

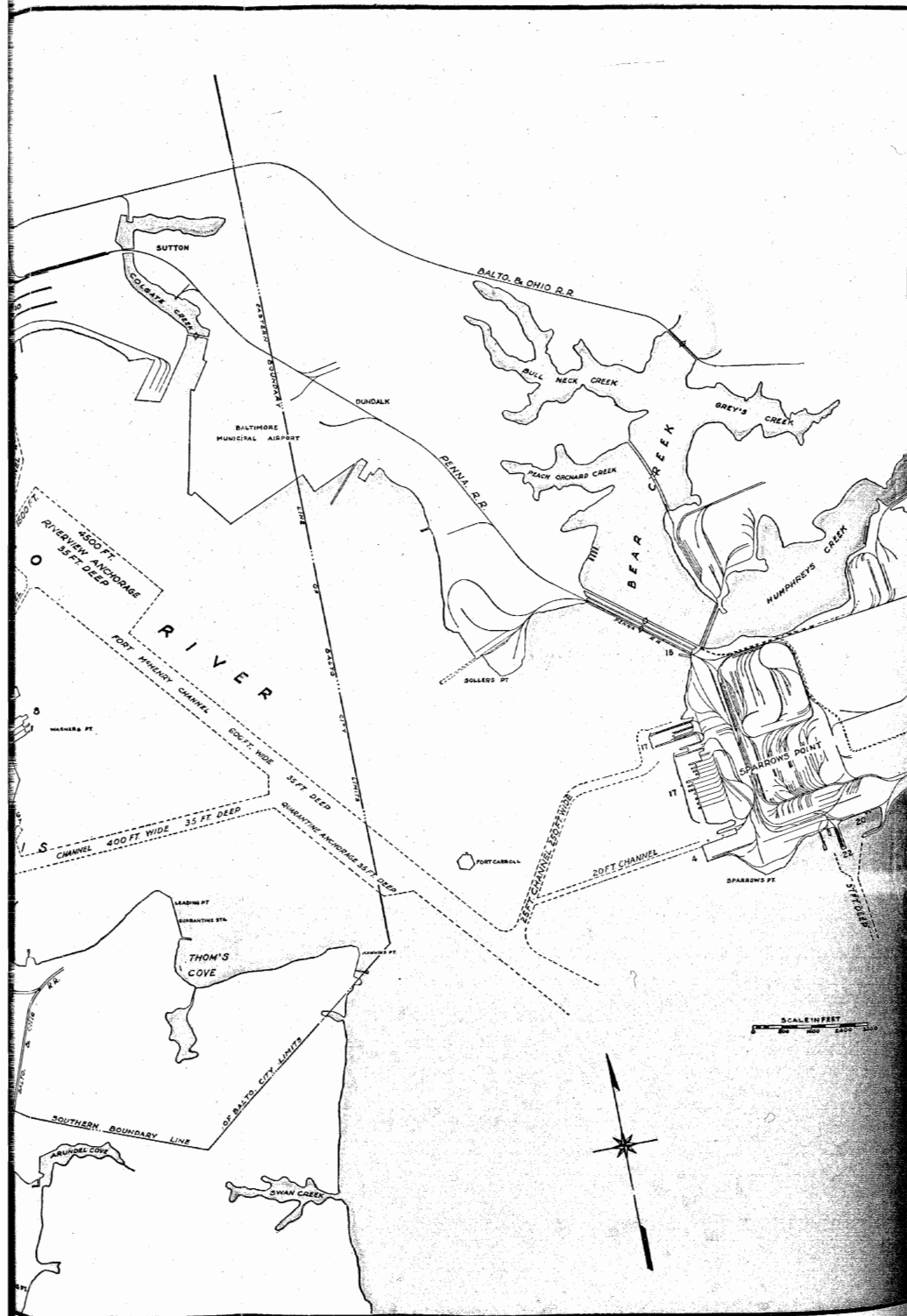
STUDIES OF THE EFFECTS OF INDUSTRIAL POLLUTION IN THE LOWER PATAPSCO RIVER AREA

1. The Curtis Bay Region, 1941

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Solomons Island, Maryland

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INTRODUCTION

Industrial effluents in the lower Patapsco area, which constitutes the navigable portion of the river and includes Baltimore Harbor, are many and include waste acid, distillery wastes, tannery wastes and copperas (ferrous sulphate) from pigment and steel industries. Preliminary studies have shown the last named waste to be most extensive. The red brown precipitate, Fe(OH)3 resulting from copperas disposal, is prevalent in Curtis Bay and can be seen in surface waters extending from Leading Point to the junction of Marley Creek and Furnace Branch, its extent and intensity depending upon variable conditions of tide and disposal. The source of the Fe(OH)3 is a paint pigment plant situated just inside the entrance of Curtis Bay opposite Sleds Point and from which it is discarded in the manufacture of titanium dioxide. On the north side of the Lower Patapsco area, originating in Humphreys Creek, copperas in pickling liquor from the steel industry produces a similar effect in Bear Creek and its tributaries (see frontispiece and Fig. 1). Also, on the north side of the area copperas is discharged by another plant which manufactures titanium pigment.

It has been possible to conduct an intensive study of the effect of copperas and its decomposition products on the biological productivity of Curtis Bay and nearby waters through the cooperation of the officials of the plants concerned and the data they have provided on the exact nature of the effluents and the conditions of their disposal. This area, polluted by copperas, is more extensive than other similarly polluted areas in the region and, moreover, its surrounding shore line has a contour that facilitates the study of such a problem.

*This is the first of a series of reports on a comprehensive and continuing hydrographic and pollution study program for the Patapsco River (Baltimore) region of Maryland. Dr. Olson is a Laboratory staff member. Mr. Brust is associated with the Department of Chemistry at the University of Pennsylvania. Dr. Tressler is Assistant Professor of Zoology, University of Maryland, and Planktologist, Chesapeake Biological Laboratory.

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GENERAL CONSIDERATIONS

The average depth of this area ranges from 5-10 meters, there being no sharp or sudden differences in depth at any given locality except at those points where artificial channels traverse the more shallow areas. Therefore, stations for sampling were chosen at convenient locations in each general area where significant differences in effects of pollution might be expected. In no case, however, was a station located directly in a main channel where dredging operations and

the frequent passage of commercial craft stir up the bottom and produce atypical conditions. The ten stations shown in Figure 1 were used in all of the work reported herein. Approximate distances in miles, by water, from each to the source of copperas disposal are as follows:

Station	Depth In Meters	Location	Distance From Source
I	6	Fort Carrol (100 yd. N.W.)	3.1 miles
IA	6	Leading Pt. (¼ mile E.)	2.0 miles
II	8	Off old wooden ships near lagoon between Sledd's Pt. and Leading Pt.	0.9 miles
III	10	Off Fire Boat dock	0.3 miles
IV	7.5	Stonehouse Cove	0.7 miles
V	6	Off Cabin Branch	0.3 miles
VI	4	Cabin Branch	0.8 miles
VII	6	Highway Bridge	0.8 miles
VIII	6	Railroad Bridge	1.4 miles
X	4	Convolute of Furnace and Marley Creek	2.7 miles

Additional stations were chosen for special purposes, as indicated later in this report.

The significance of the results of sampling at each station depends upon the velocity and direction of the flow of water and the effluent carried by it from the source of disposal during that period between the time of disposal and the time of sampling. The directions of current flow and the current velocity under various conditions are not available for the region because of the difficulties involved in their measurement. Current velocities for locations corresponding to a few of the stations in this report are given in "Tides and Currents in the Chesapeake." (Haight, 1930)

Station	Date	Location	Depth	Flood Velocity	Ebb Velocity
H 32	Aug. 19-20/27	Near Sta. I	7 ft.	.20 knots	.25 knots
			17½ ft.	.20 knots	.25 knots
			28 ft.	.30 knots	.20 knots
H 34	July 26-27/27	Near Sta. IA	7 ft.	.19 knots	.19 knots
			17½ ft.	.19 knots	.19 knots
			28 ft.	.19 knots	.19 knots
H 35	July 27-28/27	Near Sta. III	5½ ft.	All currents weak and irregular.	
			13½ ft.		
			22 ft.		

It appears that currents at stations outside of Station III average approximately .2 knots per hour, while those inside of Station III are too weak or irregular to be measured by standard methods as, for example, current meters. These measurements also show that current velocity does not vary markedly with depth outside of Curtis Bay, all of which factors are contrary to those anticipated.

While detailed measurement of current velocities and directions in Curtis Bay and nearby waters cannot be made without costly special

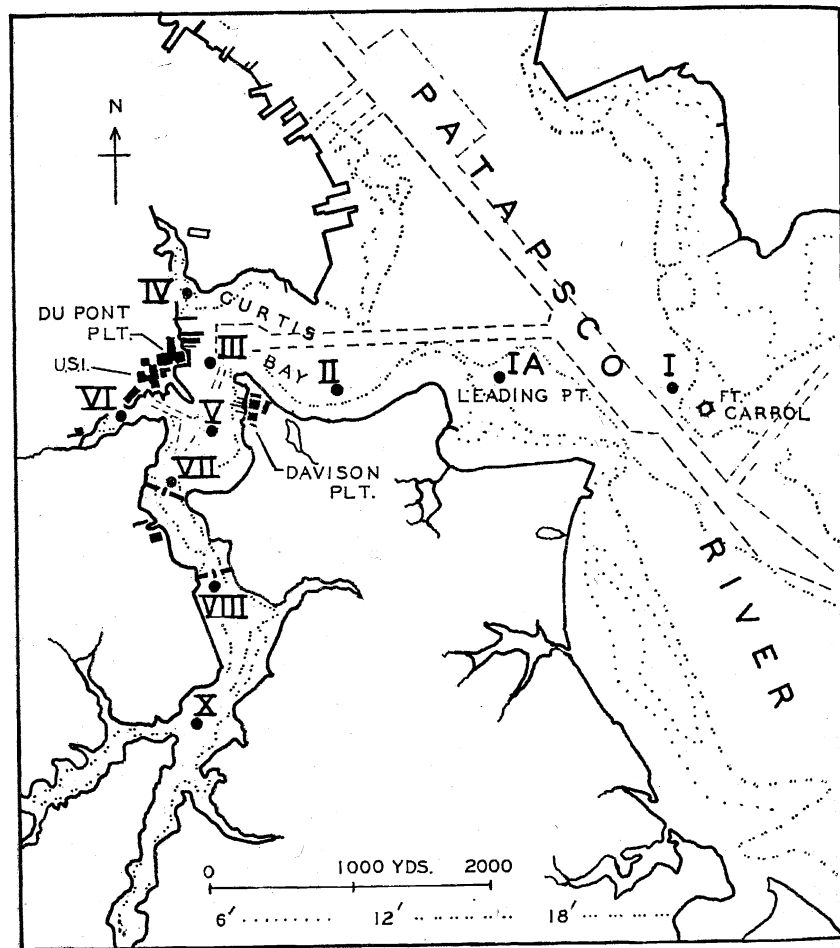


FIGURE 1.

MAP OF THE REGION SHOWING THE LOCATION OF SAMPLING STATIONS AND DISPOSAL SOURCES.

DUPONT PLT.—Krebs Pigment Division of E. I. duPont de Nemours & Co.

U. S. I.—U. S. Industrial Chemical Corporation.

DAVISON PLT.—Davison Chemical Corporation.

instruments operated by a large group of workers over a long period of time, their general trend and the time of their maxima can be determined from tide records for the area. The time and height of low and high water every day at nearby Fort McHenry, Baltimore, is predicted for each year by the Coast and Geodetic Survey. These values are predicted from harmonic constants and represent the height

of water as influenced by astronomical conditions only. However, in the upper Chesapeake Bay and tributaries the effect of astronomical influences on tide are frequently almost obliterated by such meteorological conditions as wind and precipitation. This is shown in Figure 2 by the marked difference between the predicted tide heights and the actual tide heights, as measured by the automatic tide gage maintained by the Coast and Geodetic Survey at Fort McHenry. Even greater differences than those indicated are frequent, the actual heights of tide being entirely unpredictable. Records of the tide gage, operated continuously at Fort McHenry, were made available to this study, and from them it was possible to correlate tidal height, therefore current variations with sampling data.

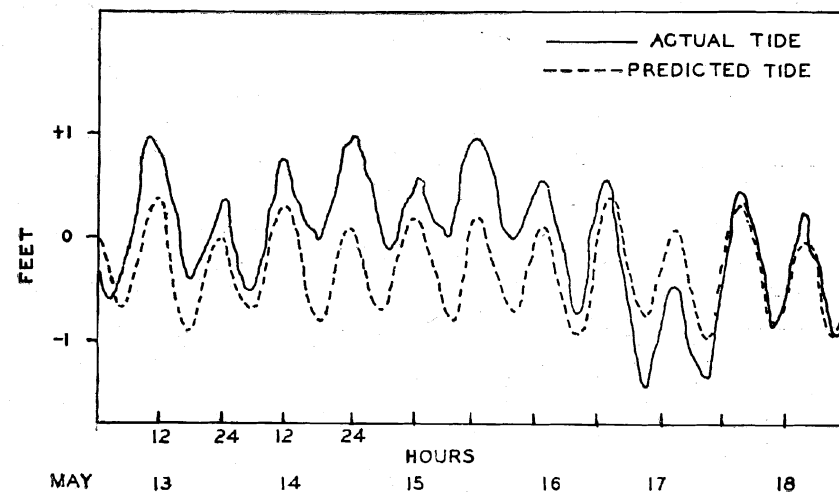


FIGURE 2.

Comparison between tides predicted by the U. S. Coast and Geodetic Survey and those measured by the automatic tide gage at Fort McHenry, Baltimore.

Copperas results at the Krebs pigment plant as a waste product in the manufacture of titanium dioxide, a white paint pigment. The pigment is extracted from ilmenite, ferrous titanate (FeTiO_3), by using sulphuric acid to dissolve out the iron, and the ferrous sulphate which occurs is discarded. Since copperas has not yet found any marketable use, and is of little commercial value (Hodges, 1939) it is dumped into Curtis Creek along with a small amount of titanium dioxide and a variable amount of unclaimed free acid.

The rate of disposal of copperas in Curtis Bay was increased during 1940 to the point where the average sometimes exceeds 150 tons per

day. Records of rates of disposal supplied by the plant authorities were correlated in every case with the time of sampling, the effect of tide, and the results of analyses. A typical record of disposal rate is shown in Table I.

TABLE I
COPPERAS DISPOSAL
Pounds Accumulated by Shifts*

Date	7-3	3-11	11-7	Date	7-3	3-11	11-7
6/1/40		150,870	163,710	16	128,361	98,688	101,629
2		139,635	123,906	17	100,974	112,822	128,766
3		138,030	175,266	18	147,660	176,550	
4		170,130	105,288	19	154,080	227,910	
5	166,920	221,490		20	195,810	195,810	
6	186,180	202,230		21	126,994	152,905	108,343
7	166,920	190,600		22	131,610	182,970	
8	160,500	202,230		23	121,980	173,340	
9	163,710	192,600		24	154,080		170,130
10	97,048	113,586	127,244	25	186,180		176,550
11	108,797	104,582	132,242	26	112,350		176,550
12	170,130		147,660	27	121,980		179,760
13	163,710		154,080	28	131,200		208,000
14	144,450		173,340	29	201,600		198,400
15	192,600		192,600	30		166,400	172,800

*Disposal occurs twice daily one hour after each flood tide.

It was the practice during the past year at the Curtis Bay pigment plant to accumulate copperas throughout the day in large storage bins. One hour after each predicted flood tide these bins were flushed out and their contents discharged into the Bay. This practice was suggested in order to minimize the accumulation of copperas and its products of decomposition in Curtis Bay. During 1938-39 this practice was carried out only during the summer months in order to reduce the number of complaints by summer residents in the Marley Creek and Furnace Branch areas. The inconvenience of accumulation of large quantities of exposed copperas on the plant floor led to the construction of permanent storage bins and the present regular practice of disposal on ebb tide, throughout the year.

When copperas is flushed into the Bay water the dissolved ferrous sulfate hydrolyzes rapidly lowering the pH and forming basic ferrous salts. In the presence of dissolved oxygen, ferrous iron becomes oxidized to ferric iron. This ferric iron is most prevalent in the form of ferric hydroxide, a yellow brown insoluble precipitate which first exists in the colloidal form and through subsequent "salting out" and flocculation becomes heavy enough to settle out. From the standpoint of pollution the first noticeable effect is the increase in acidity due to hydrolysis; the second effect is a decrease in available dissolved oxygen through Fe⁺⁺ to Fe⁺⁺⁺ oxidation, and the final effect is flocculation and settling of Fe(OH)₃. The ionic reactions, in condensed form, are represented in Figure 3.

A variable amount of free acid sometimes finds its way into Curtis Creek from the Davison Chemical plant situated on Sledd's Point, and infrequently a discharge of oxygen-consuming distillery waste results from the U. S. Industrial Chemical plant near Cabin Branch. Since these effluents are not discharged daily their effects are atypical for the region and are thereby easily detected.

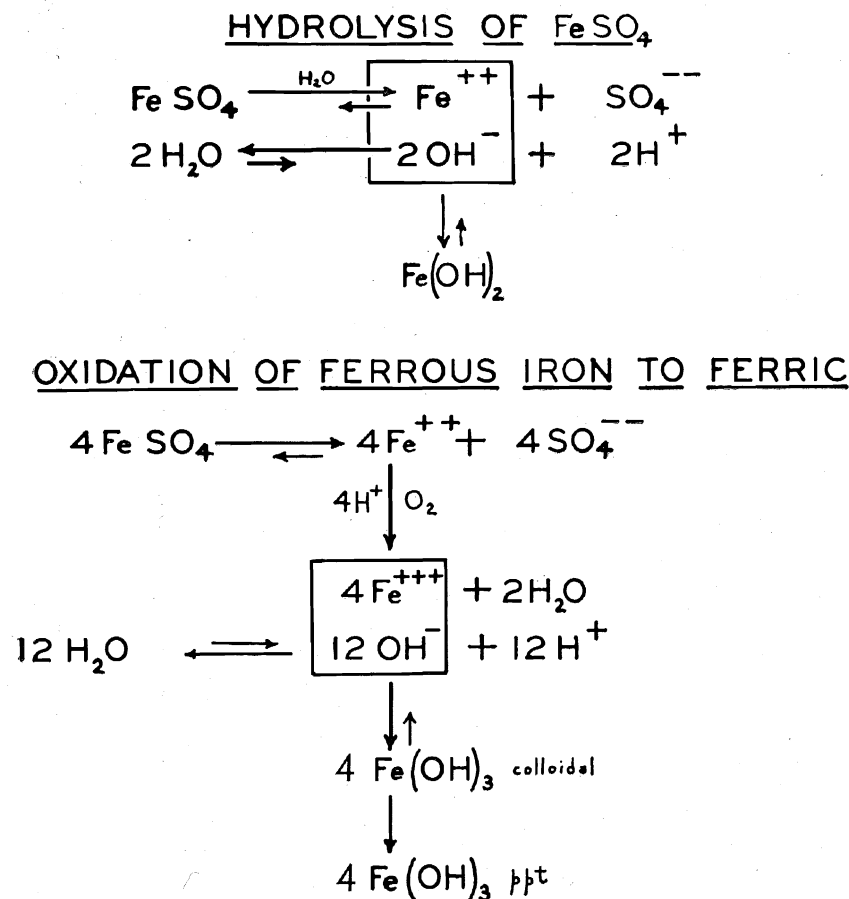


FIGURE 3.
DECOMPOSITION REACTIONS OF COPPERAS.

Analysis for dissolved oxygen, salinity, pH, and in some cases total iron, were made on samples taken at the regular stations from Fort Carroll to the head of Marley Creek over a period of two years during 1938 and 1939. Total iron in bottom muds was also deter-

ined. The results showed the degree to which copperas disposal affected the normal characteristics of nearby waters. Under the prevailing conditions of disposal the pH and dissolved oxygen anomalies were found to be largely local and effective to the limits of Curtis Bay proper, while total iron ran high as far as Leading Point. Laboratory experiments on the toxicity of copperas decomposition products also were carried out, and in a number of cases the toxic nature of these substances in concentrations that occur in Curtis Bay was clearly determined. Recent increases in the rate of copperas disposal, however, has extended the limits of detrimental effects in a degree and manner which will be pointed out in this report. Moreover, a number of problems involving a more detailed study not considered previously are treated herein.

METHODS

Station and Sampling. The ten stations established (Fig. 1) were sampled at surface and bottom depths at least once during each ten day period except when weather conditions or other uncontrollable factors made this impossible. Since the depth ranges only from 4-10 meters sampling at intermediate depths was not considered necessary except in special cases. All samples were collected with the Foerst sampler. The analytic work for dissolved oxygen, total iron, soluble iron, insoluble iron, ferrous iron, chlorinity, and pH was done in the field in those cases where unstable compounds were involved. Biological determinations were made from 250cc samples preserved with formalin and centrifuged for micro-plankton counts while macro-plankton was determined on a semi-quantitative basis by five minute surface tows with a No. 20 plankton net. Transparency was determined with the conventional Secchi disc in earlier work and whenever possible with the submarine spectroradiometer developed at the Laboratory. Temperature was measured with the usual reversing thermometers and with new rapid measuring thermoelectric equipment likewise developed during this work. Mud core samples were obtained at each station with the Woods Hole type core sampler, the core being cut into two inch segments for subsequent analysis for total and ferrous iron.

Chemical Analysis—Dissolved oxygen—Since the widely used Winkler method presents a number of difficulties and consequent errors with samples that contain ferrous and ferric iron as well as oxidizable organic matter, it became necessary to determine the extent of such

errors and the possibility of substituting some more feasible method. Other procedures include the Rideal-Stewart modification, the sodium azide method, and the Alsterberger method. Each of these was, therefore, carefully studied with respect to the extent of error caused by the presence of these interfering substances. The sodium azide method and the Rideal-Stewart modification were both found to be useful only in the presence of much organic matter, being of less value in the presence of ferrous and ferric iron than the regular Winkler method. The Alsterberger method appeared to be the most desirable when ferrous and ferric iron as well as organic matter ran high, and this method was used on many occasions. In all four procedures, as run on regular samples in Curtis Bay, results seldom differed widely enough to justify the added complexity of other methods as over and against the regular Winkler method. Moreover, oxygen values, when they are exceedingly abnormal, can be checked and corrected for the presence of ferric and ferrous iron, both of which factors were determined at all stations as conditions permitted. In all cases it was found to be absolutely essential that reagents be added in the field and that final titrations be made as soon as possible after reaching the laboratory.

Total Iron—Total iron was analyzed by the Thompson & Bremner (1935) method for sea water, the final value being determined colorimetrically. In a later stage of the problem a special photometer was devised and the values obtained electro-photometrically from galvanometer deflections. In this way values as low as 0.01 milligrams per liter could be detected with accuracy.

Soluble Iron—Soluble iron was determined by filtering samples through fine filter paper in the field, the filtrate being analysed in the same manner as for total iron. Insoluble iron was determined as the difference between total iron and soluble iron. Because of its instability it was necessary to determine ferrous iron in the field as soon as samples were collected. This presented numerous difficulties in the maintenance of standards, etc., and most of the results are not considered to be accurate within 1 mg/l. Colorimetric procedure was followed in which potassium ferricyanide was used as an indicator.

Core Samples—Total iron in bottom mud cores was determined in each two-inch segment by a modification of the Thompson and Bremner method as used for analysis of water samples. The silica and various unoxidizable solids were filtered out, following digestion, and

the regular colorimetric procedures then carried on. Ferrous iron in core segments was determined in a number of cases, qualitatively, with potassium ferricyanide, and, quantitatively, by the standard gravimetric method.

Chlorinity—Chlorinity was determined volumetrically by the standard Mohl titration method using silver nitrate with potassium chromate as an indicator.

pH—Determinations of pH in the field were made with a Beckman pH meter fitted with flow type glass electrodes, such that the sample could be poured into the electrode chamber, flushing out the previous sample and the determination carried out within fifteen seconds. Using this technique it was possible to carry out a greater number of determinations in a short time.

RESULTS AND DISCUSSION

The results from samples collected on the different trips show variations in the properties of the waters at the various stations, which results depend on the combined action of all influencing factors such as time and rate of disposal, temperature, salinity, tidal variations, etc. Therefore, the different factors and their magnitudes of variation are discussed separately while consideration is given to the interaction of these factors in certain typical cases.

Temperature—There exists but little marked temperature stratification at the several stations, since the area studied is not excessively deep and the salinity is not high, the difference between surface and bottom waters seldom exceeding 4°C. in winter and 2°C. in summer. Water temperature differences from one station to another also are slight and occur only through the slow influx of the Bay waters, that is, tidal action. Therefore, temperature differences with respect to location do not become significant except through their role in determining the degree of dissolved oxygen saturation. Of far more importance are the seasonal changes in temperature over the entire area. The higher temperatures of the summer months exert a marked influence on the degree and extent of pollution by controlling the rate of decomposition of effluents as well as growth and respiration rates of aquatic organisms, and by limiting the capacity of the waters of the region to dissolve oxygen from the air.

Seasonal changes in temperature at each depth and at all stations

were carefully followed from January, 1938, and are summarized in Table II from that date to August, 1939. The same trend occurred during 1940 but with somewhat lower values during the winter months. Average water temperatures for the region, during 1940,

TABLE II
Water Temperatures at Each Station During 1938-1939 in Degrees Centigrade

Date	Depth	I	IA	II	III	IV	V	VI	VII	VIII	X
1/20/38	Surface	7.5			7.6	6.6	5.8		7.0	6.8	7.2
	Bottom	7.6			7.9	7.5	7.0		6.5	7.1	6.7
2/15/38	Surface	5.1			4.8		5.3		5.7	5.4	5.7
	Bottom	7.8		4.8	6.6	5.0	6.5	6.1	6.1	5.9	6.2
3/22/38	Surface	11.0		11.1	11.3	11.6	11.8		11.5	11.4	11.1
	Bottom	10.6		10.5	10.6	11.5	11.7		10.7	10.8	10.9
5/6/38	Surface	21.0			20.9		20.1	23.9			
	Bottom	17.8			15.8	18.9		23.9			
6/14/38	Surface	24.0		23.7	23.5	27.0					
	Bottom	19.6		20.1	20.0	26.0					
7/15/38	Surface	32.1	31.8	32.0	31.6	34.8	31.8	32.1	32.0	32.0	31.8
	Bottom	31.0	31.6	31.0	31.4	33.8	31.5	31.7	31.7	31.4	31.4
8/31/38	Surface	30.0	30.0		29.4		30.2	31.0	30.3	31.0	30.2
	Bottom	30.1	29.4	29.3		30.3	29.5	30.3	26.3	30.3	28.3
9/15/38	Surface	32.1			28.3		26.1		27.0		
	Bottom	30.1	30.1	28.3	30.2	30.1	30.1	24.3	28.2	30.2	29.0
10/26/38	Surface	20.3			20.0		20.0		20.1	18.0	20.0
	Bottom	21.5		21.1	20.4	20.4			21.0	20.4	22.0
11/16/38	Surface	12.8			12.8		11.8		12.8	12.2	12.7
	Bottom	14.1			13.8		12.4		13.1	13.0	13.2
12/14/38	Surface	6.2	6.2		6.8				5.3	5.3	
	Bottom	6.2	6.2		6.9			6.6	5.4	5.4	6.4
1/17/39	Surface	6.0	6.0		4.1		3.1		4.4	3.3	3.1
	Bottom	6.1	6.0	6.0	5.0	5.0	6.0	4.3	4.3	4.0	3.1
3/8/39	Surface	4.6					5.4				
	Bottom	4.4	4.6	5.3	4.4	4.7	5.2	5.1	5.5	4.8	5.7
4/24/39	Surface	14.6			12.4						
	Bottom	9.7	12.2	12.8							
5/17/39	Surface	18.0							21.2	20.5	
	Bottom	17.8	17.7	19.7	19.7	20.6	20.5	20.2	19.2	18.8	23.0
6/19/39	Surface	27.1			26.3		26.0		26.3	27.3	27.2
	Bottom	26.3			26.1		25.4		26.0	26.4	25.4
8/2/39	Surface	30.2	30.3	28.2			29.4			31.1	30.2
	Bottom	27.4					28.3		28.1	28.1	29.3

ranged from 2°C. during January and February to 29°C. in July, but surface waters show a wider variation. During February ice covered the entire region with the exception of the ship channels, which were kept open. Unfortunately, no samples could be obtained at this time. Surface water during July frequently reached a temperature of 33°C. and higher. The additional effect of this upper and warmer layer, thus low oxygen water, in retarding the oxygen saturation of the underlying waters is obvious.

Chlorinity—There is but little difference in chlorinity with respect to station location, since the run off from the Marley Creek drainage area, itself small, is influenced mainly by local precipitation and is meager except during the spring thaw. Only a slight gradient exists from Station I to Station X, comprising less than one part per thousand chloride ion. Typical seasonal changes are indicated in Table III. During 1940 these values ranged from 2.0‰ in March to 8.0‰ in September.

The chlorinity stratification with depth is marked only at the deeper stations located in isolated areas where a minimum of turbulence and mixing occurs. Such is the case at Stations III, IV, and VI, where a difference of more than 1.0‰ often occurs between surface and bottom. Other stations, except in rare cases, show a surface-bottom difference of less than 0.3‰. Chlorinity, as a regional factor affecting the intensity and extent of pollution effects, cannot be considered as important in view of the slight differences experienced. As a seasonal factor it influences the rate of Fe(OH)₃ flocculation by "salting out" the colloidal particles. As an indicator of salinity, chlorinity shows the trend of the buffering action of the waters and, hence, their capacity to tolerate the contribution of added H ions. Perhaps the most significant indication from chlorinity determinations is that of the relative mixing and vertical movements of water at different depths. There are two or three instances where, in deep places, pronounced stratification and corresponding dead spots or isolated bodies of water occur in which it would be expected that effluents and their decomposition products which reach these areas would remain undissipated by decomposition. However, under exceptional tidal conditions, or by the vertical mixing that normally accompanies temperature changes in the annual turnover, the water in such areas becomes diluted.

TABLE III

Chlorinity at Each Station During 1938-1939 in Parts Per Thousand

Date	Depth	I	IA	II	III	IV	V	VI	VII	VIII	X
1/20/38	Surface	3.70			3.53	3.88	3.62		3.55	3.53	3.50
	Bottom	4.60			4.00	3.90	4.05		4.15	4.00	3.97
3/22/38	Surface	3.00		1.83	2.51	2.60	2.51		2.60	2.63	2.50
	Bottom	3.15		2.12	2.62	2.62	2.67		3.68	2.81	2.85
5/23/38	3½ meters	3.60		3.50	3.62	3.55	3.52	3.55	3.40	3.37	3.55
7/15/38	Surface	3.64	3.71	3.70	3.70	3.71	3.65	3.20	3.27	3.54	3.44
	Bottom	3.65	3.75	3.77	3.74	3.71	3.30	3.26	3.82	3.57	3.50
9/15/38	Surface	4.16			4.29		4.06		3.83		
	Bottom	4.25	4.16	4.15	4.36	4.13	4.21	4.10	4.36	3.47	3.48
11/16/38	Surface	5.77			5.67		5.63		5.54	5.48	5.24
	Bottom	6.10			5.78		6.12		5.77	5.62	5.25
1/17/39	Surface	5.08			4.97		4.86		4.73	4.70	4.28
	Bottom	5.64	4.63	4.84	6.81	5.00	6.63	4.87	6.62	7.78	4.86
3/8/39	Surface	1.64					2.07				
	Bottom	1.82	1.87	2.22	1.81	2.12	2.10	2.12	2.12	2.08	2.02
6/19/39	Surface	3.16			3.14		3.10		2.76	2.75	2.79
	Bottom	5.28			3.64		3.10		2.91	3.05	2.91
8/2/39	Surface	3.96	3.86	3.85			3.70			3.77	3.45
	Bottom	5.13					3.94		4.58	4.15	4.25

Dissolved Oxygen—The lower limit of dissolved oxygen for the normal respiration of most aquatic life has been shown to be about 4 p. p. m. or 3.5 c.c./liter (Ellis, 1937, and others). In Table IV and Table V the variation in dissolved oxygen at each station throughout the period from January, 1938 to September, 1940, is presented. The

average water temperature for each set of measurements and the saturation value for that temperature is also given.

TABLE IV
Dissolved Oxygen At Each Station in cc. Per Liter

Date	Aver. Temp.	O ₂ Sat.	Depth	I	IA	II	III	IV	V	VI	VII	VIII	X
1/20/38	7.1	8.48	Surface	7.04			6.20	4.82	5.84		6.09	6.49	7.28
			Bottom	6.93			6.13	3.21	2.07		1.97	3.47	5.63
3/22/38	11.0	7.32	Surface	6.62		6.72	6.49	3.37	5.99		5.77	5.84	5.66
			Bottom	4.85		5.91	5.74	1.81	2.71		2.71	4.00	5.41
5/6/38	19.9	6.00	Surface	6.27			5.82		5.73	1.51			
			Bottom	5.87			5.69	3.47	5.91	1.45			
7/15/38	31.5	4.95	Surface	5.47	5.35	4.35	4.53	3.59	4.20	1.76	5.11	5.71	5.50
			Bottom	4.12	4.42	4.20	2.55	0.14	1.80	1.21	3.37	5.04	0.42
9/15/38	28.6	5.20	Surface	6.07			5.20		5.72	3.56	6.63	6.10	
			Bottom	5.46	4.93	4.87	4.55	0.74	4.11		2.72		3.46
11/16/38	13.0	7.08	Surface	6.40			5.18		6.18		4.81	5.24	5.77
			Bottom	5.43			4.26		2.35		3.12	4.10	4.20
1/17/39	4.4	8.55	Surface	7.93			6.18		5.96		6.27	6.67	7.41
			Bottom	7.10	4.95	5.90	6.17	4.61	2.01	4.56	0.00	2.31	4.41
3/8/39	4.6	8.51	Surface	8.07					6.61				
			Bottom	8.06	7.54	4.55	7.44	5.81	6.09	5.96	6.18	6.78	7.56
6/19/39	26.2	5.43	Surface	4.91			4.02		3.72		3.62	4.25	6.60
			Bottom	0.00			0.33		3.62		0.76	1.16	2.18
7/10/39	30.1	5.05	Surface				5.33		4.97		6.44	6.85	6.11
			Bottom	3.96			1.97		1.85		1.26	6.72	2.63

It can be seen that harmful low values occur in Curtis Creek very frequently throughout the year, while during the summer months when the water temperatures are above 25°C. low values often occur over the entire region.

The lower values have been more intense and more frequent as the disposal rate of copperas has increased during 1939-1940 and during the summer months of 1940 (Table V) extremely low values were observed at Station I. Whether these effects are to be found beyond this station as yet have not been determined. It is obvious, however, that at these higher water temperatures (25-30°), when even fully air-

TABLE V
Dissolved Oxygen in cc. Per Liter

Date	Aver. Temp.	O ₂ Sat.	Depth	I	IA	II	III	IV	V	VI	VII	VIII	IX
3/27/40	3.9°	8.70cc/1	Surface	6.50		7.9		6.0	6.9	6.7	7.6	7.05	7.35
			Bottom	5.15		6.9		3.5	3.7	4.2	5.3	3.9	6.6
6/14/40	25.7°	5.18cc/1	Surface	4.66	4.76	2.32		4.87	6.34	6.12	7.59	6.90	6.69
			Bottom	3.27	1.60	4.52		0.00	1.66	2.77	0.41	0.00	3.99
7/9/40*	27.5°	5.04cc/1	Surface	2.66	3.38	7.74		8.44	4.58	8.27	3.08	5.32	4.36
			Bottom	0.00	1.70	5.96		6.43	6.12	8.24	5.04	8.64	7.54
8/2/40	25.0°	5.20cc/1	Surface	4.68	4.98	4.82	4.50	2.27	4.94	1.86	7.82	8.29	7.70
			Bottom	3.16	0.73	4.61	0.00	1.19	0.00	0.98	5.52	2.14	2.35
9/10/40	23.5°	5.32cc/1	Surface	4.31	5.15	5.38	3.92	3.46	4.82	1.97	6.48	7.11	8.22
			Bottom	5.37	3.58	3.17	0.78	0.41	4.42	1.88	0.00	2.61	3.94

*Winkler method used.

saturated water contains only from 5.0-5.5 cc. of dissolved oxygen per liter, further withdrawal of oxygen by copperas oxidation becomes

significant and effective in limiting the amount of O₂ needed by all aquatic organisms for normal respiration. Moreover, the normal oxygen demand of these organisms is markedly increased by these higher temperatures and the lower limits of O₂ concentration for normal function become correspondingly increased (Ellis, Weibe, and others).

TABLE VI
pH of Samples of Water

Date	Station VII	Station VIII	Plant Pier	Date	Station VII	Station VIII	Plant Pier
6/2/40	6.7	6.2		18	3.0	4.2	2.6
3	6.4	6.0		19	4.3	5.7	2.6
4	6.7	5.6		20	4.2	3.9	3.1
5	6.7	5.4		21	3.9	4.0	2.8
6	6.6	5.9	3.5	22	4.2	4.0	3.0
9	6.4	5.8	4.6	23	3.9	4.0	3.4
10	6.7	6.0	5.0	24			3.7
12	6.3	6.0	4.1	25	6.0	5.9	3.2
13	9.1	8.7	3.5	26	3.3	5.0	3.3
15			2.7	27			3.0
16	3.6	4.3	3.1	29	6.6	5.0	3.4
17	3.8	4.2	2.8	30	6.2	5.1	3.2

The detrimental effect of copperas disposal in the summer months at the increased rate prevailing during 1940 (300,000 lbs. per day) is, therefore, recognizable.

TABLE VII
pH of Samples Taken Before and During Shutdown

Date	Pier-E End	Pier Center	Pier-W End	Pier-W Center	Station VII 1st Bridge	Station VIII 2nd Bridge
Before Shutdown						
7/7/38	3.2	3.3	3.2	3.2	6.7	7.1
7/8/38	3.3	3.1	3.0	3.2	6.5	7.1
7/9/38	3.0	3.2	3.2	3.1		
7/10/38					6.7	6.9
7/11/38	3.4	3.2	3.0	3.1	6.7	7.0
7/12/38	3.3	3.7	3.4	3.7	6.8	6.9
7/13/38	3.7	3.4	3.2	3.2	6.6	7.1
7/14/38	3.4	3.4	3.2	3.3	6.8	6.9
During Shutdown						
7/16/38	4.7	3.7	3.7	3.7	6.6	6.9
7/16/38	4.7	3.7	3.7	3.7	6.6	6.4
7/17/38	6.5	6.7	6.4	6.3		
7/18/38					6.9	6.7
7/19/38	6.7	6.8	6.4	6.4	6.5	6.7
7/20/38	6.5	5.6	6.4	6.3	6.8	7.0
7/21/38	6.7	6.4	6.6	6.4	6.7	6.9
7/22/38	6.8	6.8	6.7	6.7	6.9	7.0
7/23/38	6.8	6.8	6.8	6.8	6.8	6.8
7/24/38	6.8	6.8	6.8	6.8	6.8	6.8
7/25/38	7.0	7.0	7.2	7.0	7.0	7.0
7/26/38	7.9	7.0	7.0	6.8	6.8	7.0
7/27/38	6.8	6.8	6.8	6.6	6.5	7.2
7/28/38	6.4	6.4	6.4	6.0	4.5	7.2
7/29/38	6.8	6.7	6.5	6.0	6.3	6.9

pH—Values of pH low enough to inhibit the growth and activity of aquatic life (pH 4.5 and lower) occur locally in Curtis Creek almost

continually. Records of daily sampling at Stations VII and VIII, as well as pier samples, were available for this study through the cooperation of the duPont officials. A typical record is shown for the month of June in Table VI.

It can be seen by comparing Table VI and Table I for the same month that there is no correlation between daily pH variation and the daily amount of copperas disposed. The increase in pH toward the latter part of the month appears to be associated with some other factor such as the direct disposal of waste acid from the Krebs plant, the Davison plant, and, possibly, some waste from the U. S. Industrial Chemical Corporation, as yet undetermined. Exact figures for the disposal rate of this effluent are not available at present. However, during the Krebs plant shut down from July 7-29, 1938, pH determinations were carried out daily at several stations in the region. These are presented in Table VII. It can be seen that all low pH values almost immediately returned to normal when disposal ceased. This would appear to locate the main source of waste acid during that period at the Krebs plant, although a series of local pH determinations carried out in the spring of 1940, in response to a number of complaints from Marley Creek residents, showed the occurrence of pH values of the order of pH 2.8-3.2 increasing in the direction of at least one other industrial plant. All the data indicate that the pH effects are confined to Curtis Bay and the lower portion of Marley Creek. Only in rare cases do values of less than pH 4.5 occur beyond Station II and the outer limits of Curtis Bay. All values, however, are useful in tracing the movement of waters out of Curtis Bay.

Ferrous Iron—Although the results of ferrous iron analysis are not entirely accurate with respect to absolute units, as has been pointed out, the relative differences from station to station are highly significant and can be correlated with low oxygen values. The amount of ferrous iron at a given location indicates the potential oxygen consuming capacity of that water or the chemical oxygen demand. As would be expected, values are high for those regions near disposal sources and decrease rapidly in a direction away from the source. These high values occur only in bottom samples, except in areas within a few meters of sewer outlets where they are vertically distributed. At Stations III, IV, V, and VI values as high as 15 mg/l were obtained. At Station X values often ran as high as 4 mg/l. Beyond the limits of Curtis Bay, however, only traces were detected, and these never beyond Station I. From such information it appears

TABLE VIII
Results of Sample Analysis
August 2, 1940

Station	Time	Depth (meters)	pH	Temp. °C.	Chlor. (°/°)	Oxy- gen (cc/l)	Oxy- gen Sat.	Oxy- gen % Sat.	Total Fe (P.P.M.)	Sol. Fe. (P.P.M.)	Insol. Fe. (P.P.M.)	Fe. (ous) (P.P.M.)	Trp. (cm.)	Protozoa (per liter)	Algae (per liter)	Larvae & Eggs (per liter)	Diatoms (per liter)	Obs. Tide (feet)	Prt. Tide (feet)
I	12:00 P.M.	1/2 6	7.32 7.14	27.0 26.0	4.37 4.37	4.38 3.16	5.60 5.66	83.6 53.8	447 2.28	163 .082	.284 2.20	0 0	117 0	34,600 43,300	4,730,000 4,660,000	17,300 17,300	1,790,000 5,080,000	0.9	0.1
IA	12:15 P.M.	1/2 6	6.93 6.67	26.0 25.3	4.26 4.30	4.98 0.73	5.70 5.72	87.4 12.8	848 4.68	173 1.85	.675 4.472	0 trace	86 0	17,300	5,780,000 3,940,000	17,300	1,780,000 484,400	0.9	0.1
II	12:30 P.M.	1/2 8	6.67 6.55	26.0 24.0	4.14 4.06	4.82 4.61	5.70 5.90	84.6 78.1	1.57 1.66	.220 .203	1.35 1.46	0 trace	74 0	*	*	*	*	0.9	0.1
III	12:50 P.M.	1/2 10	5.49 7.0	26.0 22.5	4.26 7.70	4.50 0.00	5.70 5.74	78.0 0.0	2.46 3.05	.246 .539	2.21 2.49	0 trace	50 0	17,300 17,300	4,610,000 4,105,000	51,900	8,550,000 2,550,000	1.0	0.1
IV	1:15 P.M.	1/2 7.5	6.33 6.33	26.5 23.0	4.08 6.82	2.27 1.19	5.55 5.83	40.9 20.8	2.45 18.9	.614 .626	1.74 12.6	1 0	44 0	34,600	16,227,400 865,000	*	1,055,300 346,000	1.1	0.1
V	1:45 P.M.	1/2 6	5.26 6.18	26.5 26.0	4.09 6.27	4.94 0.00	5.55 5.59	89.0 0.0	2.82 17.8	.244 7.54	2.08 10.3	0 12	50 0	69,200	1,077,000 41,520	34,600	7,763,000	1.2	0.1
VI	1:55 P.M.	1/2 4	4.58 4.61	26.0 26.8	4.06 4.13	1.86 0.98	5.71 5.63	32.6 17.4	2.81 4.96	.666 .764	1.64 4.20	0 trace	40 0	*	3,494,600 2,863,800	34,600	8,996,000 4,818,600	1.5	0.1
VII	2:05 P.M.	1/2 6	4.47 4.58	26.0 24.5	3.95 3.96	7.23 5.52	5.67 5.86	109.0 94.2	1.39 1.62	.207 1.80	1.18 1.44	0 trace	54 0	*	7,540,000 10,310,800	34,600	19,064,600 24,210,000	1.5	0.6
VIII	2:15 P.M.	1/2 6	4.47 5.37	27.0 24.0	3.79 4.26	8.29 2.14	5.63 5.79	147.0 37.0	1.49 8.32	.300 2.14	1.19 6.68	0 0	52 0	*	10,380,000 2,560,400	*	23,528,000 11,130,000	1.5	0.6
X	2:40 P.M.	1/2 4	5.59 5.26	27.0 26.0	3.56 3.89	7.70 2.35	5.64 5.71	137.0 41.2	.648 6.26	1.47 1.42	.501 4.84	0 0	63 0	*	5,985,800 2,699,000	34,600	13,233,200 5,293,800	1.7	0.7

*None observed in twenty counts.

**High tide predicted at 5:26 A.M.
5:23 P.M.

that under the conditions existing in Curtis Bay the oxidation Fe++ to Fe+++ does not occur immediately after disposal, but persists for some time during which oxygen is continually being removed from the water. The fact that ferrous iron is not detected beyond Station I may be due to the low sensitivity of the method under field conditions. Nevertheless, results show that oxidation of ferrous iron is nearly complete by the time contaminated waters reach Leading Point and that surface waters become oxidized almost immediately after disposal. Figures for a number of typical conditions are given in Table V and Table VI.

Total Iron—Total iron values in waters serve only to trace the path of movement and the dilution of polluted waters, and account for all of the iron containing decomposition products of copperas including those that are insoluble. The stage of oxidation and the degree of precipitation, however, can be determined only by comparison of ferrous iron and soluble and insoluble iron. During 1940 total iron values ranged from less than .5 p.p.m., at Station I, to around 25 p.p.m. at those stations near the source of disposal. Typical values are given in Tables VIII, IX, and X, as well as in Figures 4 and 5.

Further Results Involving the Interaction of Factors—Soluble iron accounts for those decomposition products of copperas that have not yet precipitated out as Fe(OH)₃ in the precipitate or flocculate form. Through comparison of these two values the stage of breakdown of copperas can be determined. Typical results are shown in Tables III, VIII and IX.

In Figures 4 and 5 the results of analysis for oxygen, pH, total iron, soluble iron, and insoluble iron are represented in graphic form for two different sampling trips. Transparency determinations were made with the Secchi disc and are, therefore, not absolute. They serve to show relative differences in the transparency of the surface layers in order that this may be correlated with the density of flocculent material or insoluble iron. This correlation is indicated in Figure 4 and again in Figure 5. In practically all cases the transparency is a reciprocal function of insoluble iron. Slight discrepancies may be caused by titanium oxide in the vicinity of the plant piers as well as by fertilizer products, refuse, oil, and other harbor wastes that find their way into the waters of the region, there to alter transparency but to affect other physical or chemical properties very slightly. Soluble iron runs high at or near the disposal source and in those more isolated

TABLE IX
Results of Sample Analysis
September 10, 1940

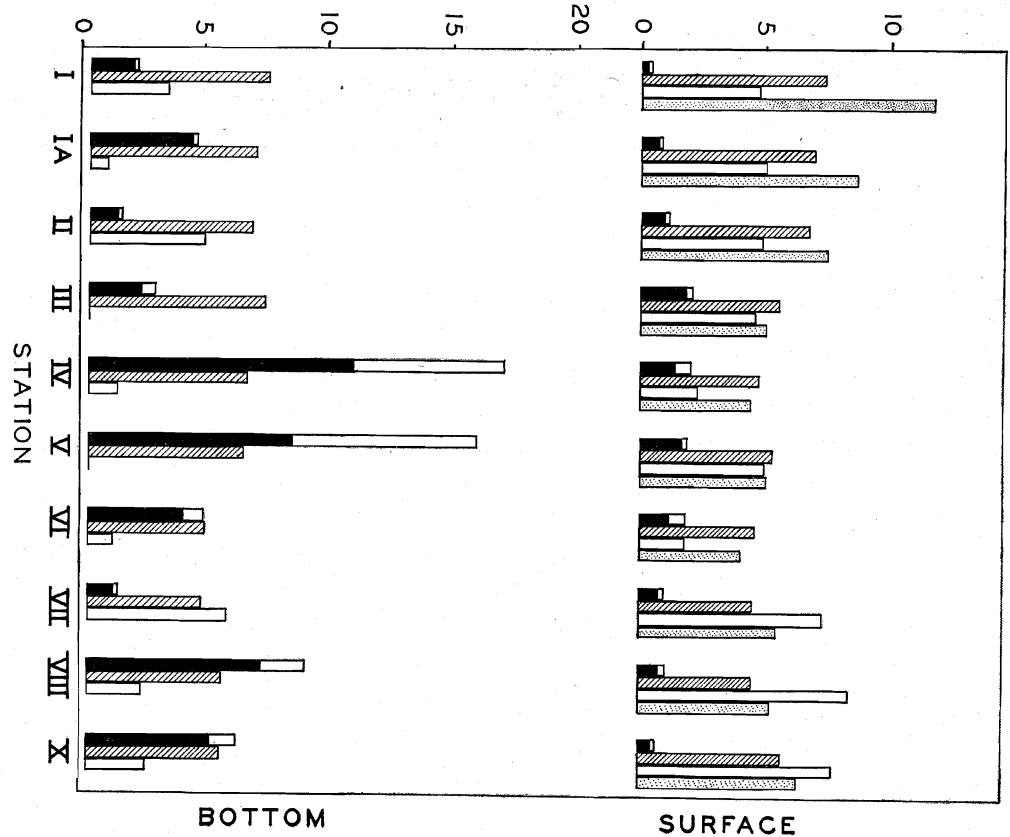
Station	Time	Depth (meters)	pH	Temp. °C.	Chlor. (‰)	Oxygen (cc/l)	Oxygen Sat.	Oxygen % Sat.	Total Fe (P.P.M.)	Sol Fe. (P.P.M.)	Insol. Fe (P.P.M.)	Fe (ous) (P.P.M.)	Trp. (cm.)	Protozoa (per liter)	Algae (per liter)	Larvae & Eggs (per liter)	Diatoms (per liter)	Obs. Tide (feet)	Pre Tide (feet)
I	10:30 A.M.	½ 6	6.87 6.77	23.5 23.1	5.21 5.74	4.81 5.37	5.47 5.46	78.7 98.3	.861 .360	.119 .068	.242 .291	0 0	143	103,800 69,200	1,315,000 1,072,600	34,600 * 1,487,800	882,300 1,487,800	1.7	1.5
IA	11:00 A.M.	½ 6	6.45 6.86	23.8 23.0	5.08 5.53	5.15 3.58	5.38 5.46	95.7 65.5	.911 2.69	.157 .160	.754 2.530	0 0	100	69,200 * 103,800	2,388,000 415,200 1,212,000	34,600 34,600 69,200	1,487,800 449,800	1.8	1.5
II	11:20 A.M.	½ 6	7.67 7.67	23.8 23.7	5.19 5.53	5.38 3.17	5.38 5.38	100.0 58.9	.493 .798	.0661 .164	.427 .634	0 0	100	242,200 103,800	1,868,000 1,212,000	* 69,200 * 2,076,000	2,076,000 485,000	1.8	1.5
III	2:55 P.M.	½ 10	6.19 6.47	23.5 22.5	5.24 7.93	3.92 0.78	5.36 5.21	73.1 14.9	2.32 4.06	.722 .370	1.598 3.690	1 3	92	69,200 * 103,800	2,147,000 242,200 * 1,038,000	* * * 346,000	1,038,000 346,000	1.9	1.5
IV	11:40 A.M.	½ 7.5	5.99 6.27	24.0 23.2	5.14 6.83	3.46 0.41	5.39 5.47	63.0 7.4	1.29 18.3	.151 14.1	1.139 4.2	0 15	80	34,600 * 103,800	3,290,000 * * 1,696,000	* * * 1,696,000	1,696,000 * * 1,696,000	1.9	1.5
V	12:10 P.M.	½ 6	6.21 5.95	24.4 22.8	4.68 4.81	4.82 4.42	5.40 5.52	89.6 80.0	.944 1.25	.148 .246	.796 1.004	0 0	80	69,200 69,200	830,000 7,000,000	311,400 69,200	934,000 1,970,000	1.9	1.5
VI	12:30 P.M.	½ 4	7.1 6.02	24.5 23.0	4.45 5.62	1.97 1.88	5.50 5.46	35.8 34.4	1.38 1.74	.179 .138	1.201 1.602	0 0	51	69,200 34,600	2,006,000 1,590,000	207,600 207,600	900,000 623,000	2.0	1.5
VII	1:30 P.M.	½ 6	6.35 6.25	24.8 23.0	4.39 6.25	6.48 0.00	5.37 5.58	120.6 00.0	2.10 26.3	.125 14.5	1.975 12.3	3 18	110	34,600 * 103,800	3,530,000 69,200 * 2,076,000	34,600 * * 103,800	2,076,000 103,800	2.1	1.5
VIII	1:50 P.M.	½ 6	6.63 6.28	22.5	3.89 5.27	7.11 2.61	5.50 5.50	47.4	.348 5.96	.0636 .935	.279 5.025	2 4	131	34,600 * 103,800	3,810,000 1,970,000 * 1,870,000	34,600 * * 761,000	1,870,000 761,000	2.0	1.5
X	2:15 P.M.	½ 4	6.07 5.87	24.0 23.0	4.16 5.03	8.22 3.94	5.51 5.18	149.1 71.8	.557 3.09	.112 .333	.445 2.757	4 4	105	346,000 1,140,000	3,220,000 3,560,000	* * * 1,800,000	3,220,000 1,800,000	1.9	1.5
V	2:35 P.M.	½ 6	0 100	1.9	1.5

*None observed in twenty counts.
**High tide predicted at 1:33 A.M.
1:24 P.M.

20

GRAPHIC REPRESENTATION OF SAMPLING DATA FOR
AUGUST 2, 1940

Figure 4.



Black and white bars represent total iron, the black portion insoluble iron, and the white portion soluble iron. All in p. p. m.
Cross-hatched bars represent pH.
White bars represent dissolved oxygen in cc./liter.
Stippled bars represent transparency in decimeters.
or deep spots found at Stations III and IV. The soluble iron values are proportional to the ferrous iron values, as was expected, except that the former are much higher in proportion. This may be caused

by the occurrence of colloidal $\text{Fe}(\text{OH})_3$ which passes through filter paper and is thereby introduced into soluble iron samples. This would also account for the relatively high soluble iron values at the surface (where oxidation should be complete) since these colloidal particles would tend to remain suspended in the upper layers until flocculation occurs. The presence of soluble ferric iron would also account for this effect.

There appears to be no consistent or direct correlation between pH and the other factors resulting from copperas disposal. Where soluble iron is high and oxygen is low there seems to be no marked lowering of pH other than the general lower pH values that occur in Curtis Bay. Surface to bottom pH differences are not great, a condition that holds with oxygen, soluble iron, total iron, etc. This, again, points to the probability of but little influence on the pH of the region by $\text{Fe}(\text{SO})_4$ hydrolysis, the general low effect being caused by disposal of waste acid from all sources in the region.

The maxima of high total iron, low oxygen, and other factors that are common to the most greatly contaminated waters do not occur at those locations where the tidal effects and disposal time would be expected to carry them. In Figure 4, the maximum falls at Stations IV and V with a secondary maximum at Station VIII, at the bottom only. Disposal occurred at the time of sampling of Station V while the previous disposal occurred twelve hours earlier. The secondary maximum appears, then, to be the effect of the previous disposal which had been carried back and has nearly dissipated itself by settling out. The slight maximum occurring at Station II, at the bottom, possibly could be the result of the disposal twenty-four hours previous. This hypothesis coincides with the observed tidal data for the period twenty-four hours previous to sampling time when the influence of secondary factors such as mixing due to harbor traffic, and other factors are considered.

Two maxima are shown in Figure 5, one at Station III and the other at Station VII. A third maximum was found to exist near the bottom at Station II. These effects also can be correlated with actual tidal conditions for the period preceding the sampling. It is obvious from this and from similar analysis of data for other periods that conditions occurring in the region are not due, alone, to the most recent disposal but are the cumulative results of the disposal occurring during two or more days. The position or location of the most severe of abnormal conditions depends mainly upon the time required for

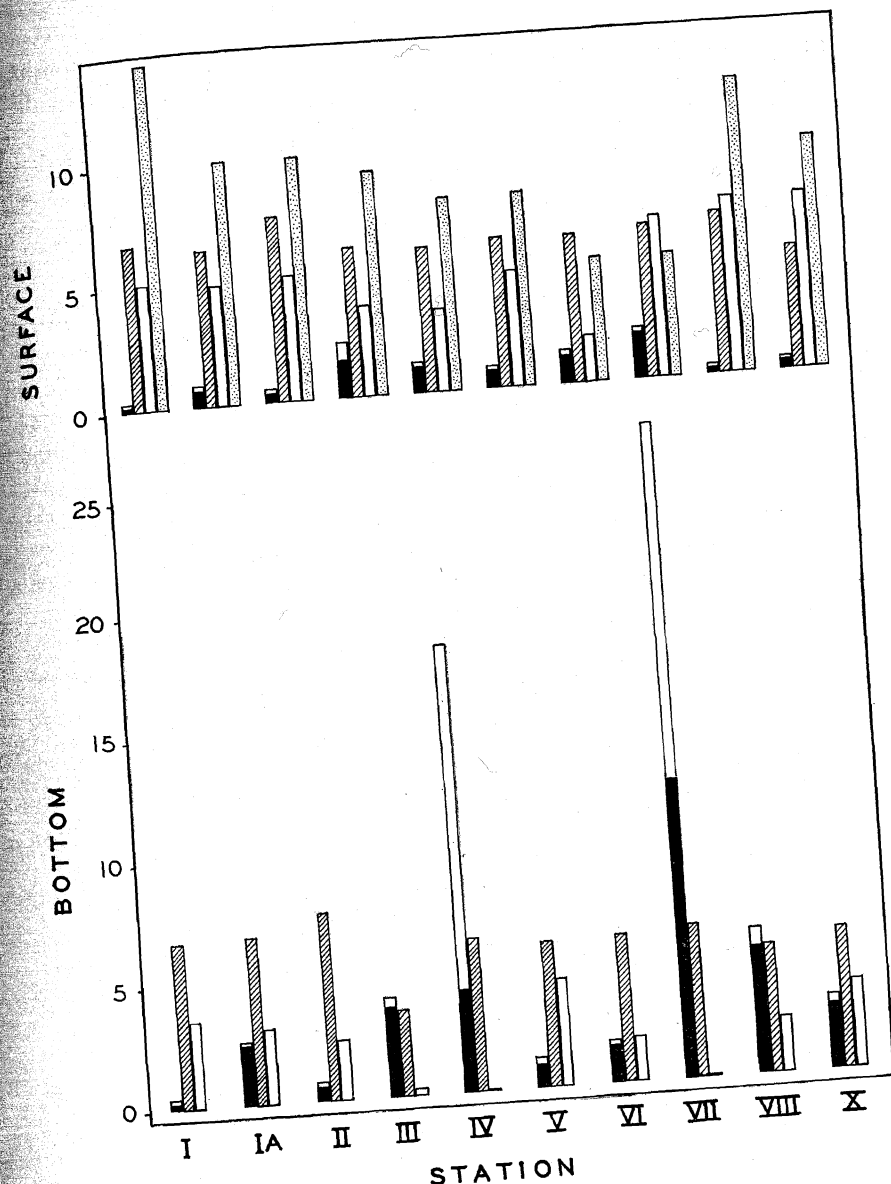


FIGURE 5.
GRAPHIC REPRESENTATION OF SAMPLING DATA FOR
SEPTEMBER 10, 1940.
Black and white bars represent total iron, the black portion insoluble iron,
and the white portion soluble iron.
Cross-hatched bars represent pH.
White bars represent dissolved oxygen in cc./liter.
Stippled bars represent transparency in decimeters.

complete dissipation of the pollutant and upon the predominating direction and rate of flow of tidal currents. Since disposal during this period was carried out so that the whole copperas accumulation (75,000 lbs., or more) was discharged into the Bay over a period of 15-30 minutes the area of immediate contamination was restricted to a limited region or mass of water which was, during its subsequent decomposition and dissipation, subject to movement by the variable currents. Knowledge of the exact changes due to oxidation, dilution and other factors that occur during this time, and the rate at which they occur, was deemed necessary in the interpretation of sampling data and in predicting the intensity of effects under various conditions of disposal. For this purpose a number of experiments on the rate of copperas decomposition at different dilutions was carried out under controlled conditions in the laboratory. With high concentrations all the oxygen in the small experimental tanks employed in the study was used up almost immediately and remained at zero concentration for several days. Stirring and aeration shortened this time to a matter of hours, but since the exact degree of mixing and dilution occurring in the field cannot be determined the results of these experiments were not applicable. The same is true for rates of hydrolysis and flocculation. However, these experiments served to show that the low pH values in Curtis Bay cannot be caused by copperas hydrolysis alone and that oxygen demand of those concentrations existing near the disposal source is high enough to deplete the waters completely of oxygen. Thus, it was necessary to find some other means to determine the time sequence and reaction rates in the field.

During regular sampling in the Curtis Bay region it has been observed often that sharp lines of demarcation persist between turbid contaminated waters and adjacent unpolluted waters. The same has been found in pH, ferrous iron and oxygen determinations. A sample taken on one side of the boat often differed tremendously from a similar sample taken simultaneously on the other side of the boat, and if the boat was held over the same mass of water the results were reproducible. From this it appears that the characteristic lack of mixing due to the slow movement of the waters in the area makes for the persistence of distinct horizontally homogeneous bodies of water which are moved as such by the slow tidal currents. If these masses can be followed accurately and sampled periodically the desired information concerning reaction rates may be obtained. Accordingly, a number of submerged-type spar buoys were devised using fourteen foot two-by-

TABLE X
Floating Buoy Study at duPont Plant, Curtis Bay

Location	Time of day	Sample time	Buoy No.	Approx. Dist. from release	Depth of Sampling	Temp. °C.	Chlor. in ‰	Oxygen cc/l	Oxygen Sat.	Total Fe. (P.P.M.)	Sol. Fe. (P.P.M.)	Insol. Fe. (P.P.M.)	Secchi Disc. cm.	pH	Obs. Tide (feet)
Midway between Sleds Point & duPonts	9:20	0	1	S 12'	26.0	4.86	2.54	5.23	4.79	2.89	1.80	057.	4.04	4.6
Going towards Davison Pt.	10:40	1 hr. 20 min.	1	300'	S 12'	25.5	4.82	3.12	5.30	2.42	.928	1.492	4.74	4.4
eventually going aground near old piling	11:45	2 hr. 25 min.	1	500' (ashore)	S 12'	24.8	4.31	3.20	5.22	2.02	.515	1.805	087.	4.75	4.2
Opposite Copper-head line	12:45	0	2	S 18(b)	26.8	4.29	1.62	5.10	15.2	13.4	1.8	3.53	4.0
Between 2 piers (D)-25 ft. End of long Pier	2:00	1 hr. 15 min.	2	150'	S 19(b)	25.5	4.39	2.87	5.24	3.51	1.39	2.12	051.	4.37	3.8
Between ends of 2 piers in Dis-gonal line	3:00	2 hr. 15 min.	2	200'	S 19(b)	24.7	4.30	2.69	5.35	2.35	1.89	2.161	057.	4.42	3.7
End of Acid Pier	1:00	0	3	S 19(b)	26.5	4.33	2.35	5.15	7.98	5.45	2.53	041.	3.90	3.8
50 ft. off Fire Boat in line with Davison Pt.	2:20	1 hr. 20 min.	3	400'	S 30(b)	25.3	4.33	2.89	5.30	8.91	2.07	6.34	5.15	3.7
Half way between "1" and Fire Boat	3:10	2 hr. 25 min.	3	600'	S 30(b)	24.0	4.34	0.04	5.17	13.8	2.05	1.72	4.39	3.7
								3.06	5.20	2.40	.736	1.664	065.	4.62	3.7
								0.04	5.45	2.99	.667	2.323	4.75	

Wind—L. N.E.
Surface—smooth.

Baltimore Harbor, August 20, 1940

Note: Copperas discharged between 12:00 noon and 12:45.

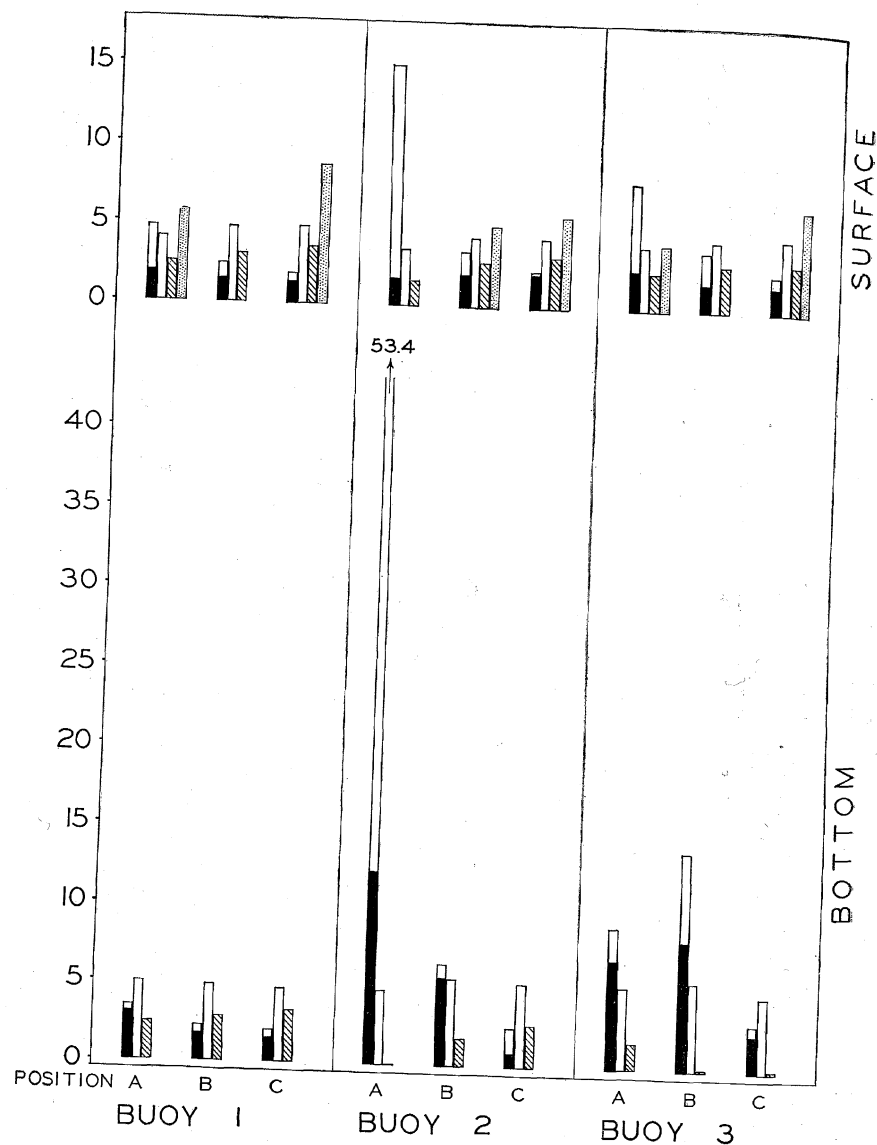


FIGURE 6.

GRAPHIC REPRESENTATION OF RESULTS OF BUOY STUDY,
AUGUST 20, 1940.

Black and white bars represent total iron, the black portion insoluble iron,
and the white portion soluble iron.
White bars represent pH.
Cross-hatched bars represent dissolved oxygen in cc./liter.
Stippled bars represent transparency in decimeters.

four timbers with suspended weights just heavy enough to allow them to remain vertical with their upper ends only a few inches above the water. Light flags with numerals were attached to these buoys so that they could be located. It was intended that these buoys should move with the stratum of water in which they were floating, namely, the upper fourteen foot layer. On August 20, 1940, three of these buoys were released from the Krebs pier. The results are shown in Table X and Figure 6. The first buoy (#1) was released as a trial, and due to persistence of the tide and a light northeast wind it traveled in a south easterly direction toward Sledd's Point, finally reaching the shoal near that point. Analysis of samples taken at the three positions of this buoy at the surface and at fourteen feet results only in a cross section of conditions in Curtis Bay at that point during the period of its excursion. Buoy #2 was released immediately after the accumulated copperas was discharged. Since the wind of the previous three hours had almost ceased and the tide had begun to ebb this buoy moved slowly in the direction of the ebbing tide. The immediate oxidation on the discharge of copperas was shown by complete absence of oxygen at fourteen feet at position C. The value of total iron and soluble iron was, as would be expected, exceedingly high. The high value for insoluble iron indicates that the flocculation of a considerable quantity of $\text{Fe}(\text{OH})_3$ had begun. pH, however, had decreased but little at the surface and practically none on the bottom. It appears that under field conditions hydrolysis is favorable in the upper strata unless, of course, some waste acid was simultaneously disposed of. One hour and fifteen minutes later at position B, 150 feet further northeast, a somewhat different situation resulted than was expected. The total iron had decreased as had the soluble and insoluble iron and the oxygen had more nearly approached the pre-disposal value. This suggested that the highly contaminated waters at position A had settled due to their greater density and had fallen below the lower level of sampling, but the rapid restoration of the oxygen at the 14 foot level was hard to account for in such slow moving waters. The same conclusion could be drawn to account for the still lower value of total, soluble and insoluble iron at position C, 200 feet from position A in the same direction, but the increase in soluble iron at 14 feet would, in light of these observations, be difficult to explain. It is more likely that there had been some difference in the movements of the water at the two sampling levels and that the buoy had moved with a direction and rate which was the resultant of the two components of force. The unexpected results at position B of buoy #3 also bear this

out. In Curtis Bay, water movements are known to be irregular and the possibility of opposing currents at different levels is greater than in the somewhat less restricted waters in the direction of Fort Carroll. Moreover, the turn of the tide is known to affect bottom and surface currents at a different rate in all bodies of water. It appears that buoys 2 and 3 were moved to positions B further into the disposal mass by stronger surface currents and were retarded by weaker surface currents to a position C lagging behind the now deeper lying and diluted mass. These results do not provide all of the expected information, but they do show the trend of movement of the disposal masses and

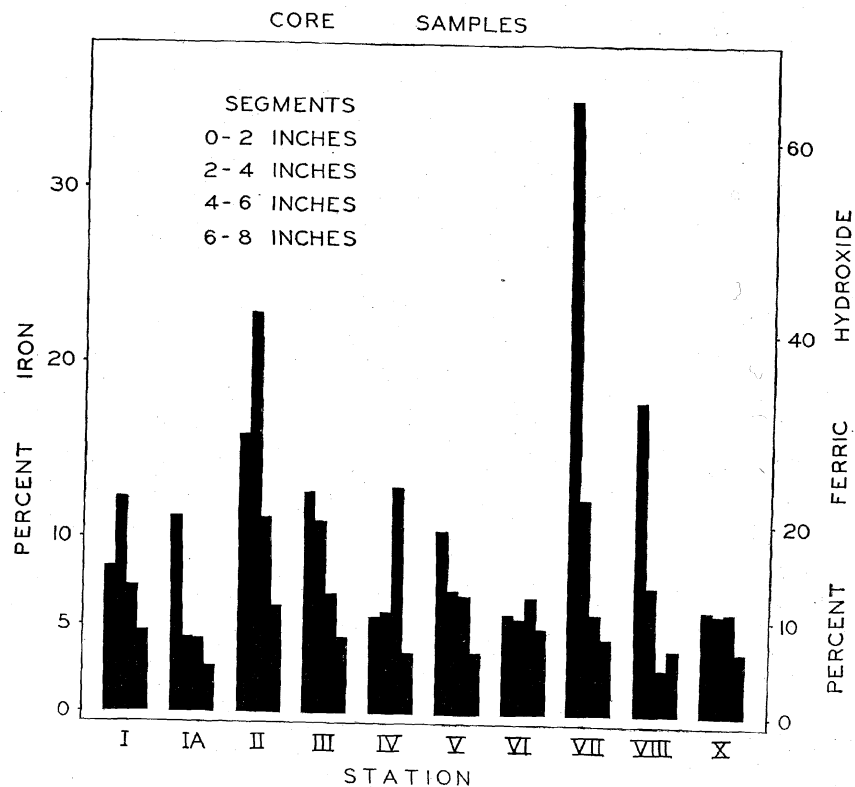


FIGURE 7.

Results of core sample analyses for November, 1939. Each bar represents a two-inch segment, the surface segment being represented in each case by the bar to the left.

relative rates of the initial reactions. The most significant information derived from them is the unexpected slow rate of tidal movement in this small region, the greatest distance covered in two and one-half

hours being only 600 feet and the shortest distance only 200 feet. The difficulty in following the movements of disposal products is thus clearly shown.

The results of core sample analysis show the degree of ferric hydroxide accumulation on the bottom. The samples taken during November, 1939, show in Figure 7 the depth of their accumulation at each station during that period. In the right hand ordinates the values are represented as the per cent weight of apparent ferric hydroxide, or the amount of ferric hydroxide that would be present if all the total iron present were in the form of ferric hydroxide. This, of course, is not the case, there being from 2-4% iron in normal river muds in the region. Nevertheless, comparison of these relative values should give a fairly good indication of accumulation at different levels and at different locations with an error of not much more than 4% weight. It will be seen that total iron values as high as 12% occur at Station I, at a depth of four inches, and decrease to 4% at eight inches. Maxima occur at Station I and Station VIII with values exceeding 35% for total iron corresponding to over 70% ferric hydroxide. Similar core samples collected during August, 1940, (Fig. 8) show a marked

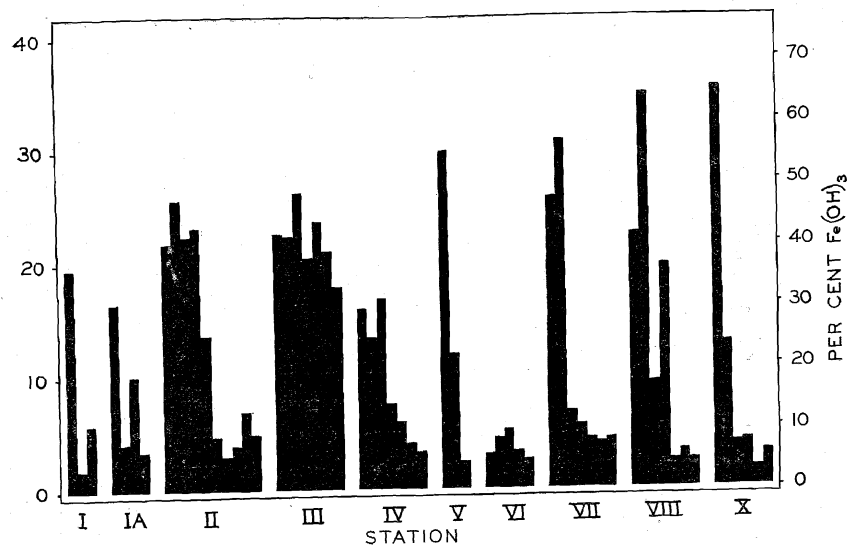


FIGURE 8.

Results of core sample analyses for August, 1940. Each bar represents a two-inch segment, the surface segment being represented in each case by the bar to the left.

increase in all values with a corresponding increase in the depth of the high concentration layer. The values are subject to slight error due to the impossibility of securing a second set of cores in exactly the same locations, but the general increase in both concentration of ferric hydroxide and in the thickness of this high concentration layer is obvious. These increases may be attributed to the increase in disposal rate of 1940, since no other factor showed marked change during the interval. The increase in disposal rate apparently favored heavier flocculation so that particles in turn settled to the bottom and became fixed there. On the other hand, apparently, the former lower disposal rate developed smaller particles and their consequent distribution over a larger area. Further work on particle size analysis is needed in elaboration of this point. The influence of the normal rate of silting also is in need of further consideration.

Qualitative tests with potassium ferricyanide showed the presence of what appeared to be large amounts of ferrous iron in core samples. Attempts at quantitative determination by digestion of the sample in hydrofluoric acid in an inert atmosphere of carbon dioxide and steam, followed by titration with potassium dichromate, were carried out. Interfering quantities of sulphides and organic matter, however, make the results of such analyses only indicative, and until some improved method can be devised it can only be said that the amount of oxidizable material in core samples is greater in Curtis Creek than in the surrounding area.

The effect of the accumulation of ferric hydroxide on the bottom is highly detrimental to the normal function of the bottom organisms which play an important role in the productivity of the region. Aquatic plants and animals, as well as bacteria, are crowded out or covered by the waste, and the resulting upset of the normal ecological balance gives rise to new and undesirable forms such as the iron and the sulphur bacteria. The result is a foul-smelling muck which supports no other type of marine life.

Biological Effects—Plankton counts were made at 200 power in a Sedgwick-Rafter counting cell; identification of organisms was carried as far as genera where possible and the totals for each group lumped together as shown in Tables No. VIII and IX and Figures 9 and 10. Identifications of the more common forms were made under higher power and are shown listed below.*

*These identifications were made by Dr. James B. Lackey, U. S. Public Health Service, Cincinnati, Ohio, whose cooperation is gratefully acknowledged.

Diatoms

Amphiprora sp.
Asterionella sp.
Chaetoceras sp.
Coscinodiscus sp.
Cyclotella meneghiniana
Melosira granulata
Navicula spp.
Nitzschia acicularis
Nitzschia closterium
Synedra biceps
Synedra delicatissima
Synedra ulna

Dinoflagellates

Amphidinium sp.
Exuviella sp. (shells)
Gymnodinium gracilis
Noctiluca miliaris
Peridinium sp.
Prorocentrum micans
Prorocentrum triangulatum

Euglenophyceae

Trachelomonas eurytoma
Trachelomonas volvocina

Cryptophyceae

Cryptomonas eroas
Rhodomonas lacustris

Chyrsophyceae

Chrysococcus cinctus
Chrysococcus rufescens
Dinobryon (cysts)

Chlorophyceae-Volvocales

Carteria sp.
Chlamydomonas sp.
Chlorella sp. (?)
Ankistrodesmus falcatus

Flagellates

Domatomonas cylindrica

Ciliates

Cyclidium sp.
Mesodinium sp.
Paramecium caudatum
Strobilidium humile
Strobilidium sp.
Tintinnidium fluviatile
Urotricha farota

The effect of the various physical and chemical disturbances on the micro-plankton of the region is shown in Tables VIII and IX. These effects on the organisms are compared graphically with values for oxygen, insoluble iron and pH in Figures 9 and 10. The effect of low oxygen on protozoa, larvae and eggs is a severe one in all cases, as is demonstrated by the data from samples in which oxygen is less than 3.5 cc/l and other conditions approach normal. Figure 9, Stations III to VII, and Figure 10, Stations IA to VIII.

It is well known that those forms which lack a rigid cell membrane rapidly break down and disintegrate in the presence of inadequate oxygen, low pH, and other abnormal conditions (Kitching, 1939, and others). Algae and diatoms, however, persist in preserved samples even when they have been killed by toxic influences. Moreover, these phytoplankton forms have a much lower oxygen consumption rate than animal forms and can tolerate far more severe conditions of oxygen depletion. Protozoa, in turn, are far more vulnerable to low pH values, as indicated in Figure 9, at Stations VII and VIII, when oxygen values were not a limiting factor.

Since it is not possible to determine the exact period of exposure of these organisms to the conditions under which they were found, many of them may be counted which were in the process of injury at the time collected and later would have disintegrated. These forms

are planktonic, that is, their motion from one location to another is effected by water movements alone. Algae in general seem to be less

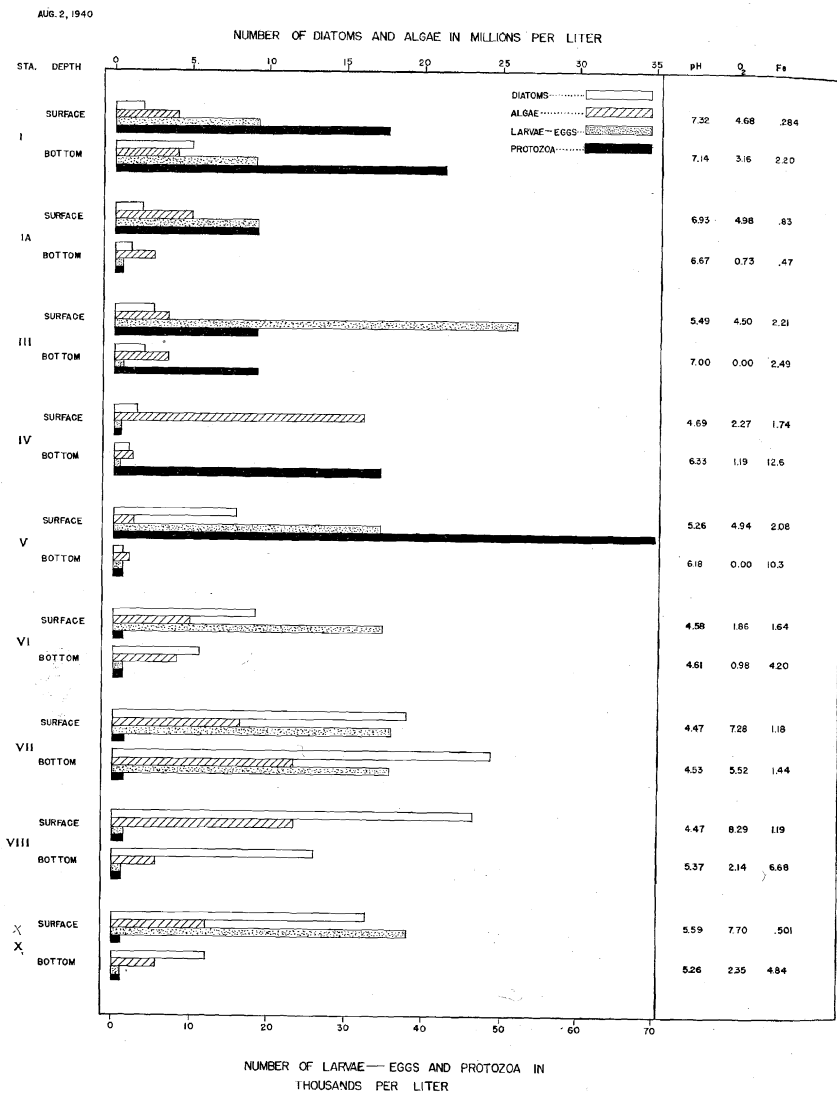


FIGURE 9.

Graphic comparison of plankton data with pH, dissolved oxygen, and total iron at each station for August 2, 1940.

affected by pH than their diatom relatives, but their disintegration, when killed, is more rapid. Diatoms persist in samples even when

they are dead, due to the stability of their silicious shells, so that their numbers indicate favorable or unfavorable conditions for growth

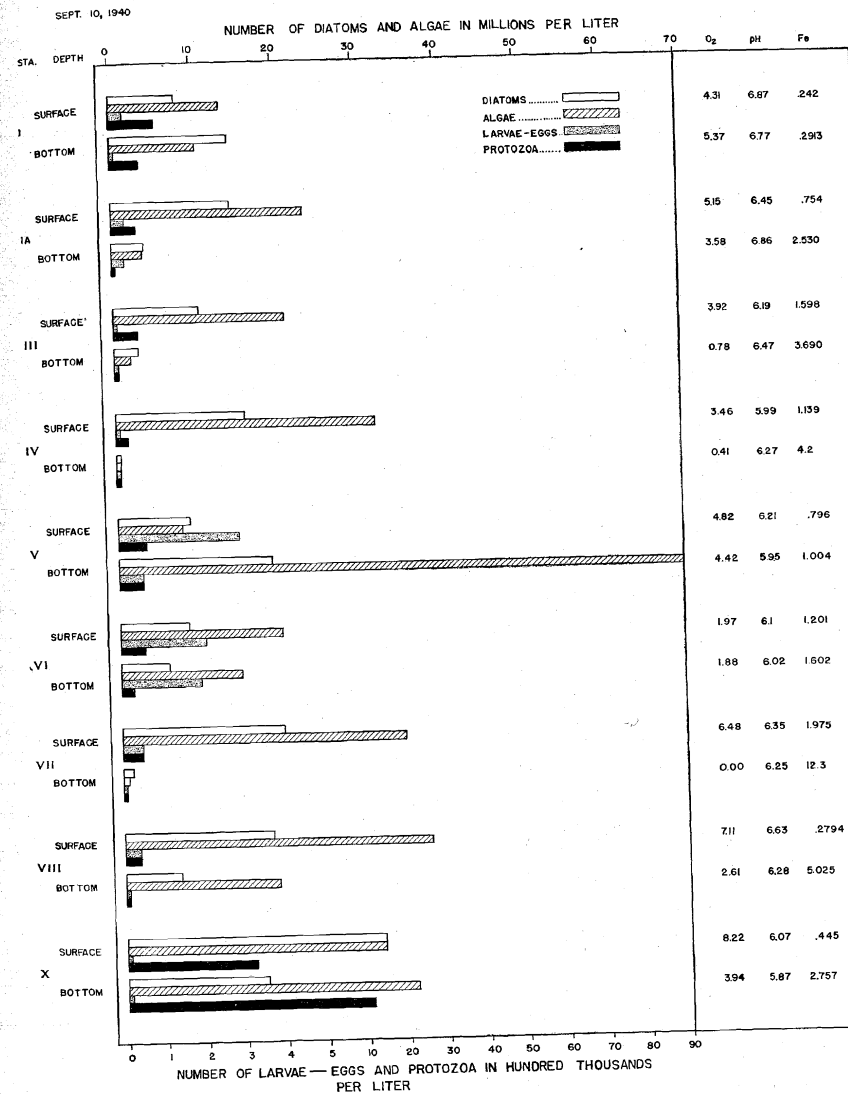


FIGURE 10.

Graphic comparison of plankton data with pH, dissolved oxygen, and total iron at each station for September 10, 1940.

and reproduction over longer periods and not direct effects of pH, low oxygen, and other conditions by which they may be killed in a

short time. Where living diatoms persisted in great numbers along with other algae, super-saturation values for dissolved oxygen were often found due to their oxygen production in photosynthesis. Since diatoms persist even though dead their complete absence in a number of bottom samples would seem difficult of explanation. This condition suggested a significant detrimental effect of flocculating ferric hydroxide.

The property of ferric hydroxide to "seed out" and precipitate on the surface of small particles is well known and is used to advantage in several methods of water purification. The colloid ferric hydroxide particles are attracted, through the charge on their surface, to surfaces bearing an opposite charge. At a low pH value ferric hydroxide particles bear a positive charge. Diatoms are small enough to have several of the properties of colloidal particles and bear a negative charge on their surfaces due to the silicious shell and possibly due to a negative charge on the cytoplasm beneath. Therefore, these diatoms provide, along with other colloidal material in natural waters, excellent nuclei or centers for the flocculation of ferric hydroxide (Harvey, 1937). The course of this process is shown in Figure 11. Soon after copperas is added to water containing diatoms a thin surface film of submicroscopic particles of $\text{Fe}(\text{OH})_3$ is laid down on the diatoms. This film is rapidly built up by the additional particles until the diatoms become heavily coated with a floc of the red-brown precipitate as can be seen in Figure 11, (lower right). Further addition of the material by subsequent flocculation eventually covers the diatoms completely so that they can no longer be recognized and are lost in the precipitate. This phenomenon occurs readily in concentrations where total iron runs as low as 2 p.p.m. and therefore occurs in the entire sampling area at some time. When bottom samples are centrifuged and the organisms in them are counted, the diatoms are so completely covered by $\text{Fe}(\text{OH})_3$ masses that they cannot be recognized (Fig. 9, Sta. 5; Fig. 10, Sta. IV and VII). From this it becomes evident that settling of ferric hydroxide involves the settling out of diatoms and their removal from the waters above. Small algae and other organisms also exhibit this phenomenon. The smaller the organisms the greater the effect. This detrimental effect of copperas in removing and destroying the basic source of food for all higher animal organisms is highly significant.

The chitinous membrane of copepods appears to be but slightly affected by flocculation in this way. Surface tows around Station V show large numbers of active copepods which do not show adhering

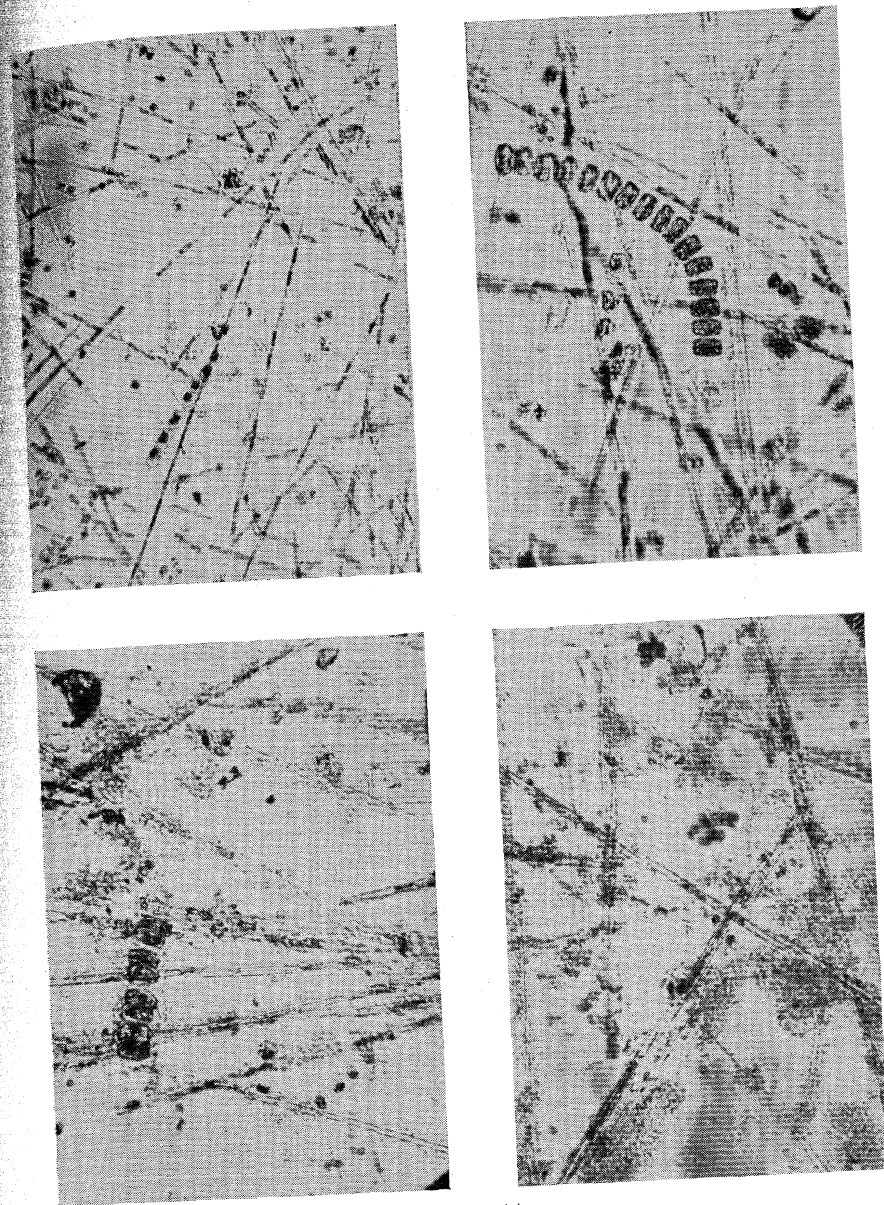


FIGURE 11.
PHOTOMICROGRAPHS SHOWING THE COURSE OF FLOCCULATION OF FERRIC HYDROXIDE ON THE SURFACES OF DIATOMS.

Upper left—diatom group before addition of copperas (Mag. 500X). Upper right—Portion of same group (Mag. 1000X). Lower left—Same group one hour after addition of copperas (Mag. 1000X). Lower right—Same group two hours after addition of copperas (Mag. 1000X).

floc of $\text{Fe}(\text{OH})_3$. Numbers decrease in tows around Stations IX and X, but this, apparently, is the effect of lower salinity or of chance distribution. Further experiments with copepods are to be carried out. The microscopic units of the highly diversified surfaces of a number of animal membranes also are small enough to bear a surface charge which favors the accumulation of ferric hydroxide. The gill membrane of a fish, with its thousands of protruding filaments, and the ciliated membranes of other organisms, become coated in a similar manner, as established by field observations. In the laboratory this principle was demonstrated by placing fish in tanks containing copperas. The pH was adjusted to about 6.0 through addition of buffering mixture, and oxygen was provided through constant aeration. Minnows (*Fundulus*), Silversides (*Menidia*), and White Perch (*Morone*), fishes common to the Patapsco, were used in the experiment and in every case the characteristic coating appeared on the gills. Microscopic examination showed flocculation on the membrane of the capillary bearing ridges borne by the gills. This coating became a heavy coagulum after several hours and appeared to restrict the oxygen diffusion to the underlying capillaries. Silversides and white perch died several hours after the formation of this coating, while fundulus, a hardy form, remained alive for several days. Various dilutions of copperas were tested. However, since the rate of flocculation and particle size were variable due to the difficulty of controlling the supply of oxygen and other factors, only positive evidence of the injurious effects of $\text{Fe}(\text{OH})_3$ was shown from these experiments.

Solar Radiation—Using the vacuum thermocouple submarine radiometer (Olson, 1941) especially developed for this work a study of the effect of ferric hydroxide suspension on the available solar energy at various depths was carried out. Typical results are shown in Figure 12. Curve 1 of that figure shows the variation of the intensity of total radiation with depth at Station III. Curve 2 shows the results of a similar series of measurements at a point in the unpolluted area of the Patapsco River proper north of Curtis Bay. In Curve 3 results are given for a point in the Chesapeake Bay near Matapeake. As indicated by the figure, the effect of the ferric hydroxide suspension at Station III is severe enough at one meter depth to cut down the total radiation by eighty-five per cent of the total found in the unpolluted area of the Patapsco at the same depth. Comparing curves 2 and 3, the effect is shown of normal silt suspension in the Patapsco during the period in which the measurements were being carried on.

Since the productivity of any body of water is directly dependent upon the amount of solar radiation which reaches its depths this decrease becomes most significant. The photosynthesis carried out by the diatoms and algae is all important in building up those carbohydrate

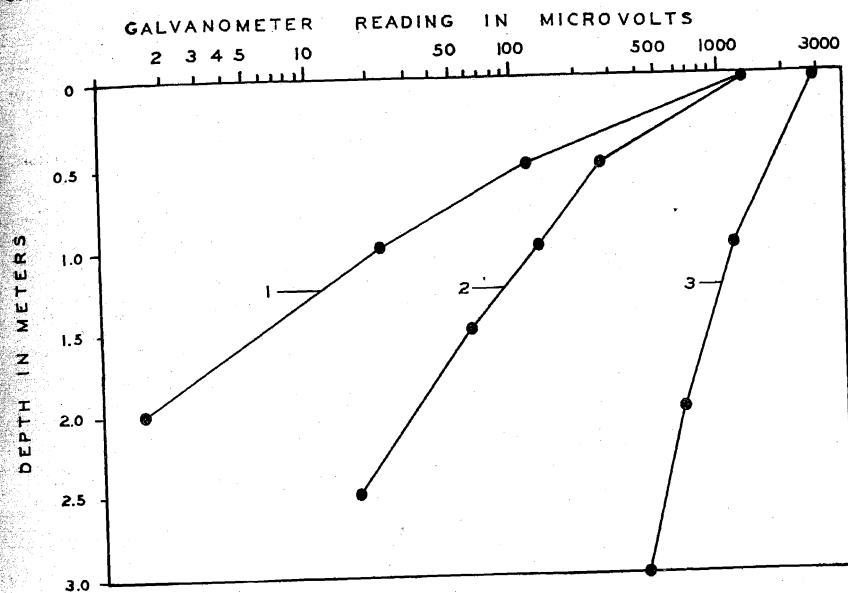


FIGURE 12.
THE INTENSITY OF TOTAL RADIATION AT DIFFERENT DEPTHS OF THREE REGIONS IN THE AREA STUDIED.
(Curve 1—Station III; Curve 2—Adjacent uncontaminated region in the Patapsco River; Curve 3—Chesapeake Bay beyond the river mouth).
1 microvolt = ± 3 ergs/mm²/sec.

reserves which serve as food material for higher aquatic organisms. An eighty-five per cent reduction of energy for this process when considered with other detrimental effects of copperas, offers a serious handicap to diminished aquatic population.

CONCLUSION

The most severe effect of copperas disposal in Curtis Bay appears to be that of lowered oxygen tension of the subsurface waters over the general region during the summer months when the saturation concentration of oxygen is normally low. Its deleterious effect is demonstrated by the data on plankton determinations, thus indirectly it adversely affects higher organisms dependent on such matter and, directly, it adversely affects them by asphyxiation. pH, however,

appears to be less significant. Plankton analysis shows some serious but local effects, although with a slight lowering in pH at distances beyond the immediate area of discharge. Even these effects appear to be the result, in part at least, of waste acid disposal and not entirely due to the hydrolysis of copperas discharge. Ferric hydroxide flocculation, due to its adsorptive properties, has been shown likewise to be detrimental to both micro-organisms and macro-organisms. It has been shown, as well, that it contributes to a marked ecological unbalance on the entire bottom of the area through its continual accumulation. The effect of this flocculent substance is more widespread than the data indicate. Approximately 100,000,000 pounds of ferric hydroxide should be formed from the copperas disposal products during a single year. This would result in a volume of the precipitate, in the anhydrous form, equal to that of a cube measuring nearly one hundred feet on edge, while in the hydrated form that occurs in Curtis Bay it would amount to a much greater volume. If deposition of this amount of material occurred only in the region studied during the year there should be found a much heavier deposit on the bottom than is shown from the core sample studies. From this it appears that the floc must continue beyond Station I before it has entirely settled out to the bottom. Both laboratory and field studies show that three days or more are often required for complete settling to the bottom and that abnormal conditions may greatly prolong this period. The distribution of this detrimental product is, therefore, undoubtedly, greater than that of any of the other products of pollution. It is hoped that future study will throw light on this subject.

The effects of tide in the region have been shown to be far less significant than they were thought to be in previous studies, since the maximum of current strength, which averages one tenth of a knot per hour, can carry the effluents less than one-half a mile away from the source of disposal under normal conditions. The effect of this factor in the dilution of the discharge is important. It was previously recommended that disposal be effected one hour after maximum flood tide, and this has been carried out during the present year. It is evident, however, that such a practice, while it minimizes the occurrence of visible disposal products in the upper reaches of Curtis Creek, allows the effluent to be discharged in one local mass which can move only a short distance before the disposal of the subsequent accumulation of copperas is discharged. This mass of polluted water remains undiluted, and its effects are severe because it is confined to a relatively

small area, even though a moving area. Moreover, if its recovery to normal condition is retarded by natural causes, as pointed out, it is possible, under extreme condition of wind and precipitation, for such contaminated bodies of water to accumulate and exert their detrimental influences over larger areas. When the accumulated copperas is discharged during a short period of time on the ebb tide the oxygen requirement entirely depletes the local area into which it is discharged. The subsequent reoxygenation requires far more mixing and diluting than does the depletion caused by a disposal of the same amount of copperas over a long period.

It is suggested from the above that the practice of disposal on the ebb tide be continued but that the flushing action and the resulting discharge be carried out at such a rate that disposal will continue over the entire ebb tide. This should allow for greater dilution by the waters moving by even though they move slowly. The resulting less severe conditions of pollution should be more easily brought to recovery by dilution, wind action, and mixing. This will not remedy the situation, however, and it is hoped that some method of disposal can be devised which will minimize or localize the effects of copperas decomposition. The use of aeration towers or spray heads in order to pre-oxidize the material should, if feasible, prove effective. The resulting ferric hydroxide sludge could be carried to evaporation basins for drying and disposal either commercially or on dumps. Such a procedure would minimize if not completely eliminate pollution of local waters.

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