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AN EVALUATION OF A COMBINED PROCESS FOR THE CONTROL

OF AIR AND WATER POLLUTION

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LIST OF ABBREVIATIONS

a	-	acres
cc	-	cubic centimeters
cf	-	cubic feet
cf/d/lb	-	cubic feet per day per pound
cfh	-	cubic feet per hour
cfm	-	cubic feet per minute
deg	-	degrees
ft	-	feet
ft-c	-	foot candles
gal	-	gallons
in	-	inches
lb	-	pounds
lb/a/d	-	pounds per acre per day
lb/d	-	pounds per day
lpd	-	liters per day
lpm	-	liters per minute
mg/1	-	milligrams per liter
ml	-	milliliters
oz/d	-	ounces per day
ppm	-	parts per million
sq in	-	square inches

w - watts

μl - microliters

°C - degrees centigrade

°F - degrees Fahrenheit

AN EVALUATION OF A COMBINED PROCESS FOR THE CONTROL

OF AIR AND WATER POLLUTION

CHAPTER I

INTRODUCTION

One of the problems that civilization has created in the de-
velopment of today's society has been the crowding together of people.
As urbanization, centralization, and industrialization continued to be-
come even more dominant, so the lives of the people have continued to
become more complex, overlapping, demanding, and especially more con-
flicting. The same could be said for the surroundings of these people.
As each step in the progression of mankind has been made, the following
step has become more precarious.

An example of the above situation is illustrated by the most
discussed domestic issue of today, the environment. Politicians, pro-
fessors, engineers, industrialists, bureaucrats, and laymen are all con-
cerned about this vital subject called the environment. Environmental
discussions cover such diverse areas as welfare, over-population, trans-
portation, urban renewal, the aged, poverty and pollution. Each of these
problem areas is intertwined with the other and, therefore, so are the
solutions.

Each facet of the environment has an effect on society and the

degree of effect dictates its priority in the scheme of solutions. Considering all these areas of the environment, currently high on the list of priorities is pollution. Although itself a diverse field, encompassing air, water, and solid wastes, pollution makes up a compatible and rather complete grouping of the environment.

This grouping together of air, water, and solid waste in this phase of environmental concern has not been evident until more recent years. Probably the earliest phase of pollution to be considered was the bacterial pollution of water. This was brought about by its effect on the health of the people and thereby water pollution was made a concern of the public health profession. This role was expanded as water demands grew and the need for increased and more thorough treatment and monitoring became evident. Because of this history in water, when an air pollution episode struck in Donora, Pennsylvania, and demonstrated serious health effects, air too, came under the auspices of health officials. Likewise, solid waste came under scrutiny as a health problem due to its putrefying nature which was followed by infestation and disease. The necessity of the "unification" of the three phases of environmental pollution has been exemplified by the creation of the Environmental Protection Agency of the United States Government which has jurisdiction in these as well as other environmental areas.

At the present time these areas have been "joined together" in government because of the likeness in effects, but the degree to which they can be brought together as a part of a solution is still in the future. These concepts are all interrelated with the problems of society and tremendous conflicts are ahead as new and better solutions are

envisioned.

There are many instances of environmental conflict and several deserve mentioning as examples. People demand superhighways in order to shorten driving time and prevent accidents and at the same time become upset because these highways divide neighborhoods, create lines of pollution, increase noise levels, and disfigure landscapes. Paper, supplied at very low prices, is one of the keys to the development of civilization today, but to provide this paper, trees, and therefore forests, are cut, wildlife is disturbed, flooding may occur, and the landscape suffers.

In another more specific example, air pollution control methods create water pollution as is the case with a scrubbing process that uses water where this water is returned to a receiving stream untreated. Also solid waste pollution control becomes an air pollution problem as demonstrated by an incinerator without adequate air pollution control equipment.

Another paradox that has become increasingly pressing was described in an editorial in the Journal of the American Medical Association (1). The city of New York City was faced with a serious power shortage during the summer months when air conditioning and other power demands were highest. Accompanying this dilemma was the fact that New York City's sulfur dioxide (a serious air pollutant that is a by-product of combustion) levels have been three times the level considered safe for human life by the federal government. Therefore, if the city increases power production, sulfur dioxide levels would also increase. If power production is not increased such problems as the great blackout experienced in 1965, reducing the number of commuter trains by one-third, running these

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trains at half speed, reducing air conditioning use, and voluntary power conservation programs would result. In short, the city must choose between a lack of power or an excess of pollution.

As with any complex problem, there is also disagreement and conflict in the search for solutions. An issue of current concern is the very basic and most important problem of answering the question, "When does pollution exist to such a degree as to be harmful to health?"

According to de Villiers (2), when discussing health effects, the fundamental meaning of health must be considered. He said that the process of living is the interplay between the individual and the stresses of his external environment and that to counterbalance these stresses, highly complex physiological or internal adoptive mechanisms are evoked in order to maintain an optimum equilibrium. Therefore, it is this optimum equilibruim that characterizes good health and maladjustment, bad health. Also reported was a figure credited to Hatch (Figure 1) that depicts the relationship between impairment scale and disability scale that is particularly apt in this discussion. It is the problem of environmental leadership to place definite numbers, be they concentration, dose-rate or whatever, in the place of the relative terms of the horizontal axis. These people in decision making positions are faced on the one hand with the clamor of the populace for strong and direct action, and on the other with a lack of complete scientific and technical knowledge on which to base the above decisions which must be made as a premise for action.

The information that is available upon which to base these decisions is both massive and fragmentary. Much research has been completed, volumes of publications printed, and there have been many people
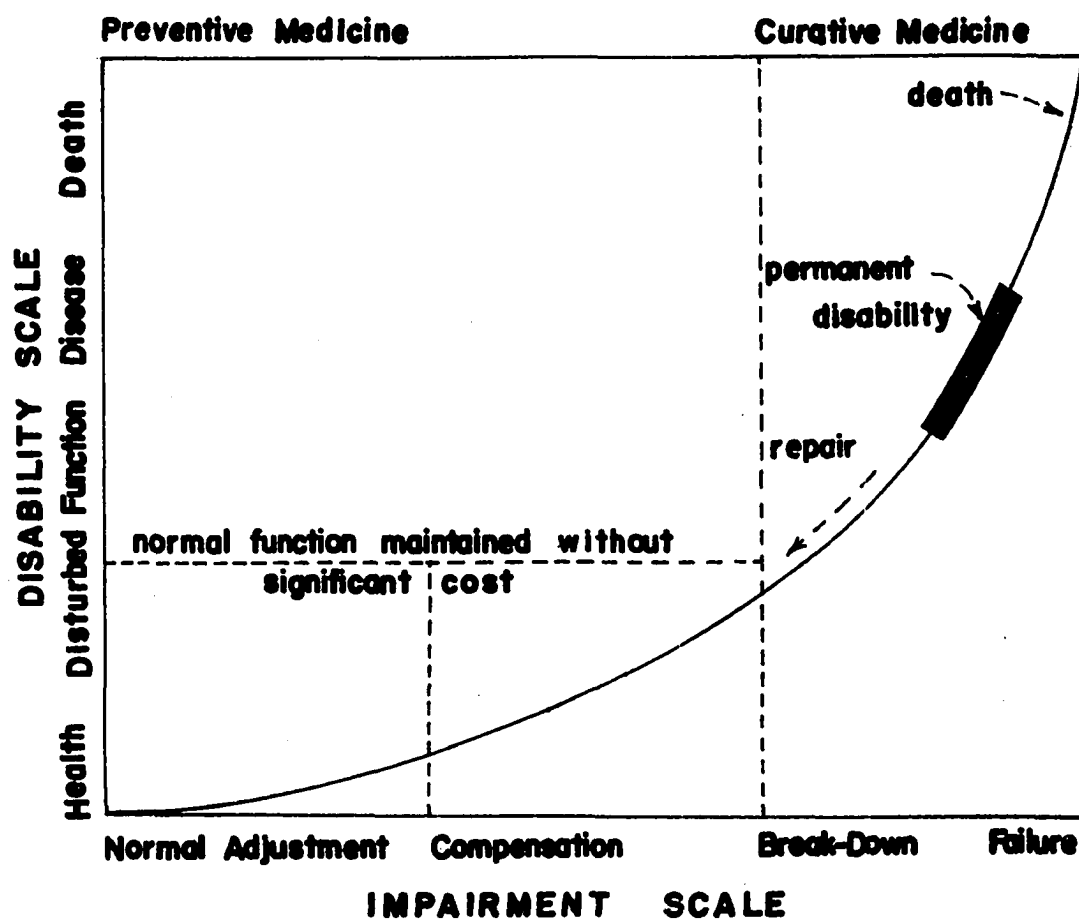
Figure 1--Multifactor relationships in the etiology of disease.

who have devoted a tremendous amount of time to these studies. However, researchers are just beginning to uncover the necessary information required and many years of diligent work remains. Therefore, it would seem that, because these decisions must be made now, the wisest course would be to consult those experts available and arrive at the best decisions possible based on all the information at hand. In an editorial in the Journal of Occupational Medicine, O'Conner (3) points out that this is not always the case.

The object of study was the Air Quality Criteria on Sulfur Oxides published by the National Air Pollution Control Administration. This document was to be used to base the aforementioned decisions pertaining to sulfur oxides. Dr. O'Conner reported that he was consulted by NAPCA to review the first draft of the criteria in June, 1966, and that he carefully reviewed many of the included references quoted and much to his surprise, "many of the references were inaccurate and, more surprising, they often were quoted out of context or grossly misquoted." This resulted in a letter of comments and detailed corrections which he returned to NAPCA (then the Division of Air Pollution Control, USPHS).

Subsequently he attended a meeting of six physicians from industry and NAPCA, was presented with a completely rewritten document, and was told they had that 1 day to examine it and make comments. The new document was 175 pages long. This was the document that was published as the official criteria but was subsequently recalled due to protest.

After this Dr. O'Conner again was consulted by NAPCA along with other physicians, this time only two were from industry, and again reviewed the new proposed document. There was complete agreement that

extensive and detailed rewriting was needed and this was promised by

NAPCA by July, 1968, at which time the consultants were promised a copy

to reconsider.

Now, according to Dr. O'Conner (3),

> In September, a rewrite much modified from the recommenda-
> tions of the consultants was distributed. Then, in October, a
> complete rewrite done by an outside consulting laboratory was
> distributed. This version was far more acceptable, at least to
> this commentator, than any previous version he had seen, and
> comments to this effect were dispatched immediately to NAPCA.
>   Then, for some reason completely unknown to this commen-
> tator, in January, 1969, a version was distributed quite simi-
> lar to the one which had been distributed in September. It
> was this version which ultimately was issued....

Dr. O'Conner then goes on to tell of the futility he experienced in this

horrendous task.

The above examples and experiences point out the tenor of this

thesis. New approaches to pollution, the environment and to the problems

that surround these are needed that include complete considerations.

While it is impossible to find solutions that will be correct for every

situation each time they are applied, certainly a better job could be done

than that of the past.

Because these problems are so immense, this dissertation encom-

passes but a small part of the overall problem, more specifically that

of air and water pollution control, with consideration given to solid

waste. The approach presented here was a continuation of work on a com-

pletely new application of a conventional system previously reported by

this author (4, 5). By combining into one control system the facilities

for treatment of water pollution and air pollution, the cost to industry,

and therefore, the consumer, stands to be greatly reduced. Also such a

method would be more efficient than conventional methods due to its

ability to prevent the pollution of another phase of the environment.
The ultimate of this, or any other system, is the returning of pollution
components to the life cycle or rendering them completely inert in the
smallest quantity. This project proposes to establish the feasibility,
at the bench scale level, of removing high concentrations of sulfur di-
oxide from an air stream using waste stabilization ponds (WSP) as a scrub-
bing media. As was the case with this example, it was believed that what
was needed in many cases was a new look at the old, not necessarily new
technology. Thus, this approach was not inventive, but simply innovative.

CHAPTER II

LITERATURE REVIEW

Sulfur Dioxide

The combustion of fuels, refuse, wood and many other materials that contain sulfur leads to the generation of sulfur dioxide. If this release is uncontrolled, as it usually is, then sulfur dioxide pollutes the atmosphere. This has been the case for many years and as the population has grown and combustion increased, pollution of the air with sulfur dioxide has increased.

In a study made by Robinson and Robbins (6) considering gaseous sulfur pollutants including sulfur dioxide, sulfates, and hydrogen sulfide, it was estimated that the annual worldwide sulfur dioxide emissions were 146×10^6 tons. Of this total, 70 per cent was estimated to result from coal combustion and 16 per cent from the combustion of petroleum products while the remainder resulted from the smelting of copper, lead and zinc. Pollutant sulfur emissions were also compared by world distribution which revealed that 93 per cent or 136×10^6 tons were released in the northern hemisphere. It was also estimated that the northern hemisphere annually receives over twice as much total gaseous sulfur as does the southern hemisphere. Figure 2 shows the environmental sulfur circulation cycle with the amounts and transport mechanisms indicated. Previous estimates of world sulfur dioxide emissions by Katz for the years
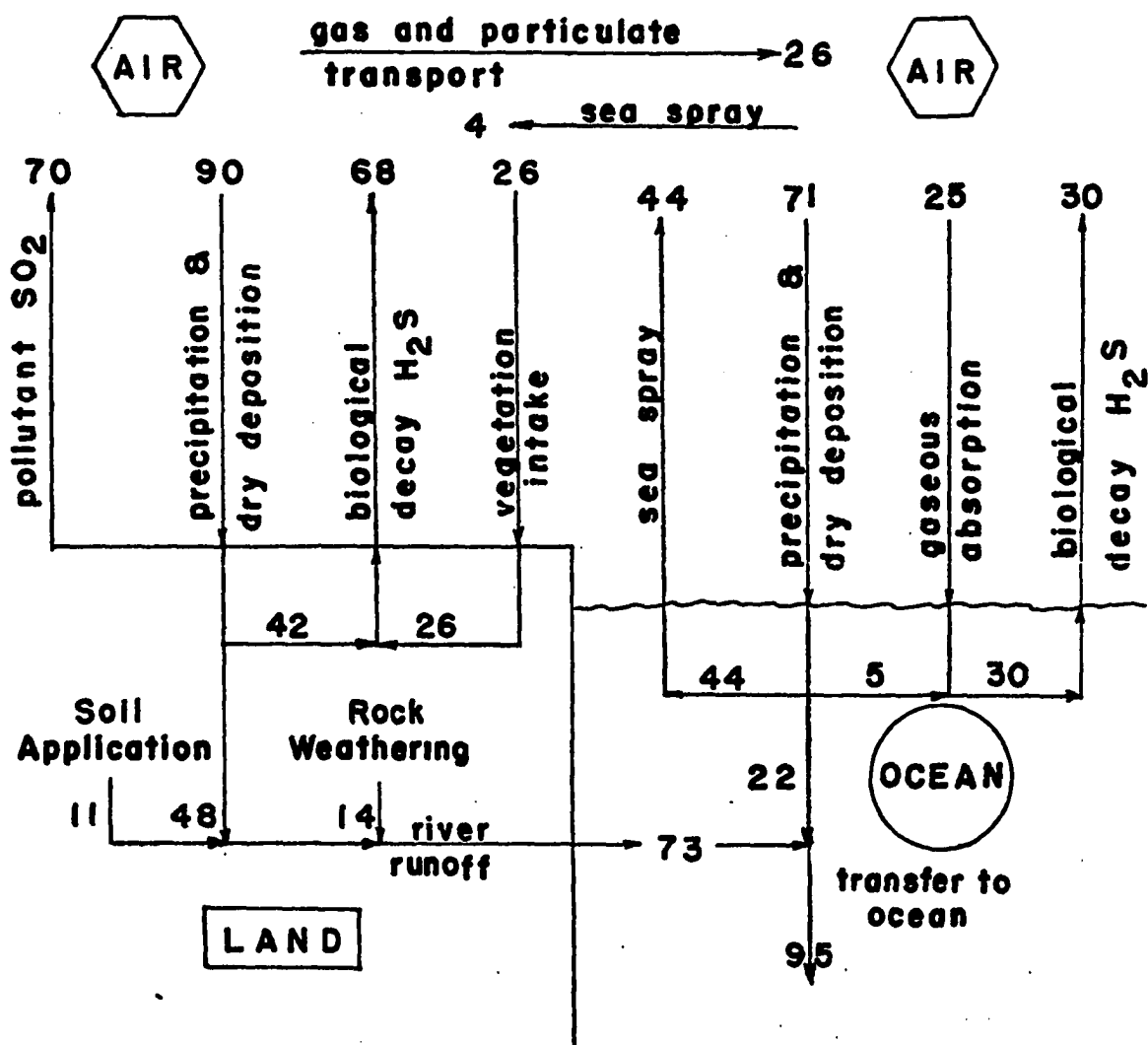
Figure 2--Environmental sulfur circulation (tons/yr sulfur) (6).

1937 and 1940 were also given. This indicated an increase from 69×10^6 tons and 78×10^6 tons, respectively, to the 146×10^6 tons reported or an increase of almost 100 per cent between 1940 and 1965, thus showing the definite increase in sulfur dioxide emissions.

With the continued increase of sulfur dioxide pollution of the atmosphere, many effects on man and the environment have been noted and studied. Daines (7) presented a thorough review of the effects sulfur dioxide had on vegetation and cited papers dealing with sulfur dioxide damage to conifers, cotton, alfalfa, potatoes, tomatoes, and other plants. From the discussion in this paper it would appear that ambient air concentrations of sulfur dioxide began to show effects on plants at about 0.5 to 0.6 ppm.

A summary of toxicologic studies pertaining to oxides of sulfur was given by Amdur (8) in which she reported that some individuals have shown detectable responses to 1 ppm sulfur dioxide but also notes that most respond to levels between 5 and 10 ppm as reflected by the industrial Threshold Limit Value of 5 ppm. She pointed out that sulfur dioxide alone is a mild irritant of the respiratory tract but when it is considered with specific particulates such as salts of ferrous iron, manganese, and vanadium, a three or fourfold potentiation of the irritant response was observed.

In another review of health effects due to sulfur dioxide by Battigelli (9), the author concluded somewhat differently than many other researchers and his results are presented in the following:

> In summary, the search for an acceptable rationale, or
> for reasonable evidence documenting a toxicological relevance
> of SO_2 levels, as these are encountered in urban air pollution,

has thus far failed. If urban pollution has a measurable effect on the health and disease of exposed populations, as it appears to have, on basis of available information, this phenomenon does not appear to involve sulfur dioxide in its mechanism.

Speizer (10) reviewed the epidemiological studies of the effects of sulfur dioxide on health as related by mortality and morbidity and discussed subjects such as increased respiratory morbidity versus air pollution. For example, in Japan respiratory disease morbidity rates were four to six times higher in polluted areas as in rural areas. It was also stated that, "major prevalence surveys from Japan, the United States, Scandinavia, and Great Britain have all reached approximately the same conclusions. Once the data are standardized for smoking habits and age, significant correlations with smoke and SO_2 levels are usually found."

The above lead to the conclusion that sulfur dioxide has been of considerable concern when the quality of the air and effects on materials, animals, and human health are at stake. For this reason many attempts have been made to find suitable, economical methods of controlling sulfur dioxide emissions at the source.

One method of sulfur dioxide removal was presented by Kiyoura (11) and used vanadium oxide to oxidize SO_2 to SO_4 at temperatures from 380° to 450°C. The sulfate is then combined with ammonia to generate ammonium sulfate which may be sold as fertilizer after collection by an electrostatic precipitator. The maximum efficiency of the system is 95 per cent and 70 to 80 per cent is considered industrially economical. However, if a system produces 1,000 ppm SO_2 a minimum emission of 50 ppm would remain and thus the problem would not be solved.

In a paper by Reid (12), the current methods of removing sulfur dioxide from stack gaseous were reviewed. Oldest of these methods was

employed at the Battersea power station in London which was installed in 1934. This method utilizes the alkaline water of the Thames River to wash the plant's stack gases in two large towers. Calcium carbonate is added to the second tower to increase the alkalinity of the water and the SO_2 is converted to calcium sulfate which along with the water is drained back into the river untreated. This system is reported to be only 90 to 95 per cent efficient and therefore has the same drawbacks as the previous method.

A successful scrubbing method for smelters is the Cominco process which uses ammonia liquor to react with the SO_2 to form ammonium sulfate, however, this method was reported unsatisfactory for power stations which have a much lower SO_2 emission (12).

Also discussed was the limestone-dolomite process which uses these chemicals either in solution to scrub the stack gases or dry by injecting them directly into the furnace or, in some instances, both processes are combined. Efficiencies of these methods range from 91 to 83 per cent removal of SO_2 and therefore have serious problems remaining also (12).

Included in this paper was a discussion of the Bureau of Mines proposed alkalized alumina process which not only removes SO_2 but yields elemental sulfur as a by-product. SO_2 laden gases pass over pellets of alkalized alumina which absorbs the SO_2 and oxidizes it to a sulfate. This is then removed to a regenerator which strips off the sulfur with hydrogen and produces H_2S which is then used as the sulfur source in the sulfur recovery unit. No efficiencies for this process were reported (12).

Another process currently under study is the Reinluft system

which uses activated charcoal as an adsorption media for the SO_2. The SO_2 is then later removed by elevating the temperature to 750° F when it is converted to sulfuric acid or elemental sulfur. Efficiencies of the method were not revealed (12).

There are many more different methods for removing SO_2 from source gases and there are more currently being developed. However, the most critical test that thus far most have failed has been that of economics. Emission standards for SO_2 will be strict and this will drive the cost of SO_2 removal upward because of the high removal efficiencies required. Economics that are unfavorable mean more expense for production and this will be passed on to the consumer in the form of higher prices. Thus any system that is brought forth for consideration by industry must be extremely efficient with very favorable economics that will not significantly effect the cost of production. The ideal process would not only cost very little but would actually produce a profit by the recovery of a marketable by-product, which in the case of sulfur dioxide might be sulfuric acid or elemental sulfur.

Waste Stabilization Ponds

Treatment of liquid carried wastes has been practiced since the turn of the century and the WSP is one of the simplest and oldest methods to be devised. The WSP can be described as a natural or man-made detention pond in which liquid carried wastes are acted upon by an active microbiological population that continually inhabits the reservoir. In the classical WSP, this would mean a population that consists mostly of algae and bacteria that act in a mutually beneficial manner. The algae provide oxygen, by photosynthetic processes, which is utilized by the

bacteria, and the bacteria produce carbon dioxide, ammonia, and other nutrients needed by the algae. However, because of the widespread and varied use of the WSP it is very difficult to describe a typical micro-biological population.

Caldwell (13) reported the use of WSP in California as early as 1924 and observed the influence of algae on the pond as reflected by pH values as high as 9.5 and increased dissolved oxygen values.

Since the original conception of the WSP, many improvements by way of modification have been developed and the most popular of these has been aeration. In most cases, the limiting factor for loading rates and detention times in the WSP has been dissolved oxygen. Because of this, aerators, either surface or sub-surface in nature, have been installed in the WSP. This has sizeably increased loading rates and shortened de-tention times which in turn has permitted the use of smaller land areas to treat wastes.

An example of sub-surface aeration of WSP was given by the Hinde Engineering Company (14, 15, 16, 17) which used perforated plastic tubing, installed at regular intervals, on the bottom of the WSP through which compressed air was vented. Design loading rates for this system ranged from 1,000 to 1,300 persons per acre for 10 to 12 ft of water depth with air requirements of approximately 700 cf/d/lb of biochemical oxygen de-mand (BOD). This would compare to typical nonaerated WSP loading rates of 200 persons per acre (18) with an average operating depth of 4 ft. The aeration rate given above is slightly less than that mentioned by Steel (19) for design of activated sludge systems which calls for rates from 750 to 1,000 cf of air per lb of BOD.

Aerated WSP have been used for treating many forms of wastes including raw domestic wastes (20, 21) tertiary treatment of domestic wastes (22), paper mill wastes (23, 24, 25), chemical and refinery wastes (26, 27), animal wastes (28, 29), and cannery wastes (30), to mention but several large general categories.

Oswald (31), considered one of the experts in WSP investigation, design, and operation, presented a very detailed account of nonaerated WSP design which included factors such as surface reaeration, sludge deposition, methane fermentation, and algal photosynthesis. In a paper by Thirumurthi (32), the approaches of chemical engineering unit operations and reactor design concepts were applied to the basic design of WSP and were compared to conventional design methods. Duttweiler and Burgh (33) report on WSP designs for military installations in South Vietnam where normal BOD loading rates for nonaerated WSP were 160 lb/a/d and one installation was constructed with a loading rate of 2,000 lb/a/d. A study of the influence of shape on mixing and loadings of WSP was made by Shindala and Murphy (34) and they concluded that rectangular WSP were superior over circular and irregularly shaped WSP.

Several studies dealing with WSP microbiology have been made with emphasis focused on the algae and bacteria. Gann (35, 36) examined the aerobic bacteria and algae in a laboratory WSP and verified his findings with samplings from a field pond. He found that the predominant bacteria were of the genera Achromobacter, Pseudomonas, and Flavobacterium while the most common genera of algae were Chlorella, Euglena, Scenedesmus, Chlamydomonas, and Ankistrodesmus. The anaerobic bacteria that inhabit the bottom or sludge layer of the WSP were studied by Parker and Skerry

(37) for the case of the anaerobic WSP in Australia. They reported the development of techniques to determine the amount and function of BOD removal due to sludge and discussed the fact that at times when methane production was completely inhibited, BOD removal was still possible due to sulfate reducing bacteria thus confirming a definite role for this group of bacteria. He observed this group uniformly across the sludge layer in numbers varying from 9×10^8 to 5×10^6 per 100 ml which indicated a relatively large population present.

Toerien, et al. (38) determined the number of sulfate reducing bacteria in three anaerobic digestors, two of which received sludge from domestic waste and one which received sulfate-rich mine drainage in addition to the same type of sludge as the others. He observed 3×10^6 to 5×10^6 organisms per 100 ml for the domestic sludge but reported that this number greatly increased in the sulfate enriched sludge to a value of 2×10^7 organisms per 100 ml. All of the organisms isolated and identified in this study were of the species Desulfovibrio desulfuricans.

Gloyna and Espino (39) conducted studies on sulfide production in WSP and related sulfide concentrations in the WSP to the influent sulfate concentrations. Sulfate concentrations from 23 to 400 mg/l were used in a buffered system of synthetic sewage to load the WSP from 68 to 136 lb/a/d of BOD. Algal growth were observed to disappear at sulfide concentrations from 6.5 to 8.5 mg/l which occurred at a sulfate concentration of 400 mg/l.

A detailed analysis of the role of sulfate reducing bacteria in the environment was given by Postgate (40) in which he reported on their metabolism, growth and nutrition, classification, and economic value

besides other properties.

In a series of reports to the London County Council, several researchers (41, 42, 43, 44) reported on a project to recover elemental sulfur from sulfide gases emitted from calcium sulfate enriched sludge. The sulfide rich gas was removed by a carbon dioxide carrier gas to a converter where elemental sulfur was processed as the end product. The pilot plant process could produce 10 oz/d of sulfur from a 50-gal sludge tank to which 5 lb of calcium sulfate had been added. No cost figures were included in the reports.

It is generally accepted that a WSP will not operate satisfactorily at extremes in pH. In a study by Pipes (45), he reported that as pH values increase in the WSP, BOD reduction decreases for the pH range of not less than 6.5 nor greater than 8.7.

At very low pH values, in the range of 2.5 to 6.0, few groups of microorganisms will survive in large numbers; however, one significant group of plant life that will thrive at low pH values is the fungi. Cooke (46) has studied fungi in acid mine drainage and reported that fungi are very common species found and discussed their role in stabilization of pollution. This included the statement that fungi reduced the BOD of artificial sewage at pH 2.9 "rather quickly." Similar work by Harvey (47), Lackey (48), and again Cooke, et al. (49, 50, 51) substantiate the presence and role of fungi in acid, polluted waters.

In summary, the WSP has demonstrated its effectiveness as a valuable and dependable waste treatment method. When the WSP is employed in a new application it can be expected that the microorganism that will inhabit the pond will be somewhat different from those found in other

situations. This is primarily due to different substrates being present for the principal microbial growth and it then follows that the entire population will be affected because of this. While prior experience with WSP operation is necessary, each new application will necessitate a thorough study to determine just what changes have occurred.

CHAPTER III

PURPOSE AND SCOPE

Previous investigations were conducted by this author (4, 5) in which a WSP operating at an organic loading rate of 30 lb/a/d of BOD was used to scrub sulfur dioxide from an air stream at a concentration of 25 ppm and an air flow rate of 0.5 cfh at ambient air temperatures. This study demonstrated that the combining of two pollution control methods did merit further investigation and it was suggested that more parameters of this system be examined.

The purpose of the present investigation was to determine the feasibility of using WSP to remove high concentrations of sulfur dioxide from an air stream as determined by scrubbing efficiencies, and to investigate the effects of these concentrations on the WSP as determined by examining treatment efficiencies and the WSP effluent. Also studied were the effects of elevated temperature, various aeration rates and organic loading rates and the resulting form and location of the sulfur removed from the air.

Utilized in this investigation were four laboratory WSP, continuously loaded with settled domestic sewage at a rate of approximately 100 lb/a/d of BOD. One WSP acted as a control and was aerated with air only at a rate of approximately 1.3 lpm. A second WSP was aerated with 1000 ppm sulfur dioxide in air at a rate of 1.3 lpm. The third and fourth

WSP were aerated with 500 ppm sulfur dioxide in air at a rate of 0.3 lpm with the fourth WSP heated to a temperature approximately 18°C above the others or 41°C. Aeration rates of 0.3 lpm and 1.3 lpm were the same as 5,280 cf/lb of BOD and 22,900 cf/lb of BOD respectively.

Scrubbing efficiencies were determined by analysis of the gaseous effluent following the introduction of sulfur dioxide into the aeration system. The effects on waste treatment efficiencies were evaluated by comparing BOD reduction values, nitrogen reduction values, and pH determined before and after the introduction of sulfur dioxide and by comparison to a control WSP. Effects of the sulfur dioxide on the WSP and the disposition of the sulfur after removal were determined by microbiological examination of the WSP contents, by monitoring sulfate concentration in the WSP effluent, by qualitative analysis of the sludge layer for elemental sulfur, and by quantitative analysis of the sludge layer for total sulfur.

CHAPTER IV

MATERIALS AND PROCEDURES

Four laboratory WSP were constructed, each consisting of a 10-gal glass aquarium with a surface area of 200 sq in, and a liquid depth of approximately 11 in. Each aquarium had a length of 20 in and a width of 10 in. An overflow weir to maintain a constant liquid level was installed in each WSP at the end opposite the influent by using a 1.5-in glass funnel inserted into a glass tube which extended through the bottom of the pond to a container. The four WSP were mounted on the middle shelf of a metal stand constructed of 1.5- by 1.5-in angle iron. This arrangement of equipment, shown in Figure 3, allowed for ample working space and full utilization of gravitational forces for constant flow feeding.

Light was provided by five, 15-w Sylvania Gro-Lux fluorescent light bulbs which were located 12 in above the liquid surface of each WSP and produced an intensity of 350 ft-c at the surface of the ponds. Two Intermatic timer switches were used to obtain a 12-hour on; 12-hour off light cycle. WSP-4 was heated an average of 18°C above ambient temperature by placing the face of a 150-w, General Electric, infrared light bulb against the side of the glass aquarium.

In each WSP, an aerater, made of four lengths of 0.5-in diameter PVC plastic water pipe connected as shown in Figure 4, was placed at an average depth of 6 in below the liquid surface. Bubblers were made by

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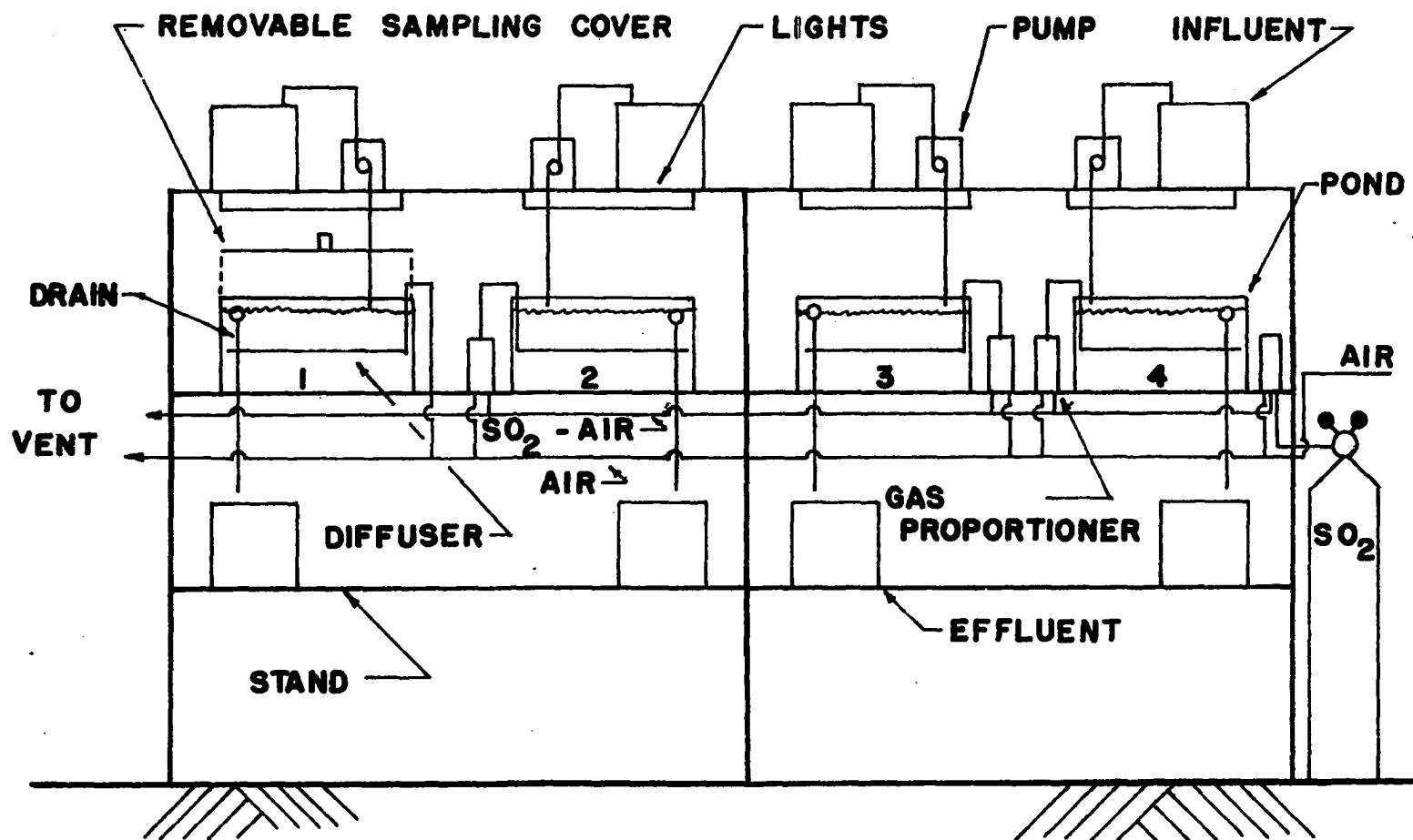
Figure 3--Arrangement of WSP and equipment in the laboratory.

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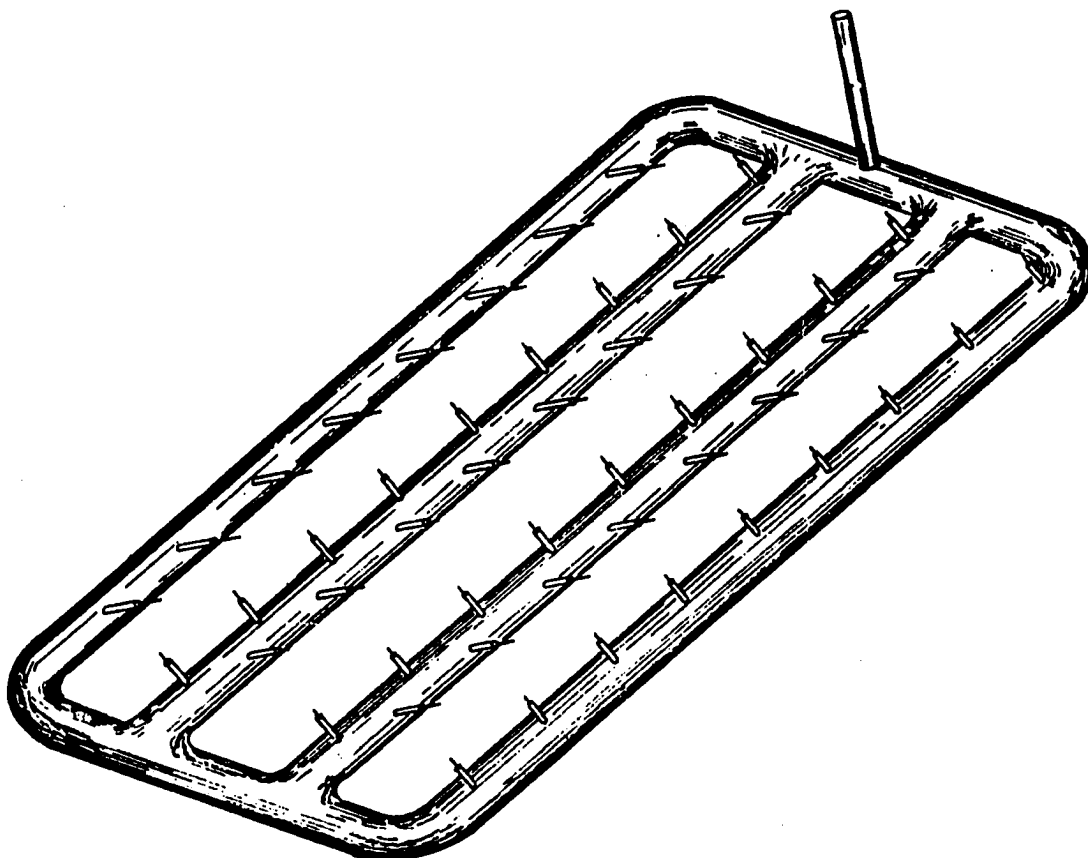
Figure 4 --Aeration device for laboratory WSP.

cutting the last inch from the end of 1-cc tuberculin syringes and attach-
ing 0.5-in, 26-g needles. These were placed every 2 in on the outside
lengths and every inch on the center lengths offset so that each of the
three spaces between the lengths had one needle every inch. The bubblers
were slanted at approximately 45 deg so as to extend over the spaces.

The four WSP used in this study had a very long history of opera-
tion in the laboratory. WSP-1 and WSP-2 were initially put into operation
in November, 1968, and WSP-3 was begun in mid December, 1968. These three
WSP were used in earlier studies (4, 5) in which WSP-3 was dosed with
sulfur dioxide at a concentration of 25 ppm for a 2-week period. In
September, 1969, WSP-4 was placed in service and all ponds began a long
period of self adjustment. The ponds were fed 2 lpd of feed and were
aerated at a rate of approximately 1.3 lpm until September, 1970, when
the feeding rate was increased to 8 lpd and WSP-4 was heated.

The four WSP were maintained under these conditions until
December 7, 1970, when WSP-3 and WSP-4 were aerated with 500 ppm sulfur
dioxide at a rate of 0.3 lpm and March 22, 1971 when WSP-2 was aerated
with 1,000 ppm sulfur dioxide at a rate of 1.3 lpm. This set of para-
meters was maintained until April 23, 1971, when the project was completed.

Sulfur dioxide was supplied by the Matheson Gas Company in com-
pressed gas cylinders and an Air Products regulator was used for dispens-
ing the gas to the system. Desired concentrations of sulfur dioxide were
obtained with Matheson Gas Company gas proportioners by diluting the pure
sulfur dioxide with air. The pure sulfur dioxide was first diluted by a
primary proportioner to 5,000 ppm in air and this was then further di-
luted by a secondary proportioner at each WSP to obtain 500 ppm for WSP-3

and WSP-4 and 1,000 ppm for WSP-2. The proper flow rate was maintained by using needle valves at the proportioners and a needle valve at the vent which produced the necessary back pressure for aeration.

The experimental WSP were fed by Sigmamotor pumps (one for each WSP) raw, settled, domestic waste obtained from the effluent of the grit chamber of the Oklahoma City North Side Sewage Treatment Plant. Although each WSP system had its own reservoir for sewage, all ponds received the same influent which was collected in the field approximately once every 5 or 6 days and then stored under refrigeration until used. The WSP were fed continuously at a rate of 8 lpd calculated to approximate the desired BOD loading rate of 100 lb/a/d.

Analysis for BOD and total Kjeldahl nitrogen were made according to Standard Methods for the Examination of Water and Wastewater (52). These tests were made on the pond influent and effluent each working day early in the sampling period but were reduced in frequency as conditions were determined to be nearly stable. For WSP effluent that had pH values below 6.0, samples were neutralized to a pH of 7.0 with sodium hydroxide solution and seeded with sewage to insure that there was no interference with organic stabilization during the BOD test. Other samples were not pre-treated.

Determinations of sulfates were made turbidimetrically on an almost daily basis in both the influent and effluent of the WSP by means of procedures outlined by the Hach Chemical Company (53) using the DR Spectrometer.

In order to sample the gaseous effluent from the WSP, a plexi-glass cover was constructed that sealed the top of the WSP. Enough time

was allowed to elapse after installation so as to displace, by several times, the volume of gas between the surface of the liquid and the cover, then the sample was taken through a 2-in hole in the cover. Sulfur dioxide emitted from the WSP surface was measured by use of the West and Gaeke Method as described in Selected Methods for the Measurement of Air Pollutants (54). In determining the calibration curve for this method, it was observed that in the range 0 to 0.15 µl of sulfur dioxide per 10 ml of sample, the curve was not linear. Therefore, any samples that were analyzed and found to be in this range were reported as "trace" amounts. The normal sampling rate was 0.25 lpm for a period of 30 minutes. Using these parameters and considering the above range, a 0.15 µl sample would represent a concentration of 0.002 ppm which would indicate that any sample reported as trace had this concentration or less, and that some sulfur dioxide was present. The sampling rate of 0.25 lpm was used throughout this project but the sampling time was shortened accordingly for higher sulfur dioxide concentrations, so as not to saturate the absorbing reagent.

A 20-ml sample from the effluent of each WSP and the sewage being fed was analyzed every sampling day by means of a Beckman expanded scale pH meter.

Samples for bacteriological cultures in the liquid part of the pond were taken by pipette. Sludge samples for this purpose were taken by coring the sludge with a 0.25-in I. D. glass tube. For studies involving location by depth, portions of the sludge was siphoned from the appropriate level using the above tube with rubber tubing attached. Bacteriological samples were cultured to determine both most probable

number (MPN) and the presence of sulfate reducing bacteria. Procedures
and medias described in Standard Methods for the Examination of Water and
Wastewater (52), were used for MPN counts and Sulfate Reducer API Agar
(55) was used to culture, anaerobically, sulfate reducing bacteria. Bac-
terial identifications were made according to Bergey's Manual of Deter-
minative Bacteriology (56).

In order to determine whether sulfur was being deposited in the
sludge layer, a 400-ml sample of sludge was taken from both WSP-1 and
WSP-3. These samples were dried by evaporation in an oven at 60°C and
extracted with carbon disulfide in a soxhlet type apparatus. The carbon
disulfide was then volatilized at room temperature and the extract was
sent to the Research and Development Laboratory, Continental Oil Company,
Ponca City, Oklahoma. Personnel at the Continental Oil Laboratory ex-
amined the extract using a total sulfur analyzer for gross sulfur com-
parisons and by x-ray defraction for crystalline forms of elemental
sulfur.

CHAPTER V

OBSERVATIONS AND DISCUSSIONS

BOD reduction in the WSP was probably the best indicator of over-all WSP function as far as its ability to treat liquid carried waste. A comparison of WSP-1 BOD to the influent BOD gave the results of a typical aerated WSP. Influent BOD had a mean value of 163 mg/l and WSP-1 a value of 10 mg/l for a total BOD reduction of slightly over 90 per cent. This was considered very good for a single cell, aerated WSP and demonstrated that the control was indeed functioning at a very high efficiency. The mean and standard deviation of BOD values are given in Table 1 and Figure 5 is a presentation of a 3-day rolling average of the BOD values and as such, shows trends in BOD rather than specific BOD values which are tabulated in the appendix.

WSP-2 was operated under two conditions, first without sulfur dioxide in the aeration air and then with 1,000 ppm sulfur dioxide. From Table 1, before sulfur dioxide aeration WSP-2 had a mean BOD value of 9 mg/l which represents a treatment efficiency of slightly over 90 per cent. After sulfur dioxide introduction, WSP-2 had a mean BOD value of 42 mg/l which was a very definite increase. This resulted in the treatment efficiency dropping to just over 74 per cent which is not as favorable as before introduction of sulfur dioxide but would be considered a moderate efficiency rate for a typical WSP. However, for a WSP aerated

TABLE 1

SUMMARY OF WSP DATA

		Influent	WSP-1	WSP-2 (Before SO_2) Introduction	WSP-2 (After SO_2) Introduction	WSP-3	WSP-4[a]
Concentration SO_2 (ppm)		–	0	0	1000	500	500
Aeration Rate (1pm)		–	1.3	1.3	1.3	0.3	0.3
pH	μ	7.19	7.81	7.82	2.71	4.28	3.35
	σ	1.82	0.15	0.16	0.19	1.13	0.90
BOD (mg/1)	μ	163.	10.	9.	42.	63.	29.
	σ	103.	11.	8.	28.	35.	22.
Total Organic Nitrogen (mg/1)	μ	32.07	2.98	2.97	38.61	36.98	44.44
	σ	12.97	2.27	1.48	17.28	10.27	12.13
Sulfates (mg/1)	μ	210.	235.	199.	304.	313.	975.
	σ	42.	52.	62.	22.	59.	302.
Temperature (°C)	μ	–	23.	23.	23.	23.	41.
	σ	–	2.	2.	3.	3.	2.

μ = mean

σ = standard deviation

n = Number of observations, can be obtained from Appendix.

[a]Not corrected for evaporation (see text)
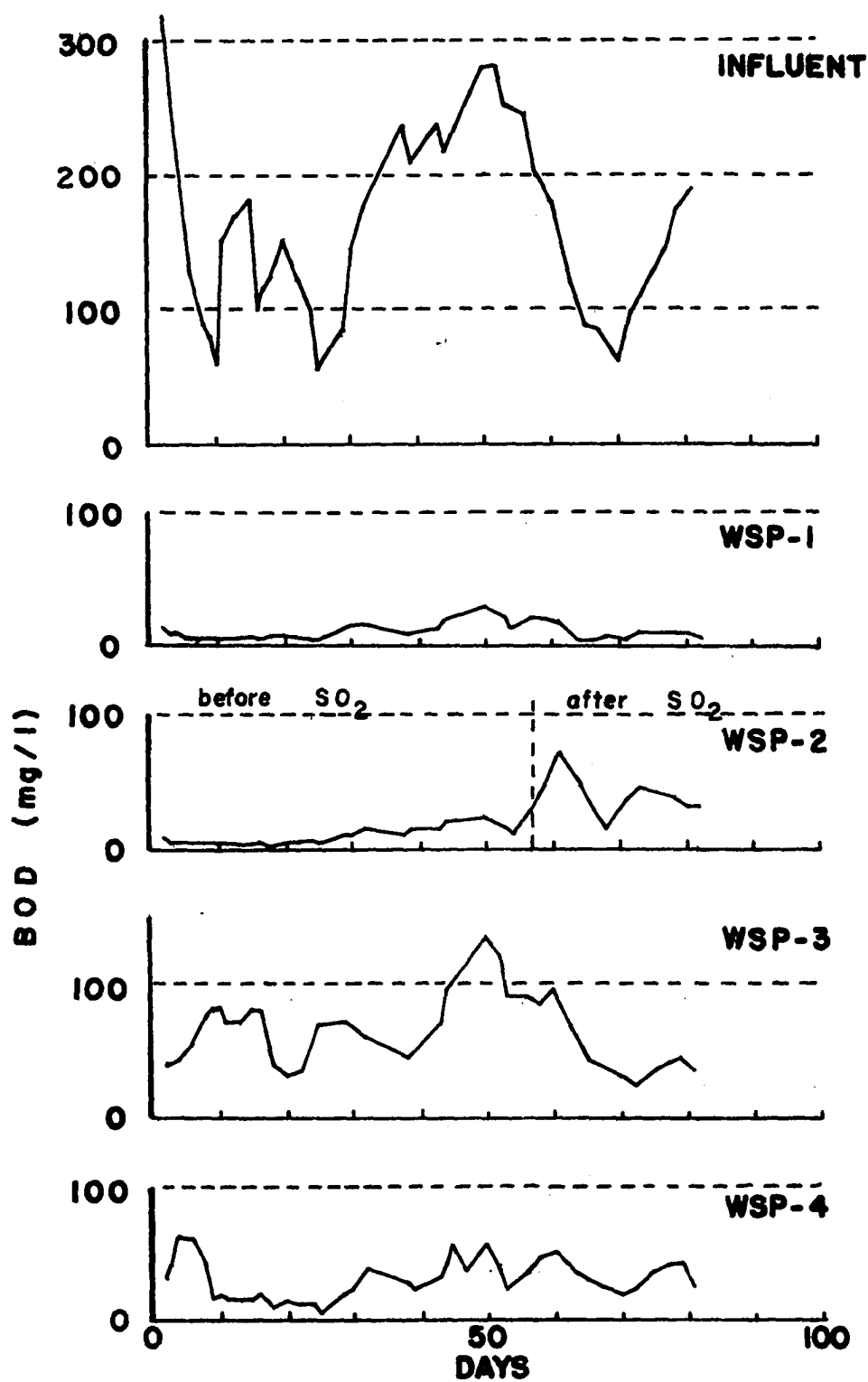
Figure 5—BOD trends for influent and effluent of WSP.

with 1000 ppm sulfur dioxide this must be considered good treatment.

Upon introduction of sulfur dioxide to WSP-2 several effects were noted. As shown in Table 1, there was a severe drop in pH from an average value of 7.82 to a value of 2.71. Accompanying this was a definite increase in total organic nitrogen from an average of 2.97 mg/l to 38.61 mg/l. Also, there was an increase in average sulfates in the liquid phase of the pond from 199 mg/l to 304 mg/l. It should be noted that all the above changes were significant at the 95 per cent confidence level when analyzed by Duncan's New Multiple Range Test. When sulfur dioxide addition was begun there was an immediate level of 8 ppm sulfur dioxide in the effluent gases but as the WSP acclimated to this condition the concentration continually dropped until only trace amounts remained. However, even with an effluent concentration of 8 ppm sulfur dioxide, this represents a removal of over 99 per cent of the sulfur dioxide which was considered to be extremely good. It should be noted that a pH change alone would cause a shift in ion concentrations but it was felt that the changes in magnitude experienced here were due to more than pH alone.

A comparison of WSP-2 to the control pond, WSP-1, showed that before sulfur dioxide introduction there was little difference in BOD reduction. However, the use of 1000 ppm sulfur dioxide aerated at the same rate caused the BOD reduction rate to be considerably less. Further comparison with WSP-3 shows that lowering the concentration and the aeration rate and therefore the total amount of sulfur going into the WSP produced even less desirable effects on BOD reduction. From this it would appear that the higher aeration rate produced the best BOD reduction rate with sulfur dioxide concentration having no obvious effect.

WSP-3 was aerated with 500 ppm sulfur dioxide in the aeration air and had a mean effluent BOD value of 63 mg/l. Therefore, the pond would have a treatment efficiency of approximately 60 per cent which must be considered marginal at best for a typical WSP. Again, this must be considered rather good treatment since the pond was also receiving large amounts of sulfur dioxide. Although dissolved oxygen was not considered as an operational parameter, it was noted that when BOD samples were analyzed this was the only WSP of the four that always had a dissolved oxygen value of zero. This may have been partly due to the lower aeration rate of 0.3 lpm as compared to WSP-1 and 2 at 1.3 lpm but does not seem consistent with WSP-4. This WSP was operated under the same conditions as WSP-3 except for the temperature difference.

WSP-4 was operated at a sulfur dioxide concentration of 500 ppm and an aeration rate of 0.3 lpm and had a mean effluent BOD value of 29 mg/l. Due to the higher temperature in this WSP, evaporation reduced the volume of the effluent to nearly one-half that of other WSP. This yielded a liquid waste treatment efficiency of slightly greater than 90 per cent, corrected for evaporation, which would be judged very good for a typical WSP. When aeration with 500 ppm sulfur dioxide was considered, this was indeed very good treatment.

The comparison of WSP-3 and WSP-4 shows that temperature had a large and beneficial effect on BOD removal. By increasing the WSP temperature an average of 18°C, the BOD removal rate increased from 60 per cent to 90 per cent or an increase of 50 per cent. This would indicate that elevated temperatures from hot aeration gases could be beneficial. The benefit might have been due to a more free exchange of energy in both

chemical and biochemical reactions.

From the above it appeared that the best combination of parameters would be an aeration rate of 1.3 lpm at elevated temperatures. Concentration of sulfur dioxide in the aeration gas did not seem to demonstrate as much effect as the above parameters, however, in all cases but WSP-4, an increase in BOD loading rate would have lowered effluent qualities below acceptable limits.

As seen in Table 1, the large standard deviation for influent BOD indicated that BOD at the sewage treatment plant fluctuated greatly and this variation was passed on to the ponds. This contributed to the study by allowing an evaluation of the effects of shock loads on the WSP. Observation of Figure 5 indicated that ponds whose contents were not exposed to sulfur dioxide, WSP-1 and WSP-2 before sulfur dioxide introduction, did not respond to changes in influent BOD in as great a magnitude as did ponds that had been exposed to sulfur dioxide. This would indicate that ponds receiving sulfur dioxide would be more susceptible to shock loading.

Total organic nitrogen is a parameter used to measure microbiological activity in a WSP. In a normal WSP, such as WSP-1 and WSP-2 before sulfur dioxide introduction, a decrease in total organic nitrogen would be expected and would be a measure of efficiency. For this to happen, microorganisms in the pond stabilize the organic material and change the nitrogen thus contained to other forms such as nitrates and nitrites. This was indeed the case as the average total organic nitrogen removal rate was over 93 per cent in these two ponds.

In WSP receiving sulfur dioxide, such as WSP-2 after sulfur

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dioxide introduction, WSP-3 and WSP-4, total organic nitrogen was also a measure of microbiological activity but in another way. In these ponds the pH dropped to acid levels and the ponds microbiology changed drastically, the greatest change being a dense growth of fungi. Total organic nitrogen values for these ponds increased above that of the influent and was probably due to and a measure of the nitrogen fixing powers of the fungi. Therefore, for ponds receiving sulfur dioxide, this parameter is suitable for a measure of microbiological activity but should not be used as a parameter for pond efficiency.

Observation of mean and standard deviation values for total organic nitrogen in Table 1 indicated that standard deviations for ponds receiving sulfur dioxide were less than those of ponds receiving no sulfur dioxide. This could be the result of the fungi having a stabilizing influence on the pond thus making the effluent values somewhat more centralized.

As noted in the literature review evidence that fungi played a part in the stabilization of organic material was reported (46). Since the efficiency of the WSP was not severely affected, it is believed that this project helps confirm this report.

Sulfates were monitored in the influent and in the WSP and the mean and standard deviation values are given in Table 1. Comparison of WSP-1 and WSP-2 before sulfur dioxide introduction, to the influent, showed that only small changes are to be expected in sulfate concentration in WSP where no sulfur dioxide is present. However, all WSP where sulfur dioxide was used indicated a very definite increase in sulfates. This helped to verify the hypothesis that sulfur dioxide would be oxidized to

the sulfate form upon going into solution in the liquid of the pond.

A comparison of mean sulfate values from Table 1 for WSP-2 after sulfur dioxide introduction and WSP-3 shows that no significant change occurred even though the first pond received twice the concentration of sulfur dioxide and at a much higher aeration rate. This would definitely indicate that sulfur was either being deposited in the sludge layer or leaving the pond in a form other than sulfate or sulfur dioxide, perhaps even as part of the biochemical makeup of microorganisms.

By comparing WSP-4 to WSP-3 and WSP-2 after introduction of sulfur dioxide, it could be seen that temperature had a definite effect on increasing the sulfate concentration. This could have been also due to greater ease in chemical and biochemical reactions and/or different solubilities due to temperature.

Values of sulfur dioxide concentrations in the effluent gases from the WSP are given in the appendix. These values can be summarized by the following: concentrations of 1,000 ppm and 500 ppm sulfur dioxide were almost completely controlled in all WSP. A period of several weeks was necessary for the WSP to acclimate to sulfur dioxide aeration and was probably dependent on the time necessary for microbiological population to adjust.

Because of the low pH values encountered in the ponds with sulfur dioxide, there was some doubt as to the survival of a bacterial population capable of organic degradation and, therefore, their role in the stabilization of organic material. To determine the extent of bacterial inhabitation of the ponds MPN counts were made and the results given in Table 2.

TABLE 2

WSP MOST PROBABLE NUMBER (MPN) OF BACTERIA
PER 100 ml OF SAMPLE[a]

	WSP-1	WSP-2[b]	WSP-3	WSP-4
Effluent MPN/100 ml	3.5×10^4	1.4×10^4	4.9×10^4	4.0×10^4
Percentage Reduction	96	98	95	96

[a]Average influent MPN - 9.7×10^5.

[b]After sulfur dioxide introduction.

These data showed that normal bacterial reduction rates were in evidence and that bacterial were present in sufficient numbers to play a part in the stabilization of organic material.

Sulfate reducing bacteria was examined in WSP-1 and WSP-3 as a possible mechanism for the changing of sulfate, and therefore sulfur dioxide, into other forms of sulfur such as sulfide and elemental sulfur. Results of this investigation are given in Table 3. These data show that there were very few sulfate reducers in the control pond, which had not had sulfur dioxide in the aeration air, compared to WSP-3 which was aerated with 500 ppm sulfur dioxide. It was also observed that these anaerobic bacteria predominated in the sludge layer which would be expected to have the least amount of dissolved oxygen.

Further investigation of the sludge layer in WSP-3 for sulfate reducing bacteria was made to determine if the bacteria favored a particular area of the pond or a certain depth in the sludge layer. Results are given in Table 4 and indicate that most sulfate reducing bacteria were found at the inlet and center of the pond and at a depth of midway through the sludge layer. The average depth of the sludge layer in WSP-3 was approximately 1.5 in. These bacteria are probably found in this general area because of the availability of unstabilized settleable solids that were deposited near the inlet and were kept from the surface of the sludge by concentrations of dissolved oxygen. During this phase of study two sulfate reducing organisms were isolated and identified to be Thiospira biponctata and Thiobacterium by Ernest D. King, Microbiologist and Graduate Fellow, University of Oklahoma.

Analysis of the carbon disulfide extracts of the sludge from

TABLE 3

SULFATE REDUCING BACTERIA COUNTS BY LOCATION
IN WSP-1 AND WSP-3

Location	WSP-1		WSP-3	
	No./1.0 ml	No./0.1 ml	No./1.0 ml	No./0.1 ml
Inlet-Liquid	0	0	0	0
Inlet-Liquid	0	0	0	0
Center-Liquid	1	0	0	0
Outlet-Liquid	13	0	0	26
Outlet-Liquid	0	0	0	0
Inlet-Sludge	0	0	TNTC	27
Inlet-Sludge	0	0	TNTC	65
Center-Sludge	98	3	18	2
Outlet-Sludge	0	0	0	0
Outlet-Sludge	0	0	8	1

TNTC - Too Numerous To Count.

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TABLE 4

NUMBER OF SULFATE REDUCING BACTERIA PER 10 ml SAMPLE
IN THE SLUDGE LAYER BY GENERAL AREA OF THE POND
AND DEPTH FOR WSP-3

Depth in Sludge	Right of Inlet	Left of Inlet	Right of Center	Left of Center	Right of Outlet	Left of Outlet
Surface	0	33	0	0	0	0
Middle	264	TNTC	532	428	2	0
Bottom	0	3	3	0	0	17

TNTC – Too Numerous To Count.

WSP-1 and WSP-3 for total sulfur showed that the sulfur content of WSP-1,
or the control, was 5.18 per cent by weight and WSP-3 was 6.50 per cent.
This increase of 1.32 per cent sulfur by weight or a total increase of
25 per cent strongly indicated that sulfur was being accumulated in the
sludge layer of the pond and should be considered a prime source for
sulfur recovery. X-ray defraction of the extract indicated that no ele-
mental sulfur was present in crystalline form. It was also observed that
when the sludge layers were being sampled WSP-3 had a very pungent sulfide
odor in the sludge while WSP-1 had almost no odor at all. This would in-
dicate that the excess sulfur noted above was in the sulfide form.

Of interest to the future development of this type of control
process was the extrapolation of the laboratory study to a full scale
plant. Using a typical hypothetical sulfuric acid plant with an exit gas
rate of 10,000 cfm and a sulfur dioxide concentration of 0.1 per cent by
volume or 1,000 ppm (57), the size of a control facility using aerated
WSP was calculated. For an aeration rate of 1.3 lpm per 200 sq in of
surface area, the facility would require a WSP of approximately 7 a in
area. Using the design BOD loading rate of 100 lb/a/d and a per capita
BOD generation rate of 0.2 lb/d, a 7-a facility could treat the waste of
3,500 people or the population of a small city.

The economics involved in this type of system may make it possible
to completely replace more costly systems for treating water and air pol-
lution now proposed or in use. There are no catalysts to buy, very little
equipment to maintain, and a comparatively small initial equipment cost.

In addition, the recovery of sulfur or a sulfur compound could
make this system even more inviting to industry. This might be possible

by removing the sludge, stabilizing it under anaerobic conditions so as to produce large amounts of hydrogen sulfide, and then convert this to sulfur or sulfur compounds for marketing. The British system reported in the literature review used sulfate enriched sewage sludge in the generation of elemental sulfur. It would seem that this process would fit this system almost ideally as all the components are already present.

CHAPTER VI

SUMMARY AND CONCLUSIONS

Four 10-gal aerated WSP were o ..ated in the laboratory in order
to study the combination of air and water pollution control processes.
One WSP was aerated at a rate of 1.3 lpm with a concentration of 1,000
ppm sulfur dioxide, a second at 0.3 lpm with a concentration of 500 ppm,
a third at 0.3 lpm with a concentration of 500 ppm and heated an average
of 18°C above ambient temperature, while a fourth WSP aerated with air at
1.3 lpm was used as a control.

In order to determine the value of the pond as both an air pol-
lution and water pollution control, BOD, total organic nitrogen, bacterial
reduction, pH, and sulfur dioxide were measured over a 5-month period.
To determine the ultimate disposition of the sulfur being introduced as
sulfur dioxide, sulfates, elemental sulfur, total sulfur and sulfate re-
ducing bacteria were also studied.

Based on the results and observations of this experiment the
following were concluded:

1. The combination of two pollution control systems into one pro-
    cess, in this case a WSP for water pollution control and wet
    scrubbing for sulfur dioxide, was successfully accomplished in
    the laboratory and should be feasible on a larger scale.

2. WSP could remove concentrations of 500 and 1,000 ppm sulfur

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dioxide from aeration gases with extremely high efficiencies and perform at a reasonable level of BOD reduction.

3. For a typical sulfuric acid plant emitting 1,000 ppm sulfur dioxide in 10,000 cfm of gases, a WSP-wet-scrubbing system with an area of 7 a would be necessary. At the same time the WSP could treat the domestic waste of 3,500 people or a small city.

4. Heating of the pond contents to simulate aeration with hot gases improved treatment efficiency and did not seem to effect sulfur dioxide removal.

5. It appeared that sulfur was being deposited in the sludge layer of ponds receiving sulfur dioxide and was found to exceed the level of the control pond by 25 per cent. This sulfur may have been present in the sulfide form as indicated by odor, but no elemental sulfur in crystalline form was found.

6. Sulfate reducing bacteria were found in much greater numbers in the sludge layer of WSP receiving sulfur dioxide than in the control. Also these bacteria favored areas toward the inlet and center of the pond at approximately the middle of the sludge layer.

7. BOD analysis seemed to indicate that WSP aerated with sulfur dioxide responded more to changes in influent BOD than did the control WSP. This would suggest that WSP aerated with sulfur dioxide were more susceptible to shock loads.

8. Fungi in the WSP aerated with sulfur dioxide seemed to play an important role in the stabilization of organic material.

9. It appeared that nitrogen was being added to the WSP receiving

sulfur dioxide by nitrogen fixing fungi which were present in
very large numbers in the ponds.

10. Further investigations of this system should be carried on at the
pilot plant size for long periods of study. Also an upper limit
on the concentration of sulfur dioxide that can be effectively
removed from the aeration gas should be determined. Other para-
meters that should be of interest include other aeration rates
and devices, other organic loading rates, increased temperatures,
and better physical design parameters for the WSP itself.

11. The economics of the system should be maximized by the incorpora-
tion of sulfur recovery into the process which might be possible
by chemical treatment of accumulating sludge.

12. The combination of pollution control processes into a single
system should be further expanded to include not only other
gaseous and liquid pollutants but also solid waste as well. The
ultimate system would treat all three phases of waste and provide
economic benefits through product recovery.

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APPENDIX

TABLE 5

CHEMICAL AND BIOCHEMICAL ANALYSES OF INFLUENT

Day Sampled	pH	BOD (mg/l)	Total Org. Nitrogen (mg/l)	Sulfates (mg/l)
1	7.05	235	35.84	
2		515	38.64	
3	7.05	201	32.37	
4	7.15		35.90	190
6	7.14	53	27.08	155
7	7.19			
8	7.21	121	27.55	170
9	7.10	94	23.24	150
10	7.24	20	21.50	240
11	7.11	64	22.96	165
13	7.20	363	34.72	210
14	7.17			
15	7.24	75		275
16	7.15	106	21.34	250
17	7.11	116	10.14	150
18	7.14	125	9.58	170
20	7.09	125	35.17	190
21	7.11			
22	7.11	204	11.20	170
23	7.11		18.20	180
24	7.15	41	26.88	210
25	7.13	50	25.82	
27	7.40		30.24	
29	7.32	74	29.40	190
30	7.28	135	26.04	210
32	7.32	224		180
34	6.79		22.34	260
35	7.27			
36	7.18		44.13	280
37	7.31			230
38	7.11	171	32.42	190
39	7.16	312		210
42	7.09			
43	7.13	145	34.66	260
44	7.24	251	30.13	190

TABLE 5--Continued

Day Sampled	pH	BOD (mg/1)	Total Org. Nitrogen (mg/1)	Sulfates (mg/1)
45	7.27			230
46	7.26		29.23	
50	7.19	255	89.26	290
51	7.23			
52	7.17	324	48.22	290
53	7.25	260		250
56	7.06	172	36.51	190
57	7.13			
58	7.21	296	30.63	270
59	7.20			
60	7.10	122	34.50	270
63	7.31	118	30.35	280
64	7.27			
65	7.33	121	35.78	220
66	7.30			
67	7.14	26	37.80	
70	7.39	107	18.42	150
71	7.30			
72	7.41	55	46.20	210
73	7.21			
74	7.23		42.84	200
77	7.15	130	39.82	220
79	7.19	249	28.39	180
80	7.26			
81	7.28	143	30.63	140
84	7.27	176	31.64	190
85	7.19			180
86	7.19		58.41	
87	7.21			
88	7.13		35.06	210

TABLE 6

CHEMICAL AND BIOCHEMICAL ANALYSES OF WSP-1[a]

Day Sampled	pH	BOD (mg/l)	Total Org. Nitrogen (mg/l)	Sulfates (mg/l)	Temp. (°C)
1	7.82	24	1.25	120	26
2	7.84	5	2.74	120	26
3	7.85	10	2.61	120	24
4	7.86	12	3.36	310	25
6	7.78	1	5.15	150	28
7	7.64				25
8	7.81	3	5.00	140	25
9	7.58	8	5.34	180	24
10	7.55	5	2.87	180	25
11	7.80	4	1.29	170	22
13	7.92	13	2.31	185	20
14	7.84				19
15	7.82	6	2.20	190	21
16	7.76	9	1.12	200	22
17	7.82	0	0.47	220	24
18	7.89	4	1.79	210	25
20	7.57	18	2.33	215	25
21	7.78				24
22	7.75	3	0.88	230	25
23	7.97		2.33	220	24
24	7.87	1	0.93	230	24
25	7.81	8	1.12	210	19
27	7.90		3.29		19
29	7.86	4	2.54	220	23
30	7.55	31	1.89	250	23
32	7.59	9	2.76	240	22
34	7.82		0.47	230	24
35	7.77				22
36	7.82		2.31	220	23
37	7.68		0.49	220	
38	7.65	4	1.36	260	
39	7.89	12		250	24
42	7.78				24
43	7.86	4	2.35	270	25
44	7.90	22	1.47	250	24

TABLE 6--Continued

Day Sampled	pH	BOD (mg/1)	Total Org. Nitrogen (mg/1)	Sulfates (mg/1)	Temp. (°C)
45	7.83			270	24
46	7.89		1.94		
49	8.35				19
50	7.65	33	5.66	270	19
51	7.70				20
53	7.82	29	5.77	280	24
54	7.89	0		280	22
57	8.13	11	5.45	250	22
58	8.21				24
59	7.83	52	7.76	250	22
60	7.79				23
61	7.63	0	9.44	250	23
64	7.69	1	8.25	240	24
65	7.52				
66	7.87	8	1.59	260	27
67	7.85				17
68	7.76	0	2.33	290	19
71	7.85	15	9.95	250	19
72	7.72				19
73	7.89	0	1.94	290	
74	7.75				19
75	7.80		4.05	310	23
78	7.74	18	2.87	300	23
80	8.10	12	1.33	310	21
81	8.13				21
82	8.15	2	1.68	290	20
85	7.87	4	2.39	290	22
86	7.91			300	22
87	7.61		3.04		
88	7.73				24
89	7.62		0.95	310	23

[a] Control Pond - No sulfur dioxide, aeration rate of 1.3 lpm.

TABLE 7

CHEMICAL AND BIOCHEMICAL ANALYSES OF WSP-2[a]

Day Sampled	pH	BOD (mg/l)	Total Org. Nitrogen (mg/l)	Sulfates (mg/l)	Temp. (°C)	SO$_2$ (ppm)
1	7.67	16	3.70	81	25	
2	7.60	3	1.96	79	25	
3	7.87	4	2.12	100	24	
4	7.81	4	4.97	120	25	
6	7.75	7	7.65	120	28	
7	7.65				26	
8	7.75	2	5.07	140	25	
9	7.66	3	3.15	140	25	
10	7.86	11	3.30	130	24	
11	7.84	4	0.39	145	21	
13	8.14	0	2.59	175	19	
14	8.02					
15	7.93	6	1.62	180	21	
16	7.80	8	1.03	170	23	
17	7.75	0	3.14	190	24	
18	7.80	1	2.58	130	25	
20	7.66	7	2.15	215	25	
21	7.64					
22	7.75	9	2.35	215	24	
23	7.75		0.93	210	24	
24	7.71	7	4.27	200	25	
25	7.75	6	2.37	220	19	
27	7.90		2.13		19	
29	7.93	2	3.17	210	23	
30	7.63	29	2.80	230	24	
32	7.59	5	4.41	210	21	
34	7.73		1.94	250	24	
35	7.86				24	
36	7.75		2.31	240	23	
37	7.83		1.49	250		
38	7.83	19	2.18	250		
39	7.95	13		250	25	
42	8.01				24	
43	8.09	19	2.41	250	25	
44	8.04	20	2.97	230	24	

TABLE 7--Continued

Day Sampled	pH	BOD (mg/1)	Total Org. Nitrogen (mg/1)	Sulfates (mg/1)	Temp. (°C)	SO_2 (ppm)
45	7.86			250	25	
46	7.76		3.94		19	
49	8.37				19	
50	7.58	26	4.22	300	19	
51	7.63				20	
52	7.82	25	6.05	310	25	
53	7.92	0		290	23	
56	7.87	12	2.61	280	23	8.000
57	7.96				24	
58	3.00	79	15.21	260	23	6.125
59	2.58				23	
60	2.52	52	16.50	290	24	6.000
63	2.58	81	13.70	310	24	3.333
64	2.52					
65	2.56	10	35.78	330	28	1.000
66	2.55				18	
67	2.65	4		300	19	Trace[b]
70	3.09	33	32.20	290	18	Trace
71	3.13				19	
72	2.79	78	38.83	320		Trace
73	2.89				19	
74	3.01		41.38	330	24	Trace
77	2.52	28	37.24	340	20	Trace
79	2.65	10	34.78	270	21	Trace
80	2.69				20	
81	2.65	57	45.08	290	20	Trace
84	2.59	28	53.09	300	23	Trace
85	2.63			310	22	
86	2.53		73.58			
87	2.71				23	
88	2.71		64.62	320	22	Trace

[a] Sulfur dioxide begun on 56th day of sampling, 1000 ppm, aeration rate of 1.3 1pm.

[b] Trace amount is 0.002 ppm or less.

TABLE 8

CHEMICAL AND BIOCHEMICAL ANALYSES OF WSP-3[a]

Day Sampled	pH	BOD (mg/l)	Total Org. Nitrogen (mg/l)	Sulfates (mg/l)	Temp. (°C)	SO_2 (ppm)
1	7.16	36	34.76	360	26	
2	5.24	30	36.37	360	26	
3	5.84		36.81	360	25	
4	4.26	55	35.47	380	26	
6	3.05	46	22.54	300	28	
7	3.49				25	4.300
8	3.44	67	45.98	320	26	
9	3.88	117	37.07	270	24	Trace[b]
10	3.24	62		300	24	0.073
11	3.55	72	19.60	350	21	0.650
12						6.208
13	4.13	79	26.04	225	19	1.500
14	4.09				19	
15	7.78	66	25.31	235	20	Trace
16	7.72	98	21.95	230	22	0.333
17	7.73	78	29.90	290	24	1.700
18	4.40	17	31.75	310	26	
19						Trace
20	3.75	18	31.47	440	25	1.050
21	4.38				23	Trace
22	3.89	57	31.70	320	25	
23	4.58		39.92	360	24	Trace
24	4.15		26.66	370	25	Trace
25	4.21	66	34.05	380	19	Trace
27	4.47		32.09		19	
29	4.27	85	31.36	350	19	Trace
30	4.59	64	30.86	370	23	Trace
32	4.62	55	41.61	370	22	Trace
34	6.42		38.98	340	24	Trace
35	4.22				23	
36	4.25		32.82	360	23	Trace
37	4.31		26.82	350		Trace
38	4.31	62	39.70	240		Trace
39	4.26			230	23	Trace
42	4.23				25	

TABLE 8--Continued

Day Sampled	pH	BOD (mg/l)	Total Org. Nitrogen (mg/l)	Sulfates (mg/l)	Temp. (°C)	SO₂ (ppm)
43	4.16	21	25.03	210	25	Trace
44	3.92	126	24.64	200	25	Trace
45	4.50			240		Trace
46	4.48		30.02			Trace
49	3.42				18	
50	4.38	141	30.35	370	20	Trace
51	4.29				21	Trace
52	4.62	140	30.41	380	24	Trace
53	4.65	85		350	24	Trace
56	3.82	47	41.78	330	22	Trace
57	3.79				23	
58	4.18	138	51.24	350	22	Trace
59	4.31					
60	3.42	71	56.34	330	23	Trace
63	6.38	77	53.76	370	24	Trace
64	5.21					
65	3.49	39	40.15	370	27	Trace
66	4.10				17	
67	4.71		39.26	350	18	Trace
70	4.75	14	34.22	350	19	Trace
71	4.80				18	
72	3.54	38	47.15	270		Trace
73	3.61				18	
74	3.58	21	51.80	260	24	Trace
77	3.11	50		270	23	Trace
79	3.00	52	48.78	240	22	Trace
80	3.04				22	
81	3.09	30	61.04	230	19	Trace
84	3.17	27	51.41	240	22	Trace
85	3.21			250	21	
86	3.14		46.20			
87	3.09				23	
88	3.21		59.14	270	23	Trace

[a]Sulfur dioxide begun 12/7/70, first day sampled 1/26/71, 500 ppm, aeration rate of 0.3 lpm.

[b]Trace amount is 0.002 ppm or less.

TABLE 9

CHEMICAL AND BIOCHEMICAL ANALYSES OF WSP-4[a]

Day Sampled	pH	BOD (mg/1)	Total Org. Nitrogen (mg/1)	Sulfates (mg/1)	Temp. (°C)	SO_2 (ppm)
1	7.50	45	39.05	460	41	
2	7.06	24	37.80	450	41	
3	7.02	27	37.02	375	41	
4	3.78	75	42.98	355	42	
6	3.42	87	46.93	600	43	
7	3.38				41	Trace[b]
8	2.92	22	51.80	620	42	
9	3.02	18	47.21	640	42	Trace
10	3.02	12	44.41	640	41	Trace
11	3.05	24	33.60	875	39	Trace
12						Trace
13	3.19	8	47.71	1100	37	Trace
14	3.16				38	
15	3.30	14	42.17	900	38	Trace
16	3.23	24	36.40	950	39	Trace
17	3.25	19	28.06	900	41	Trace
18	3.05	2	72.80	1000	42	
19						Trace
20	3.54	10	43.68	825	42	Trace
21	3.10				41	Trace
22	3.21	29	45.58	800	42	
23	3.29		48.05	850	42	Trace
24	3.16	0	35.73	750	42	Trace
25	3.48	11	38.25	700	38	Trace
27	3.24		30.30		38	
29	3.10	6	30.86	680	40	Trace
30	2.87	49	32.59	700	41	Trace
32	2.91	16	36.34	720	41	Trace
34	3.08		28.22	900	41	Trace
35	3.22				41	
36	3.19		31.42	1400	42	Trace
37	3.27		38.92	1100		Trace
38	3.29	30	32.54	1000		Trace
39	2.75	34		1050	41	Trace
42	2.89				42	

TABLE 9--Continued

Day Sampled	pH	BOD (mg/l)	Total Org. Nitrogen (mg/l)	Sulfates (mg/l)	Temp. (°C)	SO_2 (ppm)
43	2.90	4	28.95	950	43	Trace
44	2.96	61	39.20	1000	43	Trace
45	3.00			1350	42	Trace
46	3.02		39.42		37	Trace
49	3.20				40	
50	3.16	60	31.30	1140	40	Trace
51	3.19				41	Trace
52	3.09	47	35.28	1150	42	Trace
53	3.12	3		1100	40	Trace
56	4.20	19	37.30	1000	41	Trace
57	3.92				42	
58	3.25	84	42.28	1000	41	Trace
59	3.27				42	
60	3.16	34	45.75	1150	42	Trace
63	3.27	33	43.12	1100	43	Trace
64	3.41					
65	3.39	40	58.58	1150	45	Trace
66	3.49				35	
67	3.42	13		1000	39	Trace
70	3.51	19	58.80	1250	38	Trace
71	3.61				39	
72	3.50	22	55.44	1400		Trace
73	3.48				40	
74	3.56	31	62.38	1500	41	Trace
77	3.03	50	63.67	1400	41	Trace
79	2.74	45	63.28	1500	40	Trace
80	2.81				40	
81	2.78	30	58.24	1400	38	Trace
84	2.51	1	73.19	1450	42	Trace
85	2.71			1400	42	
86	2.41		60.09			
87	2.53				.43	
88	2.63		67.42		42	Trace

[a]Sulfur dioxide begun 12/7/70, first day sampled 1/26/71, 500 ppm, aeration rate of 0.3 lpm.

[b]Trace amount is 0.002 ppm or less.