An Assessment of the Hoosac Water Quality District Wastewater Treatment Plant

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ES 102

5/12/89 12:00 midnight

Professor Susan Kegley

A Nice job!

INTRODUCTION

The Hoosac Water Quality District wastewater treatment plant is located on the north/east side of the Hoosic River, north and west of the Williams College campus. The original plant at that site was built in 1963 and worked in conjunction with the plant in North Adams, which began operation in 1935. These were *primary plants*, meaning the water was cleared once in an aeration tank and solids allowed to settle out, chlorinated and then discharged into the river. The North Adams site was closed in 1977 and in the same year the Williamstown site was replaced by the plant now functioning. The existing plant handles the wastewater from North Adams and Williamstown, as well as the town of Clarksburg. It is a *secondary* treatment plant, meaning that the plant contains a second aeration tank, and therefore discharges cleaner water. (personal interview, George Heisler; Hoosac Water Quality District wastewater treatment facility brochure) For a complete description of the wastewater treatment process, see Appendix A.

The plant does its own quality control tests, according to standards set by the state and by the Environmental Protection Agency. The purpose of this study was to duplicate some of those tests to assess the success of the treatment processes and get a general idea of water

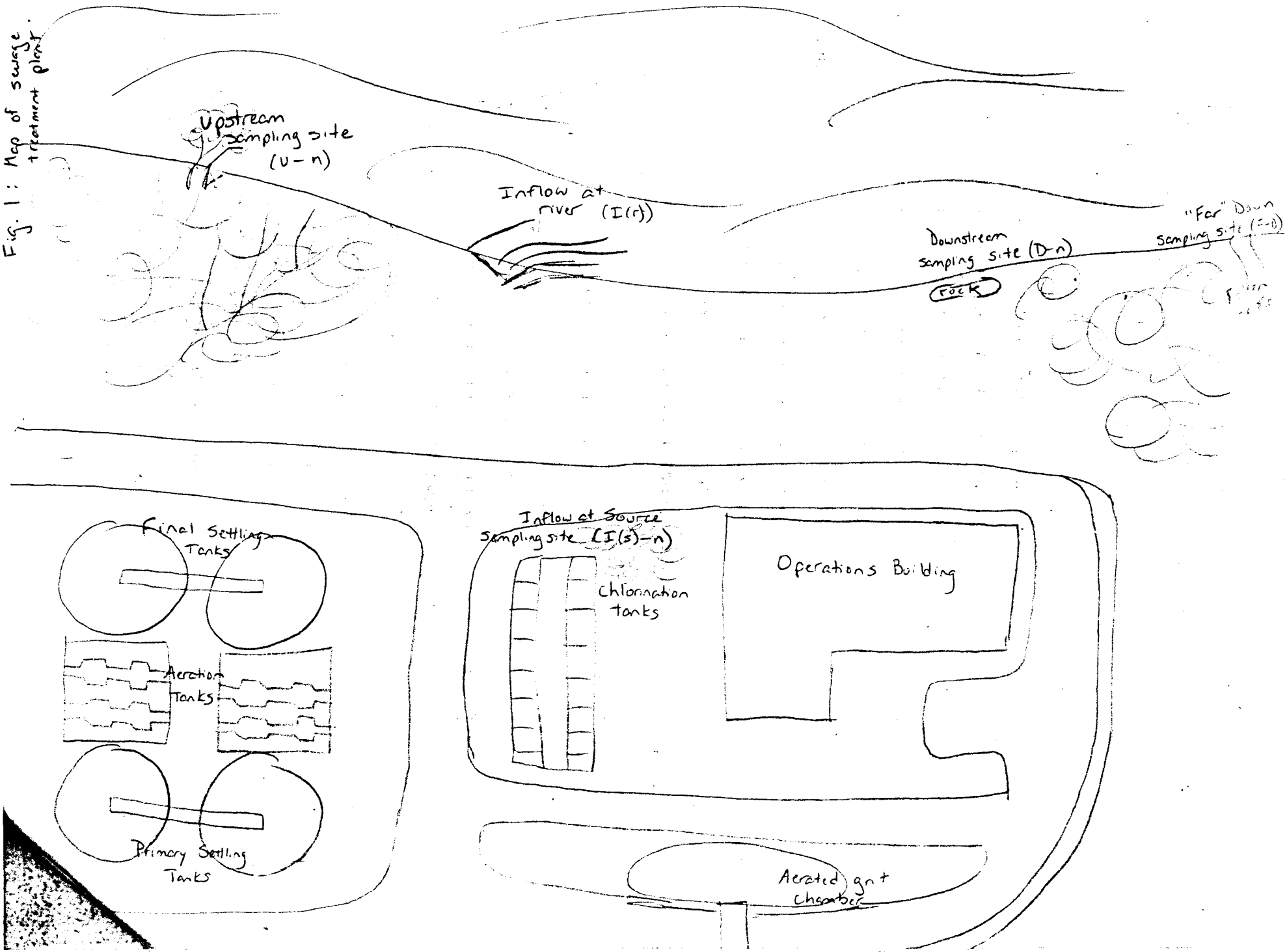
conditions around the plant. We were also aware, at the start, of the chlorination and warming of the water within the plant, and were interested in finding out just how much chlorine was discharged into the river and what the impacts are of the chlorination and increased temperature.

Methods & Materials

In order to get as complete a picture of water quality as possible, many more tests were possible than one person could have done in the allotted time. Therefore, three ES 102 students and one student from Biol 302 collaborated on the collection of data.

Trips were made to the treatment plant on three occasions. Samples were collected from four sites along the river and from the chlorination tanks, just before the flow was directed into the river. (see figure 1) Three samples were taken upstream of the inflow, two were taken from the chlorination tanks, one from the river at the pipe from which the effluent was discharged, two downstream of the inflow and a final one further downstream. Samples numbered "1" were taken close to the bank; "2" and "3" were taken from progressively farther into the flow. The upstream, first downstream and chlorination sites were also the

Fig. 1 :: Map of sewage treatment plant.



sampling sites used by the plant project engineer. We chose to use his sites so as to compare our results with his.

On April 21, the first set of samples was collected. It was sunny and warm, and the river flow was higher than usual.. Samples were held in sterile plastic bottles and brought back to the lab for testing. The pH, ANC and conductivity of each sample was measured in the laboratory as per the lab instructions handed out for the week of Feb. 20 (results shown in table 1). Petri dishes were set up in which to test for the presence of total and fecal coliform bacteria in the samples (results shown in table 1). The samples, contained in the plastic bottles, were then refrigerated until April 26.

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On that day, the Atomic Absorption Spectrometer was used to detect the sodium (Na^+) content in the samples. Because of the high presence of Na^+ in the samples, dilution was necessary. The upstream and downstream samples were diluted 1 ml. of sample in 10 ml. doubly-distilled water. The inflow samples still showed a Na^+ content far exceeding the standard curve (fig. 2) and so were diluted once again, to a final dilution of 1 ml. of sample in 20 ml. doubly-distilled water. The procedures for both the bacterial culturing and atomic absorption were provided in the lab. handout, week of March 13.

We returned to the plant on May 3. The same number of samples was taken at each site. On this day, the temperatures of each of the samples was recorded immediately upon placement in the bottle. May 3 was also a warm, sunny day but there had been heavy rains the two preceding days. Again the flow was higher than normal, according to the plant project engineer, but it was considerably lower than it had been the day before. These samples were taken at aproximately 5:00 pm, and brought back to the lab where they were refrigerated. At 7:30 they were removed from the refirgerator and brought to the lab where the DPD (N,N-Diethyl-p-phenylenediamine) test for residual chlorine was prepared. The samples sat unrefrigerated for almost 3½ hours until they were used.

This is a lot of detail. How about "Two hours elapsed between sampling time & analysis."

DPD an be used as an indicator of free chlorine because it reacts with the chlorine to produce a red color. (Greenberg, et al, 1985) The DPD test, taken from Standard Methods for the Examination of Water and Wastewater (Greenberg, et al, 1985), is a colorimetric procedure, meaning that concentration of a solution is determined by comparing the color of the solution of unknown concentration with the color of a solution of a known concentration (McGraw-Hill Dictionary of Scientific Terms). The test is based on the principle quantified in Beer's Law, which says that the absorption of a specified wavelength of light by a

solution increases with its concentration. Specifically, Beer's Law is: $A=abc$ (a= absorptivity, b= path length, c= concentration).

We used a spectrophotometer, which measures percent transmittance of light through a medium. We established a standard curve by finding the absorption of five known concentrations of potassium permanganate. We then measured out 10 ml. of each of the nine samples, added 0.5 ml. each of phosphate buffer and DPD solution, and percent transmittance was determined. Using the formula A= -log T (A= absorbance; T= transmittance) we determined the absorbance of each sample, and then applied Beer's Law to get the concentration of free chlorine present in the water. We added potasium iodide solution to one sample to test for residual chlorine but, because there was no change in the reading, we did not do this for any of the other samples. (For detailed procedures and instructions on mixing solutions, see Appendix B)

On May 5 we returned one final time to the plant to test for dissolved oxygen in the river. This was done with a portable oxygen meter. One oxygen reading was taken at each of the five sampling sites. Temperature readings were also taken, this time directly in the river, using the oxygen meter.

Data / Results

Table 1: tests run on samples collected 4/21/89

sample	tot col.	fec. col.	pH	ANC	Conductivity
U-1	0	0	7.78	4.4	1.61 x 10^2
U-2	0	0	7.77	4.4	1.5
U-3	0	1	7.70	4.4	1.52
I(s)-1	0	0	7.55	12.4	7.5
I(s)-2	0	0	7.50	12.4	7.1
I(r)	3	0	7.65	9.2	6.0
D-1	0	0	7.77	7.6	3.6
D-2	0	1	7.66	6.4	2.52
F-D	1	0	7.54	4.9	2.7

Table 2: Atomic Absorption testing for Na^+ - sample from 4/21, tested 4/26

sample	dilution	% absorban	absorbance	conc (ppm)	corrected
U-1	1 in 10 ml	.051	.0227	.781	7.81
U-2	" "	.051	.0227	.781	7.81
U-3	" "	.049	.0218	.746	7.46
I(s)-1	1 in 20 ml	.167	.0794	2.95	59.0
I(s)-2	" "	.160	.0757	2.81	56.2
I(r)	" "	.155	.0731	2.71	54.2
D-1	1 in 10 ml	.215	.1051	3.94	39.4
D-2	" "	.110	.0506	1.85	18.5
F-D	" "	.166	.0788	2.93	29.3

Table 3: DPD test results for Cl^-, 5/3/89

sample	temp 5/3	turbidity	%transmtnce	absorbance	conc (ppm)
U-1	7.5 C	97	100	0	0
U-2	7.5	96	99	4.36	0.02
U-3	7.5	97	97.5	0.01	0.07
I(s)-1	10.5	97	95	0.02	0.14
I(s)-2	10.5	97	95	0.02	0.14
I(r)	10.5	98	95.5	0.02	0.14
D-1	7.9	97	96	0.11	0.73
D-2	8.0	96	95.5	0.02	0.14
F-D	8.0	96.5	96.5	0.02	0.14

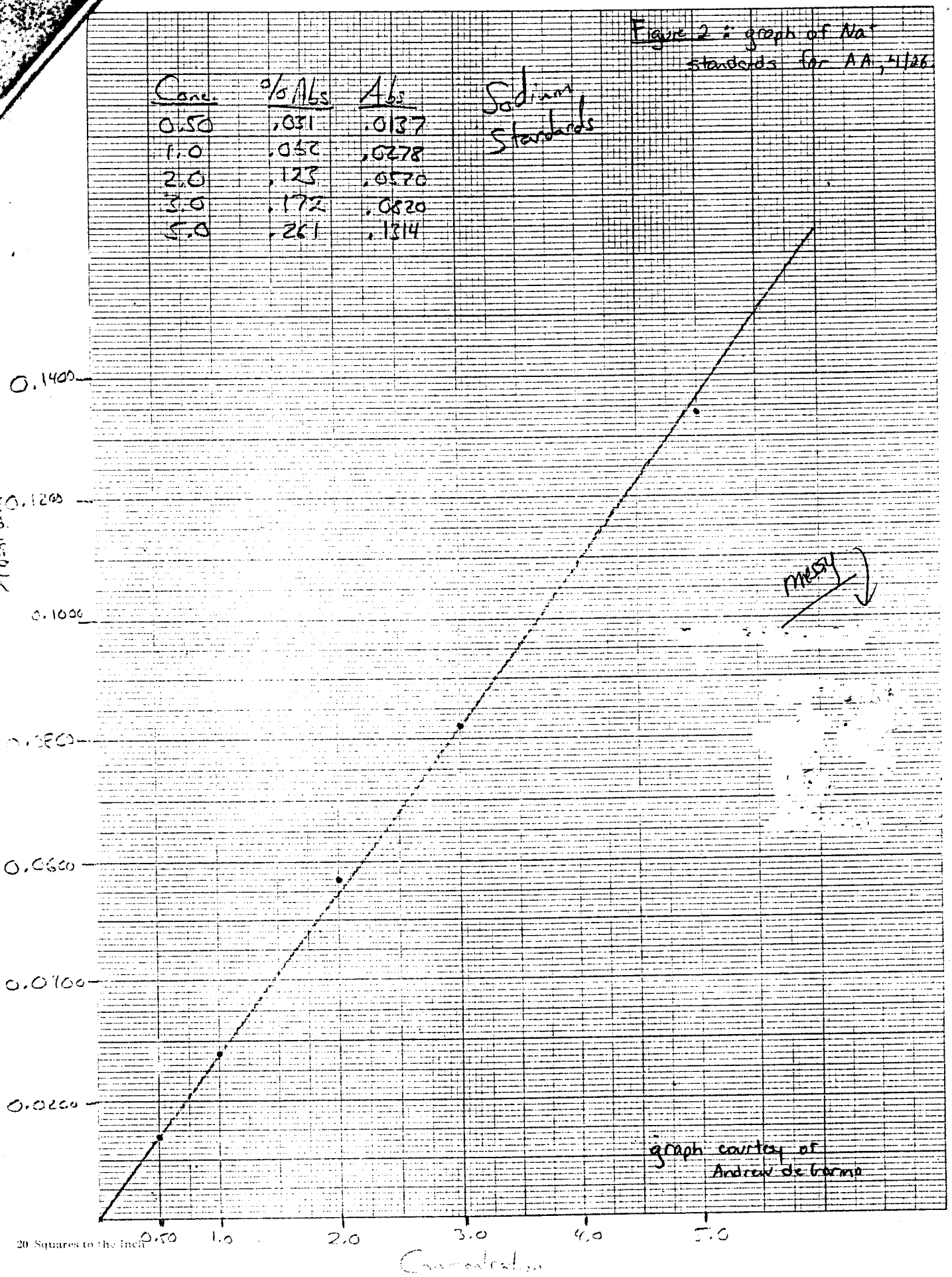
Table 4: Dissolved O_2, 5/5/89

sample	temp 5/5	DO
U-1	8.5	11.2
U-2	?	
U-3		
I(s)-1	11	2.4
I(s)-2	?	
I(r)	10	10
D-1	10.5	9.9
D-2		
D-3	9.2	14.8

Figure 2 : graph of Na^+ standards for AA, 4/26

Conc.	% Abs	Abs
0.50	.031	.0137
1.0	.062	.0278
2.0	.123	.0570
3.0	.172	.0820
5.0	.261	.1314

Sodium Standards



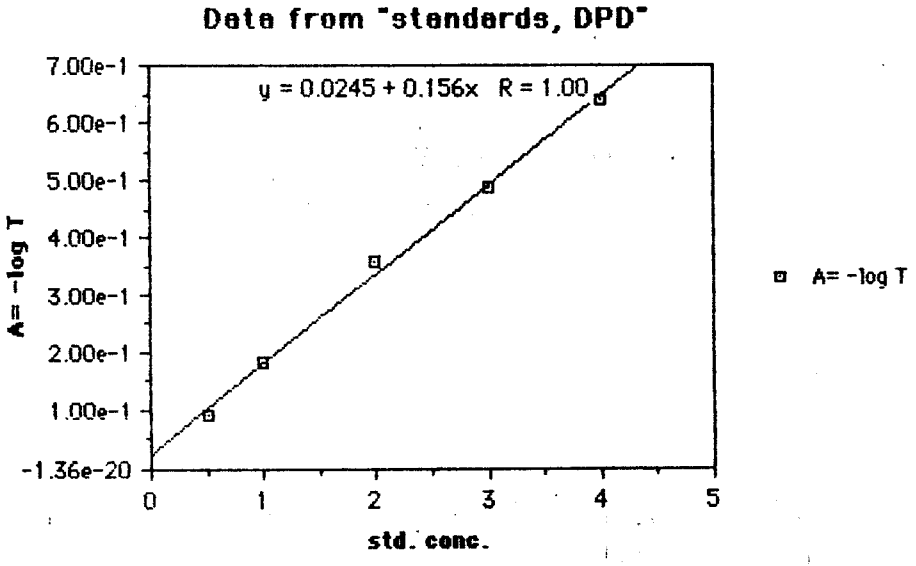
20 Squares to the inch

✓ Figure 3: Standard curve for Cl^- concentrations

standards, DPD

Thu, May 11, 1989 10:43 AM

	std. conc.	% transmitt.	A= -log T
1	0.5	81	0.09
2	1.0	66	0.18
3	2.0	43.5	0.36
4	3.0	32	0.49
5	4.0	23	0.64



graph courtesy of Jennifer Austin

Table 5: Plant data on fecal and total coliform bacteria

date	tot efflue	fec efflue	tot upstr	fec upstr	tot downst	fec downst
4/4	7800	21	1000	300	1600	0
4/11	TNTC	TNTC	5060	500	9000	6300
4/18	20	10	1400	300	2000	0
4/25	61	0	200	0	0	0
5/2	TNTC	TNTC	5800	2300	8000	2800

Table 6: Plant data on pH

date	pH
4/1	7.8
4/2	7.8
4/3	7.5
4/4	7.6
4/5	7.5
4/6	7.3
4/7	7.6
4/8	7.7
4/9	7.6
4/10	7.2
4/11	7.7
4/12	7.3
4/13	7.6
4/14	7.4
4/15	7.7
4/16	7.5
4/17	7.5
4/18	7.4
4/19	7.5
4/20	7.6
4/21	7.5
4/22	7.6
4/23	7.5
4/24	7.4
4/25	7.6
4/26	7.9
4/27	8.5
4/28	7.4
4/29	7.5
4/30	7.6

Table 7. Plant data on residual Cl⁻

date	Cl ppm	time 1	Cl ppm	time 2
4/3	.01	1:50	.01	
4/4	.1	8:15	.1	12:40
4/5	.2	10:55	.2	
4/6	.3	11:15	.3	
4/7	.56	1:45	.56	
4/8	.3	10:30	.3	
4/9	.2	11:00	.2	
4/10	.4	10:55	.4	
4/11	.0	8:15	.0	2:45
4/12	.3	10:45	.3	
4/13	.4	10:45	.4	
4/14	1.75	1:30	1.75	
4/15	.7	7:40	.7	
4/17	.0	8:05	.0	
4/18	.2	11:10	.2	2:30
4/19	.5	11:00	.5	
4/20	.2	10:00	.2	11:40
4/21	.5	9:40	.5	2:25
4/22	.3	10:30	.3	
4/23	.0	9:00	.0	
4/24	.0	2:45	.0	
4/25	.3	9:55	.3	
4/26	.3	9:30	.3	10:55
4/27	.3	11:05	.3	
4/28	.2	9:45	.2	
4/29	.3	7:35	.3	
4/30	.2	7:40	.2	

Table 8. Plant data on dissolved O_2 (DO)

Date	Final Effl	Upstream	Downstream
4/4	8.0	8.8	8.8
4/5	8.0	10.8	10.5
4/6	9.0	10.6	10.4
4/10	7.2	9.8	9.8
4/11	9.4	9.5	9.5
4/12	9.5	11.4	10.5
4/18	8.4	9.0	9.0
4/19	8.8	10.0	10.0
4/20	7.8	11.4	11.0
4/25	8.8	11.6	11.2
4/26	8.8	11.6	11.0
4/27	9.0	10.4	10.0

Table 9 Plant data on Biochemical Oxygen Demand (BOD)

date	effluent (ppm)	upstream	downstream	% removal
4/5	3.4	1.0	.5	94.3
4/6	4.1	1.4	1.4	91.8
4/12	4.6	2.2	6.8	9.0
4/13	5.7			89.5
4/19	1.5			96.6
4/20	2.6	1.6	1.6	95.3
4/26	2.8	2.4	3.2	97.8
4/27	2.4	2.0	1.6	97.3
5/3	6.8	1.1	.9	87.6

datum ⇒ singular
data ⇒ plural

Discussion

Almost all of the data collected shows a marked difference between upstream, inflow and downstream results. The temperature (May 3, table 3; May 5, table 4) was consistently highest at the inflows, slightly lower downstream and lowest upstream of the inflow, with the extreme difference being 3°C from the highest inflow temperature to the lowest upstream temperature. This difference is the result of the water's being heated in the aeration chamber (see Appendix A). It is cooled considerably as it passes through the rest of the treatment system, but is still warmer than the river water. It is interesting to note in addition that when the ES 102 Wednesday lab did the Hoosic River Flotilla, temperature readings show 6.5°C at the DeMayo outlet into the river, upstream of the plant, 9.0°C at the plant (reading taken between the inflow and downstream sites) and 7.3°C at the Hemlock Brook outlet, downstream of the plant.

Will to integrate this other data

The coliform counts (table 1), on the other hand, were not nearly as illustrative. The numbers present were so small that no significant conclusions can be drawn about relative presence of coliform in the river and in the effluent. It is fairly certain that our counts are not too inaccurate, as the counts done by the plant four days later

what happened on 9/11 & 5/12 in Table 5. Why so different?

(table 5) also show a minimal presence.* Examining their counts over a period of time, the numbers seem to show the highest counts of bacteria in the effluent, lower numbers downstream, and the lowest count is upstream of the inflow.

While this is an obvious source of pollution, an examination of the plant's data on biochemical oxygen demand (BOD) shows that they are doing a good job cleaning out the water despite the coliform. The BOD test consists of taking an oxygen reading in a sample of water, incubating it for five days, and taking a second reading. The loss of oxygen is a measure of the amount of organic material in the sample (personal interview, Richard McKnight). The plant's readings (table 9) show that while the presence of organic material is high in the effluent (to be expected because of the inflowing sewage material and the growth of bacteria in the aeration chamber--see Appendix A), the oxygen demand is minimally higher, if at all, downstream than upstream. This indicates that the treatment process is removing most of the pollutants in the wastewater and the chlorination is killing most of the bacteria. This may be corroborated by dissolved oxygen readings. Both our measurements (table 4) and theirs (table 8) show slightly less oxygen in the effluent than either upstream or downstream. This may be due to the higher presence of bacteria which is consuming the oxygen.

* The low coliform count may be due to the heavy rain the day before. When the plant recieves a higher volume of sewage water than usual, it has to be pushed through the treatment process more quickly than usual. This would lead to proportionally less bacteria in the water, as so much more water passes through in so much less time. (personal interview, George Heusler)

Or could it lead to more bacteria, since the water can't be treated for the same length of time?

While pH readings (table 1) do not vary greatly--the water is mildly basic at all three sites and only slightly less so at the chlorination tanks--the buffering capacity (ANC, table 1) shows a sharp contrast between sites. All three samples from the upstream site had an ANC of 4.4. The samples taken from the chlorination tank had an ANC of 12.4. This sharp increase in neutralizing capacity can be explained by the abundance of ~~Cl~~ No CO_3^{-2}. Cl^- doesn't buffer. present in the water. At the inflow point on the river, the ANC was 9.2, lowered probably by the dilution of the chlorine as it mixed with the river water. The first downstream had two ANC readings of 7.6, close to the bank, and 6.4, farther out into the stream, where more mixing and dilution is taking place. The "far down" reading was 4.9--almost the same as the upstream readings. The presence of the added ions is also reflected in the conductivity readings (table 1), which are very low upstream, considerably higher at the chlorination tanks, slightly lower at the inflow and lower still downstream, though not as low as upstream. This is probably also a reflection of other materials present in the effluent, including, possibly, traces of cadmium or arsenic. ⇒ Not good to say this unless you have data to back it up.

The chlorination of the water is an interesting point of discussion. Our DPD test results (table 3) showed overall less chlorine present in the water than their data (table 7). This may be due to the fact that we only tested for

Chlorine is Cl_2. It is not an ion
Chloride is Cl^-. It is an ion.

free chlorine ions. However, we tested one sample for residual chlorine and got no readings. This probably has at least two sources: the samples were sitting, unrefrigerated, for over three hours before testing. Chloramines, in higher temperatures, have a tendency to react, thus increasing the apparent free chlorine count (Greenberg et al, 1985). It is possible that much of the residual chlorine was detected as free chlorine. Anther source of error is the exposure of the DPD standards to air. We did not add sodium arsenite to the solution, a substance that prevents oxidation. It was noticed that, over time, the color of the standards darkened, a sign of oxidation. Therefore, in re-calibrating the spectrophotometer, it was standardized on an incorrect transmittance, which would make the samples appear less concentrated than they actually were.

I thought you only did it once.

With only two exceptions (4/7 and 4/14), the plant's records of ~~Cl^-~~ Cl_2 in the river is .4 ppm or less. Until the end of April, E.P.A. and state regulations require that the water contains at least .5 ppm of residual ~~Cl^-~~ Cl_2. After that, however, the regulations have been changed so that the water may contain *no more than* .5 ppm ~~Cl^-~~ Cl_2. This change is due to increasing concern with the possible hazards of chlorine to river life and to the environment in general.

Conlusion

The Hoosac Water Quality District wastewater treatment plant is carefully controlling the quality of the water it discharges into the Hoosic River, but further study is necessary to fully assess the effects of the increased buffering capacity, the temperature difference and, most importantly, the addition of chlorine to the river. As many of the papers delivered at the Fifth Conference on Water Chlorination (1984) tell us, the hazards presented by chlorination of water are many and not completely known. Although chlorination of the effluent is successful in disinfecting the water, it may have impacts that far outweigh the benefits of its use as a disinfectant.

Do you think this is bad?

Chlorination aside, it was a comfort to find out for myself that the wastewater treatment plant is keeping the water very clean, and doing far less apparent damage to the river environment than I had expected at the beginning of this project.

Appendix A

The water treatment process consists of six separate steps. Sewage water flows by gravity to the treatment plant, where it enters the influent pump station. Large solids are removed by a bar screen and the water is then pumped into an aerated grit chamber. There, heavier particles settle and are eventually trucked to the landfill. The aeration serves to keep organic matter in suspension. Next, the water is directed to the primary settling tanks, where the settleable material forms sludge. The material that floats to the top is skimmed off and later processed with the sludge: it is dewatered by vacuum filter units and then mixed with wood chips in a 2:1 wood chips to sludge ratio. This mixture is aerated in cement bins at a minimum of 55°C, to kill any bacteria that might be present. The wood chips are later filtered out for re-use and the treated sludge is used as landfill cover. Meanwhile, the water minus the settled solids moves on to the aeration tanks. There, the water is oxygenated to promote the growth of bacteria which feeds on the organic matter in the water (this is together known as *activated sludge*). After leaving the aeration tanks, the water enters the final settling tanks. Here, any remaining activated sludge is settled out and returned to the aeration tanks. The clarified water is

then directed to the chlorination tanks where chorine is added as a disinfectant, and finally flows out into the Hoosic River.

Appendix B: DPD Method of Cl^- detection

4500-Cl G. DPD Ferrous Titrimetric Method

1. General Discussion

a. Principle: N,N-diethyl-p-phenylenediamine (DPD) is used as an indicator in the titrimetric procedure with ferrous ammonium sulfate (FAS). Where complete differentiation of chlorine species is not required, the procedure may be simplified to give only free and combined chlorine or total chlorine.

In the absence of iodide ion, free chlorine reacts instantly with DPD indicator to produce a red color. Subsequent addition of a small amount of iodide ion acts catalytically to cause monochloramine to produce color. Addition of iodide ion to excess evokes a rapid response from dichloramine. In the presence of iodide ion, part of the nitrogen trichloride (NCl_3) is included with dichloramine and part with free chlorine. A supplementary procedure based on adding iodide ion before DPD permits estimating proportion of NCl_3 appearing with free chlorine.

Chlorine dioxide (ClO_2) appears, to the extent of one-fifth of its total chlorine content, with free chlorine. A full response from ClO_2, corresponding to its total chlorine content, may be obtained if the sample first is acidified in the presence of iodide ion and subsequently is brought back to an approximately neutral pH by adding bicarbonate ion. Bromine, bromamine, and iodine react with DPD indicator and appear with free chlorine.

b. pH control: For accurate results careful pH control is essential. At the proper pH of 6.2 to 6.5, the red colors produced may be titrated to sharp colorless end points. *Titrate as soon as the red color is formed in each step.* Too low a pH in the first step tends to make the monochloramine show in the free-chlorine step and the dichloramine in the monochloramine step. Too high a pH causes dissolved oxygen to give a color.

c. Temperature control: In all methods for differentiating free chlorine from chloramines, higher temperatures increase the tendency for chloramines to react and lead

Source: Greenberg, Arnold, et al. Standard Methods for the Examination of Water and Wastewater, 16th ed. Wash. DC: American Public Health Ass'n., 1985. p.302-310.

to increased apparent free-chlorine results. Higher temperatures also increase color fading. Complete measurements rapidly, especially at higher temperature.

d. Interference: The most significant interfering substance likely to be encountered in water is oxidized manganese. To correct for this, place 5 mL buffer solution and 0.5 mL sodium arsenite solution in the titration flask. Add 100 mL sample and mix. Add 5 mL DPD indicator solution, mix, and titrate with standard FAS titrant until red color is discharged. Subtract reading from Reading *A* obtained by the normal procedure as described in ¶ 3*a*1) of this method or from the total chlorine reading obtained in the simplified procedure given in ¶ 3*a*4). If the combined reagent in powder form (see below) is used, first add KI and arsenite to the sample and mix, then add combined buffer-indicator reagent.

As an alternative to sodium arsenite use a 0.25% solution of thioacetamide, adding 0.5 mL to 100 mL sample.

Interference by copper up to approximately 10 mg Cu/L is overcome by the EDTA incorporated in the reagents. EDTA enhances stability of DPD indicator solution by retarding deterioration due to oxidation, and in the test itself, provides suppression of dissolved oxygen errors by preventing trace metal catalysis.

High concentrations of combined chlorine can break through into the free chlorine fraction. At 10°C this amounts to 2% and at 25°C to 4% of the monochloramine present that reacts after standing 1 min. Adding thioacetamide (0.5 mL 0.25% solution to 100 mL) immediately after mixing DPD reagent with sample completely stops further reaction with combined chlorine in the free chlorine measurement. Continue immediately with FAS titration to obtain free chlorine. Obtain total chlorine from the normal procedure, i.e., without using thioacetamide.

Because high concentrations of iodide are used to measure combined chlorine and only traces of iodide greatly increase ramine interference in free chlorine urements, take care to avoid ic contamination by rinsing between san or using separate glassware.

See 408.1 for a discussion of othe terferences.

e. Minimum detectable concentra Approximately 18 µg Cl as Cl_2/L.

2. Reagents

a. Phosphate buffer solution: Dissolve g anhydrous Na_2HPO_4 and 46 g anhydr KH_2PO_4 in distilled water. Combine w 100 mL distilled water in which 800 disodium ethylenediamine tetraacetate hydrate (EDTA) have been dissolved. I lute to 1 L with distilled water and add mg $HgCl_2$ to prevent mold growth and i terference in the free chlorine test caus by any trace amounts of iodide in the r agents. (CAUTION: *$HgCl_2$ is toxic—tal care to avoid ingestion*).

b. N,N-Diethyl-p-phenylenediamin (DPD) indicator solution: Dissolve 1 g DP oxalate,* or 1.5 g DPD sulfate pentahy drate,† or 1.1 g anhydrous DPD sulfate i chlorine-free distilled water containing mL 1 + 3 H_2SO_4 and 200 mg disodium EDTA. Make up to 1 L, store in a brown glass-stoppered bottle in the dark, and discard when discolored. Periodically check solution blank for absorbance and discard when absorbance at 515 nm exceeds 0.002/cm. (The buffer and indicator sulfate are available commercially as a combined reagent in stable powder form.) CAUTION: *The oxalate is toxic—take care to avoid ingestion.*

c. Standard ferrous ammonium sulfate (FAS) titrant: Dissolve 1.106 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in distilled water containing 1 mL 1 + 3 H_2SO_4 and make

*Eastman chemical No. 7102 or equivalent.
†Available from Gallard-Schlesinger Chemical Mfg. Corp., 584 Mineola Avenue, Carle Place, N.Y. 11514, or equivalent.

up to 1 L with freshly boiled and cooled distilled water. This standard may be used for 1 month, and the titer checked by potassium dichromate. For this purpose add 10 mL 1 + 5 H_2SO_4, 5 mL conc H_3PO_4, and 2 mL 0.1% barium diphenylamine sulfonate indicator to a 100-mL sample of FAS and titrate with 0.100*N* primary standard potassium dichromate to a violet end point that persists for 30 s. The FAS titrant is equivalent to 100 µg Cl as Cl_2/1.00 mL.

d. Potassium iodide, KI, crystals.

e. Potassium iodide solution: Dissolve 500 mg KI and dilute to 100 mL, using freshly boiled and cooled distilled water. Store in a brown glass-stoppered bottle, preferably in a refrigerator. Discard when solution becomes yellow.

f. Potassium dichromate solution: See 408A.2*c*2).

g. Barium diphenylaminesulfonate, 0.1%: Dissolve 0.1 g $(C_6H_5NHC_6H_4\text{-}4\text{-}SO_3)_2Ba$ in 100 mL distilled water.

h. Sodium arsenite solution: Dissolve 5.0 g $NaAsO_2$ in distilled water and dilute to 1 L. (CAUTION: *Toxic—take care to avoid ingestion.*)

i. Thioacetamide solution: Dissolve 250 mg CH_3CSNH_2 in 100 mL distilled water. (CAUTION: *Cancer suspect agent. Take care to avoid skin contact or ingestion.*)

j. Chlorine-demand-free water: See 408B.3*m*.

3. Procedure

The quantities given below are suitable for concentrations of total chlorine up to 5 mg/L. If total chlorine exceeds 5 mg/L, use a smaller sample and dilute to a total volume of 100 mL. Mix usual volumes of buffer reagent and DPD indicator solution, or usual amount of DPD powder, with distilled water *before* adding sufficient sample to bring total volume to 100 mL. (If sample is added before buffer, test does not work.)

a. Free chlorine or chloramine: Place 5 mL each of buffer reagent and DPD indicator solution in titration flask and mix (or use about 500 mg DPD powder). Add 100 mL sample, or diluted sample, and mix.

1) Free chlorine—Titrate rapidly with standard FAS titrant until red color is discharged (Reading *A*).

2) Monochloramine—Add one very small crystal of KI (about 0.5 mg) or 0.1 mL (2 drops) KI solution and mix. Continue titrating until red color is discharged again (Reading *B*).

3) Dichloramine—Add several crystals KI (about 1 g) and mix to dissolve. Let stand for 2 min and continue titrating until red color is discharged (Reading *C*). For dichloramine concentrations greater than 1 mg/L, let stand 2 min more if color drift-back indicates slightly incomplete reaction. When dichloramine concentrations are not expected to be high, use half the specified amount of KI.

4) Simplified procedure for free and combined chlorine or total chlorine—Omit 2) above to obtain monochloramine and dichloramine together as combined chlorine. To obtain total chlorine in one reading, add full amount of KI at the start, with the specified amounts of buffer reagent and DPD indicator, and titrate after 2 min standing.

b. Nitrogen trichloride: Place one very small crystal of KI (about 0.5 mg) or 0.1 mL KI solution in a titration flask. Add 100 mL sample and mix. Add contents to a second flask containing 5 mL each of buffer reagent and DPD indicator solution (or add about 500 mg DPD powder direct to the first flask). Titrate rapidly with standard FAS titrant until red color is discharged (Reading *N*).

4. Calculation

For a 100-mL sample, 1.00 mL standard FAS titrant = 1.00 mg Cl as Cl_2/L.

408 E. DPD Colorimetric Method

1. General Discussion

a. Principle: This is a colorimetric version of the DPD method and is based on the same principles. Instead of titration with standard ferrous ammonium sulfate (FAS) solution as in the titrimetric method, a colorimetric procedure is used.

b. Interference: See 408.1 and 408D.1*d*. Compensate for color and turbidity by using sample to zero photometer.

c. Minimum detectable concentration: Approximately 10 µg Cl as Cl_2/L.

2. Apparatus

Colorimetric equipment: One of the following is required:

a. Spectrophotometer, for use at a wavelength of 515 nm and providing a light path of 1 cm or longer.

b. Filter photometer, equipped with a filter having maximum transmission in the wavelength range of 490 to 530 nm and providing a light path of 1 cm or longer.

c. Glassware: Use separate glassware, including separate spectrophotometer cells, for free and combined (dichloramine) measurements, to avoid iodide contamination in free chlorine measurement.

3. Reagents

See Section 408D.2*a, b, d, e, h, i,* and *j*.

4. Procedure

a. Calibration of photometer or colorimeter: Calibrate instrument with chlorine (1) or potassium permanganate (2) solutions.

1) Chlorine solutions—Prepare chlorine standards in the range of 0.05 to 4 mg/L from about 100 mg/L chlorine water standardized as directed in Section 409A.3*g*. Use chlorine-demand-free water and glassware to prepare these standards. Develop color by first placing 5 mL phosphate buffer solution and 5 mL DPD indicator reagent in flask and then adding 100 mL chlorine standard with thorough mixing as described in *b* and *c* below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with standard FAS titrant as a check on chlorine concentration.

2) Potassium permanganate solutions—Prepare a stock solution containing 891 mg $KMnO_4$/1000 mL. Dilute 10.00 mL stock solution to 100 mL with distilled water in a volumetric flask. When 1 mL of this solution is diluted to 100 mL with distilled water, a chlorine equivalent of 1.00 mg/L will be produced in the DPD reaction. Prepare a series of $KMnO_4$ standards covering the chlorine equivalent range of 0.05 to 4 mg/L. Develop color by first placing 5 mL phosphate buffer and 5 mL DPD indicator reagent in flask and adding 100 mL standard with thorough mixing as described in *b* and *c* below. Fill photometer or colorimeter cell from flask and read color at 515 nm. Return cell contents to flask and titrate with FAS titrant as a check on any absorption of permanganate by distilled water.

b. Volume of sample: Use a sample volume appropriate to the photometer or colorimeter. The following procedure is based on using 10-mL volumes; adjust reagent quantities proportionately for other sample volumes. Dilute sample with chlorine-demand-free water when total chlorine exceeds 4 mg/L.

c. Free chlorine: Place 0.5 mL each of buffer reagent and DPD indicator reagent in a test tube or photometer cell. Add 10 mL sample and mix. Read color immediately (Reading *A*).

d. Monochloramine: Continue by adding one very small crystal of KI (about 0.1 mg) and mix. If dichloramine concentration is expected to be high, instead of small crystal add 0.1 mL (1 drop) freshly prepared KI solution (0.1 g/100 mL). Read color immediately (Reading *B*).

e. Dichloramine: Continue by adding several crystals of KI (about 0.1 g) and mix to dissolve. Let stand about 2 min and read color (Reading *C*).

f. Nitrogen trichloride: Place a very small crystal of KI (about 0.1 mg) in a clean test tube or photometer cell. Add 10 mL sample and mix. To a second tube or cell add 0.5 mL each of buffer and indicator reagents; mix. Add contents to first tube or cell and mix. Read color immediately (Reading *N*).

5. Calculation

Reading	NCl_3 Absent	NCl_3 Present
A	Free Cl	Free Cl
B-A	NH_2Cl	NH_2Cl
C-B	$NHCl_2$	$NHCl_2$
N-A		NCl_3
2(N-A)		NCl_3
C-N		$NHCl_2$

In the event that monochloramine is present with NCl_3, it will be included in Reading *N*, in which case obtain NCl_3 from 2(*N-B*).

References

class lab handouts, weeks of Feb. 20 and March 13

Greenberg, et al. Standard Methods for the Examination of Water and Wastewater, 16th ed. Wash. DC: American Public Health Association, 1985. p. 302-310.

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Many thanks to Richard McKnight, Project Engineer, and George Heisler, Chief Operator, of the Hoosac Water Quality District wastewater treatment plant for their generosity with their time and information.
Thanks also to Jennifer Austin, Holly Christoffersson and Camille Uterback for their help with collecting and interpreting data.
Finally, thanks are due to Prof. Susan Kegley for her help and donation of what should have been personal time.