ALKYL BENZENE SULFONATE REMOVAL IN RAW SEWAGE STABILIZATION LAGOONS

by

Bill B. Dendy

A Thesis Submitted to the Faculty of the

DEPARTMENT OF CIVIL ENGINEERING

In Partial Fulfillment of the Requirements

For the Degree of

MASTER OF SCIENCE

In the Graduate College

UNIVERSITY OF ARIZONA

1962

STATEMENT BY AUTHOR

This thesis has been submitted in partial fulfillment of requirements for an advanced degree at The University of Arizona and is deposited in the University Library to be made available to borrowers under rules of the Library.

Brief quotations from this thesis are allowable without special permission, provided that accurate acknowledgment of source is made. Requests for permission for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in their judgment the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Bill B. Dendy

APPROVAL BY THESIS DIRECTOR

This thesis has been approved on the date shown below:

Quentin M. Mees
QUENTIN M. MEES
Professor of Civil Engineering

January 26, 1962
Date

ABSTRACT

A raw sewage stabilization lagoon located near Tucson, Arizona, and owned and operated by Pima County Sanitary District No. 1 was subjected to a four-month study in an attempt to determine whether or not the Alkyl Benzene Sulfonate (ABS) in raw sewage entering the lagoon was being degraded by the treatment process.

In the preparation of this thesis it was found that the Methylene Blue method employed for ABS determinations in both raw sewage and lagoon water was satisfactory for the desired degree of accuracy. ABS profiles for the lagoon indicated that concentrations near the bottom were 25% to 30% higher than those near the surface. There was no evidence of ABS degradation. It was apparent that some measure of buildup in ABS concentration was occurring in the lagoon. Several possible explanations for the buildup were proposed, based on the interrelationship of seepage, evaporation, and effluent flow.

ACKNOWLEDGMENTS

The author is deeply indebted to Professor Quentin M. Mees for his assistance in the preparation of this thesis.

To Pima County Sanitary District No. 1 goes another expression of gratitude for making available the facilities at which the study was conducted. The Department of Civil Engineering at the University of Arizona is commended for making available necessary laboratory facilities.

Fellow students at the University of Arizona deserve a special note of gratitude for their suggestions and criticisms. The author is indebted, also, to a friend whose kind assistance made this thesis possible.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Chapter I

INTRODUCTION

1.1 General Discussion

The majority of sewage treatment processes consist of providing an environment by which naturally occurring organisms may best perform the task of reducing the constituents of wastes to an innocuous state. Any portion of the waste which cannot be so treated poses a threat to the efficiency of the process. A raw sewage stabilization lagoon is one of the many devices employed to create the necessary environment.

Increasing use of synthetic detergents since World War II has brought about an equally increasing problem for those concerned with sewage treatment. The major reason for this problem is the fact that Alkyl Benzene Sulfonate (ABS), which is the basic molecule for most synthetic detergents, does not lend itself readily to biological decomposition.

The final product of sewage treatment is usually disposed of in one of two ways: by dilution or by allowing it to seep into the earth. In either case, the effluent is likely to find its way back to our water supplies. This fact alone emphasizes the necessity for removing any and all materials that might later prove toxic or unpalatable to the populace. Further proof of the necessity for thorough treatment is pointed up by the realization that whatever constituents are not removed by the treatment process will probably not be removed later by the actions of nature.

1.2 Purpose and Scope of Thesis

The purpose of this study is to attempt to discover what effect raw sewage stabilization lagoons have on the concentrations of ABS which are imposed upon them. An existing installation will be subjected to a thorough scrutiny consisting of the following:

(1) A careful analysis of raw sewage entering the lagoon to determine exactly what concentrations of ABS it contains.

(2) The establishment of an ABS profile in the lagoon to discover how ABS concentrations vary as treatment progresses.

(3) An analysis of effluents in an attempt to arrive at some conclusion as to overall treatment efficiency.

(4) An attempt to correlate operational data with applicable ABS study results.

Chapter II

GENERAL ASPECTS

2.1 Definitions

To avoid later misunderstanding, some of the terms associated with synthetic detergents, and their definitions, are presented as follows:

(1) Surfactant (Surface Active Agent) - Any organic compound which affects interfacial tension. Although soap is such a material, the term as generally used applies to the organic derivatives which are used for detergents, wetting agents, penetrants, spreaders, dispersants, foamants, or related purposes.

(2) Detergent - A substance or mixture that has cleaning action due to a combination of properties including the lowering of surface tension, wetting, emulsification, and dispersive actions.

(3) Soap - A metallic salt or mixture of salts of the various fatty acids of natural oils or fats.

(4) Synthetic Detergent (Syndet) - A non-soap product having detergent properties. It is compounded from a manufactured surfactant with additive materials to enhance its detergent and other characteristics.

(5) Alkyl Benzene Sulfonate (ABS) - The most common surfactant molecule used in synthetic detergents. It consists of:

a. a tetrapropylene side chain

b. a benzene ring

c. a sulfonate radical

2.2 Basic Chemistry

Surface active agents are recognized as substances which in dilute solution are responsible for wetting, emulsification, dispersing, foaming, and related phenomena. For any given compound to display surface activity, there must be present in the molecule a hydrophobic hydrocarbon portion, to which is attached one or more hydrophilic groups. Since most of these compounds dissociate in solution, it is possible to classify them into anionic, cationic, and nonionic surfactants, according to their ionization. Figure 2.1 illustrates a representative molecule for each type (1).

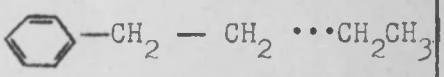
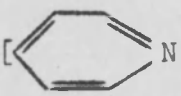
With anionics, the molecules dissociate in solution to yield a hydrocarbon anion of large mass and a cation of small mass. The majority of commercial surfactants, including ABS, belong to this class. The molecules of cationic surfactants dissociate in solution to give a cation of large mass and an anion of small mass. Nonionics do not dissociate in solution.

The raw material for surfactants of the ABS type is propylene, which is obtained from petroleum. By alkylation, the three-carbon propylene is expanded into a longer chain hydrocarbon. Reaction is initiated by addition of a proton, from the proper catalyst, to a propylene molecule to yield a carbonium ion:

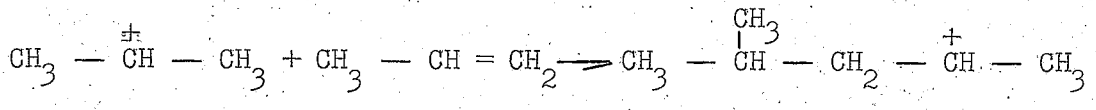
$$\underset{\text{Propylene}}{CH_3 - CH = CH_2} \xrightarrow[200^\circ C.\ 150\ psi]{H_3PO_4} \underset{\text{Carb. ion}}{CH_3 - \overset{+}{C}H - CH_3} + H_2 + PO_4^-$$

FIGURE 2.1

STRUCTURES OF TYPICAL SURFACTANTS

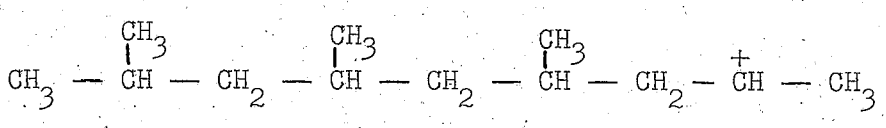
	Hydrophilic Portion	Hydrophobic Portion
Typical Soap	$[\ Na]^{+}\ \ ^{-}[\ OOC$	$-\ CH_2\ -\ CH_2\ \cdots\ CH_2CH_3]$
Typical Anionic	$[\ Na]^{+}\ ^{-}[\ O-S(=O)(=O)$	
Typical Cationic	$[\ Cl\ ]^{-}\ ^{+}[$ 	$-\ CH_2CH_2\ \cdots\ CH_2CH_3]$
Typical Nonionic	$HO(CH_2CH_2O)_mOC$	$-\ CH_2CH_2\ \cdots\ CH_2CH_3$

The carbonium ion adds, according to Markownikoff's Rule, to another propylene molecule, forming a new carbonium ion:

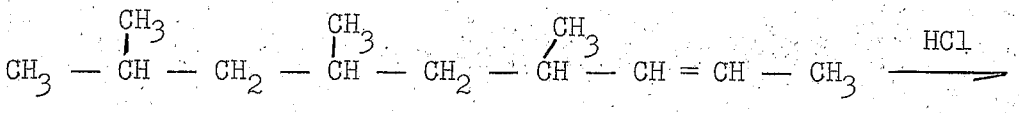


Carb. ion Propylene Carb. ion

This cycle is repeated twice more to yield a twelve-carbon ion:

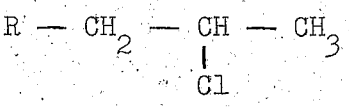


Through self-alkylation the ion loses a proton from either carbon 1 or 3 to yield tetrapropylene:



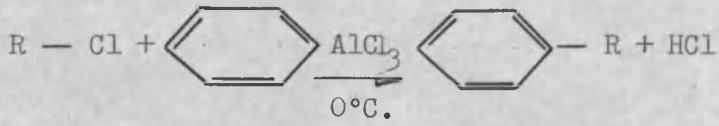
Tetrapropylene

Halogenation with HCl yields tetrapropylene chloride:

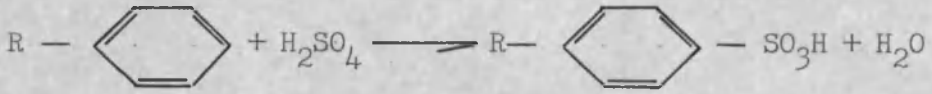


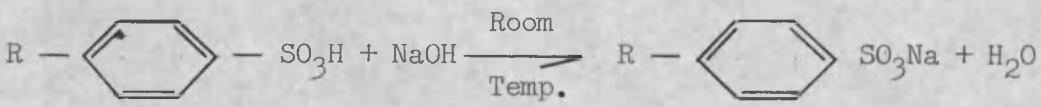
According to Markownikoff's Rule, the chlorine may be attached to either carbon 2 or 3.

An alkylbenzene compound is produced by alkylation of benzene by the Friedel-Crafts reaction, using aluminum trichloride as a catalyst:

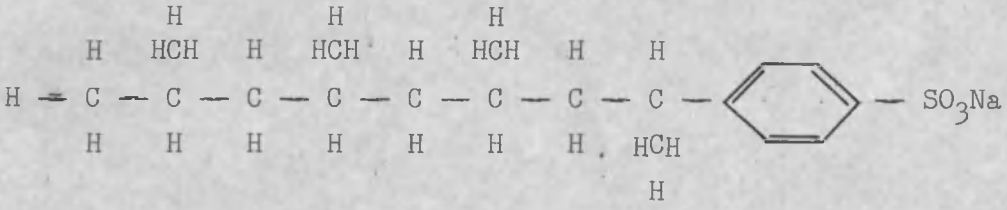


Subsequent sulfonation of the alkyl benzene compound yields ABS. The sulfonation is accomplished by reaction with sulfuric acid to form tetrapropylbenzenesulfonic acid, which is then treated with sodium hydroxide to form ABS. The alkyl radical is para-directing.

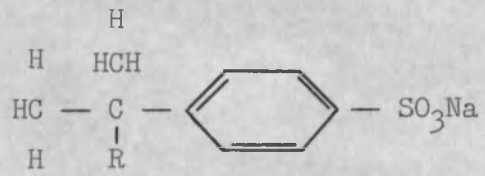




The theoretical structural formula formed is: (2) (3)



However, a report by Continental Oil Company (4) stated that the molecule actually produced in that company's commercial preparation of ABS is:



The most important difference between the two structures is the fact that the theoretical formula has a tertiary carbon where the side chain joins the benzene ring, whereas the actual structure contains a quaternary carbon at that point.

2.3 Bacterial Degradation of ABS

A report by McKinney and Symons (5) has furnished some interesting facts concerning the degradation of ABS by bacteria. They stated that bacteria have three common amino acids in their protoplasm which are made up of a hydrocarbon side chain and a benzene ring: phenylalanine, tyrosine, and tryptophan. Bacteria can both synthesize and degrade these three compounds. This indicates that they should be able to degrade ABS. The sulfonate group seemed to furnish a greater problem, but the limited information available was favorable. The authors concluded that common soil and water bacteria can utilize ABS as their sole source of organic matter. They found further that the failure of certain bacteria to completely metabolize the ABS molecule is caused primarily by a quaternary carbon block in the side chain. This quaternary carbon was believed to exist where the hydrocarbon chain joins the benzene ring.

Cohen (1) states that extensive biochemical studies by a group of researchers at Massachusetts Institute of Technology have conclusively shown that the quaternary carbon prevents microbial oxidation. He further stated that if the ABS molecule did not contain this quaternary carbon, microorganisms would have little difficulty in decomposing and removing this compound from solution.

McKinney and Symons (5) explained it more completely as follows:

> "The metabolism of organic matter by activated sludge follows a definite pattern. With ABS it is believed that metabolism starts with the terminal methyl group on the hydrocarbon side chain. The terminal methyl group is oxidized by enzymes to a carboxyl group. From this point the hydrocarbon side chain is metabolized by beta oxidation until it reaches the quaternary carbon. The quaternary carbon prevents further oxidation and thereby blocks metabolism.
>
> "The concept of a quaternary carbon block is based on the mechanism of hydrogen removal from organic matter. Inside the microorganism enzymes remove two hydrogen atoms at a time and oxidize them to water. These hydrogen atoms are removed in pairs from adjacent carbon atoms. With the quaternary carbon there is no hydrogen to be removed so that metabolism stops at this point. The ABS and the enzyme are bound together in a complex and so remain. This means that unless more enzymes are made the ABS metabolism will cease and free ABS will remain in solution."

Chapter III

PREVIOUS INVESTIGATIONS

3.1 Activated Sludge

A review of available literature reveals that a wealth of research has been done in an attempt to discover a solution to operational problems in the activated sludge process which have been attributed to ABS. As syndets became more and more popular with the public, sewage treatment plants the world over began to report the appearance of excess froth or foam formation on aeration tanks. In nearly every case the froth was attributed to increases in syndet usage. More specifically, the surfactant ABS has proved to be by far the worst offender.

In addition to being unsightly, the froth has been found to be an accident and health hazard. The foam leaves a greasy film on surrounding buildings, walkways, and work areas, making it dangerous for personnel to perform their usual duties (6). It has also been found that bacterial counts in the froth are as much as twenty times as great as in the liquid phase at the same relative point in the aeration tank (7).

Several methods of froth control have been attempted. Among these are the use of antifoam agents and the use of sprays which are directed onto the foam. One of the more successful attacks has been that of suspended solids control in the aeration tank. Several sources have discovered that mixed liquor suspended solids concentrations in the

range of 3000 to 5000 mg/l seem to give at least partial froth control. (8) (9)

A report by McGauhey and Klein (10) reached the following conclusions:

a. Those factors which govern ABS removal in the activated sludge process evidently cannot be correlated with any of the factors normally employed as controls for efficient sewage treatment by the process.

b. If the factors which govern the ABS removal can be isolated and controlled, a single stage activated sludge unit should consistently remove 50 to 60 percent of the influent ABS, while a removal of 70 percent is feasible when a second stage is utilized.

3.2 Trickling Filters

Research into the effect of ABS on trickling filter performance has been more limited than that in activated sludge. Consequently, only inconclusive results are available at the present time.

Lumb (11) tested the effects of detergents on laboratory trickling filters and reported no evidence of significant effects on nitrification, filter appearance, or on surface growths. Sperry (12) showed that increased use of syndets corresponded with a decrease in efficiency of trickling filters in removal of suspended solids and BOD.

McGauhey and Klein (10) conducted studies using laboratory model trickling filters with recirculation ratios of 3:1 and 9:1. Although filter efficiency was increased appreciably with the higher ratio, no significant increase in ABS removal occurred. In both cases the removal was about 25 percent.

The overall viewpoint concerning the effect of surfactants on trickling filters seems to be that there might be a slight decrease in BOD removal efficiency in connection with increased syndet loadings.

3.3 Primary Sedimentation

Research into the effects of ABS on the efficiency of primary sedimentation has revealed some interesting facts. ABS has been reported as interfering with both sedimentation and coagulation processes.

Manganelli (13) reported that a detergent containing the surfactant ABS caused a decrease in suspended solids removal and an increase in the grease remaining in the effluent. This detergent interfered with flocculation and coagulation when an iron salt was used as a coagulant.

Sperry (12) studied treatment plant operation records and reported that the great increase in household detergent use coincided with a reduction in the efficiency of primary sedimentation. McGauhey and Klein (10) found that the maximum ABS removal that is likely to occur in normal primary sedimentation tanks is of the order of 2 to 4 percent. However, they observed no interference with normal sedimentation.

3.4 Surface Stripping

Probably the most efficient and most effective way yet devised for ABS removal at the sewage treatment plant is a process termed "surface stripping". McGauhey and Klein (10) investigated this method and reported encouraging results.

Surface stripping consists of removing froth from the surface of the sewage being treated and then burning the froth. Since ABS tends to agglomerate in a foam, greater volumes of froth should take more ABS

from the sewage. Frothing may be induced by aeration alone or in conjunction with a foaming agent. It has been found that foam produced by aeration alone will burn more easily than that produced with the aid of a foaming agent. However, ABS removals seem to be a little higher in the latter case.

McGauhey and Klein reported further that removals of 83.2 percent were effected when foam was produced by aeration only and 90 percent when a foaming agent was used. They concluded that surface stripping would be an economically feasible ABS removal method if it proves necessary to remove more detergent than is normally degraded by activated sludge.

Chapter IV

SAMPLING PROCEDURES AND ANALYSES

4.1 Lagoon Description

The raw sewage stabilization lagoon at which the major part of this study was conducted is located 12 miles morthwest of Tucson, Arizona. It is owned and operated by Pima County Sanitary District No. 1 and has been in operation approximately a year and a half.

The Sanitary District is responsible for the disposal of sewage and wastes in Pima County which do not originate in municipalities. Its lagooning program is an attempt to determine whether or not this type of treatment is compatible with the type of weather and soil present in the area being served. The lagoon now serves residential areas lying immediately outside the city limits of Tucson.

Due to rapid development in the area, some sections of sewer have not been connected to collector and main line sewers. In those cases, sewage is allowed to accumulate in local lines for 24-hour periods, after which it is pumped into trucks. The sewage is then hauled to a point some distance from the lagoon and emptied into the main line. Although the use of trucks in the manner described provides a shock load situation at the lagoon, no resulting ill effects have been observed.

Sewage entering the lagoon is almost entirely domestic raw sewage. The flow is metered by means of a Palmer-Bowlus flume and a Leupold-Stevens recorder. There are two submerged inlet structures, located near the north end of the lagoon. The lagoon is operated at a depth of 5 feet,

at which depth it has a water surface area of two acres. Flow into the lagoon at present is approximately 60,000 gallons per day. A sketch of the lagoon site is shown in Figure 4.2.

4.2 Laboratory Procedures

A review of available literature failed to produce any evidence that ABS analyses had ever been made of samples taken from a raw sewage stabilization lagoon. However, several procedural outlines were obtained (14) (15) for detecting ABS concentrations in both water and raw sewage. These methods were compared to determine their relative values with reference to the following points:

(1) Accuracy and duplication of results

(2) Convenience as routine procedure

(3) Adaptability to the media being analyzed

The recommended procedure (16) for determining ABS concentrations in sewage was found to be much too complicated and time consuming for use as a routine method. The method finally selected, though not as precise, proved to be effective for the purposes of this study. It is outlined as follows:

METHYLENE BLUE METHOD, ARS MODIFICATION (15) (17)

APPARATUS:

Spectrophotometer, for use at 650 mμ, providing a light path of at least 1 cm.

Separatory funnels, 250 or 500 ml.

Filtering funnels, long stemmed

Volumetric flasks, 50 ml.

Pipettes, assorted sizes

Absorbent cotton

REAGENTS:

Methylene blue solution - dissolve 0.35 gms. methylene blue in one liter of 0.01 N sulfuric acid.

Chloroform, C.P.

Sulfuric Acid, 5 N

Stock standard ABS, 1.00 mg/ml.

Working standard ABS, 0.010 mg/ml.

PREPARATION OF STANDARDS:

Stock Standard: Weigh out an amount of Primary Standard ABS powder equal to 1.000 gm. ABS on a 100 percent active basis, transfer to a 1.0 liter volumetric flask and add 500 ml. of distilled water. Swirl gently until all of the powder is dissolved, let stand for one-half hour or until most of the foam breaks and then make up to the mark with distilled water. This solution contains 1.00 mg/ml. of ABS.

Working Standard: Pipette 10.0 ml. of the stock standard into a 1.0 liter volumetric flask and make up to mark. This solution contains 0.010 mg/ml. of ABS. Prepare fresh daily.

PREPARATION OF STANDARD CURVE:

(1) Add 0, 1.0, 2.0, 5.0, 10.0, 20.0, and 25.0 ml. of working standard ABS to separatory funnels and make up to 100 ml. with distilled water. These standards contain, 0, .01, .02, .05, .10, .20, and .25 mg. of ABS.

(2) Add 1.0 ml. of 5 N sulfuric acid and 5.0 ml. of methylene blue solution to each separatory funnel and mix.

(3) Add 10 ml. of chloroform to each funnel, invert and shake once a second for 25 seconds. Allow the chloroform

layer to separate.

(4) Draw off the chloroform layer and filter through a plug of absorbent cotton into a 50 ml. volumetric flask. Repeat the extraction twice more, using 10 ml. portions of chloroform, collecting the extracts in the same flask.

(5) Rinse the cotton plugs with chloroform into the 50 ml. volumetric flask, make up to the mark with chloroform, mix well and let stand for 5-10 minutes.

(6) Read the optical density of the reagent blank and standards against chloroform as a reference blank at 650 mμ in a suitable spectrophotometer and prepare a standard curve.

SAMPLE ANALYSIS:

Procedure for sample analysis is the same as for preparing the standard curve. If less than 100 ml. aliquots of the sample are used, dilute to 100 ml. Preliminary analyses should be made to determine what sample volumes to use. Duplicate analyses should be made to verify results.

DISCUSSION:

The method depends on the formation of a blue-colored salt when methylene blue reacts with anionic surfactants, which include not only ABS, but alkyl sulfates as well. The salt is soluble in chloroform, and the intensity of color is proportional to the concentration.

Both organic and inorganic compounds interfere with the determinations. Positive errors are much more common than negative. Therefore, the reading obtained represents that of maximum ABS concentration.

A sample of river water to which was added sufficient ABS to bring the concentration to 1.31 mg/l, was determined with a standard deviation of ± .25 mg/l in 40 laboratories with this method.

4.3 Verification of Standard Curve

Investigations of the selected laboratory method to verify its use as a routine procedure were conducted as follows:

(1) Various dilutions of the working standard ABS in distilled water were subjected to spectrophotometric analysis. The resulting percent transmittances are tabulated in Column 4, Table I and plotted as Curve A, Figure 4.2.

(2) It was necessary to find whether or not Curve A could be used for lagoon water analysis. Equal amounts of a well-mixed composite sample of lagoon water were added to each of the prepared dilutions of (1) The results of the analyses of these samples are tabulated in Column 4 of Table II and plotted as Curve B in Figure 4.2. The fact that Curves A and B are parallel shows that a constant ABS concentration in the lagoon water was being detected over the entire range of the curve. Thus, one very important quality of the curve has been verified.

(3) It was also necessary to determine whether or not the selected method would detect constant ABS concentrations in different volumes of lagoon water sample. Three of the dilutions from (1) were selected at random. To each of these were added graduated amounts of the same lagoon sample (see Column 2, Table III). Analysis by spectrophotometer yielded the results shown in Column 7 of Table III. Maximum variation from the average is only 1.8 percent, well within the acceptable limits for this

method. The insignificant variance of values obtained further verifies the use of Curve A for ABS determinations in lagoon water.

The final investigation involved justification of the use of Curve A for raw sewage analysis. A procedure similar to that of (2) produced the results tabulated in Table IV and plotted as Curve C in Figure 4.2. That Curve C is parallel to Curve A is obvious, and gives rise to the conclusion that a constant ABS concentration was being detected over the entire range of the curve. Further verification was obtained as in step (3). The results of this test are shown in Table V. There is a maximum variation from the average of 0.19 mg/l, or 2.3 percent. This, again, is well within practical limits of variance for the method.

FIGURE 4.1

SPECTROPHOTOMETER CURVES FOR
DETERMINING ABS CONCENTRATIONS

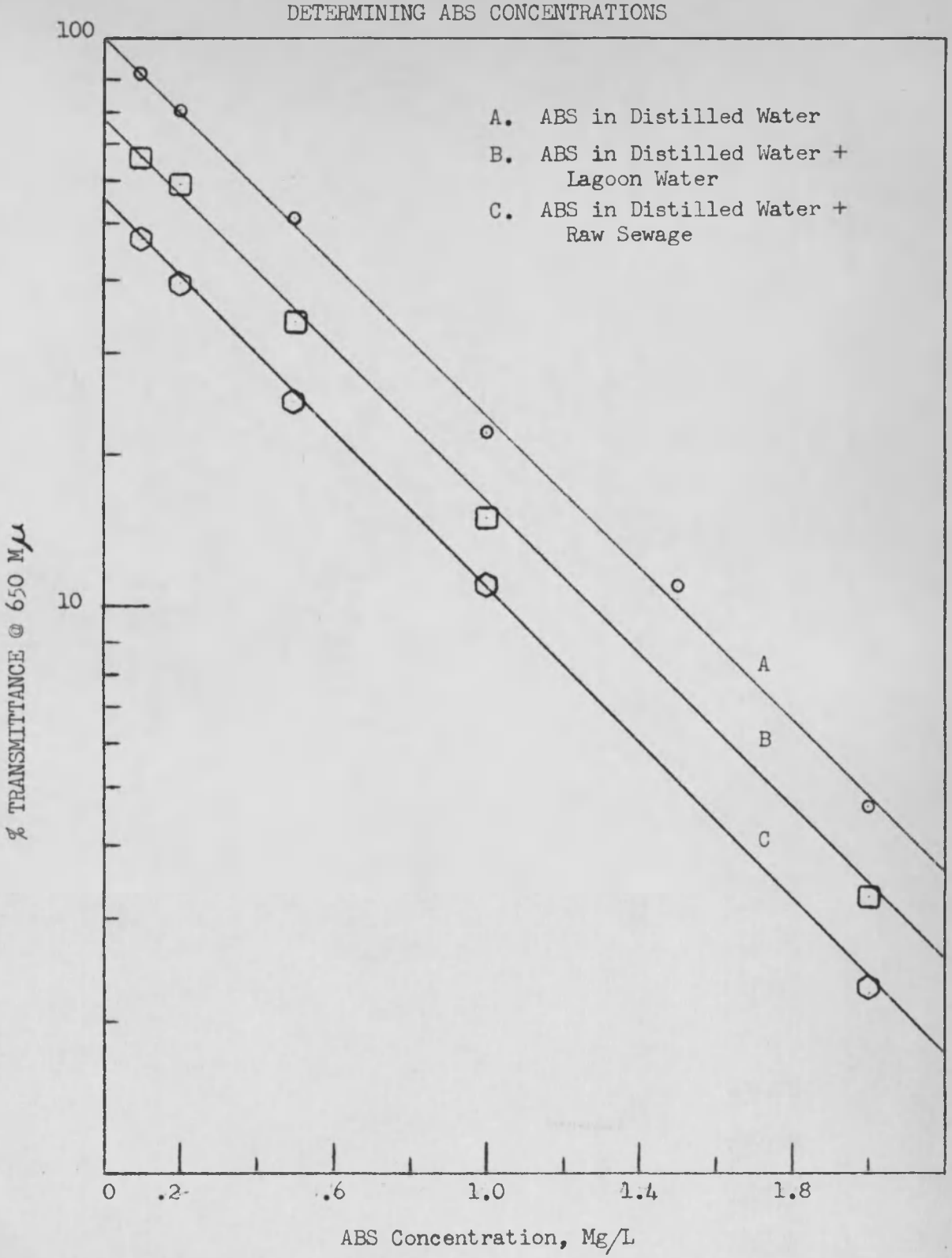


TABLE I

DATA FOR CURVE A

ABS in Distilled Water

ABS, mg/L	% Transmittance	Sensitivity	Adjusted % Transmittance
0	100.0	1	100.0
0.1	91.75	1	91.75
0.2	80.25	1	80.25
0.5	50.25	1	50.25
1.0	72.25	2	22.9
1.5	32.25	2	10.05
2.0	49.0	3	4.9

TABLE II

DATA FOR CURVE B

ABS in Distilled Water + 3.0 ml. Lagoon Composite

ABS, mg/L	% Transmittance	Sensitivity	Adjusted % Transmittance
0	100.0	1	100.0
0.1	66.0	1	66.0
0.2	60.0	1	60.0
0.5	34.0	1	34.0
1.0	53.0	2	16.8
2.0	34.0	3	3.4

TABLE III

VERIFICATION OF CURVE A

Known ABS, mg.	Lagoon Water Added, ml.	% Trans-mittance	Sensi-tivity	Adjusted % Trans-mittance	Total ABS, mg.	ABS in Lagoon Water, mg/L
0.02	0	83	1	83	0.02	-
	5.0	38	1	38	0.068	9.6
	10.0	55	2	17.5	0.116	9.6
0.05	0	50	1	50	0.05	-
	5.0	74	2	23.5	0.097	9.4
	10.0	35	2	11	0.147	9.7
0.10	0	73	2	23	0.010	-
	5.0	33	2	10.5	0.148	9.6
	10.0	49	3	4.9	0.195	9.5

TABLE IV

DATA FOR CURVE C

ABS in Distilled Water + 5.0 ml. Raw Sewage Composite

ABS, mg/L	% Transmittance	Sensitivity	Adjusted % Transmittance
0	100.0	1	100.0
0.1	47.5	1	47.5
0.2	39.5	1	39.5
0.5	79.0	2	25.0
1.0	38.0	2	12.0
2.0	23.5	3	2.35

TABLE V

VERIFICATION OF CURVE A

Known ABS, mg.	Raw Sewage Added, ml.	% Trans-mittance	Sensi-tivity	Adjusted % Trans-mittance	Total ABS, mg.	ABS in Raw Sewage, mg/L
0.02	0	83	1	83	0.02	-
	5.0	41.5	1	41.5	0.062	8.4
	10.0	69.5	2	22	0.103	8.3
0.05	0	50	1	50	0.05	-
	5.0	84	2	26.5	0.091	8.2
	10.0	44	2	14	0.130	8.0
0.10	0	73	2	23	0.10	-
	5.0	38	2	12	0.141	8.2
	10.0	62	3	6.2	0.182	8.2

4.4 Sampling Procedures for Raw Sewage

Three types of raw sewage samples were utilized in order to obtain as accurate an estimate of ABS concentration as possible:

(1) Grab samples taken at the flow-measurement flume

(2) Representative samples from truck loads of sewage which were pumped into the sewer line

(3) Composite 24-hour samples

The samples from the trucks were to serve as indicators of the true ABS concentrations being imposed upon the lagoon. The grab samples were to be used as indicators of interim fluctuations in ABS concentration. The composite samples furnished a means of refereeing the results of the other two.

4.5 Lagoon Sampling Procedures

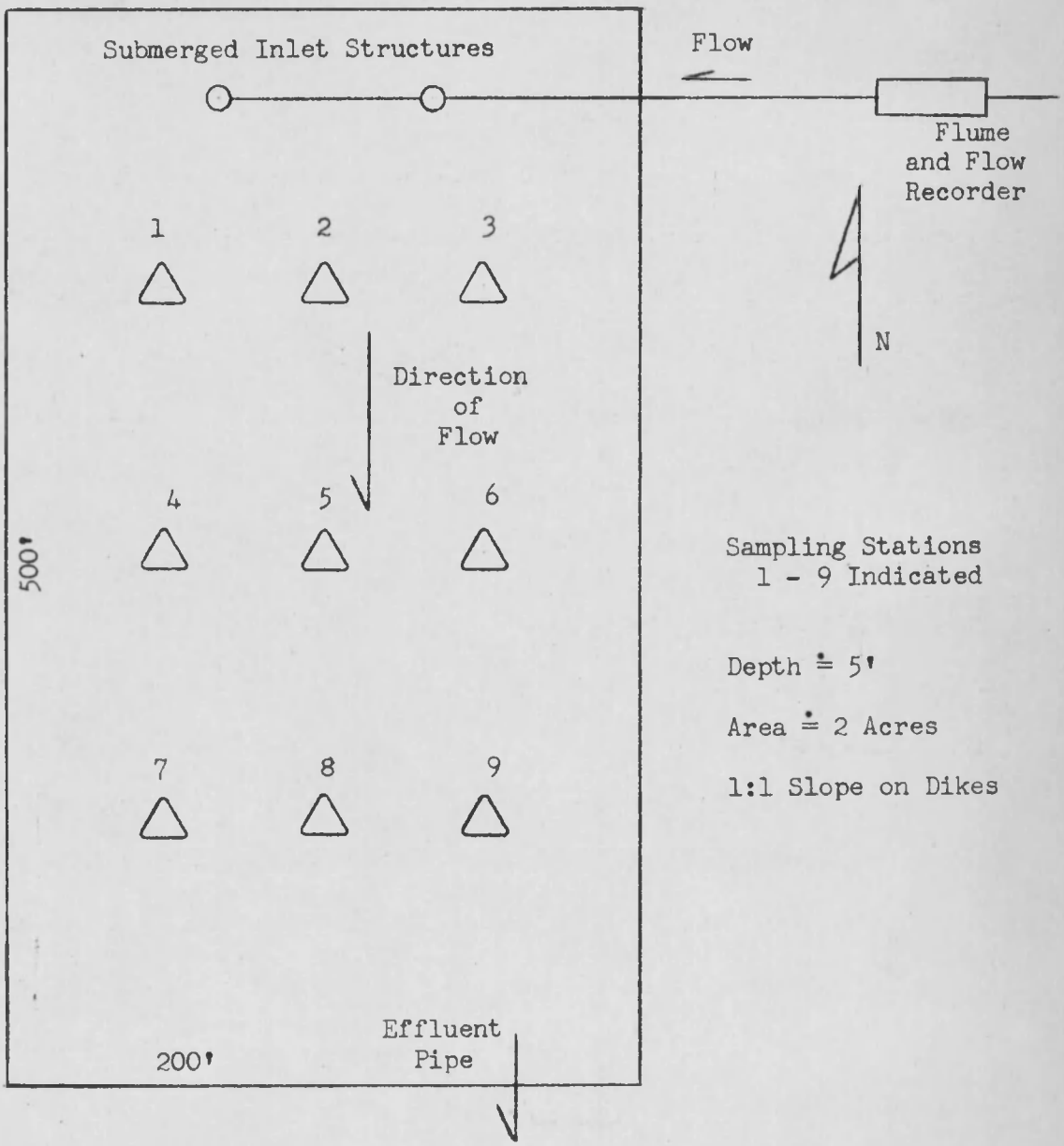
To establish ABS profiles of the lagoon, nine sampling stations were established as indicated in Figure 4.2. At each of these points samples were taken at depths of one foot and four and one-half feet. A standard 300 ml. dissolved oxygen sampler was used.

It was not possible to collect samples at the outfall end of the effluent pipe since that is submerged in an adjacent lagoon; however, it was decided that concentrations at the surface of Station 9 would represent very nearly the values in the effluent.

Composite 24-hour samples were collected at three of the sampling points on several days during the study and served as a further check on ABS concentrations.

FIGURE 4.2

SKETCH OF LAGOON SITE



Chapter 5

DATA PRESENTATION

5.1 ABS in Raw Sewage

Figure 5.1 is a record of ABS concentrations found in raw sewage entering the lagoon during the period of study. Values for both grab samples from the flume and representative samples from trucks are shown. The range of values for both curves is approximately the same. In addition, several maxima and minima on the two curves occur simultaneously or very nearly so.

Figure 5.2 shows ABS concentrations found in raw sewage composites. The range of values compares favorably with those presented in Figure 5.1.

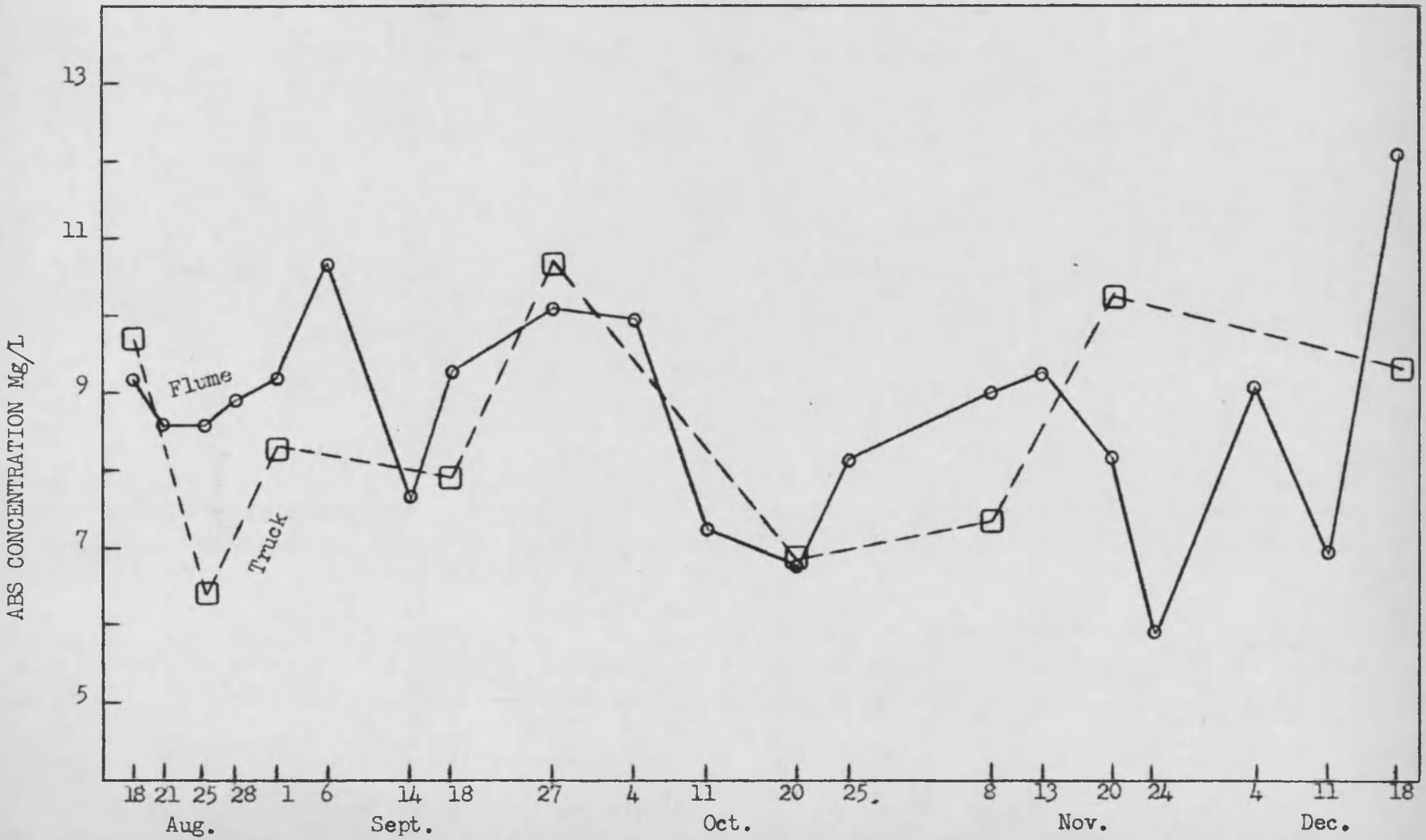
It may be concluded from the close correlation of the three curves that analytical techniques and sampling procedures were accurate for the purposes of this study. The fluctuation in values is an innate characteristic of domestic sewage.

5.2 ABS in Lagoon

Figures 5.3, 5.4, and 5.5 represent ABS profiles in the lagoon. The values plotted are averages of all determinations for the indicated sampling stations. Reference to Figure 4.2 will establish the location of the profiles within the lagoon.

The use of averages would seem justified when one realizes that the detention time in the lagoon is approximately 50 days. It hardly seems feasible that significant short term variations in ABS

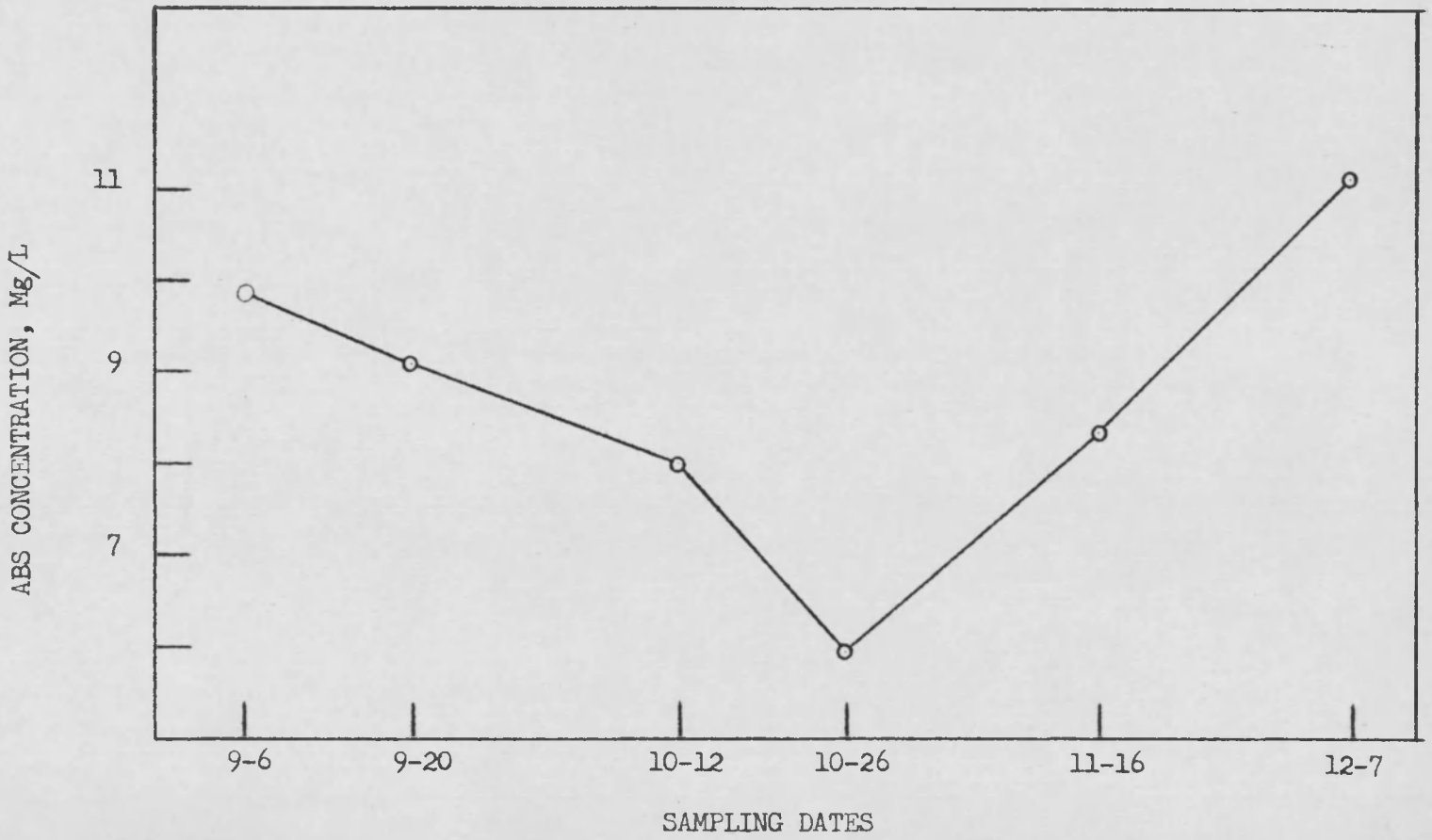
FIGURE 5.1



ABS IN RAW SEWAGE FROM TRUCKS & FLUME

FIGURE 5.2

ABS IN RAW SEWAGE COMPOSITES



concentrations should occur in an installation of this type.

The most striking characteristic of the profiles is the difference in values at the top and bottom in all three figures. This difference varies from 2.5 to 3 mg/l at every sampling point.

In Figure 5.6 overall average values have been plotted to yield one set of profiles for the entire lagoon. Concentrations near the surface are seen to decrease slightly from north to south, while bottom values suggest a reverse trend.

Figure 5.7 is a plot of average ABS concentrations in the lagoon (Stations 2, 5, and 8) as determined from composite 24-hour samples. This curve substantiates the above stated suspicion that very little variation in concentration occurred during the study.

Maximum deviation from the arithmetic mean of values determined at any one sampling station was 6.8% at Station 7. This percentage is well within accepted limits of variation for the Methylene Blue Method.

5.3 Discussion of Results

Average ABS concentration in raw sewage samples analyzed was 8.70 mg/l, while that in the lagoon was 11.35 mg/l. An attempt was made to explain the 2.65 mg/l increase on the basis of three factors:

(1) Evaporation

(2) Seepage

(3) Effluent flow

For comparison purposes, a 50-day period (approximate detention time) from October 18 to December 7 was selected for studying the three factors. During that time the average daily flow of raw sewage into the lagoon

FIGURE 5.3

ABS PROFILES IN LAGOON

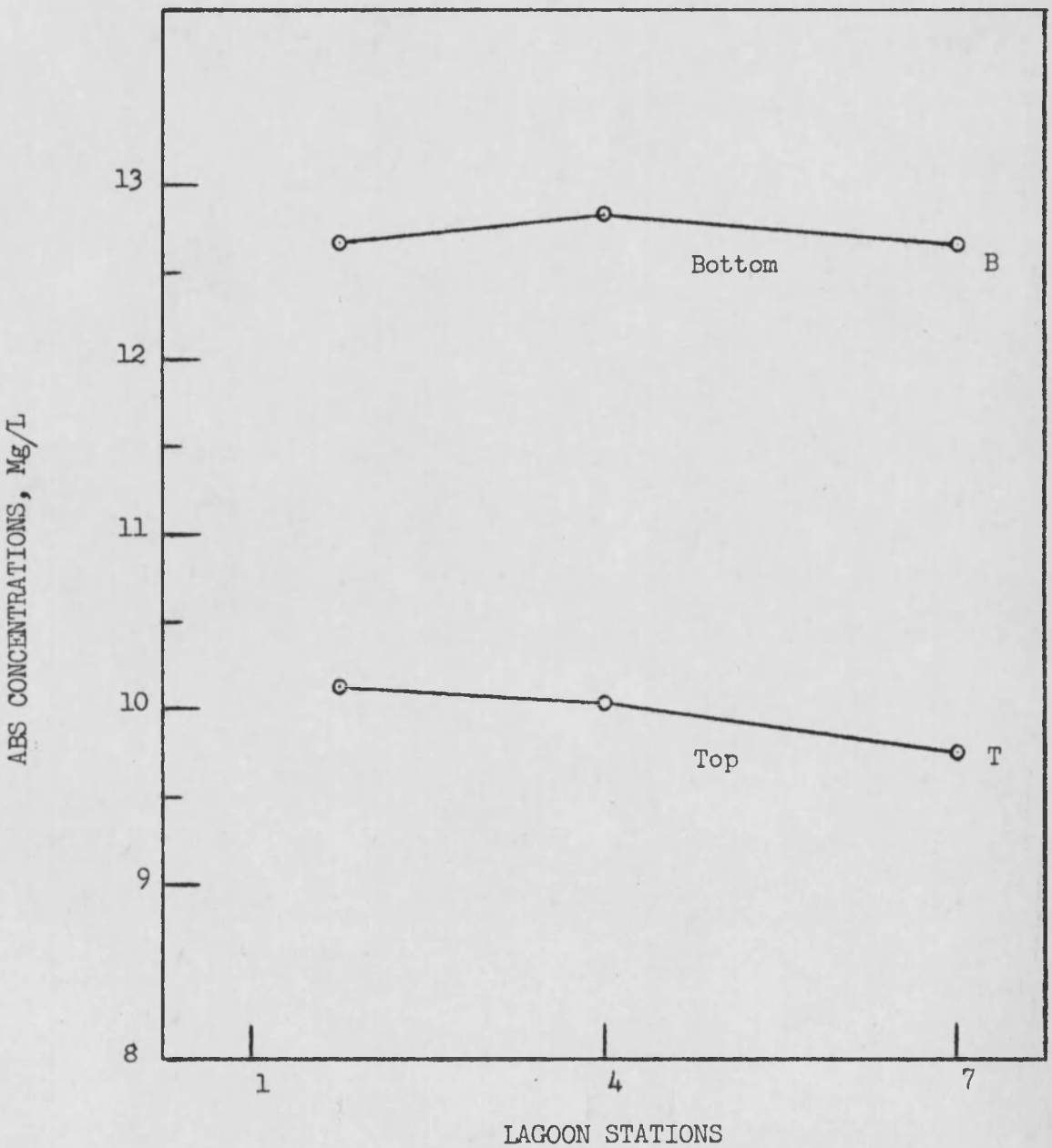


FIGURE 5.4

ABS PROFILES IN LAGOON

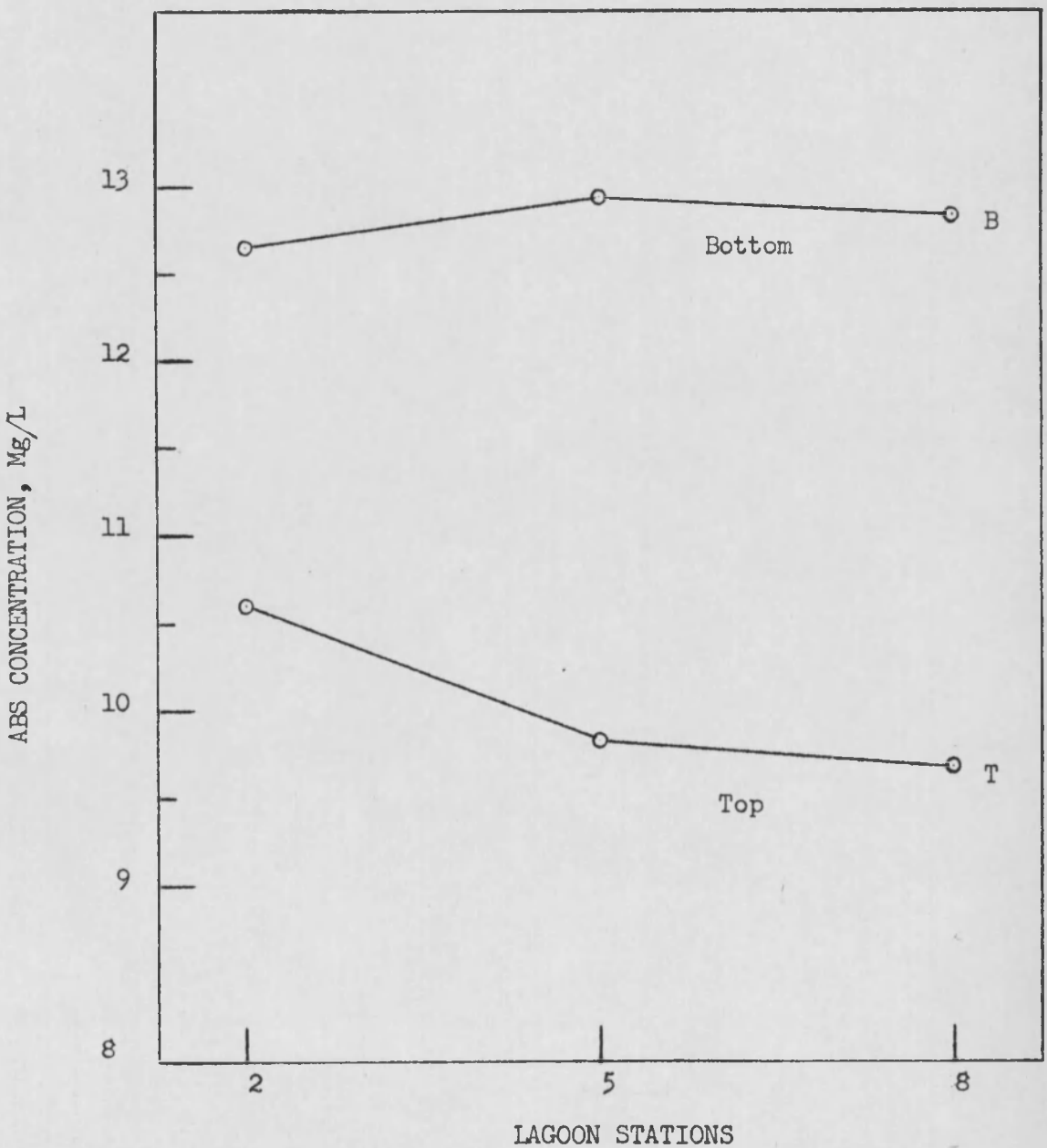


FIGURE 5.5

ABS PROFILES IN LAGOON

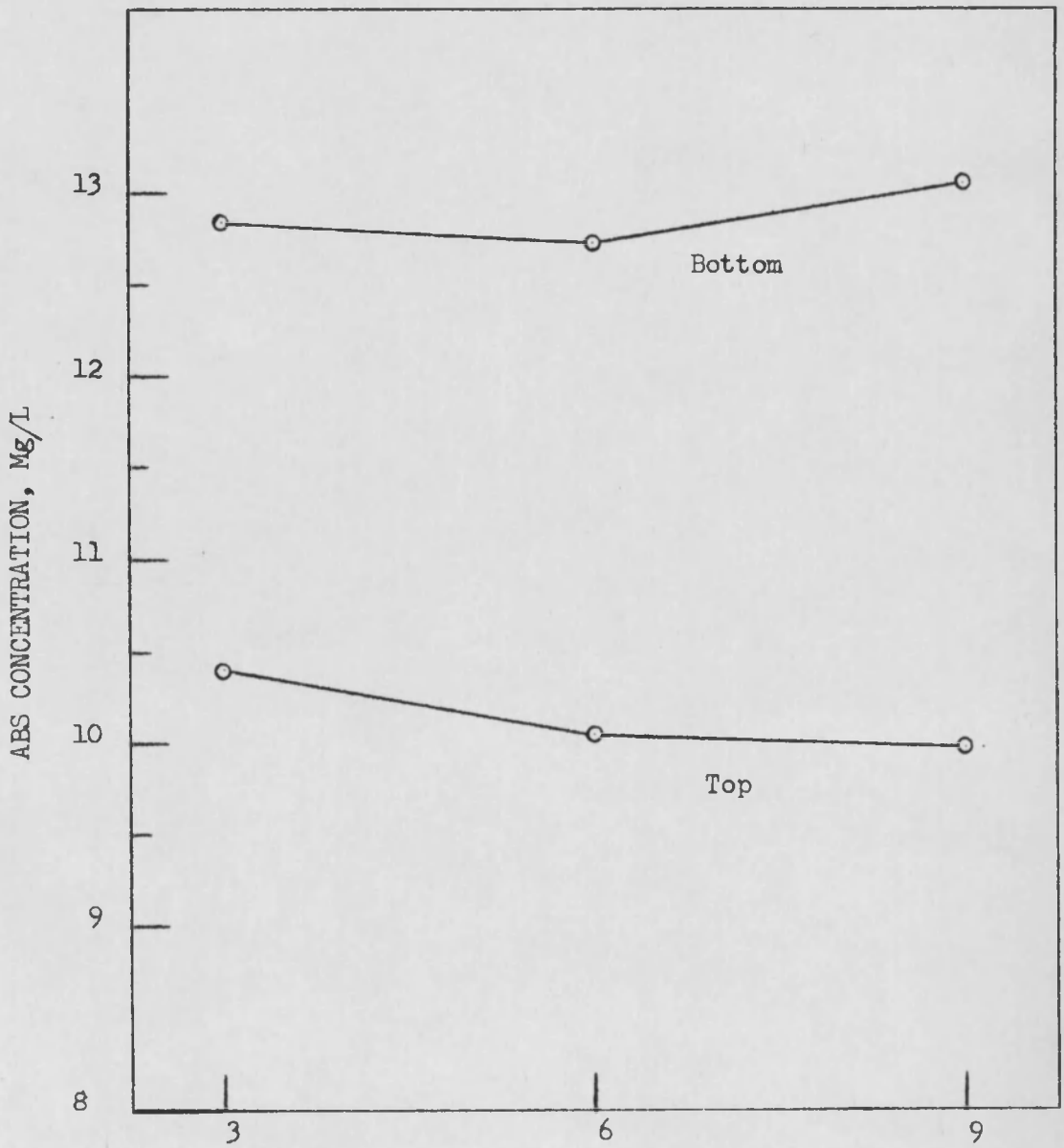


FIGURE 5.6

ABS PROFILES IN LAGOON
(AVERAGE)

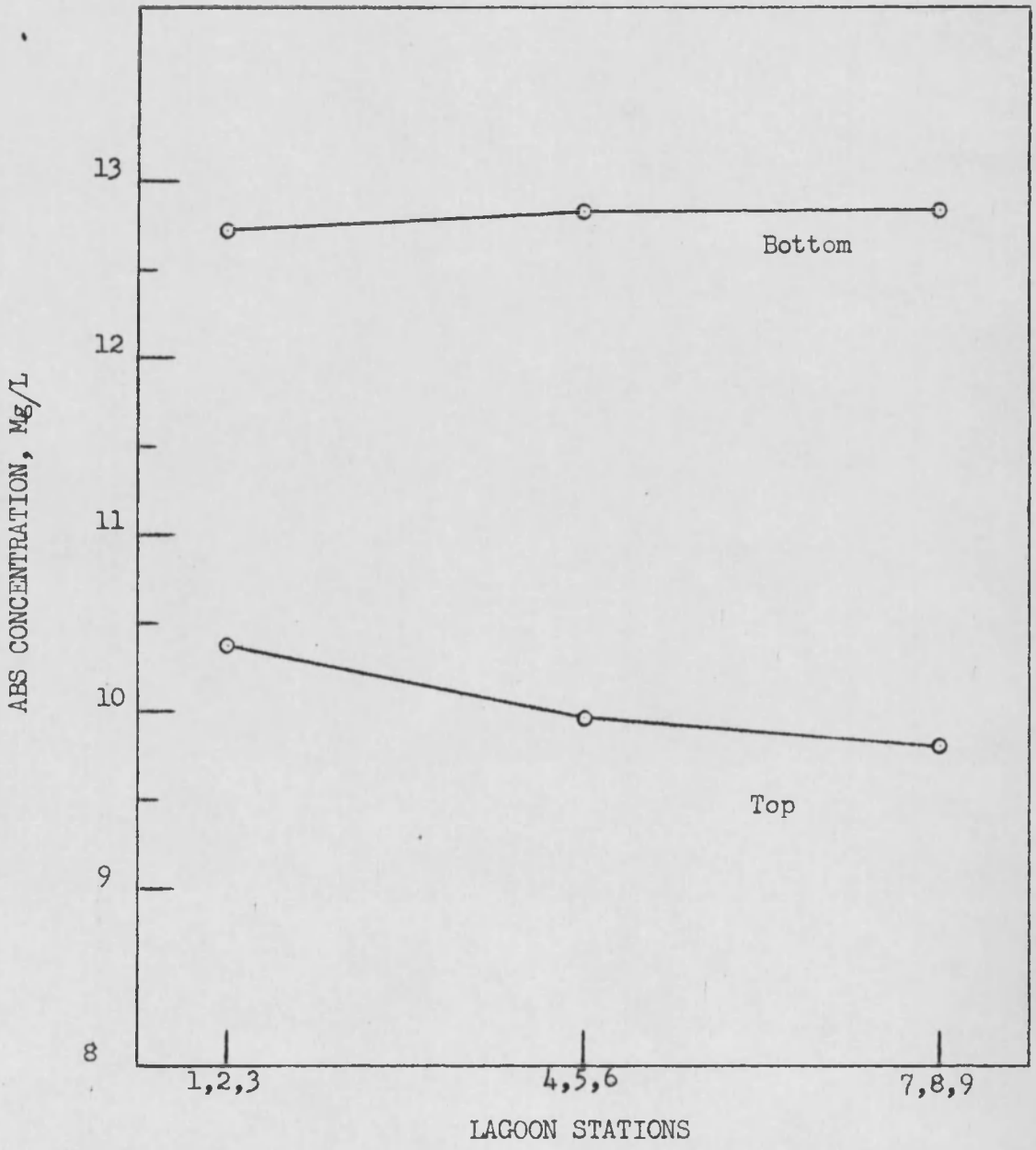
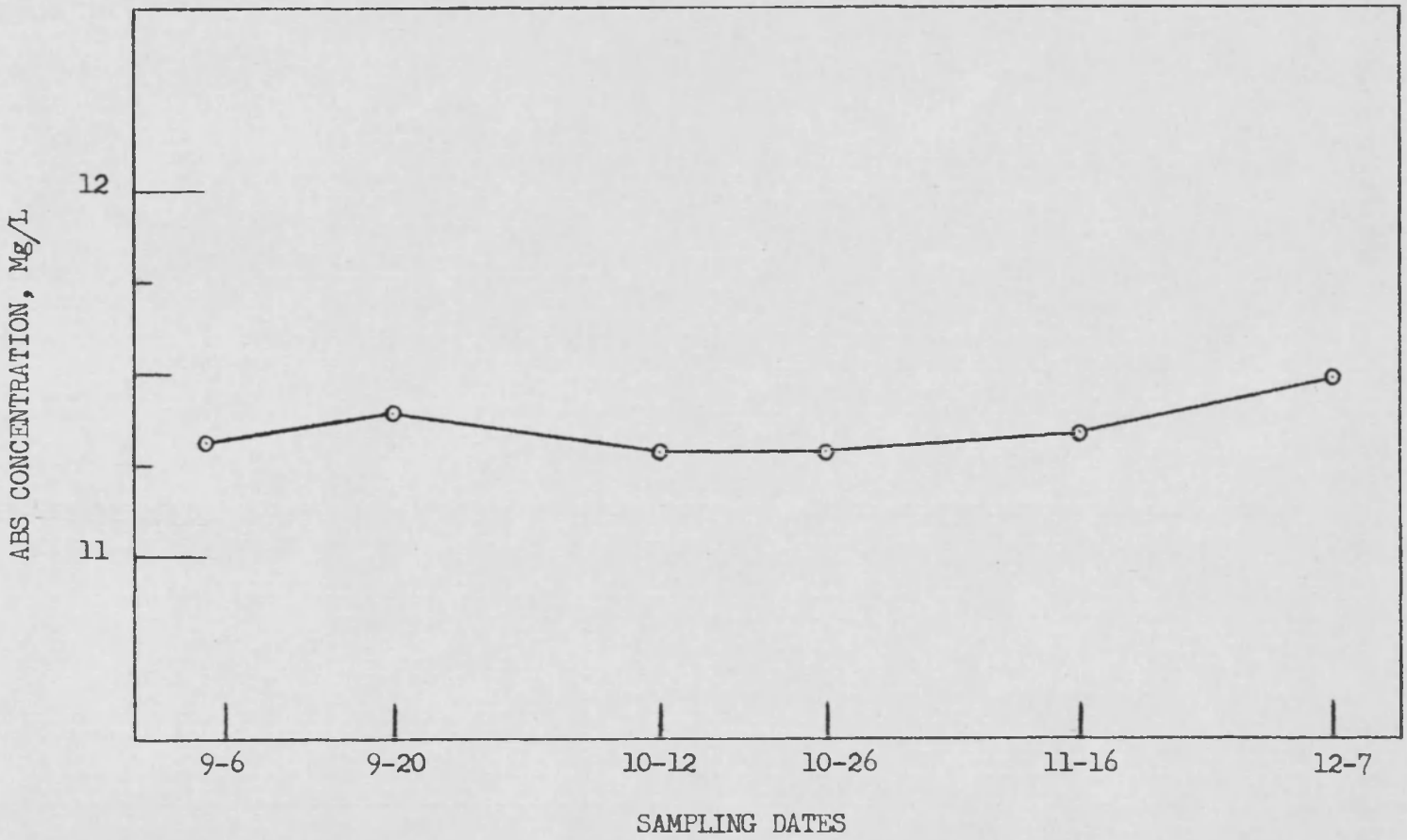


FIGURE 5.7

ABS IN LAGOON COMPOSITES



was 57,000 gallons, yielding a total influent volume of 2.86 million gallons. Evaporation accounted for a loss of 5.28 inches, or 0.29 million gallons (18). No measurement of seepage was possible, but it was hoped that some estimate of seepage rate could be arrived at by studying the other factors involved.

Since no arrangement had been made for measuring effluent flow, an estimate of the flow was made by taking a crude measure of flow velocity through the effluent pipe and measuring the depth of flow. Results of this test, extending over a 10-hour period, showed a flow of approximately 69,000 gallons per day, compared to a peak flow of 62,000 gallons per day recorded during the period of study. Extrapolation to 50 days yields a total effluent of 3.35 million gallons. Obviously, this figure is too high, since it is greater than total inflow. However, it does show that seepage probably accounts for only a negligible portion of outflow.

Using an average raw sewage ABS concentration of 8.70 mg/l, the total amount of ABS which entered the lagoon during the 50-day period was 207 lbs. Assuming that the ABS concentration in the effluent was about the same as at the surface of Station 8, or 9.7 mg/l, and that actual effluent flow was equal to the difference between inflow and evaporation, or 2.57 million gallons, it was found that 207 lbs. of ABS was removed from the lagoon during the same period. Therefore, ABS concentration in the lagoon appeared to be held at a constant level. This conclusion is borne out by the consistency of values, shown in Figure 5.7, for lagoon composites analyzed during the study period.

The question arises as to how the increase in concentration came about if the quantities of ABS entering and leaving the lagoon were equal. A look at evaporation rates for an entire year furnishes a possible explanation. In Table XI are listed average monthly evaporation rates for the Tucson area. Highest evaporation rates occur during the summer months of May, June, July, and August. If a 50-day period during June and July were selected for study, total evaporation from the lagoon could amount to 17.85 inches, or 0.98 million gallons. Assuming an influent flow of 2.86 million gallons (207 lbs. of ABS), it is apparent that only 1.88 million gallons (136 lbs. of ABS) would be lost from the lagoon by means other than evaporation. Thus, ABS concentrations in the lagoon would be increased from 8.70 mg/l to 13.2 mg/l. During periods of lowest evaporation rates, ABS concentrations probably should decrease slightly. If the average value of 6.08 inches per month is used, it may be shown that ABS concentration in the lagoon will increase from 8.70 mg/l to 10.8 mg/l in a 50-day period. On the basis of these figures, it seems reasonable to conclude that a gradual buildup in ABS concentration is taking place.

Since the lagoon had been in operation for approximately one year prior to initiation of this study, the question might possibly arise as to why the ABS concentration has increased only 2.65 mg/l. The explanation may be found by a study of seepage rates. At the time of lagoon construction, soil samples were taken at the site and subjected to permeability tests (19). A coefficient of permeability of 0.085 feet per day per foot of head was determined for untreated soil samples. Soil treated with 0.5% (by dry weight) bentonite or cement indicated a

decreased coefficient of 0.0195. When the lagoon was built, no treatment was employed except for some compaction. However, the very fine solids resulting from sedimentation and benthal decomposition probably had about the same sealing effect as bentonite or portland cement. This sealing process takes time, however, and until sufficient solids had accumulated to provide a seal, seepage rates were quite high. During the time this seepage was occurring, more ABS was leaving the lagoon than at the time of this study. Due to the higher concentrations near the bottom (Figure 5.6), water lost by seepage would have had a higher ABS content than that flowing through the effluent pipe.

Another condition obtaining, and worthy of explanation, was the striking difference in ABS concentration in the vertical profile. One possible cause for this phenomenon might stem from settling. No literature was found to substantiate this hypothesis, but it is possible that the ABS might be adsorbed to particulate matter in the lagoon. Then, as the solids settle, the adsorbed ABS is carried toward the bottom with them.

A second explanation could possibly be attributed to interferences in analytical procedures. Interfering substances could have been in greater concentration near the bottom, or might have been dislodged from the bottom and into suspension in the course of sampling. The sampling device was allowed to rest on the bottom of the lagoon while bottom samples were being taken.

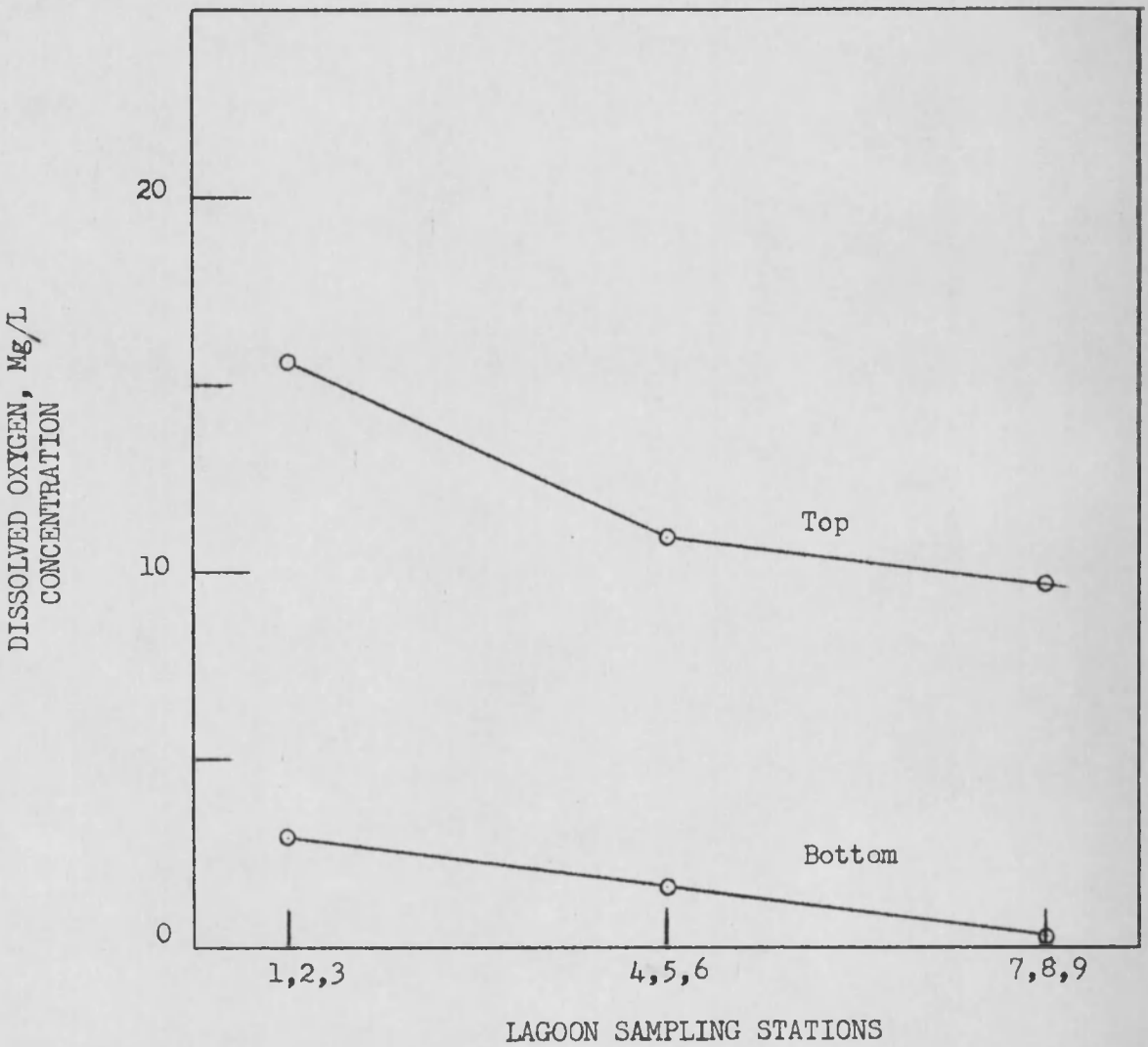
Some thought was given to the possibility that, if bacterial decomposition of ABS were taking place in the lagoon, degradation near the surface, where dissolved oxygen concentrations were highest (Figure 5.8), might be more rapid than at greater depths. However, since

it appears that no decomposition of the molecule is occurring, that theory was not explored further.

FIGURE 5.8

LAGOON DISSOLVED OXYGEN PROFILES

(AVERAGES FOR PERIOD OF STUDY)



Chapter 6

CONCLUSIONS AND SUGGESTIONS FOR FURTHER STUDY

6.1 Methods of Analysis and Sampling

It was found that the Methylene Blue method employed in ABS determinations was definitely satisfactory for the degree of accuracy required in this study. This statement held true for both raw sewage and lagoon water analyses. Evaluation of interferences in the method was not possible, however.

Sampling procedures and sample selections were justified by the consistency of results. A rather wide fluctuation of values was observed in the raw sewage, but that may be attributed to the normal fluctuations in domestic sewage characteristics.

6.2 ABS Profiles

The marked difference between ABS concentrations at the surface and near the bottom of the lagoon did not lend itself to a satisfactory explanation. Further investigations are necessary to evaluate the real causes for that variation. Two possible explanations based on settling and determinative interferences were forwarded.

6.3 Overall Treatment

It was established, that, in all probability, no reductions in ABS concentration was effected by the treatment process. On the contrary, there was an increase in concentration in the lagoon over that in the raw sewage. Probable reasons were given for the increase, based on

evaporation rates, seepage, and effluent flow. The buildup will probably continue with time until ABS concentration in the effluent is high enough to permit the removal of ABS as fast as it enters the lagoon. At that point the concentration will probably remain constant.

6.4 Suggestions for Further Study

The following is a list of projects which the author believes to be worthy of further investigation:

(1) Long-term studies of variation in ABS concentration in lagoons to determine whether or not an annual buildup does occur and, if so, whether or not a constant value will eventually be reached.

(2) Smaller scale investigations of lagoons with controlled seepage, evaporation, effluent flow, and ABS loading in an attempt to find the answers to some of the questions which arose during the preparation of this thesis.

(3) Attempts to develop a surfactant molecule which will perform as well as ABS, and yet be subject to more rapid bacterial degradation.

(4) Further attempts to discover exactly what organisms are most proficient in metabolizing ABS and to find a medium in which those organisms will abound.

(5) Studies to determine whether or not the presence of ABS interferes with the metabolic processes of biologic systems.

APPENDIX

TABLE VI

ABS IN RAW SEWAGE

GRAB SAMPLES FROM FLUME

Date	ABS, Mg/L 1	2	3	Avg.
8-18-61	8.9	9.6	9.1	9.20
8-21-61	8.0	9.0	8.8	8.60
8-25-61	8.2	8.7	8.9	8.60
8-28-61	8.9	8.35	9.5	8.92
9-1-61	9.2	9.2	9.2	9.20
9-6-61	10.3	11.0	10.8	10.70
9-14-61	7.7	7.5	7.6	7.60
9-18-61	9.0	9.5	9.4	9.30
9-27-61	10.1	9.9	10.3	10.10
10-4-61	10.0	10.0	9.95	9.98
10-11-61	7.25	7.1	7.3	7.22
10-20-61	6.6	6.75	6.9	6.75
10-25-61	8.25	8.1	8.1	8.15
11-8-61	9.0	-	-	9.0
11-13-61	9.3	9.25	9.25	9.27
11-20-61	7.9	8.2	8.3	8.13
11-24-61	5.7	5.9	6.0	5.87
12-4-61	9.1	9.1	8.95	9.05
12-11-61	6.75	6.85	7.0	6.87
12-18-61	12.2	11.95	12.0	12.05

Arithmetic Mean = 8.73 Mg/L

Max. Deviation From A. M. = 38%

TABLE VII

ABS IN RAW SEWAGE

REPRESENTATIVE SAMPLES FROM TRUCKS

Date	ABS, Mg/L 1	2	3	Avg.
8-18-61	10.3	9.2	9.6	9.70
8-25-61	6.0	6.6	6.6	6.40
9-1-61	8.0	8.4	8.5	8.30
9-18-61	7.8	7.9	8.0	7.90
9-27-61	10.6	11.0	10.5	10.70
10-20-61	6.8	7.1	6.65	6.85
11-8-61	7.3	7.45	-	7.37
11-20-61	10.1	10.25	10.4	10.25
12-18-61	9.3	9.3	-	9.30

Arithmetic Mean = 8.53 Mg/L

Max. Deviation From A.M. = 25%

TABLE VIII

ABS IN RAW SEWAGE

24-HOUR COMPOSITES

Date	ABS, Mg/L			
	1	2	3	Avg.
9-6/7-61	9.7	9.9	10.0	9.87
9-20/21-61	9.3	8.9	-	9.10
10-12/13-61	7.9	8.1	-	8.00
10-26/27-61	5.7	6.2	-	5.95
11-16/17-61	8.35	8.3	8.4	8.35
12-7/8-61	10.6	10.75	11.0	11.12

Arithmetic Mean = 8.73 Mg/L

Max. Deviation From A.M. = 32%

TABLE IX

ABS IN LAGOON GRAB SAMPLES

Date	Sample No.	Sta. 1	Sta. 2	Sta. 3	Sta. 4	Sta. 5	Sta. 6	Sta. 7	Sta. 8	Sta. 9
9-14-61	(Top)									
	1	10.3	10.5	10.3	10.1	10.0	10.25	9.8	9.6	10.05
	2	10.3	10.8	10.55	9.9	9.8	9.9	9.8	-	10.2
	3	10.5	10.7	-	10.2	9.9	10.0	9.6	9.8	-
	Avg.	10.37	10.67	10.43	10.07	9.9	10.05	9.73	9.70	10.13
	(Bottom)									
	1	12.75	12.6	12.75	12.6	12.9	12.8	12.0	12.8	13.1
	2	12.5	12.3	12.6	12.6	12.7	12.75	11.8	12.8	12.9
	3	12.4	12.2	12.0	12.65	13.1	-	11.9	12.8	13.4
	Avg.	12.55	12.37	12.75	12.62	12.90	12.78	11.90	12.80	13.13
10-4-61	(Top)									
	1	10.1	10.5	10.2	10.1	9.7	10.0	9.75	9.7	10.1
	2	10.0	10.75	10.4	10.3	9.8	10.0	9.8	9.85	10.0
	3	10.3	10.6	10.6	9.95	9.9	-	9.85	9.7	-
	Avg.	10.13	10.62	10.40	10.12	9.80	10.00	9.80	9.75	10.05
	(Bottom)									
	1	12.6	12.8	12.9	12.9	12.7	12.7	12.5	12.9	13.1
	2	12.7	12.5	-	13.1	12.9	12.6	12.7	-	12.8
	3	-	-	-	12.5	12.9	12.0	12.85	12.8	-
	Avg.	12.65	12.65	12.90	12.83	12.83	12.43	12.68	12.85	12.95
10-25-61	(Top)									
	1	10.0	10.55	10.3	10.1	9.75	10.05	9.8	9.8	10.2
	2	10.2	10.7	10.65	10.3	9.95	10.1	9.8	9.75	-
	Avg.	10.10	10.63	10.48	10.20	9.85	10.03	9.80	9.78	10.20
	(Bottom)									
	1	12.8	-	12.8	13.0	12.95	12.55	12.7	12.0	12.75
	2	12.8	-	13.2	-	-	-	12.55	13.0	13.0
	Avg.	12.80	-	13.00	13.0	12.95	12.55	12.63	12.50	12.87
11-13-61	(Top)									
	1	9.8	10.5	10.5	10.05	9.8	-	9.8	9.7	10.0
	2	10.1	10.75	10.5	-	9.6	10.2	9.8	9.75	-
	Avg.	9.95	10.63	10.50	10.05	9.20	10.2	9.80	9.73	-
	(Bottom)									
	1	12.75	12.9	12.8	-	13.1	12.9	12.8	-	13.2
	2	-	12.95	12.85	13.0	-	13.0	13.1	13.0	13.0
	Avg.	12.75	12.93	12.83	13.0	13.1	12.95	12.95	13.0	13.1
12-4-61	(Top)									
	1	9.9	10.3	10.2	9.8	9.75	10.1	9.5	9.45	9.6
	2	10.1	10.55	10.25	9.6	9.9	9.8	-	9.4	9.7
	Avg.	10.0	10.42	10.23	9.70	9.87	10.25	9.5	9.43	9.65
	(Bottom)									
	1	12.7	12.8	12.75	12.85	12.9	13.1	13.0	12.95	13.15
	2	12.75	12.8	12.8	13.1	13.2	-	13.05	13.25	-
	Avg.	12.73	12.80	12.78	12.97	13.05	13.1	13.03	13.10	13.15
Arith. Mean	(Top)	10.13	10.60	10.40	10.03	9.82	10.04	9.75	9.68	9.97
	(Bottom)	12.68	12.65	12.84	12.83	12.94	12.71	12.66	12.83	13.04

Arithmetic Mean (All Values) = 11.42

Max. Deviation From A. M. = 24%

TABLE X

ABS CONCENTRATIONS IN LAGOON

24-HOUR COMPOSITES

Date	Station 2	Station 5	Station 8	Avg.
9-6/7-61	11.68	11.35	10.90	11.31
9-20/21-61	11.90	11.50	10.77	11.39
10-12/13-61	10.95	11.68	11.22	11.28
10-26/27-61	11.73	11.30	10.82	11.28
11-16/17-61	11.58	11.40	11.05	11.34
12-7/8-61	12.03	11.48	10.93	11.48

Arithmetic Mean = 11.35

Max. Deviation From A. M. = 12%

TABLE XI *

AVERAGE MONTHLY EVAPORATION RATES

Months	Evaporation, Inches
January	2.02
February	2.72
March	5.10
April	7.57
May	9.87
June	11.20
July	10.31
August	8.25
September	7.05
October	5.08
November	2.93
December	0.96
Average	6.08

* Figures obtained from Solar Energy Laboratory and Institute of Atmospheric Physics at The University of Arizona.

LIST OF REFERENCES

(1) Cohen, Jesse M., "Effects of Synthetic Detergents on Water Treatment and Quality of Water." Paper presented at a meeting of the Conference of State and Provincial Public Health Laboratory Directors in Atlantic City, N. J., Oct. 18, 1959.

(2) Noller, Carl R., Textbook of Organic Chemistry, 2nd. Ed., W. B. Saunders Co., Philadelphia, 1958.

(3) Hart, H., and Schaetz, R. D., A Short Course in Organic Chemistry, 2nd Ed., Houghton Mifflin Co., Boston, 1959.

(4) "Structure of Alkyl Benzene Sulfonates", Report No. 139-55-503, Continental Oil Co., Central Research Laboratories (Aug. 11, 1955).

(5) McKinney, Ross E. and Symons, James M., "Bacterial Degradation of ABS, Part I., Fundamental Biochemistry", Journal, Federation Sewage & Industrial Wastes Association, 31, 549 (1959).

(6) Anon., "From Activated Sludge to Activated Suds at Batavia, Illinois." Journal, Federation Sewage & Industrial Wastes Association, 22, 362 (1950).

(7) Berg, H. E., "Operating Experiences With Detergents at Washington, D.C." Discussion. Journal, Federation Sewage & Industrial Wastes Association, 25, 281 (1953).

(8) Anon., "Hints on Froth Control." Journal, Federation Sewage & Industrial Wastes Association, 24, 679 (1952).

(9) Central States Sewage Works Association - Operators' Forum, "Frothing of Aerators" Journal, Federation Sewage & Industrial Wastes Association, 22, 1238 (1950).

(10) McGauhey, P. H., and Klein, Stephen A., "Removal of ABS by Sewage Treatment." Journal, Water Pollution Control Federation, 31, 877 (1959).

(11) Eumb, C., "Experiments on the Effects of Certain Synthetic Detergents on the Biological Oxidation of Sewage." Water and Sanitary Engineering, 4, 305 (1953-4).

(12) Sperry, W. A., "Detergents and Their Influence on Sewage Treatment." Journal, Federation Sewage & Industrial Wastes Association, 23, 1469 (1951).

(13) Manganelli, Raymond, "The Effects of Detergents on Sewage Treatment Processes." American Society Testing Materials Bulletin 192, 57 (September, 1953).

(14) Hirlinger, K. A., personal correspondence.

(15) Association of American Soap and Glycerin Producers, Inc., (AASGP), personal correspondence.

(16) House, R., et. al., "Determination of Alkyl Benzene Sulfonates in Sewage." Journal, Water Pollution Control Federation, 33, 85 (1961).

(17) Standard Methods for the Examination of Water, Sewage, and Industrial Wastes, American Public Health Association, New York, 11th Edition, (1960).

(18) Institute of Water Utilization, Agricultural Experiment Station, University of Arizona, Tucson, Arizona, personal correspondence.

(19) Mees, Q. M., personal correspondence.