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From Anaerobic Lagoons by
Purple Sulfur Bacteria

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Theodorus Johannes Maria van Lotringen

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John B. Gerrish
Major professor

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CONTROL OF HYDROGEN SULFIDE ODORS FROM ANAEROBIC LAGOONS BY PURPLE SULFUR BACTERIA

By

Theodorus Johannes Maria van Lotringen

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ABSTRACT

CONTROL OF HYDROGEN SULFIDE ODORS
FROM ANAEROBIC LAGOONS BY
PURPLE SULFUR BACTERIA

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Purple sulfur bacteria have been found to reduce the odor levels of anaerobic lagoons. A serious problem is getting a culture of purple sulfur bacteria to survive a cold winter season. This thesis puts forward a quantitative analysis of the purple sulfur bacterial processes in a lagoon environment. A model based largely on literature expresses these processes in mathematical equations. Also presented are experiments to support the model where critical values were unavailable. The processes considered in the model are the major components of the sulfur cycle, since hydrogen sulfide is believed to be an important contributor to lagoon odor. The physical environment (with special emphasis on heat balance) is modeled in order to obtain better insight into its influence on odor production.

In support of the heat balance model a temperature history was recorded during the spring warm-up of an

anaerobic swine waste lagoon. Evidence suggests that a froth-type scum cover increases the heat loss of such a lagoon system, tending to prolong the warm-up period.

In support of the model of the sulfur cycle, the rate at which hydrogen sulfide is oxidized and the rate at which sulfate is formed were measured under various light- and temperature conditions. At low light intensities the rate of oxidation of hydrogen sulfide seems to be independent of the temperature.

The work with the anaerobic swine waste lagoons at MSU has led to new insights in design and management of such lagoons. A system involving two lagoons has been shown effective in reducing the time during which odors can be produced; the basic features of the system include a strategy to preserve a population of purple sulfur bacteria during the cold Michigan winter.

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Symbol	Description	Units
A	Surface area	m^2
A_b	Surface area of a bubble	m^2
A_h	Cross-sectional area of the lagoon at height h above the bottom	m^2
A_s	Atomic weight of sulfur	u
a	Constant	-
B	Fraction of the sky covered by clouds	-
b	Constant	-
C_d	Drag coefficient	-
c	Constant	-
c'	Velocity of light in vacuo	m/s
D	Diffusivity	m^2/s
D_{H_2S}	Diffusivity of hydrogen sulfide in water	m^2/s
d	Constant	-
d_e	Equivalent diameter of a bubble	m
d_o	The actual diameter of a bubble	m
E	Radiant energy at a wavelength	W/m^2 m
Eo	Eötvös number	-
F	Rate of feces production per unit weight of animal	m^3/kg s
Fr	Froude number	-
g	Gravitational acceleration	m/s^2

Symbol	Description	Units
H	The total water depth in a lagoon	m
h	Variable height measured from the lagoon bottom	m
h'	Planck's constant	Js
h_1	Height of compensation point	m
h_b	Rise of a bubble	m
I	Incident light intensity	lx
I_1	Compensation point for purple sulfur bacteria	lx
I_h	Light intensity at height h above the bottom of a lagoon with total height H	lx
K_1	Saturation constant for the reduction of sulfate	$mole/m^3$
K_2	Saturation constant for the oxidation of hydrogen sulfide	$mole/m^3$
K_3	Saturation constant for the oxidation of sulfur	m^2/m^3
K_4	Saturation constant for the reduction of sulfur	m^2/m^3
K_5	Saturation constant of light	lx
K_{CO_2}	Henry's constant for carbon dioxide	$mole/m^3$ Pa
K'_{CO_2}	First dissociation constant for H_2S	$mole/m^3$
K_{H_2S}	Henry's constant for hydrogen sulfide	$mole/m^3$ Pa
K_I	The inhibition constant for hydrogen sulfide	$mole/m^3$
K'	First dissociation constant for H_2S	$mole/m^3$
K''	Second dissociation constant for H_2S	$mole/m^3$
k	Boltzmann constant	J/K
k_b	Mass transfer coefficient for H_2S at the bubble surface	m/s

Symbol	Description	Units
k_c	Factor depending on the cloud type	-
k_{CO_2}	Mass transfer coefficient for carbon dioxide	m/s
k_{H_2O}	Mass transfer coefficient for water	m/s
k_{H_2S}	Mass transfer coefficient for hydrogen sulfide	m/s
Le	Latent heat of evaporation at T_w	j/kg
L_o	Length of the lagoon at the bottom	m
M_a	Molecular weight of air	kg/mole
M_w	Molecular weight of water	kg/mole
m	Constant	-
N	The number of animals whose manure is transported to the lagoon	-
N_b	Number of bubbles in the lagoon	-
N_{CO_2}	Mass transfer rate of carbon dioxide	mole/s
N_{H_2O}	Mass transfer rate of water	mole/s
N_{H_2S}	Mass transfer rate of hydrogen sulfide	mole/s
N_o	Average number of sulfur globules in a cell	-
Nu	Nusselt number	-
n	Constant	-
n'	Refractive index of an emitter	-
P	Atmospheric pressure at the altitude of the surface above sea level	Pa
P_{CO_2}	Partial pressure of carbon dioxide in the gas phase	Pa
P_{H_2S}	Partial pressure of hydrogen sulfide in the gas phase	Pa

Symbol	Description	Units
Pr	Prandtl number	-
p'	Instantaneous deviation of the water vapor pressure from the time-averaged water vapor pressure	Pa
p_w	Vapor pressure of water	Pa
p'_w	Saturated water vapor pressure at T_w	Pa
p_{w_1}	Water vapor pressure at height z_1	Pa
p_{w_2}	Water vapor pressure at height z_2	Pa
Q_A	Long wave radiant energy from the atmosphere	W
Q_g	Gas production rate	m^3/s
Q_H	Indirect solar radiation	W
Q_R	Reflected solar radiation	W
Q_S	Direct solar radiation	W
Q_W	Long wave radiant energy from the water	W
Q_ε	Net input of heat by evaporation and condensation	W
Q_θ	Net total input of heat	W
Q_λ	Net input of heat by radiation	W
$Q_{\lambda n}$	Net input of heat by radiation during the night	W
Q_ρ	Net input of heat by rainfall	W
Q_σ	Net input of heat by direct heat transfer	W
R	Gas constant	m^3Pa/mole K
R'	Reflectivity	-
Rb	Bowen ratio	-
R_b	The radius of the bubble surface	m
Re	Reynolds number	-

Symbol	Description	Units
S	Surface area of the sulfur globules per unit volume lagoon water	m^2/m^3
Sc	Schmidt number	-
Sh	Sherwood number	-
S_h	Specific surface of the bubbles	m^2/m^3
T	Absolute temperature	K
T_a	Absolute temperature of the air	K
T_R	Reference temperature	K
T_w	Absolute temperature of the water	K
t	time	s
U	Rate of urine production per unit weight of animals	$m^3/kg\ s$
U_b	Rising velocity of a bubble	m/s
u	Wind velocity in main air stream	m/s
u_1	Wind velocity at the height z_1	m/s
u_2	Wind velocity at the height z_2	m/s
u_z	Wind velocity at a height z	m/s
V	The total volume of a lagoon	m^3
V_b	The volume of a bubble	m^3
V_h	Volume of the lagoon below height h	m^3
V_m	Molecular gas volume	m^3/mole
W_o	Width of the lagoon at the bottom	m
w	Average weight of the animals	kg/animal
w'	Instantaneous deviation of the vertical velocity from the time-averaged vertical velocity	m/s
X_1	Concentration of desulfurizing bacteria	$cells/m^3$

Symbol	Description	Units
X_2	Concentration of purple sulfur bacteria	cells/m^3
x	Size parameter of the lagoon surface	m
Y_1	Yield coefficient for the reduction of sulfate	cells/mole
Y_2	Yield coefficient for the oxidation of hydrogen sulfide	cells/mole
Y_3	Yield coefficient for the oxidation of sulfur	cells/mole
Y_4	Yield coefficient for the reduction of sulfur	cells/mole
Z	Group, defined in equation (6.22)	
Z1	Group, defined in equation (6.28)	
z_1, z_2	Two different heights above the water surface	m
α	Heat transfer coefficient	W/m^2K
α'	The angle of the side slopes of a lagoon	deg
η	Extinction coefficient	1/m
θ	temperature	°C
λ	Wavelength measured in vacuo	m
λ_a	Heat conductivity of air	W/m K
λ_w	Heat conductivity of water	W/m K
μ	growth rate	1/s
μ_1	Specific growth rate of the desulfurizing bacteria	1/s
μ_2	Specific growth rate of the purple sulfur bacteria oxidizing hydrogen sulfide	1/s
μ_4	Specific growth rate of the purple sulfur bacteria, reducing sulfur	1/s
μ_5	Specific growth rate of the purple sulfur bacteria for light-limited growth	1/s

Symbol	Description	Units
μ_a	Dynamic viscosity of air	kg/m s
μ_{max1}	The maximum growth rate of the desulfurizing bacteria	1/s
μ_{max2}	The theoretical maximum growth rate for the oxidation of hydrogen sulfide	1/s
μ_{max3}	The maximum growth rate for the oxidation of sulfur	1/s
μ_{max4}	The maximum growth rate for the reduction of sulfur	1/s
μ_{max5}	The theoretical maximum growth rate for light limited growth	1/s
μ_R	Reference dynamic viscosity	kg/m s
μ_w	Dynamic viscosity of water	kg/m s
ρ_a	Density of air at T_a	kg/m^3
ρ_s	Density of sulfur in globules	kg/m^3
ρ_w	Density of water	kg/m^3
$\Delta\rho$	The density difference between a bubble and water	kg/m^3
σ	Surface tension of water	kg/s^2
σ'	Stefan-Boltzmann constant	W/m^2K^4
τ	Contact time of a water particle with a bubble	s
τ_b	The time a bubble is in the water	s
Ψ_i	Angle of incidence	rad
Ψ_r	Angle of refraction	rad
Ψ_s	Solar angle	rad
[ ]	Concentration	$mole/m^3$
[ ]'	Equilibrium concentration	$mole/m^3$

Subscripts:

a	air
b	bubble
f	feces
g	gas
h	height
s	sulfur
u	urine
w	water

INTRODUCTION

Since the introduction of confined housing for animal production, manure management has become a problem: the manure was not defecated directly on pasture but in a building. Consequently, manure had to be transported. It is possible to design different combinations of storage and transport techniques, which vary from labor-intense systems with low capital investment to systems having almost no labor but requiring a high capital investment.

The system under consideration in this thesis treats the manure as a liquid. Swine manure is transported out of a slatted-floor growing-finishing building several times each day by flushing with water. The manure thus diluted is carried to an anaerobic lagoon. In order to have adequate storage capacity in a small volume lagoon, water is pumped back to the building and used for the flushing operation. An anaerobic lagoon is currently considered to be the most economical and convenient system for storage and stabilization of manure. A major disadvantage of the anaerobic lagoon is the potential for odor production.

The simple storage of animal manure in an anaerobic lagoon is an example of the complexity of nature. Not only

do the processes of anaerobic digestion take place, but also photosynthesis by bacteria or algae. The open structure makes it also susceptible to variations induced by meteorological and climatic conditions. Consequently the processes and their rates are functions of time and place.

In this thesis I will evaluate a number of variables, which play a role in the behavior of an anaerobic lagoon. In Part I the basic characteristics are described. In Part II these variables are integrated into a model, designed to improve the understanding of the complex interactions. I will attempt to make the model credible by comparing it with experimental results. Finally I will use this model to propose management practices which will result in a better lagoon performance. Particular attention is paid to lagoon operation in the North Central States, where anaerobic lagoons work in less than favorable climatic conditions.

PART I

REVIEW OF LITERATURE

CHAPTER 1

LAGOONS

1.1 Introduction

A lagoon is an open structure in the soil for the storage and/or treatment of wastewater. There is no clear distinction between different types of lagoon, but rather a continuum from one extreme to the other. Generally lagoons are subdivided into aerobic, facultative and anaerobic lagoons. This subdivision is based on the availability and presence of oxygen.

Other subdivisions, which can be made, are according to the type of waste (i.e., agricultural, industrial or municipal) according to the type of discharge (i.e., no discharge, irrigation or discharge to surface waters) according to the type of climate (i.e., cold, warm or tropical, wet or dry climates) or according to the depth (i.e., shallow or deep lagoons). All these subdivisions are arbitrary and examples of all of these can be found.

The lagoon type of interest in this thesis could be described as an anaerobic cool-and-wet climate lagoon for swine waste with land application as discharge.

Major sources of information about lagoons are conference papers, edited by Gloyna et al. (1976) and the annual literature reviews of the Water Pollution Control Federation (Burkhead and O'Brien, 1974; and O'Brien, 1975, 1976 and 1977).

The following general discussion will be based on the subdivision into aerobic, facultative and anaerobic lagoons.

1.2 Aerobic lagoons

Aerobic lagoons are characterized by the presence of oxygen throughout the body of water. They are used for the storage of irrigation and drinking water and as a polishing step for wastewater treatment. Aerobic lagoons are only used for wastewater treatment in cases where stringent odor or effluent requirements exist. Design of these lagoons is based on the use of the receiving water. Therefore criteria are used such as algal growth potential, median toxicity limits for fish, viral plaque forming units and selective disinfection kinetics of algal-bacterial effluents. Consequently the treatment is directed toward reduction of suspended solids, such as algae, reduction of enteric bacteria and reduction of nutrients such as nitrogen and phosphorous. If the effluent is used for irrigation, additional criteria such as the sodium:potassium ratio and dissolved salt limit should be considered (Gloyna, 1976).

Generally aerobic lagoons are shallow to permit natural aeration, but sometimes they are built with a considerable depth and forced-aeration is applied at a low rate. Aerobic lagoons are not suitable for the treatment of wastes from livestock production units. These wastes are too concentrated.

1.3 Facultative lagoons

Facultative lagoons are lagoons in which an anaerobic and an aerobic environment coexist. Sometimes a lagoon is facultative the whole year around, but quite often an aerobic lagoon turns anaerobic near the bottom during adverse conditions or an anaerobic lagoon acquires an aerobic layer at the surface during periods of lower loading rates or other action which reduces the biochemical oxygen demand (BOD).

Facultative lagoons are also called waste stabilization ponds, since their main application is in the reduction of the BOD of wastewater. Compared with activated sludge processes, in which forced aeration is applied, a facultative lagoon requires more land and has a higher content of biological solids, such as algae. There are however, many advantages, such as a higher BOD removal, less energy and chemical consumption and much lower manpower requirements. In addition, lagoons are less sensitive to influent characteristics than are activated sludge treatment plants.

The anaerobic environment at the bottom of a facultative lagoon serves to keep nutrients available for the

algae. Gloyna (1971) describes an empirical relationship for the design of facultative lagoons, which includes a correction factor for the temperature and for sulfide toxicity. A sulfide concentration of 7 ppm is toxic to algae. A facultative lagoon will function at temperatures above 5°C. The most important design parameter is, however, the surface area. Loading rates are therefore expressed per unit area of lagoon surface. A larger area will result in a larger input of oxygen from the air and will permit the penetration of more light into the water. Shallow lagoons are very susceptible to mixing by the wind resulting in the suspension of solids and reduced light penetration.

Photosynthetic bacteria can occur in facultative lagoons at the upper boundary of the anaerobic zone. Their coloring of the lagoon water is, however, masked by the large number of algae, which predominate in these lagoons.

1.4 Anaerobic lagoons

Characteristic of anaerobic lagoons is the complete absence of oxygen. Oxygen which enters via the surface is very rapidly consumed in the uppermost film of lagoon water. Although all lagoons, which lack oxygen are called anaerobic, there is still quite a variation possible depending on how low the oxidation-reduction ("redox") potential is. With decreasing redox potential, the following processes take place: denitrification, acid fermentation, sulfate reduction and finally, methane fermentation. In the next chapter

these processes will be discussed in greater detail. In an anaerobic lagoon the several processes will occur simultaneously with process rates being affected by depth.

Anaerobic lagoons can be built much deeper than aerobic or facultative lagoons. A minimum depth is required, however, to maintain anaerobic conditions. Since anaerobic bacteria have low growth rates, an anaerobic lagoon should not be pumped out completely because it is necessary to retain a minimum bacterial culture. This lowest allowable level is called the design volume. Consequently the design of anaerobic lagoons is not based on the load per unit surface as for facultative lagoons, but on the load per unit volume.

If conditions are suitable, photosynthetic bacteria can establish themselves in large numbers in anaerobic lagoons. Their characteristics and their occurrence in lagoons are described in Chapter 3.

Most types of algae cannot survive in anaerobic lagoons because of their oxygen requirement. There are however, some types which can perform fermentative reactions (Wiedeman and Bold, 1965). Often, however, the sulfide concentration is above the toxic level of 7 ppm. Photosynthetic sulfur bacteria can stimulate the occurrence of these algae.

CHAPTER 2

ANAEROBIC TREATMENT

2.1 Introduction

In the presence of high concentrations of organic material, anaerobic processes will occur as long as the supply of oxygen is insufficient. Even in ancient times, it was known that in swamps a combustible gas is formed. This is mentioned, for example, in the Historia Naturalis of Pliny (Haberly, 1957). For centuries this gas has been used for cooking and heating. It was Volta (1776) who discovered that the formation of this gas was related to the decomposition of organic material.

For about a century, use has been made of the anaerobic processes in the treatment of organic waste. This has developed in a wide variety of constructions in which the environment is controlled. Starting in 1860, the first anaerobic digesters were developed especially for the treatment of sewage sludge (Cameron and Travis in England, Mouras in France and Imhoff in Germany). In 1906 the Imhoff-Tank or Emscherbrunnen was used for the first time (Imhoff, 1916). In the Imhoff-tank, the digestion area is built directly under the sedimentation basin of a sewage treatment plant.

In 1914 Imhoff improved the distribution of the sludge supply and in 1916 he introduced the principle of mixing the incoming sludge with the content of the digester. Since that time, study of many environmental factors has resulted in the design of improved systems.

These developments were generally accompanied by an increase in complexity of operation, by an increase in cost and therefore by an increase in the economical size of operation. In comparison, farms are small scale systems. Farming is already such a diverse enterprise that one must avoid any unnecessary complication in equipment and management. A gas collection system was shown to contribute more costs than benefits (Nordstedt, 1976).

The principal biological processes for anaerobic lagoons and anaerobic digestion and the governing natural laws are the same. The anaerobic lagoon, however, avoids the complexity introduced in the environment controlled digestion process. Some important sources of information about the anaerobic treatment processes include the bibliography of Shadduck and Moore (1975) about the digestion of livestock wastes, the review of Regan (1975) and the annual literature review of the Water Pollution Control Federation (Ghosh and Conrad, 1974 and 1975; Ghosh et al., 1976 and 1977).

2.2 Anaerobic digestion processes

The basic feature of these processes is the degradation of volatile organic compounds through the action of microorganisms. These compounds are hydrolyzed with the aid of extracellular enzymes to a form which can be taken up by the microorganisms. The organisms which produce these extracellular enzymes are named acid-forming microorganisms or "Acid-formers," because they convert these hydrolyzed organic compounds mainly into lower molecular weight fatty acids. These acids can be used directly or indirectly by methane forming organisms, which convert them into methane and carbon dioxide. As a result of the methane digestion, organic compounds are converted almost completely into gases. The principle organic compounds in sludge and manure are carbohydrates, proteins and fats. Each of these will be described shortly in the following discussion.

The most important carbohydrates are starch, cellulose and glucose. Starch and glucose are decomposed along well known pathways. Their decomposition is a relatively fast process. The breakdown of cellulose, however, requires specific environmental conditions (Bryant, 1973 and Leatherwood, 1973). The predominant cellulose-hydrolyzing bacteria use ammonia as the only source of nitrogen and are unable to use amino acids. These bacteria also need sodium, B-vitamins and branched volatile fatty acids for the synthesis of amino acids. The most important form of the enzyme cellulase is

supposed to be built up of two groups: a hydrolyzing group and a group which attaches itself to the cellulose (Smith, 1973). The intensity of attachment to cellulose is strongly reduced by the presence of lignin and silicon, and by the crystallinity of the cellulose. If the attachment were not reduced by lignin and the other factors, hydrolysis would proceed much faster. The enzyme cellulase can be excreted by the following organisms (Leatherwood, 1973 and Dehority, 1973): Ruminococcus albus, Butyrivibrio fibrisolvens and Bacteroides ruminicola. The cellulose is converted by cellulase to the disaccharide cellobiose, which is further converted intracellularly to glucose. The decomposition of cellulose is a slow process.

Proteins are broken down outside the cell by proteolytic enzymes. A wide variety of organisms can do this. The resulting amino acids are used within cells for biosynthesis or are further broken down with the formation of CO_2, H_2, H_2S, NH_3 and HCN (Chanin, 1961).

Fats are hydrolyzed by the enzyme lipase to glycerol and fatty acids. The glycerol is converted to pyruvic acid. The fatty acids are decomposed by β-oxidation (Jeris and McCarty, 1965). The decomposition of fats results, therefore, mainly in production of acetic acid. According to Jeris and McCarty (1965) formic acid is converted into methane by reduction and acetic acid is converted into carbon dioxide and methane by transmethylation.

Acetic and formic acid are intermediate products formed during the degradation of all longer-chain fatty acids. Formic acid is converted so fast that it is seldom detected.

Methane forming organisms can utilize only a limited range of compounds. The most important substrates are hydrogen (with carbon dioxide) and formic acid. Andrews (1965), Cookson and Burbank (1965) and Laskin and Lechevalier (1973) list a number of methane forming organisms with their substrates. Some of the organisms listed are now considered to be symbiotic associations between two organisms. The best known example for this is Methanobacterium omelianskii. Each organism performs a part of the ethanol decomposition (Bryant et al., 1967 and Bryant, 1967).

$$2\ CH_3\ CH_2\ OH + 2\ H_2O \rightarrow 2\ CH_3\ COOH + 4\ H_2$$

$$CO_2 + 4\ H_2 \rightarrow CH_4 + 2\ H_2O$$

The first organism is inhibited by hydrogen which makes isolation difficult.

Winfrey and Zeikus (1977) and Winfrey et al. (1977) describe how methanogenesis is inhibited by small quantities of sulfate. The results of measurements in Lake Mendota sediments are explained very well by the pure culture studies of Bryant et al. (1977). Bryant et al. found, that desulfurizing bacteria can have a similar symbiotic association with H_2-utilizing methanogenic bacteria as

described for Methanobacterium omelianskii, provided sulfate is absent. Not only will this association metabolize ethanol as described above, but the desulfurizing bacteria produce acetate, hydrogen and carbon dioxide from lactate. Small concentrations of sulfate, however, change the metabolism of the desulfurizing bacteria. Instead of producing hydrogen they will use it seemingly at a much faster rate than the methanogenic bacteria, resulting in suppression of methanogenesis.

D'Allessandro et al. (1974) describes how the desulfurizing bacteria use the hydrogen from lactate metabolism for the reduction of sulfate:

$$3\ SO_4^{2-} + 4H^+ + NH_4^+ + 7\ CH_3\ CHOHCOO^- \rightarrow$$

$$3HS^- + 6\ CO_2 + C_5\ H_7\ O_2\ N + 5\ CH_3\ COO^- + 9\ H_2O$$

In the anaerobic environment, denitrification also takes place. Nitrates and nitrites are reduced to the gaseous products nitrous oxide and molecular nitrogen. This loss of nitrogen out of the environment is considered as a favorable aspect in wastewater treatment. For agricultural purposes, however, this means a loss of fertilizer value. Since nitrates and nitrites are unlikely to form in anaerobic lagoons, this loss is probably negligible in comparison with the loss of nitrogen by the volatilization of ammonia.

2.3 The influence of the physical environment

The most important physical factors in the anaerobic treatment are the intensity of mixing, the temperature and the availability of light.

As mentioned above, Imhoff (1916) found that mixing can considerably improve the rate of digestion. Some twenty years ago, Myers (1961) and Schreiber (1962) worked on the effects of mixing on the anaerobic digestion process. Their recommendations are incorporated by Bargman (1966) in a Manual of Practice for sludge digestion. Mixing has the following positive effects.

a. Newly introduced sludge comes rapidly to the same temperature as the bulk of the digestion tank.
b. The mixing of new sludge with large quantities of digesting and buffered sludge causes a fast contact between substrate and microorganisms resulting in a rapid start of the decomposition process.
c. By maintaining a uniform mixture of all compounds the negative effect of high local concentrations of decomposition products and toxic substances is diminished.
d. By mixing a digester, the whole volume is used. If "dead" corners are avoided in this way the size of the digester can be reduced.
e. Mixing results in a better separation of the produced gas and therefore reduces the accumulation

of scum. Scum is a layer of solids and gas at the surface.

The negative effects of mixing are:

a. It requires energy.

b. Some gas is lost.

Because of the negative effects, mixing is generally limited to short periods before and after the introduction of new sludge, which takes place once or twice daily. In order to obtain the beneficial effects of mixing, the viscosity has to be kept low. The viscosity rises dramatically with an increase in total solids. A practical upper limit for the total solids is therefore about twelve percent.

The temperature has a strong influence on the digestion process. Most attention has been given to mesophilic digestion (15-35°C) because this temperature range is fairly close to environmental conditions. In a few instances, thermophilic digestion (about 60°C) is applied. Psychrophilic organisms can occur during the winter in unheated digesters and lagoons. Digestion is then very slow and incomplete.

Fair and Moore (1937), Burd (1968) and Maly and Fadrus (1971) present graphically the influence of temperature on the time after which the digestion can be considered as completed. These times apply to digesters in which the environmental conditions are kept fairly constant. At higher temperatures the decomposition is more complete,

resulting in an increased gas production. Thermophilic digestion, however, requires a lot of energy and results in a bad-smelling effluent. According to Garber (cited in Burd, 1968) thermophilic-digested sludge has better dewatering characteristics because of the more complete degradation of proteins and the formation of larger particles.

Speece and Kem (1970) studied the influence of short-time temperature variations as they occur during the introduction of new sludge. Even if the temperature drops a few degrees the gas production stops. After a time which depends on the time and intensity of the temperature disturbance, gas production will resume. Organisms require about two hours to adapt after a step decrease in temperature of 10°C. Up to 45°C an increase in temperature will result in an increased rate of decomposition. Above this temperature, however, a rapid decrease occurs. In lagoons the temperature will never become too high.

Light plays no role in digesters, because of the closed structure. Besides the influence on photosynthetic organisms in lagoons (to be discussed in the next chapter), light can also influence the performance of some methanogenic bacteria. Pantskhava (1973a and b) studied the conversion of methanol to formaldehyde, carbon dioxide, pyruvic acid and vitamin B_{12} by cell-free extracts of Methanobacterium kuzneceovii in the light. The influence of light is

stronger at higher temperatures. Light has also a stronger effect when the reaction occurs in a hydrogen atmosphere rather than a nitrogen atmosphere. Light is thus reversing the degradation processes which take place in the dark. Light seems to inhibit methane formation in at least some methanogenic organisms.

2.4 The influence of the chemical environment

The most important chemical factors in the anaerobic environment are the pH, the concentration of volatile organic acids and the concentration of cations. In some cases compounds foreign to the system have a detrimental effect on the decomposition process.

After the start-up of a digestion process the pH will go down, because the acid forming bacteria grow faster than the methane forming bacteria. When the number of methanogenic bacteria increases, the pH will be restored to near neutral conditions. At the same time the alkalinity builds up, protecting the system against fast pH changes. If, however, the loading rate is increased too fast or if the loading is irregular the methane formers cannot keep pace with the acid formers and the alkalinity drops. Once the alkalinity becomes too low the pH starts falling. As this happens methane formation is the first process to be inhibited. Since the acid-forming bacteria have a lower pH optimum (Albertson, 1961) the pH will initially fall

faster and faster until a pH of about 6 is reached. If no action is taken the pH can go down as low as a value of 3. The above sequence of events can be initiated by an increased loading, a drop in temperature or introduction of inhibitors of methanogenesis (e.g., oxygen).

In animal waste lagoons the alkalinity is generally quite high. A rapid change in pH is therefore unlikely. If, however, a farmer discharges the contents of a manure storage pit into a lagoon, the tolerable loading rate can be far exceeded. Andrews and Graef (1971) among others describe the action of the bicarbonate buffer. Carbon dioxide occurs in several different forms: $[CO_2]$ gas, $[CO_2]$ dissolved, $[H_2CO_3]$, $[H\ CO_3^-]$ and $[CO_3^{2-}]$. The equilibrium between gaseous CO_2 and dissolved CO_2 is described by Henry's Law:

$$[CO_2]'_w = K_{CO_2} * P_{CO_2} \qquad (2.1)$$

in which:

$[CO_2]'_w$ = the saturated concentration of dissolved carbon dioxide gas in equilibrium with the carbon dioxide in the gas phase (mole/m^3)

K_{CO_2} = Henry's constant for carbon dioxide (mole/m^3. Pa)

P_{CO_2} = partial pressure of carbon dioxide in the gas phase (Pa).

In reality, equilibrium is never attained because there is a resistance to mass transfer at the gas-liquid interface. The mass transport rate becomes:

$$N_{CO_2} = k_{CO_2} * A * ([CO_2]_w - [CO_2]'_w) \qquad (2.2)$$

in which:

N_{CO_2} = mass transfer rate of carbon dioxide (mole/s)

k_{CO_2} = mass transfer coefficient for carbon dioxide (m/s)

A = transfer surface area (m^2/m^3)

$[CO_2]_w$ = actual concentration of carbon dioxide in water ($mole/m^3$)

At equilibrium the concentration of $[CO_2]_w$ far exceeds the concentration of H_2CO_3. The concentration of CO_3^{2-} is negligible as a pH of about 7. ($pK''_{CO_2} = 10.25$). There remains the equilibrium between carbonic acid and bicarbonate:

$$K'_{CO_2} = \frac{[H_3O^+]\ [HCO_3^-]}{[H_2\ CO_3]} = 4.3 * 10^{-7} \qquad (2.3)$$

According to Andrews, neglecting the resistance to mass transfer at the interface causes an error of about 10%.

Wood (1962) demonstrates the strong influence of pH on the reaction mechanism with an experiment in which Escherichia coli was grown on glucose at a pH of 6.2 and

7.8. At the higher pH for example, the enzyme is inhibited which dissociates formic acid into hydrogen and carbon dioxide. Albertson (1961) among others gives a pH optimum for the anaerobic digestion between 6.8 and 7.2. At a higher pH (pH > 8) free ammonia can become toxic.

According to Andrews and Graef (1971) the inhibition of methanogenic bacteria at a lower pH is caused by the concentration of undissociated volatile fatty acids. In the next section I will come back to this point.

McCarty and McKinney (1961b) on the other hand state, that more often digester indigestion occurs because of excessive concentrations of cations rather than anions. Kugelman and McCarty (1965) introduce a 50% inhibition index, i.e., the concentration of a cation (in eq/l) at which the reaction rate is decreased to 50% of the rate of a control unit. They get the following results:

cation:	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
50% inhibition index:	.32	.25	.15	.23	.16

Low concentrations of cations other than the one applied reduce the effect. The inhibition by Na^+, K^+ and NH_4^+ can be eliminated almost completely by the antagonistic action of Mg^{2+} and Ca^{2+}. Optimum concentrations for all cations appear to be around .01 eq/l.

The wastewater from industry often contains chemical compounds which are normally not found in the natural anaerobic environment. The suitability of a lagoon or

digester treatment depends, then, on the tolerance of the system towards these compounds. In the most favorable case, the system is not affected. Waste from animal production units can also be toxic, e.g., because of antibiotics or because of copper additives to the feed.

McDermott (1963a and b, 1965) finds that nickel concentrations below 40 ppm have almost no effect. Copper on the other hand inhibits the organisms above 10 ppm. Zinc has an effect intermediate to those of copper and nickel. Pallasch and Triebel (1969) state that concentrations of 1 wt% copper, chromium and nickel based on dry solids will totally inhibit the fermentation and concentrations of respectively .5, .5 and .3 wt% will reduce the gas-production to 50%. Hydrogen sulfide gives a precipitate with heavy metals. Lawrence and McCarty (1965), Masselli (1967) and Goebgen and Brockman (1969) suggest, therefore, the use of H_2S to counteract heavy metal toxicity.

Tenney and Budzin (1972) state that fluoride is toxic at a concentration of about 1000 ppm. Such a concentration of fluoride normally does not occur.

Much is written about the inhibition by chlorinated hydrocarbons. Prins (1972) states that chlorinated analogs of methane inhibit in the micromolar range. According to Bauchop (1967) the methane forming bacteria are quite specifically inhibited by chloroform. Sykes and Kirsch (1972) give a concentration of 16 ppm above which carbon

tetrachloride becomes toxic. Carbon tetrachloride has also a direct influence on the acid production: hydrogen accumulates, production of acetate and propionate is reduced and the production of valerate and caproate increases.

According to McBride and Wolfe (1971) 1 μM DDT inhibits the rate of methane formation by 75%. Albone (1972) and Jensen (1972) report however, that after 7 hours 50% of the DDT is converted into analogs.

Hernandez and Bloodgood (1971) studied the influence of linear alkyl benzene sulfonates (ABS). Concentrations above 1 wt % on a dry matter basis cause inhibition. The ABS can, however, be degraded by the process.

Nitrilotriacetate (NTA), used as a substitute for phosphates in detergents, is degraded by anaerobic fermentation and can serve even as the sole source of carbon (Enfors and Molin, 1973a and b).

Bishop (1972) studied the conversion of mercury to the very toxic methylmercury. Mercuric salts, however, in the presence of H_2S result in the very insoluble HgS.

2.5 Models and simulation of the anaerobic treatment

Many authors have composed models of the digestion process in order to obtain a better understanding of the process dynamics and of the microorganism-substrate interactions under different environmental conditions.

In 1967 Lawrence and McCarty (1969) tested the Monod model for application to steady state anaerobic

digestion and in 1969 they added to this the possibility of varying the solids retention time to account for the recycling of solids. They found that the Monod model gave a good description of the system. An increase in the solids retention time permits higher loading rates. Concurrently, Pfeffer (1968) modeled the influence of the recycling of solids. Pfeffer's model was later extended by Fan (1973) to a two stage digestion with mixed cultures.

In the meanwhile Andrews and Graef (1971) developed their model based on earlier experimental results (Andrews, 1965). The improved model included an inhibition function with undissociated acetic acid as both growth limiting substrate and inhibitor. The model also included the interactions between gas, liquid and biological phases. An important aspect is the above mentioned bicarbonate buffer (Andrews, 1971 and Graef and Andrews, 1973). Later Andrews and Graef added to their model the influence of base addition, organism recycling and gas scrubbing. Base addition counteracts pH and alkalinity decreases and organism recycling conserves the slow growing biomass. Gas scrubbing removes ammonia, hydrogen sulfide and carbon dioxide.

The basic features of their model are applied by Hill and Barth (1974) to explain the results of bench-scale lagoon models. By empirically adjusting certain values (1975) they could approximate the bench-scale lagoon behavior at different temperatures; much deviation between

model and experimental results still remains, however. In 1977, Hill and Nordstedt added ammonia inhibition to this model in order to account for failure at a high pH. Ammonia inhibition is illustrated by Abeliovich and Azov (1976) who observed complete inhibition of algal growth at ammonia concentrations above 3 mole/m^3.

A more experimental approach was taken by Ghosh and Pohland (1974), who measured the performance of a two stage digester with recycling of solids.

McCarty (1971) added to the modeling literature a completely different aspect by taking as basis for his calculations the energy transformation of the different metabolic processes.

The major discrepancy in applying the results of process simulations to practical situation arises from the occurrence of process instabilities, caused by large variations in influent flow rate and influent concentrations. This is obvious from the results of Hill and Barth, who loaded their units once a week. The transient behavior of biological processes was modeled by three investigators at the Rice University in Houston: Schaezler, McHarg and Busch (1971) present a model which takes into account such features as the lag phase, linear growth, and logarithmic growth. Their model uses three sets of relationships, one of which operates according to the growth phase of the organisms. The transition algorithm which selects the

operating relationships is missing from their paper, however. They managed to make their model describe the experimental results quite well.

CHAPTER 3

PURPLE SULFUR BACTERIA

3.1 Introduction

In several instances purple sulfur bacteria have been found in waste treatment lagoons (van Lotringen and Gerrish, 1977). Where found, they are always associated with reduced odor levels. George (1976) estimates that about 40% of all livestock waste lagoons in Missouri are purple as a result of these organisms.

In order to be able to make use of these bacteria for odor control it is important to know which types of bacteria are active, what metabolic characteristics might possibly be important in odor control and which environmental factors influence their proliferation. It is clear that the major environmental factors are the type of waste and the lagoon management program. This will also set the limitations on their use.

As will be described more extensively in one of the following paragraphs, the most frequently identified purple sulfur bacteria in lagoons are Chromatium vinosum, Thiocapsa roseopersicina and Thiopedia rosea. Therefore I will

direct the following discussion mainly to the characteristics of these species.

Comprehensive descriptions of photosynthetic bacteria are given by van Niel (1931) and Kondrat'eva (1965). A more recent review is written by Pfennig (1967).

3.2 Classification

The purple sulfur bacteria can be classified in several different ways as to motility, morphology, photosynthetic pigments, formation of gas vacuoles, distribution of sulfur-globules, ability to form slime capsules, metabolism, formation of poly-β-hydroxy butyrate (PHB) granules, storage carbohydrates or phosphate deposits and to the redox potential at which they occur.

The description of Pfennig in Bergey's Manual (1974) serves as a guide for the classification. The purple sulfur bacteria belong to the order Rhodospirillales and form the family of the Chromatiaceae. Members of this family are defined as "cells which are able to grow with sulfide and sulfur as the sole photosynthetic electron donors. In the presence of sulfide, globules of elemental sulfur are formed inside or outside the cells and further oxidized to sulfate."

The first criterion for subdividing the Chromatiaceae is the site of storage of sulfur globules:

I. Sulfur globules stored inside the cells.

II. Sulfur globules stored outside the cells.

To the second group belongs only one genus of purple sulfur bacteria: Ectothiorhodospira.

The first group is further subdivided into:

A. Cells without gas vacuoles.

B. Cells with gas vacuoles.

Both of these are further subdivided as to motility.

To the motile cells without gas vacuoles belong:

a. Chromatium, cells ovoid to rod-shaped.

b. Thiocystis, cells spherical, typically diplococcus-shaped before cell division.

c. Thiosarcina, cells spherical to ovoid. Grouped as regular sarcina packets.

d. Thiospirillum, cells clearly spiral-shaped.

The non-motile cells without gas vacuoles are represented by the Thiocapsa.

The motile cells with gas vacuoles are the Lamprocystis.

To the non-motile cells with gas vacuoles belong:

a. Thiodictyon, cells rod shaped.

b. Thiopedia, cells spherical to ovoid, characteristically arranged in regular platelets (flat sheets).

c. Amoebobacter, cells spherical.

Above are given the main characteristics of the 10 genera. Another important aspect is the composition of bacteriochlorophyll (BChl) and carotenoids, which helps in recognizing the cells. Belonging to the suborder

Rhodospirillineae the purple sulfur bacteria contain BChl a or b. According to Meyer (1973) Thiocapsa pfennigii is the only species of purple sulfur bacteria and Rhodopseudomonas viridis (a purple non-sulfur bacterium) the only other known bacterial species having BChl b.

The subdivision according to carotenoids places the phototrophic bacteria (including purple sulfur bacteria) into one of five groups:

1. The normal spirilloxanthin series with lycopene, rhodopin and spirilloxanthin as major components.
2. The alternative spirilloxanthin series and keto-carotenoids of the spheroidenone type. The major components are spheroidene, hydroxyspheroidene, spheroidenone, hydroxyspheroidenone and spirilloxanthin.
3. Okenone series with okenone as major component.
4. Rhodopinal series with lycopenal, lycopenol, rhodopin, rhodopinal and rhodopinol as major components.
5. Chlorobactene series with chlorobactene, hydroxychlorobactene, β-isorenieratene and isorenieratene as major components.

Thiocapsa pfennigii is again an exception. It contains Tetrahydrospirilloxanthin as major carotenoid. There are no purple sulfur bacteria known to belong to the groups 2 and 5. Much work on the identification and biosynthesis of the carotenoids of the purple sulfur bacteria has been

done by Jensen (1963), Schmidt et al. (1963), Schmidt (1963), Jensen and Schmidt (1963) and Schmidt et al. (1965). The results of these reports are summarized in an article by Schmidt et al. (1965). (See also Pfennig in Bergey's Manual, 1974.)

To group 1 belong Chromatium vinosum, C. gracile, C. minutissimum and Thiospirillum jenense, Thiocapsa roseopersicina, the Amoebobacter sp., Thiopedia sp. and Ectothiorhodospira sp.

To group 3 belong Chromatium okenii, C. weissei, C. minus and Thiocystis gelatinosa.

To group 4 belong Chromatium warmingii, C. buderi, C. violascens and Thiocystis violacea, the Lamprocystis sp. and Thiodictyon sp.

In general, Schmidt et al. (1965) and Pfennig (writing in Bergey's Manual (1974) agree on the carotenoid classification of the purple sulfur bacteria.

In contradiction to the above, Pfennig (1974) describes Thiopedia rosea as belonging to the okenone series, based on a completely different group of pigments. In Schmidt et al. (1965), the carotenoid compositions were reported as listed in Table 3.1. Okenone doesn't even appear as a minor constituent of Thiopedia rosea. Although Chromatium vinosum appears to have a different carotenoid composition, the absorption maxima of the carotenoids are very close to each other. The use of spectra for

Table 3.1--Carotenoid composition (as % of total carotenoids) of three purple sulfur bacteria, the absorption maxima of these carotenoids and the extinction coefficients of the middle main maxima (Schmidt *et al.*, 1965).

	Thiocapsa roseopersicina	*Thiopedia rosea*	*Chromatium vinosum*	Abs. maxima in petroleum ether				$E^{1\%}_{1cm}$
Lycopene	0 - 1	0 - 1	6	(345,363)	445	472	504	3400
Rhodopin	0 - 4	0 - 3	62	(345,363)	445	472	503	3000
3,4 Dehydro-rhodopin	0	0	10	(354,376)	454	483	517	2700
Anhydro-rhodovibrin	0 - 3	0 - 1	5	(354,375)	454	483	516	2700
Rhodovibrin	0 - 4	0 - 1	0	(354,375)	454	483	517	2700
Monodemethylated spirilloxanthin	0 - 2	0 - 1	2	(365,385)	465	493	527	2400
Spirilloxanthin	90 - 100	93 - 100	14	(365,385)	465	493	527	2400
Okenone	-	-	-	(360,375)	460	485	516	3000

( ) is the position of the cis-peak

identification is further complicated by the variability in the quantitative composition of carotenoids in a cell, which not only changes the intensity of absorption at different wavelengths, but also causes a shift of the absorption peaks. This can be caused by a difference in substrate, as is clearly demonstrated by Clayton (1963).

All forms of purple sulfur bacteria are able to develop as single cells. Under unfavorable conditions and in many natural environments the cells can occur in more or less regular aggregates surrounded by slime. Thiocapsa roseopersicina is always surrounded by a slime capsule. In contrast to most other purple sulfur bacteria Thiopedia rosea is normally arranged in regular platelets.

Only two species of purple sulfur bacteria, Thiocapsa roseopersicina and Amoebobacter roseus are shown to be able to grow under aerobic conditions in the dark (Kondrat'eva et al., 1975).

Both Thiocaposa roseopersicina and Chromatium vinosum can store polysaccharides, poly-β-hydroxybutyrate (PHB) and polyphosphates. Thiopedia rosea can store PHB; other storage products have not been shown.

3.3 Metabolism

The purple sulfur bacteria display a wide range of metabolic processes. As source of energy they can use light, for which they can synthesize the necessary pigments, but during the dark they can use storage products.

Thiocapsa roseopersicina has even been shown to be capable of chemolithoautotrophy and chemolithoheterotrophy (Kondrat'eva, et al., 1975, Krasil'nikov et al., 1975). As a source of carbon the purple sulfur bacteria can use carbon dioxide, alcohols, carbohydrates and a variety of simple organic acids. As source of reducing power they can use a whole range of reduced sulfur compounds and many strains are able to use molecular hydrogen. As a source of nitrogen several species can fix molecular nitrogen. Moreover, they can use ammonium salts and urea and a few use glutamate and aspartate as nitrogen sources.

Purple sulfur bacteria, like the other photosynthetic bacteria, don't evolve oxygen during their photosynthetic activities. This led to a new concept of photosynthesis (van Niel, 1931). The fixation of carbon dioxide was studied by Eymers (1938) and later by Fuller et al. (1961) who identified several enzymes of the Calvin cycle and the citric acid cycle in Chromatium extracts. Fuller found that the glyoxylate cycle is modified in that the malic dehydrogenase reaction is missing. Trüper (1964) found that acetate is used preferentially to carbon dioxide.

According to Gest (1972) the photosynthetic bacteria produce adenosine triphosphate (ATP) from radiant energy via a cyclic electron flow. Reduced nicotinamide dinucleotides are formed via a reversed electron transport chain, using organic compounds as source of reducing power.

The first extensive study of the sulfur metabolism of the purple sulfur bacteria was performed and published by Trüper and Schlegel (1964), Trüper (1964), Trüper and Pfennig (1966) and Thiele (1968 a and b). They found a maximum storage of sulfur of 30.5% and a minimum content of .7% of the dry weight. In agreement with their results, van Gemerden (1968a) reported that the oxidation of internally stored sulfur occurs simultaneously with the oxidation of sulfide. As a result, 58% of the sulfide is oxidized to sulfate at the moment of sulfide depletion. Using a maximum storage of elemental sulfur of 30% of the cells dry weight he was able to quantitatively associate this oxidation with the production of bacterial cell material, which appears to have the approximate molecular formula $C_5 H_8O_2N$ (van Gemerden, 1968b). With ammonia as the source of nitrogen, van Gemerden gives the following overall reactions:

$$10\ CO_2 + 21\ H_2S + 2\ NH_3 \rightarrow 2\ (C_5H_8O_2N) + 21S + 16\ H_2O \qquad (3.1)$$

$$30\ CO_2 + 21\ S + 6NH_3 + 36\ H_2O \rightarrow 6\ (C_5H_8O_2N) + 21\ H_2SO_4 \qquad (3.2)$$

$$40\ CO_2 + 21\ H_2S + 8\ NH_3 + 20H_2O \rightarrow 8(C_5H_8O_2N) + 21\ H_2SO_4 \qquad (3.3)$$

These reactions are valid, however, only if carbon dioxide is used as source of carbon. In the presence of acetate the consumption of reduced sulfur compounds will be:

$$5\ C_2H_4O_2 + H_2S + 2NH_3 \rightarrow 2\ (C_5H_8O_2N) + S + 6\ H_2O \quad (3.4)$$

$$15\ C_2H_4O_2 + S + 6\ NH_3 \rightarrow 6\ (C_5H_8O_2N) + H_2SO_4 + 14\ H_2O \quad (3.5)$$

$$20\ C_2H_4O_2 + H_2S + 8NH_3 \rightarrow 8\ (C_5H_8O_2N) + H_2SO_4 + 20\ H_2O \quad (3.6)$$

The above reactions lead me to estimate that for the same increase in cellular material, the carbon dioxide reduction would use 21 times the amount of sulfide as is used for acetate incorporation.

For the production of storage carbohydrates, the overall equations with the use of carbon dioxide are (representing the carbohydrates by $(C_6H_{10}O_5)_n$):

$$12n\ CO_2 + 28\ nH_2S \rightarrow 2\ (C_6H_{10}O_5)n + 14n\ H_2O + 28nS \quad (3.7)$$

$$42\ n\ CO_2 + 28\ nS + 63\ nH_2O \rightarrow 7\ (C_6H_{10}O_5)n + 28\ n\ H_2\ SO_4 \quad (3.8)$$

$$54\ n\ CO_2 + 28\ n\ H_2S + 49\ n\ H_2O \rightarrow 9\ (C_6H_{10}O_5)n + 28\ n\ H_2\ SO_4 \quad (3.9)$$

and using acetate:

$$3\ n\ C_2H_4O_2 \rightarrow (C_6H_{10}O_5)_n + n\ H_2O \qquad (3.10)$$

So no H_2S is used in the formation of storage carbohydrates from acetate. According to Hendley (1955) and van Gemerden (1968c) the storage carbohydrates are converted into PHB in the dark. During this conversion, internally stored sulfur is converted to sulfide:

$$(C_6H_{10}O_5)_n + n\ H_2O + 3nS \rightarrow (C_4H_6O_2)_n + 2nCO2 + 3n\ H_2S \qquad (3.11)$$

Not only CO_2 but also acetic acid is formed. In the light the reverse overall process will take place. Consequently a lagoon with purple sulfur bacteria will theoretically produce more hydrogen sulfide, and thus theoretically more odor, during the night. During the day, the hydrogen sulfide, and thus odor, is diminished.

If colloidal sulfur is added to a culture, it can also be used by the purple sulfur bacteria. The rate of sulfur metabolism is determined by the available sulfur surface (intra- and extracellular sulfur combined) (van Gemerden and Jannasch, 1971), rather than by the sulfur concentration.

3.4 Interactions with the environment

Although none of the purple sulfur bacteria (except Thiocapsa roseopersicina and Amoebobacter roseus)

have been shown able to grow in the presence of oxygen, Hurlbert (1967) found, that oxygen is not toxic to Chromatium strain D. Oxygen completely prevented the synthesis of BChl, but the cells were still able to oxidize thiosulfate and internally stored sulfur. This sulfur could not be oxidized to sulfate. If acetate is present it is mainly converted into PHB. As follows from the reactions given above, this conversion would result in a net production of reducing power. Hurlbert observed also, that in the presence of oxygen cells are unable to divide. Whether the cells were actually using oxygen was not determined.

Holm and Vennes (1970) report an optimum concentration of sulfide of 1.4 to 1.9 mmol/l for the growth of Thiocapsa roseopersicina and Chromatium vinosum (at pH between 7.5 and 8.2). Van Gemerden (1974) found an optimum concentration (at pH = 7.0) of about 0.08 mmol/l for Chromatium weissei and 0.11 mmol/l for Chromatium vinosum with saturation constants of 0.010 and 0.007 and inhibition constants of 0.7 and 2.5 mmol/l, respectively. Since undissociated hydrogen sulfide is the substrate and inhibiting agent (van Gemerden and Jannasch, 1971) the optimum concentration will be lower at a lower pH. Pfennig (1967) gives the following order for tolerance to high concentrations of sulfide: Thiocapsa > Amoebobacter > Thiodictyon > Thiopedia. The above sequence is in agreement with the

observations of McFarlane and Melcer (1977) for lagoon bacteria arranged in order of decreasing lagoon load (and presumably sulfide load):

Chromatium → Thiocapsa → Thiopedia

For the optimum pH Holm and Vennes report 7.5 to 8.2. Meredith and Pohland (1970) report an optimum pH of 7.5 for a Chromatium sp. from a lagoon. As suggested above, the optimum pH and the optimum sulfide concentration are not independent. Generally the values reported for the optimum pH are between 7 and 8.5 (Kondrat'eva, 1965).

The purple sulfur bacteria are found in nature at temperatures ranging from 8 to 80°C. Most species, however, have an optimum between 18 and 30°C. For a lagoon system this means that on a couple of warm and sunny days, when the surface temperature can get as high as 35°C, the activity of the purple sulfur bacteria will be reduced, while the activity of the sulfide producing bacteria remains very high. Consequently a lagoon might be expected to produce more odor under these conditions.

Obviously, the light intensity has a strong influence on the purple sulfur bacteria. Light is often the growth limiting factor under natural conditions, because of a requirement for anaerobic conditions (i.e., the surface water which would get the most light may become aerobic). Kondrat'eva (1965) reports a light saturation at intensities from 3 to 40 klx. Trüper (1964) gives a light saturation

of 2 klx for Chromatium okenii and C. vinosum and van Gemerden (1968a) 1 klx for a Chromatium.

Takahashi et al. (1970, 1972) studied the influence of the light intensity on Chromatium strain D. They found an optimum intensity of 2 klx and a compensation point between 0.05 and 0.01 klx. At the lower light intensities the bacteria show an increase in BChl content and an increase in efficiency of this BChl. At 1 and 20 klx they found growth rates of 0.087 and 0.179 hr^{-1} respectively.

The significance of the above-mentioned light intensities is only relative, since no description is given of the quality of the light. As described by Kondrat'eva (1965) the bacteria are only active at specific ranges of the spectrum.

From the metabolic features it follows that the purple sulfur bacteria interact with many other species of bacteria. From the work of van Gemerden (1968c) it is clear, that different types of purple sulfur bacteria can exist at the same time, competing for the same substrates. By closing the sulfur cycle, purple sulfur bacteria and desulfurizing bacteria will stimulate each other. This effect is studied by Matheron and Baulaigue (1976) who tested it for the green sulfur bacteria.

Since the purple sulfur bacteria use acetate preferentially to carbon dioxide they will enhance the removal of volatile fatty acids from the lagoon environment.

Though they don't consume oxygen for this process, the purple sulfur bacteria will actually lower the biochemical oxygen demand levels in the liquid phase, as was found by Holm and Vennes (1970) and McFarlane and Melcer (1977).

In their observations on lagoons Holm and Vennes found that the viable counts of the purple sulfur bacteria was usually about a factor of ten lower than the total counts. The maximum number of purple sulfur bacteria was reached after the desulfurizing bacteria reached a maximum, but before the other heterotrophic and the methanogenic bacteria reach their respective maxima.

McFarlane and Melcer (1977) list as suitable conditions for the bacteria to flourish:

1. underloaded anaerobic lagoons
2. overloaded facultative lagoons
3. selective effluents

The first indication of the presence of the purple sulfur bacteria was the change in pH. In the succession of dominant organisms they place the purple sulfur bacteria between the primary anaerobes and the algae. By lowering the sulfide concentration the purple sulfur bacteria make the growth of algae possible. This would explain the frequent observation that a lagoon will turn from purple to green during the summer.

CHAPTER 4

SWINE WASTE MANAGEMENT AT MSU

This chapter is a description of the swine waste management system on which most of the work in this thesis has been done. The system consists of a slatted floor growing-finishing building from which the waste is transported by flushing to two lagoons of equal volume, further identified as the east lagoon and the west lagoon.

The growing-finishing building houses an average of 250 hogs with an average weight of 60 kg. For the first 8 weeks these hogs receive the standard grower ration MSU 16 (see Table 4.1) as their weight increases from approximately 18 to 50 kg. For the next 8 weeks, the animals receive the standard finisher ration MSU 13 (see Table 4.1) as their weight goes from approximately 50 to 90 kg (see Miller, 1975).

Nutrient and amino acid composition of the dried swine feces were reported by Orr (1971, 1973) (see Table 4.2 and 4.3).

A mineral analysis of the swine manure has been made by Ngoddy (1971). His results are reproduced in the

Table 4.1--Swine Feed Mix.

	Grower MSU-16 wt %	Finisher MSU-13 wt %
Ground shelled corn	78.25	85.00
Soy bean meal (49% protein)	18.00	11.50
Calcium carbonate	.75	.75
Defluor phosphate	1.25	1.25
MSU-VTM premix	.50	.50
Salt	.50	.50
Sel. E. premix	.50	.50
Aureomycin SP-250	.25	--
	100%	100%

Table 4.2--Nutrient Composition of Dried Swine Feces (DSF).

Nutrient	DSF[a]	
	1	2
Protein-nitrogen, %	3.48	3.44
Non-protein-nitrogen, %	--	--
Crude protein, %	21.8	21.5
Calcium, %	2.8	2.2
Phosphorus, %	1.8	1.5
Sulfur, %	1.0	1.1
Potassium, %	1.2	0.9
Sodium, %	0.3	0.2
Chlorine, %	--	--
Magnesium, %	0.1	0.1
Manganese, ppm	213	141
Iron, ppm	513	397
Zinc, ppm	432	586
Copper, ppm	117	98

[a]Analyses of dried swine feces by P. K. Ku.

Table 4.3--Amino Acid Composition of Dried Swine Feces (DSF).

Amino Acid	DSF[a]
	%
Lysine	1.11
Histidine	0.40
Arginine	0.67
Aspartic acid	1.37
Threonine	0.80
Serine	0.58
Glutamic acid	3.37
Proline	0.91
Glycine	1.51
Alanine	1.14
Cystine	0.12
Valine	1.04
Methionine	0.58
Isoleucine	1.03
Leucine	1.57
Tyrosine	0.65
Phenylalanine	0.87

[a]Analysis by W. G. Bergen.

Tables 4.4, 4.5, and 4.6. The ratio of urine to feces as is given by Ngoddy is quite high in comparison with the values of Pratt (1975).

The swine manure in transported to the two lagoons twice daily (at about 8:00 A.M. and 4:00 P.M.) by a flushing system. For this flushing operation, use is made of three tipping tanks and a sudden release tank, each having a volume of about 0.7 m^3. A Y-valve is used to distribute the incoming manure to the two lagoons. Inlet conduits are corrugated plastic tubing, 0.15 in. diameter. A sketch of the lagoons is presented in Figure 4.1. Lagoon liquid is recycled to the barn for the flushing operation. Twice a year in April and November the lagoons are pumped out with a tractor-driver centrifugal pump. The lagoon is pumped via an irrigation line to the nearby cornfields.

The lagoon operation at the MSU Swine Research Center was started in 1972. At that time, the lagoons were designed using the figure of 0.062 m^3/kg of animal weight and each lagoon was to receive wastes from 140 hogs with an average weight of 57 kg. Added to this was a 200 m^3 volume to allow for the treatment of effluent from the oxidation ditches of two nurseries, each containing an average of 120-14 kg hogs. In summary, the design of each lagoon consisted of the following components (T. L. Loudon, 1977):

TABLE 4.4 SWINE INPUT-OUTPUT SUMMARY

Trial Number	Period (Week)	Average weight (lbs)	Rate of gain (lbs/day)	Feed Rate (lbs/day)	Feed: Water Ratio	Feed Ration (% Protein)	Efficiency ($\frac{\text{lb feed}}{\text{lb gain}}$)	Elimination Rate (lbs/day) (Feces + Urine)	Elimination Rate $\frac{\text{lbs/day}}{\text{1000 lbs live weight}}$	Parts urine to one part feces	Elimination Rate as Percent of Feed-Water intake.
(1)	1	55		2.2				2.65	48	2.5	
initial wt	2	60		2.2				2.5	42	3.0	
52 lbs	3	67		3.3				3.0	45	2.3	
final wt	4	76		3.3				5.3	69	3.0	
110 lbs	5	87		4.4				5.6	64	3.0	
	6	100						4.2	44	2.1	
AVERAGE			1.3		1:2	16	2.6		52	2.6	45
(2)	1	102		3.3				4.3	42	2.5	
initial wt	2	110		3.3				5.7	51.5	3.9	
97 lbs	3	118		3.3				4.5	38	3.65	
final wt	4	124		4.4				5.4	43	3.7	
168 lbs	5	136		4.4				6.0	44	3.55	
	6	156		5.3				6.5	41.5	3.7	
AVERAGE			1.6		1:2	16	3.9		43	3.4	48
(3)	1	142						5.6	39.5	2.9	
initial wt.	2	150						6.3	41	2.4	
138 lbs	3	158						4.8	30.5	1.8	
final wt	4	164						6.0	36	2.6	
179 lbs	5	173						6.3	36.5	3.0	
	6	178						6.1	34	2.6	
AVERAGE			1.05	4.4	1:2	13	4.3		36	2.5	46
(4)											
initial wt	1	168						6.0	36	3.5	
164 lbs	2	175						5.9	33	4.5	
final wt	3	178						5.9	33	4.0	
180 lbs											
AVERAGE			0.9	4.4	1:2	13	5.5		34	4.0	45
(5)											
initial wt	1	57		2.5				4.6	80	5.0	
53 lbs	2	64		2.5				4.6	71	4.75	
final wt	3	73		2.5				5.3	69	5.25	
90 lbs	4	81		5.2				5.8	72	4.9	
AVERAGE			1.1		1:3	16	2.7		73	4.7	44
AVERAGE OF ALL TRIALS									50	3.4	45
		40-80							70		
Average values by weight range		80-120							50		
		120-160							42		
		160-200							34		

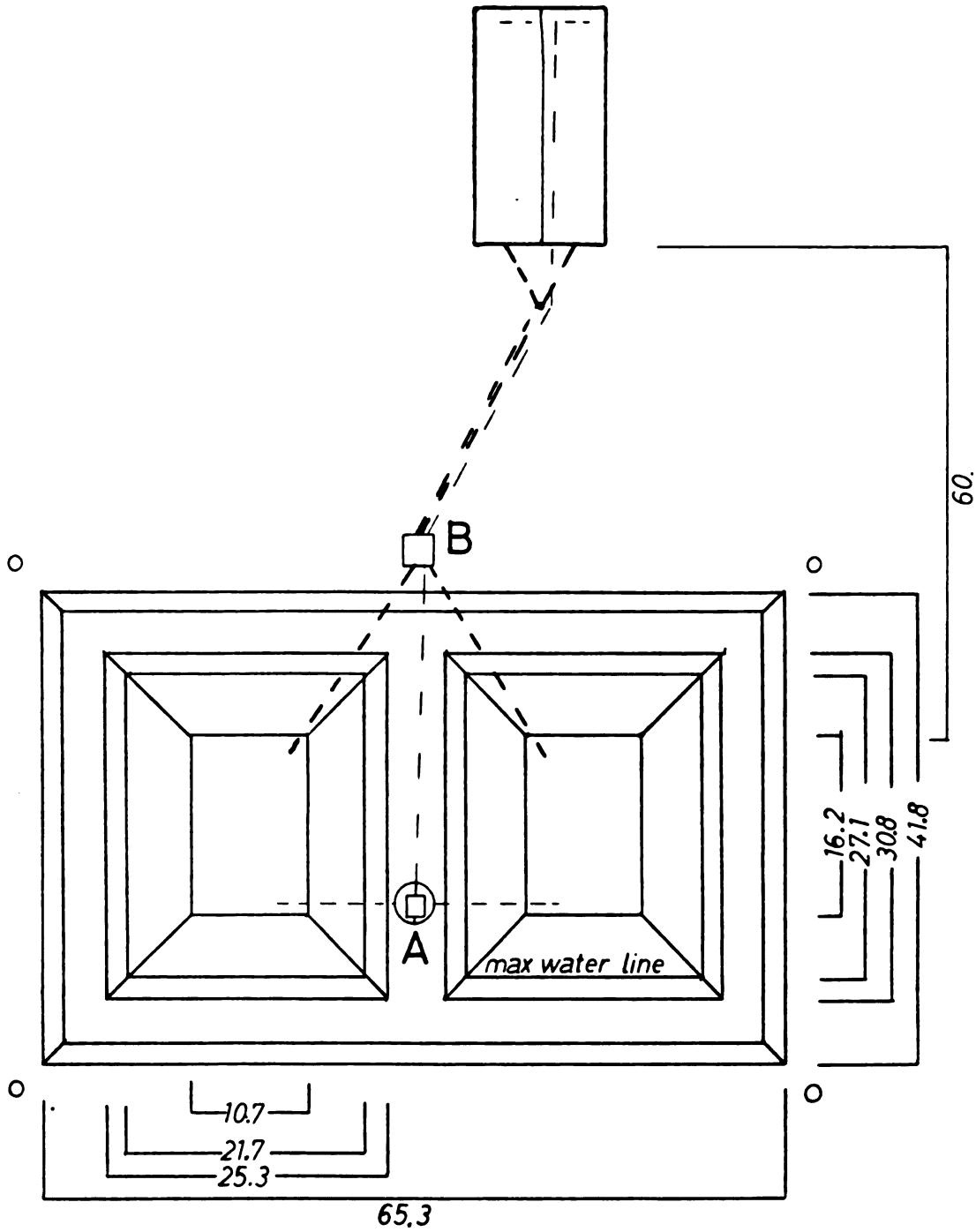
TABLE 4.5 POLLUTIONAL CHARACTERISTICS OF SWINE WASTE

Weekly Composites	COD (mg/1)	BOD_5 (mg/1)	TOTAL N (mg/1)	NH_3 - N (mg/1)	% NH_3 - N OF TOTAL N	% TS*	% VS
1	86,000	32,000	8540	4611	54	8.7	80
2	76,000	30,000	7000	3780	54	8.0	84
3	61,000	27,000	5600	2856	51	6.3	82
4	68,000	29,000	5950	2915	49	5.6	83
5	90,000	47,000	9170	3668	40	9.56	83.3
6	80,000	43,000	6160	3449	56	8.00	83
7	74,000	41,000	6500	1950	30	8.3	82
8	69,000	29,000	6000	3240	54	8.5	83
9	81,000	44,000	8000	4240	53	10.5	84
10	70,000	30,000	5900	3186	54	8.2	81
Average	80,000	35,000	6880	3390	49	8.16	83

* Average less than normal because of greater than normal water intake.

TABLE 4.6 MINERAL ANALYSIS -- (FEED, FECES, URINE) SWINE

	Feed 13% Moisture	Feces 65% Moisture (Trial 1)	Feces 65% Moisture (Trial 2)	Urine 96% Moisture (Trial 1)	Urine 96% Moisture (Trial 2)
Ca (ppm)	7,980	27,780	22,520	168	511
Mg (ppm)	1,690	9,300	6,740	68	109
Zn (ppm)	106	432	585	3.1	1.5
Cu (ppm)	19	117	98	.16	.17
Fe (ppm)	140	513	398	1.1	1.2
Mn (ppm)	34.7	213	140	.32	.31
Na (ppm)	2,170	3,060	2,210	1,510	1,090
K (ppm)	5,930	11,730	8,770	2,300	2,330
P (ppm)	6,450	18,110	15,360	224	133
S (ppm)	3,960	1,010	1,070	980	1,230
N (ppm)	24,700	34,800	34,400	5,190	4,770
Expressed as Grams/Gram Solids					
Ca	.009172	.078474	.063615	.0041379	.01258
Mg	.0019425	.026271	.019039	.001674	.002684
Zn	.001218	.001220	.0016525	.0000763	.0000369
Cu	.00002183	.0003305	.000276	.0000039	.0000041
Fe	.0001609	.001449	.001124	.000027	.0000295
Mn	.0000398	.0006016	.000395	.000008	.0000076
Na	.0031149	.008644	.0062429	.037192	.026847
K	.006816	.033135	.024774	.056650	.057389
P	.0074137	.0511582	.043389	.005517	.003275
S	.0045517	.002853	.0030225	.024137	.03029
N	.0283908	.098305	.097175	.12783	.11748



A = Wet/dry well for pumps to recycle. Water back to building.

B = Junction box.

Scale 1:600

Figure 4.1 MSU Swine Farm Lagoons

growing - finishing building design volume	500 m^3
nursery design volume	200 m^3
three years' sludge accumulation	200 m^3
six months' liquid accumulation	88 m^3
Total volume of each lagoon	988 m^3

Each lagoon was designed with a 10.7 m by 16.2 m rectangular flat bottom and side slopes of two (horizontal)-to-one (vertical), resulting in a water surface of 21.6 m by 27.1 m at a maximum depth of 2.7 m. Added to this depth was 0.9 m freeboard. Each lagoon has two inlets, one 1 m above the bottom of the lagoon and one above the water surface. At the other side of the lagoons a line connects the lagoons with a 3 m diameter dry well (actually a below-grade concrete stave silo) from which the liquid can be pumped back to the flushing tanks. Transfer of liquid between the two identical lagoons is also possible.

The first years, both lagoons received the same waste load. In the spring of 1974, the west lagoon was inoculated with about 10 liters of a laboratory-grown culture of purple sulfur bacteria. The lab culture was started from a sample of lagoon water from the Iowa State University Swine Waste Lagoon which had been purple for several years. The inoculation presumably resulted in a bloom of purple sulfur bacteria in September of the same year. No further inoculations were attempted. In 1975, a bloom of purple sulfur bacteria occurred in the east lagoon in August. In September 1975, I got involved in the

lagoon operation. I decided to change the distribution of the waste load from an equal load for each lagoon to a 1:3 ratio, i.e., into the west lagoon went three times as much waste as into the east lagoon. The surplus volume of the west lagoon was allowed to flow to the east lagoon via the silo. This practice resulted in a bloom of purple sulfur bacteria in the east lagoon at the end of June 1976. Reversing the loading rate at this point gave a bloom of purple sulfur bacteria in the west lagoon in July 1976 with a concomitant decrease in population in the east lagoon.

A normal procedure until then was to pump the lagoons from the west lagoon to the field. In order to preserve the population of purple sulfur bacteria, I decided that pumping should now be done from the east lagoon. This strategy proved to be very successful. In May 1977, the blooming of purple sulfur bacteria in the west lagoon was stronger than ever before. Reversing the loading rate resulted in a strong blooming of purple sulfur bacteria in the east lagoon in June, while no change in population density occurred in the west lagoon. It thus appears that once a population of purple sulfur bacteria has established itself in large enough numbers this population can cope with the heavier waste load caused by reversing the loading rate.

Each incidence of blooming by purple sulfur bacteria in our lagoons resulted in a dramatic reduction of odors. As a first search for the agents which could be involved in this effect, several properties of the lagoon

liquid were analyzed in 1974. The results of these analyses are presented in Table 4.7. Notice the differences in sulfide and iron concentrations.

Table 4.7--Lagoon Analysis in 1974. (Values in mg/l). (Gerrish, 1975).

Parameter	East Lagoon*	West Lagoon*
COD	1170	1260
TS	2020	2280
VS	860	1080
S^{2-}	13	3.4
NH_4+	347	352
PO_4^{3-}	21.8	31.5
Kjeldal-N	108	111
Fe	2.71	0.99
Zn	0.30	0.12
Cd	<0.01	<0.01
Pb	0.07	0.07
Ca	140	132

* The east lagoon was at this time black and malodorous; the west lagoon was purple and much less odorous.

Figure 4.2 The color of the west lagoon in the Summer of 1977. The card being held is a photographer's "grey standard."

PART II

THEORY AND MODEL DEVELOPMENT

CHAPTER 5

HEAT BALANCE

5.1 Introduction

In the North Central United States, a lagoon will typically be covered by ice during the winter and throughout the lagoon the temperatures will be low. Consequently biological conversions will be very slow. During the spring the lagoon will be warmed up and conversion rates will rise. Since liquefaction and putrefaction are the first processes to take place, a lagoon can produce considerable odor during this warm-up period. This is comparable to the start up of an anaerobic digester (Filbert, 1967). It is desirable to keep this period as short as possible.

Since the temperature plays an important role in the microbial activity with a special consideration of the activity of sulfide producing and purple sulfur bacteria an analysis of the heat balance of a lagoon is likely to be helpful in developing odor control strategies.

Almost all heat exchange between a lagoon and its environment will take place via the surface. For a certain lagoon volume the surface area will be determined by the

depth, the angle of the sideslopes and the shape. As a result, there is a direct relation between the heat balance and the lagoon design.

During the spring a lagoon will often be covered by a layer of scum. One needs to know whether the scum layer is beneficial to the production of purple sulfur bacteria (and the associated decrease in odor production). The scum layer may affect heat exchange, light penetration and mass transfer. The mechanism of scum formation would provide valuable insight if the scum layer were found to have either a positive or negative effect on lagoon performance.

For the following heat balance I will assume that:

1. The lagoon contains pure water.
2. The lagoon is located in an open area.
3. Neither heat transfer nor heat storage takes place at the bottom.
4. No water enters or leaves the lagoon via advective flow or seepage through the bottom.

The exchange of heat with the environment will then consist of the following contributions:

a. radiation (Q_λ)
b. evaporation or condensation (Q_ε)
c. rainfall (Q_ρ)
d. sensible heat (Q_σ)

The change in stored heat (Q_θ) becomes:

$$Q_\theta = Q_\lambda + Q_\varepsilon + Q_\rho + Q_\sigma \qquad (5.1)$$

Precipitation can change the water temperature by adding a volume of water with a different temperature. Not much is known about the temperature of rain, because it is a difficult quantity to measure and it can change during the course of a rainfall. Most of the time, precipitation will have a lower temperature than the water because of evaporation as the drops fall. A normal rainfall has but minor and brief influence on the temperature of a body of water (Hutchinson, 1957). In the following discussion the influence of rainfall is therefore neglected.

5.2 Transfer of heat by radiation

Radiation is considered to be the most important factor in the heating of a body of water. The radiation surplus (Q_λ) is composed of several parameters:

a. direct solar radiation arriving at the surface (Q_S)
b. indirect or scattered solar radiation from the sky and clouds (Q_H)
c. solar radiation reflected from the surface (Q_R)
d. long wave radiation from the atmosphere (Q_A)
e. long wave radiation emitted from the body of water (Q_W)

Other sources of radiation like the moon and the stars are negligible. The radiation surplus becomes then:

$$Q_\lambda = Q_S + Q_H - Q_R + Q_A - Q_W \qquad (5.2)$$

During the night this reduces to:

$$Q_{\lambda n} = Q_A - Q_W \qquad (5.3)$$

The intensity of the direct solar radiation which arrives at the water surface, depends on factors like the solar height, the altitude of the lagoon (both of which determine the pathlength of the radiation through the atmosphere), the moisture content of the atmosphere and the presence of clouds. Since the surface of a lagoon is horizontal the angle of incoming radiation is determined by the solar height, in turn a function of the time of the day, the time of the year and the latitude.

Hutchinson (1957) gives an estimate of the total direct radiation at different latitudes on the 15th day of each month. At a latitude of 45°N this is (in W/m^2): January-177, February-285, March-427, April-575, May-678, June-728, July-703, August-625, September-483, October-331, November-209, December-151. (See Figure 5.1)

The influence which cloud cover and moisture content of the atmosphere have on incoming radiation depends on local conditions. A heavy cloud can reflect and absorb all direct solar radiation. Direct measurements of these factors are required.

The indirect or scattered solar radiation varies from about 10% to 40% of the total direct radiation. Hutchinson gives 20% as an average value.

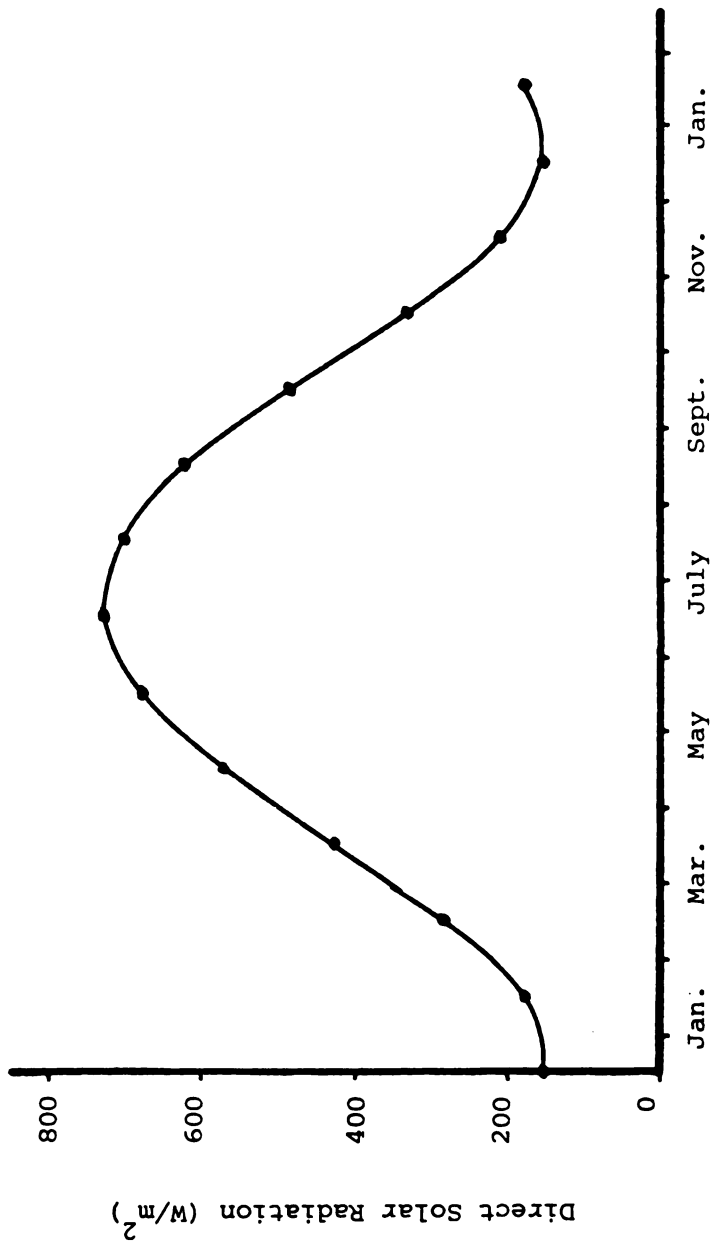


Figure 5.1 Direct Solar Radiation as a Function of the Time of the Year at 45°N Latitude.

The reflected solar radiation is directly proportional to the incident radiation:

$$Q_R = R' * Q_S \tag{5.4}$$

in which R' is the reflectivity for direct solar radiation. The reflectivity depends on the solar height (which dependence is expressed in Fresnel's law as a function of the angle of incidence, Ψi) and the angle of refraction (Ψr). For an undisturbed water surface:

$$R' = \tfrac{1}{2} \left\{ \frac{\sin^2 (\Psi i - \Psi r)}{\sin^2 (\Psi i + \Psi r)} + \frac{\tan^2 (\Psi i - \Psi r)}{\tan^2 (\Psi i + \Psi r)} \right\} \tag{5.5}$$

Anderson (1952) gives an empirical formula for clear days:

$$R' = 1.18 \ \Psi s^{-0.77} \tag{5.6}$$

in which Ψs is the solar angle. This empirical formula accounts for reflection of sun and sky radiation together. The reflection of radiation from the sky is estimated to be 7% for the total reflectivity. Johnsson (cited in Hutchinson, 1957) gives a value of 6% in summer and 10% in winter.

The long wave radiation from the atmosphere will depend on the temperature, and the quantity and type of cloud cover. Bolz and Fritz (1950) give the following equation:

$$Q_A = \sigma' * T_a^4 \ (1 + k_c * B^{2.5}) * (.820 - .250 * 10^{-.126 * Pw}) \tag{5.7}$$

in which Q_A is in cal/cm^2 min and

σ' = Stefan-Boltzmann constant

T_a = air temperature

B = fraction of the sky covered by clouds

P_w = the vapor pressure of water

k_c = factor depending on cloud type:

Cloud type	k_c
cirrus	.04
cirro-stratus	.08
altocirrus	.17
altostratus	.20
cumulus	.20
stratus	.24

The long wave radiation emitted from the water surface has a spectrum somewhat different from black body radiation. Anderson gives an emissivity of 97%:

$$Q_W = .97\ \sigma' * t_w^4 \qquad (5.8)$$

in which t_w is the water temperature. Johnsson assumes for both air and water blackbody radiation:

$$Q_W - Q_A = 8.26 * 10^{-11}\ (t_w^4 - t_a^4) \qquad (5.9)$$

in which Q is in cal/cm^2 min. For the usual environmental temperatures he simplifies this formula further to:

$$Q_W - Q_A = 11\ (t_w - t_a)\ \text{cal/cm}^2\text{.day} \qquad (5.10)$$

Using this equation we obtain for the radiation surplus during the night:

$$Q_{\lambda n} = 11\ (t_a - t_w)\ \text{cal/cm}^2\text{.day} \qquad (5.11)$$

5.3 Transfer of heat by evaporation or condensation

Since the temperature of the air is most often higher than the dew point temperature, the heat lost by evaporation plays a much more important role than the heat gained by condensation. Consequently Q_ε is generally negative. The main driving force for evaporation is the vapor pressure difference between the atmosphere and the water surface. Several empirical equations have been proposed for the relation between evaporation rate and more easily measured parameters. On the basis of the type of equation there are three different groups:

1. Equations based on the vapor pressure deficit and the wind velocity.
2. Equations based on the vapor pressure gradient and the heat or momentum flux.
3. Equations based on the vapor pressure fluctuations according to the Eddy correlation method.

The first type of equation has the following general form:

$$Q_\varepsilon = Le * \rho_w\ (a + b * u_z^n)\ x^{-m}\ (p_w - p_w') \qquad (5.12)$$

in which

Le = latent heat of evaporation at t_w (cal/g)

t_w = surface water temperature (K)

p'_w = saturated vapor pressure at t_w (m bar)

u_z = wind velocity at a height z above the water (cm/s)

x = size parameter of the surface (cm)

ρ_w = density of water at t_w (g/cm^3)

a, b, m, n = parameters, which vary within a small range, depending on the roughness of the surface, the wind speed, the stability of the atmosphere and (except for n) the size of the water surface.

The oldest form of this equation is obtained by substituting m = 0 and n = 1. Brutsaert and Yu (1968) brought the result of ten articles together in an equation for which a = 0. Using the Bowen ratio Dingman et al. (1968) arrived at an equation with m = 0 and n = 1. Yen and Landvatter (1970) reported an equation with m = 0. The different parameters from these articles are represented in Table 5.1.

Since most of these equations are derived from the researchers' specific equipment, they have a limited range of application.

Obviously, the empirical equation (5.12) is dimensionally inhomogeneous. In principle it is based on the general equation for mass transfer:

$$N_{H_2O} = k_{H_2O} * A * ([H_2O]_a - [H_2O]'_a) \qquad (5.13)$$

Table 5.1--Parameter Values for the Equation Based on Vapor Pressure Deficit and Wind Velocity.

Author		m	n	$a*10^3$	$b*10^4$
Carpenter	(1891)	0	1	2.17	.233
Rohwer	(1931)	0	1	2.44	.148
Johnsson	(1946)	0	0.8	0	2.40
Kohler	(1952)	0	1	1.18	.132
Brutsaert	(1968)	0	1	1.80	25.3
Brutsaert	(1968)	.124	.60	0	3.80
Dingman	(1968)	0	1	1.08	25.3
Yen	(1970)	0	1.52	5.17	33.2

in which

N_{H_2O} = mass transfer rate of water (mole/s)

k_{H_2O} = mass transfer coefficient for water (m/s)

A = surface area (m^2)

$[H_2O]_a$ = concentration of water vapor in the air ($mole/m^3$)

$[H_2O]'_a$ = saturated water vapor concentration in the air at T_w ($mole/m^3$)

The mass transfer rate is related to the heat transfer rate via the latent heat of evaporation (Le); the concentration of water vapor is related to the vapor pressure via the ideal gas law. The k_{H_2O} can be expressed as a function of

the wind velocity and a size parameter with the dimensionless Sherwood number (Sh):

$$Sh = \frac{k_{H_2O} * x}{D_{H_2O}} = a + b * Re^c * Sc^d \qquad (5.14)$$

D_{H_2O} = diffusivity of water in air (m^2/s)

x = size parameter of the surface (m)

Re = Reynolds number (dimensionless)

Sc = Schmidt number (dimensionless)

a, b, c, d = dimensionless parameters

The Reynolds and Schmidt numbers can be expressed as:

$$Re = \frac{\rho_a * u * x}{\mu_a} \qquad (5.15)$$

and

$$Sc = \frac{\mu_a}{\rho_a * D_{H_2O}} \qquad (5.16)$$

in which

ρ_a = density of air at T_a (kg/m^3)

u = wind velocity of the main air stream (m/s)

μ_a = viscosity of the air (kg/m s)

Combining the equations (5.14), (5.15) and (5.16) k_{H_2O} can be expressed as:

$$k_{H_2O} = a * \frac{D_{H_2O}}{x} + b * \frac{\rho_a^{c-d} * u^c * x^{c-1} * D_{H_2O}^{1-d}}{\mu_a^{c-d}} \qquad (5.17)$$

Comparing this with equation (5.12) shows, that the parameters m and n are not independent (m + n = 1). The value for c is generally between .5 and .8 and the value for d is 1/3. a and b have to be determined experimentally. At very low wind velocities the second part of this equation becomes many times larger than the first part. As a result the first part can generally be neglected.

Several equations are based on the vapor pressure gradient and the heat or momentum flux; two such equations are the relation of Thornthwaite and Holzman, as given by Rosenberg (1974):

$$Q_\varepsilon = Le * a * \rho_a * k^2 * \frac{(P_{w2} - P_{w1})\ (u_2 - u_1)}{\ln\ (z_2/z_1)^2} \qquad (5\text{-}18)$$

$$Rb = \frac{Q_\sigma}{Q_\varepsilon} = 61 * 10^{-5} * \frac{T_w - T_a}{P_w - P_w'} * P \qquad (5.19)$$

in which:

P_{w1}, P_{w2} = water vapor pressure at two different heights z_1 and z_2 (Pa)

u_1, u_2 = wind velocities at the corresponding heights z_1 and z_2 (m/s)

k_{H_2O} = mass transfer coefficient (m/s)

Rb = Bowen ratio

P = atmospheric pressure at altitude h of the surface above sea level.

Use of these equations requires a large number of variables to be measured and requires a correction factor for the stability of the atmosphere. In these equations it is assumed that the Reynolds analogy is valid. The Reynolds analogy describes the transfer of heat with equations similar to the equations (5.13) and (5.17) and assumes that the transfer of mass and heat by conduction is negligible. In addition the coefficients b,c and d in equation (5.17) are assumed equal for heat and mass transfer. This means, that the heat transfer is described with:

$$Q_\sigma = \alpha * A * (T_w - T_a) \qquad (5.20)$$

in which

α = heat transfer coefficient (W/m^2k)

T_w = temperature of the water

T_a = temperature of the air

The heat transfer coefficient is related to the wind velocity and the above mentioned size parameter via the Nusselt number (Nu):

$$Nu = \frac{\alpha * x}{\lambda_a} = b * Re^c * Pr^d \qquad (5.21)$$

in which

λ_a = heat conductivity of the air (W/mK)

Pr = Prandl number (dimensionless)

The Prandl number can be expressed as:

$$Pr = \frac{\mu_a c_p}{\lambda_a} \tag{5.22}$$

in which c_p is the heat capacity of air.

With the equations (5.13) and (5.20) the Bowen ratio can be expressed as:

$$Rb = \frac{Q_\sigma}{Q_\varepsilon} = \frac{\alpha * A * (T_w - T_a) * R * T_a}{Le * M_w * k * A * (P'_w - P_w)} \tag{5.23}$$

in which R is the gas constant (m^3Pa/mole K). At an air temperature of 20°C and standard atmospheric pressure the Bowen ratio is:

$$Rb = 5.34 * 10^{-7} * \frac{\alpha}{k_{H_2O}} * \frac{T_w - T_a}{P'_w - P_w} * P \tag{5.24}$$

The values for R, P, Le and M_w are given in Appendix A.2. The value for α/k_{H_2O} can be calculated from the equations (5.21) and (5.14) by substituting d = 1/3:

$$\frac{\alpha}{k_{H_2O}} = \frac{\lambda_a}{D_{H_2O}} * \left(\frac{Pr}{Sc}\right)^{1/3} \tag{5.25}$$

A value for Pr can be calculated with the data in Appendix A.2, but can also be found directly in Perry (1973). Substitution of the constants in equation (5.25) results in a value of $\alpha/k_{H_2O} = 1.17 * 10^3$. With equation (5.24) this results in a constant in the equation for the Bowen ratio of

$6.2 * 10^{-4}$ as is given in equation (5.19). The equations based on the vapor pressure fluctuations according to the Eddy correlation method describe the flow of water vapor in the vertical direction as follows:

$$Q_\varepsilon = Le * \frac{M_w/M_a}{P} * \rho a * \overline{w'*p'} \qquad (5.26)$$

in which

M = molecular weight

w' = instantaneous deviation of the vertical velocity from the time-averaged vertical velocity.

p' = instantaneous deviation of the water vapor pressure from the time-averaged water vapor pressure.

In order to be able to measure instantaneous temperature, wind velocity and vapor pressure, the instrumentation has to be quite sensitive and responsive. The combination of anemometer, humidity sensor and thermometer give a large quantity of data which make an on-line computer arrangement almost a necessity. Golz et al. (1970) find with their instruments a good agreement with lysimeter measurements, although their system still had many problems.

5.4 Transfer of sensible heat

Sensible heat is transported to and from the water surface by conductive and convective transport. As described above the contribution of conductive transport is already negligible at very low wind speeds. Johnsson (as

cited by Hutchinson (1957)) gives the following relationship for the convective transport:

$$Q_\sigma = 4.4 * (T_w - T_a) * u^{0.8} \qquad (5.27)$$

in which Q_σ is expressed in cal/cm^2 day and u in m/s.

Comparison of Johnsson's equation with the equations (5.20) and (5.21) results in a value for b and c of 4.59 and 0.8 respectively. In most cases the convective heat transfer is smaller than the heat transfer by evaporation. If, however, the surface is covered by ice the opposite can be true.

The transfer of sensible heat can, of course, also be calculated with the Bowen ratio, making use of the Reynolds analogy.

5.5 The distribution of heat in the lagoon

The transfer of latent and sensible heat depends on the surface temperature and the surface roughness. The surface temperature is a function of the distribution of heat in the lagoon and is affected by mixing. The intensity of mixing depends on the wind velocity and the stability of stratification. Mixing is also caused by density currents.

Generally stratification in a shallow lake is neglected and ideal mixing is assumed. Stahl and May (1967), however, report on the temperature distribution in

a 1 m deep rat waste lagoon and in two 1.3m dairy waste lagoons and find temperature decreases of more than 10°C in the top .5m on most summer days. Under otherwise identical conditions the average temperature of a stratified lagoon will be lower than the temperature of a mixed lagoon, since a stratified lagoon has its highest temperature at the surface which increases the loss of heat. Stratification will thus reduce the rate at which a lagoon warms up.

After the various coefficients are determined (see Chapter 7) the equations in this chapter would make it possible to predict the warm-up of a particular lagoon under specified climatic conditions.

5.6 Scum formation

After the ice cover disappears from the surface, a lagoon will be covered with scum for some time. Subsequently the scum will appear with several variations until summer when scum formation is at a minimum. Scum has a very important influence on the proliferation of purple sulfur bacteria, since it almost completely absorbs all available solar radiation.

The formation of scum needs to be understood. As a gas bubble rises in a lagoon, solid particles are entrained in the wake from the time that the bubble emerges from the sludge layer at the bottom. If the anaerobic digestion processes are close to completion, the solid

particles will be high in inert material and low in proteins and fats. In addition, the volatile fatty acids, which are known to reduce the surface tension, are in low concentration. Arriving at the surface the liquid film of the bubble evaporates, the bubble collapses and the solids sink back to the bottom. If, however, the digestion processes are incomplete, the solid particles at the surface can stick together and form a mat until after evaporation of the water content they are dense enough to sink. A high concentration of volatile fatty acids will promote formation of a solid mat or scum because surface tension is reduced and it therefore takes longer for a bubble to collapse. This results in a higher concentration of solid particles at the surface and consequently increases the probability that the solid particles will stick together. In addition, the longer existence of a solid mat can entrap other gas bubbles which keeps the mat floating.

The liquid film of a bubble doesn't evaporate if the temperature of the air is equal to or less than the dew point temperature. On the contrary, water will be added. Bubbles will less easily collapse and will coalesce to very large sizes as can be seen from the picture (Figure 5.2) which was taken on a spring morning when such conditions occurred. Later in the day the temperature rises, the bubbles collapse and typically, a large solid mat is formed.

⊢ 10 cm at the center of the photo.

Figure 5.2 Scum formation in Spring.

Unless there is a strong wind or precipitation, such a mat can cover most of the lagoon for a large portion of the day.

I have considered the possibility that low temperatures would inhibit the acid consuming bacteria more strongly than the acid forming bacteria which would explain the same phenomena. Volatile fatty acids (VFA) concentrations were measured with a gas chromatograph during a day-night period when the scum cover ranged from 5 to 100% of the lagoon surface. I could not detect a change in VFA concentrations.

I conclude that the influence of VFAs on the scum formation is more of a seasonal character, while diurnal variations of the scum cover are caused by the changes in relative humidity of the air.

Table 5.2--Volatile Fatty Acids in the Lagoons on April 30, 1977.

	Scumcover %		Acetic Acid mole/m^3		Propionic Acid mole/m^3		Butyric Acid mole/m^3	
	W	E	W	E	W	E	W	E
3:35 A.M.	100	100	1.63	--	.32	--	.11	--
4:45 A.M.	100	100	1.45	2.25	.29	.60	--	.10
5:30 A.M.	100	100	1.48	2.57	.30	.72	.07	.12
6:30 A.M.	100	100	1.45	2.50	.29	.71	.08	.10
8:30 A.M.	100	100	1.47	2.33	.27	.61	.05	.10
10:30 A.M.	40	100	1.37	2.33	.25	.65	.06	.11
11:30 A.M.	20	80	--	--	--	--	--	--
12:30 P.M.	--	--	1.50	2.47	.29	.72	.07	.13

CHAPTER 6

THE SULFUR CYCLE AND KINETICS

6.1 Introduction

In the Chapters 1, 2 and 3 a description was given of the microbial populations and their interactions with the environment. Since these interactions are very complex, it would be very time-consuming to test all variations in the lagoon situation or even in the lab. With certain simplifications and therefore some loss in accuracy these interactions can be simulated on a computer with an appropriate model. In this way other researchers have had great success in revealing details in the behavior of the anaerobic digestion process. In paragraph 2.5 a short description of the models for anaerobic digestion was given. These models describe the behavior of acid and methane forming organisms.

No similar models exist for the sulfur cycle. Principal differences with the anaerobic digestion model are:

1. The purple sulfur bacteria and the sulfate reducing bacteria cause sulfur to move in a cyclic process, while the carbon path in the anaerobic digestion follows a sequential process from acid formers to methane formers.

2. The gaseous product H_2S is an odorous pollutant and therefore unwanted, whereas the gaseous products methane and carbon dioxide are valued products of anaerobic digestion.
3. Sulfur is stored in the purple sulfur bacteria, while no storage products are considered in anaerobic digestion.
4. Purple sulfur bacteria are light-dependent, while light has no significance in anaerobic digestion.
5. Almost all models of anaerobic digestion consider the steady state. Because of the storage of sulfur and the changing meteorological conditions (including the availability of light), the steady state is not applicable.

In the following model of the sulfur cycle in the lagoon, I will include all these features.

Before assembling the total model I will discuss the different components:

a. Description and mathematical formulation of the lagoon.
b. Description and mathematical formulation of gas bubbles rising in the lagoon liquid.
c. Transfer of hydrogen sulfide between the gas bubbles and the liquid.
d. Transfer of hydrogen sulfide from the liquid to the air.

e. The microbial conversion processes and growth rates.

f. The influence of the pH.

g. The influence of the temperature.

h. Changes in the lagoon volume.

6.2 Description and mathematical formulation of the lagoon

Most lagoons are designed as trapezoidal structures as shown in Figure 6.1.

The cross sectional area at depth h, measured from the bottom, becomes then:

$$A_h = L_o * W_o + 2h\ (L_o + W_o)\ \cot\ \alpha' + 4h^2\ \cot^2\alpha' \qquad (6.1)$$

in which:

A_h = area at depth h (m^2)

L_o = length of the lagoon at the bottom (m)

W_o = width of the lagoon at the bottom (m)

α' = angle of the side slopes (deg)

The volume below the depth h becomes:

$$V_h = L_o * W_o * h + h^2\ (L_o + W_o)\ \cot\alpha' + \frac{4}{3}\ h^3\ \cot^2\alpha' \qquad (6.2)$$

The lagoon liquid is assumed to be ideally mixed. This means that the input of manure is evenly distributed over the whole volume and that the concentrations of sulfide, sulfate, sulfur and microorganisms show no spatial differences.

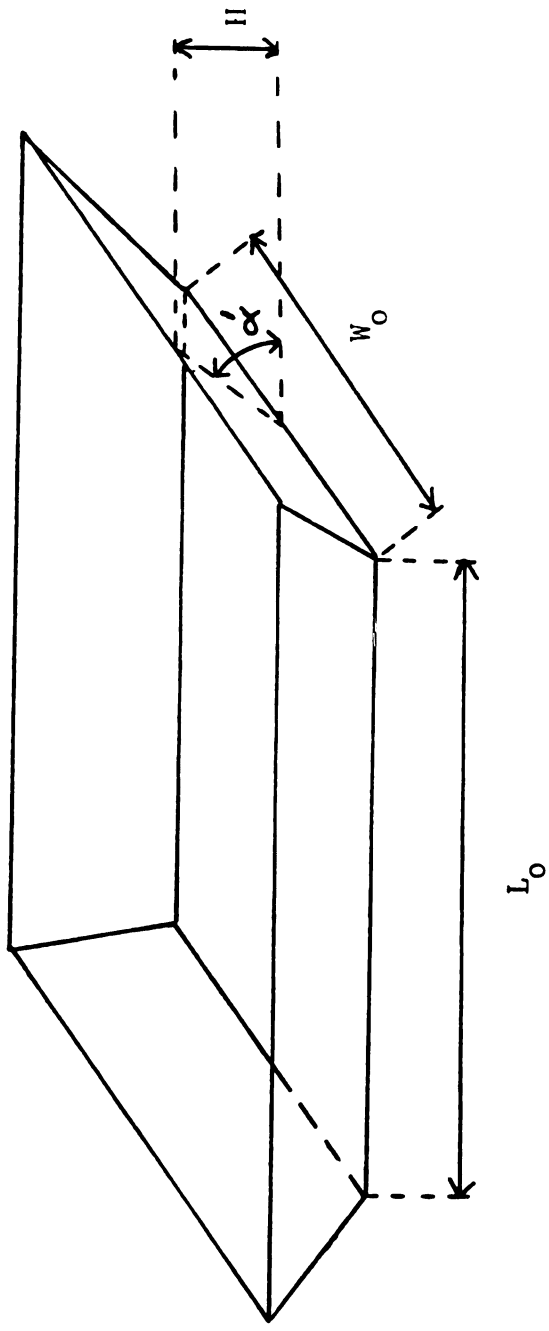


Figure 6.1 The Trapezoidal Shaped Lagoon

Further I have assumed, that the urine enters the lagoon via the liquid phase and that the feces are part of the sediment. The feces are degraded in the sediment layer and provide a steady production of gas containing all the sulfur of the feces in the form of sulfide. Since the urinal sulfur is mainly sulfate the urine addition raises only the level of sulfates.

At the bottom of the lagoon, then, the concentration of sulfide in the gas bubbles $[H_2S]_{go}$ becomes:

$$[H_2S]_{go} = \frac{[TS]_f * F * N * w}{Q_g} \qquad (6.3)$$

in which:

$[TS]_f$ = the total sulfur concentration in the feces (mole/m^3)

F = the rate of feces production per unit weight of animals (m^3/kg s)

N = the number of animals whose manure is transported to the lagoon

w = the average weight of the animals (kg)

Q_g = flowrate of the gas (m^3/s)

The flowrate of the gas can be expressed as:

$$Q_g = [C]_f * F * N * w * V_M \qquad (6.4)$$

in which:

$[C]_f$ = the concentration of organic carbon in the feces (mole/m^3)

V_M = molecular gas volume (m^3/mole)

The change of sulfate concentration caused by the introduction of the urine is equal to:

$$\frac{d[SO_4]}{dt} = \frac{[TS]_u * U * N * w}{V} \qquad (6.5)$$

in which:

U = the rate of urine production per unit weight of animals

$[TS]_u$ = the total sulfur concentration in the urine (mole/m^3)

V = the total volume of the lagoon (m^3)

6.3 Description and mathematical formulation of gas bubbles rising in the lagoon liquid

For the following derivations I have assumed that:

1. gas production takes place only at the bottom surface
2. the gas bubbles have a constant equivalent diameter d_e of 1 cm (see equation 6.17)
3. as the gas bubbles rise, they remain equally distributed over the lagoon area

Knowing the equivalent diameter the Eötvös number (Eo) can be determined, which is related to the shape of a bubble:

$$Eo = \frac{\rho_w * g * d_e^2}{\sigma} \qquad (6.6)$$

in which:

ρ_w = the density of water (kg/m^3)

g = gravitational acceleration (m/s^2)

d_e = the equivalent diameter (m.)

σ = surface tension of water (kg/s^2)

For pure water $\sigma = 7.275 * 10^{-2} kg/s^2$ and the Eötvös number becomes 13.5, at which value the bubbles have the shape of a spherical cap as is drawn in Figure 6.2.

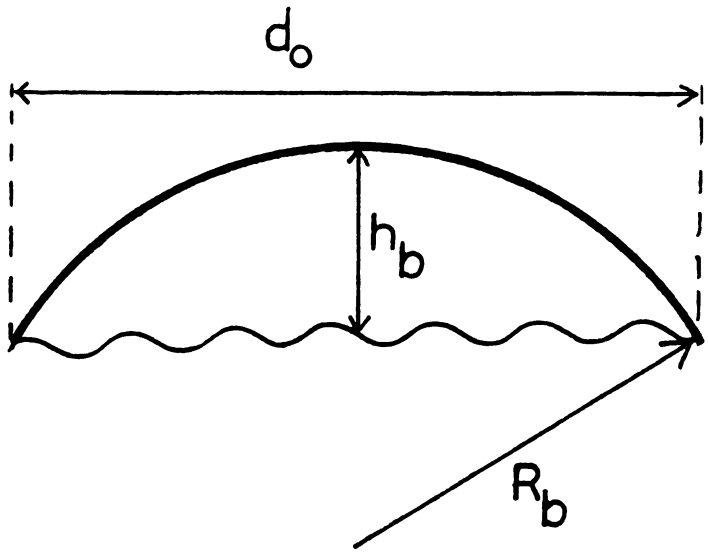


Figure 6.2 A Spherical Cap.

If the Reynolds number (Re) for the bubble is larger than 800, the drag coefficient (C_d) of the gas bubbles is constant and equal to 0.95. The bubbles will quickly reach their terminal velocity, at which velocity the buoyant force, is equal to the resistance of the water:

$$\frac{\pi}{6} * d_e^3 * \Delta_\rho * g = \tfrac{1}{2} * \rho_w * U_b^2 * C_d * \frac{\pi}{4} * d_o^2 \qquad (6.7)$$

in which:

U_b = rising velocity of a bubble (m/s)

d_o = the actual diameter of a bubble (m)

Δ_ρ = the difference in density between bubble and water (kg/m^3)

This equation can be rearranged to:

$$U_b = \sqrt{\frac{4 * g * d_e^3}{3 * C_d * d_o^2}} \qquad (6.8)$$

According to Davies and Taylor (1950) and Wu et al. (1974):

$$\frac{d_o}{d_e} = 3.65 * Fr \qquad (6.9)$$

in which Fr is the number of Froude:

$$Fr = \frac{U_b^2}{g d_e} \qquad (6.10)$$

The equations (6.8), (6.9) and (6.10) give:

$$Fr = \frac{U_b^2}{g d_e} = \frac{4 * d_e^2}{3 * C_d * d_o^2} = \frac{4}{3 * .95 * (3.65)^2 * Fr^2} \qquad (6.11)$$

As a result, Fr = .47. From equation (6.10) the U_b can be calculated:

$$U_b = \sqrt{Fr * g * d_e} = .22 \text{ m/s} \qquad (6.12)$$

The Reynolds number becomes then:

$$Re = \frac{\rho_w U_b d_e}{\mu_w} = 2100 \qquad (6.13)$$

The value of .95 for the drag coefficient is thus justified. A simple calculation shows, that the bubble will reach a velocity of 99% of the terminal velocity within 1 cm of the point of release. The velocity of the bubble can therefore be considered constant.

The surface of the sphere segment A_b in Figure 6.2 is:

$$A_b = 2\pi * R_b * h_b \qquad (6.14)$$

in which

$$h_b = -\tfrac{1}{2} \sqrt{4 * R_b^2 - d_o^2} + R_b \qquad (6.15)$$

Davies and Taylor (1950) give for the radius R_b:

$$R_b = \frac{9}{4} * Fr * d_e \qquad (6.16)$$

By definition of the equivalent diameter the volume of each bubble is:

$$V_b = \frac{\pi}{6} * d_e^3 \qquad (6.17)$$

The time a bubble is in the water:

$$\tau_b = \frac{H}{U_b} \qquad (6.18)$$

Combination of the equations (6.4), (6.17) and (6.18) makes the number of bubbles in the lagoon at any time (N_b) a calculable quantity:

$$N_b = \frac{Q_g * \tau_b}{V_b} \qquad (6.19)$$

The specific surface of the bubbles (S_h) will decrease with increasing height in the lagoon, because of the increasing cross sectional area of the lagoon:

$$S_h = \frac{N_b * A_b}{H * A_b} \qquad (6.20)$$

Substitution of N_b and A_b (equations (6.19) and (6.14)) gives:

$$S_h = \frac{Q_g * \tau_b * 2\pi * R_b * h_b}{V_b * H * A_h} \qquad (6.21)$$

Rearranging this equation and substitution of τ_b, R_b, h_b and V_b results in:

$$Z \equiv \frac{S_h * A_h}{Q_g} = 25.2 * Fr^{3/2} * d_e^{-3/2} * g^{-1/2} \qquad (6.22)$$

This specific surface group, further identified with the symbol Z, provides the surface through which mass exchange between the bubbles and the lagoon liquid takes place.

For this mass transfer, which takes place according to an equation similar to the equations (2.5) and (5.13), it is important to know the mass transfer coefficient k_b. This coefficient can be found by using the penetration theory of Higbie (1935). This theory can be used, because gas bubbles of the size assumed have an internal circulation, which keeps the concentration of gases uniform inside the bubble.

$$k_b = 2 \sqrt{\frac{D_{H_2S}}{\pi * \tau}} \qquad (6.23)$$

in which:

D_{H_2S} = diffusivity of H_2S in water (m^2/s)

τ = contact time of a water particle with the bubble (s)

This contact time can be taken as:

$$\tau = \frac{d_e}{U_b} \qquad (6.24)$$

6.4 Transfer of hydrogen sulfide

As was mentioned earlier, hydrogen sulfide is transported between the gas bubbles and the liquid and from

the liquid to the air. Both transfer processes can be described by the equation:

$$N_{H_2S} = k_{H_2S} * A * ([H_2S]'_w - [H_2S]_w) \qquad (6.25)$$

in which:

N_{H_2S} = mass transfer rate of H_2S (mole/s)

k_{H_2S} = mass transfer coefficient for H_2S (m/s)

$[H_2S]_w$ = concentration of H_2S in the water (mole/m^3)

$[H_2S]'_w$ = concentration of H_2S in the water, which would be in equilibrium with the concentration of H_2S in the air or in the bubbles (mole/m^3)

If the concentration of hydrogen sulfide in the air is neglected, this last concentration becomes zero in the calculation of transport of H_2S to the air. For this process the transfer area A is equal to the lagoon surface area, which can be obtained from equation (6.1), assuming that the surface is smooth. Gloyna and Espino (1969) have determined the mass transfer rate for H_2S from pond water, when there is no mixing and the water is under an atmosphere of carbon dioxide. They found a transfer coefficient of $2.3 * 10^{-3}$ m/s. They claimed that this coefficient increases by a factor of 20 when "slow mixing" was applied by means of air jets. In this last case the transfer of oxygen and subsequent oxidation of H_2S could have interfered with their measurements, resulting in an excessive value for the

mass transfer coefficient, since the transfer of oxygen is faster than the transfer of H_2S. (The diffusion coefficient for oxygen is 1.5 times that of H_2S.)

For the transfer of hydrogen sulfide between the bubbles and the liquid the transfer coefficient is given by equation (6.23). Substitution of the values for τ and D_{H_2S} gives a value for k_b of $2.2 * 10^{-4}$m/s.

The equilibrium concentration can be calculated with Henry's law:

$$[H_2S]'_w = K_{H_2S} * P_{H_2S} \qquad (6.26)$$

This equation is identical with equation (2.4).

The concentration of hydrogen sulfide in an ascending bubble is a function of its height above the bottom of the lagoon. To obtain the total amount of H_2S transferred, the transfer rate has to be integrated over the height. The partial pressure in Henry's law can be replaced by concentration using the ideal gas law. As a result, the concentration of hydrogen sulfide in the bubbles at the surface of the lagoon (height H) becomes:

$$[H_2S]_{gH} = \frac{[H_2S]_w}{Zl} + \left([H_2S]_{go} - \frac{[H_2S]_w}{Zl}\right) * \exp\left(- \frac{Z}{Zl} * k_b * H\right) \qquad (6.27)$$

in which:

$$Z1 = K_{H_2S} * R * T \qquad (6.28)$$

R = gas constant (m^3Pa/mole K)

T = absolute temperature (K)

The value for Z is obtained from equation (6.22). The amount of H_2S transferred is then:

$$Q_g \ ([H_2S]_{go} - [H_2S]_{gH}) \qquad (6.29)$$

The total rate of H_2S leaving the lagoon as an odorous air pollutant is the sum of the mass transfer rate at the surface and the product of gas flow rate and sulfide concentration in the bubbles at the surface ($[H_2S]_{gH}$).

6.5 Microbial conversion processes

6.5.1 Sulfide Balance.--Although in the last paragraph a relation was given for the air pollution, this relation contains still an unknown quantity: the sulfide concentration in the water phase. In order to determine this quantity a mass balance has to be made for the processes which introduce sulfide and the processes which remove sulfide. Two of these processes have been identified in the previous section (section 6.4). The others are:

1. Conversion of sulfide to internally stored sulfur by the purple sulfur bacteria in the light.
2. Conversion of internally stored sulfur to sulfide by purple sulfur bacteria in the dark.

3. Conversion of sulfate to sulfide by the sulfate reducing bacteria.
4. Chemical oxidation of sulfide by oxygen. (The concentration of oxygen in an anaerobic lagoon is so low, that I will neglect this.)
5. Dissociation of hydrogen sulfide in its ionic form.
6. Precipitation of sulfides with a low solubility. This process requires a complete model for itself. Moreover I don't think that heavy metals play an important role in the treatment of animal waste. Therefore I decided to neglect it.

The fifth process will be discussed in the next paragraph. This process is so fast as compared with the first three microbial processes that equilibrium can always be assumed.

For the three microbial processes I will assume, that the Monod model is applicable. In many microbial treatment processes this assumption has been shown to lead to a good simulation of practical results.

Analogous to the inhibition of methanogenic organisms by undissociated acid, mentioned in paragraph 2.5, van Gemerden (1974) reports that the purple sulfur bacteria are inhibited by undissociated hydrogen sulfide, which also serves as a source of reducing power. To express this inhibition, he introduces a function similar to the one used by Andrews. I will make use of the same function:

$$\mu_2 = \frac{\mu_{max2} * [H_2S]_w}{(K_2 + [H_2S]_w (1 + \frac{[H_2S]_w}{K_I}} \qquad (6.30)$$

in which:

μ_2 = the specific growth rate for purple sulfur bacteria, using H_2S as substrate. (1/s)

μ_{max2} = the theoretical maximum growth rate for this process without inhibition (1/s)

K_2 = the saturation constant for the oxidation of H_2S (mole/m^3)

K_I = the inhibition constant for H_2S (mole/m^3)

The rate of sulfide oxidation becomes then:

$$\frac{d[H_2S]_w}{dt} = - \frac{\mu_2 X_2}{Y_2} \qquad (6.31)$$

in which:

t = time (s)

X_2 = concentration of purple sulfur bacteria (cells/m^3)

Y_2 = yield coefficient for the oxidation of hydrogen sulfide (cells/mole substrate converted)

The yield coefficient depends on the source of carbon as is explained in paragraph 3.3.

The rate of the second microbial process, the reduction of internally stored sulfur, will be determined by the surface area (S) of the sulfur granules:

$$S = 4 * \pi * N_o * X_2 \sqrt[3]{\left(\frac{A_s * [S] * 3}{4 * \pi * \rho_s * N_o * X_2}\right)^2} \qquad (6.32)$$

in which:

N_o = the number of sulfur globules per cell

A_s = atomic weight of sulfur

[S] = the concentration of elemental sulfur in the lagoon (mole/m^3)

ρ_s = the density of sulfur in the globules (kg/m^3)

The specific growth rate (μ_4) for this process becomes then:

$$\mu_4 = \frac{\mu_{max4} * S}{K_4 + S} \qquad (6.33)$$

in which:

μ_{max4} = the maximum growth rate of PSB using internally stored sulfur

K_4 = the saturation constant for the use of internally stored sulfur (m^2/m^3)

The rate of sulfide production becomes:

$$\frac{d[H_2S]_w}{dt} = \frac{\mu_4 * X_2}{Y_4} \qquad (6.34)$$

in which Y_4 is the yield coefficient for the reduction of internally stored sulfur.

The reduction of sulfate depends on the specific growth rate of the desulfurizing bacteria (μ_1):

$$\mu_1 = \frac{\mu_{max1} * [SO_4]_w}{K_1 + [SO_4]_w} \qquad (6.35)$$

in which:

μ_{max1} = the maximum growth rate of the desulfurizing bacteria (1/s)

$[SO_4]_w$ = the concentration of sulfate in the lagoon (mole/m^3)

K_1 = the saturation constant for sulfate (mole/m^3)

The resulting rate of sulfide production is:

$$\frac{d[H_2S]_w}{dt} = \frac{\mu_1 * X_1}{Y_1} \qquad (6.36)$$

in which Y_1 is the yield coefficient for the reduction of sulfate to sulfide (cells/mole of substrate converted).

The equation (6.31) is only valid if sulfide is the growth rate limiting substrate. If light is limiting, the growth rate has to be calculated for the available light intensity. The light intensity as a function of the depth can be described by Beer's law:

$$I_h = I * \exp(-\eta * (H - h)) \qquad (6.37)$$

with:

I_h = light intensity at height h above the bottom of a lagoon with total height H (lx)

I = incident light intensity (lx)

η = extinction coefficient (1/m)

This equation assumes that incident light is normal to the water surface. For the photosynthetic bacteria, let the transition from light zone to dark zone occur at a height h_1 (less than the lagoon depth H) at which the light intensity I is just sufficient to permit phosynthesis:

$$h_1 = H + \eta * \log (I_1/I) \qquad (6.38)$$

From the measurements of van Gemerden (1968a) of the growth rate at different light intensities a relationship can be derived. I have put his data on a Lineweaver-Burk plot (Figure 6.3); the convincing straight line makes it possible to determine the growth rate (μ_5) with a Monod-type equation:

$$\mu_5 = \frac{\mu_{max5} * I_h}{K_5 + I_h} \qquad (6.39)$$

in which:

μ_{max5} = the theoretical maximum growth rate for light limited growth

K_5 = light saturation constant

μ_5 will be the growth rate from the height h_1 (the compensation point) up to the level where the combined rate of sulfide and sulfur oxidation becomes the limiting factor. This Monod-type equation is comparable with the equation for a rectangular hyperbola, which is discussed by Takahashi and Ichimura (1970). I chose for the Monod-type equation, because the constants in this equation are more meaningful.

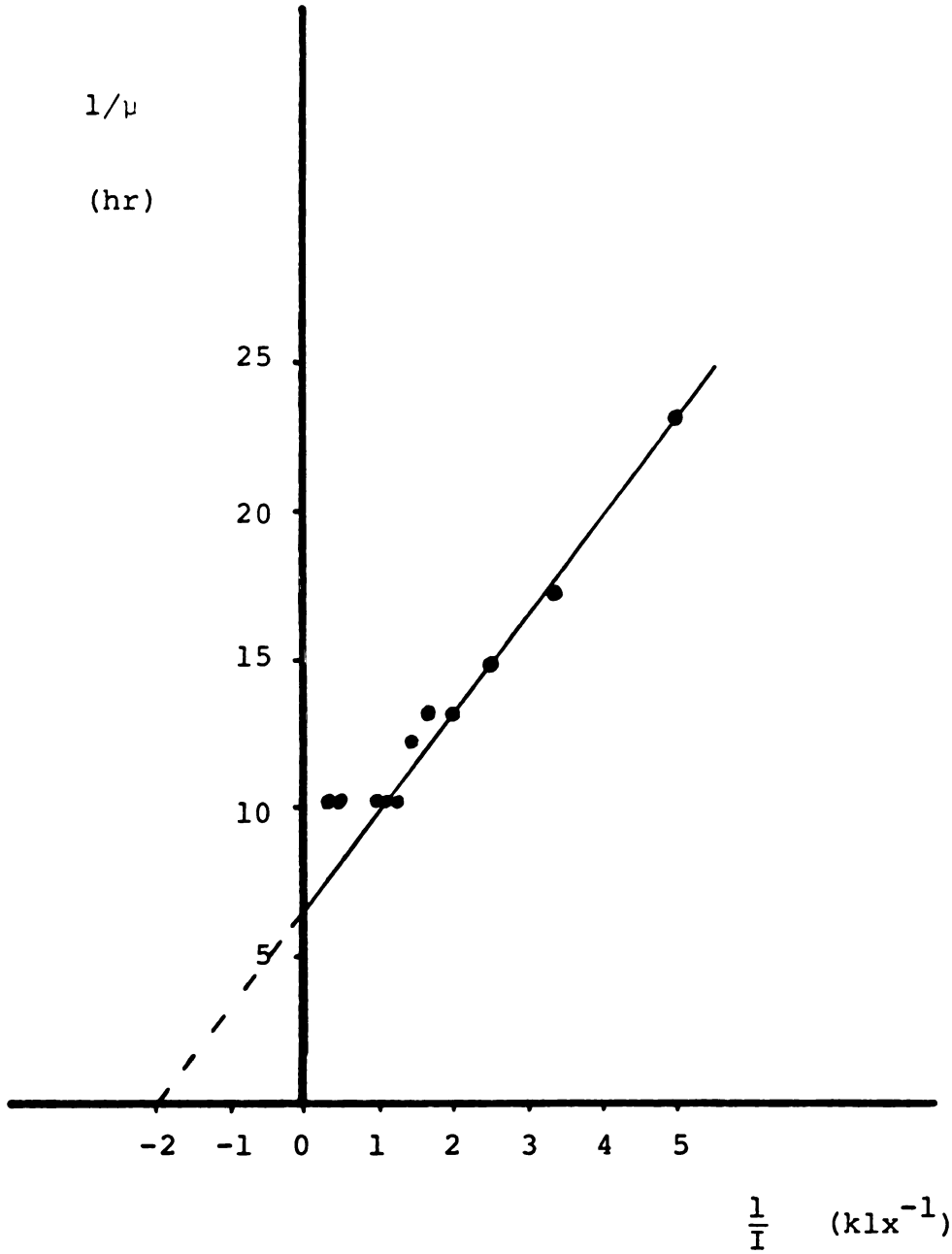


Figure 6.3 Lineweaver-Burk plot for light-limited growth.

Now all the components for a sulfide balance are described. For the equations (6.30) to (6.39) one must supply the model with values for μ_{max2}, K_2, K_I, Y_2, N_o, ρ_s, μ_{max4}, K_4, Y_4, μ_{max1}, K_1, Y_1, I, η, I_1, μ_{max5} and K_5. (A complete list of parameters and their values is given in Appendix A.) The values for X_2, [S], X_1 and $[SO_4]_w$ can be calculated with mass balances for sulfur, sulfate and the microorganisms, as will be described later in this chapter. Furthermore, a starting value for the sulfide concentration must be established.

6.5.2 Sulfate Balance.--For the sulfate balance the following components have to be considered:

1. Introduction of sulfate into the lagoon via the urine (equation 6.5).
2. The reduction of sulfate to sulfide by desulfurizing bacteria (equation 6.36).
3. The oxidation of internally stored sulfur to sulfate by the purple sulfur bacteria.

The last component is a function of the sulfur surface as is given by equation (6.32). The specific growth rate (μ_3) for the oxidation of sulfur is:

$$\mu_3 = \frac{\mu_{max3} * S}{K_3 + S} \tag{6.40}$$

The resulting production rate of sulfate is:

$$\frac{d[SO_4]_w}{dt} = \frac{\mu_3 * X_2}{Y_3} \tag{6.41}$$

in which Y_3 is the yield coefficient for the oxidation of sulfur. This coefficient is likely to be three times the yield coefficient for the oxidation of hydrogen sulfide as can be seen from the apparent reducing power in the equations (3.1), (3.2) and (3.4), (3.5).

For the sulfate balance an initial sulfate concentration has to be supplied.

6.5.3 Sulfur Balance.--Three processes take place with the internally stored sulfur:

1. Formation of sulfur from the oxidation of hydrogen sulfide (equation 6.31).
2. Consumption of sulfur for the oxidation to sulfate (equation 6.41).
3. Consumption of sulfur for the reduction to hydrogen sulfide (equation 6.34).

All the components of the sulfur balance are given in the previous paragraphs. An initial sulfur concentration has to be supplied.

6.5.4 Balance of purple sulfur bacteria.--In order to find the growth of purple sulfur bacteria over a certain time span the contributions to the growth rate from equations (6.30), (6.33), (6.39) and (6.40) have to be integrated over that part of the lagoon volume, in which they are active. Since μ_2 and μ_3 represent growth based on coupled phenomena their sum is limited by μ_{max2} (Trüper, 1964).

An initial concentration of bacteria has to be supplied. Over longer periods of time a death rate has to be taken into account. For the short simulations in this thesis, the death rate has been neglected.

6.5.5 Balance of desulfurizing bacteria.--In this model the growth of the desulfurizing bacteria is considered to depend only on the reduction of sulfate.

The specific growth rate is obtained from equation (6.35) and the death rate is neglected. An initial concentration of bacteria has to be supplied.

6.6 The influence of pH

The pH has a strong influence on the performance of the microbial populations under consideration. In order to keep the complexity of this model within limits, the influence of the microbial activities on the pH and the influence of the pH on the maximum growth rates of the microorganisms have been neglected.

The only pH effect which has been considered is in the formation of a sulfide buffer. As is described above, only undissociated hydrogen sulfide can serve as a substrate and inhibiting agent for the purple sulfur bacteria and only undissociated hydrogen sulfide is transferred from the gas phase and to the air. The total available amount of sulfide is, however, the sum of undissociated and ionic forms:

$$[H_2S]_{w,total} = [H_2S]_w + [HS^-]_w + [S^{2-}]_w \qquad (6.42)$$

Using known dissociation constants K' and K'', this can be written as:

$$[H_2S]_{w,total} = [H_2S]_w \left\{1 + \frac{K'}{[H^+]} + \frac{K' * K''}{[H^+]^2}\right\} \qquad (6.43)$$

The hydrogen sulfide formed, consumed and transferred in the equations (6.25), (6.31), (6.34) and (6.36) has to be corrected by this factor.

6.7 The influence of temperature

The maximum growth rates of the microorganisms are functions of the temperature. Below the optimum temperature an Arrhenius type of relationship is displayed. Gloyna (1971) gives the equation:

$$\mu = \mu_R * (1.085)^{T - T_R} \qquad (6.44)$$

The mass transfer processes are also influenced by the temperature. The temperature dependence of the diffusion coefficient, which is important for the mass transfer processes is given by the law of Nernst-Einstein:

$$\frac{D_{H_2O} * \mu_w}{T} = \text{constant} \qquad (6.45)$$

in which μ_w is the dynamic viscosity. The temperature dependence of the dynamic viscosity of water is:

$$\mu_w = .1 * 10^{\left(a + \frac{b}{c + d\,(\theta - 20) + e\,(\theta - 20)^2}\right)} \qquad (6.46)$$

in which:

θ = temperature (°C)

a,b,c,d and e are constants:

a = -3.30233 b = 13.01

c = 998.333 d = 8.1855

e = .00585

For short periods of time the temperature of a waterbody can be treated as constant, but for longer time spans temperature variation plays an important role.

6.8 Changes in the lagoon volume

For short periods of time the volume of a lagoon can be considered constant. Over longer periods several factors change the volume:

1. The volumetric loading with manure
2. Precipitation
3. Evaporation and condensation (see paragraph 5.3)
4. Pumping of the lagoon contents to the field

The volumetric loading rate doesn't require any additional information since it uses the feces and urine production rates as were used in the equation (6.3) and (5.5):

$$\frac{dV}{dt} = (F + U) * N * w \qquad (6.47)$$

This amounts to a very small percentage daily addition to total lagoon volume.

The precipitation has to be obtained from climatic or meteorological data or can be simulated by a random variable appropriately distributed. Precipitation dilutes the lagoon contents. Although it can have an important influence on the surface roughness and therefore on the transfer of hydrogen sulfide to the air, I have neglected these effects on the grounds that the duration of precipitation events is not great.

The pumping of the lagoon contents causes an occasional drastic change in the lagoon volume. For the microbial processes, lagoon pump out will act as a step increase in all loading rates and can therefore greatly upset the system. I have not simulated pumping of the lagoon since pumping usually occurs prior to and at the end of the lagoon's May to November operating season.

Volumetric changes will thus play no role in this model.

6.9 The total model

The total model can best be illustrated by a few diagrams. In figure 6.3 the different processes are represented schematically and in figure 6.4 a flow diagram of the major part of the computer program is given.

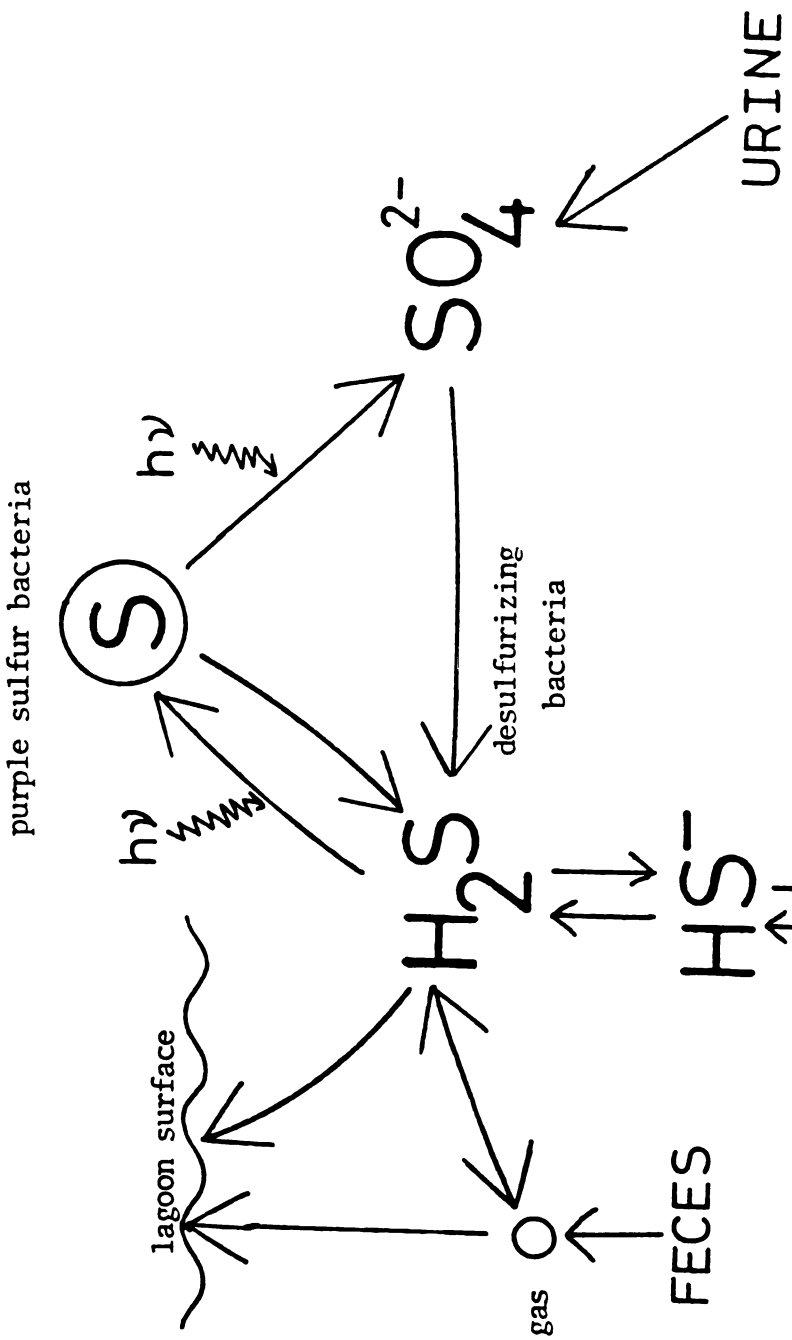


Figure 6.4 Model of the Sulfur Cycle.

Flowchart of the main loop.

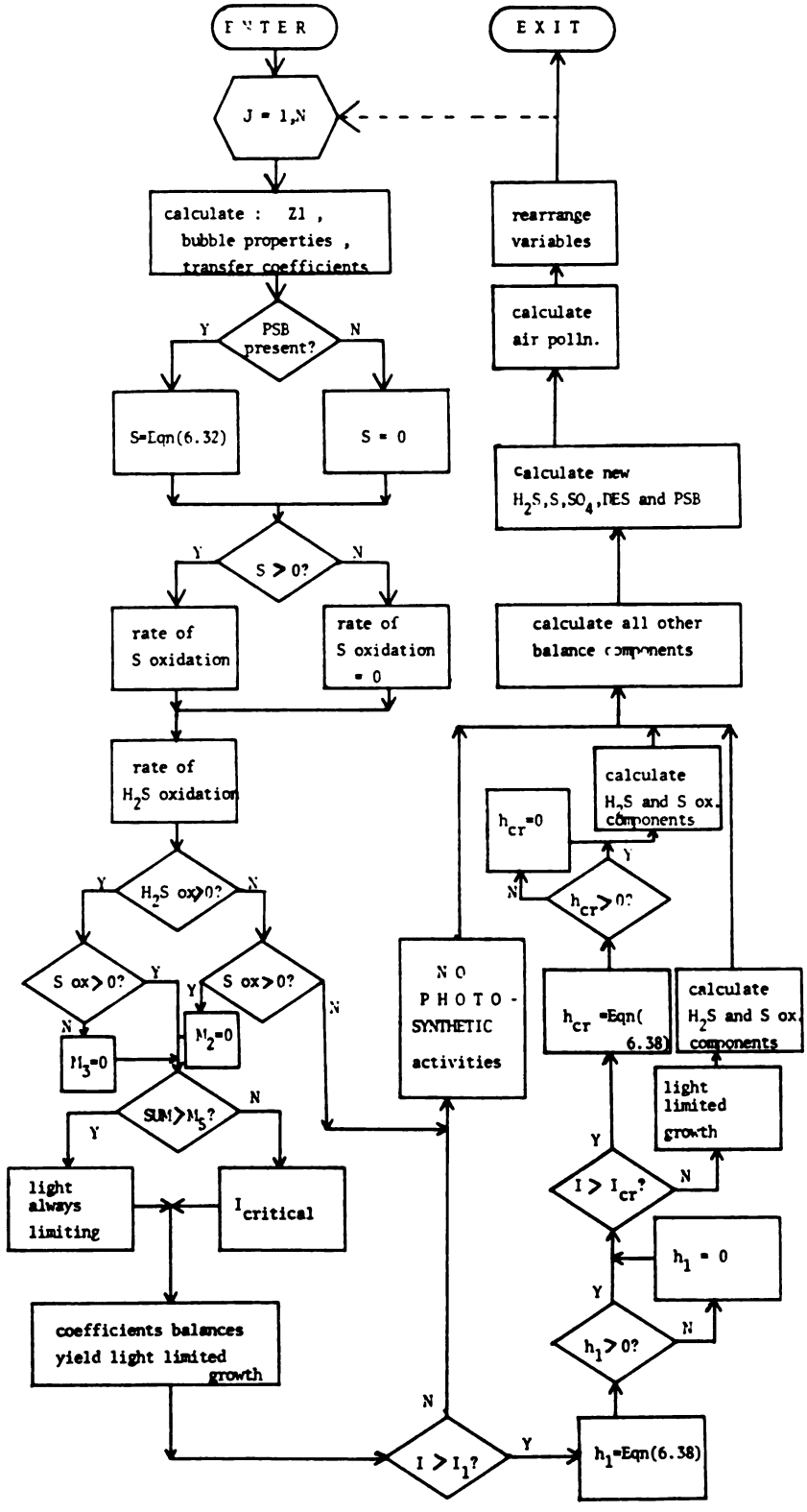


Figure 6.5 Flowchart of the Main Loop.

PART III

EXPERIMENTS

CHAPTER 7

HEAT BALANCE

7.1 Introduction

In Chapter 5 a theoretical model for the heat balance of a lagoon was described. In that model there are a number of unknowns which have to be determined experimentally. The most important of these unknowns are the parameters in the equations for the evaporation and condensation (a and b in equation 5.14).

These parameters can be determined by supplying all the data necessary for a complete heat balance. These data are:

1. The solar radiation (Q_s)
2. The temperature of the air (T_a)
3. The temperature of the lagoon surface (T_w)
4. The surface area of the water (A)
5. The water vapor concentration in the air ($[H_2O]a$)
6. The saturated water vapor concentration in the air at T_w ($[H_2O]'_a$)
7. The wind velocity (u)
8. The density of the moist air (ρ_a)
9. The temperature distribution in the lagoon

10. The shape of the lagoon

The data for solar radiation were kindly supplied by D. E. Linvill. The data for the air temperature, the wind velocity and the humidity of the air were derived from the monthly reports of the National Weather Service. These data are tabulated in Appendix C. From these data the density of the air is calculated with a psychrometric computing routine.

In the following paragraphs I will describe the measurements of the shape of the lagoons and the temperature distribution in these lagoons. Thereafter the data will be applied to the model developed in Chapter 5.

7.2 The shape of the lagoons

The heat content of a lagoon is determined by the temperature and the volume or the temperature at each depth and the corresponding volume at that depth. From equation (6.2) one can see, that the volume is determined by the length, the width, the angle of the side slopes and by the depth. In Chapter 4 the design values for these dimensions are presented. In order to know the actual sludge accumulation and the actual dimensions, a depth-profile of the west lagoon was measured.

On February 1, 1977, when the lagoons were covered with ice, 21 holes were drilled through the ice as indicated in Figure 7.1. The water depth was measured with a sand filled bottle on a rope and the total depth was measured

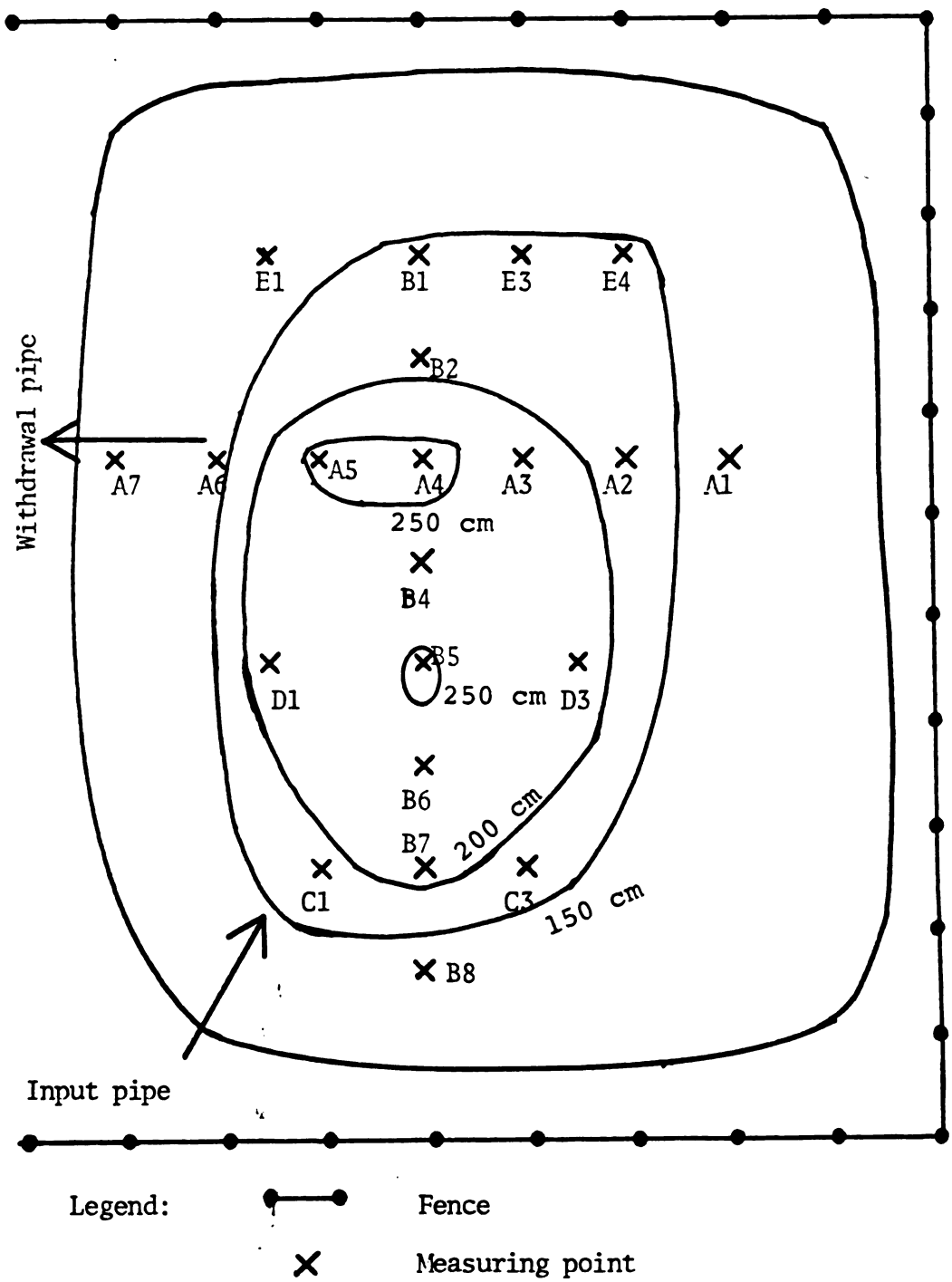


Figure 7.1 Water Depth of the West Lagoon.

using a metal stick. A measurement was also made of the ice thickness. The results are tabulated in Table 7.1 and the corresponding profiles for the water-depth are drawn in Figure 7.1. Also given in this figure is the shoreline, which was established by measuring distance from the fence-line on April 27, 1977. In Figure 7.2 the approximate lines of equal sludge accumulation are drawn. From these graphs one can conclude that the locations of the inlet and outlet structures of the lagoon have a marked influence on the depth profile. In general the sludge tends to accumulate in the deeper parts of the lagoon. In the immediate vicinity of the inlet and outlet, however, the flow of water scours the sludge.

The depth profile of the east lagoon was not measured because the ice was too weak. A single depth measurement for the east lagoon was made at one point corresponding to point A4 of the west lagoon. Since the values were the same, and the construction of the east lagoon is identical to that of the west lagoon is, it is assumed that both lagoons have similar bottom profiles.

The side slopes of both lagoons have been measured in a way similar to that described above for the water depth. For both lagoons the side slope had an approximate 1:3 ratio.

Table 7.1--Depth Profile of the West Lagoon.

Point	Total depth cm	Water depth cm	Sediment depth cm	Ice cover cm
A1	191	112	79	48
A2	259	188	71	27
A3	271	216	55	20
A4	282	269	13	14
A5	284	267	17	17
A6	198	132	56	25
A7	79	38	41	23
B1	224	165	59	30
B2	272	178	94	32
B3 = A4				
B4	281	226	55	15
B5	267	254	13	18
B6	272	244	28	22
B7	244	224	20	24
B8	119	102	17	33
C1	236	188	48	4
C2 = B7				
C3	224	178	46	20
D1	271	211	60	20
D2 = B5				
D3	263	204	59	20
E1	152	124	28	34
E2 = B1				
E3	211	160	51	36
E4	216	168	48	46

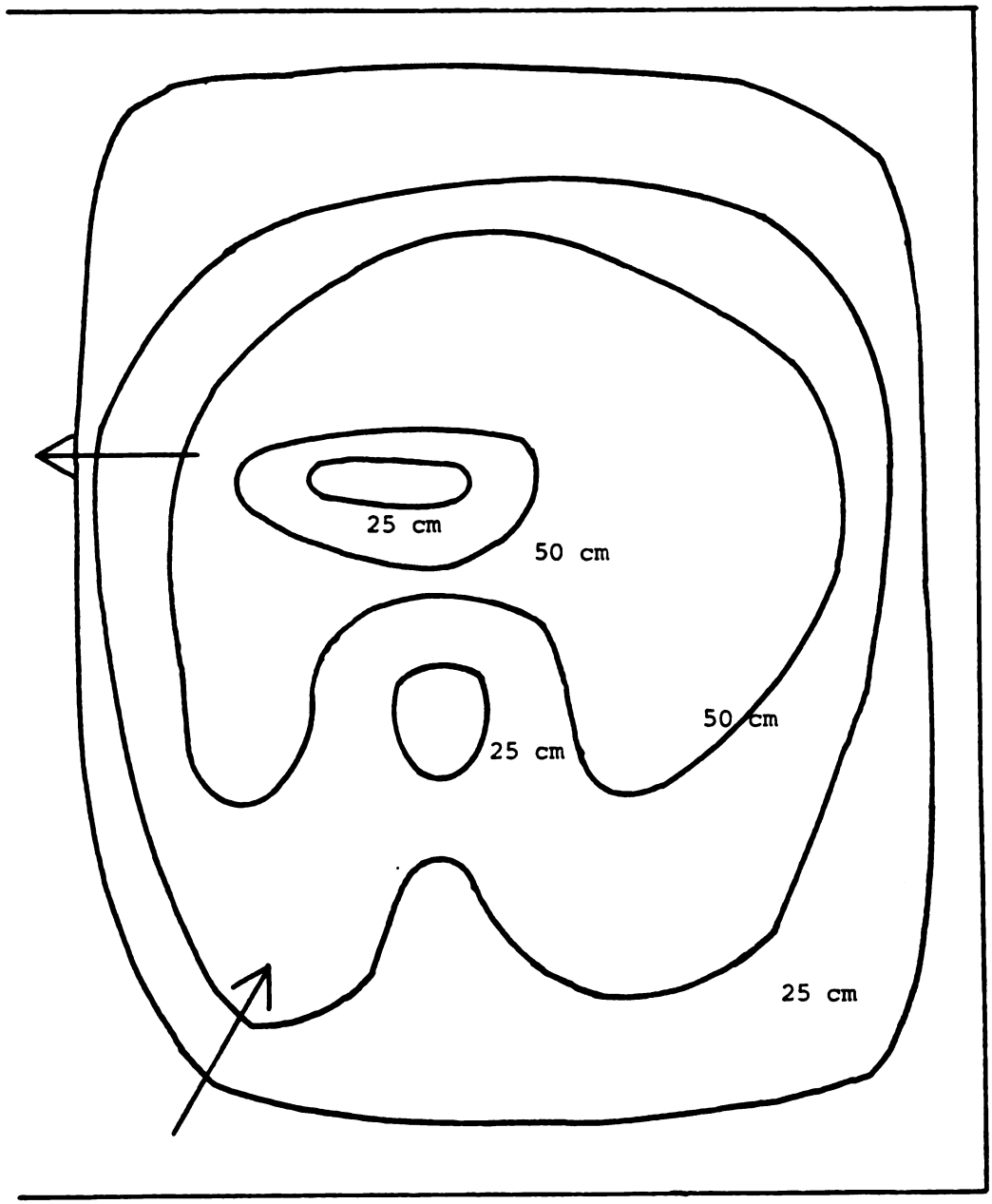


Figure 7.2 Sediment Depth of West Lagoon.

7.3 Temperature distribution

At point A4 in both lagoons a float with copper-constatan thermocouples was installed. At each float two thermocouples measured the air temperature. From the float a line of thermocouples hung down into the water with a distance of .3m between thermocouples. The thermocouples' millivolt outputs were recorded hourly by an Esterline Angus Data Collection System. These mV recordings converted into degrees Celsius with the following equation:

$$°C = 25.86 * (mV - c) - .651 * (mV - c)^2 \qquad (7.1)$$

in which c is a correction faction. A comparison with the accepted tables (Omega, 1974) shows that this equation gives the temperature within .03°C for temperatures between -20 and 40°C.

During the period in which measurements were made, the most reliable results were obtained during the first 20 days of May 1977. This period happens to be the critical period for odor production. With the aid of a computer plotting routine a series of bi-hourly measurements for air, surface and bottom temperatures are presented in Figures 7.5 - 7.8. Figure 7.5 shows that in the beginning of May the water temperature of the east lagoon has a value equal to the average daily air temperature. One can also deduce that little or no stratification occurs in the east lagoon and that the bottom temperature is almost constant.

Figure 7.3 Installation of Temperature Measurement System

Figure 7.4 Temperature Measurement System in Operation.

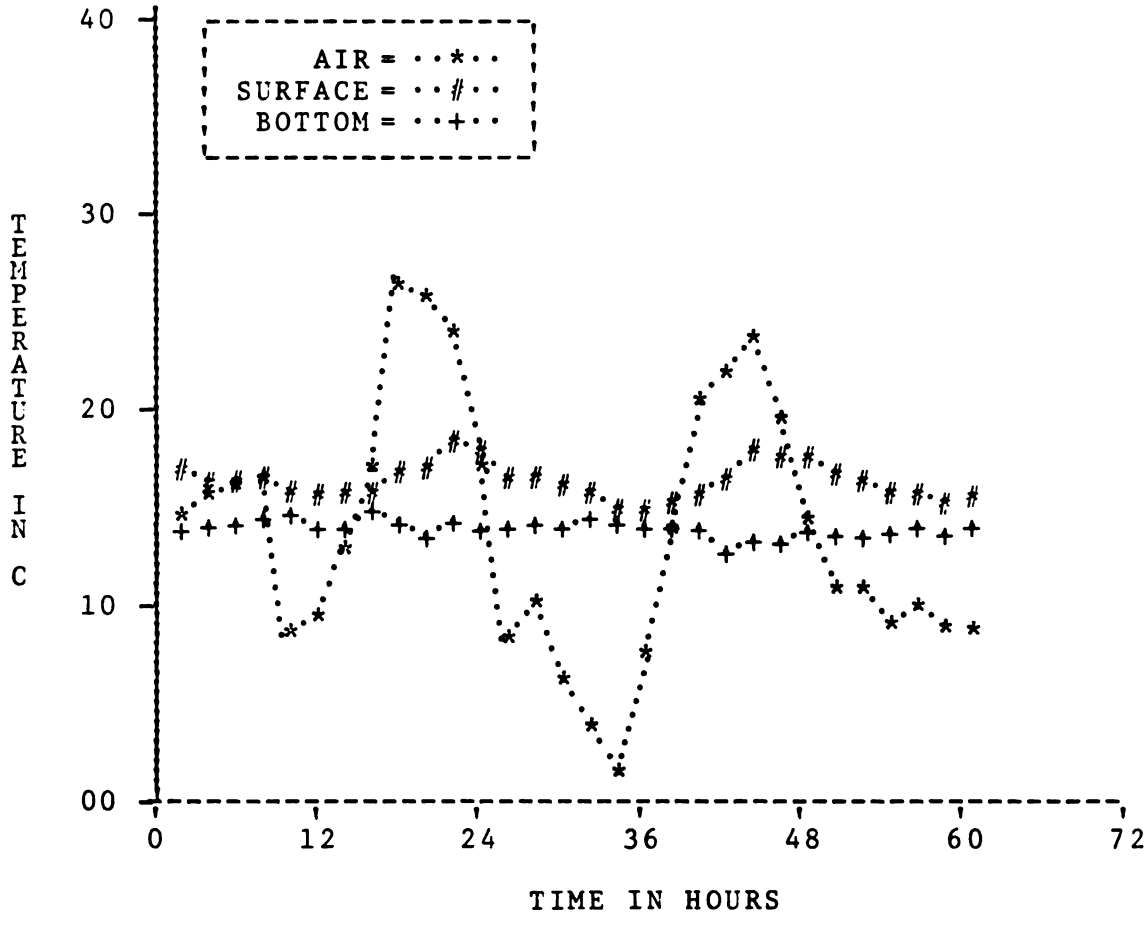


Figure. 7.5 Temperatures in the East Lagoon from May 1, 9 P.M. to May 4, 8 A.M.

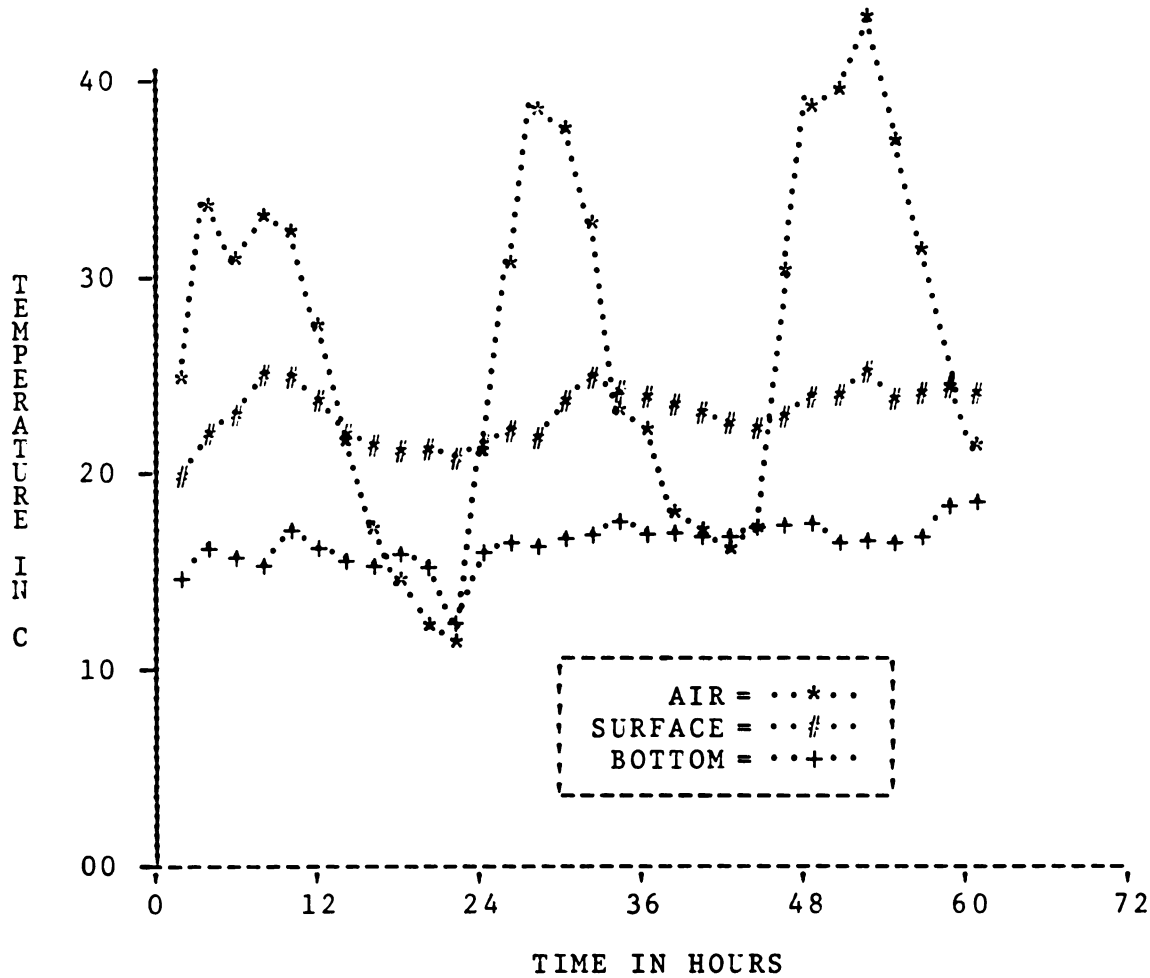


Figure 7.6 Temperatures in the East Lagoon from May 18, 9 A.M. to May 20, 11 P.M., with a Three Hour Interruption at the Thirtieth Hour.

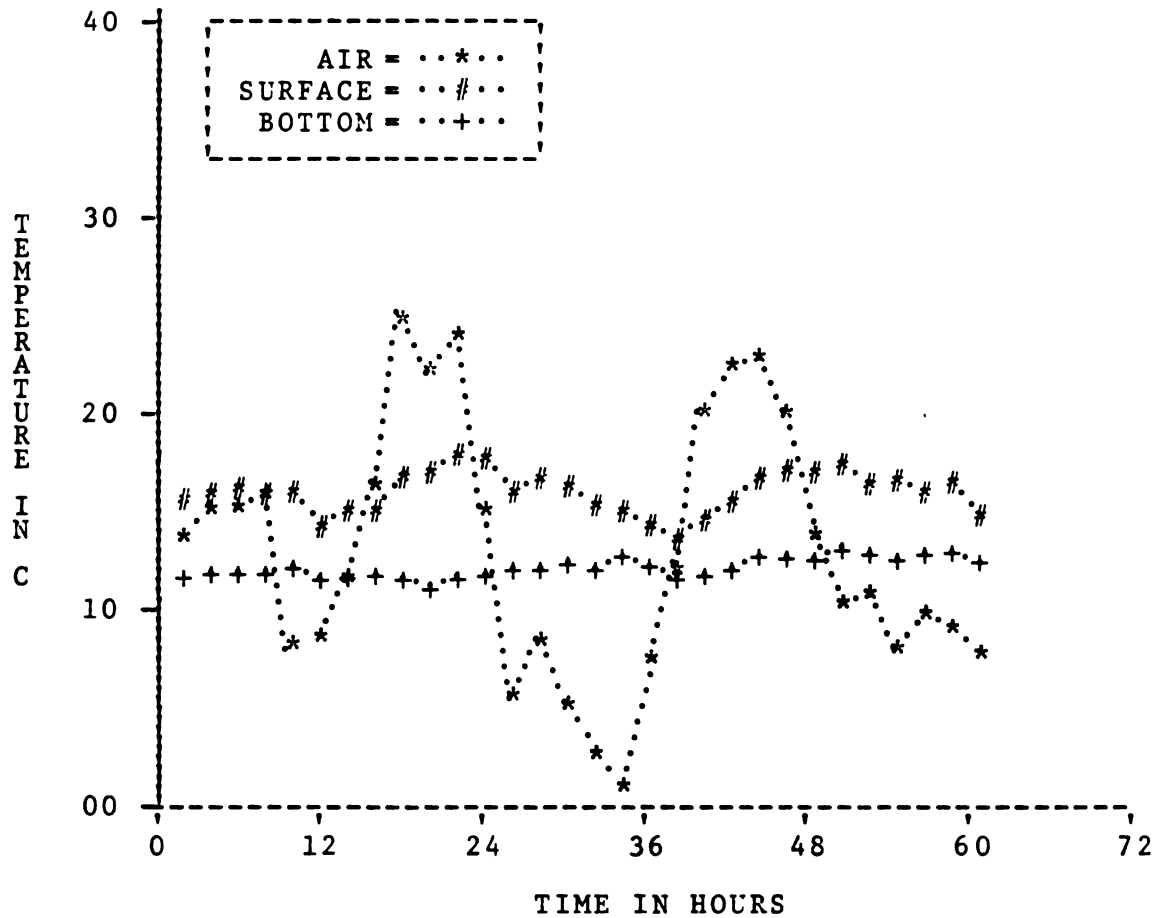


Figure 7.7 Temperatures in the West Lagoon from May 1, 9 P.M. till May 4, 8 A.M.

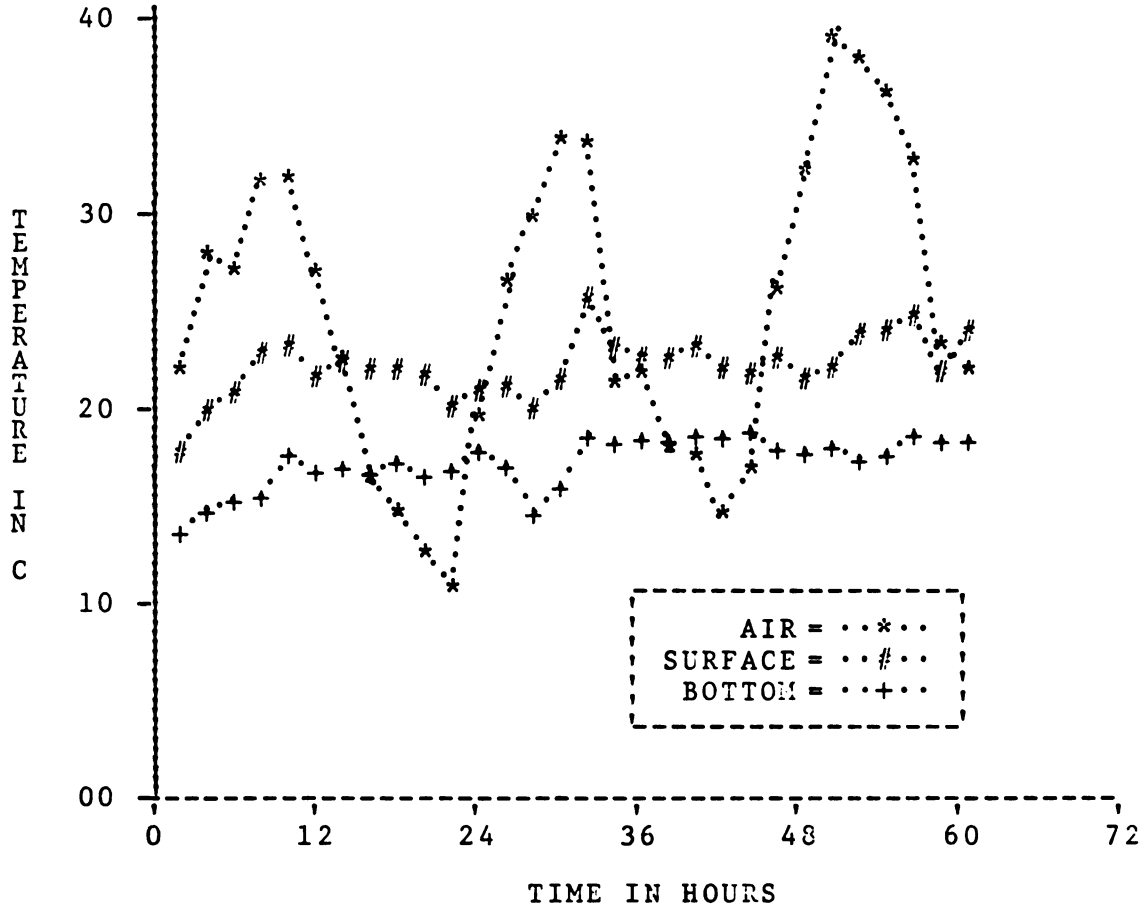


Figure 7.8 Temperatures in the West Lagoon from May 18, 9 A.M. till May 20, 11 P.M. with a Three Hour Interruption at the Thirtieth Hour.

It is important to note that the bottom temperature is high enough to allow substantial microbial activity. Comparison of Figure 7.6 with Figure 7.5 shows that during May 1977, the bottom temperature increased only slightly, while the surface temperature remained close to the daily average air temperature. Consequently temperature differences of five to ten degrees developed between the surface and the bottom.

In the beginning of May, the west lagoon (Figure 7.7) has the same surface temperature as the east lagoon, but a lower bottom temperature. The west lagoon thus shows a more stable microstratification. This difference can be explained by the higher loading rate which was applied to the east lagoon, causing greater mixing, and consequently a reduced heat loss, as is explained in Chapter 5. At the end of May this difference was no longer as pronounced. The temperatures in the west lagoon were then slightly higher than those in the east lagoon.

Because of the above mentioned higher loading rate, the east lagoon developed a more extensive scum cover than the west lagoon during the month of May. Consequently, temperature profiles can possibly be explained by a larger heat loss in the east lagoon as result of the greater surface roughness. Scum thus seems to increase the heat loss or reduce the heat gain or both.

To further verify this I calculated the heat input and output of the two lagoons, except the heat lost by evaporation. I then set the heat lost by evaporation equal to the difference between the net heat input to the lagoons and the change in heat content. The heat content of the two lagoons is plotted in the Figures 7.9 and 7.10. A linear regression, which I subsequently performed on log (Sh) against log (Re), resulted in the following values for the parameters b and c: (equation 5.14)

	b	c
East	1070	-.65
West	1.29	.32

The two linear equations are different with a 90% confidence (N = 32). The differences in b and c show, that not only are heat losses greater for the east lagoon, but also the heat loss increases with decreasing wind velocity. This phenomenon can be explained by the scum removal action of the wind.

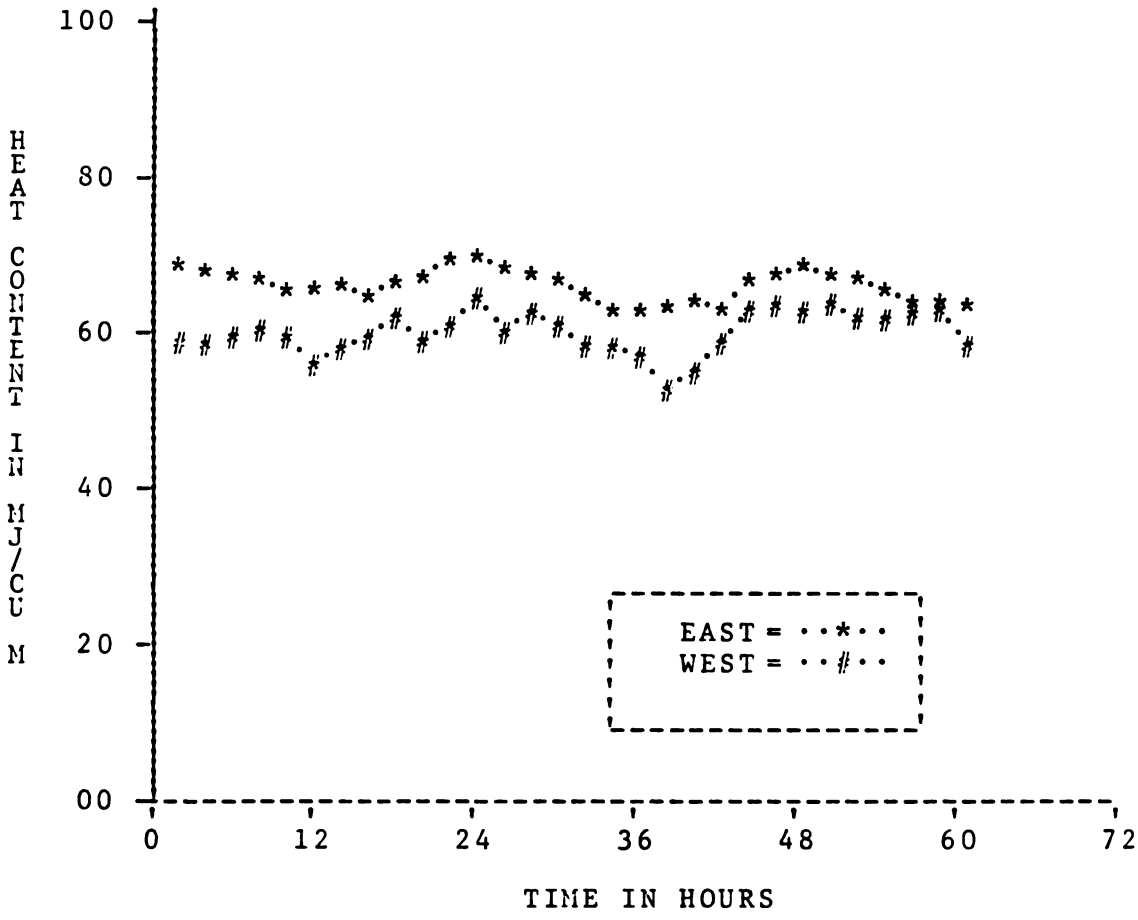


Figure 7.9 Heat Content of the Two Lagoons From May 1, 9 P.M. to May 4, 8 A.M.

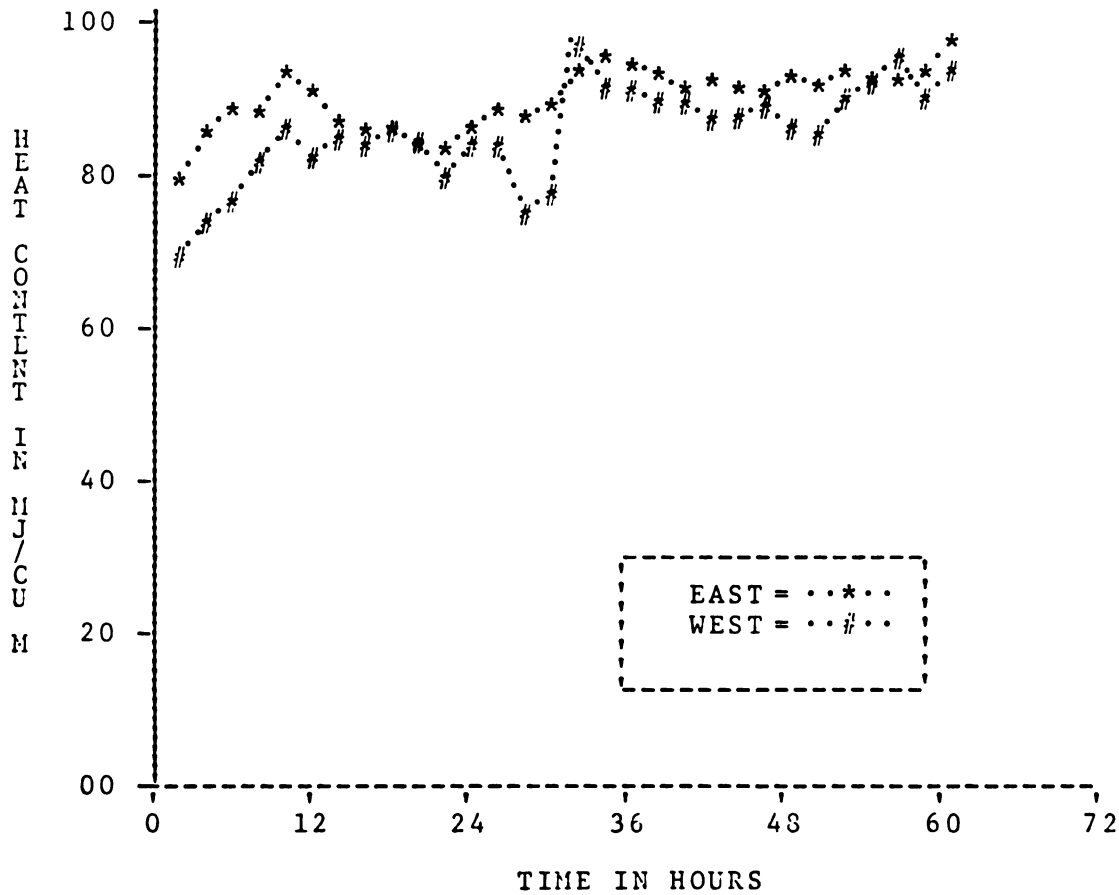


Figure 7.10 Heat Content of the Two Lagoons from May 18, 9 A.M. to May 20, 11 P.M., with an Interruption at the Thirtieth Hour.

CHAPTER 8

KINETICS

8.1 Introduction

In support of the model which I described in Chapter 6, I have conducted a series of experiments. In the following paragraphs I will describe the experimental procedures, the results obtained, and the simulation of these experiments with the model. The goal of these experiments is to determine at what rate the purple sulfur bacteria perform the conversion of hydrogen sulfide to sulfate with the intermediate storage of elemental sulfur. They are intended to show the influence of various temperatures and light intensities in the chemical and microbial environment of an anaerobic swine waste lagoon.

8.2 Experimental Procedures

Late in the afternoon, test tubes were filled with liquid from the purple west lagoon, which is described previously. In order to avoid contact of the lagoon liquid with air, the tubes were filled and closed with rubber stoppers under the surface at about the center of the lagoon. The outsides of the tubes were cleaned with distilled water to prevent formation of light-absorbing

spots and the tubes were placed in the dark as soon as possible. One hundred of such tubes were divided into four groups and exposed to light intensities of 11, 75, 205 and 540 lux after an incubation period of about 14 hours in the dark. The light and temperature regime were provided by a Sherer environmental chamber (model CEL25-7HL), which is equipped with 12 frosted incandescent light bulbs of 25 W each.

The spectral distribution of the incandescent light source is given in Figure 8.1. This spectral distribution can be approximately described by the black body relationship:

$$E = \frac{2\pi\, h'c'^{2}\, n'^{2}}{\lambda^{5}\,(\exp(h'c'/k\,T)-1)} \qquad (8.1)$$

in which:

E = Radiant energy at a wavelength ($W/m^2 \cdot m$)

h' = Planck's constant (J·s)

k = Bolzmann constant (J/K)

c' = Velocity of light in vacuo (m/s)

n' = Refactive index of an emitter

T = Absolute temperature of the body (K)

λ = Wavelength (m)

The spectral distribution of Figure 8.1 results in a value of $2.89 \cdot 10^{34}$ (including an equipment correction factor) for the group $2\pi\, h'c'^{2}\, n'^{2}$ and a value of $5.86 \cdot 10^{-7}$ for the group h'c'/kT. These values go into equation 8.1 to

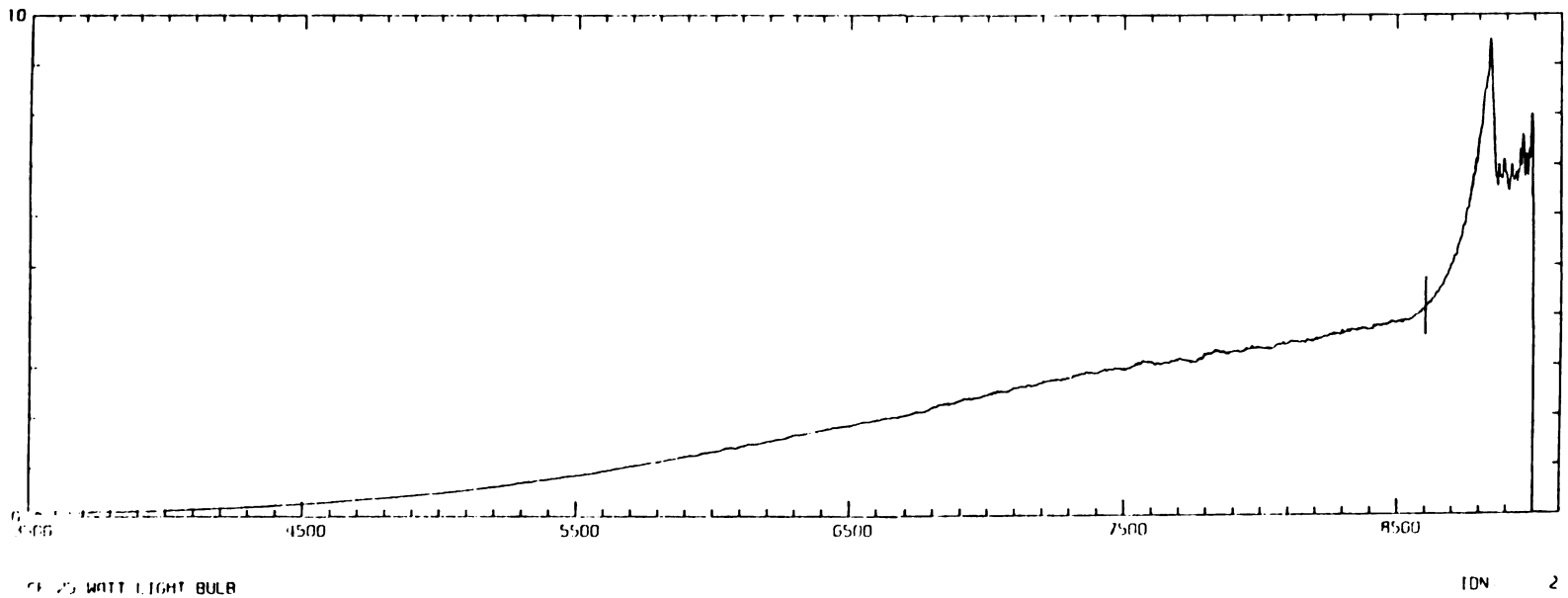


Figure 8.1 Spectral Distribution of the Incandescent Light Source.

provide a value for E which can deviate 25% for wavelengths of about $4 \cdot 10^{-7}$m and 0.3% or less at wavelengths about $5 \cdot 10^{-7}$m. Thus, the bulbs have a black body temperature of 2455 K.

Since the 12 light sources are equally distributed over the ceiling of the 0.55m by 1.25m environmental chamber, the test tubes were placed in a horizontal position at a distance of 0.9m from the light sources. The various light intensities were obtained by covering the test tubes with stretched layers of black nylon netting, which were fixed on a frame. For the light intensities of 540, 205, 75 and 11 lx, I used respectively 0, 8, 16 and 32 layers of netting.

Three temperatures were used: 10, 20 and 25°C. Every four hours, the series were sampled for sulfide and sulfate analysis and occasionally for sulfur analysis, microscopic examination and microorganism counts.

Total sulfide was analyzed with a specific ion electrode as described in Appendix B.1. Sulfate was analyzed gravimetrically as described in Appendix B.2. For the analysis of sulfur the cells were centrifuged and extracted with ethanol. The extract was transferred in the dark and the absorption spectrum was measured with a Cary double beam spectrophotometer. As described in van Gemerden (1968a), the solution of sulfur in ethanol absorbs at 260 nm. Since the absorption peak for sulfur

has to be corrected for the presence of bacteriochlorophyll and since organic contaminants from the lagoon liquid contribute to the absorption the analysis of sulfur is not very accurate in my situation. The results are therefore only used as an indication.

Occasionally, I made counts of purple sulfur bacteria with a Petroff Hauser counting chamber, but since the lagoon liquid was often contaminated with particles, the results are somewhat inaccurate.

I counted desulfurizing bacteria with a most-probable-number technique, using the medium of Baars as described by Pankhurst (1971). As reducing agent, I used titanium (III) citrate instead of sodium thioglycolate (Zehnder and Wuhrmann, 1976).

In order to obtain a more accurate description of the oxidation of sulfide I made duplicate measurements at 25°C and 540 lx, sampling the cultures every two hours. The data from these measurements were later used to support a computer simulation.

At the end of Fall, 1977, I set up an experiment to determine the maximum sulfide removal rate at 540 lx, since none of the previous experiments had sulfide concentrations which were high enough to provide this information. For this experiment, the test tubes were filled with lagoon water from a bucket, to which various quantities of a sodium sulfide solution were added.

8.3 Results and Discussion

Microscopic examination indicated the presence of Thiocapsa roseopersicina as the dominant species:

-- The cells contained globules which were light in the center and a dark ring around them, characteristic for sulfur globules.
-- The cells were round, often occurring as diplococci.
-- I could not detect any motility.
-- India ink stain indicated the typical capsulated structure.

Supporting evidence was found in the spectral measurements:

-- Ethanol extracts gave a peak at 775 nm, which is characteristic for bacteriochlorophyll a.
-- Cells suspended in a sucrose solution gave peaks at 370, 480, 511, 547, 587, 670, 798, 855 and 895 nm. Takacs (1971) gives for Thiocapsa roseopersicina cells absorption maxima at 375, 495, 515, 550, 590, 800, 850 and 890 nm.

The lagoon samples showed a sharp decrease of the H_2S concentration in the light, while the concentration increased slightly in the dark. This shows the presence of a photosynthetic sulfur bacterium. The concentration of these bacteria was about 10^8 cells/ml at the height of the bloom (September 1977).

T. roseopersicina are immotile. Turbulence such as that generated by the wind keeps these bacteria in suspension in a lagoon. In test tubes, no such mixing is available; as a result, cells tended to settle during the course of a day. Some initial longer experiments (not reported) showed a compaction of cells at the bottom of the tubes. Most of these experiments were carried out during Fall 1977. At the end of this testing program, the cells taken from the lagoon showed a tendency to settle faster in test tubes. Although cell counts in the lagoon were similar to the counts at the beginning of Fall, the activity of the cells was much lower at the end of Fall. This is probably caused by a reduction in the number of viable cells as a result of the rapidly decreasing temperatures (see also Figure 8.8).

The results of the sulfide and sulfate measurements for the experiments with various light intensities were presented in Tables (8.1, 8.2, 8.3) and Figures (8.2) through (8.7). At 11 lx, no significant removal of hydrogen sulfide occurred at any of the three temperatures. This is in agreement with a previously-mentioned compensation point figure of about 10 lx as reported by Takahashi et al. (1972).

At 75 lx the rate of sulfide oxidation seems to be almost independent of the temperature; the light intensity appears to be the rate limiting factor. For an unknown reason, the rate at 10°C, as measured, was higher than at the other two temperatures. All three temperatures show an

Table 8.1--Oxidation of Hydrogen Sulfide at 10°C and Four Light Intensities.

Light Intensity	Concentration of Soluble Sulfide at Indicated Time ($mole/m^3$)			
	9 A.M.	Noon	4 P.M.	8 P.M.
11	.60	.50	.55	.58
75	.58	.53	.45	.30
205	.57	.51	.42	.36
540	.57	.48	.39	.30

Light Intensity	Concentrations of sulfate at indicated time ($mole/m^3$)			
	9 A.M.	Noon	4 P.M.	8 P.M.
11	.64	.45	.64	.78
75	.71	.73	.57	.61
205	.65	.83	.82	.91
540	.59	.93	.94	.89

Table 8.2--Oxidation of Hydrogen Sulfide at 20°C and Four Light Intensities.

Light Intensity	Concentrations of sulfide at indicated time ($mole/m^3$) 8 A.M.	Noon	4 P.M.	8 P.M.
11	.57	.58	.58	.56
75	.57	.54	.49	.41
205	.53	.48	.38	.29
540	.54	.32	.17	.12

Light Intensity	Concentrations of sulfate at indicated time ($mole/m^3$) 8 A.M.	Noon	4 P.M.	8 P.M.
11	.29	.41	.32	.24
75	.60	.53	.46	.42
205	.48	.63	.61	.38
540	.56	.50	.67	.84

Table 8.3--Oxidation of Hydrogen Sulfide at 25°C and Four Light Intensities.

Light Intensity	Concentrations of sulfide at the indicated time (mole/m^3)		
	8 A.M.	11:10 A.M.	3:30 P.M.
11	.53	.52	.52
75	.54	.51	.46
205	.54	.46	.34
540	.53	.29	.13

Light Intensity	Concentrations of sulfate at the indicated time (mole/m^3)		
	8 A.M.	11:10 A.M.	3:30 P.M.
11	.29	.35	.42
75	.27	.40	.66
205	.27	.42	.79
540	.29	.48	.85

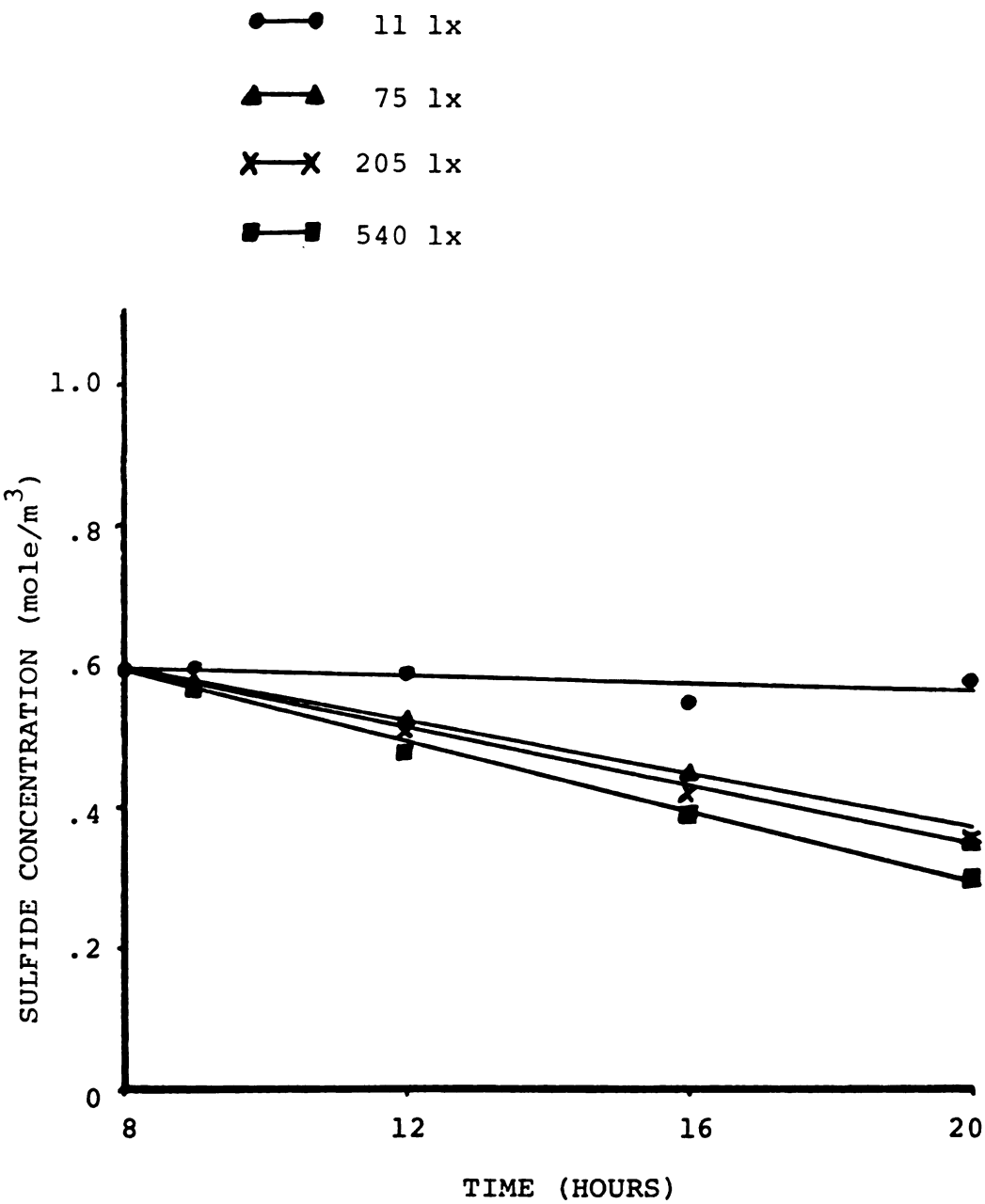


Figure 8.2 Oxidation of Hydrogen Sulfide at 10°C and Four Light Intensities.

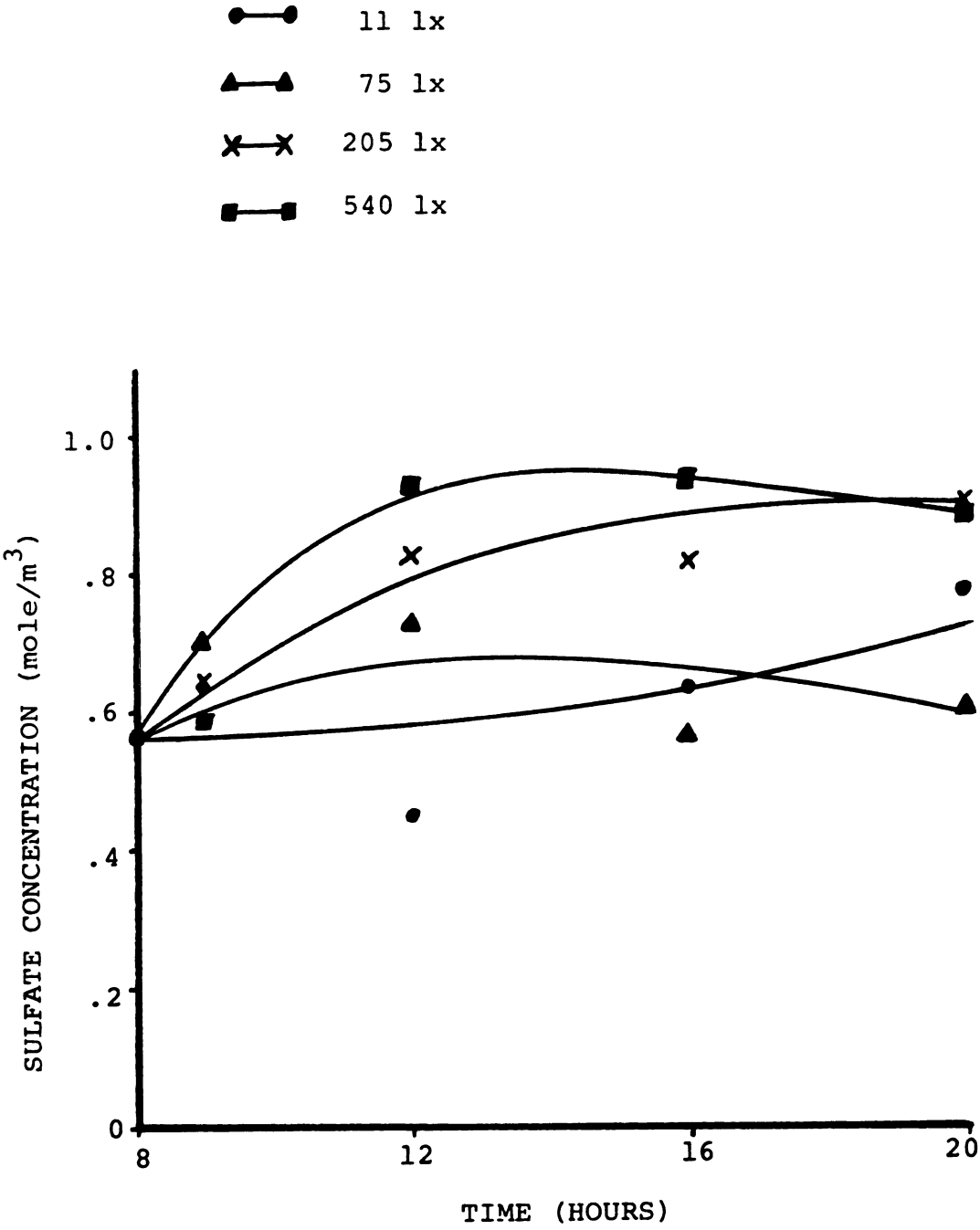


Figure 8.3 Formation of Sulfate at 10°C and Four Light Intensities.

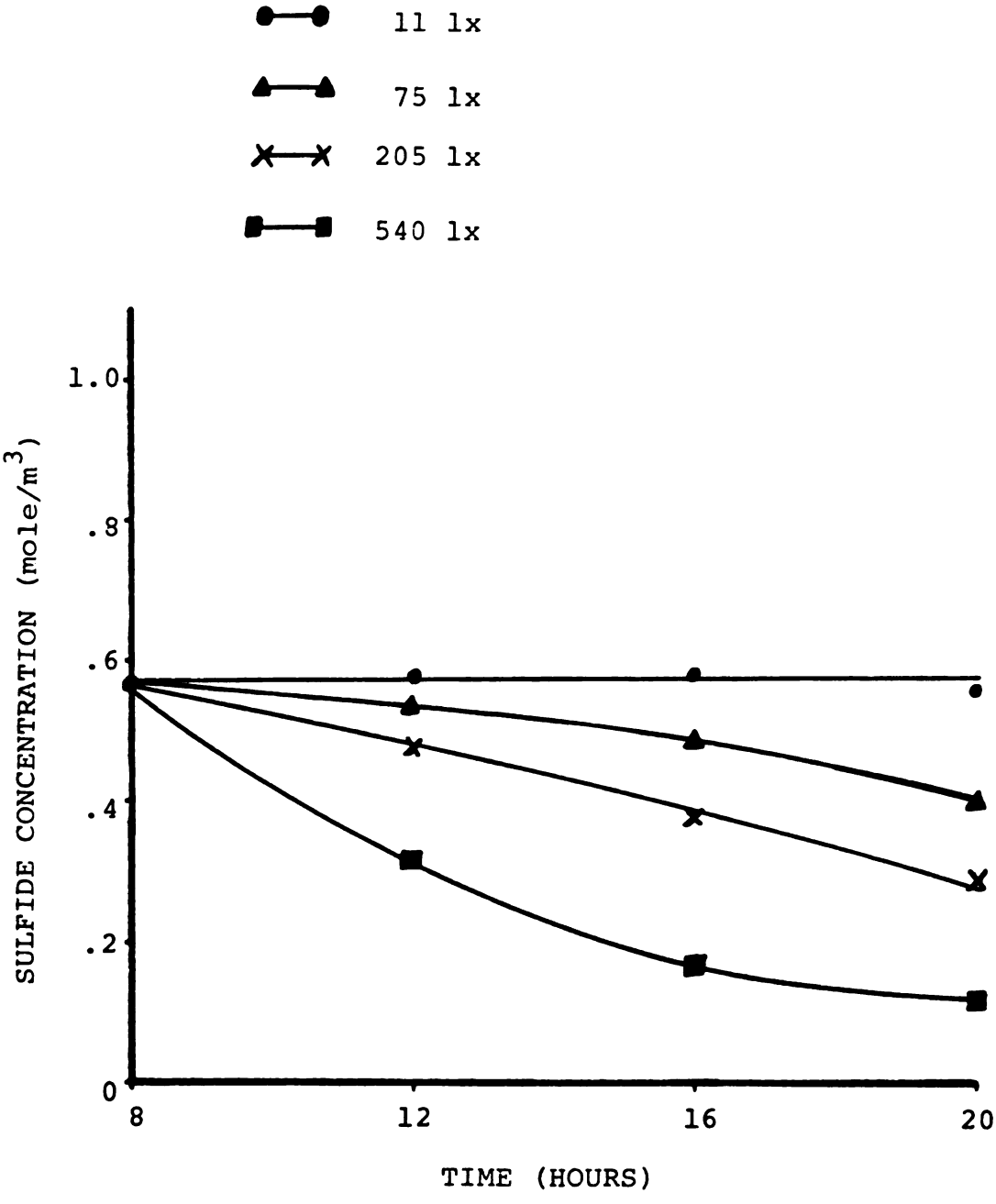


Figure 8.4 Oxidation of Hydrogen Sulfide at 20°C and Four Light Intensities.

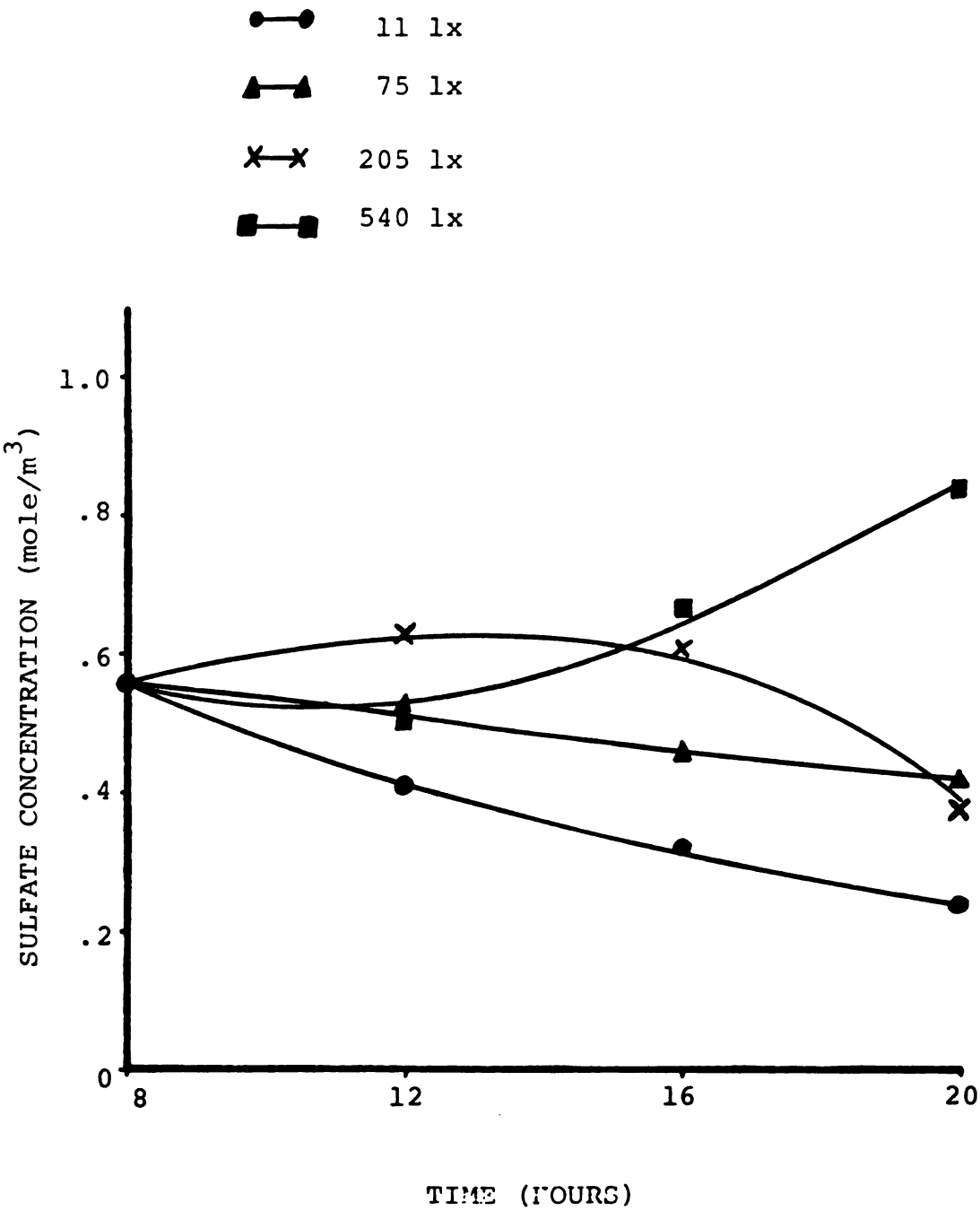


Figure 8.5 Formation of Sulfate at 20°C and Four Light Intensities.

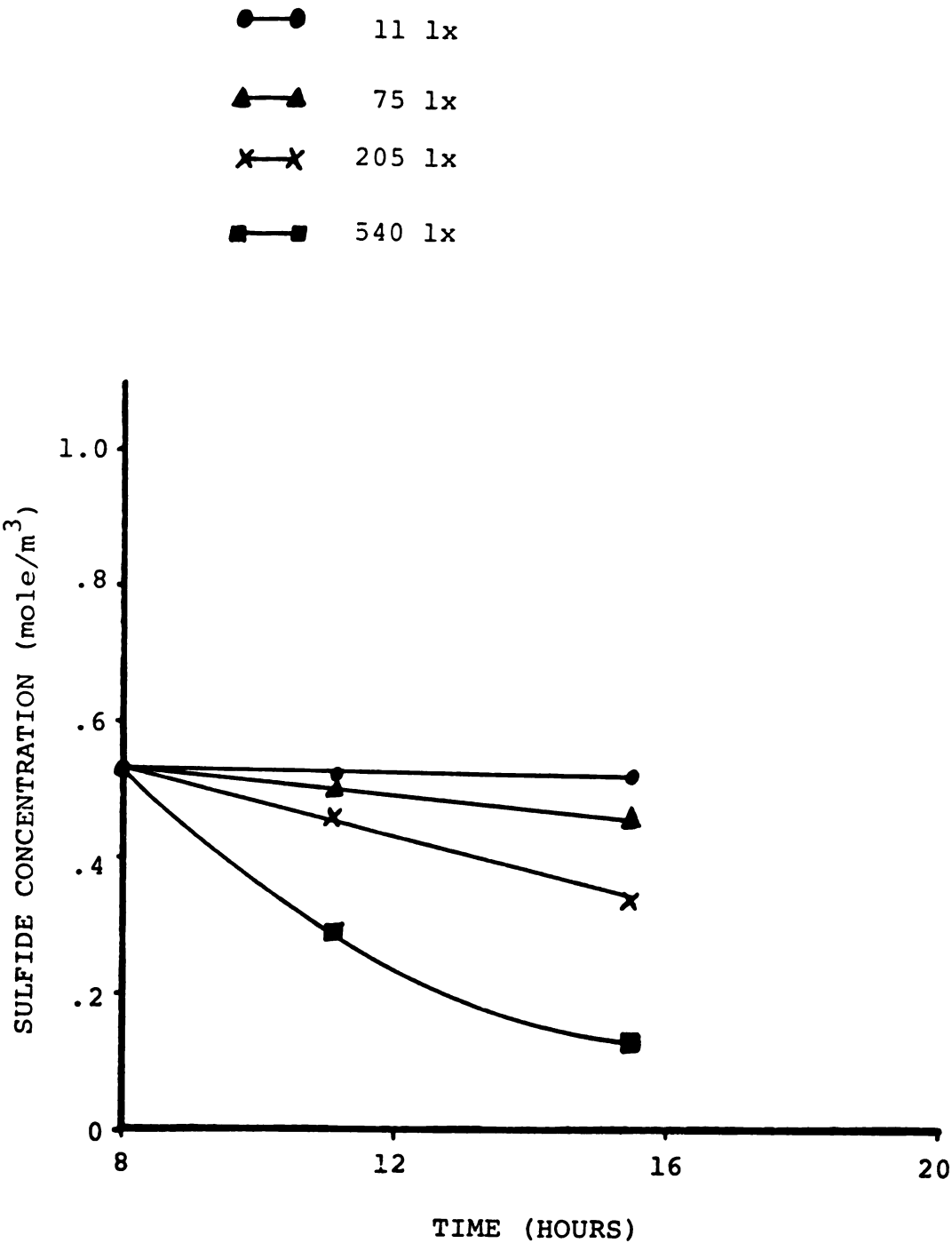


Figure 8.6 Oxidation of Sulfide at 25°C and Four Light Intensities.

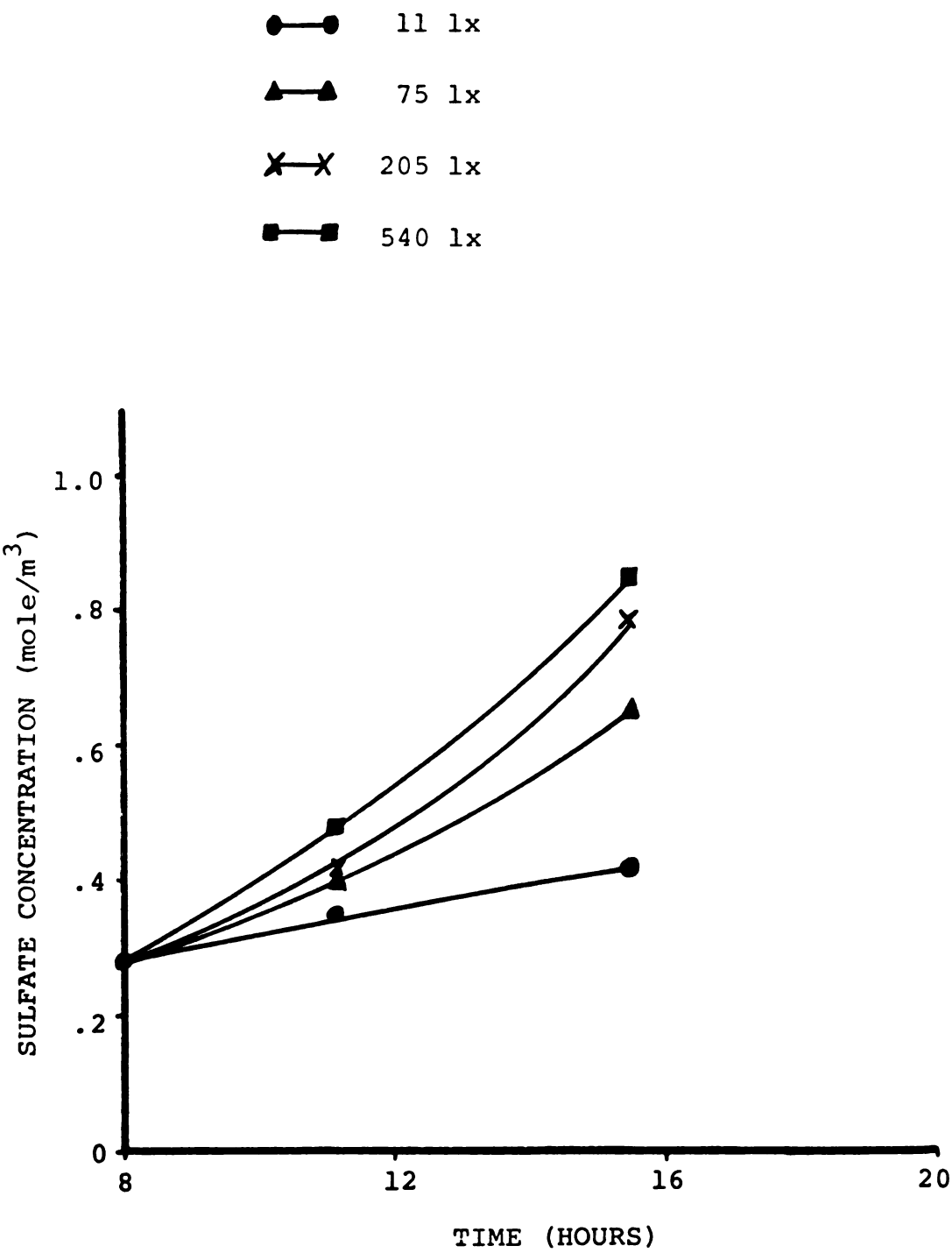


Figure 8.7 Formation of sulfate at 25°C and Four Light Intensities.

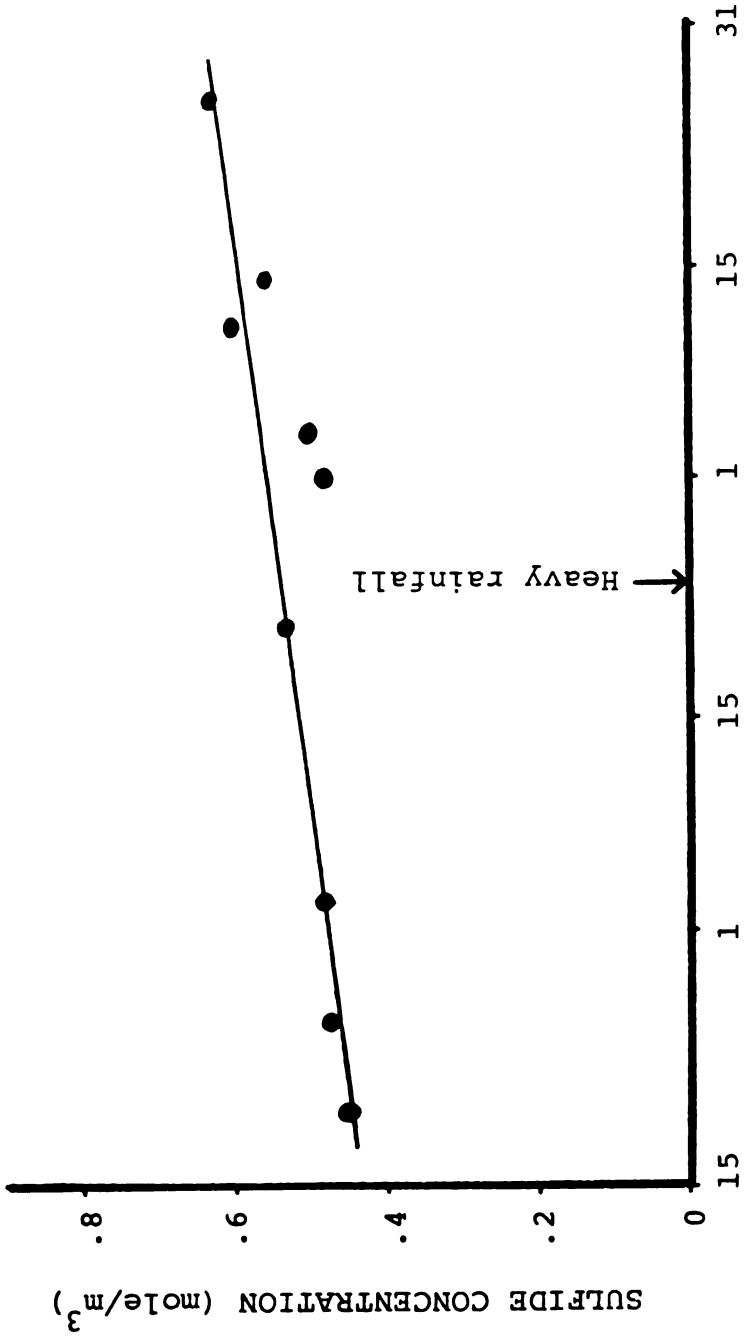


Figure 8.8 Concentration of Hydrogen Sulfide in the West Lagoon During the Fall of 1977 (measured at 5-6 P.M.).

increasing rate of sulfide oxidation with time. This is especially clear for the 20°C measurements (Figure 8.4). This can likely be explained by an adaptation of the purple sulfur bacteria to the low light intensity, resulting in an increase in concentration of bacteriochlorophyll.

At 205 lx, the rate of sulfide oxidation shows a dependence on the temperature between 20 and 25°C, resulting in a higher rate at 25°C. Between 10 and 20°C no significant change is apparent. As at 75 lx, so also at 205 lx a slight increase with time in the rate of sulfide oxidation appears. The increase in rate is with time, however, less pronounced at 205 lx.

At 540 lx a strong dependence of the rate of sulfide oxidation on temperature shows up. Comparison of the three figures (Figure 8.2, 8.4, and 8.6) reveals that below 0.3 mole/m^3 the sulfide concentration is a limiting factor in the oxidation of sulfide. No influence of desulfurizing bacteria is apparent from the sulfide measurements. The increasing rate of sulfate formation at 540 lx, while the rate of sulfide oxidation decreases, can probably be explained by the increasing reliance of the PSB on the oxidation of internally stored sulfur. The concentration of sulfate at 8 A.M. is surprisingly low for the 25°C measurements, but almost exactly the same for the different samples. The variation in samples as obtained from the lagoon is not likely to be the cause of this. In Figure

8.8, I have plotted the sulfide concentrations in the lagoon during the period that these measurements were made. All samples were taken between 5 and 6 P.M.

The average values of duplicate measurements of sulfide and sulfate concentrations for 25°C and 540 lx are presented in Table 8.4 and Figure 8.9. The slight increase in the sum of sulfide and sulfate concentration could have been caused by oxidation of internally stored sulfur. At the end of the afternoon, the sulfate concentration shows a decrease, possibly caused by an increase in the number of desulfurizing bacteria as a result of the high sulfate concentrations.

As I mentioned previously, these data were used for a computer simulation. In order to permit an accurate comparison between data and computer simulation, I have plotted the data with the computer plotting subroutine (see Figure 8.10). For the simulation of this experiment, I simplified the model presented in Chapter 6 by removing all terms which involved the addition of feces and urine, the action of gas bubbles and the release of hydrogen sulfide to the air. Basically, the data as supplied by Appendix A were used. The initial measured values for sulfide, sulfate and microorganisms were supplied. Based on the change in the sum of sulfide and sulfate, I estimated the concentration of internally stored sulfur as .05 mole/m^3. Assumed values for μ_{max4} and Y_4 were supplied,

Table 8.4--Oxidation of Hydrogen Sulfide at 25°C and 540 lx.

Time	$[H_2S]$	$[SO_4]$	$[H_2S + SO_4]$
8	.47	.16	.63
9	.27	.28	.55
10	.22	.46	.68
12	.11	.58	.69
14	.05	.66	.70
16	.04	.68	.72
18	.04	.65	.69
20	.03	.62	.65

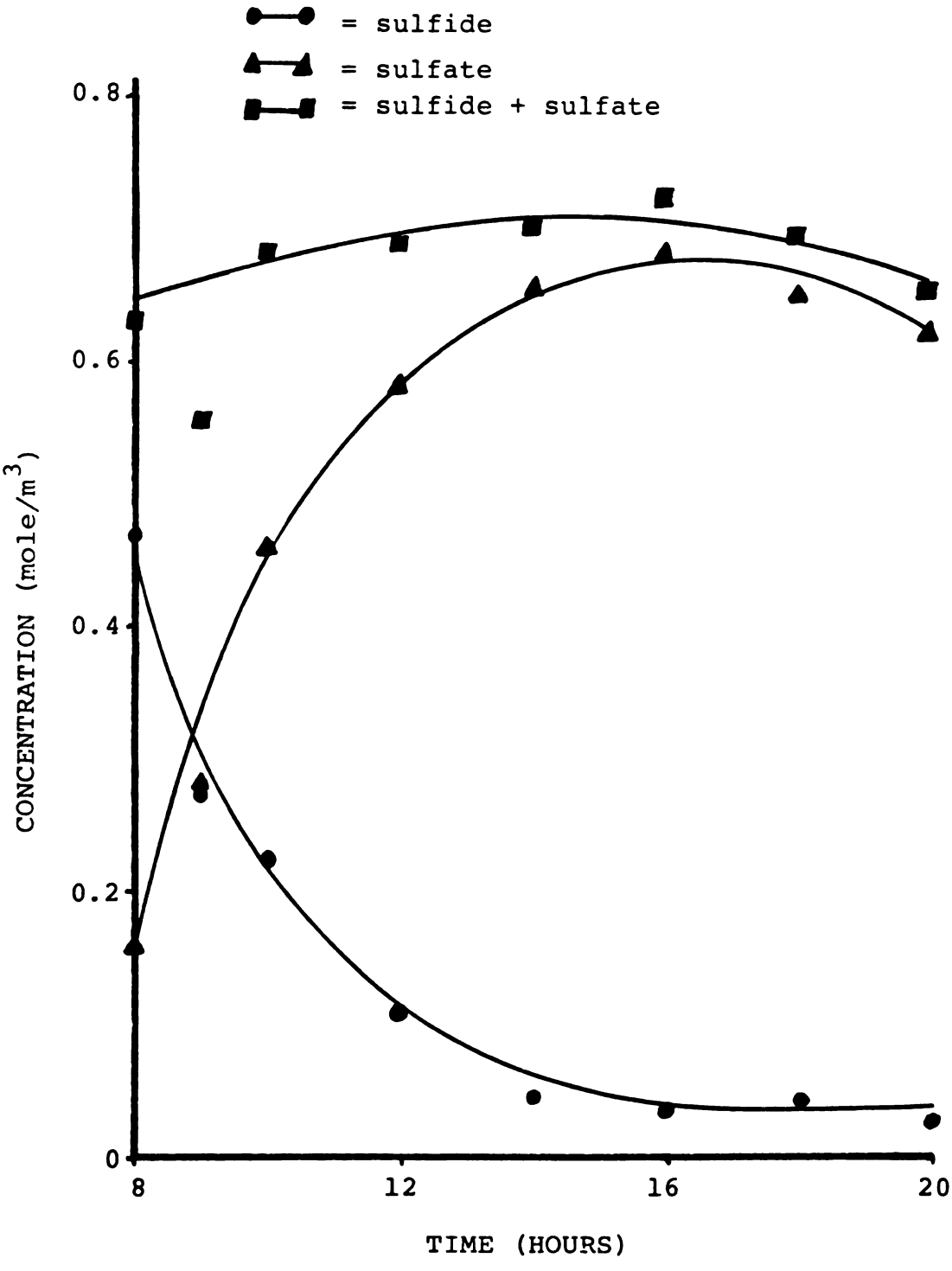


Figure 8.9 Oxidation of Hydrogen Sulfide at 25°C and 540 lx.

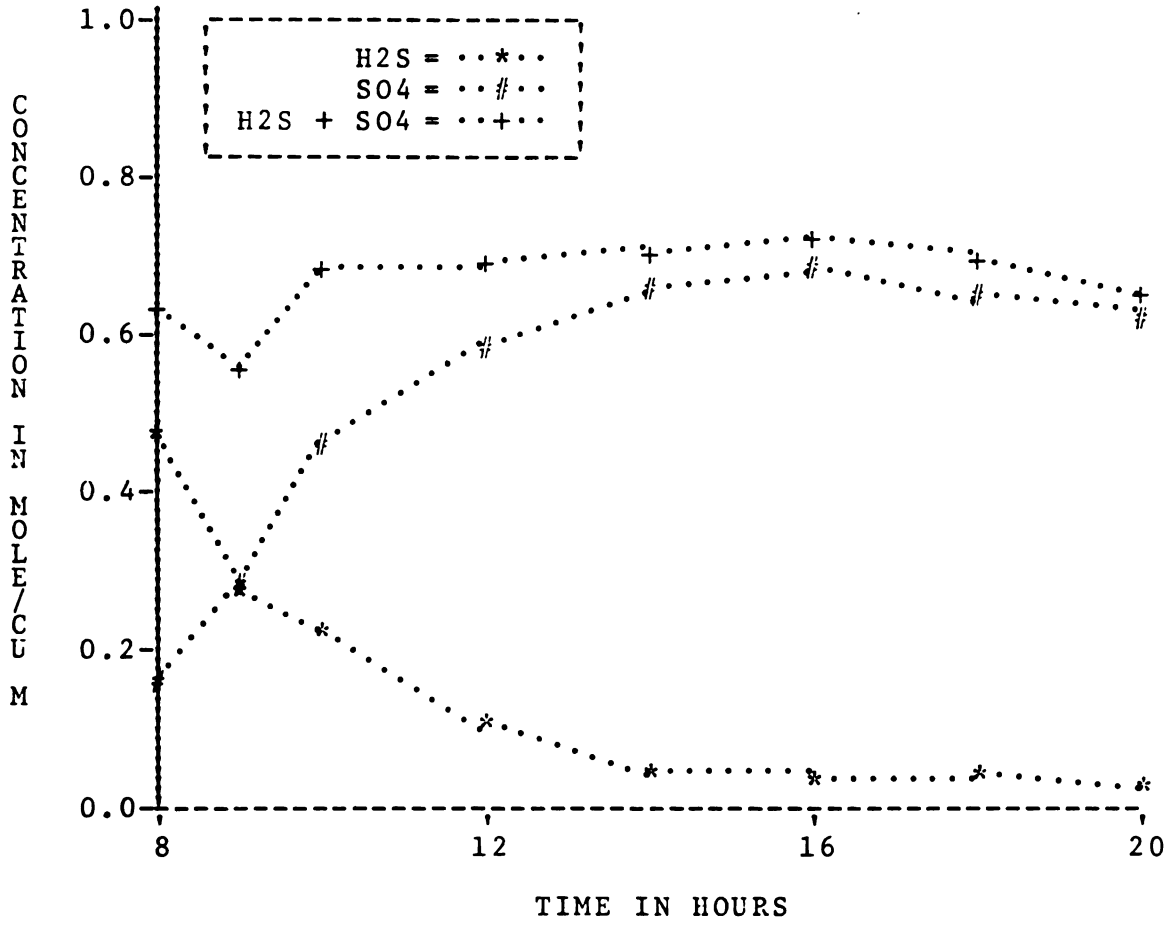


Figure 8.10 Oxidation of Hydrogen Sulfide at 25°C and 540 lx (plotted by computer subroutine).

although they appeared not to be important, since at a depth of 2 cm the light intensity is still above the compensation point (for I = 540 lux).

The computer simulation calculated rates of microbial processes which were many times too high. So I adjusted a few parameters based on the following assumptions.

1. The number of viable cells of purple sulfur bacteria is less than the direct count.
2. Under natural conditions a certain substrate is likely to be in a less accessible form as it is in a laboratory medium. This will result in an increase of the saturation constants.
3. The value for Y_2 (the yield coefficient for the oxidation of sulfide) which is unknown, is likely to be close to 1/4 of the yield coefficient for the desulfurizing bacteria, since 1/4 of the electrotransfer takes place. The formation of storage carbohydrates will temporarily lower the yield coefficient. The net effect is probably negligible since the yield coefficient is higher when storage carbohydrates are converted to structural cell material.

The best fitting simulation, as is plotted in Figure 8.11, was obtained by substituting the initial microbial concentrations of 10^{12} and 10^{10} for respectively purple sulfur and desulfurizing bacteria and K_2 = .1 and K_1 = .15 mole/m^3.

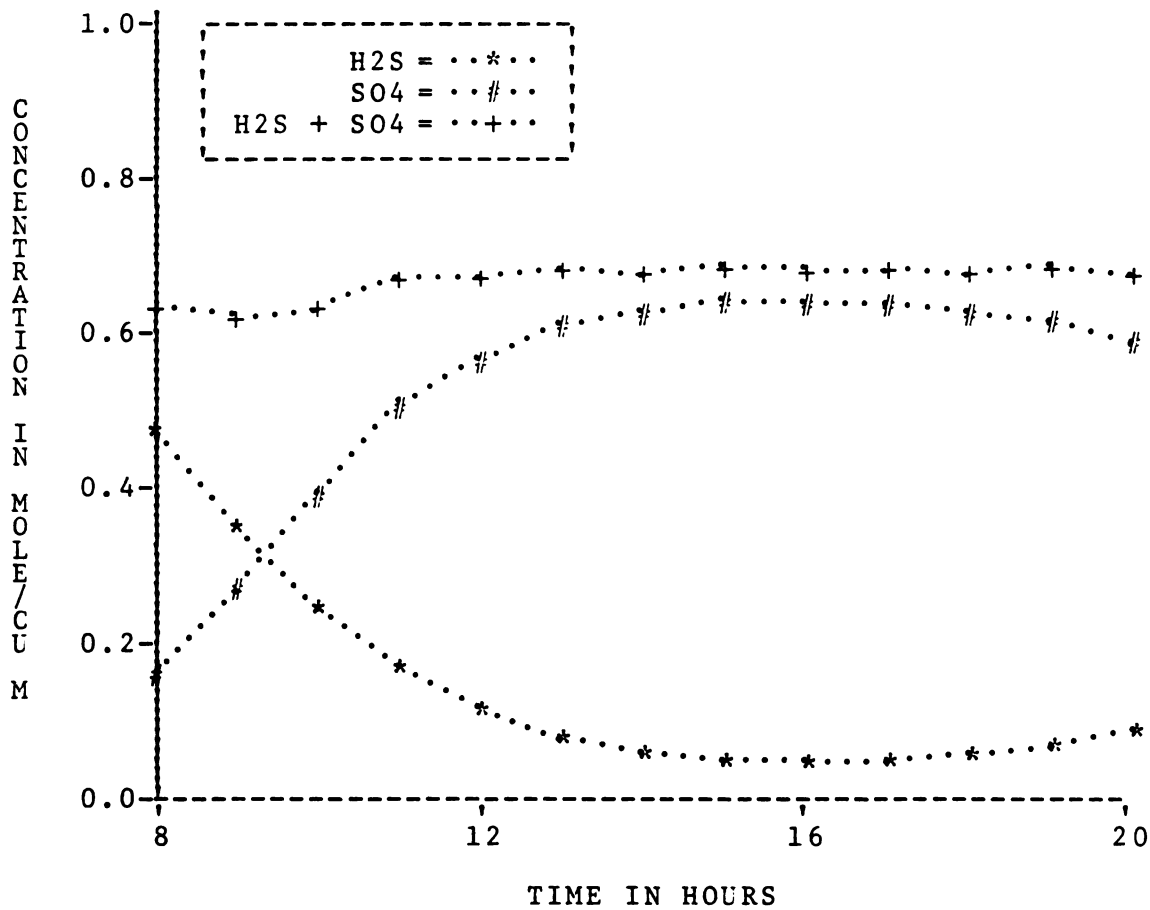


Figure 8.11 Computer Simulation of the Oxidation of Hydrogen Sulfide at 25°C and 540 lx.

As was noted above, the only effect apparent on the graph (Figure 8.9), which could possibly result from the desulfurizing bacteria would be the lowering of the sulfate concentration at the end of the afternoon. In addition to this, the desulfurizing bacterial processes probably affect the exact shape of the curves, but their influence is minor. As far as the computer simulation is concerned, the cell concentration of 10^{10} and the K_1 of .15 need not be very accurate. The K_2 of .1, however, appears to be quite critical.

The results of the measurements made to obtain the maximum hydrogen sulfide oxidation rate at 25°C and 540 lx are presented in Table 8.5 and Figures 8.12 and 8.13. A comparison with Figure 8.9 or 8.6 shows, that the maximum rate of sulfide oxidation must be decreased. This could possibly be caused by a reduction in the number of viable cells which I postulated previously.

The low point in the concentration of sulfate (Figure 8.13) is a bit strange. A possible but unlikely explanation is that the temperature in the lagoon liquid is very low, resulting in a reduced microbial activity. By introducing the liquid into a 25°C environment the desulfurizing bacteria could have become much more active, resulting in a decrease of sulfate and a slight increase in hydrogen sulfide. This is however, not in agreement with the rest of the curves. Therefore, it remains an unexplained phenomenon.

Table 8.5--Oxidation of Hydrogen Sulfide at 25°C 1x and 540 1x with Increased Starting Concentrations.

Serie	Concentrations of Sulfide at Indicated Times (mole/m^3)				
	8 A.M.	9:30 A.M.	Noon	4 P.M.	8 P.M.
1	1.25	1.06	1.00	.74	.47
2	1.13	1.02	.87	.59	.33
3	.93	.86	.69	.39	.25
4	.85	.78	.64	.33	.20
5	.63	.59	.44	.18	.15

Serie	Concentrations of Sulfate at Indicated Times (mole/m^3)				
	8 A.M.	9:30 A.M.	Noon	4 P.M.	8 P.M.
1	.24	.09	.20	.43	.48
2	.31	.09	.20	.49	.68
3	.32	.15	.34	.67	.82
4	.33	.08	.25	.52	.67
5	.37	.20	.18	.41	.52

Table 8.6--Oxidation of Hydrogen Sulfide at 540 lx and Four Temperatures.

Date*	Temperature	Concentration of sulfide at indicated times (in between parenthesis the % of the initial)				
		8 A.M.	9 A.M.	10 A.M.	11:10 A.M.	Noon
8/27	25°C a	.47 (100)	.27 (57)	.22 (47)		.11 (23)
9/22	25°C b	.53 (100)			.29 (55)	
10/5	20°C	.54 (100)				.32 (59)
9/4	15°C	.48 (100)		.35 (73)		.27 (56)
10/12	10°C	.60 (100)	.57 (95)			.48 (89)
		2 P.M.	3:30 P.M.	4 P.M.	6 P.M.	8 P.M.
	25°C a	.05 (11)		.04 (9)	.04 (9)	.03 (6)
	25°C b		.13 (25)			
	20°C			.17 (31)		.12 (22)
	15°C			.13 (27)		.07 (15)
	10°C			.39 (65)		.30 (50)

* See Figure 8.8

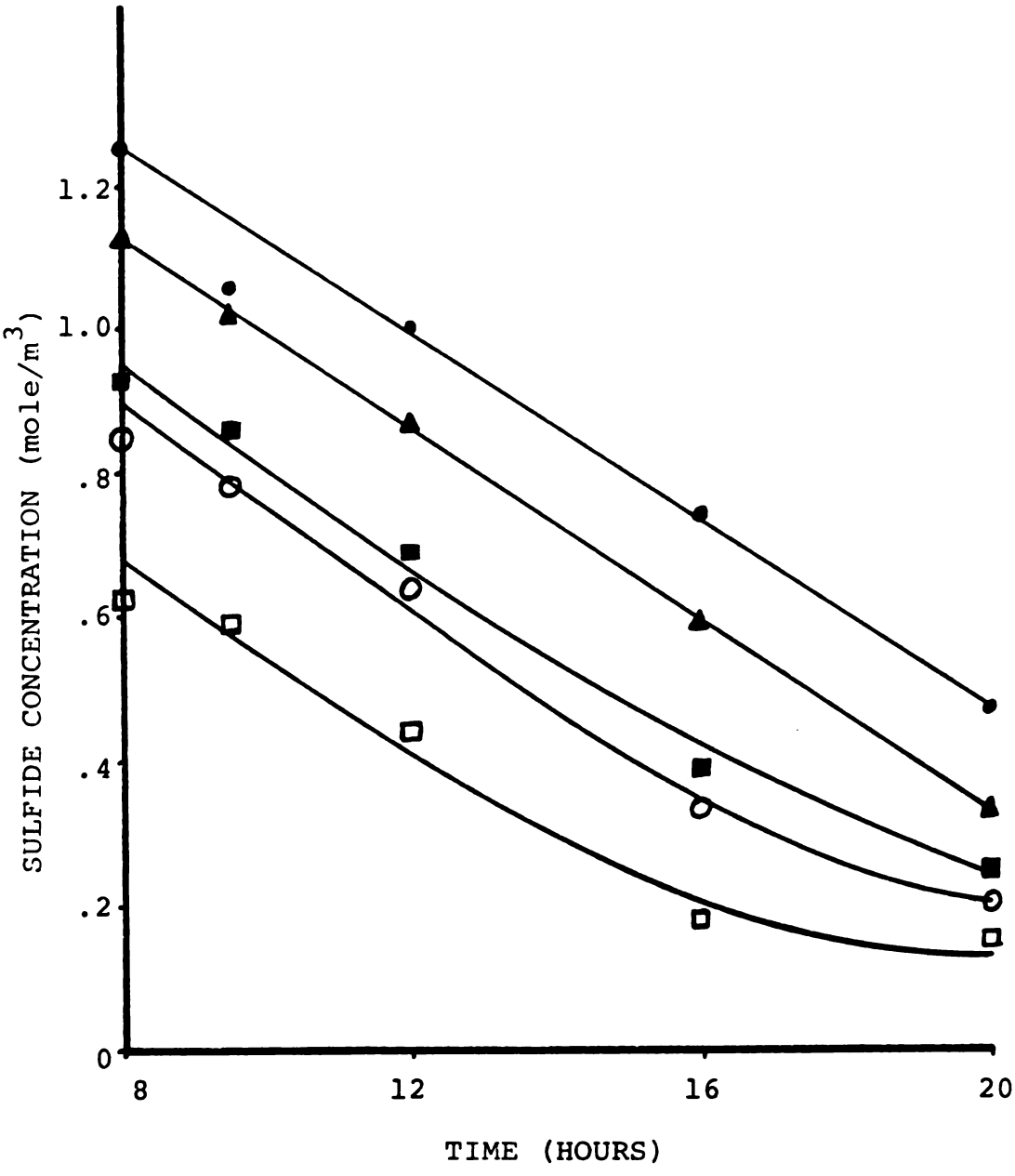


Figure 8.12 Oxidation of Hydrogen Sulfide at 25°C and 540 lx with Increased Starting Concentrations.

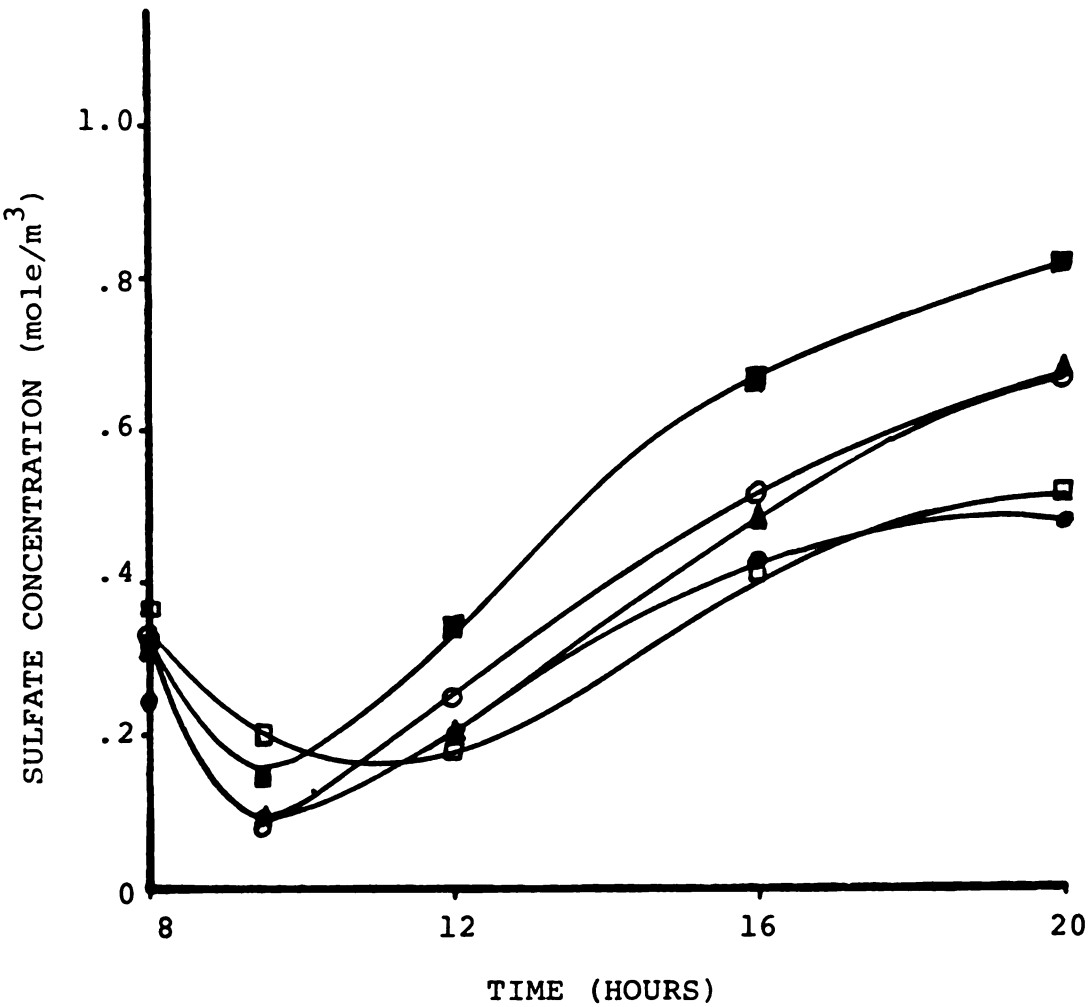


Figure 8.13 Formation of Sulfate at 25°C and 540 lx with Increased Starting Concentrations of Hydrogen Sulfide.

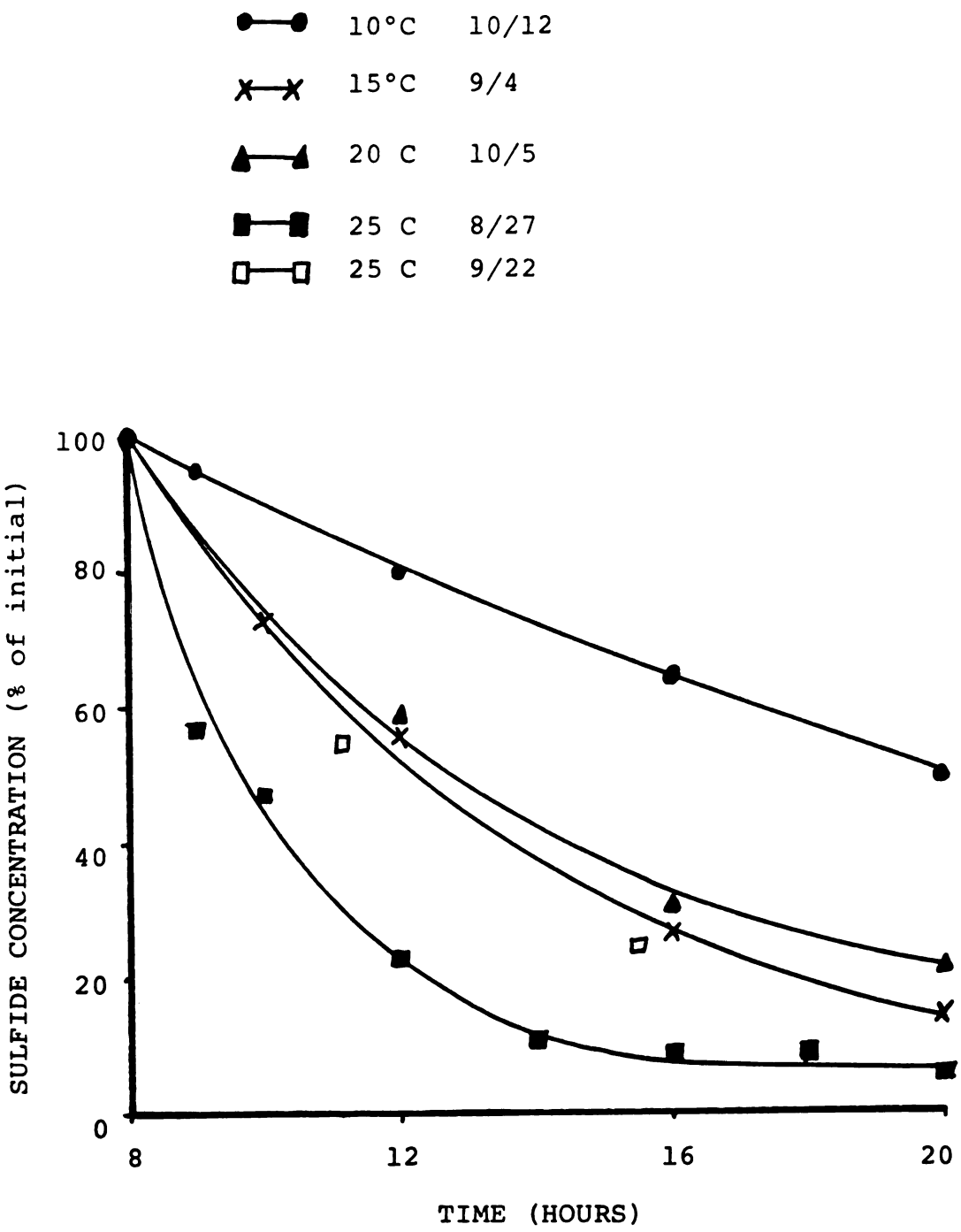


Figure 8.14 Oxidation of Hydrogen Sulfide at 540 lx and Four Temperatures.

PART IV

DISCUSSION

CHAPTER 9

MANAGEMENT IMPLICATIONS

In this chapter I will discuss various management criteria which are important in the proper operation of an anaerobic lagoon and how these management criteria are influenced by the purple sulfur bacteria. Some of these management criteria will be the same as the ones for anaerobic digestion since the basic anaerobic treatment processes, as described in Chapter 2, are the same. Some other management criteria are related to the specific properties of an anaerobic lagoon and to the specific needs of a farmer. Lagoon design criteria will also be affected by the decision to foster purple sulfur bacteria in the lagoon.

The loading rate is an important factor for lagoons as well as anaerobic digesters. Since a lagoon is not equipped with specific devices which control the environment and since a lagoon is a semi-batch system, from which the contents are removed about twice a year, the loading rate, as based on volume and quality of organic material per unit lagoon volume, has to be much lower than for an anaerobic digester. Similar to the anaerobic digestion

loading has to occur on a regular and frequent basis, (i.e., once or twice daily) to prevent conditions which upset the microorganisms. A farmer, who empties the contents of a pit into a lagoon, asks for problems. In Chapter 4, I reported that the lagoons at MSU were designed using the figure of 0.062 m^3/kg of animal weight. This is equal to the loading rate recommended by Smith and Miner (1975) and equivalent to 0.077 kg volatile solids (VS) per cubic meter (0.048 kg VS/kg animal daily manure production). In the presence of purple sulfur bacteria this loading rate does not lead to malodorous conditions.

In the design of the lagoon system at MSU, 200 m^3 were included to account for a three years' sludge accumulation. In Table 7.1 the sludge accumulation is given as measured at the beginning of 1977. From this table I estimate that the total sludge volume is slightly more than 200 m^3. The design value for sludge accumulation appears to be correct. This value is twice the volume given by Smith and Miner (1975) (i.e., 20% of the design volume).

The lagoon system at MSU consists of two identical lagoons. In Chapter 4, I described some management features which I tried out on these lagoons and which proved to be successful. I took advantage of the existence of the two lagoons by using one of them to preserve a favorable bacterial culture during the winter. Since the purple sulfur bacteria were able to survive anaerobically in the

refrigerator for more than two years, it seemed possible to obtain winter survival at culture densities that would be immediately beneficial for Spring odor control. I reduced the amount of organic material going to the purple sulfur bacteria by diverting the winter accumulation mostly to one lagoon. By pumping the most heavily loaded lagoon in the Spring, the purple sulfur bacteria in the other lagoon were preserved in a condition in which they could immediately photosynthesize in the Spring. Thus the odorous Spring episode could be avoided. The reduction of organic material can also be obtained with a single lagoon system by pumping the lagoon down to a low level in Spring and filling it partly with fresh water. The latter procedure results, however, in a larger loss of the bacterial population. The preservation of the bacterial population in the two-lagoon system can be compared with the increase in solids retention time (i.e., microorganism retention time) which is obtained in two-stage digestion and the activated sludge process by separation and recycling of solids (i.e., microorganisms).

In my opinion, the best time to pump a lagoon is the time that a noticeable increase in odor occurs. At this time the bacterial activity has substantially increased and as a result the concentration of suspended solids will be very high as compared with other times. The operator can select his/her pumpout time to take advantage of wind velocity and direction.

Figure 9.1 Pumping the East Lagoon in Fall 1977.

The purple sulfur bacteria are considered ubiquitous. In principle, therefore, inoculation is unnecessary. As described in Chapter 4, the purple sulfur bacteria don't seem to be able to cope with an increased loading rate if their number is limited. This means that a bloom of purple sulfur bacteria will only survive in a lagoon when they get a chance to develop in sufficient numbers. In marginal cases, inoculation of a lagoon with a culture can make the difference between establishment or failure of a population of purple sulfur bacteria.

Conclusions

1. Once purple sulfur bacteria have established themselves in large numbers in a lagoon it is possible to increase the loading rate of this lagoon to a certain extent without causing malodorous conditions.
2. A method of increasing the microorganism retention time has been successfully applied to an anaerobic lagoon system.
3. The MSU swine waste lagoon system appears to be working according to the design; the 1972 design criteria are satisfactory for a relatively odor-free anaerobic lagoon.
4. It is possible to operate an anaerobic lagoon in Michigan's cool-wet climate, without odor problems by following simple management guidelines and proper design criteria.
5. A froth-type scumcover on a lagoon is likely to increase the heat losses.
6. Changes in sulfide and sulfate concentrations in a mixed lagoon culture under laboratory environmental conditions are a repeatable phenomenon which can be modeled and predicted.
7. In Fall the rate of sulfide oxidation decreases resulting in rising sulfide concentrations in a lagoon. This is considered to be caused by a

decrease in the number of viable cells of purple sulfur bacteria.

8. Diurnal temperature fluctuations are not seriously affecting bacterial activity.

APPENDICES

APPENDIX A

CONSTANTS AND PARAMETER VALUES

APPENDIX A-1

Table A-1--Conversion of Units (Weast, 1976).

From	To	Multiplication Factor
Acres	m^2	4046.8564
Atmospheres	Pa	$1.01325*10^5$
Btu	J	1054.18
Btu/lb	J/kg	2324.44
Calories	J	4.184
Centipoise	kg/ms	10^{-3}
Cubic feet	m^3	0.028316847
Feet	m	0.3048
Foot-candles	lx	10.763910
Gallons	m^3	0.0037854118
Inches of Hg	Pa	3386.39
Knots	m/s	0.514444
Lamberts	lx	10^4
mm of Hg	Pa	133.3224
Phots	lx	10^4
Pounds	kg	.45359237
Square feet	m^2	.09290304
Stilbs	lx	$3.1415927*10^4$

APPENDIX A-2

Table A-2--Physical Constants (Weast, 1976).

Constant	Value	Units
A_c	0.012011	kg/at
A_s	0.03206	kg/at
c	$2.9979*10^{7}$	m/s
c_{pa} (300K)	1004.6	J/kg K
c_{pw} (273K)	4217.7	J/kg K
D_{H_2O} (281K)	$0.239*10^{-4}$	m^2/s
D_{H_2S} (289K)	$1.77*10^{-9}$	m^2/s
g	9.807	m/s^2
h'	$6.6256*10^{-34}$	J.s
K^1 (291K)	$9.1*10^{-5}$	$mole/m^3$
K^2 (291K)	$1.1*10^{-9}$	$mole/m^3$
k	$1.3805*10^{-23}$	J/K
Le (273K)	$2.50*10^{6}$	J/kg
M_w	0.01801534	kg/mole
P	$1.01325*10^{5}$	Pa
R	8.314	m^3.Pa/mole.K
λ_a (300K)	$2.64*10^{-2}$	W/m.K
λ_w (280K)	0.574	W/m.K

Table A-2 Continued.

Constant	Value	Units
μ_a (300K)	$1.84*10^{-5}$	kg/ms
μ_w (293K)	$1.002*10^{-3}$	kg/ms
ρ_a (273K)	1.2929	kg/m^3
ρ_w (273K)	1000	kg/m^3
σ'	$5.67032*10^{-8}$	W/m^2K^4

APPENDIX A-3

Table A-3--Waste Characteristics.

Parameter		Units	Reference
F	$4.1*10^{-10}$	m^3/s	Pratt et al. (1975)
U	$3.4*10^{-10}$	m^3/s	Pratt et al. (1975)
$[TS]_u$	35	$mole/m^3$	Ngoddy et al. (1971)
$[TS]_f$	33	$mole/m^3$	Ngoddy et al. (1971)
$[C]_f$	4500	at/m^3	Humenik (1977)
N	125	--	1)
w	60	kg	(Personal communication M. G. Hogberg, MSU)

1) This is a principle variable in the process of establishing an optimal loading rate for the anaerobic swine waste lagoon.

APPENDIX A-4

Table A-4--Lagoon Characteristics.

Parameter	Value	Units
L_o	10	m
W_o	5	m
$\cot\alpha$	3	--
H	2.7	m
T	15-20	^oC
$[H^+]$	$2.5*10^{-5}$	eq/m^3

All these parameters are measured. The description of the shape parameters is given in Chapter 7.

APPENDIX A-5

Table A-5--Microbial Characteristics [1)]

Parameter	Value	Units	Source
μ_{max1}	$1.4*10^{-4}$	1/s	Senez (1962)[2)]
μ_{max2}	$3.6*10^{-5}$	1/s	van Gemerden (1974)
μ_{max3} =	μ_{max2}	1/s	Trüper (1964b)
μ_{max4}	not known	1/s	
μ_{max5}	$4.22*10^{-5}$	1/s	Figure 6-3
Y_1	$1.4*10^{10}$	cells/mole	Senez (1962)[3)]
Y_2	$\sim.25*Y_1$	cells/mole	4)
Y_3	$= 3*Y_2$	cells/mole	Eqns. (3-1), (3-2) and (3-4), (3-5)
Y_4	not known	cells/mole	
K_1	.15	$mole/m^3$	From computer simulation
K_2	.007	$mole/m^3$	van Gemerden (1974)
K_3	55	m^2/m^3	van Gemerden (1971)
K_4	$=K_3$	m^2/m^3	5)
K_5	200	lx	Figure 6-3
K_I	2.5	$mole/m^3$	van Gemerden (1974)
I_1	10	lx	Takahashi et al. (1972)
N_o	2	--	Microscopical observation
ρ_s	2000	kg/m^3	van Gemerden (1968a, 1971) and Weast (1976)

APPENDIX A-6

Comments on Table A-5.

1. Since Thiocapsa roseopersicina and Chromatium vinosum show in many aspects an identical behaviour I have used the reported values for C. vinosum, if none were available to me for T. roseopersicina.
2. Value is given for Desulfovibrio desulfuricans.
3. I deduced this value from the yield coefficient (in grams of cellular material per mole of substrate) which is given by Senez (1962) for the reduction of sulfate with pyruvate and with acetate as source of carbon.
4. This is just a first estimate.
5. It is likely, that both sulfur consuming processes are governed by the same saturation constant, since not the metabolic process itself, but the transport from the globules is rate limiting, as far as these two processes can be considered separately.

APPENDIX B

ANALYTICAL METHODS

APPENDIX B

ANALYTICAL METHODS

B.1 The sulfide analysis

Many procedures have been developed for the analysis of hydrogen sulfide. Benthge (1953) describes three groups of analytical methods which are based on the oxidation of the sulfide. He concludes that the iodine method is the most accurate, but relatively insensitive and that the alkaline hypochloride method is the most sensitive, but relatively inaccurate. For all methods the precision depends on suitable oxidation conditions. In the analysis of sulfide in lagoon water many interferences for these oxidative methods can be expected, since the anaerobic environment contains many compounds in the reduced form.

The analytical methods discussed by Bethea (1973) concern the analysis of hydrogen sulfide as an odorous pollutant. All these methods are quite elaborate and are influenced by the many possible interferences. In the following I will describe the use of a specific ion electrode which I have used for my measurements. The advantages of the specific ion electrode are the simplicity of the procedure and the low number of interfering compounds.

(Mercury is known to interfere with the electrode performance. Free mercury is, however, not present in sulfide containing samples.)

The sulfide ion electrode used is the model 94-16 solid state electrode of Orion (1974). In addition to the electrode the instrumentation consists of a double junction reference electrode, a digital pH/mV meter, an electrode holder, a magnetic stirrer and stirring bar, a buret and sample beakers.

Chemicals which were used are:

- sodium hydroxide
- sodium salicylate
- ascorbic acid
- lead perchlorate (10^{-1}M, 10^{-2}M, 10^{-3}M and 10^{-4}M)
- potassium nitrate (1M)
- nitrogen

For the preservation of samples a sulfide anti-oxidant buffer (SAOB) was prepared by adding 40 g sodium hydroxide, 160 g sodium salicylate and 36 g L-ascorbic acid to 500 ml distilled water (flushed with nitrogen). The final volume was made up to 1 liter with distilled water (flushed with nitrogen). Sample bottles were filled for half of the volume (i.e., 50-60 ml) with the SAOB solution and flushed with nitrogen. At the time of sampling the content of two test tubes with sample of a combined volume of 50 ml was added to the sample bottle with SAOB and the tubes were once rinsed with a small quantity of distilled water.

Samples were titrated with a lead perchlorate solution. After each addition of lead perchlorate, a millivolt reading with the specific ion electrode was made. Small additions near the endpoint resulted in an accurate titration curve from which the endpoint was graphically determined.

After each addition of lead perchlorate, it is necessary to reach equilibrium before a millivolt reading is made. The time required for this process appeared to be a function of the age of the sample. While no significant change in the endpoint was observed, the time required for the titration could be reduced considerably by storing the sample for about 24 hours. A possible explanation for this phenomenon might be the breakdown of organic complexes.

The analysis of sulfide with a specific ion electrode gave generally values within 1% accurate. A few values will deviate 5-10% as result of a choice for a too concentrated lead perchlorate solution.

B.2 The sulfate analysis

Sulfate was determined gravimetrically with barium chloride. The content of two test tubes (50 ml) was added to a sample bottle, which contained a small quantity of activated carbon powder. The sample was subsequently acidified with a few drops concentrated hydrochloric acid and stored in a refrigerator. After centrifugation, the sample was filtered through a previously washed millipore

filter (.45 μm) and the filtercake was washed with distilled water. The filtrate was heated till the boiling point and a filtered warm solution of barium chloride was slowly added till an excess barium chloride was present. After 2 hours, the filtrate was cooled down and filtered through a washed, dried and weighed millipore filter (.45 μm). The resulting filter and filtercake were washed with warm distilled water (with a drop of ethylene glycol to reduce the surface tension) till no precipitate was formed (in the filtrate) with a silver nitrate solution. As a final step, the filter was dried till constant weight.

The experimental error in the sulfate analysis is estimated to be about 15 to 20%.

APPENDIX C

ENVIRONMENTAL DATA

Table c1. Solar radiation data.

Day \ Time	6–7	7–8	8–9	9-10	10-11	11-12	12-13	13-14	14-15	15-16	16-17	17-18	18-19	19-20	20-21
5/1	0.1	7.7	20.2	33.6	37.0	50.2	39.3	42.2	38.4	44.8	25.8	16.6	9.5	6.2	1.0
5/2	0.0	1.4	4.6	7.9	15.5	18.1	53.9	67.0	64.3	58.3	48.1	36.7	23.9	9.4	1.1
5/3	0.4	7.4	20.4	36.4	49.3	60.1	67.2	68.3	64.3	53.2	43.8	28.9	16.7	4.9	0.7
5/4	0.0	0.7	1.0	7.1	20.8	17.9	15.6	11.0	15.6	12.2	10.6	6.2	3.0	.3	0.4
5/5	0.0	2.8	11.8	10.4	14.3	51.4	66.2	68.2	63.5	56.4	47.0	34.2	22.0	8.6	1.1
5/6	?	?	?	?	?	?	?	?	?	?	?	?	?	?	?
5/7	?	?	?	?	?	?	?	?	?	?	?	?	25.3	10.9	1.4
5/8	?	?	24.0	37.2	50.9	62.6	69.4	71.0	68.4	61.8	51.5	39.4	26.0	11.5	1.6
5/9	0.6	10.2	24.1	40.4	55.9	66.6	73.1	74.2	70.3	62.6	51.7	39.1	26.2	11.2	1.6
5/10	1.1	9.8	24.1	38.2	51.2	62.3	70.3	72.5	68.9	61.9	52.3	38.6	25.3	11.5	1.6
5/11	1.4	10.9	24.6	38.6	51.7	62.8	69.2	70.8	67.4	60.4	49.6	37.1	24.0	10.2	1.6
5/12	0.6	5.5	12.1	15.8	31.1	48.1	43.4	40.9	40.8	50.3	41.8	34.4	22.1	8.0	1.9
5/13	1.2	8.6	21.2	34.8	46.7	56.8	62.4	65.6	63.0	57.2	48.1	36.0	24.0	10.3	1.7
5/14	1.2	8.8	20.3	34.5	48.5	59.4	66.7	70.0	65.6	58.4	49.1	36.8	24.2	10.8	1.3
5/15	1.4	10.9	24.6	38.8	51.5	62.4	70.3	72.0	67.3	60.2	48.0	37.3	24.6	11.4	1.7
5/16	1.1	7.3	19.1	32.2	39.8	54.2	61.3	64.1	62.8	55.3	43.6	34.1	21.6	9.4	1.4

MAY 1977
LANSING, MICHIGAN
NATIONAL WEATHER SERVICE OFC
CAPITAL CITY AIRPORT

Local Climatological Data

MONTHLY SUMMARY

MAY 1977 LANSING, MICHIGAN

LATITUDE 42° 47 'N LONGITUDE 84° 36 'W ELEVATION (GROUND) 841 FT. STANDARD TIME USED: EASTERN WBAN 14836

DATE	TEMPERATURE °F MAXIMUM	MINIMUM	AVERAGE	DEPARTURE FROM NORMAL	AVERAGE DEW POINT	DEGREE DAYS BASE 65° HEATING (DAILY)	DEGREE DAYS BASE 65° COOLING (DAILY)	WEATHER TYPES OR DATES OF OCCURRENCE	SNOW, ICE PELLETS OR HAIL ON GROUND AT 0700 LST IN.	PRECIPITATION WATER EQUIVALENT IN.	PRECIPITATION SNOW, ICE PELLETS IN.	SEA LEVEL PRESSURE MEAN MB ELEV. 879 FEET M.S.L.	WIND RESULTANT DIR.	WIND RESULTANT SPEED M.P.H.	WIND AVERAGE SPEED M.P.H.	WIND FASTEST MILE SPEED M.P.H.	WIND FASTEST MILE DIRECTION	SUNSHINE MINUTES	SUNSHINE PERCENT OF POSSIBLE	SKY COVER TENTHS SUNRISE TO SUNSET	SKY COVER TENTHS MIDNIGHT TO MIDNIGHT	DATE
1	75	41	58	0	48	7	0		0	.01	0	29.16	20	8.5	8.8	18		603	82	8	7	1
2	68	48	58	0	46	7	0	1	0	.02	0	29.19	04	3.9	7.6	16		567	67	9	7	2
3	68	37	53	0	38	12	0		0	0	0	29.27	08	8.7	8.2	17		712	84	8	8	3
4	83	48	66	13	51	0	1	1	0	.03	0	29.02	06	8.3	7.3	17		89	11	10	10	4
5	80	54	67	14	55	0	2	1	0	.02	0	28.76	25	8.0	13.7	28	W	0	0	9	9	5
6	78	50	64	10	48	1	0		0	0	0	28.82	28	8.8	8.8	20	W	857	101	9	9	6
7	81	48	65	11	50	0	0		0	0	0	29.16	02	9.8	7.8	19	W	880	100	0	1	7
8	86	53	70	16	52	0	5		0	0	0	29.08	32	10.9	12.8	32	W	885	100	1	1	8
9	86	56	71	17	53	0	6		0	0	0	29.20	01	7.5	8.6	20	W	885	100	1	1	9
10	86	48	67	13	53	0	2		0	0	0	29.18	30	4.0	4.6	14	W	887	100	1	1	10
11	71	50	61	7	49	4	0		0	0	0	29.20	27	9.8	8.8	19	W	888	100	1	1	11
12	78	49	64	10	49	1	0		0	0	0	29.18	27	10.7	10.8	26	W	885	100	1	0	12
13	86	57	72	18	55	0	7		0	0	0	29.04	28	11.4	12.9	28	W	838	94	4	4	13
14	78	48	63	7	50	2	0		0	0	0	29.08	07	9.3	8.2	21	W	788	91	4	4	14
15	81	48	65	9	50	0	0		0	0	0	29.16	14	7.3	7.8	13	E	811	91	4	3	15
16	80	55	68	12	48	0	3		0	0	0	29.20	30	8.2	8.4	18	E	729	82	4	3	16
17	88	63	76	20	55	0	11	1	0	0	0	29.13	22	8.8	10.8	28	E	672	76	8	8	17
18	88	62	75	19	55	0	10	1	0	0	0	29.08	27	10.8	12.4	30	E	784	90	8	8	18
19	80	60	70	12	55	0	5	1	0	0	0	29.18	12	6	5.0	14	E	807	91	8	8	19
20	83	56	70	12	50	0	5		0	0	0	29.15	18	6.4	6.0	16	E	838	94	8	8	20
21	88	66	80	22	58	0	15		0	0	0	29.11	17	10.4	11.1	21	E	788	88	7	7	21
22	88	70	80	21	59	0	15	3	0	.01	0	29.11	18	11.8	12.2	24	E	852	73	7	8	22
23	81	68	80	21	61	0	15		0	1	0	29.21	20	8.8	7.8	21	E	862	73	7	8	23
24	87	61	74	14	63	0	9		0	1	0	29.24	23	2.8	3.3	20	E	728	81	8	8	24
25	88	60	74	14	61	0	9	1	0	1	0	29.18	09	4.1	5.3	14	E	815	91	8	8	25
26	81	48	64	4	51	1	0		0	0	0	29.14	08	5.8	6.3	11	E	872	97	3	2	26
27	84	41	63	2	47	2	0		0	0	0	29.02	07	2.8	2.8	8	E	900	100	2	1	27
28	81	48	65	4	48	0	0		0	0	0	28.86	35	3.1	4.2	12	E	877	97	3	2	28
29	77	54	66	5	62	0	1		0	0	0	28.88	07	8.4	8.8	18	E	868	77	10	9	29
30	80	47	64	2	48	1	0		0	0	0	29.13	08	7.9	7.8	15	E	743	82	4	5	30
31	82	52	67	5	57	0	2	3	0	.02	0	29.12	01	1.8	10.9	25	W	901	95	8	8	31
	HIGH 88	LOW 37				TOTAL 137	TOTAL 124			TOTAL .62	TOTAL 0	29.10	22	1.0	8.4	32	W	TOTAL 23018		FOR 154	FOR 133	
	AVG 2964	AVG 1921						NUMBER OF DAYS										AVG 742		AVG	AVG	
	AVG 78.5	AVG 48.1	AVG 64.3	DEP 7.5	AVG 49	DEP -143	DEP 88	PRECIPITATION .01 INCH OR MORE		7		DEP -2.70						DATE 08				
						SEASON TO DATE		SNOW, ICE PELLETS 1.0 INCH OR MORE		0								TOTAL 27218		5.0	4.3	

NUMBER OF DAYS MAXIMUM TEMP. ≤ 32°	MINIMUM TEMP. ≤ 32°	MAXIMUM TEMP. ≥ 90°	MINIMUM TEMP. ≥ 70°	HEATING DEGREE DAYS TOTAL	HEATING DEGREE DAYS DEP	COOLING DEGREE DAYS TOTAL	COOLING DEGREE DAYS DEP
0	0	0	0	845	117	12	8

GREATEST 1 TO 24 HOURS AND DATES			GREATEST DEPTH ON GROUND OF SNOW, ICE PELLETS OR ICE AND DATE
PRECIPITATION	SNOW, ICE PELLETS		
.52 31	0		0

THUNDERSTORMS	2
HEAVY FOG	0
CLEAR 12	PARTLY CLOUDY 10
CLOUDY 8	

- EXTREME FOR THE MONTH - LAST OCCURRENCE IF MORE THAN ONE.
T TRACE AMOUNT
+ ALSO ON AN EARLIER DATE, OR DATES.
WEATHER TYPES - VISIBILITY 1/4 MILE OR LESS.
FIGURES FOR WIND DIRECTIONS ARE TENS OF DEGREES CLOCKWISE FROM TRUE NORTH: 00 = CALM. DATA IN COLS. 6 AND 12-15 ARE BASED ON 7 OB

HOURLY OBSERVATIONS PER DAY AT 3-HOUR INTERVALS. FASTEST MILE WIND SPEEDS ARE FASTEST OBSERVED ONE-MINUTE VALUES WHEN DIRECTIONS ARE IN TENS OF DEGREES. THE / WITH THE DIRECTION INDICATES PEAK GUST SPEED
ANY ERRORS DETECTED WILL BE CORRECTED AND CHANGES IN SUMMARY DATA WILL BE ANNOTATED IN THE REMARKS SUMMARY

SUMMARY BY HOURS

HOUR LOCAL TIME	AVERAGES SKY COVER TENTHS	STATION PRESSURE IN.	TEMPERATURE DEW PT.	TEMPERATURE WET BULB °F	TEMPERATURE DRY BULB °F	RELATIVE HUMIDITY %	WIND SPEED M.P.H.	RESULTANT WIND DIRECTION	RESULTANT WIND SPEED M.P.H.
01	5	29.11	47	52	61	72	6.8	17	2.2
04	5	29.10	45	49	58	80	5.8	16	1.3
07	5	29.19	45	49	57	84	6.6	16	1.3
10	5	29.14	48	52	64	81	8.8	27	1.3
13	6	29.11	49	51	61	68	10.7	28	1.0
16	9	29.07	48	51	60	72	11.2	28	3.5
19	8	29.08	49	50	60	69	8.8	24	1.7
22	7	29.08	47	50	60	65	7.8	19	1.8

HOURLY PRECIPITATION (WATER EQUIVALENT IN INCHES)

DAY	A. M. HOUR ENDING AT 1	2	3	4	5	6	7	8	9	10	11	12	P. M. HOUR ENDING AT 1	2	3	4	5	6	7	8	9	10	11	12	DAY
1																		.01	T						1
2					.01	.01																			2
3						T	T	.01	.03																3
4				.01	.01	T																			4
5																									5
6																									6
7																									7
8																									8
9																									9
10																									10
11																									11
12																									12
13																								.01	13
14	T																								14
15																									15
16																									16
17																			T	T					17
18																									18
19																									19
20																									20
21															T	T		.01	T						21
22																			T						22
23																									23
24																									24
25																									25
26																									26
27																									27
28																									28
29																									29
30																									30
31										.37	.19	.01													31

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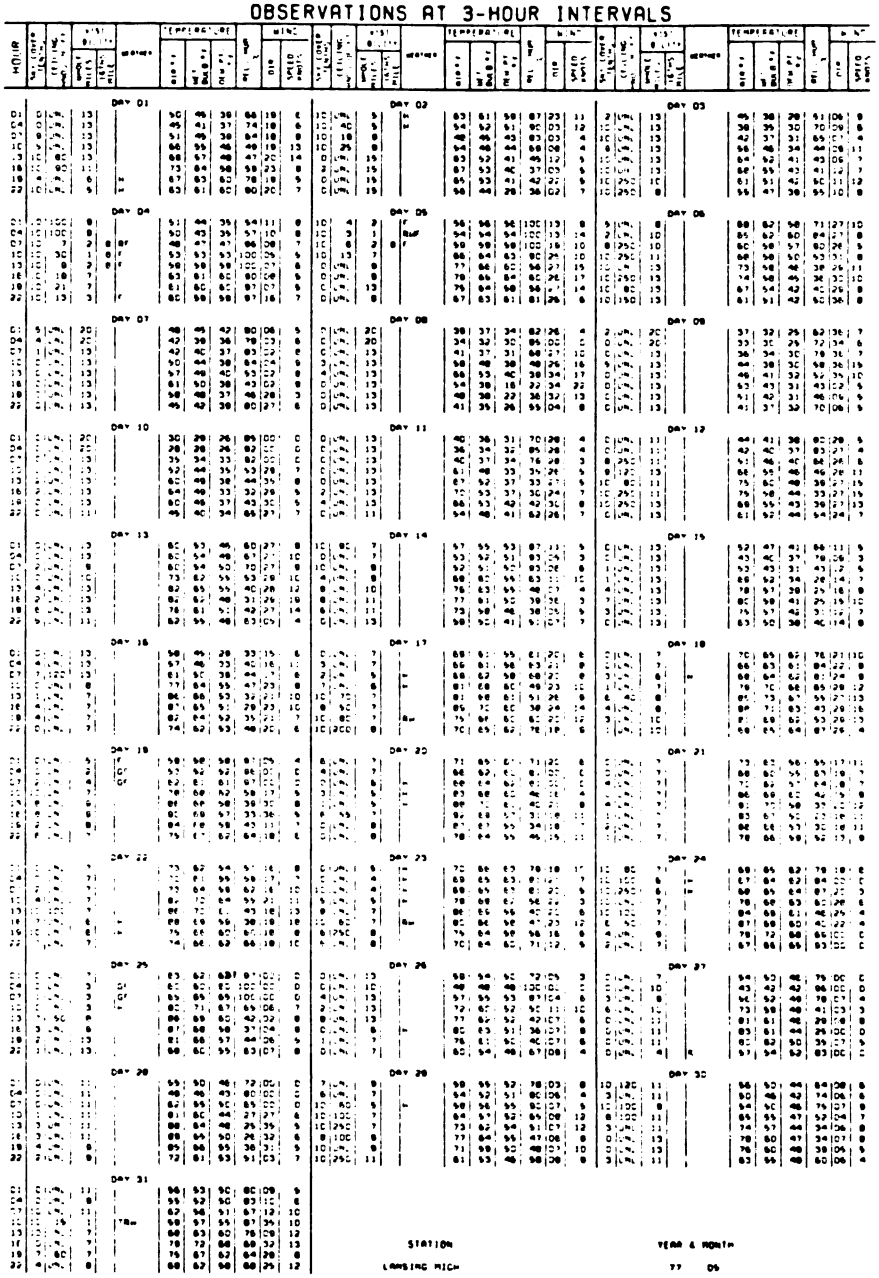
Daniel B. Mitchell
DIRECTOR, NATIONAL CLIMATIC CENTER

USCOMM--NOAA--ASHEVILLE 08/17/77 475

OBSERVATIONS AT 3-HOUR INTERVALS



STATION
LANSING MICH

YEAR & MONTH
77 05

NOTES

CEILING

WEATHER

- + TORNADO
- T THUNDERSTORM
- R RAIN
- RW RAIN SHOWERS
- ZR FREEZING RAIN
- L DRIZZLE
- ZL FREEZING DRIZZLE
- S SNOW
- SP SNOW PELLETS
- IC ICE CRYSTALS
- SW SNOW SHOWERS
- SG SNOW GRAINS
- IP ICE PELLETS
- A HAIL
- F FOG
- IF ICE FOG
- GF GROUND FOG
- BS BLOWING SNOW
- BD BLOWING DUST
- BN BLOWING SAND
- K SMOKE
- H HAZE
- D DUST

WIND

DIRECTIONS ARE THOSE FROM
WHICH THE WIND BLOWS. INCLUDE
CALM IN TERMS OF DEGREES
FROM TRUE NORTH. (I.E. 09
FOR EAST, 18 FOR SOUTH, 27
FOR WEST, ENTER 00 FOR CALM
THE DIRECTION FROM THE
GREEN DROP.

SPEED IS EXPRESSED IN KNOTS.
TO CONVERT
TO MILES PER HOUR

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