

Proceedings of the Eighth Annual

**AIR AND WATER
POLLUTION
CONFERENCE**

**November 13, 1962
Columbia, Missouri**

**RALPH H. LUEBBERS, P. E., Editor
Professor of Chemical Engineering**

"Is it Safe?"

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The Ninth Annual Air and Water Pollution Conference will be held on Tuesday, November 12, 1963 in the Student Union on the Campus in Columbia

Cover Photo by Massie—Missouri Commerce

“PROGRESS REPORT OF THE WATER POLLUTION BOARD IN MAKING SURVEYS OF THE STREAMS OF MISSOURI”

Edward S. Lightfoot, Water Pollution Board of Missouri, Jefferson City, Mo.

We are told today the United States uses water at the rate of 270 billion gallons per day and by 1980 we will use 600 billion gallons per day which will be close to the nations limit of fresh daily water supply. This does not imply that 270 billion gallons per day is consumed and therefore not available again. Only 75 billion gallons a day is consumed for irrigation, rural use, industrial and steam power. It does mean that water must be re-used many times over if we are to meet the future demands. If water is to be re-used, it must be of a quality suitable to the many users such as municipalities for a water supply, industries and mining for their many and varied processes, agriculture for stock watering and irrigation, and recreational, fish and wildlife interests.

The Missouri Water Pollution Law defines pollution as “The discharge or deposit of sewage, industrial waste or other wastes into the waters of the State in such condition, manner or quantity which causes the waters to be contaminated, unclean, impure, odorous or noxious to such an extent as to be detrimental to public health, to create public nuisance, to kill or have harmful effect on fish or other aquatic life, or upon game or other wildlife or unreasonably detrimental to agricultural, industrial, recreational or other reasonable uses.” The potential pollutants may be classified under the following general categories:

1. *Sewage and other oxygen demanding wastes*—These are the traditional putrescible organic substances which come from domestic wastes and from industries such as food processing plants. If this class of pollutant in sufficient concentration can remove the dissolved oxygen in a stream and smother aquatic life.
2. *Infectious agents*—The disease causing organisms discharged into streams mainly by municipalities.
3. *Plant nutrients*—Mineral substances, primarily nitrogen and phosphorus in solution which serve as food for aquatic plant life, such as algae and water weeds, which cause taste and odor in water supplies.
4. *Organic chemicals*—Including household detergents, pesticides and herbicides which are being increasingly used. The human physiological effects of these are relatively unknown when consumed in a water supply.
5. *Dissolved mineral and chemical substances*—from various mining and industrial processes and land drainage.
6. *Sediments*—which are primarily soils and mineral particles washed from the land by rain.
7. *Radioactive substances*—from bomb testing, industrial use, medical use to name a few.
8. *Heat*—added to water used for industrial cooling processes. This can have a direct detrimental effect on aquatic life by reducing the amount of oxygen that can be held in solution.

Reasonably effective treatment has been developed for only the first two of these eight classes of pollutants although research is proceeding at the Taft Engineering Center of the U.S. Public Health Service to develop new methods to treat the dissolved organic chemicals.

For many years the Water Pollution Control agency in Missouri has been aware of the urgent need for a stream survey program. What concentration of potential pollutants are already present in our streams? What low flow duration can we expect in our streams? What uses are made of our streams? These questions along with others must be answered if we are ever able to arrive at a rational solution to the problem of what degree of treatment is needed for municipal and industrial wastes. Admittedly, we have had to make an “educated guess” in the past. We have been in the position of “prescribing” without benefit of a diagnosis. A case in point was the location of Solar Nitrogen Chemicals Incorporated on a stream in southwest Missouri. This company was formed as a subsidiary of Atlas Chemical Corporation and Standard Oil Company of Ohio. Their representatives contacted our office for information on receiving stream flow, analysis of receiving stream and degree of treatment required. We knew there was no information on water quality in the receiving stream, we found there was no gauge on the receiving stream—hence no flow measurements were available and we were at a loss to determine degree of treatment needed. There was no alternative but to be completely frank and admit we couldn’t supply the answers. The industry was very cooperative and furnished us with expected flow data using flow and run off data from an adjoining stream. They sampled the stream for about a week’s period and supplied us with water quality data. Based on this information, we arrived at the treatment required for this industry’s waste. You may say “What meager data to base a conclusion.” We will agree but we felt this was better than no data at all.

Stream surveys in Missouri were begun in 1958 when Dr. Joe Neel, U.S. Public Health Service gave technical assistance to a Missouri team composed of myself, Wesley Smith, aquatic biologist with the Division of Health and Herbert Fisher, Fisheries Biologist with the Conservation Commission made studies of chemical, biological and bacteriological characteristics of Turkey Creek and Shoal Creek in the Spring River Watershed. These streams were studied because we had received numerous pollution complaints on Turkey Creek, and Shoal Creek was in the near vicinity and was used as a public water supply for Neosho and Joplin. Reports of these two surveys are published.

On October 1, 1959 the Water Pollution Board was established as a separate state agency and without suf-

ficient funds to carry on the stream survey program. The succeeding legislature convened and on April 24, 1962 the Governor authorized the money to begin this program. In the meantime, the Federated Womens' Clubs of Missouri became interested in the state's water resources and initiated a project to raise money to purchase a mobile laboratory for the Water Pollution Board. The chairman for this statewide project is Mrs. L. B. Obermiller of Columbia and she reports good progress.

The first consideration in planning a program of this scope is personnel needed. We knew we would need one engineer to work in the mobile laboratory to collect chemical data and one engineer to work full time making industrial waste surveys. The mobile laboratory will be in the field the great majority of the time and the two men will be alternated in their jobs to give them well rounded experience. We are fortunate to have Bill Sankpill and Tom Carter to fill these two positions. The Conservation Commission furnishes an aquatic biologist for full time work on the field crew. The Stream and Industrial Waste Survey Section is in charge of John Schondelmeyer who will direct the program and will review and interpret the data and help prepare the reports for the state stream inventory.

The Water Pollution Board is housed in the Old Post Office Building in Jefferson City. This building is old and we could not believe it would be economical to plan for a large scale laboratory in this building. We compared the cost of analysis by private laboratory with a cooperative program with the Water Quality Section of the U.S. Geological Survey. We found we could obtain more data for the same money with the U.S. Geological Survey since they would match dollar for dollar on all work done. The cost of this cooperative program will be discussed later under the budget.

We looked at many plans other states had used for mobile laboratories. Many of them used large house trailers converted into laboratories. We finally concluded that we needed a vehicle which could be driven right out to the site of sample collection. After looking at several possibilities, we concluded that the Chevrolet Greenbrier served our needs best. We are presently leasing one until the Federated Women's Clubs raise the necessary funds to present one to us.

The budget for the program consists of the following:

July 1, 1962 to June 30, 1963

Routine chemical analyses	\$10,000.00
Special chemical analyses	3,000.00
Salaries, 3 engineers, 1 clerk-typist	26,136.00
Operations (travel, lodging, meals, etc.) ..	8,810.00
Equipment	1,500.00
TOTAL	\$49,446.00

The \$10,000.00 for routine chemical analyses will be matched by \$10,000.00 by U.S. Geological Survey.

Since the Water Pollution Board would be the only agency collecting water quality data we met with other state and federal agencies dealing with water in Missouri to find out if any additional data could be collected which would be useful to them in their work. It was concluded after this meeting, the data we proposed to collect would answer the questions the other state agencies had.

The program has the following objectives:

1. To determine the extremes or range of quantity, the increment of ground flow in total stream quantity, the pattern of availability and mass movement of water in the stream, and the loss of stream flow to underground aquifer.
2. To determine the present water use, the anticipated use, and speculation as to the quantity and quality requirements for municipal water supplies, sewerage disposal, industrial use, recreation use, fish and wildlife, agriculture and others.
3. To establish trends of the chemical, physical, biological, and radiological characteristics of the water, as peculiar to the geological formations and the physical characteristics, both natural and man made for each of the various stream basins.
4. To locate all sources of wastes including estimates of quantity and quality of discharges.
5. Thru the initial survey and continuous monitoring; establish changes in the characteristics of the water, due to pollution.
6. To compile data on the effects of various waste discharges upon the stream under different natural conditions for future pollution abatement activities.
7. To establish water quality objectives where needed.
8. To collect data useful to municipal, industrial, agriculture, recreational, fish and wildlife, individual and all other legal users.
9. To procure data useful and necessary for securing public action toward the preservation of streams for all beneficial uses.

We have completed our preliminary planning for the program, the next step is the decision of where to begin operations. The decision on priority is made by the Board with staff guidance.

The Meramec Development Corporation was formed by citizens in the area to make a study of and recommend water resources development in the Meramec Basin. When their report was published, one of the recommendations included a water quality investigation of the waters of the State be initiated since they could not find much data for their report. The Corps of Engineers are also developing a plan for comprehensive development in the Meramec Basin and they have requested water quality information on streams in that basin.

They have also requested we furnish them with a quantity of water needed to effectively dilute treated wastes.

The urgent need for information on water quality in the Meramec Basin led the Board to its decision to begin our program in this basin.

The first order of business included making a survey of the industries and other waste discharges in the basin. The industrial waste surveys include interviewing officials of companies to determine the quantity and source of their water supply, the raw materials consumed, the products manufactured and the quantity and quality of the wastes discharged. These sources of wastes are plotted on a map which is used to locate appropriate sampling points on the stream.

A Corvair Greenbrier has been leased until such time as the Federated Women's Clubs complete their collection and a vehicle may be purchased. We plan to collect samples on the main stem and important tributaries of the Meramec, Bourbeuse and Big Rivers during the four seasons of the year to reflect changes in weather, stream flow, waste discharges etc. Chemical samples will be collected and analyzed immediately for turbidity, temperature, pH, phenolphthalein and methol orange alkalinity, dissolved oxygen, phosphate, $\text{NH}_3\text{-N}$, $\text{NO}_2\text{-N}$, $\text{NO}_3\text{-N}$, specific conductance and hardness. If a complex waste source needs to be analyzed, a sample is collected and sent to the U.S. Geological Survey laboratory at Little Rock, Arkansas.

The appropriate biological samples are collected by the Conservation Commission biologist at each station. The collection of this sample requires about the same amount of time as the chemical analysis, however, the separation of the organisms and identification, which is accomplished in the Commission's laboratory in Columbia, requires about 2-4 hours per sample. Although the chemical analysis reflects the condition of the stream at the time of collection, the biological sample gives information on the history of pollution for the past 6 months to a year. The Commission will also do some fish population studies.

The concentration of coliform bacteria will be measured at each station utilizing the membrane filter technique. Some difficulty was experienced with the media, however, a new supply of media was obtained and we are now in a position to obtain the desired results.

Radiological samples are needed to present background levels of radiation in our streams. The Division of Health is presently collecting some information in this regard and we plan to supplement their information if this is indicated.

Information we need in regard to stream flows or quantities of ground water within a basin will be supplied by the State Geologist, Dr. Tom Beveridge. We plan the number of stream gaggings which will be needed and Dr. Beveridge arranges for an engineer from the U.S. Geological Survey office at Rolla to accompany our survey crew. He makes flow determinations at each of our sampling stations each time a sample is collected.

Field work was begun in the Meramec Basin on July 16, 1962. To date the main stems of the Meramec and Bourbeuse Rivers have been completed. No work has been accomplished on the Big River.

Statistics are monotonous and I will give you only a few which have been compiled so far;

1. Man days in field	77
2. Miles traveled	4853
3. Samples collected	539
4. Sampling points investigated	95
5. Industrial waste surveys	18
6. Industrial waste treatment surveyed	1
7. Municipal treatment plants surveyed	8
8. Waste outlet locations	75
9. Man days work in office	41

Some interesting features noted so far include:

1. The PO_4 below the Salem treatment plant in Spring Creek amounted to 9 mg/1. with a flow of 1.9 cfs. The normal PO_4 content is a trace.
2. At another sampling station $\text{NO}_2\text{-N}$ and $\text{NH}_3\text{-N}$ were increased considerably due to cattle manure on a ranch 1 mile upstream.
3. We found cases where stream flow disappears and goes underground and where stream flow doubled due to influence of springs.
4. Specific conductance is a very useful parameter in locating unusual discharges to streams. For example the specific conductance was quite steady at 250-350 Mhos in the Little Courtois Creek until a sample was collected just below the entrance of the tailings pond discharge from the Pea Ridge Mining Company. The specific conductance suddenly raised to 800 Mhos. We knew about Pea Ridge operations and expected this increase, however, you can see the potential value of this parameter in locating unknown discharges.

The \$10,000 matching fund program previously referred to under our budget discussion is used to establish a monitoring network for the streams in the State. I have a map with me today which illustrates the various geological formations in the State. The chrome pins indicate the stations at which samples are being collected now. These locations were selected to reflect the quality of water from each of the different formations. As each basin is surveyed, these stations will be strategically relocated in that basin to furnish continuous water quality information. The U.S. Geological Survey provides for a chemist to sample each of the 24 stations once a month. Nine times each year, an analysis will be made for Sodium, alkalinity, sulfate, chloride, kjeldahl nitrogen, nitrate, phosphorus, hardness, non-carbonate hardness, pH, specific conductance and turbidity. Three times a year, an analysis will be made for silica, iron, manganese, calcium, magnesium, sodium, potassium, alkalinity, sulfate, chloride, fluoride, kjeldahl nitrogen, nitrite, nitrate, phosphorus, dissolved solids, hardness, non-carbonate hardness, pH, specific conductance, color, turbidity and detergents. We will

continue to collect as much useful data as possible for the least cost. If a piece of equipment is found which can do a job more efficiently, we will incorporate it into our program.

We hope to be able to complete at least one drainage basin per year. Upon conclusion of the sampling, a report will be written containing the following information:

1. Historical background
2. A physical description of the basin including geology, topography, climate and hydrology.
3. Economic development
4. Use of the water resources including municipal, industrial and mining, navigation, fish and wildlife, recreation, agriculture and dilution for treated waste.
5. The survey methods used explaining the field investigations and laboratory operations.
6. A presentation of the data composed of a list of municipal and industrial water supplies, waste discharges, low flow frequencies, hydrograph and ground water available, the laboratory results and any special studies.
7. A discussion of the data including surface water quality and quantity and a general discussion of quantity of ground water available by Dr. Beveridge. A discussion of damages to water resources by pollution and benefits to be derived from pollution abatement.

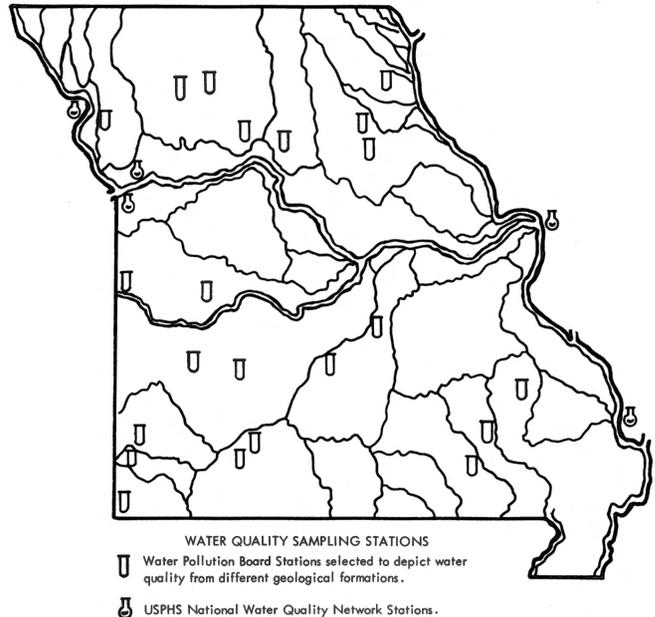
As was previously stated, this will be the first time data will be available on water quality in our streams. We will know how water uses are being impaired and we will be able to demonstrate how the effects of pollution and pollution abatement by drainage basins can be initiated.

The Water Pollution Law provides the Board with power to establish standards of water purity for any of the waters of the State. This may be done only after public hearings. Some states have adopted this plan, however, it has proved to be a long drawn out process and if a standard is found to be unreasonable the same procedure must be followed to change it. We might add that one industrial group has requested the legislature to change the law to force us to adopt "stream standards", however, we feel they are in the minority. We would rather develop the degree of treatment needed for a proposed waste discharge based on the location and the use of the receiving stream below the point of discharge. We have developed what we prefer to call "Water Quality Objectives" for the Blue River in Kansas City. Kansas City has enacted a sewer use ordinance providing for charges

based on quantity and quality of waste entering their sewer system. Some industries along the Blue River had an economic choice to make. They could discharge their waste to the city sewers and pay the monthly use charge or they could provide their own treatment acceptable to the Water Pollution Board. In order to make the decision they had to know the limits of the constituents in their waste we would allow in the river. We developed our objectives after reviewing the uses of the Blue River. It so happened we divided the river into 3 zones, each based on a different use of the stream and other considerations. The industries are now developing treatment in accordance with these objectives.

We feel the stream inventory for the State will be a valuable contribution in the following manner:

1. It will aid the Water Resources Board in developing a plan for Water Resource Utilization in Missouri.
2. The agriculture department will know what kind of water is available for irrigation.
3. The Conservation Commission is interested in the quality of water available for the fishery habitat.
4. It will aid municipalities in developing water supplies.
5. It will be useful to industry in development of new plant sites particularly where a certain quality of water is needed for a specific process.
6. It will help the Water Pollution Board evaluate waste treatment needs and the adequacy of present treatment.



THE REMOVAL OF Sr-85 AND I-131 BY RUNOFF WATER AS INFLUENCED BY THE SOIL'S COVER CROP AND THE AMOUNT OF RAINFALL*

E. R. Grabam, Professor of Soils, University of Missouri, Columbia, Mo.

Introduction

With the development of the power reaction program, a potential source of environmental contamination and fallout from fission products, it becomes important to investigate the possibility of runoff water being contaminated with such products as Sr-90 and I-131. It has been forecast that the world-wide average fallout of Sr-90 will be 26 millicuries per square mile by 1965. The concentration of the nuclide per square foot is in the order of 3×10^{10} molecules or 10^6 molecules per gram of soil. Natural radioactivity in the soil will contribute to this amount; however, if the nuclides remain in the soil, they will be harmless. The amount of radioactivity removed from the soil by runoff water is dependent in part upon the amount, frequency and duration of the rainfall, and whether the land is being cropped or is in fallow. The anticipated amount removed in runoff water will probably be small if fallout does not occur at rates greater than at present. This will not be true in the case of an emergency such as would be brought about by an all-out use of nuclear bombs or a reactor accident such as the Windscale incident in England. It was the objective of this study to investigate the concentration of Sr-85 and I-131, which would be found in runoff water in relation to the soil's cover crop and the amount of rainfall.

Plan and Method of Investigation

A study was made on Putnam silt loam (located at the Missouri Claypan Station, McCredie, Missouri). This soil is representative of the northeast claypan area of Missouri. It is classified as being flat to gently rolling having a claypan at a depth of about 6 to 10 inches. The claypan restricts the downward movement of water; therefore, the rate of internal drainage is slow.

The study was made on plots which were 10.5 x 90 feet, and so arranged that the long direction goes down the slope. The slope of the area is near 3%. The Sr-85 was added to the plots in .535 mc per each plot as strontium nitrate dissolved in weak nitric solution diluted in three gallons of water. Ten milligrams of strontium chloride were added as a carrier to each three gallons. The solutions thus prepared were sprayed on the plots. A pressure atomized type of sprayer was used to simulate rain and insure good coverage.

The first series of I-131 studies were carried out by applying .912 mc of I-131 as sodium iodide in a basic

sodium sulfite solution, which was diluted as above and applied in the same manner.

In the second study, 2 mc of I-131 as sodium iodide were applied to each plot. Ion exchange experiments on the solution indicated that most of the iodine was in the anion form and that the strontium was in the cation form.

After each rainstorm which resulted in runoff, the runoff water was collected and the activity was determined with the use of a gamma-ray-spectrometer. The resulting count was corrected for background, counting efficiency, and decay, and the data recorded.

In the strontium experiments and the first I-131 experiment, 250 or 500 ml. of runoff water were concentrated to 4 mls. and counted in a well type NaI scintillator gamma ray spectrometer. In the final I-131 experiment, a liter of solution was counted with a 5-inch diameter plastic covered NaI scintillation gamma detector. This arrangement resulted in sufficient count to allow for accuracy without concentration of the runoff water.

The plots used in the first Sr-85 experiment were fallow, corn fodder, and A and B plots growing clover and weeds in a wheat stubble. The 1961 and 1962 ex-



Fig. 1. Runoff collection tanks. The plot in the center is the fescue meadow used in the fall of 1961 and 1962.

*Contribution from the Missouri Agricultural Experiment Station. Journal Series No. 2559 Approved by the Director.

periments were carried out on fallow, corn fodder, and fescue meadow. The fallow plot was kept clean by frequent cultivation. The soil remained loose and was free of weeds. Since the experiment was done in the fall, the corn plot had a full crop of corn stover. There was a thick stand of large corn plants on the corn plot. The yield of corn was approximately 100 bushels per acre.

The wheat stubble plots used in the 1960 experiment had large amounts of straw which had fallen over, matting the soil, with some clover and weeds growing up between the semi-rotted matted straw. This condition resulted in higher amounts of runoff than is usually normal for a cropping system of this type.

The fescue meadow used in the 1961 and 1962 experiments was excellent, with plants covering every square inch of the area. The crop was green, lush, and growing vigorously at the time the experiment was carried out.



Fig. 2. Collecting samples of radioactive grass from the fescue meadow plot ten days after the application of I-131 solutions.

Results and Discussion

The results of the 1960 experiments carried out with Sr-85 are presented in tables 1, 2, and 3. The highest amount of removal was from the fallow plot and for the fall season of 1960, this amounted to .097% of the added activity. This amount is by a factor of .10 that reported by Menzel** in his studies at Tifton, Georgia and La-Crosse, Wisconsin. This is to be expected since the soil

in Georgia was a sandy loam and the slope of the Wisconsin plots was 16%. The sandy loam would result in a lower exchange capacity, which would not offer the exchange sites necessary for the absorption of strontium, as would the silt loam, and, in the case of the steeper soil the amount of runoff per given inch of rainfall would have been higher.

The fall of 1960 was somewhat drier than average for Missouri conditions, even though one rain of 2 inches was recorded. The resulting runoff was lower than has been recorded in the past.

The 1961 results of the Sr-85 experiments are presented in tables 4, 5, and 6. These tables show a removal of .98% from the fallow plot, and .04% from the meadow. This season was rather wet following good summer rains, and the November 3 rain resulted in a runoff of 63%. The above runoff values are from the fallow plots. These high rates of runoff resulted in dilution of the surface-held Sr-85, resulting in the removal of approximately 1%.

The results of the 1961 studies on the removal of applied I-131 by surface water was found to be highest on the fallow plot, being .44%, and lowest on the fescue meadow, resulting in a fantastically low value of .0003%. Since the heaviest rain and runoff occurred after the I-131 had decayed out, it is entirely possible that had the heavier rains occurred earlier in the season the amounts would have been somewhat larger.

The results obtained for the I-131 in runoff water for the tests conducted in 1962, showed the same trend that was obtained in the 1961 experiment. These results revealed that the amount of runoff obtained from the fescue meadow plots in two rainfalls was so small that it was difficult to collect runoff samples. The samples collected, when counted with the gamma ray spectrometer, revealed an activity no higher than background, (table 7).

In the case of corn fodder plots and the fallow plot, the amount of runoff obtained in the October 12 and 19 rainfalls was large enough so that a good sample of the runoff water was obtained. However, the amount of I-131 in the runoff water was relatively low, resulting in a percentage of .0005 for each of the rainfalls for the corn stover plot. The iodine in the fallow plot was by a factor of approximately ten-fold greater than that in the corn stubble. Even so this was a low amount when considered in relation to the percentage added. In the fall of 1962 experiments, 2 mc of I-131 were added to each plot; and since very little of it was found in the runoff water, it is of interest to know what happened to the iodine. The growing crop of fescue meadow was analyzed for its content of I-131. The results of a study of the fescue grass is presented in table 8. The percentage of applied I-131 on October 1, 1962, ten days after application was found to be 3.5% of that applied. Thirty-five days after application the amount was found to be .9%. This decrease in

**"Transport of Strontium-90 in Runoff." *Science*, Vol. 131, No. 3399, page 499, 1960.

TABLE 1. SR-85 ACTIVITY IN RUNOFF WATER IN RELATION TO COVER
DETERMINED AT McCREDIE - FALL, 1960

Runoff	Plot No.	Liters/Plot	Water-Held Total activity* d/m/plot x 10 ³	Inches Rain	Inches Runoff
Oct. 20	1	1.285	10.4	.45	Tr**
	2	25.666	33.9		.01
	3	5.732	31.8		Tr
	4	7.371	149.5		Tr
Oct. 27	1	2.185	34.9	.49	Tr
	2	6.917	60.9		Tr
	3	1.285	13.8		Tr
	4	2.608	13.7		Tr
Oct. 31	1	20.449	156.2	2.00	.01
	2	27.858	68.5		.01
	3	10.886	19.8		Tr
	4	12.625	22.7		.01
Nov. 16	1	48.799	751.5	.92	.02
	2	8.240	64.6		Tr
	3	2.608	14.0		Tr
	4	3.855	23.1		Tr
Dec. 11	1	0.0	0.0	.85 Snow and Rain	0
	2	8.240	32.5		Tr
	3	2.192	26.6		Tr
	4	2.192	5.5		Tr

*Activity corrected for counting efficiency and for decay to September 8, 1960.

**Tr = Trace amounts less than .01 inch.

Note: Plot 1 was fallow, Plot 2 wheat stubble, Plot 3 corn stubble, and Plot 4 was wheat stubble.

TABLE 2. SR- 85 ACTIVITY (SOIL-HELD), ERODED AS DETERMINED AT McCREDIE - FALL, 1960

Runoff	Plot No.	Grams Soils/Plot	Total activity ₃ d/m/plot x 10 ³
Oct. 20	1	19.32	2.4
	2	.92	2.0
	3	9.07	5.6
	4	4.01	16.1
Oct. 27	1	1.65	3.0
	2	.58	1.0
	3	.08	.1
	4	.54	.3
Oct. 31	1	20.77	59.7
	2	5.01	24.3
	3	4.72	16.7
	4	5.11	5.9
Nov. 16	1	150.80	99.9
	2	2.68	16.1
	3	4.35	1.3
	4	4.56	1.3
Dec. 11	1	0.00	0.0
	2	2.46	1.9
	3	2.04	.8
	4	.70	.6

TABLE 3. SR-85 ACTIVITY REMOVED BY RUNOFF AND EROSION . OCT. 20 THROUGH DEC. 11, 1960

Plot	*Sr-85 x 10 ³ activity in runoff	Sr-85 activity of eroded soil x 10 ³	Sr-85 activity removed as runoff and erosion % of total activity added
1 - Fallow	953.1	165.0	.097
2 - Stubble	260.3	45.2	.026
3 - Corn stover	107.0	24.6	.009
4 - Stubble	321.5	24.1	.028

*Sr-85 activity added/plot Sept. 8, 1960 = 1.155×10^9 d/m/plot

TABLE 4. SR-85 ACTIVITY IN RUNOFF WATER IN RELATION TO CROP COVER DETERMINED AT THE MISSOURI CLAYPAN STATION, McCREIDIE, MO., FALL, 1961

Date of runoff	Plot No.	Runoff liters/plot	Water-held total activity* ₃ d/m/plot x 10 ³	Inches rain	Inches runoff
Sept. 24	1	3.04	5.1	1.18	Tr**
	2	6.99	125.2		Tr
	3	95.00	1860.0		.05
Oct. 30	1	3.26	3.1	1.19	Tr
	2	8.62	2.6		Tr
	3	122.74	668.3		.06
Nov. 3	1	.41	.6	1.13	Tr
	2	38.76	107.1		.02
	3	680.96	2906.7		.33
Nov. 14	1	.87	.8	.45	Tr
	2	.87	1.2		Tr
	3	143.26	849.6		.07
Nov. 16	1	118.18	423.0	1.15	.06
	2	228.00	916.8		.11
	3	1516.20	5187.0		.72

*Activity corrected for counting efficiency and for decay to Sept. 25, 1961.

**Tr = Trace amounts less than .01 inch.

Note: Plot 1 was covered with a good fescue meadow, Plot 2 was in corn (estimated yield 100 bushels), and Plot 3 was clean fallow.

TABLE 5. I-131 ACTIVITY IN RUNOFF WATER IN RELATION TO CROP COVER DETERMINED AT MISSOURI CLAYPAN STATION, McCREIDIE, MO., FALL, 1961.

Date of runoff	Plot No.	Runoff liters/plot	Water-held total activity ₃ d/m/plot x 10 ³	Inches rain	Inches runoff
Sept. 24	1	3.04	6.0	1.18	Tr*
	2	6.99	10.0		Tr
	3	95.00	3863.0		.05
Oct. 30	1	3.26	7.2	1.19	Tr
	2	2.62	4.0		Tr
	3	122.74	736.4		.06
Nov. 3	1	.41	Background	1.13	Tr
	2	38.76	250.9		.02
	3	680.96	1983.6		.33

*Tr = Trace amounts less than .01 inch.

Note: Plot 1 was covered with good fescue meadow, plot 2 was in corn (estimated yield 100 bushels), and Plot 3 was clean fallow.

TABLE 6. PERCENTAGE OF ADDED SR-85 AND I-131 ACTIVITY REMOVED BY RUNOFF WATER NATURAL RAINFALL OF 1961

Plot	Sr-85 removed as runoff and erosion % of total activity added		I-131 removed as runoff and erosion % of total activity added	
1 - Fescue meadow	Sept. 24	.00043		.0003
	Oct. 30	.00021		Background
	Nov. 3	.00005		Background
	Nov. 14	Tr		Background
	Nov. 16	<u>.037</u>		<u>Background</u>
	Total	.03769	Total	.0003
2 - Corn stubble	Sept. 24	.01060		.0005
	Oct. 30	.00018		Background
	Nov. 3	.00900		.0202
	Nov. 14	.00010		Background
	Nov. 16	<u>.08050</u>		<u>Background</u>
	Total	.10038	Total	.0207
3 - Fallow (clean and loose)	Sept. 24	.1570		.1930
	Oct. 30	.0560		.0612
	Nov. 3	.2450		.1610
	Nov. 14	.0696		.0225
	Nov. 16	<u>.4550</u>		<u>Background</u>
	Total	.9826	Total	.4377

Sr-85 activity added adjusted to Sept. 25, 1961 = 1.183×10^9 d/m/plot.

I-131 activity added adjusted to Sept. 25, 1961 = 2.014×10^9 d/m/plot.

TABLE 7. I-131 ACTIVITY IN RUNOFF WATER IN RELATION TO CROP COVER AND AMOUNT OF RAINFALL.
(MISSOURI CLAYPAN STATION, McCREDIE, MO., FALL: 1962)

Date of runoff	Plot No.	Runoff liters/plot	Water-held total activity* ₃ d/m/plot x 10 ³	Inches rain**	Inches runoff	I-131 removed as runoff % of total added
Oct. 12	1	.55	Background	.93	Tr	None
	2	36.82	131.0	.93	.02	.0005
	3	116.96	635.1	.93	.06	.0022
Oct. 19	1	.65	Background	1.49	Tr	None
	2	85.81	148.4	1.49	.04	.0005
	3	321.43	487.2	1.49	.16	.0017

*Concentration/liter times the liters of runoff, adjusted for decay to Oct. 23, 1962.

**Rainfall of 1.27 inches fell during a 16 hour drizzle on Sept. 30, 1962; however, since the average rate was only .08 inches/hr. no runoff occurred.

TABLE 8. THE I-131 CONTENT OF FESCUE MEADOW GRASS

Sample date	c/m/100g	d/m/100g	Percentage applied in crops*
Oct. 1 (after 1.49 inch rain)	18,558	1.86×10^5	3.5
Oct. 26 (after 9.21 inch rain)	5,110	$.51 \times 10^5$.9

*Estimated crop yield as 2000 lbs./acre. Counted and corrected for I-131 decay to Oct. 30, 1962.

I-131 content in the plant was probably caused by the iodine being translocated to roots and loss due to rain-water solution.

Conclusions

A study of the effect of soil cover crop and the amount of rainfall as factors determining the amount of Sr-85 and I-131 in runoff water revealed the following items of importance.

The percentage of added Sr-85 removed as runoff and erosion from a fallow plot was .097% for the fall of 1960 and .982% for the fall of 1961. When the plot was covered with wheat stubble this was reduced to .026% for the fall

of 1960 and the fescue meadow covered revealed a percentage removal of .037% during the fall of 1961.

The percentage removal from corn stubble covered plots was intermediate.

The I-131 removal from a fallow plot was .438% for the fall of 1961 and .004% for 1962. The removal of I-131 from a plot covered with fescue meadow was .0003% in the fall of 1961 and zero during the fall of 1962.

Whenever rainstorms occurred at slow rates, i.e. less than .2 inches per hour, or stopped before significant amounts of rain had fallen, the plots represented in this study held the rainwater and the radioactivity.

Fig. 1. Runoff collection tanks. The plot in the center is the fescue meadow used in the fall of 1961 and 1962.

Fig. 2. Collecting samples of radioactive grass from the fescue meadow plot ten days after the application of I-131 solutions.

SOME EFFECTS OF METALS AND DETERGENTS ON FISHES

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In the past few years there has been increased concern about the sublethal effects of various types of pollutants on aquatic life. Much research has been directed toward determining the level at which mortality occurs, but little regard has been given to the consequences of exposures to low concentrations over extended periods of time. Those concerned with water pollution and its control now realize that concentrations of pollutants that are not immediately lethal may still destroy fish population, or at least shift the balance of an aquatic environment so that undesirable species become predominant. Less obvious effects might be a reduction or change in food organisms, or a decrease in productivity.

Several factors have brought about this increased interest in chronic toxicity. Certainly the population explosion has made us realize more fully the value of our aquatic habitat as a recreational resource. The disappearance from our larger rivers and lakes of desirable species of fish that are commercially important has caused concern among commercial fishermen. Widespread use of highly toxic chemicals used for pest control have stimulated interest in controlling contamination of our water supplies. The widespread appearance in many surface and ground water supplies of the common detergent, ABS, probably has caused more concern than any other single pollutant although it appears to be non-toxic in relation to many pesticides.

Research in aquatic biology conducted by the Robert A. Taft Sanitary Engineering Center is carried on at three locations. At Corvallis, Oregon, Dr. Peter Doudoroff directs a laboratory, supported jointly by Oregon State University and the United States Public Health Service. Much of the work there is of a basic nature and recently has dealt with dissolved oxygen relationships to growth and swimming performance of fishes.

At the Robert A. Taft Sanitary Engineering Center, recent research has been concentrated upon the effects of heavy metals and detergents upon fish and aquatic invertebrates. The objectives are to determine the effects that may be expected when the concentrations range from just below the lethal level to the level where there is no measurable effect. It is not enough simply to show a change in the organism as a result of a pollutant; it is necessary to evaluate the change and attempt to show its significance. This evaluation requires considerable time and is part of the reason there is hesitation in answering questions regarding the effects of toxicants on aquatic life. The aquatic toxicologist is not permitted to use the large safety factors that are commonly used in fields such as medicine. This seems to indicate that our aquatic resources are not as highly valued as perhaps they should be.

The work in Cincinnati is in two parts. Studies such as static bioassays are conducted at the Robert A. Taft Sanitary Engineering Center on Columbia Parkway. Two years ago another laboratory was established at the State Fish Hatchery at Newtown, Ohio, about three miles from the Center. At the Hatchery there is better access to fish, and, more important, a better water supply. Almost all the work at the Newtown laboratory deals with sublethal effects. Continuous flow test systems are used in order to keep conditions constant and suitable for long-term tests. Fish grow quite well in the test chambers; 2-gram bluegills may double their weight in 30-day tests. Plastic or stainless steel water lines are used to prevent contamination of the water by copper because in very soft water with a relatively low pH even minute concentrations of copper are lethal to fish.

Mr. Eugene W. Surber and his workers are engaged in extensive research to determine the toxicity of ABS (Alkyl Benzene Sulfonate) to aquatic invertebrates such as crayfish, aquatic insects, and mollusks. All of these invertebrates are important as food for fishes, and without them, fish could not thrive.

The research described on the following pages has not been published as yet. A paper on the ABS work has been submitted for publication and the rest of the work is in various stages of progress and will be published later in much more detail.

Effects of ABS on Bluegills

Previous studies of the effects of ABS on fish have been limited to five 30-day continuous-flow tests with 2-gram bluegills (*Lepomis macrochirus*). The test water was composed of 95 percent carbon-filtered and deionized water and 5 percent hard, limestone spring water. This test water has a versenate hardness of 20 mg/l (expressed as CaCO_3) and a pH of 7.3-7.4. Dissolved oxygen was near air saturation at 25°C, the test temperature. ABS was introduced by metering pumps just before the water entered the test chambers. Nominal concentrations were calculated each day on the basis of two daily measurements of flow rate and the amount of toxicant pumped during 24 hours. Grab samples were analyzed at least once weekly for ABS content and were always found to be about as expected. Each chamber had a 100-minute retention time and no attempt was made to control the light intensity or day length. Six concentrations and a control, all in duplicate, can be tested at the same time; there is room for 10 fish per chamber, or 20 fish per concentration.

ABS concentrations ranged from one high enough to produce a kill within 96 hours to one low enough to insure the survival of all fish in the two lowest concen-

trations. By using quarter points on the log scale we obtained the desired range.

There was little difference between the concentration required to kill half of the fish in 24 hours and that required for a 50 percent kill in 30 days. These TL_m (Median Tolerance Limits) values were 20 mg/1 and 17 mg/1, respectively. Actually there were few deaths after the first 24 hours, which indicates that ABS is not cumulative in its lethal effect on bluegills. The high TL_m values found were due, at least in part, to the builder salts such as sodium sulfate, present in the commercial formulation used. These apparently antagonize the toxicity of ABS.

Because the primary interest was in sublethal effects, parameters such as growth rate, histological effects, swimming performance, and blood changes were studied. There appeared to be a reduction in rate of growth at concentrations as low as 6 mg/1; not all of the tests gave consistent results, however. No histological effects were noted in any tissues except the gills, where a pronounced thickening of the respiratory epithelium was evident at 10 to 15 mg/1 and some was still apparent at 6 mg/1.

Tests on the swimming performance of the test and control fish gave negative results. There was some acclimation to ABS by test fish exposed to low levels of ABS during the 30-day test periods.

Other workers have found that ABS which has been through a sewage treatment plant is less toxic than before treatment. They also found that the toxic level depended in part on DO concentrations.

Preliminary work showed that concentrations in the range of 10 mg/1 decrease the incubation time of fish eggs and that still higher concentrations reduce the survival of the fry, or even kill the embryo before hatching.

Based on the limited data available, nuisance foams probably will appear on surface waters before acutely toxic levels of ABS are reached. This conclusion may have to be changed after the toxicity of ABS to other species and forms of aquatic life is known.

Toxicity of Heavy Metals to Fish

Considerable literature exists on the toxicity of heavy metals to fish. Extensive work has been done in this area, but there are many contradictory findings. There is little or no information on chronic effects.

Zinc was studied because it is important as a pollutant and because it has a radioisotope that can be used for tracer studies. The initial objective was to find what levels are harmless to fish and to develop an autopsy method for determining whether fish kills were zinc-caused.

The experimental system was similar to that used in the ABS studies. Adult bluegills were used; however, in order to have more tissue for analyses and to make dissection easier. The test fish were exposed to sublethal zinc concentrations for various periods of time, after which their growth rate, swimming performance, and some hematological characteristics were measured. A

complete histological examination followed. After a good procedure for rapid analysis of zinc in tissue was developed, studies were made of the uptake and accumulation as a function of time and of zinc concentration in the water.

Histological examinations showed effects only in the gill tissue. Figures 1 and 2 show gills from a normal fish and from a fish exposed to one-fourth 96 hour TL_m values, for 30 days. There is a pronounced reduction of the cell mass lying between the lamellae, and a separation of the epithelium from the supporting column of cells. Histological changes in the gills were evident at concentrations below those at which any other harmful effect was observable. The significance of this change is being studied; such effects could become important when DO is also at a critically low level.

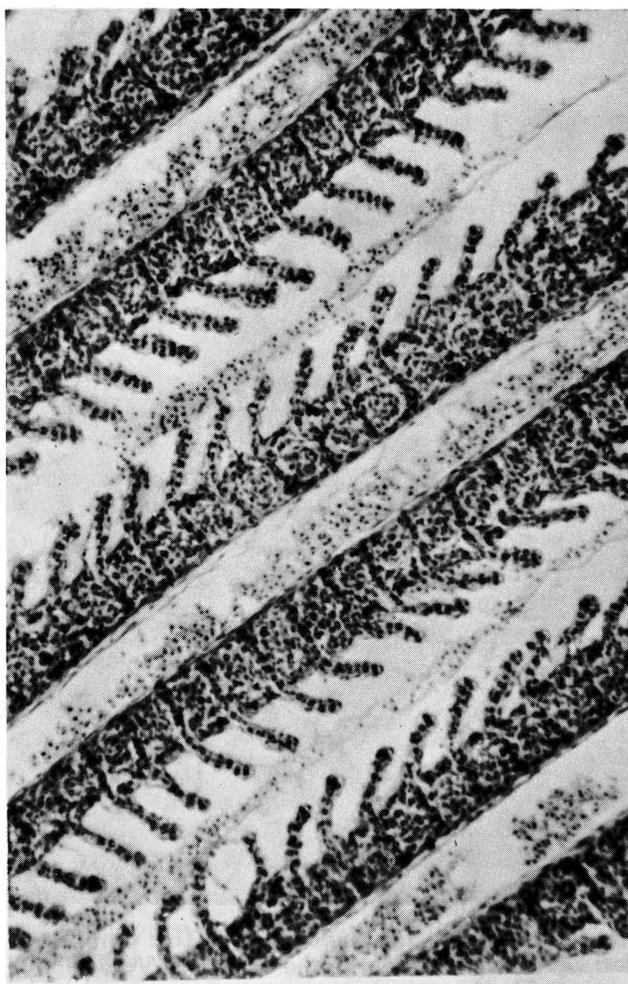


Figure 1. Normal Bluegill Gills.

In the soft water used in the experiment a zinc concentration of 3.5 mg/1 was about the maximum most of the fish could withstand. This concentration actually caused a weight loss however, and would have been fatal if the fish were exposed to it long enough. Considering mortality only, in exposures as long as 90 days, fish able

to live one week at a given concentration, will live 90 days.

Large amounts of zinc were taken up by all tissues of the body from water with concentrations ranging from 0.8 to 5.0 mg/l. The bone, scales, gut, gills, and kidney accumulated especially high concentrations. Figure 3 illustrates the pattern of uptake in a typical exposure. These data indicate that there is some intermediate zinc concentration at which accumulation is maximal. If growth rate is considered along with accumulation, the amount of zinc retained appears to be a function of growth as well as of the zinc concentration in the water.

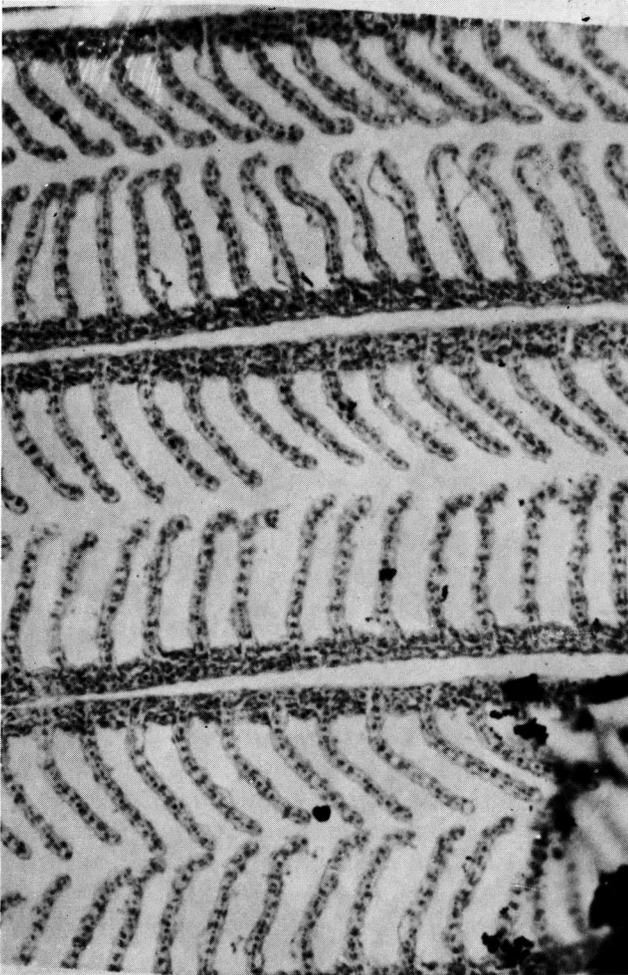


Figure 2. Bluegill Gills Exposed to a Zinc Concentration Equal to 25 percent of the 96 hr TL_m Value.

It soon became apparent that the histological damage to the gills was of a generalized type and could be produced by many different things, including other heavy metals. This left little hope that histological damage could be used as an autopsy technique. There was an obvious increase in the zinc concentration in the gills in lethal exposures; which offered some hope for autopsy analysis. However, a given level of zinc in the gill could represent a non-lethal or lethal exposure, depending on the length of time in which it accumulated.

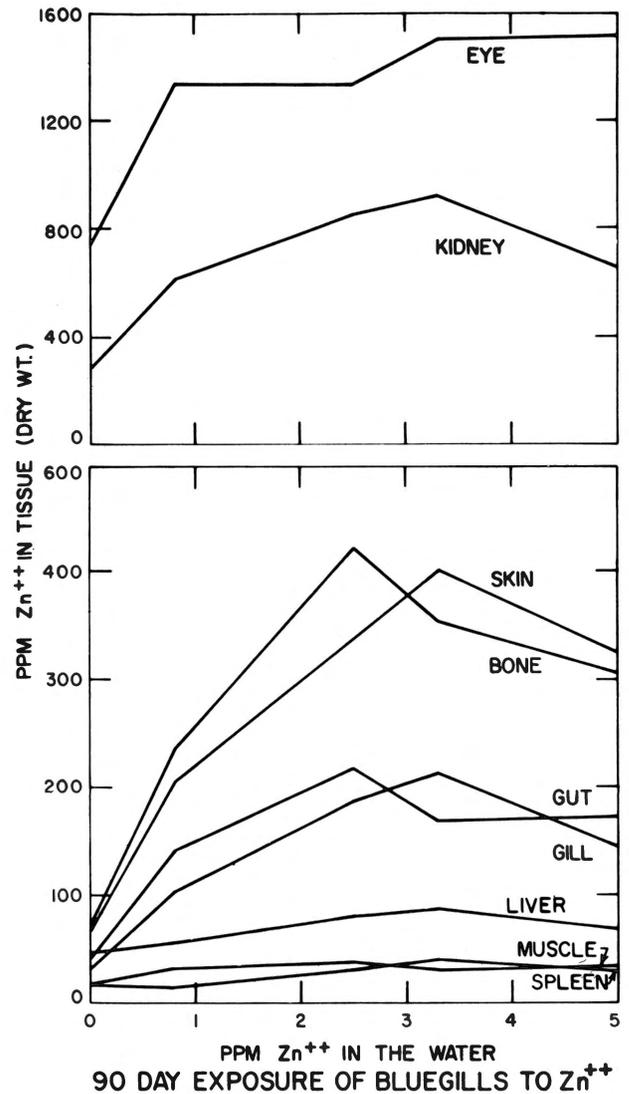


Figure 3. Uptake of Zinc in Various Tissues of Bluegills Exposed to Zinc in the Water

A comparison of curves for different tissues, such as are shown in Figure 3, suggested a new technique. A method based on the ratio of zinc found in the gills to that found in other tissues was developed to account for the effects of long-term exposure to low zinc concentrations. This method has been tested on various species, in different types of water, at different zinc concentrations, and for varying lengths of time, and the technique is reliable. Analyses were made on several thousand fish of different species from different areas of the country where the zinc concentration in the water is known and these data verify the validity of the autopsy method.

Since the basis of the method is a measure of a critical zinc concentration, it is specific for zinc mortality. Samples do not have to be carefully preserved before analysis as for histological techniques. Preliminary work indicates that the same approach can be used for other heavy metals. This autopsy method for pinpointing the actual cause of fish kills should be very useful.

There are many areas to be investigated before a complete picture of zinc toxicity is obtained. Among these are the effects of zinc intake from food on the toxic level in the water. Almost surely when the ambient zinc concentration is high, the food eaten by the fish will also contain high zinc concentrations. Does this additional intake then decrease the amount the fish can tolerate in the water?

Much research must be done in all of these areas. Future experiments are planned to determine the effect of zinc and copper and mixtures of the two on the reproduction of several generations of test animals. Needless to say, this will involve a large amount of work over a period of years to obtain a small, but important, amount of data.

Testing of the toxicity of copper, cadmium, and zinc in a block of 30 day tests, in both soft and hard water, is in progress. Evaluation of these tests should indicate some tentative levels of safety for bluegills. These tests are designed on a statistical basis to minimize variability due to different groups of fish. It is often impossible to complete an experiment with the same group of fish because of the length of time involved. Obtaining a sample large enough for these long-term tests is a problem.

The question logically arises as to how levels safe for aquatic life will compare with those already estab-

lished for purposes of human consumption. One must keep in mind that almost all mammalian toxicity is based upon an administered dose of toxicant rather than a concentration in the ambient medium, as is the case with fish. In fish toxicology one deals with a relatively continuous exposure. For this reason, the levels that are just lethal or appear to be harmless to fish are usually much lower than those established for human consumptive purposes.

A multitude of factors must be considered when one is determining safe levels; temperature, dissolved oxygen, hardness, pH, alkalinity, presence of silt, other toxicants, species of fish and fish food organisms, and many other factors influence the toxicity picture. One important consideration is that it is the extremes and not the mean that limit or determine the suitability of a habitat; weekly, monthly, or yearly averages of temperature, pH, or concentration are untenable as standards of quality. It makes little difference to fish if conditions are optimum 364 days a year; if they are intolerable on only one day, they will be killed.

Many years of research are needed to determine toxicant levels that are safe for aquatic life. Until then we must keep our waters as clean as possible and use existing data to estimate acceptable levels of contamination.

TOXICOLOGICAL EFFECTS OF HERBICIDES ON THE FISH ENVIRONMENT¹

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The effects of pesticides upon the fishery habitat commands the interest and concern of commercial and sport fishery conservationists. The careless, uninformed and indiscriminate use of these chemicals have been reported as the most frequent cause of fish kills by the U. S. Public Health Service (20). Often the subtle or chronic "trace effects" of these materials are more serious in what appear to be sub-lethal concentrations or exposures. The USPHS also has held several Biological Seminars on Water Pollution Problems (19) which emphasized many of the "trace effects" by contaminants in our most important resource: water. Their degrading action is seen in the destruction of the biological environment of desirable fish species and the depreciation of water quality for other uses.

Pesticidal chemicals are among the most difficult to study because of their great biological potency in ultra-micro quantities. They are often beyond chemical detection limits. However, new instrumentation, bioassay

methods and chemical techniques have combined to become the analytical tools in residue and toxicology studies.

The use of chemicals in the fishery environment entails a serious responsibility with respect to water usage and conservation of the resource. The biotic potential of any given species of fish is regulated by the environmental resistance of its habitat. Physico-chemical characteristics of the water and the biological complex that it supports define the parameters of the fish growth, reproduction and survival for each species. A change or imposition of any aspect of this habitat may have a profound effect upon the fishery and a reduction or depreciation of its productivity often results.

Advances in the intensive management of fishery resources require methods for control of both the fishes and the fishery habitat. The manipulation of the fish population is required to increase production of harvestable size fish. The distribution of fish food organisms and the extent of aquatic plant growth often define the limiting factors for fish production in ponds and lakes.

Pesticide chemicals have become tools of the fisheries biologist in the control of fishes and certain biological

¹Contribution from Federal-Aid in Fish Restoration Project F-1-R, Missouri.

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features of their habitat. Particular emphasis has been given to the control of aquatic vegetation constituting escape cover for forage fish populations in ponds and lakes. This is particularly important in the manipulation of the predator-prey relationship involved in the bass-sunfish stocking combinations. An abundance of plant cover results in starvation and poor reproduction of largemouth bass which is the predatory species. The more prolific forage species such as bluegill become stunted and overpopulated. This type of depreciation of the sport fishery can be corrected with chemical agents or biological controls. The new Fish Control Laboratory of the U. S. Fish and Wildlife Service, located at La Crosse, Wisconsin, has as its principal objective the development of knowledge which will lead to new and improved methods for the manipulation and control of fish populations.

The original research efforts of the author have been directed toward the development of aquatic herbicides for the control of aquatic vegetation in lakes and ponds. Intensive investigations were made during 1958-1961 while I was employed by the Fisheries Section of the Missouri Conservation Commission. They included studies on toxicological effects of herbicides on the fish, on fish habitat, on herbicides themselves, and on the degradation of residues in water and fish flesh.

Mode of Study

The pesticides were first tested in the laboratory by the bioassay methods described by Hart, Doudoroff, and Greenback (8) and others (4). The experiments to measure dose-effect relationships were made in 20-gallon aquaria at constant temperatures (Figure 1). Controls

were included. Fish were acclimatized to test waters from city taps or Little Dixie Lake for 11 days prior to toxicity tests (Table 1). Aeration and feeding were discontinued during the last 3 days of acclimatization.

After the test chemicals were introduced, observations were made at 25-hour intervals on both the test animals and the controls for a period of 96 to 254 hours. The number, size, and weight of fish per unit volume of water were taken into consideration. Measurements of differences in response to toxicity among species also were included. The results were evaluated statistically as dose-effects expressed in percent (3) (12).



Figure 1. Bioassay facilities in the temperature controlled room at the Missouri Conservation Commission's Little Dixie Laboratory.

TABLE 1. THE AVERAGE WATER QUALITY CHARACTERISTICS OF THE LITTLE DIXIE LAKE WATER SUPPLY USED IN THE BIOASSAY LABORATORY TESTS DURING 1960 AND THE COLUMBIA TAP WATER USED IN THE 1959 - 1960 PRELIMINARY SCREENING TESTS.

Chemical Constituent	Average concentration in parts per million by weight	
	Little Dixie	Columbia
Calcium	19.00	37.60
Magnesium	1.75	29.20
Potassium	5.20	46.2 ^{2/}
Ammonium	0.015	--
Nitrite	0.003	--
Nitrate	0.101	0.060
Phosphate	0.019	--
Specific conductance ^{1/}	166.7	662.0

^{1/} Specific conductance expressed in micromhos/cm. electrolytic resistance at 25° C.

^{2/} This figure includes sodium ion.

Test species included red shiner (*Notropis lutrensis*), redfin shiner (*N. umbratilis*), bluntnose minnow (*Pimephales notatus*), yellow bullhead (*Ictalurus natalis*), brown bullhead (*I. nebulosus*) black bullhead (*I. melas*), bluegill (*Lepomis macrochirus*), green sunfish (*L. cyanellus*), redear sunfish (*L. microlophus*), pumpkinseed sunfish (*L. gibbosus*), and largemouth bass (*Micropterus salmoides*). The Ozark Fisheries, Inc. supplied a carp x goldfish hybrid for use in these tests.

Seventy-two of the more promising herbicides were included in 2560 tests in the field to determine their toxicity and ecological effects. The applications of herbicides were made to open plots, whole ponds, and to the plastic enclosures developed in these studies (22). Effects of the herbicides on emergent aquatic vegetation were noted along with observations on submersed species (23) (24).

A determination of the "trace effects" of herbicides upon the fish food organisms was an important part of this study (25). Samples of bottom fauna were collected periodically with a Peterson dredge from within the plastic enclosure. Both the acute and chronic aspects of toxicity were evaluated in this phase of the investigation. In addition, the condition of plants was observed weekly during the growing season to further document the ecological situations.

A detailed study was made on the toxicology and residues of 3,6-endoxohexahydrophthalic acid (9) and its di-N,N'-dimethylcocoamine derivative (26). Laboratory and field experiments were used in tracing the degradation of these chemicals. The flax seed bioassay method (14) was supported by the endothal-armeen chemical analysis (16) for detection of the endothal cocoamine in water, fish and bottom fauna organisms. A physiological study was also made of the fish exposed and injected with the herbicidal materials. Modified hematological techniques (13) were used to document the biological features of stress.

Experimental weed control plots were located in two general areas of the state of Missouri; east central on the August A. Busch Memorial Wildlife Area in St. Charles county, and central in Boone county on private lands, U.S. Forest Service, University of Missouri Experimental Farms and the Ashland Wildlife Area.

Results and Discussion

Toxicity to Fish—Bioassay tests for fish toxicity

The acute toxicity of herbicidal materials of fishes was quite variable. Some compounds such as dalapon were relatively non-toxic at very high dosage rates which exceeded practical field application 1000-fold. Most compounds were classified as moderately or slightly toxic to fish with lethal dosages ranging between 5 and 100 ppmw, and they usually allowed a security quotient (29) of several fold. However, several herbicides were quite toxic at concentrations of less than 2 ppmw and ranging to sev-

eral ppbw. Toxicity was observed to be a function of exposure time and concentration. Figure 2, which is a plot of toxicity recorded at 48, 96 and 168 hours, illustrates this effect.

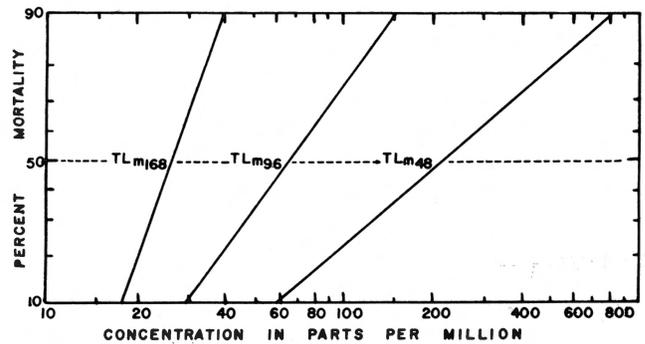


Figure 2. The per cent dose-effect curves illustrating the function of exposure time to the chemical toxicity of diquat herbicide on the carp x goldfish hybrid.

The data on fish toxicity for both the technical and formulated materials often illustrated the more toxic effects of the "inert" added ingredients. Some wetting agents, emulsifiers, and carriers were found to be either additive, synergistic or antagonistic to the toxicity of herbicides. Formulations of simazine illustrate this point (Figure 3). Toxicity may be enhanced by increased solubility, greater permeability of fish tissues, increased residual activity, complementary physiological properties supporting the direct toxic action or the actual additive poison with or without synergism (1) (8). Fish species differ in their sensitivity to herbicides as demonstrated in Figure 4.

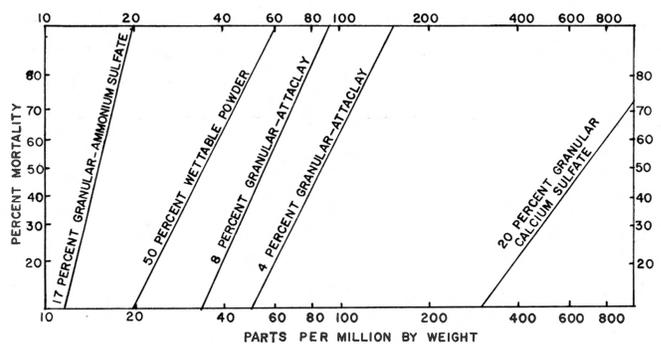


Figure 3. The per cent dose-effect curves for simazine as the active ingredient in formulations demonstrating the effect of carriers upon the chemical toxicity to bluegill, redear sunfish, green sunfish and largemouth bass in a 96-hour exposure period.

It was noted that even small changes in the chemical structure or an alteration in the side chain of the organic herbicides such as the s-triazine compounds (Figure 5) significantly affect its toxicity to fish. Similar changes in toxicity are apparent with the type of salt or ester which is used in preparation of formulations such as calvex and 2,4-D (Figure 6). The carrier is equally important in this respect (Figure 3).

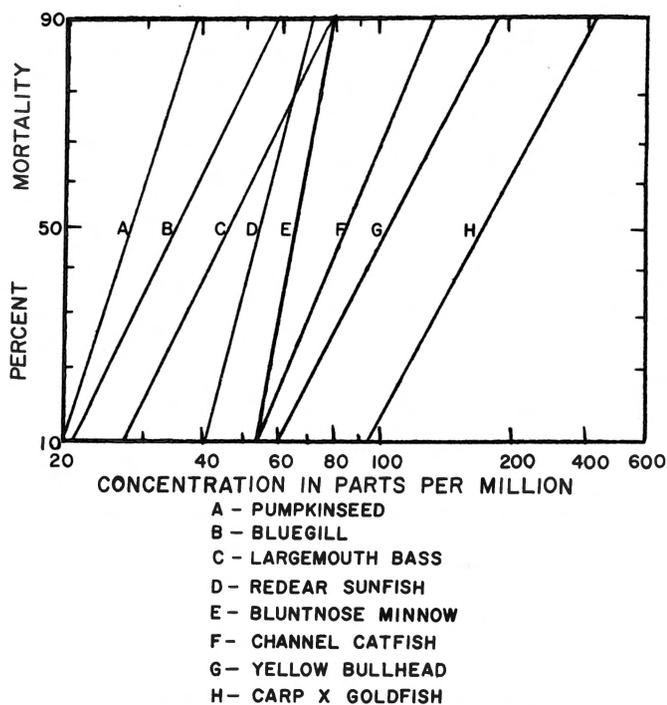


Figure 4. The per cent dose-effect curves for various species of fish exposed for 96 hours to simazine wettable powder illustrating the general pattern of sensitivity of fish species.

Methods of application can drastically affect the success of herbicidal activity as well as the toxicity to fish. The application of acrolien (Aqualin), a highly toxic lacrimator, is outlined in detail by Shell Chemical Company. Fish are repelled from the area under treatment by sublethal doses which are followed by heavier applications to achieve weed control. Acrolien or the endothal dimethylcocoamine can be used to control both fish and certain

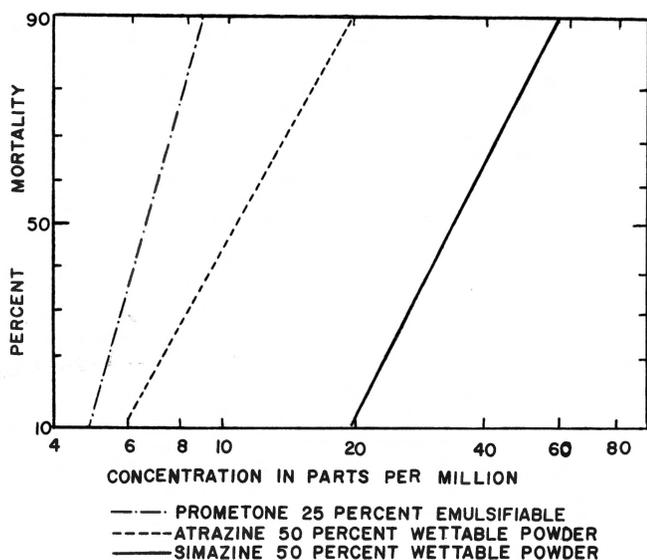


Figure 5. The average per cent dose-effect curves for various-s-triazine compounds demonstrating the significance of chemical side-chain in toxicity to bluegill, redear sunfish, green sunfish and largemouth bass in a 96-hour exposure period.

aquatic weeds (24) (26). The complete or partial renovation of fish populations is often required where aquatic vegetation contributes to over-population.

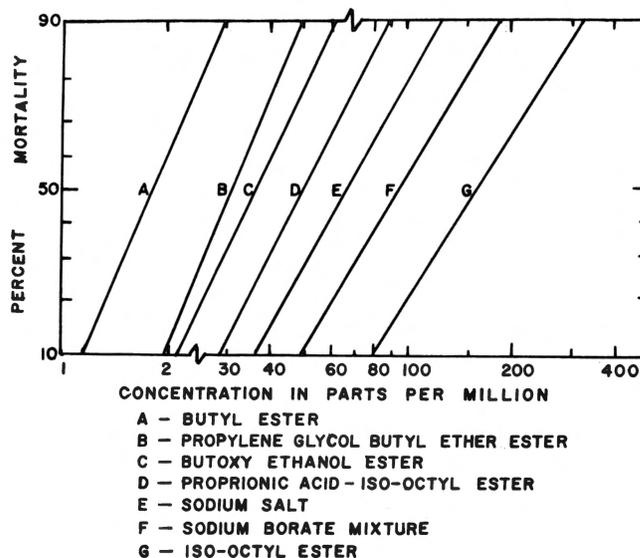


Figure 6. The per cent dose-effect curves illustrating differential toxicities of various 2,4-D formulations and one wetting agent on bluegill, redear sunfish, green sunfish and largemouth bass in a 96 hour exposure period.

The study of endothal provides us with an example of toxicological aspects of a relatively non-toxic compound. The median tolerance limit ranged from 95 to 150 ppmw in the aggregate of species and test conditions. Extended bioassay tests and higher concentrations revealed that the average minimum lethal concentrations were 60 to 120 ppmw under various temperatures and water supplies. (Table 2).

Physiological aspects of fish toxicity

The rate and mode of chemical degradation and detoxification were important from the standpoint of exposure time in relation to the concentration. The depression of oxygen tensions at higher endothal concentrations revealed a chemical oxygen demand which contributed to the asphyxiation of the test fish (Figure 7). The endothal "coco" amine derivative produced symptoms of injury to the gills.

Temperature affected both the mortality rates of fishes and the activity of endothal compounds (in the slope of the percent effect curves) as demonstrated in the example of "coco" amine (Figure 8), and in the median tolerance limits shown for endothal salt (Table 2). Reduced toxicities are probably due to higher calcium concentrations in bioassay tests made with Columbia tap water (Table 2). Increased water temperatures also produced greater gill irritation among the test species at lethal concentrations. Because of the unique proximity of the environment to the fish's physiological features, separated only by the vascular membrane of the gills, the osmotic relationship of water to the blood serum is quite significant. Under

TABLE 2. DELIMITING CONCENTRATIONS OF DISODIUM ENDOTHAL AT THE 96-HOUR EXPOSURE PERIOD FOR SPECIES OF FISH IN COLUMBIA TAP WATER (C.T.W.) OR THE LITTLE DIXIE LAKE WATER (L.D.L.W.) AT SPECIFIED BIOASSAY TEMPERATURES IN PARTS PER MILLION BY WEIGHT.

Common name	Lethal tolerance limit	Median lethal tolerance limit	Water quality (temperature °F)
Carp x goldfish hybrid	120	175	L.D.L.W. (70)
	110	145	L.D.L.W. (80)
	150	210	C.T.W. (60)
	130	190	C.T.W. (70)
Redfin shiner	60	95	C.T.W. (80)
Red shiner	60	105	C.T.W. (80)
Bluntnose minnow	90	120	L.D.L.W. (70)
	70	110	L.D.L.W. (80)
	70	120	C.T.W. (80)
Yellow bullhead	110	175	L.D.L.W. (70)
	120	170	L.D.L.W. (80)
Black bullhead	120	180	L.D.L.W. (70)
	100	185	C.T.W. (80)
Largemouth bass	95	120	L.D.L.W. (70)
	115	125	C.T.W. (70)
Bluegill	100	125	C.T.W. (80)
	105	150	C.T.W. (70)
	100	140	L.D.L.W. (70)
Redear sunfish	100	125	L.D.L.W. (70)
	100	125	C.T.W. (80)

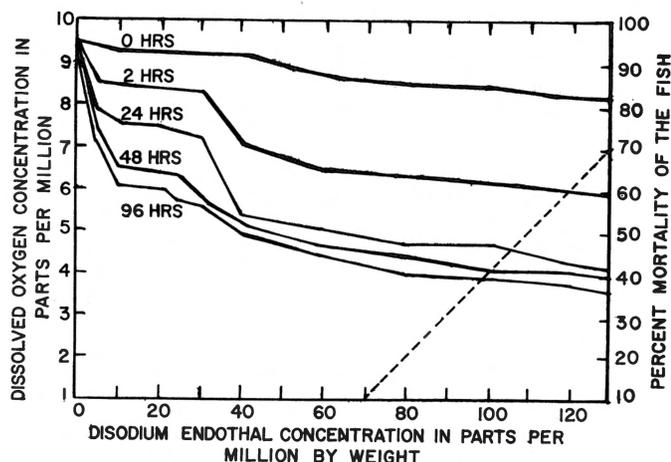


Figure 7. The effect of various disodium endothal concentrations upon the dissolved oxygen tensions with respect to exposure time (solid lines) and its relationship to the average mortality of bluntnose minnows (broken line) in bioassays at 96 hours.

stress conditions, carp x goldfish hybrids and bluegills exhibited slight changes in their hematological characteristics (Table 3 and 4). This may be explained on the basis of increased buffer action and reduction of osmotic losses of blood calcium through osmoregulation of the fish gills. Several authors have investigated the various aspects of osmoregulation relative to buffer systems (1), (8), (15), (18).

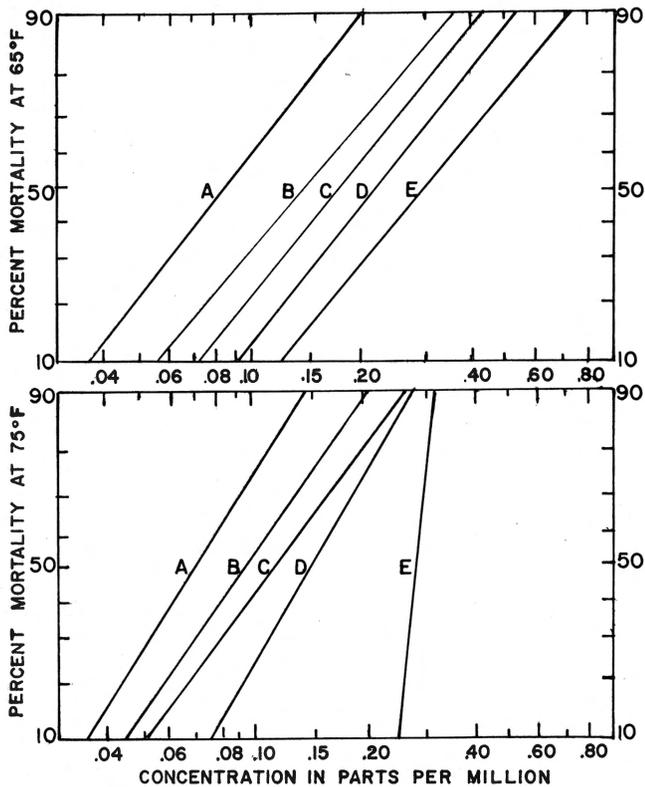


Figure 8. The per cent dose effect curves for various species of fish (A=small bluegill, B=adult bluegill, C=adult redear, D=adult largemouth bass, E=adult yellow bullhead) exposed for 96 hours to di N,N'-dimethylcocoamine salt of 3,6-endoxohexahydrophthalic acid at two water temperatures.

TABLE 3. OBSERVATIONS ON THE BLOOD OF TEST FISHES WHICH WERE INVOLVED IN THE CONTROL AND ENDOTHAL SALT OF di-N,N'-DIMETHYLCOCOAMINE ABSORPTION STUDIES. EACH OF THE EXPOSED TEST GROUPS CONTAINED 10 FISH WHICH WERE LATER ANALYZED FOR HERBICIE RESIDUES COMPARED CONTROLS CONTAINING 100 FISH EACH.

Species	Treatment	Sex	Weight (grams)	Hematological characteristics		
				Hematocrit (per cent)	Sodium ion (meq/l)	Calcium ion (meq/l)
Bluegill	control	F	11.5	44	137	5.0
	control	M	14.3	45	146	4.4
	average		12.7	44	141	4.7
Bluegill	0.05 ppm 96 hour exposure		14.6	48	149	4.6
Carp x goldfish	control		5.8	38	118	2.7
Carp x goldfish	0.05 ppm 96 hour exposure		5.8	41	122	2.5

The ability of fishes to survive in these stressed conditions depends on the structure of gills, extent of gill surface, rate of oxygen consumption, tolerance of tissues, and control of permeability as pointed out by Hart, *et. al.* (8) and other studies (1), (4), (6), (19). The differences in toxicity between species may be further explained from other experiments in fish physiology which showed significant variations in metabolic characteristics with respect to respiration, assimilation, and energy conversion of food.

Residues in the fish and their effects

Chemical analyses for herbicide residues in fish flesh were made periodically following the application of sublethal dosages in aquaria. The absorption of endothal "coco" amine into fish flesh as shown by the armeen chemical method was essentially negative. Concentrations were found to be less than 2 mg. per kg. of fish flesh over the background level found in the controls, which averaged 23.4 mg. per kg. (Table 5). This was similar to the background data obtained in aquarium experiments.

TABLE 4. OBSERVATIONS ON THE BLOOD OF TEST FISHES WHICH RECEIVED INTRAPERITONEAL INJECTIONS OF THE di-N, N'-DIMETHYLCOCOAMINE SALT OF ENDOTHAL. EACH OF THE TEST GROUPS CONTAINED 10 FISH WHICH WERE LATER ANALYZED FOR HERBICIDE RESIDUES

Species	Treatment	Sex	Weight (grams)	Hematological characteristics		
				Hematocrit (per cent)	Sodium ion (meq/l)	Calcium ion (meq/l)
Bluegill	50 mg	F	21.3	55	153	4.1
	injection		22.0	45	156	4.8
	average		21.6	51	154	4.4
Bluegill	100 mg	F	19.0	50	160	3.9
	injection		17.8	52	156	4.5
	average		18.5	51	158	4.2

TABLE 5. THE RECOVERY OF ENDOTHAL "COCO"AMINE RESIDUES FROM 20 SAMPLES OF BLUEGILL SUNFISH ANALYZED 1-2 WEEKS AND 3-4 WEEKS FOLLOWING INTRAPERITONEAL INJECTION OF 50 AND 100 MG. OF ACTIVE INGREDIENT. BACKGROUND CONCENTRATION IN 10 UNTREATED SUNFISH AVERAGED 23.4 MG/K IN THIS SERIES OF TESTS. DATA FROM METCALFE (1961) DEMONSTRATES EFFECTIVENESS OF THE CHEMICAL METHOD ON WALLEYE AND NORTHERN PIKE.

Sampling Period in weeks	Dosage injection in mg.	Average dosage in mg/k	Average amount recovered in mg/k	Percentage recovery of dosage
1 - 2	50	225.8	180.8	80.0
3 - 4	50	285.0	185.6	65.1
1 - 2	100	377.0	293.0	77.7
3 - 4	100	376.0	126.6	33.6
Walleye	5 - 100	6.0	24.1	85.8
Northern Pike	10 - 25	3.5	13.7	76.0

Intramuscular injections of endothal amine in normal saline solution produced epithelial sloughing and a resultant loss of injected material, hence this technique could not be used to determine retention time. However, intraperitoneal injections of endothal "coco" amine into bluegill were highly successful; recovery rates were comparable to those achieved by Metcalfe (18) with northern pike and walleye. Dosages of 50, 100, 500, and 1,000 mg. were used on bluegill weighing 15 to 40 grams. The higher injection rates of 500 to 1,000 mg. were lethal to the fish within 30 minutes. Endothal "coco" amine residues were recovered at levels of 78 to 95 percent in the injection experiments (Table 5). The residues from the 50 and 100 mg. injections were readily distinguished from the background amines in fish flesh 1 and 2 weeks later (Table 5). The retention of amine residues decreased appreciably in 3 to 4 weeks.

Dehydration occurred in fish at the higher rates of injection and the sub-lethal exposures at concentrations

of 0.05 ppmw. This disturbance in the osmotic regulation of the fish was indicated by an increase in the sodium ion and hematocrit values found in the blood serum (Tables 3 and 4). Higher concentrations of calcium in the water supply constituted an effective buffer effect (5) at sub-lethal concentrations in Columbia tap water (Table 2). However, losses in blood calcium were not corrected in bluegill injected with herbicide (Table 4). Carp x goldfish hybrids did not exhibit the disturbance of osmotic regulation that was evident in bluegill at those sub-lethal dosages. However, lower temperatures evidently decreased the osmotic stress and lengthened survival periods for bluegill and carp x goldfish hybrids and perhaps other species (Figure 8 and Table 3). The basic differences found between species of fish, such as metabolic rates, osmotic regulation, and other physiological factors, may be correlated with differences in the blood serum under stress (1) (4) (6) (19).

TABLE 6. AVERAGE NUMBERS OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF ENDOTHAL RANGING FROM 5 TO 10 PPMW OF ACTIVE MATERIAL IN 10 PLASTIC ENCLOSURES, 1958 - 1959.

Taxonomic group	Control	1 week	6-8 weeks	4-6 months	11-14 months
Water bugs	0.5	0.4	--	0.3	0.8
Mayfly nymphs	1.9	0.8	0.3	0.2	0.3
Horsefly larvae	4.6	3.3	2.1	1.3	0.2
Common midges	3.8	3.0	9.9	2.7	3.7
Mosquitoes	0.3	0.2	0.1	--	--
Phantom midges	3.2	3.7	6.1	8.8	20.8
Biting midges	0.4	tr.	tr.	0.4	1.7
Caddis fly larvae	3.7	5.0	4.9	--	--
Dragonfly nymphs	2.3	4.7	2.3	0.2	tr.
Damselfly nymphs	0.4	0.7	0.3	0.7	0.2
Water beetles	2.1	0.2	tr.	4.8	10.0
Aquatic worms	164.8	99.4	140.8	112.3	245.3
Leeches	0.1	0.1	0.1	0.2	0.5
Clams	27.4	33.8	7.8	1.8	0.5
Snails	2.2	0.2	--	--	--
Total numbers	217.7	155.5	174.7	133.7	284.0
Total weight	2.10	1.29	1.30	1.07	1.59

Toxicity to Fish-food Organisms

Tests for toxicity

Evaluating the effects of herbicide applications on fish-food organisms is an important aspect in its relation to the health and productive vigor of the fish population. Qualitative and quantitative samples of invertebrate populations are difficult to obtain in statistically significant numbers in the degraded type of habitats. Populations of gastropods and various aquatic worms are comparatively static while those of aquatic insects change rapidly as their larvae metamorphose and emerge in large numbers. The water quality aspects were particularly important in the numerical abundance of the organisms and the species composition. Bottom configuration, fertility, presence and form of vegetation, and water depth also have an important influence on the distribution and abundance of various species (24) (25). Obviously, adequate controls were a necessity to permit comparison of sampling results over a period of time. Therefore, control samples were taken on each sampling date and averaged for the entire sampling period. The data from 282 tests in plastic enclosures were expressed in numbers of individuals and grams of wet weight per square foot of bottom mud area (Tables 6 through 16).

TABLE 7. AVERAGE NUMBER OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF ENDOTHAL "COCO" AMINE SALT AT 1 PPMW TO 1 PLASTIC ENCLOSURE (1959).

Taxonomic group	control	3 months
Mayfly nymphs	4.5	0.7
Horsefly larvae	3.0	3.0
Common midges	3.5	0.7
Phantom midges	--	3.3
Biting midges	1.0	--
Caddis fly larvae	0.5	0.3
Dragonfly nymphs	3.0	--
Damselfly nymphs	1.5	--
Water beetles	1.7	1.7
Aquatic worms	204.0	261.7
Clams	11.0	5.0
Snails	1.5	0.3
Total numbers	229.5	273.7
Total weight	2.80	4.97

TABLE 8. AVERAGE NUMBERS OF BOTTOM DWELLING ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATIONS OF SIMAZINE RANGING FROM 0.5 TO 10 PARTS PPMW IN 14 PLASTIC ENCLOSURES, 1958 - 1959.

Taxonomic group	Control	1 week	6-8 weeks	4-6 months	11-14 months
Water bugs	0.1	0.1	--	tr.	--
Mayfly nymphs	2.5	0.3	0.4	1.7	1.0
Horsefly larvae	6.9	3.9	4.4	6.7	6.6
Common midges	7.6	9.4	3.4	6.3	3.5
Mosquitoes	0.2	--	tr.	tr.	--
Phantom midges	1.1	1.0	2.9	2.1	4.5
Biting midges	0.6	--	--	0.7	0.4
Caddis fly larvae	3.2	2.6	5.2	1.1	0.7
Dragonfly nymphs	1.8	1.9	1.1	1.0	1.3
Damselfly nymphs	0.1	--	--	0.6	0.5
Water beetles	1.4	0.1	0.2	0.6	1.1
Aquatic worms	128.6	63.9	58.5	111.2	103.8
Leeches	9.1	0.1	--	tr.	--
Clams	20.5	16.2	21.3	6.4	7.6
Snails	1.6	--	--	1.7	1.0
Total numbers	176.2	99.6	100.9	140.3	134.4
Total weight (gms.)	2.23	1.18	1.77	1.61	1.60

TABLE 9. AVERAGE NUMBER OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF ATRAZINE RANGING FROM 0.5 TO 2.0 PPMW IN 8 PLASTIC ENCLOSURES (1959).

Taxonomic group	Control	6-8 weeks
Water bugs	0.33	--
Mayfly nymphs	2.25	0.33
Horsefly larvae	8.92	1.25
Common midges	10.33	0.25
Mosquitoes	0.33	--
Phantom midges	1.00	1.25
Biting midges	1.33	0.17
Caddis fly larvae	1.25	0.17
Dragonfly nymphs	0.50	0.83
Damselfly nymphs	0.25	0.67
Water beetles	0.43	1.29
Aquatic worms	237.78	112.67
Leeches	0.08	--
Clams	6.40	0.83
Snails	0.33	1.33
Total numbers	271.80	130.83
Total weight	1.457	2.125

TABLE 10. AVERAGE NUMBERS OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF MONURON RANGING FROM 1 TO 2 PPMW IN 3 PLASTIC ENCLOSURES (1959).

Taxonomic group	Control	3 months
Mayfly nymphs	3.00	--
Horsefly larvae	2.00	4.33
Common midges	2.33	--
Phantom midges	--	0.33
Biting midges	0.67	--
Caddis fly larvae	0.33	--
Dragonfly nymphs	2.00	--
Damselfly nymphs	1.00	--
Water beetles	1.17	2.46
Aquatic worms	136.00	64.00
Leeches	0.33	0.33
Clams	7.33	1.33
Snails	0.67	0.33
Total numbers	153.00	95.00
Total weight	1.867	1.533

TABLE 11. AVERAGE NUMBERS OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF PBA (POLYCHLOROBENZOIC ACID) RANGING FROM 0.5 TO 2.0 PPMW IN 4 PLASTIC ENCLOSURES, 1958 - 1959.

Taxonomic group	Control	1 week	6-8 weeks	11-14 months
Water bugs	0.7	--	--	--
Mayfly nymphs	1.9	--	--	--
Horsefly larvae	6.8	3.2	9.5	--
Common midges	5.4	2.5	0.8	10.0
Mosquitoes	0.1	--	--	--
Phantom midges	0.7	0.3	8.0	17.0
Biting midges	0.6	--	--	24.0
Caddis fly larvae	4.1	1.7	--	--
Dragonfly nymphs	1.3	2.3	0.7	0.7
Damselfly nymphs	0.1	--	--	0.7
Water beetles	0.5	0.5	--	0.3
Aquatic worms	206.2	58.0	114.8	202.3
Leeches	0.2	--	0.2	--
Clams	31.5	75.2	6.2	1.7
Snails	0.1	--	--	0.3
Total numbers	259.4	143.7	140.2	257.0
Total weight	2.15	2.59	0.87	0.77

TABLE 12. AVERAGE NUMBERS OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATIONS OF GRANULAR SODIUM ARSENITE RANGING FROM 2.5 TO 20.0 PPMW OF ARSENITE TRIOXIDE IN 5 PLASTIC ENCLOSURES, 1958 - 1959.

Taxonomic group	Control	1 week	6-8 weeks	4-6 months	11-14 months
Water bugs	0.1	--	--	--	--
Mayfly nymphs	0.5	0.3	--	--	--
Horsefly larvae	1.1	0.7	2.0	0.3	--
Common midges	2.7	2.3	1.3	1.0	0.3
Mosquitoes	0.9	0.7	0.3	--	0.3
Phantom midges	7.6	3.2	4.0	2.3	2.3
Biting midges	1.1	0.9	--	--	--
Caddis fly larvae	1.6	1.3	--	--	--
Dragonfly nymphs	2.7	2.6	3.3	--	--
Damselfly nymphs	5.3	4.7	1.3	--	--
Water beetles	0.1	--	--	--	--
Aquatic worms	314.1	208.2	265.7	23.3	3.7
Clams	8.7	12.7	10.0	2.0	--
Snails	2.7	1.3	--	--	--
Total numbers	349.2	238.9	287.9	28.9	6.6
Total weight	1.83	1.80	1.60	0.16	1.08

TABLE 13. AVERAGE NUMBERS OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF NEBURON RANGING FROM 1 TO 10 PPMW IN 6 PLASTIC ENCLOSURES, 1958 - 1959.

Taxonomic group	Control	1 week	6 weeks	12 months
Mayfly nymphs	1.54	0.89	0.22	--
Horsefly larvae	5.04	4.44	0.56	2.56
Common midges	7.04	3.89	0.67	0.56
Mosquitoes	0.42	0.33	--	--
Phantom midges	3.58	2.78	0.67	1.00
Biting midges	0.83	0.44	--	--
Caddis fly larvae	0.67	1.22	0.44	0.22
Dragonfly nymphs	0.50	2.89	--	--
Damselfly nymphs	0.17	0.56	0.78	0.44
Water beetles	0.08	0.22	--	0.26
Aquatic worms	109.96	276.11	95.56	2.33
Leeches	0.08	0.22	--	--
Clams	3.21	7.67	0.78	0.67
Snails	2.25	7.44	16.33	--
Total numbers	136.71	308.78	116.56	10.00
Total weight	0.873	2.720	0.950	0.223

TABLE 14. AVERAGE NUMBERS OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF 2,4-D RANGING FROM 1 TO 4 PPMW IN 6 PLASTIC ENCLOSURES, 1958 - 1959.

Taxonomic group	Control	1 week	6 weeks	12 months
Mayfly nymphs	4.00	0.17	0.17	--
Horsefly larvae	12.44	4.50	4.50	3.67
Common midges	17.11	4.50	1.50	0.33
Mosquitoes	0.44	0.33	--	--
Phantom midges	3.00	1.00	3.33	0.33
Biting midges	1.22	0.33	0.50	--
Caddis fly larvae	2.78	1.33	0.17	0.33
Damselfly nymphs	0.22	0.17	--	0.67
Water beetles	0.02	--	0.17	3.33
Aquatic worms	24.11	10.00	4.50	1.67
Leeches	0.11	--	--	--
Clams	5.44	--	--	--
Snails	5.67	0.50	--	--
Total numbers	76.56	22.83	14.83	10.33
Total weight	1.299	0.733	0.175	0.127

TABLE 15. AVERAGE NUMBERS OF BOTTOM ORGANISMS PER SQUARE FOOT FOLLOWING APPLICATION OF COPPER EDTA AT THE RATE OF 1 PPMW IN A PLASTIC ENCLOSURE, 1958 - 1959

Taxonomic group	Control	6 weeks	12 months
Mayfly nymphs	2.4	1.7	0.3
Horsefly larvae	1.4	0.7	--
Common midges	3.7	2.3	0.7
Phantom midges	--	--	3.0
Biting midges	0.4	tr.	1.0
Caddis fly larvae	1.2	11.0	2.3
Dragonfly nymphs	3.7	1.7	3.3
Damselfly nymphs	0.5	--	--
Water beetles	0.6	--	2.2
Aquatic worms	119.7	91.3	48.3
Clams	4.2	--	--
Snails	0.5	--	--
Total numbers	140.4	109.7	56.0
Total weight	2.73	1.93	0.53

TABLE 16. AVERAGE NUMBER OF BOTTOM ORGANISMS RECOVERED FOLLOWING A 6-WEEK EXPOSURE TO VARIOUS CONCENTRATIONS OF COPPER SULFATE IN CANISTER LABORATORY EXPERIMENTS.

Bottom organisms	Control	Concentration in parts per million by weight									
		2.5	5.0	10.0	25.0	50.0	75.0	100	150	200	300
<i>Mayfly nymphs (Ephemeroptera)</i>											
<u>Caenis</u>	53.77	-	-	-	-	-	-	-	-	-	-
<u>Hexagenia</u>	2.00	-	-	-	-	-	-	-	-	-	-
<u>Siphonurus</u>	0.57	-	-	-	-	-	-	-	-	-	-
<i>Common midge larvae (Tendipedidae)</i>											
<u>Chironomus</u>	3.15	2.86	-	0.72	-	-	-	-	-	-	-
<u>Clinotanypus</u>	4.00	0.72	-	0.72	-	-	-	-	-	-	-
<u>Prodimesa</u>	59.49	60.06	10.73	4.29	1.43	-	-	-	-	-	-
<i>Biting midge larvae (Ceratopogonidae)</i>											
<u>Probezzia</u>	11.44	3.58	5.72	1.43	7.15	4.29	5.01	2.86	1.43	4.20	-
<i>Phantom midge larvae (Chaborinae)</i>											
<u>Chaoborus</u>	13.44	12.87	13.59	5.72	9.30	10.01	3.58	8.58	0.72	5.72	-

Toxicological effects on bottom organisms

No significant reduction in the numbers of bottom dwelling organisms was detected for those plots receiving disodium endothal, endothal dimethylcocoamine and simazine at normal herbicidal usage rates (Tables 6, 7,

and 8). Less obvious results occurred in the plots treated with atrazine, monuron, and polychlorobenzoic acid (Tables 9, 10, and 11). Only in plots receiving sodium arsenite, neburon, 2,4-D, and copper EDTA was the reduction significant following application (Tables 12, 13, 14 and 15). Although several species of bottom organisms were not completely destroyed, the more subtle effects such as change in species composition, production, and availability as fish food may have a profound influence on the ecology of fish habitat.

The application of chemicals may cause an immediate acute toxicity, a more subtle chronic toxicity, or even a very rapid increase in the production of certain organisms. Some applications strongly inhibited growth or practically eliminated several species. Acute toxicity was proportional to the concentration and was a direct function of the exposure time. This was demonstrated in the laboratory tests with copper sulfate (Table 16). Chronic toxicity was revealed by a gradual reduction in number.

Residues in bottom organisms

Residues of di-N,N'-dimethylcocoamine salt of endothal were found in detectable quantities in those plots receiving more than 0.3 ppmw. Dosage rates less than 0.1 ppmw, however, were not readily distinguished from

the natural background of amine concentrations found in the control (Table 17). This suggests that endothal residues may be more concentrated in organic matter associated with bottom muds following application of the herbicide. Most herbicides are strongly adsorbed onto the clay and organic colloids (2). The normal process of eutrophication is associated with the accumulation of organic matter from plants and siltation from watershed sources. These deposits accompanied by leaching perform the act of burying the degradation products which are not recirculated as plant and animal nutrients. The bottom organisms, which thrive on these organically enriched deposits, may have intimate contact with herbicides and degradation products. We observed the complete destruction of bottom organisms in those plastic enclosures receiving dosages greater than 1 ppmw of the di-N,N'-dimethylcocoamine salt of endothal. However, these applications exceeded those recommended for practical use.

TABLE 17. THE CONCENTRATION OF HERBICIDE RESIDUE FOUND BY THE ENDOTHAL-ARMEEN METHOD IN FISH-FOOD ORGANISM SAMPLES FROM 3 PLASTIC ENCLOSURES AND CONTROL AREA 3 WEEKS FOLLOWING THE HERBICIDE APPLICATION.

Application rate p.p.m.	Weight in grams of sample ¹	Endothal-armeens mg/k
Control	5.2	21
0.1	5.3	24
0.3	5.5	46
0.6	5.3	128

¹ Sample consisted of organisms from three square feet of bottom area.

Ecological aspects

The results from this study indicated the residual toxicity, the extent of habitat degradation, possible chronic "trace effects," and the ecological implications of the chemical application. We found that very few bottom dwelling fish-food populations were static and entirely unchanged in their numerical abundance. Several kinds of weed inhabiting species virtually disappeared after the aquatic vegetation was destroyed, whereas aquatic earthworms, dipterous larvae, and fingernail clams became abundant. Water which approached septic conditions from the decomposition of dead vegetation contained an abundance of phantom midge and mosquito larvae. In general, decomposing vegetation stimulated growth and production of all but the weed inhabiting species. However, oxygen depletion due to biochemical oxygen demand in these situations often resulted in fish mortality. Systemic or growth regulating herbicides acted slowly and minimized this problem, while contact-type

weed killers which caused rapid death and decomposition of plants accentuated fish mortalities.

Toxicity to Aquatic Plants

Tests for vegetation control

The treatment of a plant-infested body of water with a weed control chemical caused a drastic change in the natural ecology. In the case of contact herbicides, this change was comparable to that of the effects of fire upon the terrestrial environment. Sterilization of the soil occurred with the more persistent, systemic-type chemicals. The subsequent regrowth or new plant growth represented the character of the secondary succession or recovery from pollution (Table 18). These observations reveal the general abundance and occurrence of the aquatic plant species, their sensitivity to chemical control and the ecological sequence of plants which followed.

The observations on the new growth by a species indigenous to a plot indicated the relative positions of plant life in secondary succession. The algae consistently dominated the early stages of revegetation. Chara or muskgrass (*Chara vulgaris*) and filamentous algae (*Cladophora* and *Pithophora*) were more common. Slender naiad (*Najas flexilis*) followed by leafy (*Potamogeton foliosus*) and small pondweed (*P. pusillus*) or sago pondweed (*P. pectinatus*) were among the first of the higher aquatic plants to be observed. American (*P. nodosus*) and waterthread (*P. diversifolius*) pondweeds often were accompanied by coontail (*Ceratophyllum demersum*) or watermilfoil (*Myriophyllum exalbesens* and *M. heterophyllum*) in the later stage of secondary succession. The latter species also were common to mature ponds which were undisturbed.

Herbicide activity and physiology

Chemicals with soil sterilizing properties usually are nonselective and have more profound effects on pond ecology. Contact weed killers have less effect on revegetation which often occurred from the unaffected root stock. Regrowth usually was observed within a period of 3 to 6 months following chemical treatment (Table 18).

Herbicides with pre-emergent activity were most effective in inhibiting growth. Plots receiving soil sterilizing dosages of these chemicals were often barren for periods up to and exceeding two years. Viable areas of vegetation were left standing in a growth inhibited state similar to winter dormancy for as long as six months. Triazine related compounds (simazine, atrazine, and propazine) and substituted ureas (monuron, fenuron, diuron, neburon and the TCA complexes) were most effective in the control of monocots, dicots and filamentous algae. All of these herbicides have a common physiological mode of toxic action which has been elucidated as inhibitors of the electron transfer system of enzymes involved in the oxidative phosphorylation associated with

TABLE 18. FREQUENCY OF OCCURRENCE FOR 17 COMMON SUBMERSED AQUATIC WEEDS EXPRESS IN PER CENT INFESTATION FOR THE 625 WEED CONTROL PLOTS OF 1958-1960 WITH OBSERVATIONS ON THE ENSUING REGROWTH AND NEW GROWTH FOLLOWING CHEMICAL TREATMENT.

Species	Before treatment	Regrowth			Plus new growth	
		After 1 month	After 3 months	After 6 months	After 3 months	After 6 months
Filamentous algae <u>Cladophora</u> spp.	38	18	22	32	26	46
Filamentous algae <u>pithophora</u> spp.	26	8	17	23	18	26
Filamentous algae q <u>Spirogyra</u> spp.	10	4	4	5	5	8
Chara or muskgrass <u>Chara vulgaris</u> spp.	41	23	29	35	31	41
American pondweed <u>Potamogeton nodosus</u> spp.	47	13	16	22	15	22
Waterthread pondweed <u>Potamogeton diversifolius</u> spp.	18	5	7	10	7	11
Leafy pondweed <u>Potamogeton foliosus</u> spp.	12	4	5	6	5	7
Small pondweed <u>Potamogeton pusillus</u> spp.	5	tr.	1	2	1	2
Fineleaf pondweed <u>Potamogeton filiformis</u> spp.	5	1	1	2	1	2
Sago pondweed <u>Potamogeton pectinatus</u> spp.	5	tr.	1	2	1	2
Slender naiad <u>Najas flexilis</u> spp.	29	5	8	13	9	14
Waterstar grass <u>Heteranthera dubia</u> spp.	8	-	1	1	1	1
Common coontail <u>Ceratophyllum demersum</u> spp.	15	2	4	9	4	9
American elodea <u>Elodea canadensis</u> spp.	3	2	2	3	2	3
Eelgrass <u>Vallisneria americana</u> spp.	3	2	3	3	3	3
Waterhyssop <u>Bacopa rotundifolia</u> spp.	2	1	1	1	1	1
Watermilfoil <u>Myriophyllum heterophyllum</u> spp.	1	tr.	1	1	1	1

photosynthesis (2) (21). Other materials were found to be more selective as aquatic herbicides (2,4-D, silvex, polychlorobenzoic acid, diquat, endothal, acrolein, fenac and dichlobenil).

Chemicals with a high degree of contact activity (sodium arsenite, borate mixtures, acrolien, pentachlorophenol and nitrophenols) gave nonselective results of shorter duration. The herbicidal impact on enzymatic processes within the cellular structure of aquatic plants can produce drastic effects upon the exposed tissues which are vulnerable to this specific mode of action. Pentachlorophenol, dinitrophenol and many other compounds are exceedingly potent uncouplers of oxidative phosphorylation (17). According to Mitchell, these compounds are quite capable of penetrating the cell membrane and destroying its selectivity function in ion exchange (17) (21).

The same biochemical processes can occur in animals and produce subtle changes in the functions of their organs. The effects of 2,4-D upon mammalian mitochondrial membranes (5) *in vitro*, and of other physiologically active pesticides (19) *in vivo* demonstrate modes of action which cause concern regarding chronic toxicity to plant and animal life. The "trace effects" involve the critical, biochemical balances in enzyme systems which are concerned with the growth, vigor and fecundity of the organism.

Residues in the fishery habitat

The degradation of endothal dimethylcocoamine (26) provides us with an example of the ramifications of problems in residue analysis in the fishery habitat.

Studies on the degradation of this compound in aquaria revealed that a rapid breakdown takes place in

the first week. A background concentration of 0.1 to 0.5 ppmw of long-chain amines was recorded for the aquarium waters. (Table 19). The decomposition of fish flesh which contributed to background concentrations up to 0.5 ppmw did not interfere, however, with the endothal-ameen method of determination.

The absorption of endothal by aquatic vegetation within plastic enclosures within a pond was apparent immediately following the application. Endothal amines subsequently were released, along with amines of vegetative origin, as decomposition of the vegetation occurred within 3 to 5 days. Dilution of residue by rainfall during the period of determination was not significant. The enclosures were placed along the dam of the pond, and thereby inflow was kept at a minimum.

The decomposition of vegetation following herbicide application in the plastic enclosures provided much higher background concentrations of amines. The levels ranged from 0.2 to slightly over 5.0 ppmw depending upon the amount of vegetation present. The breakdown of endothal "coco" amine and the long-chain amine components of decomposing vegetation were of similar duration (Figure 9). Agreement was found in the degradation curves plotted for both the flax seed bioassay technique and the endothal-ameen chemical method of determination. The breakdown of the endothal "coco" amine exhibited a direct functional relationship of time and concentration. Rapid degradation occurred at lower herbicide concentrations (0.1 and 0.3 ppmw), while greater time was required with increased concentration. The residue from the 10 ppmw dosage rate required nearly 25 days to disappear.

TABLE 19. RECOVERY OF ENDOTHAL DIMETHYLCOCOAMINE WITH CORRECTIONS MADE FOR BACKGROUND LEVELS OF LONG CHAIN FATTY ACID AMINES (ENDOTHAL-ARMEENS) FROM WATER CONTAMINATES (.07 TO .09 PPMW) AND DECOMPOSING FISH FLESH (.10 TO .51 PPMW) INTRODUCED AT THE RATE OF ABOUT 200 MG/KG IN AQUARIA TESTS.

Dosage of endothal dimethylcocoamine	Endothal-ameen recovered after 1 day (ppmw)	Per cent recovery of endothal dimethylcocoamine	Endothal-ameen recovered after 4 days (ppmw)	Per cent recovery of endothal dimethylcocoamine
0.05	0.11	38	0.15	27
0.10	0.19	56	0.49	49
0.20	0.31	70	0.68	68
0.40	0.48	75	0.59	65
0.60	0.74	88	0.62	56
0.80	0.92	88	0.78	60
1.00	1.19	96	0.82	54
2.00	2.22	99	1.68	67
4.00	4.29	101	4.20	93
Control ¹	0.24	0	0.51	0
Control ²	0.08	0	0.09	0

¹Whole dead fish were added to aquaria and allowed to decompose at 190 mg/kg.

²Only live fish were present in a quantity equal to 200 mg/kg.

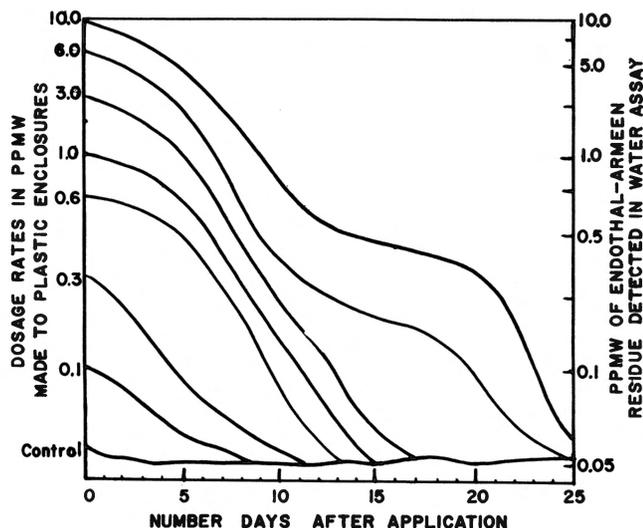


Figure 9. The degradation curves of herbicide residues showing concentrations of endothal-armeen residues, and flax-seed inhibition levels for three dilutions for the control and seven rates of application of di-N,N'-dimethylcocoamine salt of 3,6-endoxohexahydrophthalic acid in plastic enclosures.

Limnological aspects

The effects of both the endothal herbicides upon fish-food organisms did not result from direct chemical action, but from ecological and limnological changes. Table 20 illustrates the change in water chemistry resulting from plant destruction following herbicide application. The numbers and weight of bottom fauna increased following the release of plant nutrients (Tables 6 through 16). Acute toxicity was demonstrated by the immediate effect of the herbicide on the bottom fauna (Figure 10). A change in the species composition occurred in conjunction with the change in habitat. Species tolerant of the organic pollution resulting from plant decay were dominant in the period succeeding the eradication of aquatic plants (Figure 11).

TABLE 20. LIMNOLOGICAL CHANGES PRODUCED BY EFFECTIVE DOSAGES OF ENDOTHAL COMPOUNDS IN WHOLE PONDS AND PLASTIC ENCLOSURES. AVERAGE MEASUREMENTS OF PLANT NUTRIENT CONCENTRATIONS (IN PPMW) AND SPECIFIC CONDUCTANCE (IN MICROMHOS) BEFORE AND AFTER WEEDS WERE CONTROLLED (2 to 6 WEEKS) IN 38 TEST PLOTS

Plant nutrient	Before treatment	After treatment	Untreated control
Calcium	22.6	26.5	20.7
Magnesium	3.41	5.89	2.85
Potassium	4.60	5.10	4.40
Ammonium N	0.285	0.620	0.260
Nitrite N	0.006	0.015	0.008
Nitrite N	0.205	0.410	0.280
Phosphate P	0.012	0.126	0.018
Organic P	0.029	0.230	0.022
Total P	0.041	0.256	0.040
Specific conductance	130.5	195.2	120.6

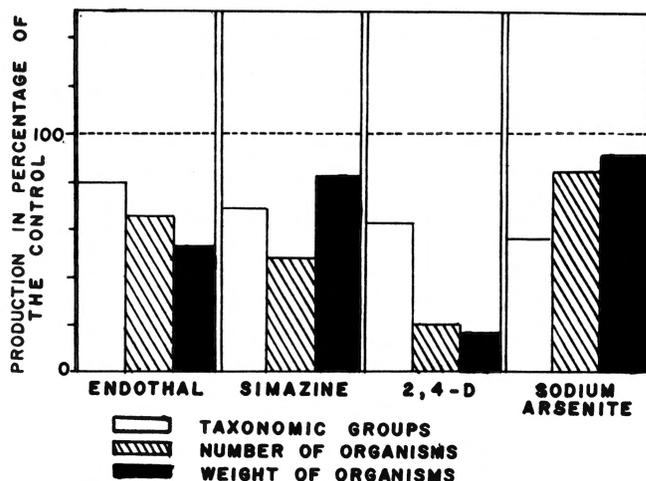


Figure 10. A graphic illustration of the comparative acute toxicity of four common herbicides to bottom dwelling fish food organisms.

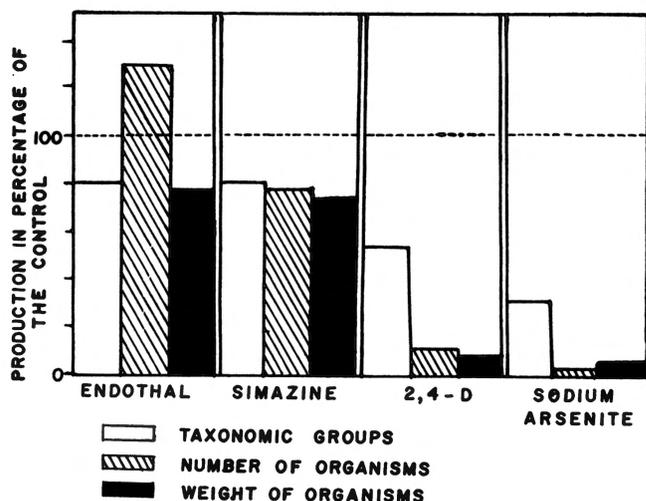


Figure 11. A graphic illustration of the comparative chronic toxicity of four common herbicides to bottom dwelling fish food organisms.

Fish are primarily opportunists in selecting foods (7) (10) (11). Bluegills have been found to feed chiefly upon insects, aquatic worms, and entomostraca (10). The habitat change caused by vegetation removal would then appear to increase the availability of food which results in the increased production of bluegills. However, some forage fish such as the redear sunfish may not benefit from this change. This species of sunfish is known to feed upon gastropods (10). Since the control of aquatic vegetation eliminates the gastropod habitat, this species of fish would suffer the adverse affects of the herbicide.

Summary

The preliminary examination of the toxicity of herbicidal materials to fish was made in the laboratory. Bioassay methods showed that acute toxicity was a function of concentration dependent upon the time of exposure and effect of water temperature. The toxicity of the chlorinated hydrocarbon pesticides was somewhat selective in

establishing an order of sensitivity for various fish species. Small variations in the side chain, alterations in the salt or ester form, manipulation of the carrier and use of wetting agent or emulsifier had a marked effect upon the toxicity of the pesticide to fishes. The mode of action of the chemical toxicity, the degradation and detoxification of the material also function in the toxicology. Subtle "trace effects" of the chemical toxicity are reflected in the physiology of the fishes.

The chemical control of aquatic vegetation resulted in a pronounced change in the limnological characteristics of the water. The water chemistry was similar in nature to organic pollution. The decomposing vegetation was often the cause of oxygen depletion and the abundance of plant nutrient released was found to stimulate growths of filamentous algae in many cases.

A detailed study was made on the degradation and residues of endothal dimethylcocoamine which was used as an aquatic herbicide. The chemical and bioassay methods of analysis revealed that the breakdown of this herbicide was a direct functional relationship of time and concentration. Rapid degradation occurred in the water at lower concentrations (0.1 to 0.3 ppmw), while greater time was required with increased concentration. The residue from the 10 ppmw dosage rate required nearly 25 days to disappear. No residues could be detected in fish at sub-lethal doses (0.05 to 0.1 ppmw). Intraperitoneal injections of 200 to 500 mg/K were found to decrease appreciably within 3 to 4 weeks in the chemical assays of the fish flesh. Although field applications in excess of the 1 ppmw dosage rate destroyed the bottom fauna, the chemical analysis recovered some residues at the sub-lethal dosage rates of 0.3 to 0.6 ppmw. Residues could not be distinguished from the natural long-chain amines at lower dosage rates.

Chemicals can significantly alter the fishery habitat with either benefit or destruction. The nature of changes in the environment may have profound influences upon the production and species composition of the fish food organisms. The effects can be measured in terms of acute toxicity featured in biological response. The long term effect of the ecological change may be described as the chronic toxicity. These factors may have a drastic impact on the nutrition of the fish. The growth, vigor, fecundity and resistance of fish to disease, and abnormal predation weigh heavily on the biological and chemical features of the habitat.

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DETERGENTS AND WATER POLLUTION— THE PROBLEM IN PERSPECTIVE

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Within recent years, increasing attention has been given to problems which appear to be scientific, or technical, but which cannot be properly evaluated in a purely scientific or technical frame of reference. Offhand, I think of the fluoridation question, or the polyunsaturated fats debate, or the proper role of insecticides.

Perhaps there should be called techno-emotional problems, for the emotional attitudes of the man-in-the-street generate pressures which call for an answer that the public, as well as the scientist, will accept.

To some extent, the problem of persistent detergent residues, as related to water pollution, falls into this class. The sight of detergent suds in the kitchen sink or laundry tub is a daily experience in almost every household. Even on TV, there is a controversy about high-suds versus low-suds in the washer. Yet, unlike the old soap bar, detergents are still new enough to generate a disquieting question or two, if not actual concern, at the possibility of their being ingested.

Thus, once foam makes an appearance on a stream, or even at a sewage treatment plant, it is not just a technical problem, but one evoking a direct public identification with "those suds-making detergents". And if foam appears on one's own well water, there is no question as to the culprit in the mind of the householder. He wants no scientific appraisal of the inadequacy of his septic tank. He finds it easy to believe that detergents have been foisted on the public, puffed up with unnecessary suds—and that a simple change in formula—bringing down the suds level—would solve all his troubles. He may even deplore "non-degradable" detergents in contrast to good old degradable soap—particularly if he never does the laundry himself. Of course, this is not the whole story.

The detergent industry, these last ten years, has approached its relationship to the pollution issue primarily as a technical one—rather than as a techno-emotional one. We followed the proceedings of national conferences on water pollution, with their record of inadequate and overloaded plants—and the continuing discharge of untreated sewage from cities and towns with 22 million population. We read of public health leaders condemning closely-located septic tanks and wells as basically unsound while their use continued to grow. And, rightly or wrongly, we evaluated the effect of our own product as a marginal one—if anything as an *indicator* of pre-existing public health hazards, rather than a "cause celebre". This, of course, was from the technical point of view.

From this viewpoint, the fact that pollution traceable to detergents is not a public health issue in itself can *still* be substantiated, as I will briefly try to show. But from the *techno-emotional* point of view—there is no arguing with the impact of water topped with a visible foam. This is now pollution personified—even though the stream beneath it has been unfit for human consumption for the past 25 years. It is also one of the few aspects of the pollution problem which can be attacked without posing the need for a substantial increase in the local tax bill for better treatment.

So, if you see us now working vigorously to change our formulations—this is not due to an initial complacency or unconcern for the actual effects of our present products on public health or convenience. The case against present-day so-called "hard" detergents, *per se*, is certainly weaker than the case against on-lot wells and septic tanks, *per se*. We now find that the sight of foam—whatever its combination of causes—is being laid directly at detergents' door. Meanwhile, a host of government

reports on the widespread unseen hazards existing before detergents were invented, and hazards that only large expenditures of tax money will clear away, are being submerged. The *technical* fact is that doing the *full job* against pollution by advanced treatment would concurrently correct the conditions under which present detergent residues cause visible foam affecting water supplies. The *techno-emotional* fact is that we cannot wait for sewage treatment methods to reach the standards they should.

That is why so much of the development work of our producers and suppliers is now being concentrated on new surfactants of greater degradability. We are still greatly heartened by the approach of the Advanced Wastes Treatment Project of the U. S. Public Health Department. When we read that in a certain sewage effluent, 65 per cent of the persistent organic pollutants are "unknowns", and only 10 per cent or so are identified as ABS (1), this appears to be the technical perspective most conducive to protecting public welfare. But as a techno-emotional answer, the goal now impinging upon us is to improve the degradability of surfactants used in detergents to a point where—even after less-than-ideal sewage treatment—they will not be a contributor to visible foam downstream.

So much for the philosophy—now what are some of the facts?

To begin with, there are few examples in industrial history where one type of chemical material—out of thousands having somewhat similar properties—has taken over a household market quite so rapidly and thoroughly as the surface active agent—or surfactant—common to most synthetic detergents. Since World War II, a negligible detergent volume has grown to some 3.5 billion pounds per year, of which some 800 million pounds is the surfactant content. Of this, it is estimated that at least 70 per cent is alkyl benzene sulfonate—the familiar ABS—derived from propylene tetramer. The structure and characteristics of the material have been thoroughly reported in the literature (2). Needless to say, those studies negate the popular public concept that surfactants can be neatly classified as "degradable" and "non-degradable". The rate and extent of breakdown of this and other surfactants in waste water is a matter of degree—and the degree is greatly affected by the composition of the waste water and its subsequent treatment and movement. None are indestructible, in the way that common salt is indestructible, in passing through a treatment plant. In surface water, the breakdown of ABS is such that the situation is self-correcting, except under unusual circumstances, before the receiving stream becomes a source of potable water.

The "whys" of the resistance rates of organic surfactants to biological breakdown have been studied for years. McKinney and others did some early work at M.I.T. which has been widely quoted (3). Dr. D. R. Swisher of Monsanto Chemical Company presented a paper at the Water Pollution Federation in Toronto just a few weeks ago which will be of particular interest to

those wishing to inform themselves in this highly technical area (4).

Initially, of course, the industry's primary concern lay elsewhere. As might be expected for a household product associated with food preparation, even before ABS came into general use, it was established that it had acceptably low levels of toxicity. Feeding tests extending up to six months or so, involving both animals and humans, went in the record as early as 1945 (5). More recently, chronic toxicity tests extending to two years or more on rats and dogs have been conducted confirming its non-toxicity over this period when ingested at rates 100 times or more higher than levels encountered in water supplies. The recommended standards of the U.S.P.H.S., setting a limit of 0.5 ppm ABS for esthetic reasons and as an indicator, also bear out this point (6).

In any event, with a satisfactory assurance of this important safety point, the industry turned to an evaluation of the relative persistence of ABS and related surfactants and the effects of such persistence, in conventional sewage treatment systems. The first such evaluation was concentrated on problems of foaming or frothing in aeration tanks of activated sludge sewage plants. We immediately ran up against a situation that has remained to plague us even today—that is, the great number of variables—over and apart from the surfactant level itself—that determine the extent of this frothing effect. Examples have been cited of two aeration tanks, side by side, handling the same sewage, one of which foamed and one did not (7). Curiously, there are some sewage plants which can generate a stiffer, more long-lasting foam than has ever been generated with ABS in the laboratory. There are other plants handling similar ABS levels where virtually no frothing occurs. For the most part, the more troublesome of these occurrences have been overcome or reduced by pragmatic remedies, rather than scientific findings. Variations in the angle of entering air, use of recirculating sprays, chemical defoamers have kept the problem under control. Aside from nuisance value, any interference with plant operation or its bacteriological processes due to surfactants has been found to be negligible (8).

It is necessary to report that tests of one "softer" surfactant—as conducted in England—do not offer any alleviation of this particular "in-plant" problem by composition change alone. In fact, the more degradable material is quoted as causing somewhat more foam on the aeration tanks, where it is presumably in the act of breaking down (9).

Also, frothing at sewage plants has its unfortunate techno-emotional side. It has probably provided more and better news pictures than any other source—complete with captions as to the detergent "menace". The rejoinder that one does not drink sewage out of aeration tanks seldom gets into print.

Technically, because "in-plant" frothing is controllable, we have always been more seriously concerned for the "throughput" aspect of surfactants under sewage

treatment: That is, their tendency to pass through into the effluent at a level still above the foaming point, or to a degree that may affect the timing or acceptability of water reuse from the receiving stream or ground water. Two approaches were used in these studies.

We investigated specific occurrences to determine the special combination of circumstances which led to high surfactant levels in the receiving streams and consequent foaming effects. In at least one spectacular case, the cause of the foaming proved not to be of detergent origin. We sponsored an analysis of the degree of breakdown taking place at typical plants. As might be expected, trickling filter plants had a low removal percentage—in the order of 25 per cent. Activated sludge plants, properly operated, were able to eliminate some 50-60 per cent of the incoming surfactant (10).

So, in view of the remaining surfactant being discharged, what happens to the recreational value of the receiving stream, its ability to support fish life, or its suitability for early reuse as potable water? Except on streams unfit for such use anyway—the horrible examples from every pollution standpoint—foam-causing levels of ABS are hard to find. A survey of Illinois streams showed ABS averaging only 0.12 ppm at 32 different locations, all far below the foaming level (11).

Monitoring of the Ohio River since 1954, for example, has established that ABS levels averaged 0.16 ppm, and that only an occasional sample reached the 0.5 ppm level considered a criterion of acceptability for potable water (12). Apparently, in surface water, we have a definite continuation of breakdown of current surfactants as well as the factor of dilution. The situation is less acute here than in England, but even there, it is reported that no foam has been detected on public water supplies being drawn for delivery to the consumer (13).

To reassure ourselves on this same point, a survey of drinking water as received in 32 American cities was conducted in 1960. The highest level of ABS detected was 0.14 ppm, and 0.02 ppm was on the high side for 68 per cent of the samples (14). It is probable that this content would not even have been detectable, except for the high sensitivity of test methods which respond to ABS. Other constituents at these same levels are not even tested-for in routine water analysis.

Frankly, when the entire picture is looked at in perspective, the presence of ABS or other surfactant residues from household sources has seldom detectably downgraded surface water that was otherwise acceptable as a potable source. More importantly, there is evidence of low-level equilibrium—not continual accumulation, as feared by those with the misconception that ABS never degrades.

Of course, this may not quite meet the standards of those who feel that potable water should have nothing in it—not even traces—that nature did not put in. If we accept this principle, however, no one should make the methylene blue test for ABS his first criterion of such

trace chemicals. A test of carbon-chloroform and carbon-alcohol extraction is more to the point. (15)

As the one trace constituent of established non-toxicity, ABS might reasonably be expected to be far down on any priority scale aimed at absolute purity. By the time it is reached—with the help of more bio-degradable products now under development—the trace-residue problem will have solved itself.

Now when we come to *ground water* we have a somewhat different situation. Let me first discuss the problem arising, primarily in lower California, where water reclamation and artificial recharge of the aquifer by sewage effluent has been essential. There is no doubt that conventional treatment may result in an effluent having, say, 6 ppm ABS, and that its direct recharge into the ground water opens up the possibility of foam-causing levels in wells downstream—in the absence of any substantial dilution. Recently, a limitation of 4 ppm on ABS has been proposed for sewage effluent to be used for such discharge at one such location. This is a genuine technical problem, to which two divergent approaches immediately suggest themselves. One is the improvement of sewage processes—or the addition of a tertiary treatment—to break down or remove the surfactant and other persistent residues; a second is to increase the bio-degradability of the surfactant to a point where even reasonably modern treatment methods can meet or exceed limits established for the effluent. Both of these are receiving continued exploration and research, within and outside the industry. Improvement in plant design and operating methods—specifically by extended aeration, has made some substantial gains—there is a difference of 20 percentage points or more between the degree of removal achieved by some plants as compared to others. An early approach which has so far not had a practical outcome is the inoculation of the plant with specially-selected or modified bacteria with above-average ability to degrade ABS. However, work is continuing along this path. Tertiary treatment through an intermittent sand filter, or use of special adsorbents such as activated carbon, appear to have definite limitations. No doubt, the most interesting special treatment proposed is the process known as froth fractionation, which was shown some five years ago by Association sponsored research to have the potential to reduce ABS levels by as much as 85 per cent (10). This process involves a deliberate aeration of the sewage to maximize foaming, followed by stripping the froth from the surface and collapsing it for disposal. The U. S. Public Health Service has been particularly attracted by the possibilities of this procedure, as it not only reduces the ABS content, but also takes with it a substantial part of the other persistent dissolved organic pollutants in the effluent. Development contracts sponsored by the Service are continuing. A still more recent advance in the procedure has been announced by the California Research Corporation (16). Here the foam, after removal, is recycled to the sewage feed, the collapsed foam stream

being about 1 per cent of the raw sewage feed stream. Because of the higher total removal achieved by recycling, there is no waste stream of ABS to be disposed of by a separate process. The effect of the foam recycle is to increase the overall efficiency of ABS removal through the plant to 85 per cent of the ABS in the incoming sewage and to boost the elimination of other persistent organics as measured by Chemical Oxygen Demand. A further advantage of the proposed system is that it could be applied to existing plants without the addition of new tanks, if a section of the aeration tank or the secondary settling tank was adapted to serve as the foamer. So, we have here a removal process that would bring ABS in the final effluent predictably below 2 ppm, in what appears to be an economically practical system, and reduction below 0.5 ppm is not out of the question.

Perhaps, this could prove to be an adequate *technical* answer to the water reclamation needs without product change—but I suspect that the *techno-emotional* solution still rests on our alternate approach—that of increasing the biodegradability of the surfactant used in our household products.

Here, we enter an area where the competitive interests of suppliers—with millions of dollars of surfactant sales at stake—limits to some extent an evaluation of progress to date. This is not slowing down the work, but it may be slowing down announcements about it. The fact is that the whole concept of relative “biodegradability” is still a fuzzy one, as it is impossible to turn to a single test method or laboratory procedure and prove the degree of advantage that one product has over another.

One of the tests commonly employed in such evaluation is the River Dieaway Test, in which surfactant at about 20 ppm concentration is added to a sample river water and the decline in surfactant content measured from day to day. A certain product may fall 50 per cent in ten days in one typical water. However, cooperative experiments by a Biodegradability Subcommittee of our industry currently shows little consistency of results from one river water to another. We are continuing our work on test methods for biodegradability—because without it, evaluation of product improvements is necessarily slow and difficult.

An alternate test method has recently been incorporated in regulations adopted in Germany within the last two weeks, regulations which will restrict after October 1964, the sale of detergents containing surfactants failing to meet the test. It provides for the inoculation of a standard sewage with airborne bacteria (to avoid acclimatization effects) and subsequent measurement of the breakdown of the surfactant when recycled in this media and tested every three days for over a twenty-one day period (17). There is reason to believe that the arbitrary level of degradability called for (80 per cent) could be met by products that will fall short of the goals American producers have in mind.

No laboratory test so far developed, here or abroad, can rank different surfactants accurately on a scale that will correlate with their degradability in actual sewage treatment with all the variables from plant to plant, in sewage composition, and in the biological and physical conditions under which breakdown takes place. So far as field experience is concerned, no supplier is yet prepared to state that under any and all conditions of use, his product will degrade at a rate so and so many percentage points better than current ABS. Until more field tests are run, the danger of some arbitrary standard for biodegradability as in Germany is that it might freeze the development work in a rut designed to meet such a standard. Later, actual use might belie the apparent gains of the test-favored formulation. Of course, the surfactants I am talking about here are those that will provide a finished product acceptable to the housewife at reasonable cost in the volume that national distribution requires. Some of the suggested quickly-degraded materials cannot meet this test.

One of the special problems with which product improvement is confronted is the foaming of water drawn from shallow, private wells, as a result of the migration of detergent residues from nearby cesspools and septic tanks. There is no evidence at this time that a “softer” surfactant—as rated on purely aerobic test procedures—will degrade faster than present materials once it is confined to anaerobic conditions or reaches the saturated soil in which most ground water movement takes place.

Yet it is clear the the sight of foam on water drawn from private wells is perhaps our most pressing techno-emotional problem. It is the aggrieved householder that is insisting most strongly that “something must be done”. Well, what can be done?

Let’s look at Proposal No. 1 which some popular writers have advocated—“Go back to using soap”. It is reasonable to believe that this might clear up the problem of foam on water drawn from private wells in an isolated situation. But to credit this to the “greater degradability” of soap is not the whole story. The initial action destroying the surface activity of soap is precipitation by the action of mineral salts in the rinse water, the sewage, or in the ground—in other words, *scum-formation*, an extension of the familiar ring around the bathtub. Once the insoluble fatty acid salts are out of solution, their anaerobic digestion along with other solids in the septic tank, or elsewhere underground, can be as leisurely as you please, or they may be part of the next year’s clog-up. This drop-out by scum formation, however, is the very reason that soaps have been so largely abandoned by the housewife in the first place. Any large-scale reversion to soap for use in the home laundry—except in the softest of water—might be expected to produce hundreds of inoperative washing machines and aggrieved housewives, for every foaming well it cured.

It is even more significant that in this area of high public complaint, many outstanding health authorities

have taken a position, not for the limitation of detergents, but for the limitation of the use of septic tanks (18). If the detergent is migrating from septic tank to the nearby well, this is presumptive evidence, according to the U. S. Public Health Service among others, that concurrent sewage pollution of a potentially hazardous kind is also taking place. Detergent residues are simply an indicator, not a stimulator, of this concurrent pollution. The tastes and odors would be there, the high nitrates, the free ammonia, even if detergents had never been invented. As V. W. Langworthy, editor of *WATER & WASTES DIGEST*, has put it: "We do not think for one minute that the cause of the problem is synthetic detergents . . . The real cause of the problem is gross overload of livable ground."

Were we operating in a completely *technical* frame of reference, we would probably do well to line ourselves up with the authorities who say: "No lasting solution to this problem exists short of public water sewer services." (19), or who admit our present product is useful to them as a pollution indicator (18).

Frankly, the indicator function is not our idea of a desirable sales point. We are more than anxious to abandon this role to some producer of tracers whose business does not depend on keeping housewives happy. Consequently, our concern is still great for the development of products, or of disposal methods, that will keep our residues out of the ground water completely—even if there is no well within miles. Here, some promising channels are opening up. Work at the U. S. Public Health Service's Robert A. Taft Sanitary Engineering Center, for example, has established that even present ABS can be substantially degraded by intermittent disposal on unsaturated soil—particularly soil near the surface where aerobic conditions exist. This suggests that, where space permits, septic tank tile fields would be made adequate to prevent any appreciable migration of undegraded residues into the ground water itself. There is also a possibility that combination filtration adsorption units designed to handle laundry wastes in unsewered areas can be simplified to a point permitting home installation. Aerobic home treatment systems have a logical place where sewers are impractical—if we really wish to protect our ground water from *all* the pollutants requiring bio-oxidation for their destruction, rather than just from the visible foam.

Nor have we given up on the possibility that, under strict standards of septic-tank installation, products now under development can be broken down, precipitated out, hydrolyzed or otherwise disposed of within a conventional septic tank and the soil around it. The fact is, we know very little of what happens to the soluble constituents which enter a septic tank and leach into the soil. Currently, we are cooperating with the Temporary State Commission on Water Resources Planning of New York State on just such a field test of ground conditions and on the fate of detergents and other pollutants discharged

in the waste water of typical households. We expect to try different materials under good, bad and indifferent conditions, and to make an accurate evaluation of their effects. Further field trials dealing with lagooning and other treatment methods, as related to product degradability, are also about to get underway.

In conclusion, I cannot help but think back to eight or ten years ago, when we approached this whole problem of detergent residue disposal as a relatively simple technical matter. Each year, with new information, we have seen the problems increase in complexity. There is the fact that residues of low-suders are no less foam-prone at sewage concentrations than high-suders, and that both may tend to complex with proteinaceous wastes over which we have no control. There is the problem of coin-op laundry wastes in unsewered areas—correctible but costly to the laundry operator. There is the question of phosphates as nutrients for algae growth, for example, that I have not even touched upon, because other sources of phosphates exceed the critical nutrient level, even without detergents' share.

Here, as elsewhere, almost all the problems have turned out to be examples of joint responsibility, of interrelationships between detergent residues and treatment methods, and the whole water pollution complex that no one of us alone has caused, or alone can remedy. We think the solutions involve joint responsibility, too. Our perspective may not be yours, but we can at least move in together on the same set of facts. Our biggest common problem, I suspect, is to overcome the *techno-emotional* view that a cheap and easy solution is being stalled by inaction, because the remedy is really just a simple matter of biodegradability, after all. If I have destroyed that illusion of simplicity for you—I have done no more than put you in the same boat with the rest of us.

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DISPOSAL OF REFINERY WASTES AT AMERICAN OIL COMPANY'S SUGAR CREEK REFINERY

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The Sugar Creek refinery of the American Oil Company is located in Jackson County on the south bank of the Missouri River approximately eight miles downstream from Kansas City, Missouri. South of the property is the municipality of Sugar Creek, Missouri. Through the heart of the refinery flows a small stream bearing the name Sugar Creek. Although the area of the refinery is about 500 acres, the total drainage to Sugar Creek comes from about 2,000 acres. The refinery produces a complete line of petroleum products, from high grade motor fuels through coke, with the exception of lubricating oils and waxes.

The refinery is divided roughly into three areas, each of which discharges water-borne wastes through its own oil-water separator into Sugar Creek. The oldest portion of the refinery, shown in the lower right portion of Figure 1, is called the Lower Refinery and is located directly on the south bank of the Missouri River. In this area are located three crude-running units, treating facilities for finishing petroleum products, a power station with associated water treating equipment, mechanical shops, offices, a laboratory, and storage tanks. Much of the old processing equipment in this area is being replaced by an entirely new and modern pipe still for processing crude oil.

An area along the south limits of the refinery is called the Crawford Tract because of historical background. In this area are located automatic equipment for

gasoline blending and for blending cutback asphalt, and loading facilities for hard asphalts and liquefied petroleum gas. Some obsolete equipment remains from former operations that included five units for low-pressure thermal cracking, gas recovery, and refractionation of polymer gasoline.

The West Plant area of the refinery is located at the extreme western edge of the property at an elevation substantially above the rest of the plant. Process operations built since 1948 are located there. These include catalytic cracking, catalytic reforming, alkylation, catalytic polymerization, crude running, and coking operations. Also in this area are several large cooling towers that furnish water on a recirculating basis for the newer units.

The refinery requires large volumes of water for its process operations. The water is used in heat-exchange and vapor-quenching equipment for cooling purposes, desalting crude, and washing some products. Prior to a major expansion in 1948, river water was pumped through heat-exchange equipment, including many ancient-type box coolers, and returned directly to the river. Since 1948 cooling towers have been provided for all new refining facilities as they have been built. By recirculation of cooling water, only a small volume of river water is required to offset losses from evaporation, blowdown, and leakage. Reducing the volume of waste water decreases the volume of refinery effluent flowing into Sugar Creek.



Figure 1. Aerial View of the Sugar Creek Refinery—1955.

Under normal weather conditions, the refinery effluent constitutes the major part of the flow in Sugar Creek. The flow will increase by three to four times in periods of wet weather as the result of run-off from the watershed. To intercept oil spills or leakage into the creek, a skimming dam has been constructed across the creek in the Lower Refinery area. The oil recovered at this dam is returned to tanks containing slop oils.

Nature and Source of Waste Products in the Refinery (Reference Table 1)

1. *Oil*

Oil enters the refinery sewers by (a) leakage from heat exchangers and pump glands into cooling water, (b) condensation of vapors into quench water, (c) emulsion formation with water, condensed from process steam

in the presence of condensing hydrocarbon vapors, (d) water-washing of crude oil and products as a means of desalting and cleaning, (e) water which is incompletely settled from oil in storage tanks. Oil is the major contaminant in the refinery waste water.

The oil content of the waste water entering the gravity-type separators varies greatly. Experience has shown that the more modern gravity-type oil-water separator can remove about 90 per cent of the entering oil. Based on processing 75,000 barrels per day of crude oil, it is estimated that the total water-borne waste from the refinery carried about 36 barrels per day of oil before the recent construction of modern recovery facilities.

2. *Sulfur Compounds, Including Hydrogen Sulfide, Mercaptan Sulfur, and Miscellaneous Organic Sulfur Compounds*

Sulfur in the contaminants arises from naturally-occurring sulfur compounds in the crude oil. In the various process operations the original compounds that are unstable break up to form mostly hydrogen sulfide and mercaptans. A large part of the hydrogen sulfide generated in process operations is removed in subsequent steps and burned at flares. Objectionable mercaptans are converted by chemical means to alkyl disulfides. However, not all of the sulfur contaminants are so easily handled. For example, the steam condensate in reflux streams contains large amounts of both hydrogen sulfide and mercaptans. These are discharged through process sewers to the separators. There they are changed by oxidation. The concentration of these contaminants in the refinery effluent, formerly discharging to the river, is about 1 ppm, measured as sulfide.

3. *Caustic Solutions*

Sodium hydroxide solutions of various strengths are used in the refinery chemical treating operations. Sodium sulfide and sodium salts of phenols and cresols concentrate in them. Because a treating operation with caustic is followed usually by a water wash to remove entrained sodium hydroxide, the water from such a process is alkaline. This discharges to the sewers and makes the total water-borne waste alkaline. The pH of the effluent water from the refinery is about 9.0.

4. *Ammonia*

Ammonia, as a contaminant in a refinery's water-borne waste, arises from two sources—ammonia added directly to process streams for the control of corrosion and the breakdown of nitrogen compounds naturally occurring in the oil. Much of the ammonia that reaches the process sewers actually exists in the water-borne waste leaving the refinery. Not all of the nitrogen appears as ammonia. Some of it is combined and reported as basic nitrogen compounds, which are not eliminated easily. The concentration of combined nitrogen in the water-borne waste under present operations is about 14 ppm.

5. *Phenols*

Phenols and cresols are produced by the various cracking processes used in refinery operations. Most of those formed leave the oil streams by solution in water condensed from steam in the reflux coolers or by combination as sodium salts in caustic solution. Spent caustic solutions that contain significant amounts of cresylate salts are sold and thus eliminated as water contaminants. Only phenols in the reflux waters get into the total water-borne waste. Consequently, contamination by phenols from the Sugar Creek refinery has been minimized for a long time. The present concentration of phenols in the water-borne waste is 0.6 ppm.

6. *Untreated Sewage*

Sanitary sewage entering Sugar Creek within the refinery arises from two sources—from the population of the refinery itself and from the discharge of the city of Independence sewer emptying into Sugar Creek within the confines of the refinery. Surveys made by the refinery from 1954 to date have shown a BOD of 143 ppm or an equivalent population of 123,000.

7. *Water Treating Sludges*

The refinery uses about 1 million gallons of water a day for generation of steam. For this purpose the chemical constituents in the water contributing to hardness must be removed. Complete water softening facilities of the most modern design exist in the refinery. In the softening process, the mud and mineral matter naturally present in the water are removed. These are subsequently re-used for clarification of additional quantities of river water in a cold process system. After final use they are discharged to the river from where they came. Chemicals used as aids in softening and clarification are lime, ferrifloc, and sodium hydroxide.

Past Programs for Refinery Waste Disposal

It may have appeared to some people that oil refineries, and other industries, have been slow to submit plans for ultimate elimination of contaminants from their waste water. However, it must be remembered that rapid changes in processing techniques have made it almost impossible to settle on a design for facilities which could be expected to fit the predicted situation.

As a matter of fact, the Sugar Creek refinery has made an almost continuous improvement in refinery effluent character. This program really began in 1948 when recirculation of treated water, through cooling towers, became a policy for all new process units. The greatly-reduced volume of waste water to the sewers resulted in comparable reduction in contaminants eliminated to Sugar Creek. The total ultimate reduction, foreseen in present plans, will be from a former volume of 20 million gallons per day to about 10 million gallons per day. Nearly all of the water must be returned to Sugar Creek by way of oil-water separators.

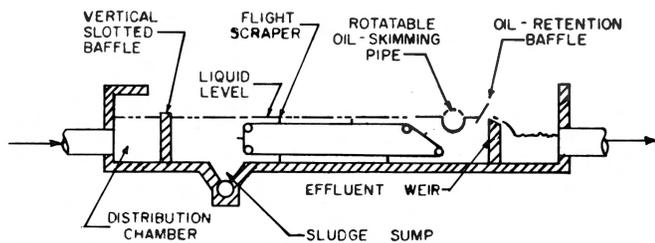


Figure 2. A.P.I. Oil-Water Separator.

The current design of the API separator was developed under the chairmanship of Dr. Roy Giles as a major assignment to one of API's committees. Dr. Giles at that time was director of Technical Service for the entire Standard Oil Company. Consequently the use of separators of API design has been prevalent within the company for a long period of time.

As mentioned above, the process equipment operating in the Lower Refinery area is of older design. Consequently, much of it used process cooling water on a once-through basis in box coolers. This required much larger volumes of water than on more modern units. Moreover, the resultant large volume of waste water had to be handled in oil recovery facilities to reduce the oil content of the effluent to the river. This area has been served by an API-type separator from almost the beginning of refinery operations. One such separator of old design was replaced by the most modern design available in 1953. The design is shown in Figure 2 and a picture of the unit in Figure 3. This unit provides for water distribution through four settling bays with mechanical oil-skimming and scraping facilities for removal of oil and sludge. Although the quantity of oil handled by this separator has been large and variable, the operation has been considered acceptable. The oil recovered in the skimmer pipe is pumped to tankage. The sludge obtained from the bottom of the separator is pumped to a sludge pond where any further separation of oil is skimmed and returned to refinery slop tanks, dehydrated in stills, and sent to coking.

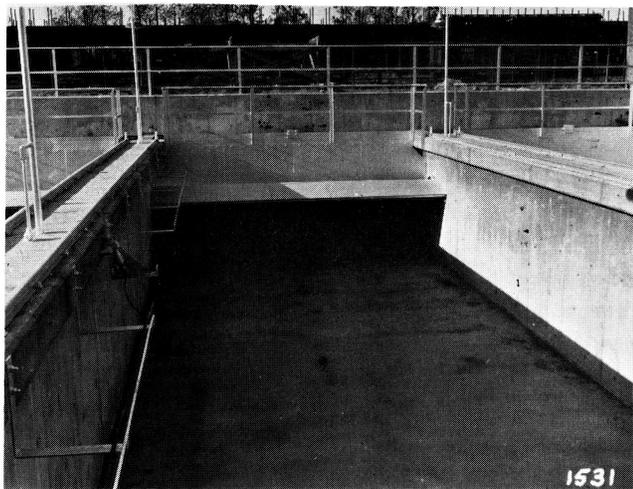


Figure 3. Lower Refinery Separator.

In the Crawford Tract area of the refinery exists the oldest oil-water separator now in use. This is truly a gravity type separator without the use of oil skimmers or scrapers. It is the old cellular type and, although of ancient design, operates with very good oil recoveries. Since the dismantling of thermal cracking equipment in July of 1959 and practical elimination of asphalt oxidation, the amount of water handled by this separator has diminished. The oil recovered is pumped to tankage and the water flows under a skimming weir into Sugar Creek.

Although most of the modern processing units located in the West Plant are served by cooling towers, there is some once-through process water associated with crude running and coking operations. The discharge of such water from the West Plant area flows into an API separator of 1948 design. This unit includes oil skimmers and flight scrapers, although they are less effective than in the more modern design of separator. The operation of this separator has been least satisfactory of the three in the refinery. This is associated largely with the presence of finely-divided particulate matter, which may come from catalytic cracking and decoking operations, and the presence of particles of wax that reach the separator from coke-drum steaming. Oil recovered in this separator is pumped to tankage; sludge from the bottom is picked up by a vacuum truck and transported to the sludge pond.

Another factor contributing to difficulty in operation of the West Plant separator is the discharge of foul steam condensate from catalytic cracking operations. This condensate is heavily contaminated with hydrogen sulfide, ammonia, and phenols. Upon contact with air, much of the ammonia escapes and much of the hydrogen sulfide oxidizes, releasing free sulfur which, as particulate matter, makes it difficult to separate oil associated with it. Process design studies have been completed for construction of a foul-water stripper. The actual installation of such equipment has been held in abeyance until an opportunity has been afforded to observe the operation of a new lagoon just recently completed.

As a normal part of refinery operations, there accumulates waste caustic containing various kinds of contaminants. Predominant are those caustic solutions that contain the sodium salts of phenols or cresols. Also accumulated are solutions that are contaminated with sodium sulfide. In the Sugar Creek refinery alkaline solutions that contain significant amounts of sodium cresylate are accumulated and sold for the recovery of the phenols and cresols. This has been done for many years and thereby prevents this type of contaminant from getting into the refinery's water-borne waste.

Recently there was constructed in the refinery, equipment for neutralizing waste caustic solutions that contain predominantly sodium sulfide as a contaminant. Operation of the equipment was successful. Because it was found to be of economic advantage to sell waste caustic solutions containing sodium sulfide for recovery of chem-

icals elsewhere, the use of the caustic neutralizer has been held in abeyance; the equipment is retained ready to operate in the event that the necessity arises.

The retirement of old processing equipment that had made control of waste elimination difficult, has been a continuing program. Exemplary of what has been done is the retirement and dismantling of thermal cracking units, the elimination of obsolete shell still coking, the elimination of asphalt oxidation formerly done by obsolete processes, the elimination of tar filtration, and now the replacement of the four old crude distillation units with one new and modern unit. The new unit will use recirculated cooling water, which greatly reduces water going

to the sewer. Also, it will eliminate a great many vessels, tanks, pumps, coolers, etc., so that the problems of leakage and separation of water-oil mixtures will be greatly reduced.

During recent years the old shell stills, which were retired from coking service, have been used to dehydrate, by heating, the slop-oil emulsions which formerly contributed important amounts of oil to the sewer. When the crude distillation side of the present Combination Crude Running and Coking Unit is retired, it is planned to revamp parts of these facilities to provide for greatly improved dehydrating and redistillation of slop oils.

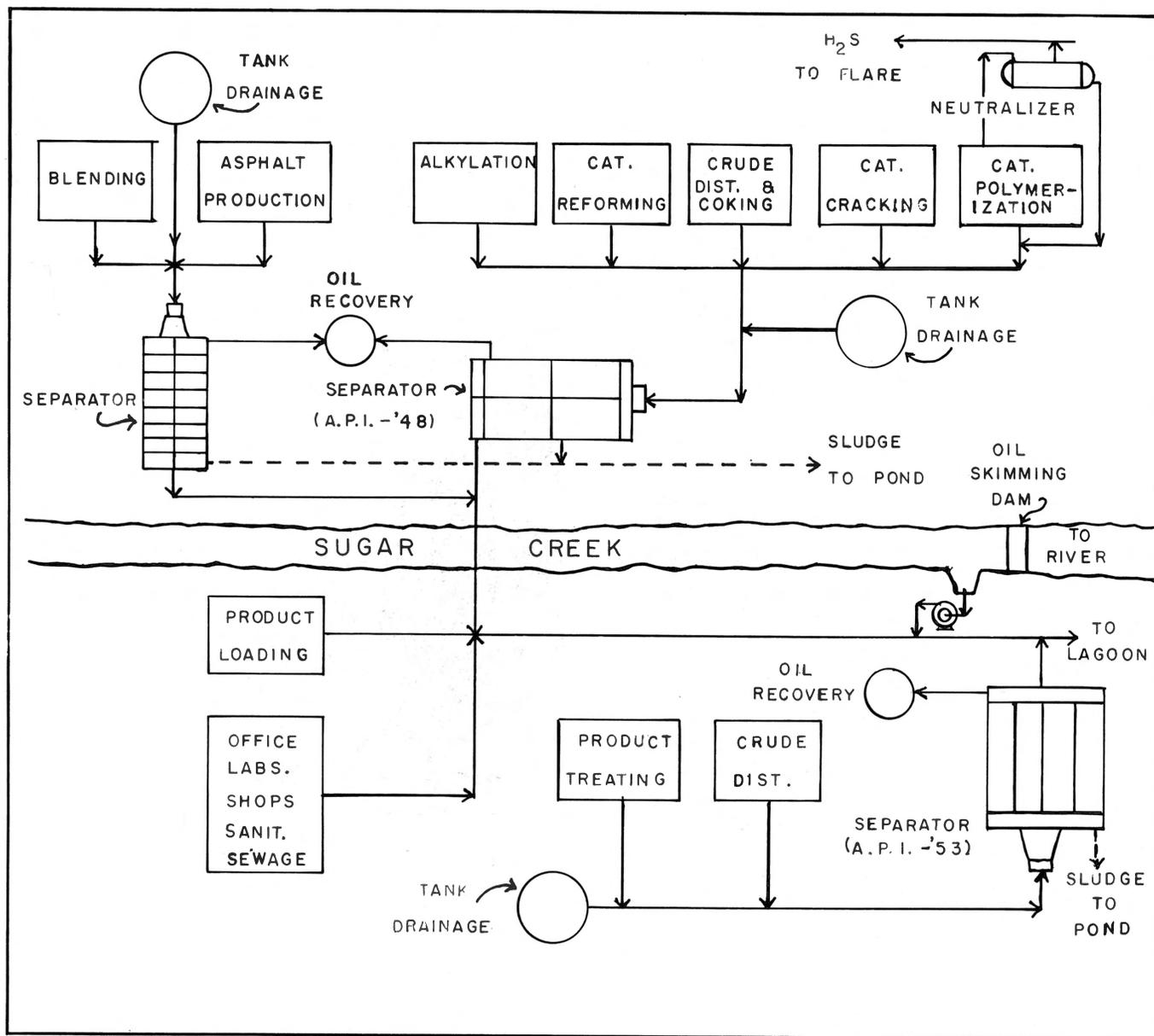


Figure 4. Modernized Sewer System.

Modernization of Waste Treating Facilities

As indicated earlier, there has been a continual improvement in the installation of waste treating facilities and in the operation of the refinery to minimize pollution. One of the most significant steps is just about to be taken. This is the operation of a 10-acre lagoon, using supplemental aeration, to improve the character of the total water-borne effluent. Associated with the construction of these facilities is a modernization of the refinery sewer system, which is shown in Figure 4. Process water has been segregated from once-through cooling water and run-off water from the watershed. Thus, only the water that is truly contaminated is treated. This change, coupled with moves for the conservation of water usage, will reduce the total effluent flow from approximately 20 to 10 million gallons per day. Whereas formerly process water from the separators entered the stream Sugar Creek and flowed through the refinery, all such water now will be accumulated in enclosed sewers and carried directly to the lagoon. In addition, sludge accumulating in the separators, which has been moved by various means to the sludge pond, now will be likewise collected in a separate sewer system and sent directly to a new sludge pond. Thus the stream of water flowing down Sugar Creek will contain only run-off water and such leakage as cannot be readily contained. To prevent the loss of contaminants directly into the river through this stream, the dam across Sugar Creek, shown in Figure 5, will be equipped with a pumping station, shown in Figure 6, so that the entire stream will flow through the lagoon. This will continue under all conditions except that of heavy rainfall. It is estimated that the lift pumps at the creek are capable of handling the run-off from a rain-storm intensity of not greater than 0.1 inch per hour rate for a 30-minute period. For a half-inch per hour rainfall, it is estimated that the dam on Sugar Creek would overflow some 25 minutes after the beginning of the storm. Thus, prior to storm run-offs spilling over the dam, a large volume of this water, including surface oil on the creek, will have been diverted to the lagoon.

Sanitary sewage arising in the refinery itself will be routed to the lagoon. However, plans are afoot for treating sanitary sewage from the cities of Sugar Creek and Independence in a separate plant operated by the city of Independence at a site northwest of the refinery.

The lagoon for the Sugar Creek refinery was constructed on company property north of the Santa Fe tracks and adjoining the Missouri River. Space was available in this area for a 10-acre lagoon which would be used with supplemental aeration. By reference to Figure 7, the operation of the lagoon is as follows: The collected waste water enters the lagoon through a sewer section designed as a mixing chamber. Acid will be added automatically as required to provide the optimum balance between acidity and alkalinity. The entrance section of the lagoon provides a minimum retention time of eight



Figure 5. Oil Skimming Dam.



Figure 6. Lift Station for Water in Sugar Creek.

hours to permit oil separation. The oil so separated is trapped by baffles and flows through slotted skimming pipes. The combination of oil-water mixture is further concentrated and pumped to heated storage tanks for final recovery.

The lagoon consists of three separate basins, 160 feet wide and 10 feet deep, comprising a storage capacity of about 30 million gallons. Water flows from one basin to the next, passing under divider walls to eliminate the flow of surface oil between the basins. Finally the water

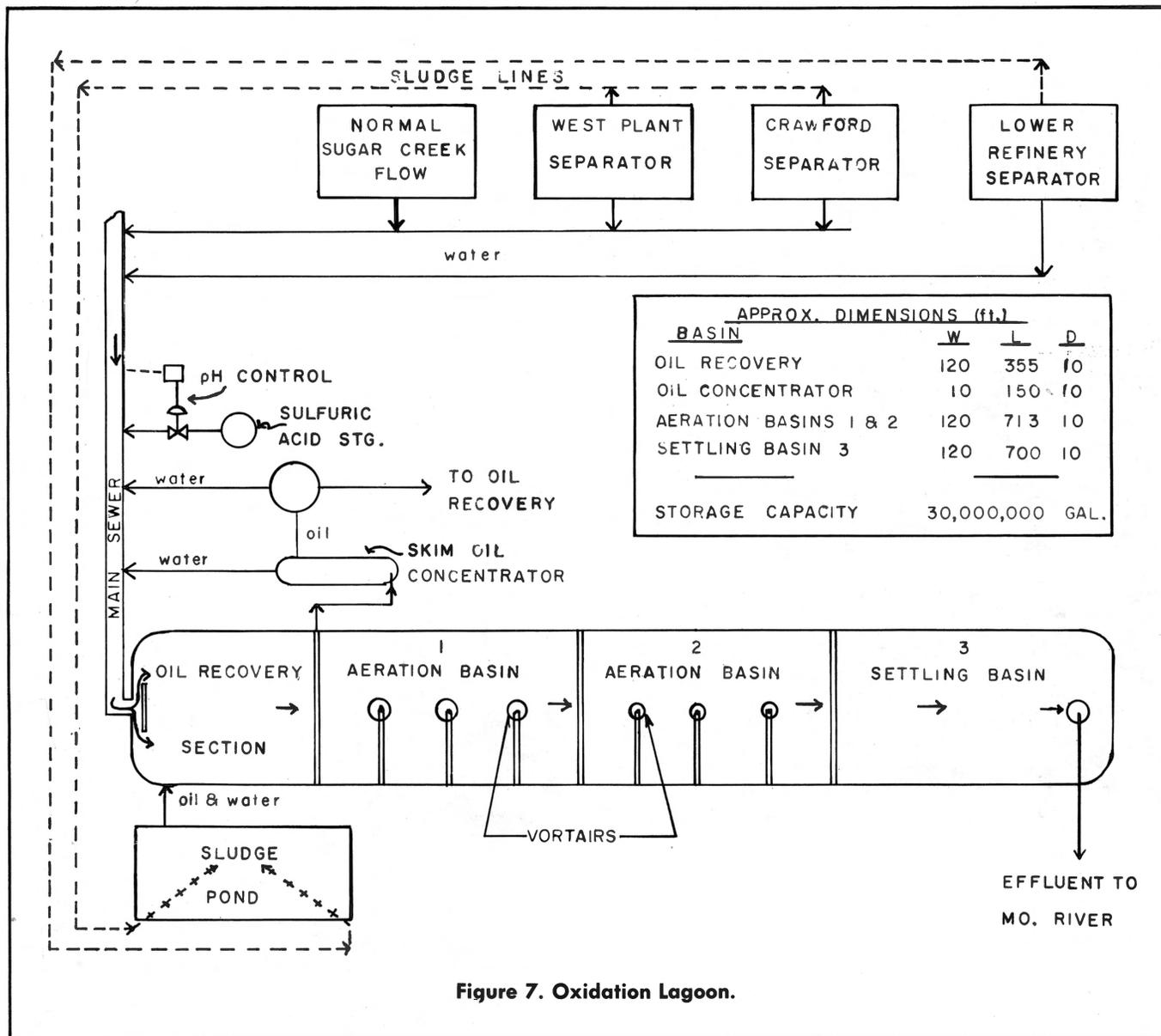


Figure 7. Oxidation Lagoon.

leaves the lagoon over an adjustable weir and enters the Missouri River. Based on the estimated future flow of water to the lagoon, the retention time is about three days.

Somewhat more detailed data on the lagoon follows. The entire waste water stream from the refinery enters the oil skimming section of the lagoon from a 60 inch sewer through an apron and head wall. The head wall is 30 feet long and 7 feet high. It serves to distribute the water evenly across the basin. The oil-skim section is 120 feet across at the base and 355 feet long. Easily separable oil rises to the surface of the water and is skimmed therefrom in slotted pipes, three of which are located across the baffle separating this section from the first aeration section. Oil so removed is transferred to a skim-oil concentrator 10 feet wide and 150 feet long that is just adjacent to the oil-skim section of the lagoon. Oil pumped from the surface of this section goes to tankage

where further treatment is given for additional concentration of the oil. Water from this section goes to the lagoon via the sludge pond.

Water flows beneath the baffle separating the oil-skim section from No. 1 aeration basin and enters this basin for further treatment. The basin is 120 feet wide and approximately 713 feet long. Located in it along the center line are three 60-H.P. Vortair units to add supplemental air as an aid to biological action. It is expected the three Vortair units in this section of the lagoon will furnish 74 per cent of the necessary supplemental oxygen. Based on calculated performance, three of them should supply 9,920 pounds of oxygen per day. Because of the turbulence created by the Vortair units, the walls of this section of the lagoon are lined with rock to prevent erosion from wave action. A view of a Vortair unit is shown in Figure 8.



Figure 8. 60-Horsepower Vortair Unit.

Separating No. 1 aeration basin from No. 2 aeration basin is a retention baffle constructed of corrugated aluminum sheeting. It extends downward to within four feet of the bottom of the lagoon. This second aeration section of the lagoon is 120 feet wide and 700 feet long. It also contains three Vortair units for adding supplemental oxygen. These are only 15-H.P. units. They will supply 26 per cent of the total oxygen demand or 3,040 pounds per day. Sections 2 and 3 are separated by a retention wall of the same design as that which separates the first two sections. Section 3 of the lagoon is 120 feet wide by 715 feet long. It is a quiescent section and dependent on its bio-action for oxygen that diffuses into the water. Bio-solids also settle here. The effluent water from the entire lagoon system passes into an outfall well 14 feet in diameter located at the far end of the settling basin. The water in turn flows into a 48-inch concrete sewer and then northward into the Missouri River.

Located directly above the outfall sewer is a sample station. Housed therein is a continuously recording flow meter and automatic equipment for compositing samples. Three samples are composited; one for oil content and two for other contaminants. In addition, it is possible to sample the stream and put it through a charcoal filter system for evaluation of taste and odor constituents. This latter system consists of a flow meter, a sand prefilter, and

two charcoal filter elements that can be used individually or in series. Various features of the lagoon are shown in photographs, Figures 9 through 16.

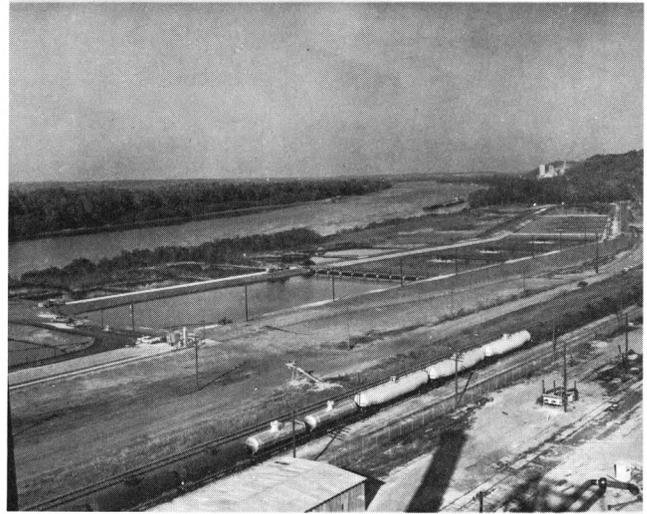


Figure 9. Lagoon from Inlet End.

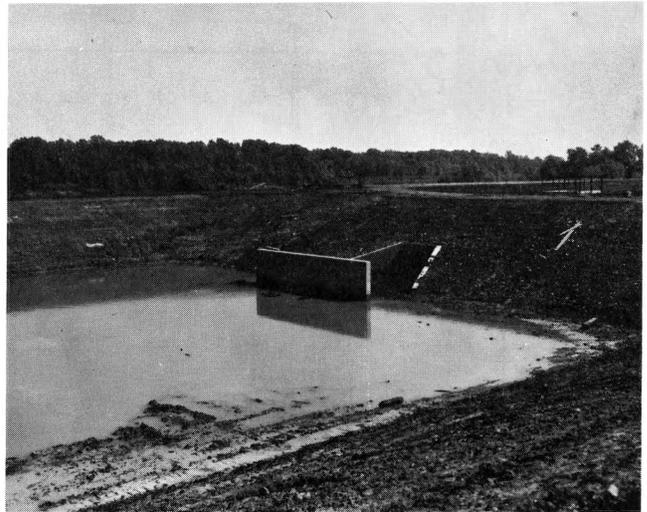


Figure 10. Inlet Distribution Baffle.



Figure 11. Oil Retention Baffle.

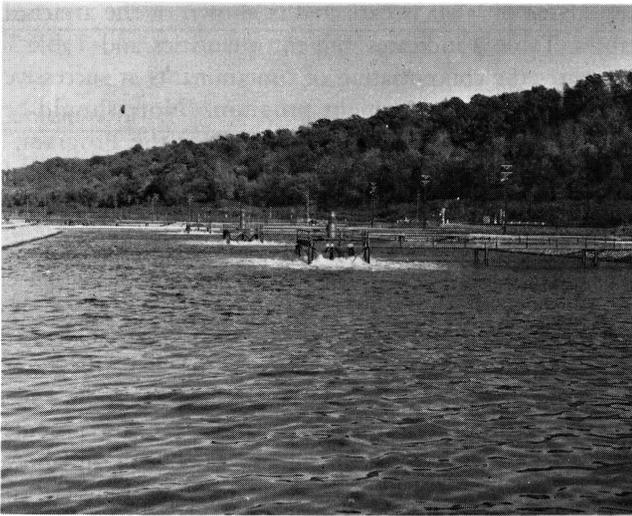


Figure 12. No. 1 Aeration Section and Vortair Units.

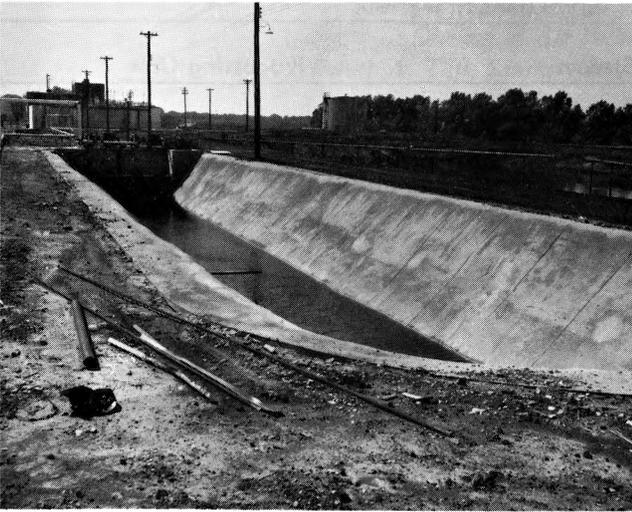


Figure 13. Skim-Oil Concentrator.

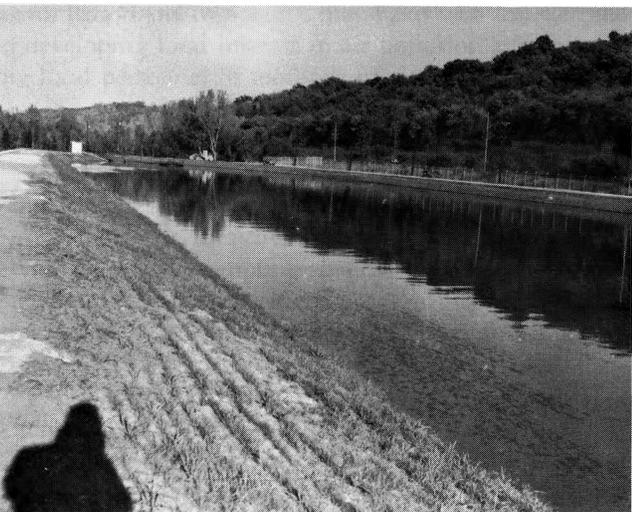


Figure 14. Settling Basin.

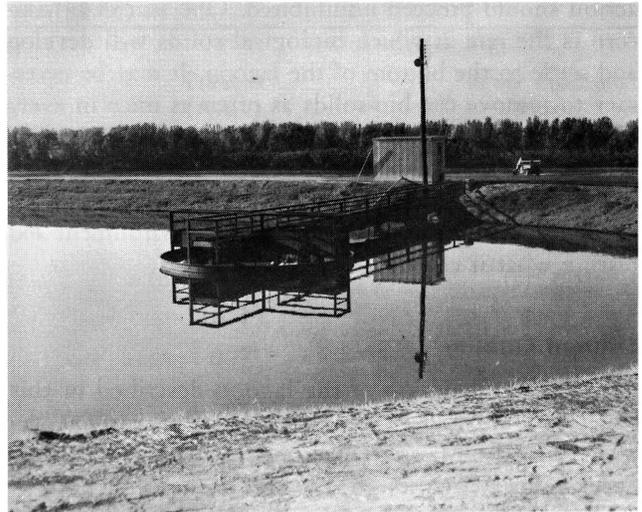


Figure 15. Outfall Well and Sample Station.

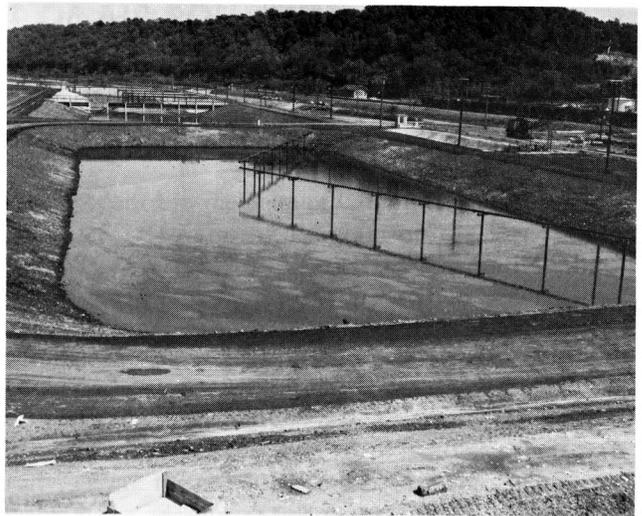


Figure 16. Sludge Pond.

Expected Biological Action

The use of supplemental aeration to augment biological action in the lagoon is not new but its application is not widespread. Therefore, the construction of the lagoon by American Oil Company serves as an interesting example of how supplemental aeration will enhance biological action. The lagoon is not large enough to handle the biological load without the addition of air; only 10 per cent of it could be treated. Consequently, it is necessary to add supplemental air by means of mechanical aeration in adequate amounts to furnish the bacteria with oxygen to decompose the organic matter into carbon dioxide and water. It is not known if there is enough sanitary sewage in the water going to the lagoon to establish the desired level of biological oxidation. Therefore, if necessary the lagoon will be seeded in the early stages of its operation so that the correct biological flora will be present. It is never expected that the phenolic load on the lagoon will be sufficiently large to have a detrimental effect upon the bio-organisms present. Ultimately they will tolerate the phenol level and, therefore, biological

action should proceed uninhibited. One matter of concern is the rate at which biological solids will develop and settle to the bottom of the lagoon. It may be necessary to remove the bio-solids as often as once in every four or five years. No clear-cut decision has been made on how this shall be handled. Obviously with a new project of this type, direct attention will be given to all aspects of creating the proper biological environment and testing what it can do.

Effluent Quality

The construction of the lagoon described in this paper should result in a higher quality of effluent delivered to the Missouri River from American's Sugar Creek refinery. Although the lagoon has not been in operation long enough to test the quality of the water,

some idea of what is expected is shown in the attached tables. Table 2 indicates effluent quantities and Table 3 compares the concentration of contaminants at successive stages of the improvement program. Note should be taken that in the section labeled "After the Program," the values are given as *maximum values*. It is expected that operation will actually indicate lower levels of all of these except ammonia. Oil content may be expected to reach levels less than 10 ppm much of the time.

It is anticipated that after the performance of the lagoon has been tested through the one-year cycle, it may be possible to report again to this group as to the exact operation. In addition, it may be possible to report some interesting information on taste and odor constituents that arise in the course of refinery operation and how they are eliminated by a lagoon of the type described herein.

TABLE 1. SOURCES OF CONTAMINATION

Contaminant	Contaminating Stream	Processing Unit
Oil	Cooling and Pump Gland Waters	All Units
S=, RSH, Phenols, NH ₃ , Nitrogen Bases, Oil	Quench and Reflux Waters	Catalytic Cracking, Crude Running and Coking
Phenols, S=, RSH	Spent Caustic Solutions	Product Treating
Oil, Solids, some- times Phenols, S=, and RSH	Tank Bottoms	Storage
Oil, Phenols, S=, RSH	Wash Waters	Product Treating and Vapor Recovery
Solids - sometimes oil laden, Coke Fines	Miscellaneous Solids	Tank and Separator Bottoms, Water Treating, Decoking
Raw Sewage	Sanitary Sewers	Offices, Laboratories, Shops, etc.

TABLE 2. WASTE WATER QUANTITIES
(MILLION GALLONS / DAY)

Source	Before Water Conservation	Present	Future (After New Pipe Still)
Lower Refinery Separator	8.0	6.0	3.4
Crawford Separator	7.0	2.0	2.0
West Plant Separator	2.0	2.0	2.0
Sanitary Sewers	0.1	0.1	0.1
Creek Flow	1.5	1.5	1.5
Miscellaneous Drains	1.5	1.0	1.0
	<u>20.1</u>	<u>12.6</u>	<u>10.0</u>

TABLE 3. QUALITY OF WATER TO RIVER

Contaminant	Before Program Started (Avg.)	Present (Avg.)	After Program (Max.)
Sulfide, Sulfur, ppm	19.6	0.9	1.0
Mercaptan, Sulfur, ppm	3.1	< 0.1	0.1
Sodium Hydroxide Equivalent, ppm	24.1	(pH 7.0-10.0)	(pH 6.0-9.0)
Ammonia, ppm	14.2	13.1	14.1
Phenols, ppm	0.6	0.7	0.5
Oil, ppm	157	120	15
BPD	75	36	3.6
BOD, ppm	150	-	70-

LOW-COST MEASUREMENT OF AIR POLLUTION

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Low-cost Measurement of Air Pollution

In the past decade, air pollution has become an increasingly greater problem throughout the United States. In some of the larger cities, such as Los Angeles, New York City and San Francisco, definite strides have been made in the solution of this problem. In other communities, however, efforts have been curtailed by a lack of funds and technical personnel trained in air pollution measurement techniques.

The Public Health Service has instituted a program of cooperative air pollution measurement studies. Such short-term cooperative studies have been carried out with state and local agencies in Tucson, and Phoenix, Arizona; Fresno, California; Providence, Rhode Island; and Birmingham, Alabama. These studies have provided much useful data; more important, they have been instrumental in developing local interest in air pollution and in training local personnel in methods of air pollution analysis.

Types of Air Pollution Studies

Air pollution measurement programs can be conveniently classified into two broad categories:

- 1) long-term measurement surveys
- 2) short-term sampling studies

Long-term measurement programs can, in turn, be divided into the expensive continuous monitoring programs and the inexpensive surveillance programs.

The expensive programs are conducted with continuous monitoring automatic recording instruments that have been developed for the analysis of a number of common gaseous pollutants such as, sulfur dioxide, the oxides of nitrogen, total oxidants, total hydrocarbons, carbon monoxide and carbon dioxide. These instruments

are widely used in the State of California and by the Continuous Air Monitoring Program of the U. S. Public Health Service. The cost of such instrumentation, however, is in the range of \$50,000 per station, and thus not within the budgetary frame work of most communities.

A surveillance measurement program, however, is relatively inexpensive to initiate and maintain. The costs of such a program are similar to those of the short-term study, except for personnel and time requirements. The program includes measurement of dustfall, operation of the high-volume sampler and the AISI strip filter paper sampler, and analysis of gaseous pollutants usually once or twice a day. These techniques constitute the core of the inexpensive air-pollution measurement program. Through the use of simplified instrumentation and sampling equipment, described herein, initial cost is reduced to a reasonable level. Particulate samples are collected on a daily or monthly basis; gaseous samples are collected for periods of 10 to 30 minutes. Hence, the manpower requirements of such a program are also low.

Short-term sampling studies entail extensive sampling for various gaseous and particulate pollutants on a regularly scheduled basis over a period of one to two weeks. Gaseous pollutants are usually collected 5 times a day on a bi-hourly basis. During the same period, nighttime pollutant levels are determined by continued sampling around-the-clock for one or more nights. Due to the nature of collection procedures, particulate sampling is similar to that in the surveillance measurement program. Sampling methods are described in detail in succeeding sections. A detailed breakdown of equipment costs is also given.

The short-term study is valuable in determining diurnal and weekly variations of the various pollutants, and "background" on normal pollutant levels. Such data are not readily determined by a surveillance procedure and before initiation of a surveillance measurement program, a related short-term study should be undertaken to predetermine background levels and diurnal variations.

Particulate Measurements

Two types of particulates are of interest in air pollution studies, namely, the coarse and the fine particles.

The coarse particulates are large agglomerates of a size greater than 10 microns, which settle from the air by gravity and are identified as sootfall and dustfall. The basic equipment is a wide-mouthed container (Figure 1), usually plastic, and enough water to keep the bottom of the container covered throughout the collection period. The collector is placed in an open area for 2 to 4 weeks, following which the water is evaporated and the residue weighed. Dustfall rates are usually calculated and reported in units of tons per square mile per month.

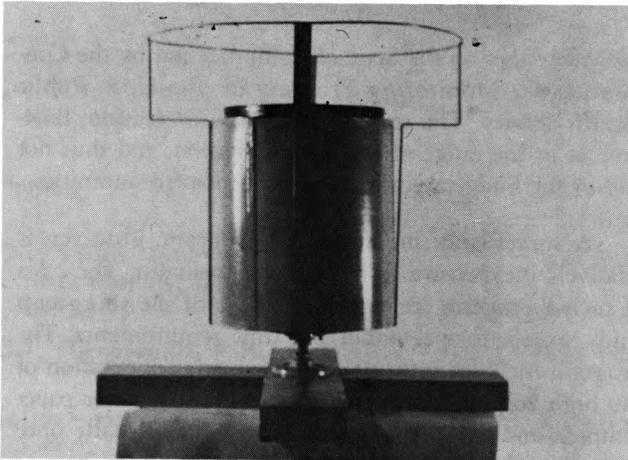


Figure 1. Dustfall Collector.

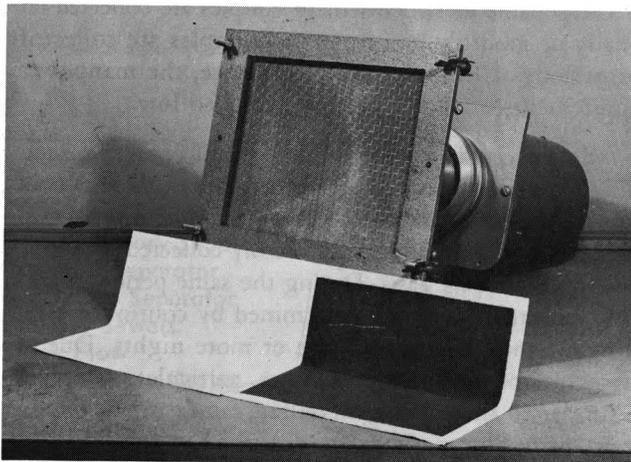


Figure 2. High-Volume Filter Sampler.

In the longer collection periods, precaution must be taken to prevent the growth of organisms in the collector that will give erroneous results. Quaternary ammonium salts are useful as an algicide, as they are readily volatilized during evaporation of the water in the course of analysis. During the winter months an antifreeze must be added to the collector; isopropyl alcohol has been used successfully.

Several other analyses of the dustfall sample may be made. Most common is the separation into water soluble and insoluble portions. Percent combustible or percent ash is also common. Among the lesser determined components are sulfates, chlorides, phosphates, and alkali metals.

Dustfall in non-urban areas is generally of the order of 10 to 15 tons per square mile per month. The central parts of many large cities, however, experience dustfall rates of 30 to 60 tons per square mile per month. Standards along this line are sparse, but rates greater than 25 tons per square mile per month are considered excessive and undesirable by some authorities.

Of equal interest is the measurement of the fine particles in the atmosphere. These particles are too small to be seen with the naked eye, but are the major components of smoke and haze. This phenomenon is a result of their effective light-scattering ability.

The concentrations of particulates in this size range are determined by two methods: suspended particulates with the high-volume filter sampler, and the soiling index by the AISI strip-filter paper sampler.

With the high-volume sampler (Figure 2), large volumes of air are drawn through tared filter webs by a vacuum-cleaner-type motor. Over a 24-hour period, about 60,000 cubic feet of air is sampled. Particulates of size 0.4 micron and larger are collected quantitatively with lesser efficiencies for smaller particles. By reweighing the filter mats to determine the amount of particulates collected, and determining the total volume of air sampled, the particulate concentration can be calculated in units of micrograms of material per cubic meter of air.

Coh's per 100 linear feet of air	Rating
0 - 0.9	Light
1.0 - 1.9	Moderate
2.0 - 2.9	Heavy
3.0 - 3.9	Very heavy
4.0 - plus	Extremely heavy

For non-urban areas, suspended particulate concentrations average about 40 micrograms per cubic meter. Average concentrations in urban air, however, range from 110 to 200 micrograms per cubic meter, depending upon size and industrial activity. In heavily polluted areas, values of 2500 micrograms per cubic meter have been recorded on heavily polluted days.

Many additional analyses can be run on the particulate samples. Benzene extracts provide an estimate of the organic portion of the material. For the most part, organic particulates are a result of poor or incomplete combustion of fuels and waste materials. Of special interest is the presence of polynuclear hydrocarbons. Several of these, such as benzo(a)pyrene, have been shown to be carcinogenic in animals, and are suspected of similar action in humans.

Aqueous extracts of the high-volume filters can be analyzed for sulfates, chlorides, nitrates, and alkali metals. Also, a portion of the filter web may be used for spectrographic analysis for metals.

With the AISI strip filter paper sampler (Figure 3), only the very minute particles are collected. The sampler collects samples automatically for periods of 1 to 4 hours at air flow rates of approximately 0.25 cubic feet per minute. By sampling at this low flow rate with a down-facing, large diameter air inlet, only the very small particles in the atmosphere are drawn into the sampler.

Air is drawn for a determined period of time through filter paper strips. Dark spots are produced on the paper. At the end of the sampling period, the filter strip is indexed to a new spot and the cycle repeated. At convenient intervals, usually within a week, the sampling strip is removed and the particulate samples evaluated.

Because of the very small weight of particulates involved, the samples are evaluated by optical methods utilizing the light scattering properties of the particles. The filter strip is placed between a light source and a photo-electric cell, and the optical density of the spot with respect to clean paper is available for use with the filter paper strips. From the optical density of the spots, the soiling index can be calculated. The soiling index is reported in units of coh's per thousand linear feet of air, where 1 coh (coefficient of haze) is that quantity of particulate matter that produces an optical density of 0.01 on filter paper.

A rating system for describing the soiling index has been devised by the New Jersey State Department of Health (1), as follows:

<u>Pollutant</u>	<u>Sources of pollutant</u>	<u>Method of measurement</u>	
Oxidant	Photochemical reactions and naturally occurring	Phenolphthalin method	(2)
Nitric oxide, Nitrogen dioxide	Combustion processes including motor vehicle exhaust	Saltzman method including oxidation of NO to NO ₂ by KMnO ₄ .	(3)
Carbon monoxide	Largely motor vehicle exhaust; some from other combustion processes	Adaptation of NBS detector tube technique	(4)
Sulfur dioxide	Combustion of sulfur-containing fuels; certain industrial processes.	West-Gaeke method	(5)

This method provides easy comparison of different sampling areas. After initial calibration of the instrument, the determination becomes a matter of reading the tapes and picking the corresponding coh values from a calibration chart.

Gaseous Pollutant Measurements

Except in special cases, gaseous pollutants of major concern are sulfur dioxide, nitrogen dioxide, nitric oxide, total oxidants, and carbon monoxide. For each of these pollutants, a suitable colorimetric determination has been adapted.

When analyzing for sulfur dioxide, the oxides of nitrogen, and oxidants, the air is metered through fritted glass bubblers or impingers as the method may require, and the pollutant scrubbed out by an absorbing reagent (Figure 4). A color change is either produced directly in the absorbing reagent or induced by additional color reagents. Then the percent transmission, or optical density, of the sample is determined against a reagent blank in a spectrophotometer at the prescribed wave length. The volume of pollutant can be determined from a standard curve for the particular method, and the concentration in the ambient air calculated in parts per million.

Carbon monoxide is determined using an adaptation of the National Bureau of Standards detector tube technique. Air is drawn through the detector tube at a rate of 100 cubic centimeters per minute with the gas being absorbed on an impregnated silica gel column. A blue complex is formed, the depth of color indicating the amount of pollutant absorbed. Ambient air concentration is determined by visual comparison to a standard color chart.

An approach to gaseous pollutant analysis that is sometimes satisfactory is to obtain accumulative indexes of pollutant concentrations over extended periods of time. Samples are usually collected for periods up to a month by greatly simplified methods such as the lead peroxide candle method for sulfur dioxide, and the rubber cracking method for ozone. Although quantitative results cannot be claimed, these methods are especially

useful for determining relative concentration levels in different areas. The cost of such operations is insignificant in comparison with the more elaborate techniques.

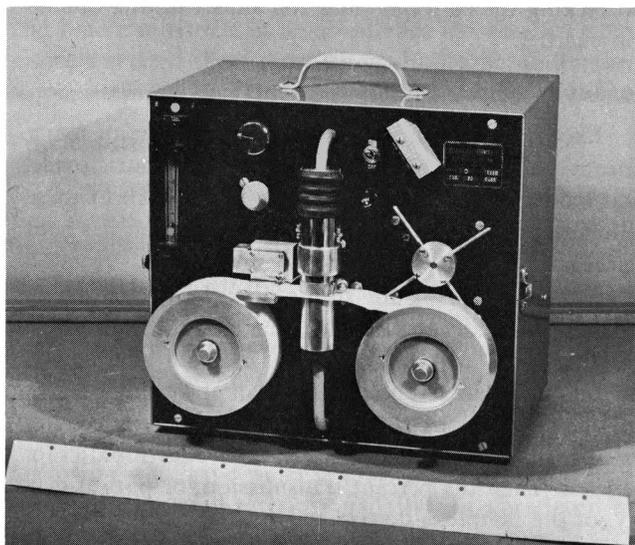


Figure 3. AISI Automatic Strip Filter Paper Sampler.

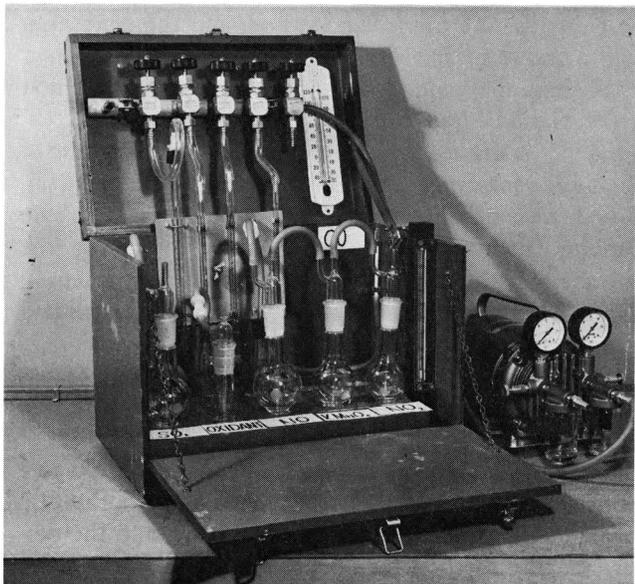


Figure 4. Multiple Gas Sampling Apparatus.

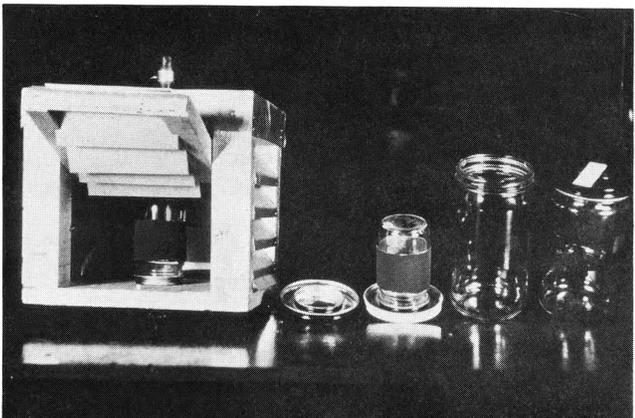


Figure 5. Lead Peroxide Candle.

In the lead peroxide candle method, a gauze strip impregnated with lead peroxide is wrapped about a cylindrical support such as a small jar (Figure 5). The collecting medium is allowed to stand open to the atmosphere with the natural air movements bringing the pollutant into contact with it. At the end of the sampling period, the gauze strip is removed, and the lead salts dissolved. Sulfur dioxide is determined, by a suitable method, as sulfate.

Similar simplified methods are available for the determination of gaseous fluorides and hydrogen sulfide, but are used to a lesser extent.

A simple method for the determination of hydrogen sulfide is through a modification of the AISI sampling procedure for soiling index. In this method a lead acetate impregnated tape is used. The air is initially filtered to eliminate interference of particulate matter. In passing through the impregnated tape, the sulfide is removed, and dark spots of lead sulfide are produced. As before, the optical density of the spots is determined and the concentration of hydrogen sulfide evaluated by use of a standard curve.

Equipment Cost

Sampling equipment required for low cost sampling is about \$1100. Of this, \$650 is allotted for particulate sampling equipment, as follows:

AISI automatic filter paper sampler	\$275
AISI spot evaluator	140
High-volume filter sampler & shelter	200
Dustfall containers & stands	5
Supplies (Filters, filter tapes, etc.)	30

In addition to various chemicals, equipment necessary for gaseous sampling includes a vacuum pump, manifold with valves, rotameters, glassware and a box to contain the sampling apparatus. With the exception of the sampling box, this equipment is available commercially and can be assembled at an approximate cost of \$375.

Fritted bubblers (4)	\$ 68
Midget impingers (4)	30
Carbon monoxide detector tubes	25
Vacuum pump	78
Rotameters (4)	100
Manifold with valves	25
Sampling kit & miscellaneous supplies	50

A spectrophotometer covering the visible spectrum is also necessary for the program. Such an instrument is usually available in a local laboratory. If it is necessary to buy such an instrument, an additional \$300 should be added.

Summary

An air pollution monitoring program is described that can be initiated and maintained by a local air pollu-

tion agency or health department at a moderate cost. Simple, inexpensive methods of sampling and analysis for gaseous pollutants and particulates are outlined and a detailed equipment cost breakdown is given.

Acknowledgments

This paper is based in part on a previous paper on low cost techniques of evaluating air pollution by Frank A. Bell, Jr. (6)

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MEASURES BEING TAKEN AT THE MONTROSE POWER PLANT TO REDUCE AIR POLLUTION

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Montrose Steam Electric Station of the Kansas City Power & Light Company is located in Henry County, about 70 miles southeast of Kansas City and about 12 miles southwest of Clinton, Missouri.

Extensive investigation indicated that it would be more economical to transport electric energy to the Metropolitan area of Kansas City than it would be to transport the coal, thus the decision was made to locate the plant in the strip mining area. All of the electric energy is transmitted to Kansas City as the plant area is outside the Company's franchise area.

For cooling condensers and plant use, a lake was constructed by building a 3600 ft earth dam on Deepwater Creek with a normal impoundment of 11,000 acre feet and 1530 surface acres of water. Judicious operation of the Tainter gates has resulted in eliminating much of the downstream flooding, making it much more likely that the farmers will be able to raise crops in the bottom land downstream from the dam. The lake and most of the land surrounding it has been turned over to the Missouri Conservation Commission for management, and affords the general area facilities for fishing, hunting of water fowl, and a wildlife refuge.

The first of three 175,000 kw steam generating units went into service in May of 1958, the second in June of 1960, and the third is scheduled for operation in March of 1964. The pulverized coal-fired boilers are rated at 1,260,000 lbs of steam per hr.

Approximately 55 million tons of coal was contracted for from the Peabody Coal Company to provide the plant with approximately 40 years' fuel supply. Of this 55 million tons of coal, approximately 45 million tons is contained in the Tebo seam. This Tebo seam of coal is and will be obtained from two mines, one in the

vicinity of the plant called the Power Mine, and the other referred to as the Tebo Mine which is approximately 25 miles from the plant near Calhoun, Missouri.

The remaining 10 million tons of coal is and will be obtained from the Power Mine near the plant site, but from a second and lower seam titled the Weir-Pittsburg seam. All of the coal obtained from the Power Mine is raw or mine run coal, whereas that obtained from the Tebo Mine is all washed coal. The principal reason for going to a washed coal at the Tebo Mine was to keep the freight cost down for this longer haul by eliminating approximately 8 per cent of the ash and pyrites by the washing process at the mine.

Prior to designing the station, extensive sampling of all the coal reserves was accomplished, which indicated a sulphur content of approximately 4 per cent. On the basis of approximately 4 per cent sulphur in the coal and 20 years' experience on operating high pressure boilers with pulverized fuel in Kansas City, the decision was made to construct smoke stacks 250 ft high and to install 85 per cent efficient mechanical dust collectors. After the plant was operating, but prior to using any of the 10 million tons of coal in the Weir-Pittsburg seam, it was determined by additional sampling that the sulphur content in the Weir-Pittsburg seam was much more erratic than originally estimated and that it ranged in value all the way from 3 per cent to 16 per cent with an average content of approximately 9 per cent. In order to utilize this coal, it was necessary for the coal company to construct a second unloading hopper at the plant so that this high sulphur Weir-Pittsburg coal could be mixed with the lower sulphur Tebo seam to give a blend that would not exceed 6 per cent. Due to the severe slagging characteristics of this fuel, it was also necessary

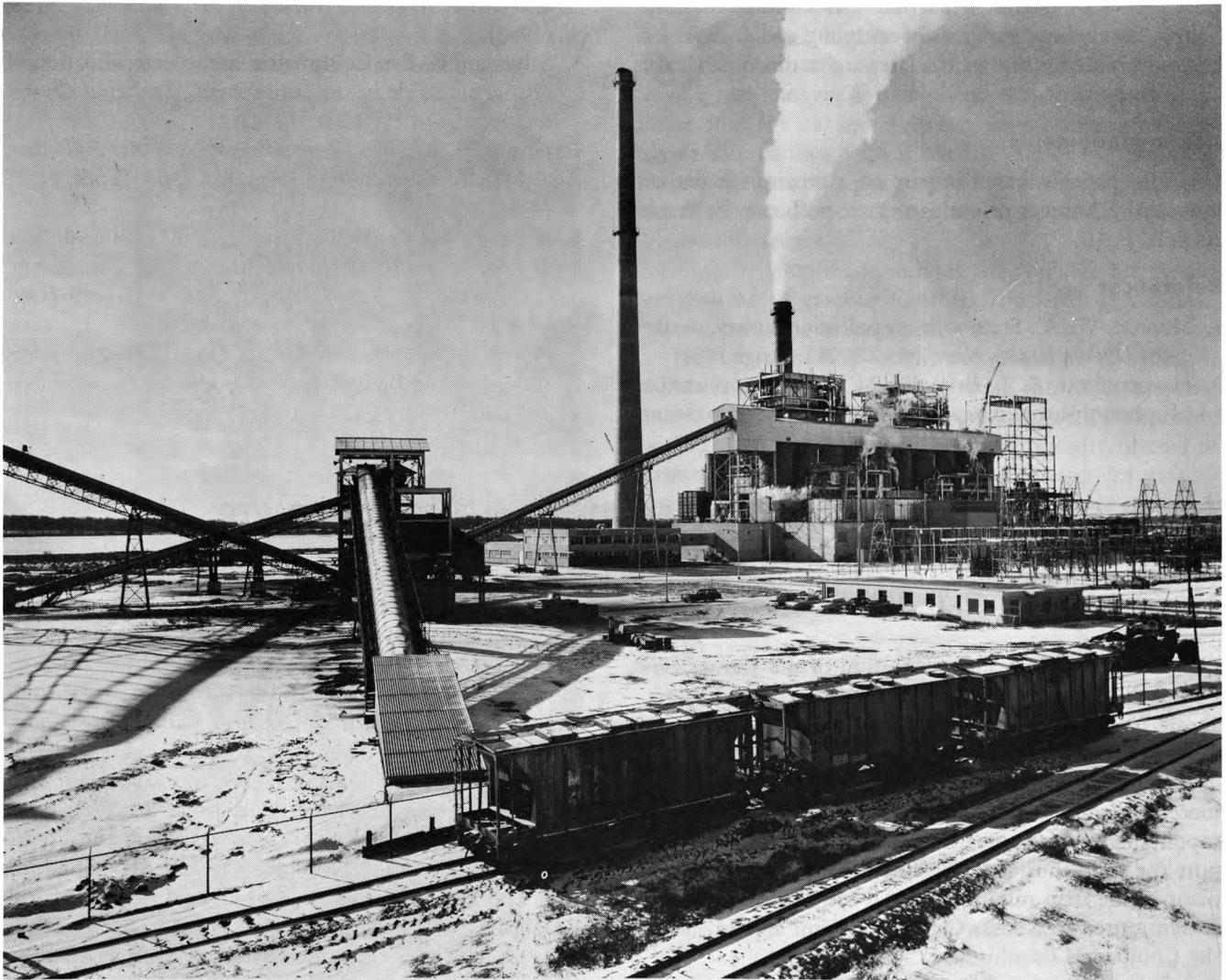


Figure 1. View of the Montrose Plant from the Northeast.

to install 12 additional soot blowers on each steam generating unit, and to reinforce the furnace bottoms to withstand greater impacts due to falling slag.

The sulphur content of the coal is determined daily on an "As Received" basis and the Tebo and Weir-Pittsburg seams are blended in the proper proportions so as to obtain a blend that has approximately 6 per cent sulphur. At the present time, a three-way blend is being fired, made up of approximately one-third raw Weir-Pittsburg, one-third raw Tebo, both from the Power Mine, and one-third washed Tebo from the Tebo Mine near Calhoun. A typical "As Received" analysis of this three-way blend is as follows:

Moisture	9.97%	Ash	15.59%
Volatile Matter	32.86%	Sulphur	6.00%
Fixed Carbon	41.58%	Btu per lb	10,679

With normal operating conditions and electrical loading of the Station, around 400 tons of fly ash are

caught and disposed of daily from two units. Most of this fly ash is sold as a substitute for cement in oil well cementing or concrete. Most of the remainder, along with bottom ash and pyrite rejects, is returned to and dumped into the strip mines.

Much of the sulphur is contained in a nodular dense type pyrite which, due to its density, is rejected by the coal pulverizers and thus does not reach the furnaces. Analyses of one set of simultaneous samples taken at pulverizer inlet and outlet showed a sulphur reduction of 2.21 per cent on a "dry" basis. While it is not certain that this reduction exists under all conditions, the amount of pyrite rejects does indicate the normal sulphur reduction to be quite significant.

From this it follows that while six per cent sulphur coal is being received, the sulphur content of the coal actually burned and which would contribute to air pollution is in the magnitude of four or five per cent.

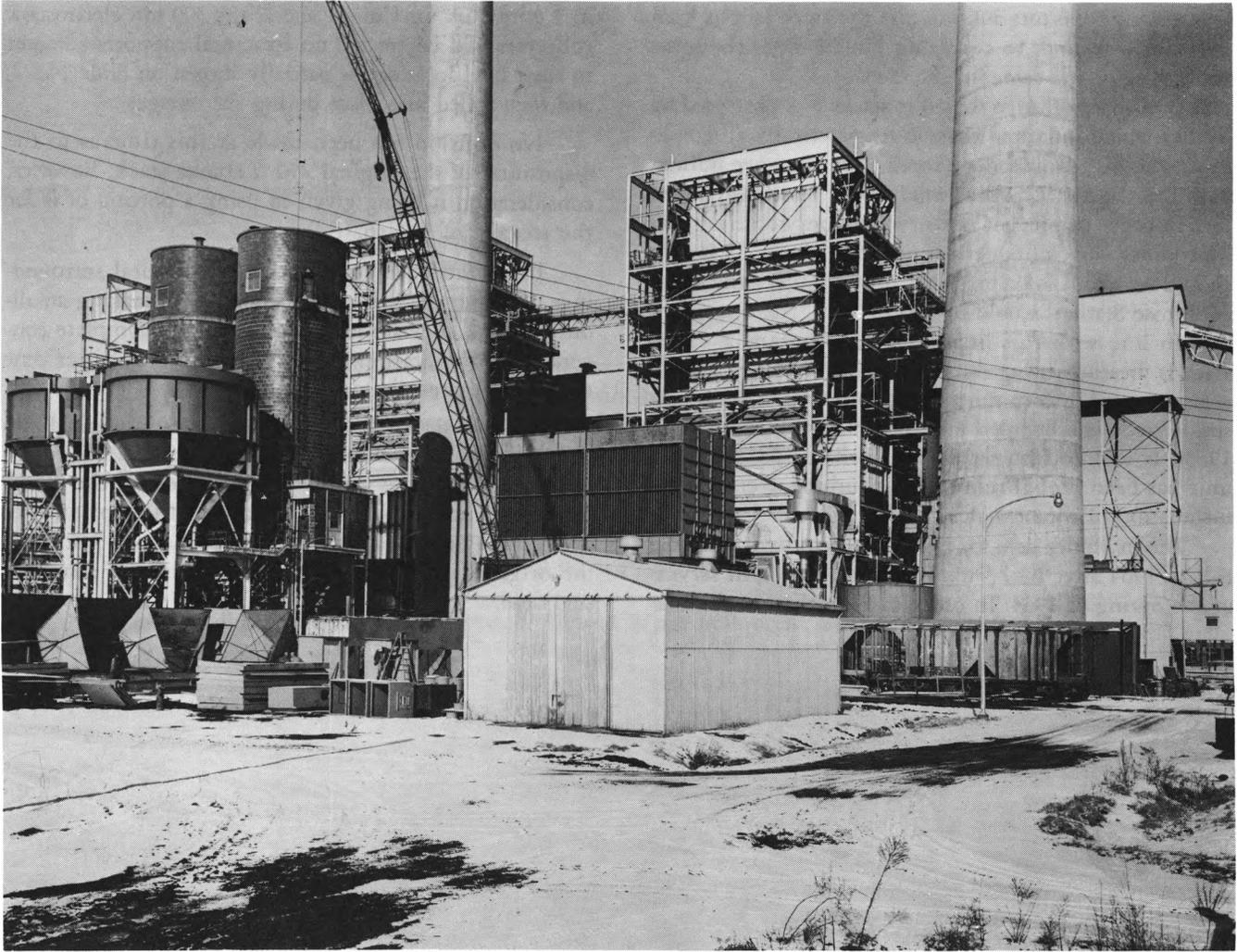


Figure 2. View from Southeast Showing Dewatering Bins and Fly Ash Silos.

Figure 2 shows the dewatering bins and fly ash silos. Ash from the furnace bottoms and pyrites are hydraulically conveyed to the dewatering bins shown on the left. After a bin is filled, the water is drained off, after which the ash and pyrites are gravity dumped into side dump railroad cars for disposal. These bins have a capacity of around 600 tons each. To the right are Nos. 1 and 2 fly ash silos which receive ash for storage and disposal from the respective boilers. Fly ash is conveyed to these silos pneumatically and dumped by gravity into cement type cars for sale, or through a dustless unloader into open top side dump railroad cars for disposal. Each silo has a capacity of 400 tons.

As mentioned previously, in spite of the remote rural location of Montrose Station, more than normal expenditures were made to keep air pollution at a minimum by the installation of 85 per cent efficiency dust collectors and a 250 ft stack; however, after about one year of operations, complaints were registered by some of the neighboring farmers. Of the complainants, only one was

really outspoken and he was located approximately a mile southeast of the plant. At times, when a temperature inversion exists, the smoke is inclined to settle down in the area of his farm. Prevailing winds are normally in this direction (SSE) around ten per cent of the time at an average velocity of 10 mph. For around 240 hours per year during the months of May through September, while the wind is in this direction, the atmosphere is sufficiently turbulent and unstable so as to cause the plume to come lower to the ground than otherwise. It follows that during such times, the ground level concentrations of SO_2 and dust will occasionally reach higher values than during times of a stable atmosphere. For the remaining time, the plume will rise and dissipate.

In view of the inclination toward pollution during certain inversion and the experience of extremely high rate of wear on the mechanical collectors, the Company adopted an all-out program for improvement. Under this program, it was decided to convert Units 1 and 2 from 85 per cent mechanical dust collectors to 95 per cent

electrostatic collectors and increase the stack height from 250 to 450 ft, and to construct Unit 3 with the same type collector and same height stack.

Decision to change to 450 ft stacks was prompted by studies which indicated that under practically all conditions, the SO₂ would not exceed 0.30 parts per million with the 450 ft stack. Also, wind tunnel tests have shown that in order to prevent down wash from occurring, except under very infrequent conditions, the stack height should be about 2.5 times that of the boiler which, for Montrose Station, would be 400 ft.

In line with this improvement program, a 450 ft stack is presently being constructed for No. 1 Unit, which is now served by a common stack with No. 2. This new single stack is scheduled for completion by February of 1963. It will go into service in April of 1963 after the unit has been brought down for a turbine overhaul and installation of the new electrostatic collector.

The in service date for Unit 2 collector will be in the Fall of 1964 after No. 3 unit has been placed in service in the Spring of 1964. In order to keep the outage time

to a minimum for Units 1 and 2, the 300 ton electrostatic collectors will be erected on structural supports adjacent to their final location, as partially shown on Slide No. 2, and then rolled into place during the outage.

No decision has been made at this time as to the disposition of the original 250 ft smoke stack; however, consideration is being given to using a portion of it for the storage of fly ash.

In summary, in spite of the remote rural surroundings of Montrose Station, the Company is making an all-out effort to alleviate local pollution by a complete conversion of the Station to 450 ft stacks and 95 per cent electrostatic precipitators.

It is our sincere belief and desire that a marked improvement will be effected and we would also like to say that in spite of the sizable expenditure and the many problems accompanying the operation of this plant, it is still working out in a very satisfactory manner, justifying the original decision of locating the plant in a nearby coal field.

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