Metallic and Non-metallic Pollutants in the Discharge Water of Varieties of Industries

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INTRODUCTION

In the present era of science and technology, the growing number and variety of industries have caused multiple problems associated with water and air pollution. Due to the adverse effects of these pollutants on the public, aquatic and plant lives, a number of studies were made to find the means of reducing the pollution; for example, waste water treatment at different plants and places, waste disposal, designing of waste water treatment, industrial sewage collection, etc. Such means could be enforced more effectively if the nature and the amount of pollutants in the discharge water of industries are known. In the present study, discharge water samples from a number of industries were analyzed for most of the metallic and non-metallic pollutants. The industries were chosen by selecting them from the heading "Critical Industrial Groups" (DEPT. OF ARMY, 1971).

EXPERIMENTAL

Collection of Sample

Most of the values reported are based on 24-hour composite samples, collected by employing automatic sampling techniques. Several commercially available instruments can be used for such purposes. An instrument manufactured by Sigma Motor Corporation of New York proved very satisfactory. The instrument can be programmed to take samples at any desired interval using 1/4 inch internal diameter tubing. The instrument pumps at a rate of 50-60 milliliters per minute. Most sampling was done at 15-minute intervals for a duration of 2 minutes. This insured a volume of approximately 2 gallons at the end of the sampling period. Shorter cycle times were used when extreme variations were suspected in the content of discharge water. Provisions were made to keep the samples at about 30-40^{o}F until they were shipped to the laboratory for analyses.

The instrument cited above is completely portable (12 V battery operated) and can withstand all weather conditions; thus, it is ideal for sampling streams, lakes, rivers, etc., when regular 115 V alternating current is not readily available.

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Sample Preservation

Most of the samples were either analyzed immediately for those substances which needed preservation or they were preserved strictly under the instructions given in "Standard Methods for the Examination of Water and Wastewater, 13th edition, 1971".

Analysis of Non-metallic Groups

Methods described in "Standard Methods for the Examination of Water and Waste Water, 13th edition, 1971" were strictly used for the analysis of all non-metallic substances.

Analysis for the Metals

A Perkin-Elmer Model 303 Atomic Absorption Spectrophotometer was used for analyzing the metals using conditions most suited for individual elements. Samples were prepared by taking an aliquot and acidifying with concentrated HNO_3 (Baker reagent grade) and evaporating to dryness at 80° C. They were cooled and additional HNO_3 was added. The beaker was covered with a watch glass and gently heated allowing a refluxing action to occur. After the digestion was completed, sufficient HCl 1:1 (Baker reagent grade) was added to dissolve the residue. Silicates and other insoluble materials were removed by filtration and the filtrate adjusted to a known volume. The solutions thus obtained were aspirated and the results were recorded.

Results and Discussion

pH

The pH of the samples were measured immediately after they were shipped to the laboratory. Samples from the industries under the classification "Industrial Inorganic and Organic Chemicals" showed a large variation ranging from 1.2 to 11.3 at room temperature. The organic chemicals industries gave a pH range of 4.9 to 11.6. Less variation was found in samples from printing and textile industries, where the pH was found in between 4.5 and 7.3. The paint industries and the industries dealing with meat products showed a less variation, the pH ranging between 7 and 9.

Generally, the pH of the samples received from refineries was between 9 and 10.

Oil and Grease

Large amounts of grease can cause difficulties in sewerage systems and receiving waters. Some of these difficulties include the clogging of wastewater conduits, interference in biological processes, slower rates of degradation of these compounds and unsightly formations at outfalls and in streams. The analysis on a number of samples (minimum of 2 and maximum of 9 from each type of industry) showed a large variation ranging from 1 mg/l to 2 gms/l. The results do not show any correlation except that refineries were found to discharge large amounts of oil and grease. The concentration of oil and grease was generally 1 gm/l in most of the samples.

Turbidity

A summary of the results obtained on different samples is given in Table I. Paint and varnish industries were found to have highest turbidity, whereas printing and textile industries were second in order. There was no high turbidity in discharges from other types of industries. A high turbidity indicates a high amount of colloidal matter in wastewater, and the presence of large amounts of colloidal matters have been found to create problems in advanced wastewater treatments, such as the fouling of ion exchange resins and electrodialysis membranes. Also, turbidity possesses a significant absorptive capacity of its own and therefore might contribute to organic recoveries by entrapment on carbon and subsequent release of organic materials during desorption.

Solids

Results on solids have been divided into three categories, e.g., total dissolved solids, total suspended solids, and total volatile solids and are given in Table I. Petroleum refineries and related industries contained the highest amount of dissolved solids, whereas the industries under the classification of Industrial Inorganic and Organic Chemicals were found to have minimum dissolved solids. The printing and textile industries were second in order. Paint and industrial organic chemical industries were very much comparable. Total suspended solids did not show any trend. A definite trend was found in the case of total volatile

TABLE I

Turbidity, Total Dissolved, Total Suspended and Total Volatile Solids Results on Different Types of Discharge Water Samples

Classification of Industry	Sample Number	Turbidity JTU	Total Dissolved Solids - mg/l	Total Suspended Solids - mg/l	Total Volatile Solids - mg/l
Industrial Inorganic and Organic chemicals	1	50	490	2	52
	2	75	621	155	41
	3	75	394	36	113
	4	21	545	30	13
	5	10	338	3	85
	6	10	821	15	98
	7	31	306	230	167
	8	10	397	2.7	72
	9	68	298	40	26
Industrial Organic chemicals	1	79	335	26	76
	2	1700	1649	2140	685
	3	3125	871	2930	2618
	4	175	405	115	70
	5	5	11028	3	337
Paint Industry	1	1015625	--	--	--
	2	41000	1573	1748	16538
	3	3125	600	332	1022
Printing and Textile	1	560	2159	116	2734
	2	850	406	128	570
	3	1125	534	360	741
	4	7500	3627	612	7182
	5	2250	1030	291	1841
Petroleum Refineries and Related	1	140	66710	104	7350
	2	3500	4745	1398	2340
Meat Products	1	58	89	143	131
	2	40	1430	324	2306

solids. Paint industries contained highest amount of volatile solids. Petroleum refineries and related industries as well as printing and textile industries gave comparable values of total volatile solids but were third in order, whereas minimum amounts of volatile solids were found in the case of industries manufacturing inorganic and organic chemicals.

Chemical Oxygen Demand (COD)

COD is considered as one of the important factors in evaluating the degree of water pollution. The results given in Table II show that the paint industries had the highest COD values, next being the printing and textile industries. Petroleum refineries and related industries as well as the industries manufacturing organic chemicals were third in order with substantial amounts of COD. Even though the industries under the group of industrial inorganic and organic chemicals were lowest in the order, they gave significant amount of COD.

Biochemical Oxygen Demand (BOD)

Biochemical oxygen demand is of major importance since it is used to measure the quantity of oxygen required during stabilization of decomposable organic matter by aerobic biochemical action. BOD values, obtained on different samples are summarized in Table II. Evidently, the discharge samples of printing and textile industries gave the highest BOD values whereas the industries under the classification of industrial organic and inorganic chemicals gave the lowest, with one exception. Paint and varnish industries were second highest. Industries under the groups industrial organic chemicals, petroleum refineries and related and meat products gave very comparable values and were third in order.

Total Organic Carbon (TOC)

One of the primary indicators of the degree of water pollution is the concentration of organic matter. The various organics, discharge from different types of industries and also from other sources into sewage collection systems and natural waterways, seriously impair water usage by causing foul taste and odor, loss of dissolved oxygen and toxicity, resulting in fish kills. The results, given in Table II, indicate that the paint industries contained the highest amount of organic carbon, whereas, printing and textile industries were second in order. Petroleum refineries and related industries and also the industries manufacturing industrial organic chemicals were comparable and were next in order. The industries under

TABLE II

COD, BOD and TOC Results on Different Types of Discharge Water Samples

Classification of Industry	Sample Number	COD mg/1	BOD mg/1	TOC mg/1
Industrial Inorganic and Organic chemicals	1	600	365	195
	2	350	5	79
	3	31	30	28
	4	20	0	32
	5	400	2	4
	6	32	2.5	7
	7	400	10	7
	8	200	15	16
	9	150	20	<1 not detecte(
	10	550	7.5	1
Industrial Organic chemicals	1	1000	3	53
	2	2800	40	879
	3	3000	85	230
	4	675	95	271
	5	115	85	38
Paint Industry	1	34000	147	20000
	2	38000	410	14980
	3	979	280	560
Printing and Textile	1	13000	110	3677
	2	7000	605	2200
	3	4858	670	3285
	4	2400	138	976
	5	1120	120	414
Petroleum-Refineries and Related	1	3259	72	167
	2	2000	30	830
Meat Products	1	2200	50	59
	2	234	70	82

the classification of industrial inorganic and organic chemicals were found to give lowest TOC values.

The results on COD, BOD, and TOC, indicate that there is no significant correlation between the amount of total organic carbon and chemical oxygen demand, which may be due to the fact that COD is greatly enhanced by oxidizable inorganic materials. BARTH, et. al. (1965) reported that the concentration of copper exceeding 1.2 mg/l was associated with a significant increase in COD. At the most, a high COD may be expected with the high TOC. Similarly, there was no distinct correlation between COD and BOD. For example, a COD value of 234 mg/l was found for a sample which gave 70 mg/l BOD; at the same time another sample with a BOD value of 50 mg/l only gave a COD value of 2200 mg/l. Several other samples gave similar results. Similarly, BOD and TOC did not show predictable correlation which may be primarily due to the fact that the biological oxygen demand depends not only upon organic carbon, but also on oxidizable nitrogen, which serves as food for specific bacteria (COURCHAINE, 1968).

There are many other factors which are also extremely important in estimating the degree of pollution. For example, a concentration of ammonia nitrogen exceeding 1700 mg/l was reported as the toxicity threshold by a number of workers (ALBERTSON, 1961; McCARTY and McKINNEY, 1961; WATER POLLUTION CONTROL FEDERATION), although, subsequently others found that it is not the concentration of ammonia nitrogen which is critical but the rate at which it is produced. Waste water from few industries when analyzed exceeded this critical number. Industries dealing with fertilizers may be expected to contain high ammonia nitrogen.

The importance of organic nitrogen can be realized by the fact that the oxygen demand for the organic material in wastewater, waste effluents, industrial wastes and polluted water is exerted by two classes of materials:

1. Carbonaceous organic materials which are usable as a source of food by aerobic organisms,
2. Oxidizable nitrogen (COURCHAINE, 1968) which serves as food for specific bacteria.

Organic carbon has been pointed out as the most important factor in discussing organic pollution, overlooking the fact that organic nitrogen could be equally important. A few samples, when analyzed, gave Kjeldahl nitrogen ranging from 10 mg/l to 25 gms/l.

SAWYER (1952) reported that when concentrations of inorganic phosphorus and inorganic nitrogen equal or exceed 0.01 and 0.30 mg/l, respectively, in lake water, nuisance algal conditions can be expected. The discharge water from some of the industries dealing with refining of metals contained very high amounts of inorganic nitrogen and phosphorus. Concentration of metallic ions such as copper, mercury, nickel, zinc, and chromium were notably high. It is a well known fact that a high concentration of metallic ions poses many problems, for example, copper contributes to high COD value. Chromium and mercury are well known toxic materials.

Summarizing the results on different discharge water samples, it can be concluded that the extent and nature of pollution could be inferred from the type of industry.

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