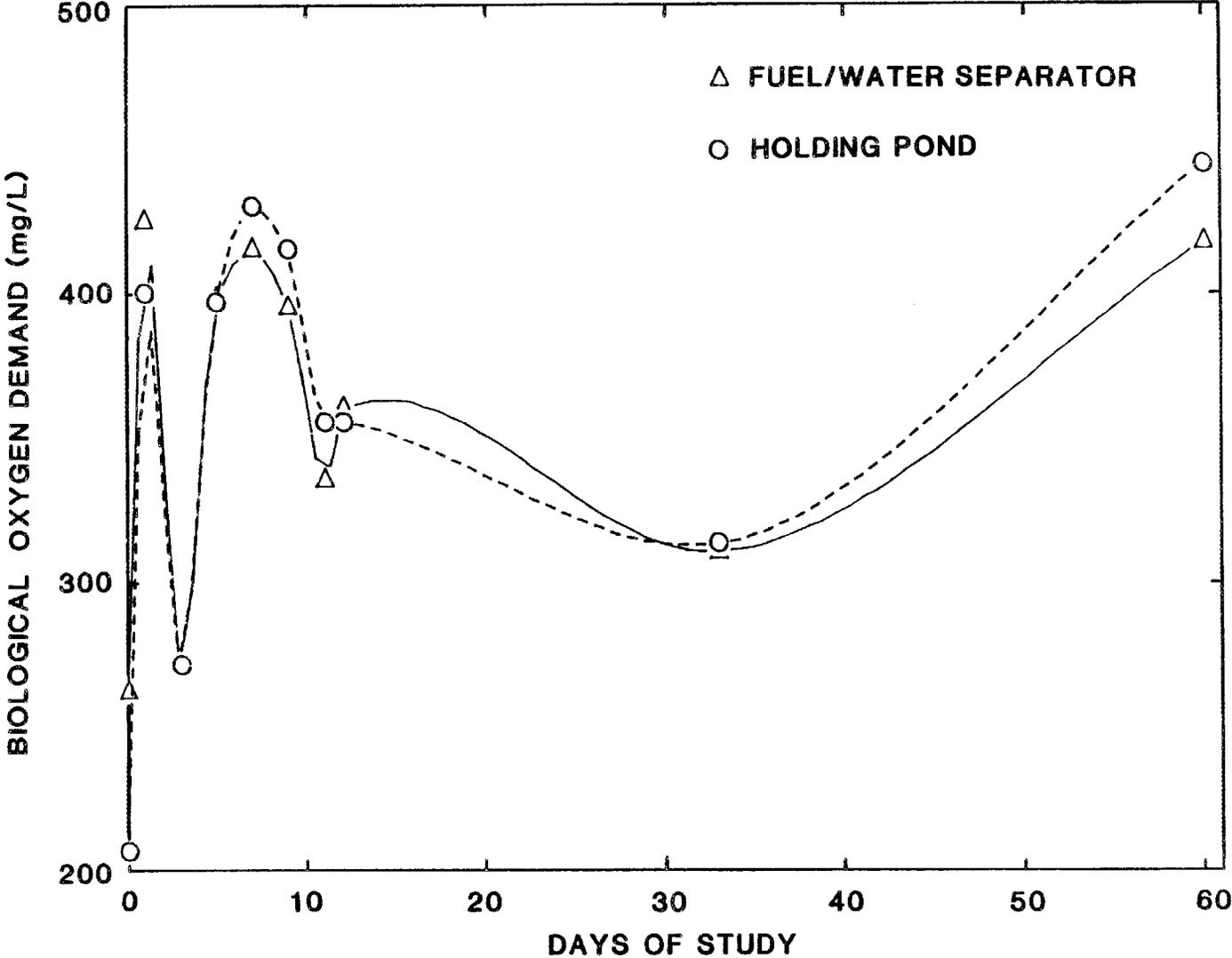


Fig. 3.11 Results of BOD analyses.

3.4.10 Fluoride

Samples submitted to determine the concentration of fluoride were analyzed by Method 340.2, which EPA reports has a 5% precision. A duplicate fluoride sample was submitted to the laboratory with the 59-d samples. Fluoride is present in the extinguishing agent (AFFF) in the form of a fluoroalkyl surfactant. The separator and the pond were sampled to determine the concentration of fluoride in the water, with the results presented in Fig. 3.12 and Tables C.2 and C.3. The data indicate an initial small increase in fluoride concentration, but the concentration remains fairly stable thereafter.

3.4.11 Temperature and pH

During sampling, the pH of the water in the separator and in the pond was monitored using a Cole-Parmer Model 5985-00 pH meter. The data are presented in Tables C.2 and C.3, and the pH data are also shown in Fig. 3.13. The pH data indicate that the training exercises had a negligible effect on the pH of the separator and a slight effect on the pH of the pond; however, the pH of the separator decreased almost one unit, and the pH of the pond decreased ~1/2 unit during the 59-d period. The pH values measured are normal values for water and do not present an adverse impact on the environment.

The temperatures of the fuel/water separator and holding pond were taken with a mercury thermometer and did not vary much according to the data. However, the temperature remained in the 8 to 16°C (46 to 61°F) range, which may be too low to stimulate biological activity.

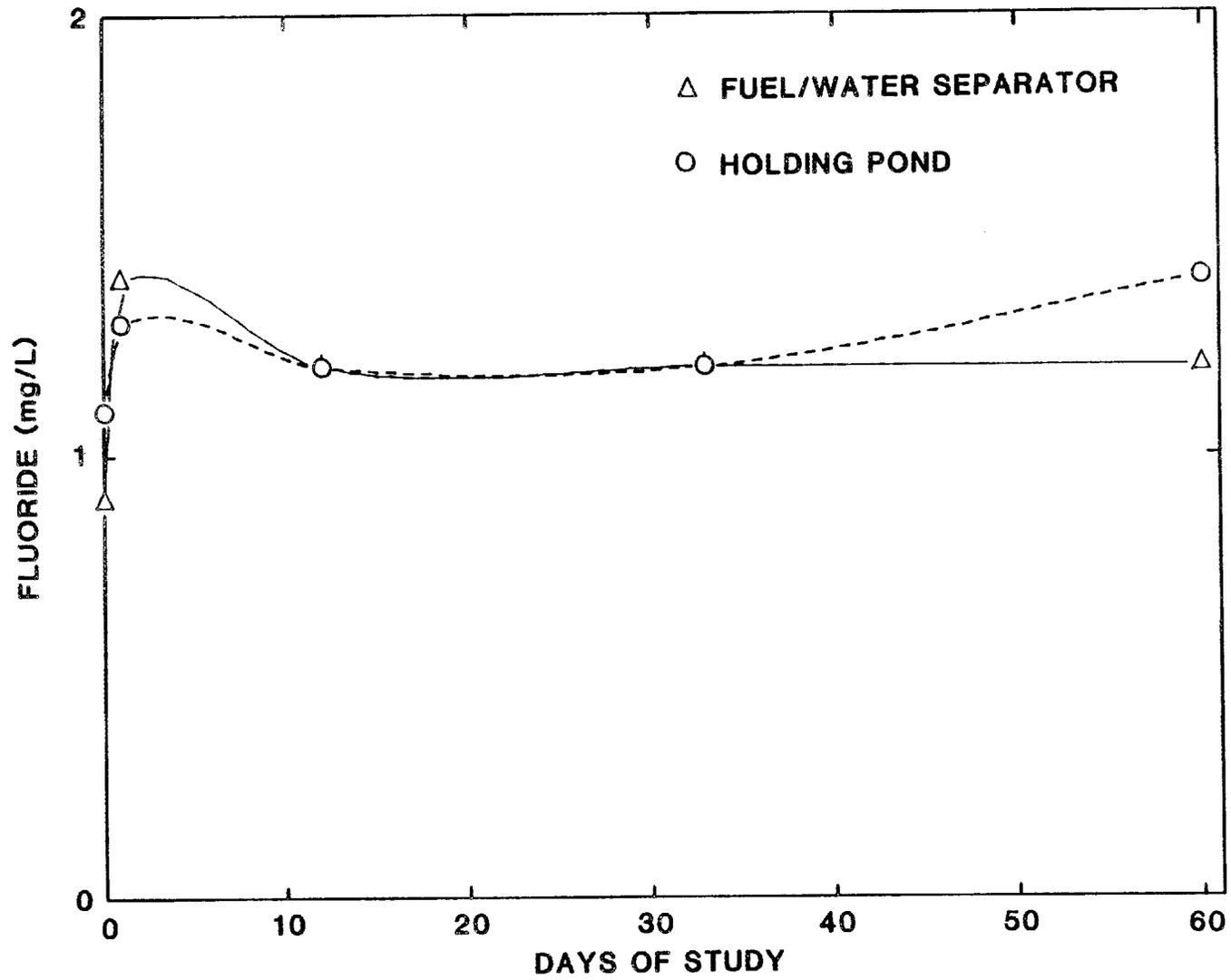


Fig. 3.12 Results of fluoride analyses.

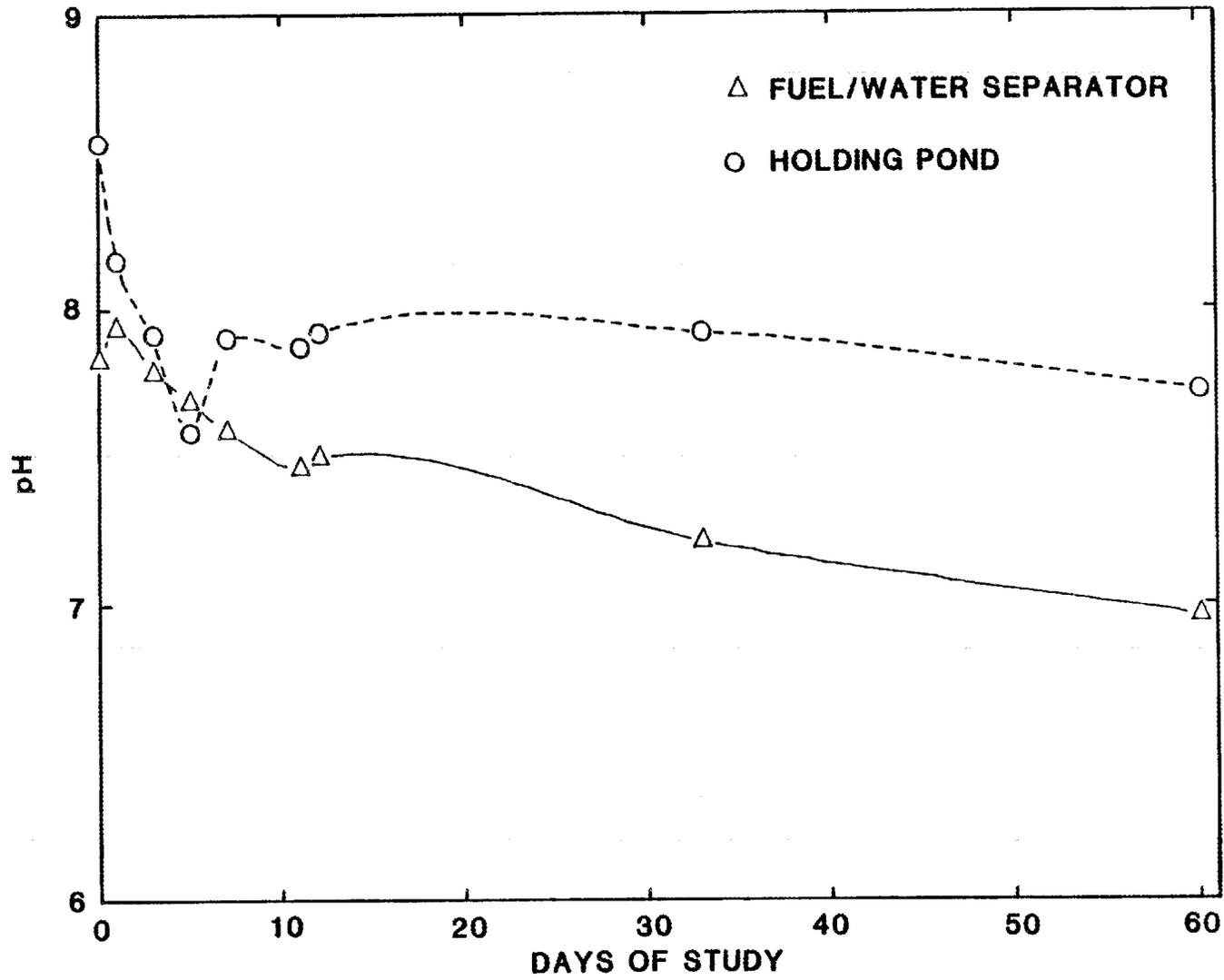


Fig. 3.13 Results of pH analyses.

3.4.12 Ignitability and EP-Toxicity Results from Burn Pit

Ignitability was evaluated in accordance with SW-846 Method 1010. The results from the ignitability samples taken from the burn pit (Table 3.1) are somewhat misleading and require some interpretation. When the samples were taken two phases were observed - aqueous and fuel - indicating that the burn pit was not flushed out well. The inadequate flushing was probably a result of (1) an improper water level in the burn pit (gravel was protruding through the liquid) and (2) the low-capacity flow rate of the portable pump that was used for these tests. A portion of each phase was tested for ignitability, and the results indicated that the fuel phase, as expected, was ignitable; however, the aqueous phase was not ignitable. These results indicate that the burn pit would not be ignitable if the procedure for flushing the pit was modified so that the fuel would be burned off at the end of a training series (if regulations would permit), and/or completely flushed out of the pit.

Table 3.1. Results of ignitability tests from burn pit at Davis-Monthan

	<u>Prior to water flush</u> Flash Point (°C)	<u>After water flush</u> Flash Point (°C)
Aqueous phase	>63	>63
Fuel phase	<24	<24

The burn pit was also sampled for EP-Toxicity metal analysis, and the aqueous phase was analyzed in accordance with SW-846 Method 1310. The results (Table 3.2) indicate that the metals in the aqueous phase are well under the maximum concentrations allowed, as listed for SW-846 Method 1310 in the Federal Register.

3.4.13 Efficiency of Fuel/Water Separator

The influent and effluent streams of the fuel/water separator were sampled during the draining and flushing of the burn pit after the second burn on the second day of the training exercises to determine the efficiency of the separator. The samples were submitted for TOC, COD, fluoride, O & G, EPA Method 8015, and EPA Method 8020 (benzene, toluene, xylene, ethylbenzene) analyses. Unfortunately, due to a labeling error in the analytical laboratory, the influent stream was not analyzed for EPA Method 8020. The results are presented in Table 3.3. The O & G results indicate a separator efficiency of ~93%. However, the O & G effluent concentration is much higher than the design concentration of 25 ppm. It is believed that this is a result of the speed by which the additions were made to the fuel/water separator.

3.4.14 Total Suspended Solids in Holding Pond

The holding pond was sampled before and after the training exercises to determine the effect of the exercises on the suspended solids. The holding pond had a total suspended solids concentration of 430 mg/L prior to the training exercises and a concentration of 530 mg/L following the training exercises.

Table 3.2 Results of EP-Toxicity metal analysis from burn pit
at Davis-Monthan

Metal	Prior to water flush (mg/L)	After water flush (mg/L)	Maximum contamination level (mg/L)
Arsenic	<0.005	<0.005	5.0
Barium	0.041	0.026	100
Cadmium	0.006	0.005	1.0
Chromium	<0.01	<0.01	5.0
Lead	0.12	0.064	5.0
Mercury	<0.001	<0.001	0.2
Selenium	<0.005	<0.005	1.0
Silver	<0.006	<0.006	5.0

Table 3.3, Fuel/water separator efficiency results

Analysis	Influent (mg/L)	Effluent (mg/L)
TOC	1250	900
COD	5500	2750
Fluoride	1.4	1.5
O & G	5700	380
NHVOs	120	120

4. CONCLUSIONS AND RECOMMENDATIONS

Except for the volatile components, contamination in the wastewater after training exercises does not diminish with time. It cannot be ascertained whether the volatile components are diminishing due to volatilization or biodegradation, but it seems likely that the components are volatilizing unless one considers that the bacteria may be selective. However, whichever mechanism is occurring, it is insufficient since the concentration of contamination appears to reach a steady state soon after the training exercises are complete. Therefore, the concentration of contaminants will continue to increase as training exercises continue. The increasing concentration of contaminants leads to several problems, including the possibilities of forming polynuclear aromatics (PNAs) and of contaminating soil if the holding pond should overflow. It is recommended that the present bioactivity be stimulated or that new bioactivity be introduced to degrade the contaminants in the wastewater. Bench-scale studies are recommended to determine the availability of bacteria to degrade the organics and the means of stimulating the bioactivity under operating conditions within the facilities. Alternatively, if present bacteria are not capable of biodegrading the contaminants, studies should focus on identifying a type of bacteria that will degrade the organics. Variables requiring more study include pH, temperature, contaminant concentration, nutrient addition to the water, etc.

The fuel/water separator was designed to reduce the effluent concentration of O & G to 25 mg/L, with the condition of allowing 45 min between additions to the separator. Analysis of the effluent sample taken to determine the efficiency of the separator indicated that the O & G effluent concentration was 380 mg/L. This result indicates that the separator was either overworked or was not working as designed. It is believed that in an attempt to get a large number of burns completed to raise the COD levels for this evaluation, the separator was overworked. Therefore, it is recommended that the design requirement of scheduling 45-min intervals between burn pit flushes be followed until more samples can be taken to verify that the separator is working as designed.

Mixed-phase samples were taken from the burn pit (1) immediately following the extinguishing of a fire and (2) immediately following the draining and flushing of the burn pit to the fuel/water separator to determine whether the solution remaining in the pit was ignitable. Analysis revealed that the fuel phase was ignitable, but that the aqueous phase was not. Therefore, it is recommended that the unburned fuel remaining in the burn pit after the completion of a series of training exercises be burned off (if local/state/federal regulations will permit this) and the pit flushed to remove all the remaining pockets of unburned jet fuel. This will probably require modification of the burn pit flush procedure, such as raising the liquid level above the gravel level before opening the drain valve so that the gravel will not interfere with the fuel being flushed out of the pit. This should also improve the removal of AFFF foam from the burn pit.

APPENDIX A**GENERAL PROCEDURE FOR CONDUCTING A TRAINING EXERCISE**

1. Water is added from the holding pond to the burn pit. The purpose of the water is to float the jet fuel.
2. Jet fuel (JP-4) is pumped from storage tanks at the facility to the burn pit. The volume of the jet fuel added is dependent on the type of fire to be simulated.
3. The jet fuel is ignited and allowed to reach full height (usually ~30 s). The fire trucks, which are carrying a mixture of water and AFFF, are called in to extinguish the blaze (extinguishment time averages 30 s).
4. The burn pit is drained and flushed to the fuel/water separator with water from the holding pond.
5. The unburned jet fuel is skimmed off of the water in the first stage of the separator and will be added to another fire as reburn material. The water passes through three settling stages before being discharged to the holding pond.
6. Steps 1-5 are repeated if another training exercise is to be done.

APPENDIX B. SAMPLE DESCRIPTIONS

Table B.1. Sample plan for preliminary studies at Tyndall AFB

Analysis	EPA Method	Burn Number						Comments
		1	2	3	4	5	6	
Total organic carbon	415.1	IE ^a	IE	E	IE	IE	IE	Samples were preserved by acidifying with H ₂ SO ₄ to pH<2.
Chemical oxygen demand	410.4	IE	IE	E		IE	IE	Samples were preserved by acidifying with H ₂ SO ₄ to pH<2.
Oil and grease	413.1						IE	Samples were preserved by acidifying with H ₂ SO ₄ to pH<2.
Fluoride	340.2						IE	
Nonhalogenated volatile organics	8015						IE	Samples were taken in amber VOA sample vials. Sample vials were completely filled with liquid.
Volatile organic components	8020						IE	Samples were taken in amber VOA sample vials. Sample vials were completely filled with liquid.

45

^aPoints Sampled: I - separator influent; E - separator effluent.

Table B.2. Analyses performed on holding pond during test program

Date	Analyses/process parameters ^a	Description
12/3/88	8270, 8015, 8020, COD O&G, TOC, BOD, DO, Fl ⁻ , temp, pH, TSS	Prior to training exercises
12/4/88	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, Fl ⁻ , temp, pH, TSS	After training exercises
12/6-14/88	COD, BOD, TOC, DO, pH, temp	Every other day for 10 d after training exercises
12/15/88	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, temp, pH	11 d after training exercises
01/05/89	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, temp, pH	32 d after training exercises
02/01/89	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, temp, pH	59 d after training exercises

^aParameters:

- BOD - Biological oxygen demand - EPA Method 405.1
- COD - Chemical oxygen demand - EPA Method 410.4
- DO - Dissolved oxygen
- Fl⁻ - Fluoride - EPA Method 340.2
- O&G - Oil and grease - EPA Method 413.1
- TOC - Total organic carbon - EPA Method 415.1
- TSS - Total suspended solids
- 8015 - Nonhalogenated volatile organics - EPA Method 8015
- 8020 - Benzene, toluene, xylene, ethylbenzene - EPA Method 8020
- 8270 - Base/neutrals, acids extractable organics - EPA Method 8270

Table B.3. Analyses performed on fuel/water separator during test program

Date	Analyses/process parameters ^a	Description
12/3/88	8270, 8015, 8020, COD O&G, TOC, BOD, DO, F1 ⁻ , temp, pH	Prior to training exercises
12/4/88	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, F1 ⁻ , temp, pH	After training exercises
12/6-14/88	COD, BOD, TOC, DO, pH, temp	Every other day for 10 d after training exercises
12/15/88	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, temp, pH	11 d after training exercises
01/05/89	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, temp, pH	32 d after training exercises
02/01/89	8270, 8015, 8020, COD, O&G, TOC, BOD, DO, temp, pH	59 d after training exercises

^aParameters:

- BOD - Biological oxygen demand - EPA Method 405.1
- COD - Chemical oxygen demand - EPA Method 410.4
- DO - Dissolved oxygen
- F1⁻ - Fluoride - EPA Method 340.2
- O&G - Oil and grease - EPA Method 413.1
- TOC - Total organic carbon - EPA Method 415.1
- TSS - Total suspended solids
- 8015 - Nonhalogenated volatile organics - EPA Method 8015
- 8020 - Benzene, toluene, xylene, ethylbenzene - EPA Method 8020
- 8270 - Base/neutrals, acids extractable organics - EPA Method 8270

Table B.4. Miscellaneous analyses performed during test program

Date	Analyses/process parameters	Description
12/4/88	TOC, COD, O & G, Fl ⁻ , 8015, 8020	Sample of influent to separator during pit flush out after 10th burn
12/4/88	TOC, COD, O & G, Fl ⁻ , 8015, 8020	Sample of effluent from separator during pit flush out after 10th burn
12/4/88	Ignitability, EP-Toxicity	Sample of burn pit immediately following extinguishing of fire
12/4/88	Ignitability, EP-Toxicity	Sample of burn pit immediately following flushing of pit

APPENDIX C. SAMPLE RESULTS

Table C.1. TOC and COD results from fuel/water separator at Tyndall AFB

Burn No.	Influent		Effluent	
	TOC (mg/L)	COD (mg/L)	TOC (mg/L)	COD (mg/L)
1	241	685	32	175
2	322	1500	226	730
3			287	900
4	303		268	
5	139	2900	366	1100
6	234	3350	369	1200

Table C.2. Results from Fuel/Water Separator at Davis-Monthan AFB

Days of Study	0	1	3	5	7	9	11	12	33	60
	Days Following Last Training Exercise									
	<u>Pre Burn</u>	<u>Post Burn</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>	<u>11</u>	<u>32</u>	<u>59</u>
TOC (mg/L)*	160	990	1110	1100	1050	1340	1200	1240	1170	1220
COD	460	3000	6250	5500	4500	8250	4500	6000	4900	4550 4380
Fluoride	0.9	1.4						1.2	1.2	1.2
Oil & Grease	4.4	170						730	180	120
BOD	262	425	270	398	415	395	335	360	310	417
8015	14	94						180	58	45
Benzene	0.77	10						5.7	3.5	1.8
Toluene	1.2	15						7.2	5.9	3
Xylene	0.7	7.3						2.5	3.2	1.9
Ethylbenzene	0.39	3.8						1	0.7	0.12
Butyl Carbitol ($\mu\text{g/L}$)	1900							88000	240000	3700
pH	7.83	7.94	7.79	7.69	7.59		7.46	7.5	7.21	6.96
Dissolved Oxygen	6.5	4.72	5	5.5	5		6.6	5	5.8	6.11
Temperature ($^{\circ}\text{C}$)	11.5		16	14	10	12	8	13	10	11

* All units are mg/L unless otherwise noted.

Table C.3: Results from the Holding Pond at Davis-Monthan AFB

Days of Study	0	1	3	5	7	9	11	12	33	60
	Days Following Last Training Exercise									
	<u>Pre Burn</u>	<u>Post Burn</u>	<u>2</u>	<u>4</u>	<u>6</u>	<u>8</u>	<u>10</u>	<u>11</u>	<u>32</u>	<u>59</u>
TOC (mg/L)*	97	370	360	370	360	340	350	350	400	530 480
COD	230	1700	1880	1780	1500	1400	1440	1380	1450	1440
Fluoride	1.1	1.3						1.2	1.2	1.4 1.4
Oil & Grease	<2.0	33						44	22	11 24
BOD	207	400	271	397	430	415	355	355	313	444
8015	2.7	80						3.9	0	0
Benzene	0.13	3						0.19	0	0
Toluene	0.34	4.9						0.34	0	0
Xylene	0.16	1.3						0.2	0	0
Ethylbenzene	0.087	2.0						0.068	0	0
Butyl Carbitol (µg/L)	1600	5500						910	50000	39000
TSS	430	530								
pH	8.56	8.16	7.91	7.58	7.90		7.87	7.92	7.92	7.72
Dissolved Oxygen	8.20	7.00	6.60	6.80	8.20		7.50	7.44	9.10	8.00
Temperature (°C)	9		16	14	6	8	8	10	11	10

* All units are mg/L unless otherwise noted.

INTERNAL DISTRIBUTION

- | | | | |
|--------|---------------|--------|-----------------------------|
| 1. | D. W. Burton | 18. | M. G. Stewart |
| 2. | R. K. Genung | 19-21. | J. F. Walker |
| 3-5. | A. N. Herron | 22-23. | J. H. Wilson |
| 6. | C. M. Holley | 24. | A. Zucker |
| 7-11. | T. D. Hylton | 25-26. | Central Research Library |
| 12. | N. A. Luedtke | 27. | ORNL-Y-12 Technical Library |
| 13. | M. S. Miller | | Document Reference Section |
| 14. | W. W. Pitt | 28-29. | Laboratory Records |
| 15. | D. R. Reichle | 30. | Laboratory Records, ORNL-RC |
| 16-17. | J. R. Russell | 31. | ORNL Patent Section |

EXTERNAL DISTRIBUTION

32. Mano Husain, CSG/DEQ, Bldg. 4300, Davis-Monthan AFB, AZ 85707-5100
33. Lt. Edward Marchand, HQ AFESC/RDVW, Bldg. 1117, Tyndall AFB, FL 32403-6001
- 34-36. Chuck Risinger, HQ AFESC/RDCF, Bldg. 1120, Tyndall AFB, FL 32403-6001
37. Neil Rochelle, Environmental Policy & Assessment Branch, HQ USAF/LEEV, Bldg. 516, Bolling AFB, Washington, D. C. 20332
- 38-40. Jay Shah, Environmental Policy & Assessment Branch, HQ USAF/LEEV, Bldg. 516, Bolling AFB, Washington, D. C. 20332
41. Dick Vickers, HQ AFESC/RDCF, Bldg. 1120, Tyndall AFB, FL 32403-6001
42. Joe Walker, HQ AFESC/RDCF, Bldg. 1120, Tyndall AFB, FL 32403-6001
43. Office of Assistant Manager, Energy Research and Development, DOE-ORO, P.O. Box 2001, Oak Ridge, TN 37831
- 44-53. Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831