

6.6.3 Results and Discussion

General Observations

The tower showed many signs of deterioration, although the stairway, top deck and fanstacks appeared to be only slightly weathered. The wooden louvers on the sides of the tower were thickly encrusted with salt and bright green algae. Makeup water was a murky gray color, and had a strong musty odor. Both the hot and cold water basin samples were yellow-green and odorless. No plumes were visible, and drift appeared to be negligible.

Temperature, pH and Chlorine

Figure 6.6-1 shows the measured values of temperature, pH and total residual chlorine for each hour of the sampling. Values are plotted to the nearest quarter-hour on the time scale. Circulating water conditions were relatively constant throughout the day, while makeup water pH dropped considerably from 0845 hours to noon. Chlorine levels in all samples averaged about 0.2 ppm.

Inorganic Constituents

Table 6.6-1 presents the results of our analyses of the inorganic constituents of the makeup water, hot water basin and cold water basin samples. Analyses were performed only on filtrates of the composite samples. Results indicate that salts in the makeup water are concentrated roughly three to four times by passage through the cooling tower. Total suspended solids and zinc appear to be lost from the system, since they are at lower concentrations in the recirculating water than in the makeup; perhaps they are deposited as sludge in the cold water basin. The only metal at a high concentration is chromium, which is added to the system as chromate. According to one of the chemical suppliers to the cooling tower operator, dissolved chromium concentrations are supposed to be between 10 and 20 ppm to be effective; our values fall within this range. It is interesting to note that metal concentrations in the makeup water are generally lower than in the treated municipal wastewater used by Burbank and Glendale.

The results of the USEPA/MERL's analysis of our samples are shown in Table 6.6-2. (Due to an error in sample collection, a makeup water sample was not sent to the USEPA/MERL.)

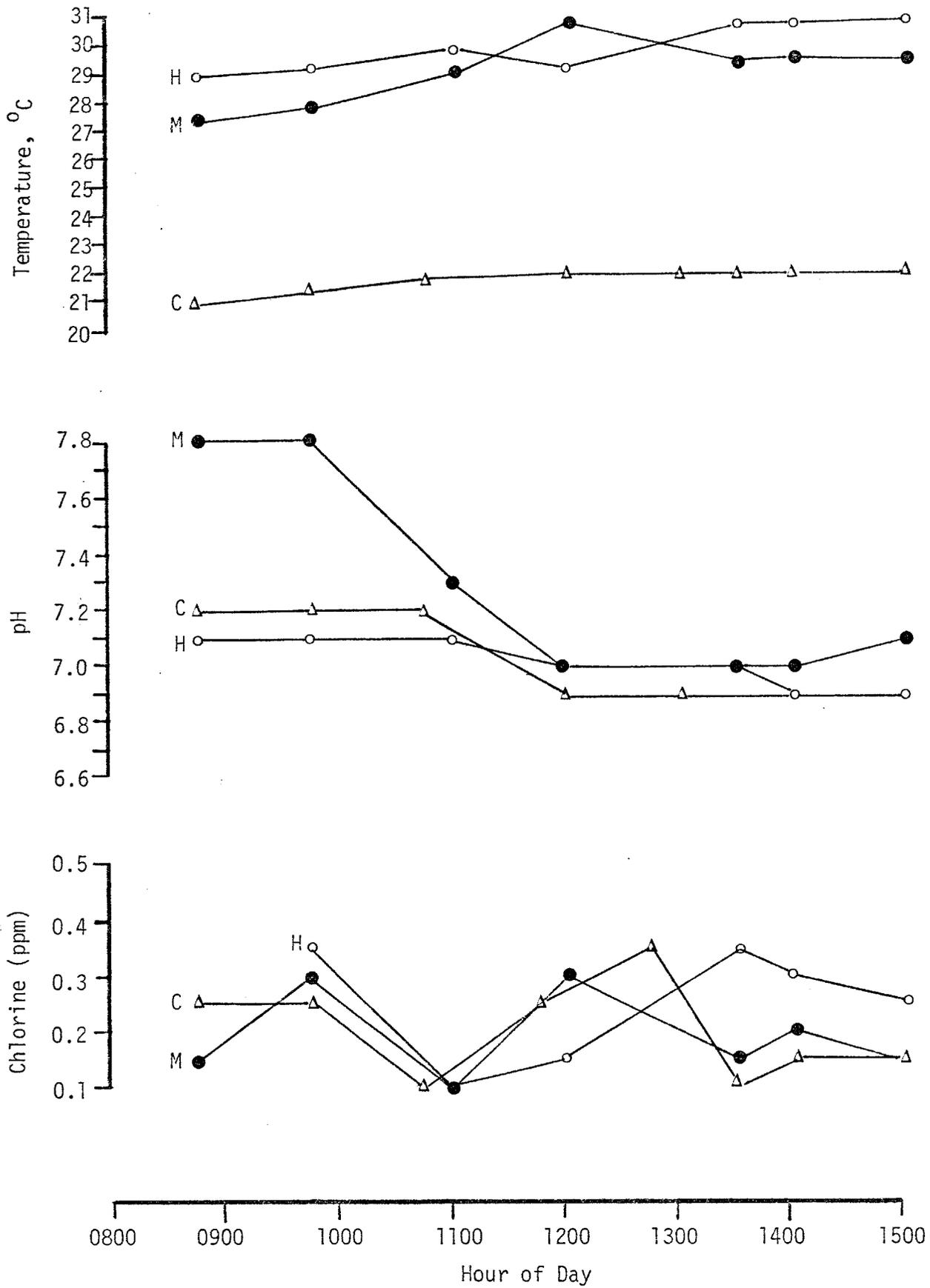


Figure 6.6-1. Temperature, pH and Free Chlorine Residual, Industrial Cooling Tower No. 1, 22 January 1981 Sampling.

Table 6.6-1

INORGANIC CONSTITUENTS IN INDUSTRIAL COOLING TOWER NO. 1
WATER, 5 AUGUST 1980 SAMPLING^a

Constituent	Units of Concentration	Makeup Water	Hot Water Basin		Cold Water Basin	
			Conc.	HW/M ^b	Conc.	CW/M ^c
Cadmium	ppb	<0.2	0.8	>4	0.8	>4
Chromium	ppm	0.013	16.1	1238	15.5	1192
Copper	ppb	3	17	5.7	19	6.3
Lead	ppb	<0.5	1	>2	2	>4
Mercury	ppt	<3	<3	1	<3	1
Zinc	ppm	2.56	2.22	0.87	2.17	0.85
Tot. Susp. Sol.	ppm	21.0	17.0	0.81	16.7	0.80
Tot. Diss. Sol.	ppm	742	2674	3.6	2584	3.5
Conductivity	µmho/cm	1050	3300	3.1	3340	3.2

^aAnalyses performed on filtrate only.

^bHW/M = ratio of hot water basin concentration to makeup water concentration.

^cCW/M = ratio of cold water basin concentration to makeup water concentration.

Table 6.6-2

RESULTS OF USEPA/MERL ANALYSES OF COLD WATER BASIN SAMPLES FROM
INDUSTRIAL TOWER No. 1, 5 AUGUST 1980 SAMPLING

Constituent	No. of Samples	Range of Concentration (ppm)
Na ⁺	3	512 - 518
K ⁺	3	47.9 - 50.0
Mg ⁺⁺	3	67.6 - 69.0
Cl ⁻	NM ^a	NM
SO ₄ ⁼	3	1450 - 4400
Total Fe	3	1.46 - 2.14
Total PO ₄ ³⁻	2	3.6 - 3.7

Source: Neill, 1981.

^aNot measured

Volatile Organics

As seen in Figure 6.6-2, our GC/MS analysis revealed the presence of a large number of volatile organic compounds in the makeup water sample. Of the numerous discernible peaks in mass spectrum, 17 could be identified with some certainty. It is evident, however, that many more compounds are present. Table 6.6-3 lists the identified compounds, along with estimates of their concentrations in the makeup, hot water basin and cold water basin. The makeup contains about 1.8 mg/L of volatile organics, the largest identifiable class of which is benzene and its derivatives, toluene and xylene.

Figures 6.6-3 and 6.6-4 show the mass spectra of the hot and cold water basin samples respectively. Concentrations of all quantifiable compounds present in the makeup water except chloroform, benzene and toluene were below detectable limits in the circulating water. Even these three components were at substantially lower concentrations than in the makeup. This finding is consistent with the idea that volatile organics are stripped effectively from the circulating water.

Nonvolatile Organics

Of the towers examined in this study, Industrial Tower No. 1 had the most complex array of nonvolatile organic compounds in its makeup and circulating water. Table 6.6-4 reports the concentrations of the acid and base-neutral extracts from the water samples. Circulating water concentrations of both fractions are somewhat lower than in the makeup, indicating losses from the system; mechanisms could include volatilization of some of the lighter molecular weight compounds, chemical transformation to volatiles, and deposition in cooling tower sludge.

Figure 6.6-5 shows GC traces for the base-neutral extracts of makeup and hot water basin samples. In comparing the traces, it should be borne in mind that the hot water basin sample injection was 1.5 times as concentrated as the makeup water sample injection. In addition, the trace for the makeup water sample was 100 times more attenuated than was that for the hot water basin. Gas chromatography/mass spectrometry (GC/MS) analyses of the makeup water show that a majority of the compounds are aromatic, with homologous series of alkyl benzenes, naphthalenes, fluorenes, and pyrenes. Table 6.6-5 presents the findings of a computer library search for the major peaks in this

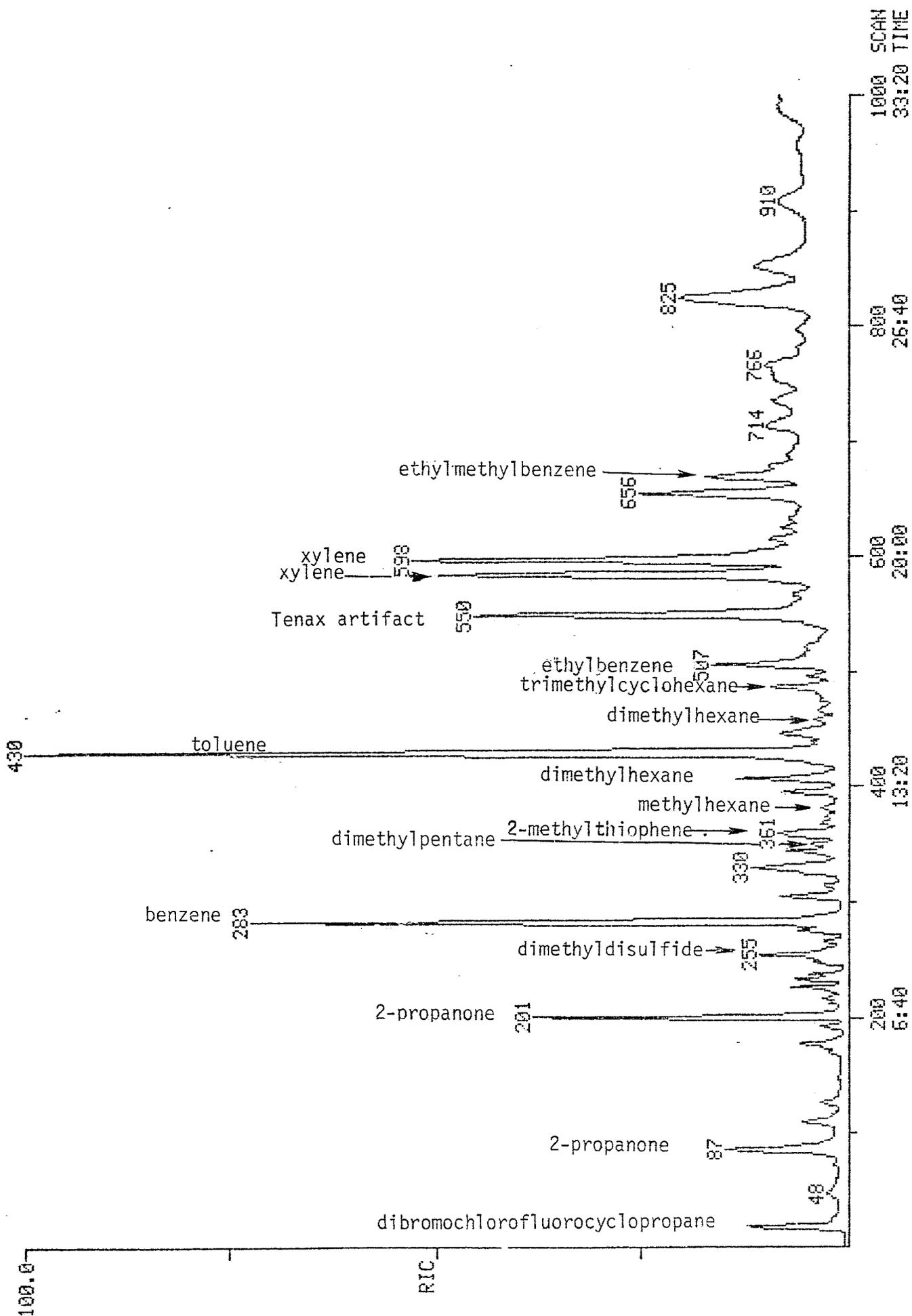


Figure 6.6-2. Mass Spectrum of Makeup Water Sample, Industrial Cooling Tower No. 1, 5 August 1980.

Table 6.6-3

VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN
INDUSTRIAL COOLING TOWER NO. 1 WATER, 5 AUGUST 1980 SAMPLING
(Concentrations in ppb)

Compound	Makeup	Hot Water Basin	Cold Water Basin
Chloroform	16	2.3	2.3
2-propanone	51	<1	<1
2-butanone	92	<1	<1
Benzene	196	2.3	2.3
Toluene	354	2.4	2.7
o-xylene, m-xylene	158	<1	<1
p-xylene	161	<1	<1
Ethyl benzene	15	<1	<1
Ethylmethyl benzene	85	<1	<1
Others ^a	1128 ^b		

^aThe following were detected in trace amounts in the makeup:

dibromochlorofluoro cyclopropane
dimethyl disulfide
dimethyl pentane
2-methyl thiophene
methyl hexane
dimethyl heptane
dimethyl hexane
trimethyl cyclohexane

^bConcentration based upon average response factors for standard n-alkanes eluting within range of sample elution times.

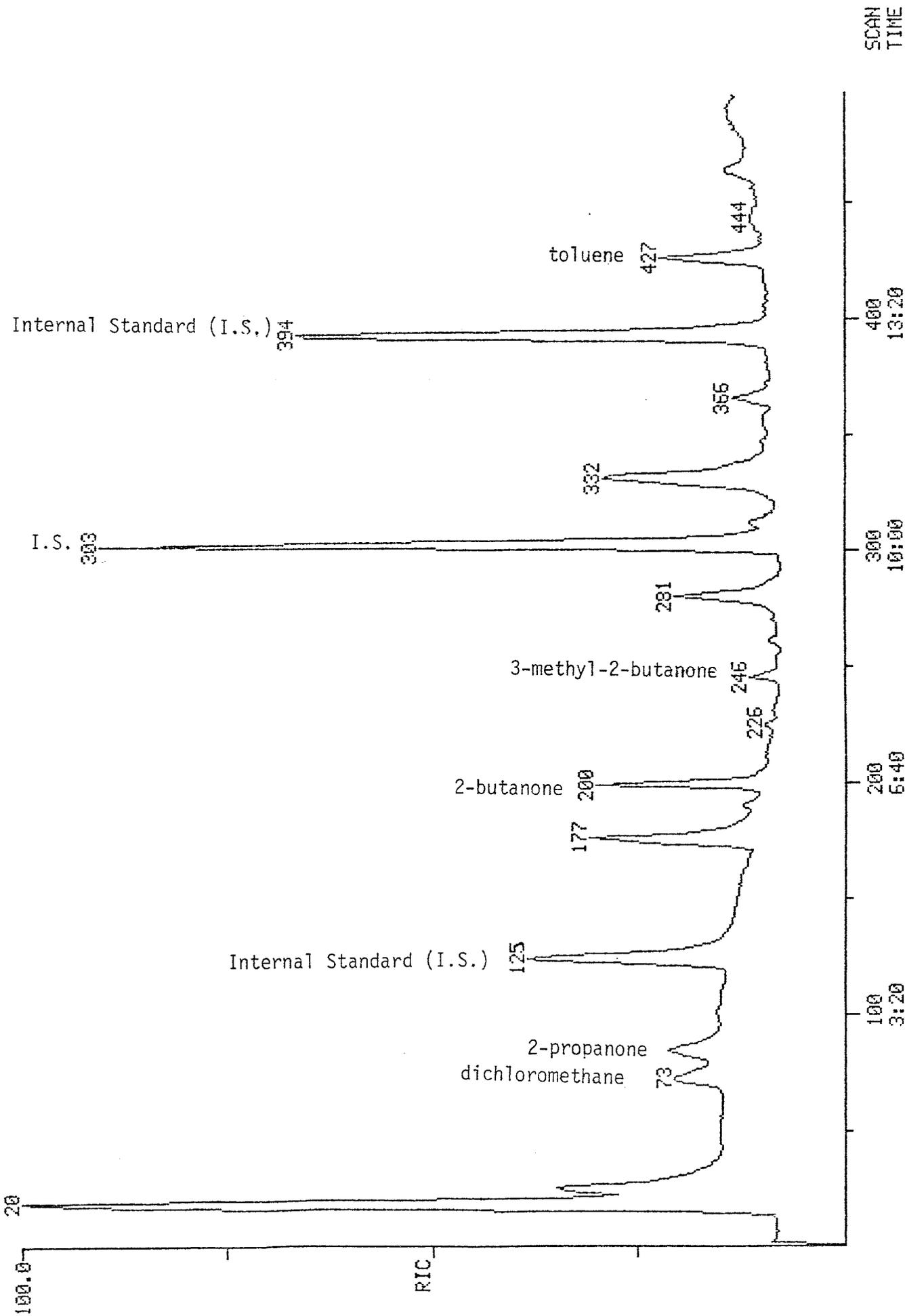


Figure 6.6-3. Mass Spectrum of Hot Water Basin Sample, Industrial Cooling Tower No. 1, 5 August 1980.

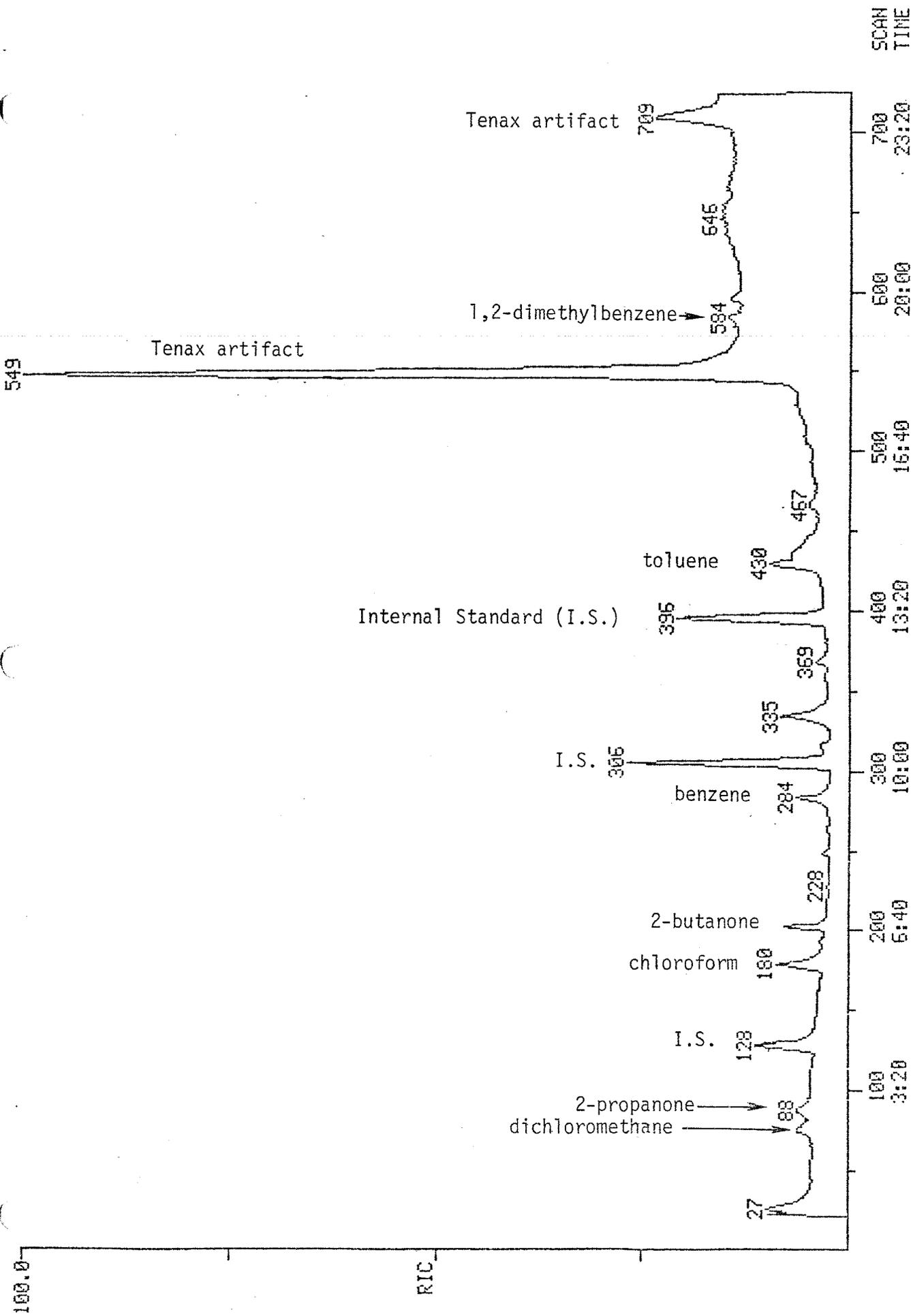


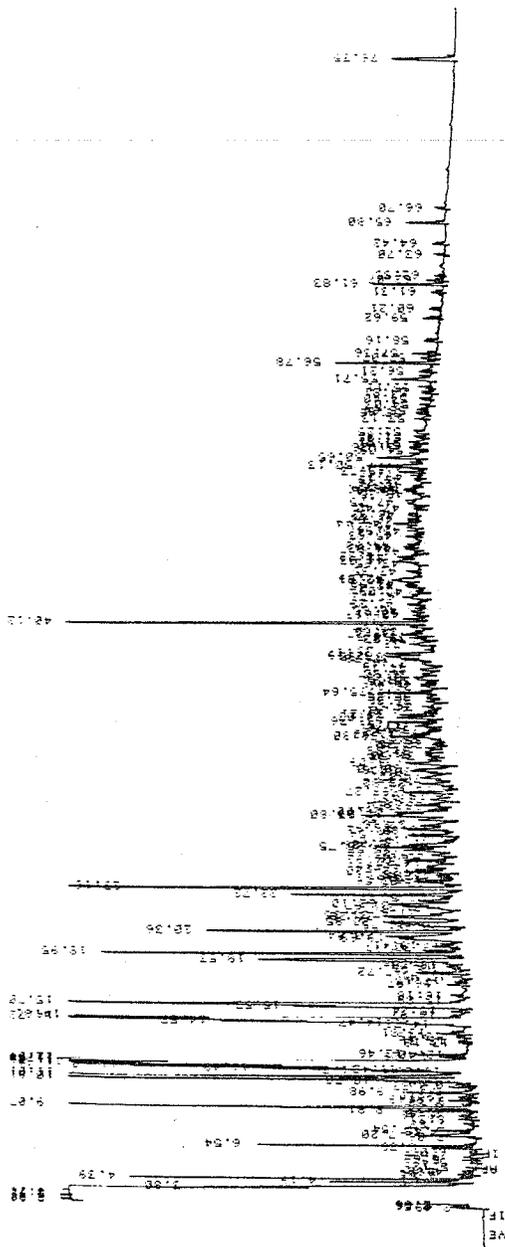
Figure 6.6-4. Mass Spectrum of Cold Water Basin Sample, Industrial Cooling Tower No. 1, 5 August 1980.

Table 6.6-4

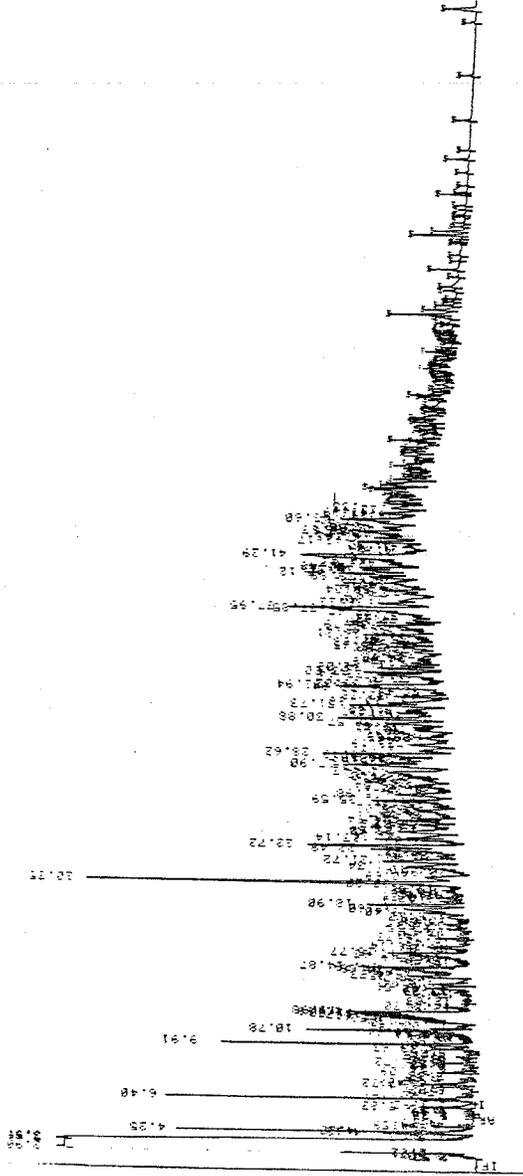
CONCENTRATIONS OF NONVOLATILE ORGANIC COMPOUNDS EXTRACTED FROM
INDUSTRIAL COOLING TOWER No. 1, 5 AUGUST 1980 SAMPLING
(Concentrations in ppb)^a

Sample Extract	Makeup Water		Hot Water		Cold Water	
	Resolved	Unresolved	Resolved	Unresolved	Resolved	Unresolved
Base-Neutral	360	1704	230	830	225	920
Acid	230	2350	140	2140	100	1740
Totals	590	4054	370	2970	325	2660
	4644		3340		2985	

^aConcentrations are based upon average response factors for standard n-alkanes eluting within range of sample elution times.



Hot Water



Makeup

Figure 6.6-5. Gas Chromatograms of Base-Neutral Extracts of Makeup and Hot Water Basin Samples, Industrial Cooling Tower No. 1, 5 August 1980 Sampling.

Table 6.6-5

COMPOUNDS IDENTIFIED THROUGH GC/MS ANALYSIS OF BASE-NEUTRAL EXTRACT OF MAKEUP WATER,
INDUSTRIAL COOLING TOWER NO.1, 5 AUGUST 1980 SAMPLING

NO	NAME	NO	NAME
1	2-PYRIDINEMETHANOL, . ALPHA. -2-PYRIDINYL-	52	BENZENEACETICACID, 4-METHOXY-
2	BENZENE, METHYL-	53	BENZENEACETICACID, 4-METHOXY-
3	THIOPHENE, 2-METHYL-	54	BENZENE, (1, 1-DIMETHYL-2-PROPENYL)-
4	THIOPHENE, 2-METHYL-	55	UNDECANE
5	THIOPHENE, 3-METHYL-	56	PHENOL, 2, 4-DIMETHYL-
6	CYANICACID, PROPYLESTER	57	UNDECANE, 2, 6-DIMETHYL-
7	CYANICACID, PROPYLESTER	58	1, 3, 6-OCTATRIENE, 3, 7-DIMETHYL-
8	AZETIDINE	59	1, 3, 6-OCTATRIENE, 3, 7-DIMETHYL-
9	CYCLOHEXANE, 1, 1, 3-TRIMETHYL-	60	QUINOLINE
10	CYCLOHEXANE, 1, 1, 3-TRIMETHYL-	61	1, 3, 6-OCTATRIENE, 3, 7-DIMETHYL-
11	BENZENE, ETHYL-	62	BENZENE, (3-METHYL-2-BUTENYL)-
12	BENZENE, 1, 3-DIMETHYL-	63	INDAN, 5, 6-DIMETHYL-
13	2-CYCLOPENTENE-1-THIONE, 3-METHYL-	64	NAPHTHALENE, 2-METHYL-
14	NOT IDENTIFIED	65	1H-INDAZOLE, 4, 5, 6, 7-TETRAHYDRO-7-METHYL-
15	BENZENE, 1, 3-DIMETHYL-	66	TRIDECANE
16	ACETICACID, \ (AMINOCARBONYL) AMINO\OXO-	67	NAPHTHALENE, 2-METHYL-
17	ACETICACID, \ (AMINOCARBONYL) AMINO\OXO-	68	UNDECANE, 2-METHYL-
18	OXIRANE	69	1, 4-BUTANEDIOL, 2, 3-BIS(METHYLENE)-
19	OXIRANE	70	2, 5-CYCLOHEXADIEN-1-ONE, 3, 4, 4-TRIMETHYL-
20	ACETICACID, \ (AMINOCARBONYL) AMINO\OXO-	71	DODECANE, 2, 6, 11-TRIMETHYL-
21	OCTANE, 2, 6-DIMETHYL-	72	BENZENE, PROPOXY-
22	BENZENE, 1-ETHYL-2-METHYL-	73	NAPHTHALENE, 2-ETHYL-
23	BENZENE, 1, 3, 5-TRIMETHYL-	74	BENZENE, (METHYLSULFONYL)-
24	BENZENAMINE	75	BUTANE, 2-1000-2-METHYL-
25	4-HEPTEN-3-ONE, 5-ETHYL-2-METHYL-	76	NAPHTHALENE, 2, 3-DIMETHYL-
26	4-HEPTEN-3-ONE, 5-ETHYL-2-METHYL-	77	NAPHTHALENE, 2, 3-DIMETHYL-
27	OXIRANE	78	BENZENE, (METHYLSULFONYL)-
28	BENZENE, 1, 2, 4-TRIMETHYL-	79	NAPHTHALENE, 1, 3-DIMETHYL-
29	PENTANAL	80	NOT IDENTIFIED
30	ACETAMIDE, N-(1-METHYLPROPYL)-	81	QUINOLINE, 2, 4-DIMETHYL-
31	ACETAMIDE, N-(1-METHYLPROPYL)-	82	QUINOLINE, 2, 4-DIMETHYL-
32	ACETAMIDE, N-(1-METHYLPROPYL)-	83	2(3H)-NAPHTHALENONE, 4, 4A, 5, 6, 7, 8-HEXAHYDRO-
33	ACETAMIDE, N-(1-METHYLPROPYL)-	84	TETRADECANE
34	BENZENE, 1, 2, 3-TRIMETHYL-	85	QUINOLINE, 2, 3, 4-TRIMETHYL-
35	1H-INDENE, 2, 3-DIHYDRO-	86	NAPHTHALENE, 2, 3, 6-TRIMETHYL-
36	BENZENE, 1-METHYL-4-PROPYL-	87	BENZOFURAN, 4, 7-DIMETHYL-
37	BENZENAMINE, 4-METHYL-	88	1H-PYRAZOLE, 4, 5-DIHYDRO-1-PHENYL-
38	BENZENAMINE, 4-METHYL-	89	QUINOLINE, 2, 3, 4-TRIMETHYL-
39	ETHANONE, 1-(METHYLPHENYL)-	90	1H-BENZIMIDAZOLE, 2, 5-DIMETHYL-
40	2-BUTANAMINE, N-(1-METHYLPROPYL)-	91	BENZALDEHYDE, 2-HYDROXY-4-METHOXY-6-METHYL-
41	3-PIPERIDINOL, 6-METHYL-	92	HEXADECANE
42	UNDECANE	93	1H-PYRAZOLE, 4, 5-DIHYDRO-3-PHENYL-
43	3-NONYNE	94	2-CYCLOHEXEN-1-ONE, 3-METHYL-
44	CYANICACID, PROPYLESTER	95	2(1H)-PYRIDINONE, 4-PHENYL-
45	1H-INDENE, 2, 3-DIHYDRO-5-METHYL-	96	1H-PYRAZOLE, 4, 5-DIHYDRO-3-PHENYL-
46	BICYCLO\3, 2, 0\HEPT-6-ENE	97	1H-PYRAZOLE, 4, 5-DIHYDRO-3-PHENYL-
47	1H-INDENE, 2, 3-DIHYDRO-4-METHYL-	98	1, 8-(EPOXYMETHANO)-2, 7-METHANODIBENZO\A, E\
48	BENZENE, (1, 1-DIMETHYLETHYL)-		CYCLOBUTA\O\CYCLOOCTEN-13-
49	NOT IDENTIFIED	99	NONANE, 2-METHYL-
50	BICYCLO\4, 1, 0\HEPTANE, 2-METHYL-	100	PYRAZOL\1, 5-ALPYRIDINE, 2, 3, 7-TRIMETHYL-
51	BENZENE, (1, 1-DIMETHYL-2-PROPENYL)-	101	2H-1-BENZOPYRAN-2-ONE, 3-METHYL-
		102	BIPHENYLENE, 1, 2, 3, 6, 7, 8, 8A, 8B-OCTAHYDRO-, TRANS-

sample. Although GC/MS was not used on the hot water basin sample, it is evident from Figure 6.6-5 that most of the lower molecular weight aromatics present in the makeup water have been lost.

GC traces for the acid extracts of makeup water and hot water basin samples are shown in Figure 6.6-6. In comparing the traces, note that the hot water sample was three times as concentrated, and its trace was one-tenth as attenuated, as the makeup water sample. The presence of neutral components (n-alkanes) in the sample is probably due to their high concentrations in the water and to the use of the continuous liquid-liquid extractor. The GC traces show a greater abundance of phenols in the makeup water and a larger unresolved complex mixture in the circulating water. The results of a GC/MS library search on the acid extract of the makeup water are shown in Table 6.6-6. The major components were phenol and dimethylphenol, whose concentrations were 28 and 16 ppb, respectively.

Legionella Assay

According to the Centers for Disease Control, the cold water basin samples were negative for Legionella pneumophila (Neill, 1981).

6.7 TASK 3 SAMPLING AT INDUSTRIAL TOWER NO. 2

6.7.1 Site Description and Sampling Conditions

Task 3 sampling was performed on 6 December 1979 on a two-cell crossflow cooling tower at a large industrial facility. The tower, which was built by Pritchard in 1969, has a nominal circulating water rate of $1.26 \text{ m}^3/\text{s}$ (20,000 gpm), and is the only one in this study with forced draft. The only chemical added is chlorine, which is slug fed to the cold water basin for 12 hours on Mondays, Wednesdays and Fridays. Chlorine had last been added at 2130 hours on the night before our sampling. The test day was warm and hazy. To the best of our knowledge, the tower was operating normally. There was no appreciable wind.

6.7.2 Procedures

Water samples were collected roughly on the half hour from 0830 to 1530 hours by SAI staff. Makeup water samples were taken from a tap in a line leading from a clarifier. Hot and cold water basin samples were collected from taps on the risers and return pipes, respectively. At 1430, additional

Table 6.6-6

COMPOUNDS IDENTIFIED THROUGH GC/MS ANALYSIS OF ACID EXTRACT OF MAKEUP WATER,
INDUSTRIAL COOLING TOWER NO.1, 5 AUGUST 1980 SAMPLING

NO	NAME	53	ISOOCTANOL
1	NOT IDENTIFIED	54	UNDECANE
2	NOT IDENTIFIED	55	1-HEXENE, 3, 5, 5-TRIMETHYL-
3	CYCLOTRISILOXANE, HEXAMETHYL-	56	NAPHTHALENE, 1, 2-DIMETHYL-
4	CYCLOTRISILOXANE, HEXAMETHYL-	57	NAPHTHALENE, 2, 7-DIMETHYL-
5	CYCLOTRISILOXANE, HEXAMETHYL-	58	PENTANOICACID, 4, 4-DIMETHYL-3-METHYLENE-, ETHYLESTER
6	OXIRANE	59	1-PENTANOL, 4-METHYL-2-PROPYL-
7	OXIRANE	60	DECANE, 2-METHYL-
8	L-LEUCINE, ETHYLESTER	61	OXIRANE, (3, 3-DIMETHYLBUTYL)-
9	L-LEUCINE, ETHYLESTER	62	1-PENTANOL, 4-METHYL-2-PROPYL-
10	2-PROPANAMINE	63	CYCLOPENTANE, 1, 1, 3-TRIMETHYL-
11	PHENOL	64	DODECANE
12	ACETAMIDE, N-(1-METHYLPROPYL)-	65	NAPHTHALENE, 1, 3, 6-TRIMETHYL-
13	HEPTANE, 2, 5, 5-TRIMETHYL-	66	NAPHTHALENE, 1, 3, 6-TRIMETHYL-
14	PHENOL, 2-METHYL-	67	NAPHTHALENE, 1, 3, 6-TRIMETHYL-
15	PHENOL, 3-METHYL-	68	NAPHTHALENE, 1, 3, 6-TRIMETHYL-
16	CYCLOPENTANECARBONITRILE, 2-IMINO-	69	CYCLOHEXANEMETHANOL
17	UNDECANE	70	BICYCLO[3. 1. 1]HEPTAN-3-ONE, 2, 6, 6-TRIMETHYL-, (1. ALPHA., 2. BETA., 5. ALPH
18	NOT IDENTIFIED	71	1-NONENE, 4, 6, 8-TRIMETHYL-
19	PHENOL, 2-ETHYL-	72	17-PENTATRIACONTENE
20	PHENOL, 3, 4-DIMETHYL-	73	OCTANE, 2, 4, 6-TRIMETHYL-
21	PHENOL, 3, 4-DIMETHYL-	74	P-MENTH-8(10)-EN-9-OL, CIS-
22	PHENOL, 3, 4-DIMETHYL-	75	2, 6-PYRAZINEDIAMINE
23	PHENOL, 3, 4-DIMETHYL-	76	1, 4-UNDECADIENE, (Z)-
24	1-PENTANOL, 4-METHYL-2-PROPYL-	77	UNDECANE, 3, 6-DIMETHYL-
25	PHENOL, 3, 5-DIMETHYL-	78	UNDECANE, 3, 8-DIMETHYL-
26	1-DODECYNE	79	1-PENTANOL, 4-METHYL-2-PROPYL-
27	PHENOL, 3, 5-DIMETHYL-	80	CYCLOPENTANE, 1, 1, 3-TRIMETHYL-
28	2-NONENAL, (E)-	81	BICYCLO[3. 1. 1]HEPTAN-3-ONE, 2, 6, 6-TRIMETHYL-, (1. ALPHA., 2. BETA., 5. ALPH
29	PHENOL, 3, 4-DIMETHYL-	82	UNDECANE, 4, 7-DIMETHYL-
30	NONANE, 2-METHYL-	83	OCTANE, 2-BROMO-
31	1-HEPTANOL, 6-METHYL-	84	1, 4-UNDECADIENE, (Z)-
32	UNDECANE, 2, 6-DIMETHYL-	85	6-TRIDECENE, 7-METHYL-
33	CYCLOPENTANE, 1, 1, 3-TRIMETHYL-	86	CYCLOPENTANE, (2-METHYLBUTYL)-
34	BENZOTHIADZOLE	87	1-NONENE, 4, 6, 8-TRIMETHYL-
35	1-PENTYN-3-OL, 4-METHYL-	88	1-PENTANOL, 4-METHYL-2-PROPYL-
36	CYCLOPENTANE, 1-ETHYL-3-METHYL-, CIS-	89	OCTADECANE, 1-(ETHENYLOXY)-
37	CYCLOPENTANE, 1-ETHYL-3-METHYL-, CIS-	90	D-10 PHENANTHRENE (I. S.)
38	ISOOCTANOL	91	PHENANTHRENE
39	NOT IDENTIFIED	92	1H-BENZIMIDAZOL-4-OL, 5-METHOXY-1-(PHENYLMETHYL)-
40	PHENOL, 4-ETHYL-2-METHYL-	93	CYCLOPENTANE, 1, 1, 3-TRIMETHYL-
41	PHENOL, 3-ETHYL-5-METHYL-	94	PENTADECANE
42	OCTANE, 2, 3, 7-TRIMETHYL-	95	NOT IDENTIFIED
43	PHENOL, 2-ETHYL-5-METHYL-	96	UNDECANE, 3, 8-DIMETHYL-
44	NAPHTHALENE, 2-METHYL-	97	1-PENTANOL, 4-METHYL-2-PROPYL-
45	CYCLOPROPANE, 1-METHYL-2-(3-METHYLPENTYL)	98	UNDECANE-6-CYCLOHEXYL-, 6-CYCLOHEXYL-
46	CYCLOPROPANE, 1-METHYL-2-(3-METHYLPENTYL)	99	1-PENTANOL, 2-ETHYL-4-METHYL-
47	UNDECANE, 4, 7-DIMETHYL-	100	HEPTADECANE
48	TRIDECANE, 6-METHYL-	101	PHENANTHRENE, 2-METHYL-
49	OCTANE, 2, 7-DIMETHYL-	102	1, 2-BENZENEDICARBOXYLICACID, DIBUTYLESTER
50	1-PENTANOL, 2-ETHYL-4-METHYL-		
51	NONANE, 3, 7-DIMETHYL-		
52	1-DECENE, 8-METHYL-		

samples of makeup and cold water basin water were collected for Legionella assay. Sampling and analysis procedures were as described in Section 6.2.

6.7.3 Results and Discussion

General Observations

All water samples were light brown or gray-brown and rather turbid. Basin samples were observed to have considerable particulate matter.

Temperature, pH and Chlorine

Figure 6.7-1 shows measured values of temperature and pH. Results are plotted to the nearest 15 minutes on the time axis. Total residual chlorine concentrations were all below 0.1 ppm; given the difficulty of establishing an end point at such low concentrations, individual values are not shown in the figure.

Inorganic Constituents

Given the nature of the industrial processes from which the makeup water was derived, it was believed that chromium and iron would be the only inorganic species of interest. Table 6.7-1 shows the results of our analyses of hot and cold water basin samples for these metals, total suspended solids, total dissolved solids and conductivity. As seen, the circulating water has lower concentrations of dissolved solids than do the other towers measured in this study. The USEPA/MERL's analyses of the cold water basin samples showed Na^+ , K^+ , Mg^{++} , and Cl^- concentrations to be 47, 5.1, 8.0 and 43 ppm, respectively (Broome, 1980). Since the same laboratory found makeup water chloride to be at 21 ppm, only about 1.7 cycles of concentration are achieved in this tower.

Organics

All volatile organic compounds for which we had standards were below detectable limits in all the water samples from this tower. Analysis of the water for nonvolatile organics showed two unidentified compounds having 14 and 16 carbons, respectively; neither was a pesticide or other priority pollutant. Total concentrations of nonvolatiles were negligible.

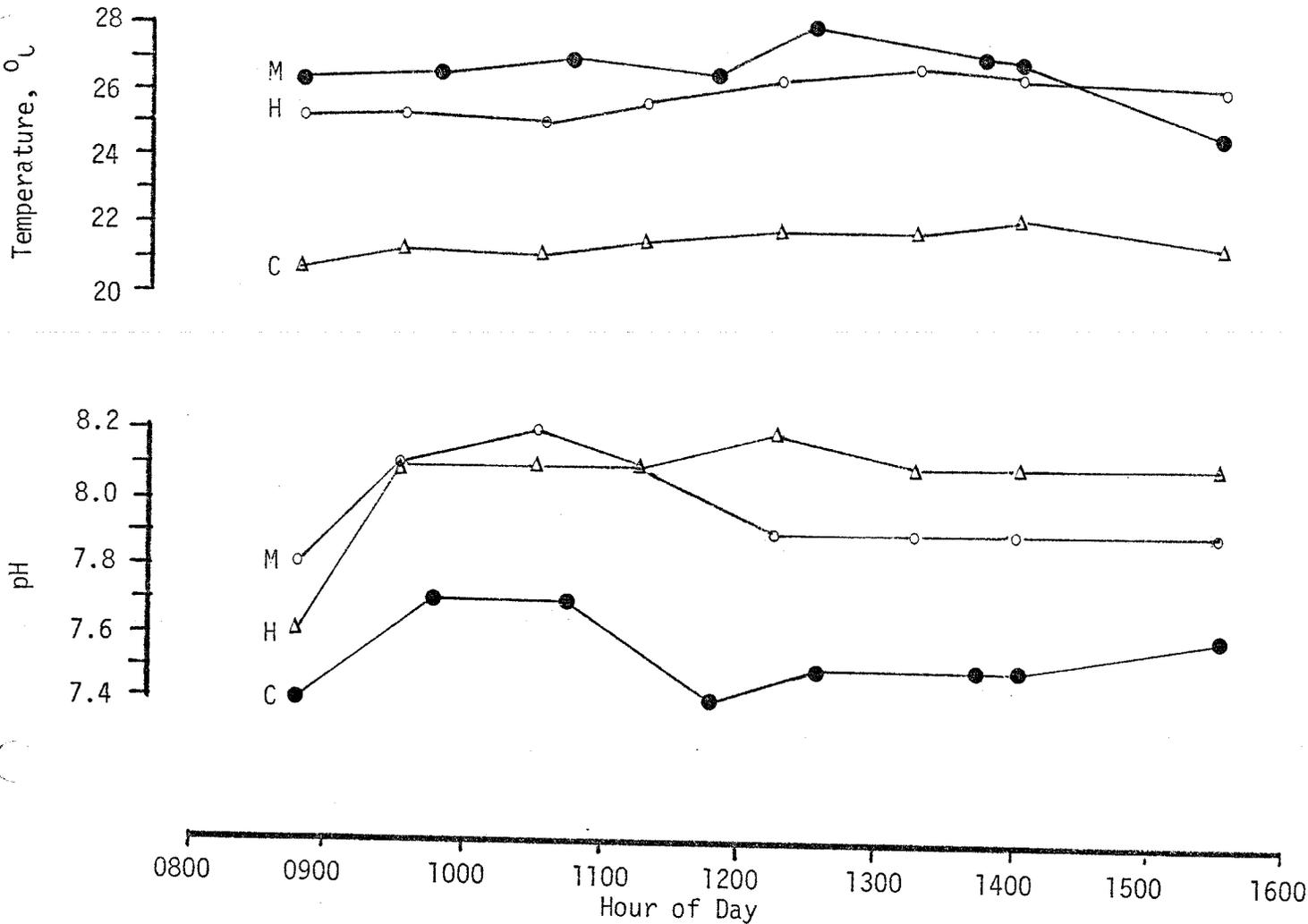


Figure 6.7-1. Temperature and pH, Industrial Cooling Tower No.2, 6 December 1979 Sampling.

Table 6.7-1
 INORGANIC CONSTITUENTS IN INDUSTRIAL
 COOLING TOWER NO. 2 WATER,
 6 DECEMBER 1979 SAMPLING

Constituent	Concentration in ppm ^a	
	Hot Water Basin	Cold Water Basin
Chromium	0.002	0.002
Iron	0.103	0.108
Total Suspended Solids	14.0	17.7
Total Dissolved Solids	272	294
Conductivity ($\mu\text{mho/cm}$)	380	409

^aMetal and TDS concentrations are for filtrate only.

Legionella Assay

According to the Centers for Disease Control, the cold water basin sample analyzed was positive for a serogroup 5 Legionella pneumophila (Broome, 1980). This finding was reported by the CDC to State and local health authorities, and it was planned to conduct emissions tests for Legionella as part of our Task 4 sampling. However, as will be explained in Chapter 7, testing protocols could not be developed in time.

6.8 TASK 3 SAMPLING AT GEOTHERMAL TOWER

6.8.1 Site Description and Sampling Conditions

Task 3 sampling was conducted on 23 January 1980 on a five-cell, mechanical draft, crossflow cooling tower serving a geothermal electric power plant. The tower, which is oriented southeast to northwest, has a nominal circulating water rate of $4.94 \text{ m}^3/\text{s}$ (78,300 gpm). The Stretford desulfurization plant associated with the tower was not operating, and noncondensable gases were injected into the north side of the tower, about 5 m from the ground. The sampling day was clear and warm. Winds were light, but there were occasional strong gusts. Cooling tower plumes rose vertically.

6.8.2 Procedures

Samples of hot and cold water basin water were collected by SAI staff on the hour from 1100 through 1700. The hot water collection point was a trough accessible from a hatch in the deck just north of the cell on the southeast end of the tower. Cold water basin samples were collected from the basin under the same cell; access was by means of a wooden walkway through the tower's plenum chamber. At 1400 and 1600 hours, samples of steam condensate were taken from a tap in the turbine building.

6.8.3 Results and Discussion

General Observations

As expected, there was a strong odor of H_2S above the hot water trough. Although the circulating water flow was greater than for most of the other towers sampled in this project, the apparent amount of drift was quite low.

Temperature and pH

Since temperature and pH varied only slightly during the test day, their measured values are reported in Table 6.8-1, rather than in a figure. Chlorine is not added to the tower, and thus was not measured. Of all the towers measured in this project, this one had the highest hot water basin temperature, as well as the greatest difference between hot and cold water temperatures.

Inorganic Constituents

The results of our analyses of hot and cold water basin and steam condensate samples for inorganic constituents are shown in Table 6.8-2. Note that analyses were performed on both filtrate and the particulate matter remaining on the filters so that the extent of partitioning between aqueous and solid phases could be ascertained. Our measured concentrations are reasonably close to those reported for earlier measurements at this tower. Our arsenic concentrations of about 0.5 ppm are similar to the values of 0.53 and 0.30 ppm measured by Robertson, et al. (1981) in June 1979 and on our test day, respectively. However, almost all of the arsenic we measured was in dissolved form, while a Battelle Pacific Northwest Laboratories study cited by Enriquez (1978) found all but a small fraction of the arsenic to be in particulate form. Our values for total mercury are quite similar to those reported by Robertson et al. (1977 and 1981), but the partitioning between aqueous and particulate phases differs. In Section 5.3.1 we presented reasons why most of the mercury in the steam condensate should be aqueous, yet in our analysis almost all of it was in particulate form. On the other hand, our findings echo those of Robertson et al. (1977) for the circulating water; most of the mercury is again in the solid fraction.

6.9 IMPLICATIONS FOR TASK 4 (STACK TESTING)

As will be discussed in Chapter 8, many of the results of our water sampling program can be used directly to estimate atmospheric emissions from cooling towers which reuse wastewater. To identify and quantify other types of emissions required direct sampling of cooling tower stack exhausts. In designing our stack testing program (Task 4), we used two guidelines:

- (1) Would stack testing provide information which would not be obtained otherwise

Table 6.8-1

MEASURED TEMPERATURE AND pH AT GEOTHERMAL
COOLING TOWER, 23 JANUARY 1980 SAMPLING

Nominal Hour of Day	Hot Water Basin		Cold Water Basin		Condensate	
	Temp. °C	pH	Temp. °C	pH	Temp. °C	pH
1100	38.5	7.8	25.7	7.75		NM ^a
1200	39.6	7.85	27.5	7.8		NM
1300	39.6	7.8	27.2	7.75		NM
1400	40.5	7.8	27.1	7.8		5.6
1500	40.2	7.75	27.4	7.8		NM
1600	40.5	7.7	27.7	7.8		5.55
1700	40.1	NM	27.4	NM		NM

^aNM = Not Measured.

Table 6.8-2

INORGANIC CONSTITUENTS IN GEOTHERMAL COOLING TOWER WATER,
23 JANUARY 1980 SAMPLING

Constituent	Units of Concentration	Hot Water Basin		Cold Water Basin		Condensate	
		Filtrate	Part.	Filtrate	Part.	Filtrate	Part.
Arsenic	ppb	474	2	479			
Cadmium	ppb	<0.2	0.2	<0.2			
Chromium	ppb	2	1	3			
Copper	ppb	1	3	2		9	
Lead	ppb	<1	<1	<1	3		
Mercury	ppt	30	5200	<3		266	23000
Selenium	ppb	<5	<5	<5			
Zinc	ppb	2	<0.2	7			
Ammonia	ppm	59.3		62.8		136	
Hydrogen Sulfide	ppm	1.62		0.87		130	
Tot. Susp. Sol.	ppm	1.70		1.90		9.10	
Tot. Diss. Sol.	ppm	606	-	434	-	233	

- (2) Would such testing be physically feasible, within the limitations of project resources?

A key consideration was the medium to be sampled. Cooling tower exhausts are complex mixtures of water vapor-laden air, organic vapors, water droplets of various sizes, dissolved and particulate salts, and encapsulated and free floating microorganisms. As will be discussed in detail in Section 7.2 and Appendix C, collection of enough drift water during one sampling day for all chemical and microbiological analyses of interest was not feasible. It was therefore necessary to set priorities for the use of any water collected. On the other hand, collection of organic vapors was relatively simple, and was conducted wherever applicable. The following subsections briefly describe our rationale for selecting the cooling tower water constituents to be sampled in stack exhaust.

6.9.1 Organic Compounds

Our water sampling program showed that several organic substances of interest, including benzene and halocarbons, were present in cooling tower makeup and recirculating water. It was originally hoped that accurate circulating water rate data could be obtained for use in a mass balance calculation. However, none of the tower operators had such data, and it was felt that, given the great day-to-day variability in tower heat load, even an extremely accurate measurement on one day would be inapplicable on another occasion. While known nominal flow rates could be used to estimate maximum potential emissions, it was clear that only a stack testing program could verify that species of interest were actually released to the atmosphere. Since sampling for airborne volatile organics was relatively straightforward, these substances were included in the testing program.

Analysis of nonvolatile organics, on the other hand, would require collection of drift water samples, since by definition these compounds could enter the atmosphere only as constituents of entrained water droplets. Task 3 sampling showed that nonvolatile organic concentrations were very low in five of the six towers. The only tower to have appreciable nonvolatiles (Industrial Tower No. 1) was observed during Task 3 testing to have a very low drift rate, so that collection of substantial water samples would not be feasible. We therefore decided to exclude nonvolatile organics from the Task 4 testing program.

6.9.2 Inorganic Constituents

Towers Using Municipal Wastewater

None of the three municipal wastewater-using towers contained enough metals of interest to make stack testing desirable. In addition, as our experience ultimately showed, it would have been infeasible to collect enough water for both microbiological and inorganic chemical analyses from these towers, and the former had higher priority. As an alternative, we used modeling to estimate maximum metal concentrations around one cooling tower, given their concentrations in the makeup and circulating water (see Section 8.5).

Towers Using Industrial Wastewater

Except for chromium in Industrial Tower No. 1, metal concentrations in these two towers were generally lower than in the circulating water of the towers using municipal wastewater. As noted above, the drift rate for Industrial Tower No. 1 was too low to allow for collection of enough water for sampling. Because the chromium in this tower was due to addition of a chromate corrosion inhibitor, rather than presence of chromium in wastewater used for makeup, emissions for this tower were not modelled.

Tower Using Geothermal Steam Condensate

For this tower, the chief metals of concern, arsenic and mercury, were found to be largely in particulate form. Because it was reasonably convenient in this case to collect these metals in both aqueous and particulate form, they were included in the stack testing. Hydrogen sulfide and ammonia emissions were also of great concern and relatively easy to measure, so they were also included.

6.9.3 Bacteria and Virus

Before this project, no one had collected microorganisms isokinetically from cooling tower stacks. Because pathogenic emissions were of primary concern to both the Air Resources Board and the Energy Commission, we developed special equipment to collect and keep alive indicator bacteria and virus. Both suspended and free-floating organisms were collected. We also added cascade impactor sampling of ambient airborne bacteria and virus.

6.10 REFERENCES

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COOLING TOWER EMISSIONS TESTING

7.1 INTRODUCTION

7.1.1 Objectives and Scope

The objectives of this portion of the research were to verify that potential airborne pollutants of concern were indeed emitted from the cooling towers at which waters were sampled, and, to the extent possible, to obtain data with which to quantify these emissions. Table 7.1-1 lists the towers at which stack testing was performed, along with the chemical and microbiological species we attempted to collect.

Two towers were dropped from the study. Analysis of water samples from Industrial Tower No. 2 had shown negligible concentrations of volatile and nonvolatile organics, and relatively low concentrations of metals. Indeed, the only finding of interest was a positive assay for Legionella pneumophila in the cold water basin. The Task 4 sampling plan for this tower was therefore changed to delete stack tests for organics and metals, and substitute downwind ambient sampling for Legionnaires' Disease bacterium. During December 1980 and January 1981, numerous discussions were held with staff of the Centers for Disease Control (CDC) to design sampling protocols. Arrangements were made with the tower operator to conduct tests in March 1981. Then, in February 1981, the CDC informed us that it was withdrawing its support from the sampling effort, since it wanted to conduct further laboratory tests of the recoverability of Legionella by the method that SAI was to use (Band, 1981).

The other tower deleted from Task 4 was Municipal Tower No. 3 (Glendale). As a result of delays in testing our microbiological stack sampler (see Appendix C), we were not ready to conduct Task 4 tests at Glendale until February 1981. On 13 February we learned that the phosphate treatment plant associated with the Glendale Public Service Department power plant had been out of service for a few weeks (Boothe, 1981). Because the municipal wastewater could not be used without phosphate removal, the cooling towers were operating on fresh water. Repair work did not begin until July 1981. Since the towers would not return to wastewater use in time for us to conduct our emissions tests (Shattuck, 1981), this facility had to be dropped.

Table 7.1-1
COOLING TOWERS TESTED IN TASK 4

Tower Designation	Sampling Date	Constituents Basin	Sampled Stack
Municipal Tower No. 1	29-30 April 1981 ^a	Microorganisms, Volatile organics	Microorganisms, ^c Volatile organics
Municipal Tower No. 2	3 - 4 February 1981 ^b	Microorganisms, Volatile organics	Microorganisms, Volatile organics
Industrial Tower No. 1	22 January 1981	Volatile organics	Volatile organics
Geothermal Tower	9 July 1981	Hydrogen sulfide, Ammonia, metals	Hydrogen sulfide, Ammonia, mercury

^aSupplementary test made on 20 November 1980; see text.

^bSupplementary test made on 30 June 1981; see text

^cAmbient bacterial aerosols also sampled.

7.1.2 Procedures

Procedures for collection and analysis of makeup and basin water samples were generally the same as for the Task 3 sampling (see Section 6.2). Since the Fischer-Porter amperometric titrator was no longer available, chlorine analysis was done by the leuco crystal violet method, Standard Method 409 G (APHA et al., 1976).

In order to estimate exhaust air flow rates, velocity traverses were made on both municipal towers and the industrial tower. (Traverse data for the geothermal tower were available from the operator.) To measure exhaust velocity, the vane of an Ota Keiki Model 29-DGDC digital air velocity meter was suspended at various points along one or two diameters of the fanstack. Because the air flow was quite turbulent, meter readings fluctuated considerably. Therefore, our procedure was to maintain the vane at one position for at least three minutes and to note a range of velocities in which about 90 percent of the readings fell. Readings were accurate to 0.1 m/s. A slender piece of tape was attached to the vane to indicate the direction of flow.

Organic vapor samples were collected by drawing air through Tenax traps with a vacuum pump. Air flow rates were determined by the falling soap film method. Backup traps were used in all cases. For Municipal Tower No. 1, the traps were attached to a special sampling port in the SAI microbiological stack sampler (see below). At Municipal Tower No. 2 and Industrial Tower No. 1, the traps were affixed to the fanstack, such that their open ends extended to the point of maximum upward air velocity. In all three cases, ambient air samples were taken at the base of the tower, where air is drawn through the louvers. Tenax traps were heat desorbed, and the collected vapors were analyzed by gas chromatography.

Special sampling trains for collection of hydrogen sulfide, ammonia and mercury were designed for use at the geothermal tower. These systems, along with the analytical techniques used, are described in detail in Section 7.6.2 below.

To collect indicator bacteria and virus from cooling tower exhaust, the SAI microbiological stack sampler was suspended at one or two positions and run for several hours. Procedures for recovery of microorganisms from the

internal parts of the sampler are discussed in detail below and in Appendix C. Samples of drift and washings were analyzed by Morning Star Laboratories by the same methods used for basin and makeup water analysis.

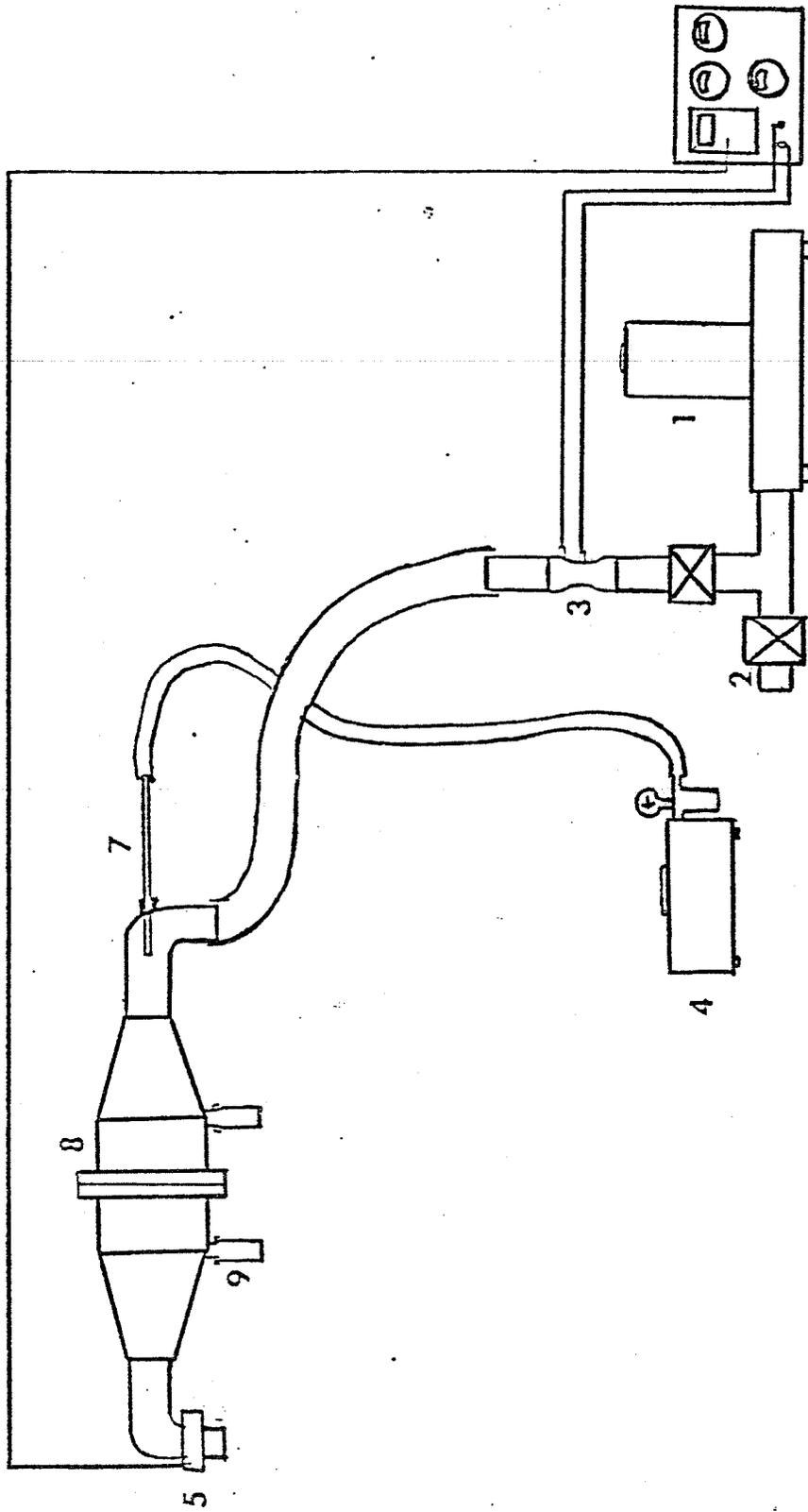
Finally, at Municipal Tower No. 1, two six-stage viable particle sizing samplers (Andersen Samplers Inc., Atlanta, Georgia) were used to collect ambient aerosol samples on the tower deck and at the base. On different runs, the sampler heads were loaded with plates coated with tryptic soy agar, KF streptococcus agar, and MacConkey's agar, for subsequent analysis of total bacteria count, fecal streptococcus, and total coliforms, respectively. All plates were incubated at 35 °C. Incubation times were 48 hours for the total bacteria count and fecal streptococcus and 24 hours for the total coliforms.

7.2 THE SAI MICROBIOLOGICAL STACK SAMPLER

One of the requirements of this project was to collect isokinetic samples of microorganisms emitted from the towers using reclaimed municipal wastewater. To this end, SAI designed, built, tested and used a stack sampling device. Details of our design and testing experience are provided in Appendix C. In this section we describe the instrument and its use.

7.2.1 Description of the Sampler

Figure 7.2-1 shows a schematic of the SAI microbiological stack sampler system. Air is pulled into the filter holder by means of a 3-hp Gast Ram II blower (Model S65-102-J700X) equipped with a Barco 1 1/2 - 427 Series V1 venturi air flow measurement system. Figure 7.2-2 shows the filter holder, which is made of stainless steel. The inlet, which is positioned perpendicular to the exhaust air flow, has a diameter of 5.08 cm (2 in). After passing through an elbow joint and into the 11.43-cm (4.5-in) cross-sectional area of the central portion of the device, the cooling tower air, whose velocity has been reduced by 80.2 percent, strikes three filter pads in series. The pads are composed of interwoven filaments of polypropylene and polyvinylidene fluoride resin (Kimre, Inc., Perrine, Florida), and are normally used as mist eliminators in chemical processes and as drift eliminators in cooling towers. The pad section is 16.5 cm (6.5 in) thick. Water droplets striking the filters flow to holes in the bottom of the sampler and then into 50-ml glass flasks.



- 1 - Blower: Gast Ram II Regenerative Blower Model S65-102-J700X 220v 10.6 amp sgl phase.
- 2 - Valves: Batterball Butterfly Valve, 2" Gast Service Milwaukee Valve Co.
- 3 - Venturi: Barco 1½-427 Series V1 (Bronze) Beta ratio of 0.427.
- 4 - Air Pump: Gast Rotary Vane Pump, Model 0522-V4B-G180DX 115v 6.0 amp single phase
- 5 - Air Velocity Meter: Weathertronics Digital Air Meter, Model 2430 115v 5 watts.
- 6 - Gauges: Dwyer Series 2000 Magnehelic Differential Pressure Gauge. 0-3 in W.C. 0-15 in. W.C., 0-50 in. W.C.
- 7 - Gas Trap: Tubing packed with Tenax. .125" O.D., .09" I.D.
- 8 - Filter Bank: Kon-Tane Tower Packing 6.5" deep, 4.5" dia.
- 9 - Collecting Bottles: 50 ml Kimble centrifuge tube.

Figure 7.2-1. SAI Microbiological Stack Sampler System

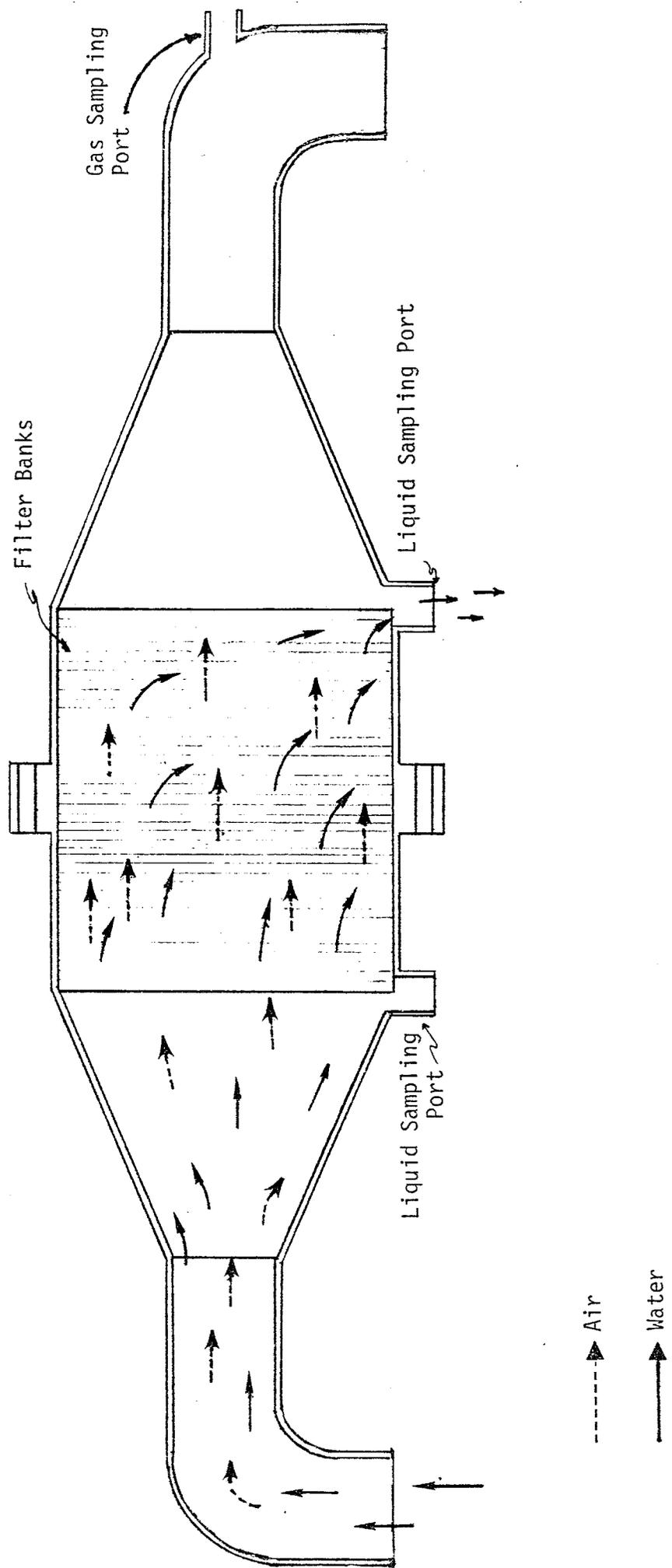


Figure 7.2-2. Interior of Filter Holder, SAI Microbiological Stack Sampler.

Downstream from the filter assembly, a sampling port for installation of Tenax traps is provided. A set of wheels, which allow the sampler to move back and forth along a track suspended over the fanstack, are clamped to the top of the device. Finally, the vane of the digital air velocity meter is attached to the inlet so that an intake flow rate corresponding to isokinetic sampling may be determined.

7.2.2 Sampling Protocol

The entire sampler, along with all auxiliary glassware, was autoclaved at SAI's La Jolla laboratories before each use. At the sampling site, a steel rail was assembled and placed on a diameter of the fanstack to be sampled. The velocity traverse was then made with the vane attached to the sampler, and the position of maximum upward velocity was determined. The sampler was stationed at this point. The blower was then adjusted so that flow into the sampler was isokinetic. Sampling time varied with each tower.

At the end of the sampling period, the blower was turned off and the glass vials were disconnected. Water collected therein was immediately transferred to sterile glass bottles containing $\text{Na}_2\text{S}_2\text{O}_3$ (to reduce any residual chlorine). The holes where the vials had been connected were closed with autoclaved Teflon plugs. The sampler was then removed from the fanstack and disconnected from the blower hose.

Since laboratory tests (see Appendix C) had shown that viable organisms adhere to the filter material, the sampler was washed with approximately 100 ml of sterile phosphate buffer solution prepared by Standard Method 905 C (APHA et al., 1976). Washings were collected in a 1-L autoclaved beaker. The sampler was then opened and the filters were removed with tweezers. Each filter was dipped in the washing solution and then shaken vigorously above the water surface until all visible water droplets had transferred to the beaker. The beaker solution was measured and transferred to autoclaved 236-ml, metal-capped plastic bottles pretreated with 10 mg of $\text{Na}_2\text{S}_2\text{O}_3$.

7.3 TASK 4 SAMPLING AT MUNICIPAL TOWER NO. 1 (BURBANK/OLIVE 1)

Task 4 sampling was conducted at Municipal Tower No. 1 on two occasions. The main purpose of the first visit, which was made on 20 November 1980, was to field-test the SAI microbiological stack sampler. In addition,

we collected hourly samples of makeup and circulating water, so that indicator bacteria levels could be correlated with concentrations of pathogens in samples collected concurrently by the UC Davis team. The organic vapor sampling system was also tested. The field test of the sampler revealed certain deficiencies in test protocol, which were corrected through the laboratory tests described in Appendix C. The second visit took place on 29-30 April 1981, and is the main subject of this section.

7.3.1 Site Description and Sampling Conditions

Although tests were made on the same tower as described in Section 6.3.1, weather conditions and the time of sample collection were quite different. In order to maximize drift water collection and avoid the toxic effects of ultraviolet radiation upon airborne microorganisms, we decided to perform the tests at night. The choice was fortunate, as the day of 29 April 1981 was hot, extremely dry, and moderately windy; the temperature in Los Angeles was a record 35 °C (95 °F). At night, however, a layer of cold marine air moved inland, lowering the temperature to about 15.5 °C (60 °C) and increasing the humidity.

7.3.2 Procedures

The afternoon of the 29th was spent erecting scaffolding, assembling the rail system, and preparing the drift sampler. The central stack of the five-stack tower was chosen for sampling. Given the need to hoist each piece of scaffolding, the blower, and other test equipment to the top of the tower; to assemble the rail system; and to place the rail in the proper position, it took about six hours to set up. A velocity traverse was then made along one diameter (out and back), from north to south. For microbiological and organic vapor sampling, the sampler was positioned at about half the fanstack radius. At that point, the average upward air velocity was 10.4 m/s. Due to an on-site calculation error, the blower was set such that the sampling rate was actually 11.8 m/s. The implications of nonisokinetic sampling are discussed in Section 7.3.3. The blower was run from 0000 to 0857 hours on 30 April. Thus the total sampling time was 537 minutes and the volume of air passing through the system was 770 m³.

Six-stage Andersen samplers were set up at two stations. The first was on the cooling tower deck, about 4 m from the base of the center fanstack.

The sampler inlet was about 0.6 m (2 ft) above the deck. The second location was about 3 m (10 ft) from the sloping, louvered west side of the tower, near the north end, and about 0.6 m (2 ft) above the ground. This "base" sampling site was chosen to characterize ambient air entering the tower. Although we had originally planned to collect an ambient sample farther upwind from the tower, variable winds made it difficult to identify a suitable site within reasonable distance. The Andersen sampler is designed to operate at an air flow rate of 0.028 m³/min (1.0 cfm). Air flow through the Andersen Model 11-000 pump was measured with a Rockwell T-110 dry gas meter having a resolution of 0.005 ft³. The minimum flow rate obtainable with our pump was 0.0298 m³/sec (1.012 cfm). This flow rate was taken into account in calculating the concentration of airborne bacteria. Since the size fractionation in this sampler depends upon air flow rate, the cutoff points for the different plates will vary somewhat from the standard Andersen calibration. The following airborne bacterial sampling runs were made:

<u>Run No.</u>	<u>Site</u>	<u>Selective Medium For</u>	<u>Hour of Day</u>	
4-3	Deck	Total bacterial count	0110	0122
4-1	Deck	Fecal streptococcus	0135	0206
3-3	Base	Total bacterial count	0315	0345
3-1	Base	Fecal streptococcus	0350	0420
4-2	Deck	Fecal coliform	0845	0950

Organic gas samples were collected on a Tenax trap (provided with a backup) installed in the sampling port at the rear of our stack sampler. An ambient sample was also obtained at the same point as the "Base" sample of ambient airborne bacteria. Stack and ambient sampling times were 145 and 140 minutes, respectively. Finally, water samples for microbiological, volatile organic, and inorganic analyses were collected from the makeup water inlet and the hot and cold water basins at 0130, 0630, 0815, and 1410 hours. Temperature measurements were made at the time of each collection. Chlorine was not measured on site; rather, additional samples were collected for analysis in our laboratory. Due to an equipment malfunction, pH readings were not made. The approximate chlorine water sample collection times were 0630, 0815, and 1410 hours.

7.3.3 Results and Discussion

General Observations

Water from all sources was similar in appearance and odor to that collected on our Task 3 sampling visit. Vapor plumes from the stacks were quite wispy and appeared to rise vertically. There was considerable fallout of large drift droplets on the tower deck.

Temperature and Chlorine

Results of our on-site temperature measurements and laboratory analyses of chlorine residual are shown in Table 7.3-1. Comparison of temperature data with those collected in our November 1979 sampling shows that the heat load on the tower was lower this time, especially during the early morning hours. This difference is understandable, since our Task 3 tests were made during the middle and late afternoon, when electricity use would be higher. Our chlorine results are less comprehensible. Hot and cold water basin values are all over 11 mg/L; in November 1979 the peak value (which lasted for about an hour) was 7 mg/L in the cold water basin. On the other hand, makeup water chlorine concentrations are within the range of those measured previously (2.1 to 5.2 mg/L in 1979), so that analytical errors may not be the cause for the discrepancy.

Fanstack Exhaust Air Flow Rate

Figure 7.3-1 shows the results of our velocity traverse measurements. Dots indicate the average velocities, while bars show the range of measurements at each point. Note that velocity measurements differed at 0.95, 1.91 and 2.86 m from the north end during the "out" and "back" traverses. The curve shown in the figure represents our best judgement as to the probable emission profile. It should be noted that visibility was quite poor (the traverse was made at night), and that the position of the velocity meter was observed from an acute angle. Therefore the positions between 2 and 6 m from the northern wall of the stack could be in error by as much as 1 m. The positive air flow rate was computed by the following formula:

$$Q_a = \sum \left(\frac{V_i + V_{i+1}}{2} \right) \frac{\pi}{n} \left| (r^2 - r_{i+1}^2) \right| \quad (7-1)$$

Table 7.3-1
 TEMPERATURE AND CHLORINE MEASUREMENTS AT
 MUNICIPAL COOLING TOWER NO.1, 30 APRIL 1981 SAMPLING

Hour of Day	Temperature (°C)		Cold Water Basin	Makeup	Chlorine (mg/L)	
	Hot Water Basin	Hot Water Basin			Hot Water Basin	Cold Water Basin
0630	23.2	24.1	19.4		. . . Not Measured . . .	
0815	22.0	26.5	19.7	2.02	11.4	13.6
1410	24.1	30.6	25.2	4.11	12.9	11.9

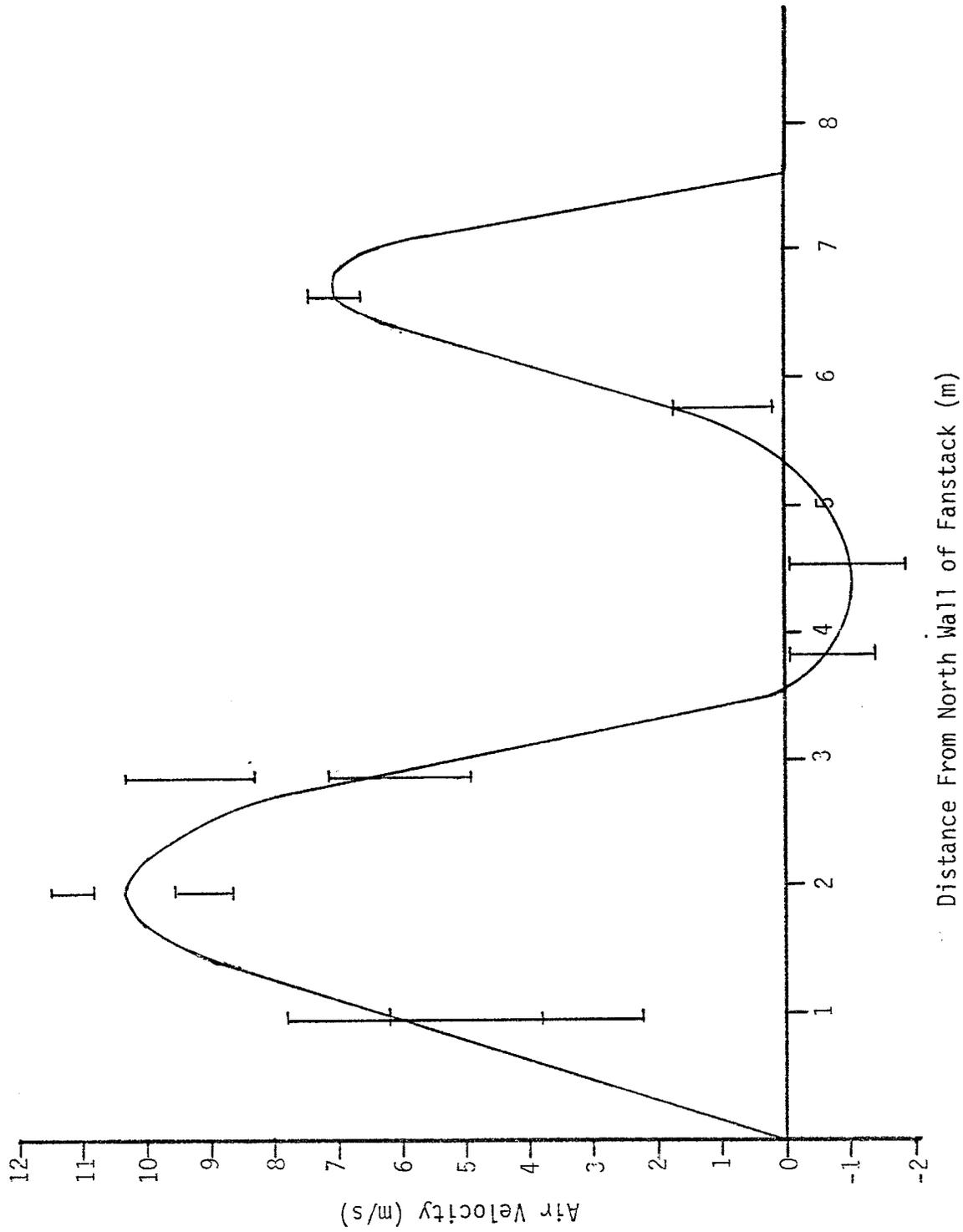


Figure 7.3-1. Velocity Profile Measured by North-South Traverse of Central Fanstack, Burbank/Olive 1 Cooling Tower, 30 April 1981.

where V_i and V_{i+1} are the velocities corresponding to radii r_i and r_{i+1} along a radial traverse and n is the number of radii measured. The positive air flow rate for this fanstack was $225 \text{ m}^3/\text{s}$. Since there are five fanstacks, the total air flow rate for the tower was approximately $1125 \text{ m}^3/\text{s}$. The mean upward air velocity in our case was 5.0 m/s .

Volatile Organics

Water Samples. The results of our analyses of the two makeup water samples taken on 30 April 1981 are shown in Table 7.3-2. Concentrations of all identifiable compounds in the hot and cold water basin samples were below detectable limits. Note that, because 1,1,2,2-tetrachloroethane and tetrachloroethylene may co-elute in GC runs, it was necessary to calculate concentration ranges based upon the response factor for each compound. It is interesting to note that none of the volatile organic compounds identified in the makeup water samples taken in November 1979 from this tower was found in the makeup in April 1981, and vice versa. Chloroform, which was detected in all parts of the cooling tower system in 1979, was not detected in 1981. The fact that circulating water concentrations of 1,1,2,2,-tetrachloroethane and tetrachloroethylene were negligible on the present occasion implies an effective loss of these compounds from the system.

Ambient Air and Stack Samples. Table 7.3-2 also shows the results of our analyses of air samples collected on Tenax traps from the cooling tower inlet and the fanstack exhaust. GC/FID traces are shown in Figure 7.3-2. Of the six species identified in the exhaust air, five were also in the ambient air; the exception is pentane. On the other hand, 1,2-dichloroethane was present in the inlet air but not in the cooling tower exhaust. While differences in ambient air and exhaust concentrations were observed for some of the compounds, it is difficult to draw conclusions about the origins of the components of the exhaust. The presence of 1,1,2,2-tetrachloroethane and/or tetrachloroethylene in the makeup water and in the stack gas, and their absence in the circulating water support the idea that these two compounds, at least, are potential air pollutants of wastewater origin. A discussion of the possible relationships between ambient air and cooling tower exhaust concentrations will be presented in Chapter 8.

Table 7.3-2

VOLATILE ORGANIC COMPOUNDS IN MAKEUP WATER, INLET AIR AND COOLING TOWER EXHAUST,
BURBANK/OLIVE 1 TOWER, 30 APRIL 1981

Compound	Makeup Water Concentration (ppb)		Concentration in Air Samples ($\mu\text{g}/\text{m}^3$)	
	0100 Hrs	0630 Hrs	Inlet Air	Exhaust
Pentane	ND ^a	ND	ND	≥ 7
1,2-Dichloroethane	ND	ND	≥ 31	ND
Bromodichloromethane	ND	ND	24	32
Benzene	ND	ND	19	10
1,1,2,2,-Tetrachloroethane	16 - 31 ^b	<30 ^b	35 - 70 ^b	33 - 64 ^b
Tetrachloroethylene				
Toluene	ND	ND	36	30
Ethylbenzene	<4	<4	ND	ND
o-xylene and p-xylene	ND	ND	7	7

^aND = Significantly below limit of detection

^bSince 1,1,2,2,-tetrachloroethane and tetrachloroethylene co-eluted, range reported is based upon response factors for the two compounds.

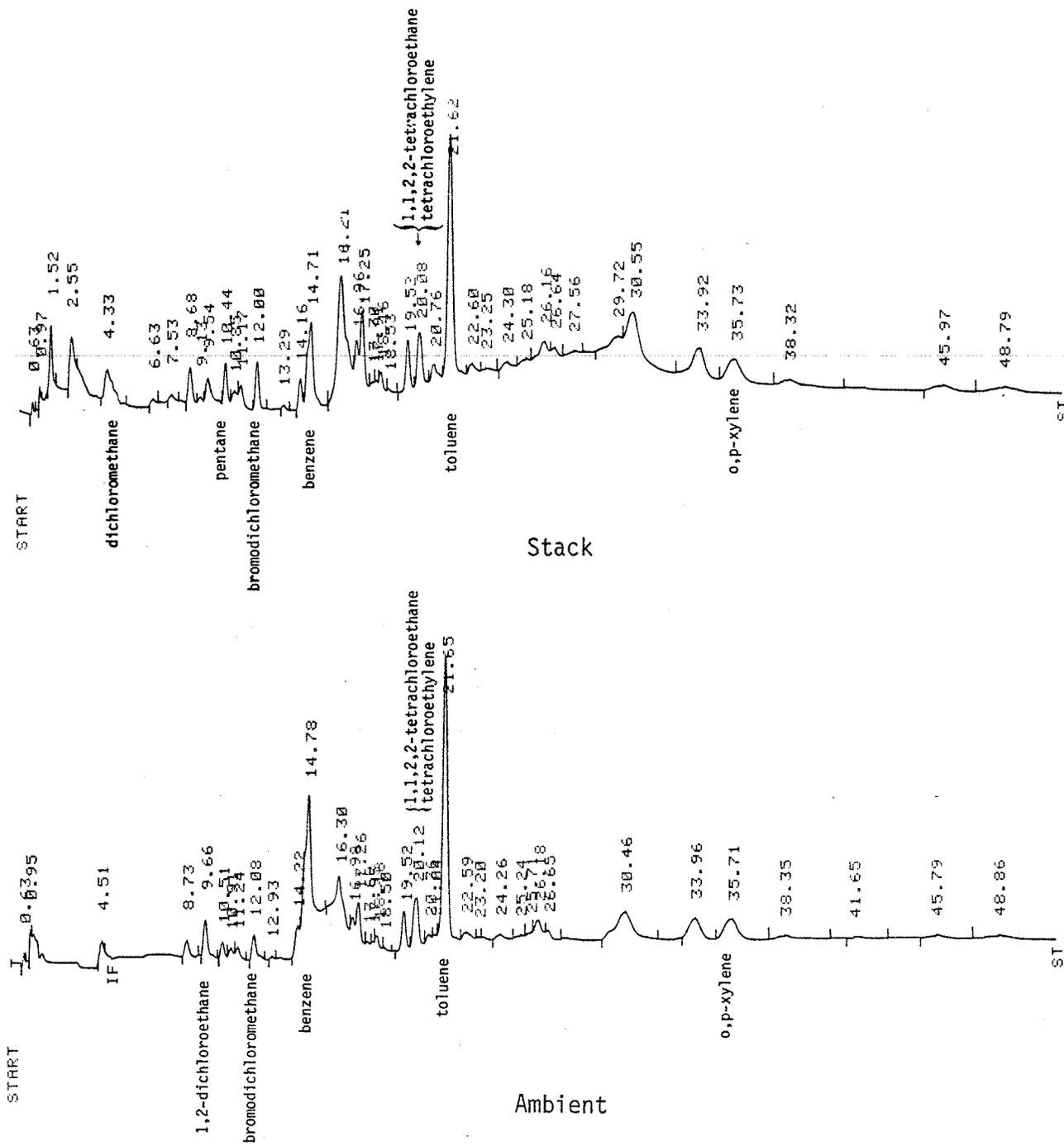


Figure 7.3-2. Gas Chromatograms of Ambient and Exhaust Air Samples Taken on Tenax, Burbank/Olive 1 Cooling Tower, 30 April 1981.

Hourly Sampling of Indicator Microorganisms (20 November 1980)

As noted above, hourly water samples were collected on 20 November 1980 so that indicator organism concentrations could be compared with those of pathogens collected concurrently by the UC Davis team. Tables 7.3-3 through 7.3-6 present our results. Indicator organism concentrations apparently did vary through the day in both makeup and recirculating water. Apparently a major change occurred in wastewater quality at about 1500 hours, since makeup water concentrations of all indicators except fecal streptococcus rose markedly at that time.

No significant correlation could be detected between the hourly total and fecal bacteria levels and the hourly pathogen concentrations determined by the UC Davis team (Fanelli et al., 1981). Although the presence of coliforms should theoretically serve as an indication of other pathogenic species, high coliform counts may also make it difficult to isolate and identify the enteric pathogens because they may overgrow the media used for isolation. In addition, because there was no discernible correspondence between indicator bacteria and other pathogens, it would require more samples per hour, perhaps taken over several days, to more accurately characterize this relationship.

There also appears to be little correlation between concentrations of a given indicator organism in different parts of the system. The two exceptions are fecal coliforms in the hot water basin and the blowdown ($r = 0.932$) and *E. coliphage* in the makeup and the recirculating water ($r = 0.860$). That cold water basin and blowdown concentrations show no clear relationship is surprising, since the blowdown is taken directly from the cold water basin.

Daily average values (excluding the peak at 1500 hours) of total and fecal coliforms are comparable to the concentrations in the composite samples collected in November 1979, and reported earlier in Table 6.3-4. Bacterial virus concentrations are about 50 percent lower. The greatest difference is in the fecal streptococcus concentrations, which were about four times their November 1979 values.

Indicator Microorganisms in April 1981 Test

Makeup and Recirculating Water. Table 7.3-7 shows the concentrations of indicator organisms in the makeup, hot water and cold water basins at the

Table 7.3-3

TOTAL COLIFORMS IN HOURLY SAMPLES COLLECTED FROM
BURBANK/OLIVE 1 TOWER, 20 NOVEMBER 1980
(Concentrations in MPN/100 ml)

Hour of Day	Makeup Water	Hot Water Basin	Cold Water Basin	Blowdown
0900	9	1100	460	>2400
1000	15	75	>2400	1100
1100	3	>2400	>2400	1100
1200	7	1100	>2400	460
1300	43	460	>2400	>2400
1400	9	>2400	>2400	1100
1500	>2400	>2400	>2400	NM ^a
mean ^b	14	>1300	>2100	>1200

^aNM = Not measured.

^bExcludes 1500 hour value.

Table 7.3-4

FECAL COLIFORMS IN HOURLY SAMPLES COLLECTED FROM
BURBANK/OLIVE 1 TOWER, 20 NOVEMBER 1980
(Concentrations in MPN/100 ml)

Hour of Day	Makeup Water	Hot Water Basin	Cold Water Basin	Blowdown
0900	<3	23	7	7
1000	<3	23	43	9
1100	<3	150	4	23
1200	<4	15	9	4
1300	<3	9	11	4
1400	<4	43	43	15
1500	150	15	15	NM ^a
mean ^b	<3	44	20	10

^aNot measured.

^bExcludes 1500 hour value

Table 7.3-5

FECAL STREPTOCOCCUS IN HOURLY SAMPLES COLLECTED FROM
BURBANK/OLIVE 1 TOWER, 20 NOVEMBER 1980
(Concentrations in MPN/100 ml)

Hour of Day	Makeup Water	Hot Water Basin	Cold Water Basin	Blowdown
0900	93	23	43	43
1000	<3	15	93	43
1100	11	43	43	23
1200	9	43	23	9
1300	23	93	43	23
1400	21	23	23	<3 ^a
1500	28	28	15	NM ^a
mean	27	38	40	24

^aNM = Not measured.

Table 7.3-6

E. COLIPHAGE IN HOURLY SAMPLES COLLECTED FROM
BURBANK/OLIVE 1 TOWER, 20 NOVEMBER 1980
(Concentrations in plaques/ml)

Hour of Day	Makeup Water	Hot Water Basin	Cold Water Basin	Blowdown
0900	5.4	0	0	0.3
1000	0.8	1.4	0	1.1
1100	3.7	1.2	0.9	0.8
1200	2.0	1.2	0.5	1.5
1300	4.3	0.8	1.4	0.6
1400	6.5	1.1	0.8	0.5
1500	36.8	2.9	2.2	NM ^a
mean ^b	3.8	1.0	0.6	0.8

^aNM = Not measured

^bExcludes 1500 hour value

Table 7.3-7

INDICATOR MICROORGANISMS IN COMPOSITE AND HOURLY SAMPLES FROM
BURBANK/OLIVE 1 TOWER, 30 APRIL 1981 SAMPLING

Organism	Units	Makeup Water		Hot Water Basin		Cold Water Basin	
		0130 +0815	1410	0130 +0815	1410	0130 +0815	1410
Total coliforms	MPN/100 ml	1100	23	460	>2400	>2400	>2400
Fecal coliforms	MPN/100 ml	93	9	<3	43	150	43
Fecal streptococcus	MPN/100 ml	<3	3	7	93	150	93
E. coliphage	Plaques/ml ^a	10.9	2.5	1.2	3.5	3.5	2.9

^aValues reported as (plaques/5 ml + plaques/1 ml + plaques/0.5 ml)/6.5.

three sampling times. (Note that the 0630 and 0815 samples were combined.) Makeup and basin water concentrations of coliform organisms were higher on this occasion than on either of the previous sampling exercises, while, except for the early morning sampling, coliphage concentrations in the makeup were lower. All organisms were at their highest concentrations at the midmorning sampling.

Stack Sample. The SAI microbiological stack sampler collected 46.3 ml of water during its 8.95 hours over the fanstack. The relative proportions of drift and fog collected cannot be determined. However, what is important is the number of organisms sampled, rather than the amount of water. After the contents of the sampler's glass vials were transferred to sterile containers, the interior of the device was washed with 360 ml of sterile buffer. Table 7.3-8 summarizes the results of our analyses of the collected water and the washings. Relatively high concentrations of total coliforms were trapped in both the sampler vials and on interior surfaces, including the filter pads. Bacterial virus particles were caught in the interior of the sampler, but not in the collected drift and fog water. Unfortunately, we did not anticipate collection of so many viable total coliform bacteria; greater sample dilution would have enabled us to set a more precise lower limit than 2400 organisms per 100 ml. Note that the finding of <3 fecal coliforms and <3 fecal streptococci per 100 ml should be interpreted to mean that there is a 95-percent probability of there being fewer than 3 organisms in the stated volume. In the MPN approach to water analysis, one cannot say for certain that no organisms are present. Because they are based upon direct counting, rather than upon probabilistic assumptions, the E. coliphage plaque numbers can be stated with greater certainty.

Since 770 m^3 of air was collected, the concentration of total coliforms in the stack exhaust was at least 1.6 particles per cubic meter. Fecal coliforms and fecal streptococci concentrations were both less than or equal to $0.016 \text{ particles/m}^3$, and there were about $0.07 \text{ virus particles/m}^3$. Actual concentrations were probably somewhat higher, since the sampling rate was about 13 percent above isokinetic. Available data are insufficient to estimate the effect of nonisokinetic sampling on our results.

Ambient Sampling. The results of our Andersen Sampler tests are shown in Table 7.3-9. Organisms of each type (total bacterial count, total

Table 7.3-8

MICROORGANISMS COLLECTED FROM COOLING TOWER EXHAUST AT
BURBANK/OLIVE 1, 30 APRIL 1981 SAMPLING

Organism	Concentration ^a in Water Collected by Sampler (Volume=46.3 ml)	Number of Organisms	Concentration ^a in Washings From sampler Interior (Volume=360 ml)	Number of Organisms	Total No. of Organisms Collected
Total coliforms	>2400	≥1194	23	83	≥1194
Fecal coliforms	<3	<1.4	<3	<10.8	0 - 12
Fecal streptococcus	<3	<1.4	<3	<10.8	0 - 12
E. coliphage	0	0	0.15	54	54

^aBacterial concentrations in MPN/100 ml, virus concentrations in plaques/ml.

Table 7.3-9
 AMBIENT BACTERIAL CONCENTRATIONS ON DECK AND AT BASE OF
 BURBANK/OLIVE 1 COOLING TOWER, 30 APRIL 1981

Run	Sampler Site	Organism ^a	Time of Day	Sampling Time(min)	6-Plate Counts	Ambient ³ Conc. (No./m ³)
4-3	Deck	TBC	0110 - 0122	12.66	26 ^b	70.9
4-2	Deck	TC	0845 - 0950	64.68	1	0.53
4-1	Deck	FS ^c	0135 - 0206	31.07	1	1.1
3-3	Base	TBC	0315 - 0345	30.07	58	66.6
3-1	Base	FS	0350 - 0420	32.37	0	0

^aTBC = Total bacterial count, TC = Total coliforms

^bPlate No. 6 was broken

^cFS = Fecal streptococci

coliforms and fecal streptococci) were detected on the cooling tower deck. No fecal streptococci were detected at the base, and fecal coliforms were not sampled at that station. In Run 3-3 (total bacteria count), two thirds of the viable particles were collected on stages five and six, which are designed to trap the smallest particles (0.65 to 2.1 μm). A similar deposition pattern was noted for Run 4-3, total bacteria count on the tower deck. Unfortunately, the sixth stage petri dish was accidentally broken and could not be incubated. If the fifth and sixth stages' catch had borne the same relation to the total catch in Run 4-3 as in Run 3-3, then the total collection would have been about 54 organisms, indicating an ambient concentration on the deck equal to about double that at the base. The single fecal streptococcus and coliform particles were detected on the second (4.7 to 7.0 μm) and fourth (2.1 to 3.3 μm) stages, respectively. As was noted above, the fact that our sampling rate exceeded the recommended 0.0283 m^3/min by about 2 percent means that the actual particle size ranges were probably slightly different.

This sampling exercise confirms that indicator bacteria exist in the ambient air above and at the base of this cooling tower. The samples taken at the tower base are probably representative of local ambient air, as the inlet was in the path of a major flow of air toward the tower louvers. Some contamination from water splashing down from the louvers was possible, however. How representative the deck samples are of fallout from tower emissions is uncertain. There is no doubt, given the heavy, visible deposition of drift on the deck, that some of the particles trapped by the samplers originated in the cooling tower basin. However, at various times during the sampling period, the deck was swept with gusts of wind from the west. Thus bacterial particles of other origins could have entered the sampler.

7.4 TASK 4 SAMPLING AT MUNICIPAL TOWER NO. 2 (BURBANK/MAGNOLIA 4)

Task 4 tests at Municipal Tower No. 2 were conducted in two phases. On 3-4 February 1981, we ran our microbiological stack sampler and collected water samples. Due to an equipment malfunction, we were unable to collect organic gas samples from the stack at that time. We returned on 30 June 1981 for that purpose.

7.4.1 Site Description and Sampling Conditions

According to the tower operators, the boiler served by the cooling tower was operating at approximately one-third its normal capacity. The recirculating water flow rate was estimated to be 75 percent of maximum, or about 1.2 m³/s. As will be discussed below, air was circulating through only four of the tower's six cells during the first two hours of the sampling period. The weather was sunny and hot during the day, and windy and cold at night.

7.4.2 Procedures

The morning of 3 February was spent in assembling the rail system and mounting the rail and sampler on the fanstack at the north end of the tower. No scaffolding was necessary, since the fanstack rim was approximately 1.8 m (6 ft) above the deck. A velocity traverse was then made. At 1100 hours, the sampler was moved to a point where the upward flow of drift droplets appeared to be quite heavy. The air speed at this point was 8.0 m/s. The blower rate was adjusted to permit isokinetic sampling, and the sampling system was turned on at 1117 hours. As the air speed at the sampling point varied occasionally, it was necessary to readjust the blower rate several times. The operating conditions were as follows.

<u>Start Time</u>	<u>Stop Time</u>	<u>Elapsed Time (min.)</u>	<u>Exhaust Air Speed (m/s)</u>
1117	1232	75	8.0
1232	1405	93	8.6
1405	1525	80	8.0
1525	1855	210	7.5
1855	1915	20	Blower off
1915	2352	277	8.85
2352	0600	36	Blower off
0600	1035	275	9.7

The blower was turned off twice during the sampling period. The first time, at 1855 hours, the front sampling vial was detached from the sampler so that we could reserve one portion of collected drift and fog water before chlorine was added to the tower at 1900 hours. Unfortunately, the container in which this portion was stored was defective, and the sample was lost. After

chlorination, the sampling system was run from 1915 to 2352 hours, and then turned off for the night. A total of 1062 m³ of air passed through the system. The volume of air sampled during the post-chlorination phase was 622.5 m³.

The temperatures and pH of the makeup, hot water and cold water basin water were measured at 9 times. Water samples for analysis of volatile organics were collected at 1400 hours on 3 February and 1100 hours on 4 February. Finally, samples for microbiological assay were taken from the makeup water supply and the hot water basin and composited as follows:

<u>Sample No.</u>	<u>Hours of Collection</u>
1	1000, 1400, 1600 (3 February)
2	2000, 2200 (3 February)
3	1100 (4 February)

No chlorine analyses were performed.

On the afternoon of 30 June 1981 we returned to the site to perform the organic gas sampling. Tenax trap collection times for stack emissions and ambient air were 120 and 110 minutes, respectively. The sampling flow rates were 29 and 19 ml/min.

7.4.3 Results and Discussion

After mid-morning on both 3 and 4 February, the plumes from the stacks of this tower were barely visible. Considerable drift was observed, however. The entire sampler, as well as much of the rail, was dripping with condensate and attached drift droplets. At 1400 hours on 3 February we noticed that the fan in the cell next to the one we were testing had been turned off. At least one other fan was also off. Concerned that air could be drawn into the tower through the stacks of the other cells and then into the one we were testing, we asked the plant operator to turn on all the fans except the one at the extreme south end of the tower. This was done.

Temperature and pH

Table 7.4-1 shows measured values of temperature and pH of the makeup and of the hot and cold water. Makeup water temperatures varied only slightly during the test period. The late morning-early afternoon peak of the

Table 7.4-1

TEMPERATURE AND pH MEASUREMENTS AT
MUNICIPAL COOLING TOWER NO. 2, 3-4 FEBRUARY 1981 SAMPLING

Date	Hour of Day	Makeup	Temperature (°C) Hot Water Basin	Cold Water Basin	Makeup	pH Reading Hot Water Basin	Cold Water Basin
3 Feb.	1200	20.9	18.4	15.0	7.0	6.7	6.7
3 Feb.	1400	20.8	23.0	17.4	6.8	6.3	6.6
3 Feb.	1515	20.9	21.3	16.0	. . . Not Measured . . .		
3 Feb.	1615	20.9	19.1	14.5	6.7	6.5	6.6
3 Feb.	1710	20.9	18.3	13.5	7.0	6.9	6.8
3 Feb.	1910	20.8	17.0	12.7	. . . Not Measured . . .		
3 Feb.	2010	20.8	16.9	12.4	6.6	6.3	6.3
3 Feb.	2205	20.7	16.0	11.8	6.7	6.3	6.4
4 Feb.	1130	20.7	20.5	16.2	6.9	6.8	6.8

hot water basin temperature, followed by a gradual decline through the afternoon and evening, mirrors the changes in demand upon the power plant. Values of pH were slightly lower than during the Task 3 sampling.

Fanstack Exhaust Air Flow Rate

Using the traverse data shown in Figure 7.4-1, we estimate that the upward air flow rate for the stack we tested was $160 \text{ m}^3/\text{s}$. The mean upward air velocity was 6.6 m/s . Since there are six stacks, the total exhaust air flow is estimated to be $960 \text{ m}^3/\text{s}$.

Volatile Organics

Water Samples. Concentrations of all volatile organic compounds for which we had standards were below detectable limits in the makeup and circulating water samples collected for these analyses. It will be recalled that our Task 3 water sampling at this tower yielded the same result.

Ambient Air and Stack Samples. GC/FID chromatographic traces for the ambient air and cooling tower exhaust samples taken on 30 June 1981 are shown in Figure 7.4-1. Both samples contain many compounds for which we had no GC standards. (A GC/MS analysis was not performed.) Compounds which could be identified and quantified are listed in Table 7.4-2. Note that, in several cases, measurable concentrations were detected in both the front and backup Tenax traps. Because we cannot be certain that there was no breakthrough of these compounds from the backup traps, their concentrations are expressed as minima.

It is of interest to compare ambient concentrations measured at the Magnolia 4 tower with those measured in April 1981 at the Olive 1 tower, which is about 50 m to the southwest. (See Table 7.3-2.) Tetrachloroethylene, toluene and xylene were detected at both towers, while ethylbenzene was present at neither. The inlet air at Olive 1 had significant concentrations of 1,2-dichloroethane, bromodichloromethane, and benzene, while none was detected at Magnolia 4. On the other hand, only the Magnolia 4 tower had trichloroethylene and hexane in its inlet air. (Note that, while hexane may be an analytical artifact in many cases, it was not present in GC runs on field sample blanks in this instance.) The presence of hydrocarbons such as

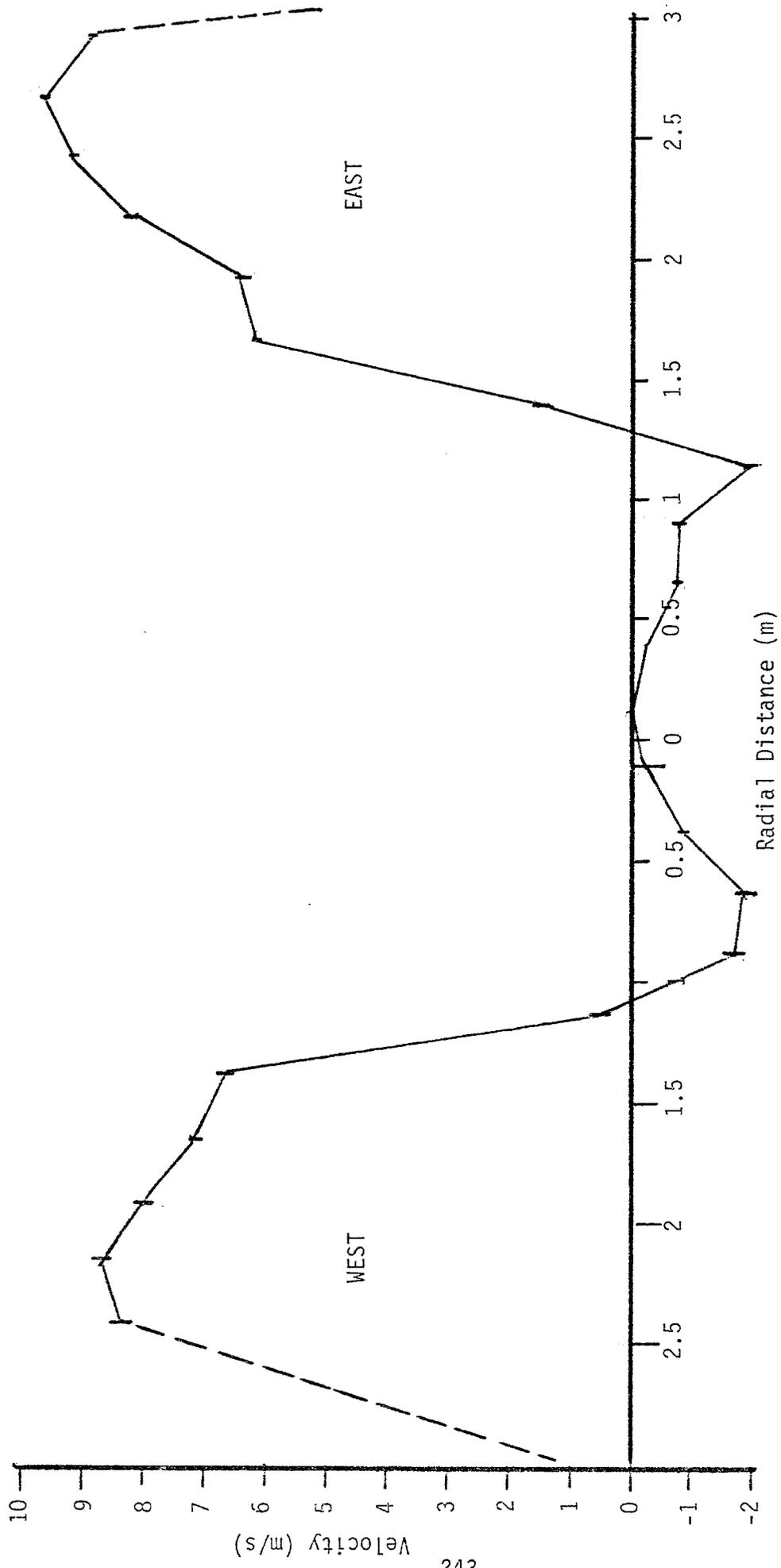


Figure 7.4-1. Velocity Profile For Northernmost Fanstack, Burbank/Magnolia 4 Cooling Tower.

Table 7.4-2

VOLATILE ORGANIC COMPOUNDS IN INLET AIR AND COOLING TOWER EXHAUST,
BURBANK/MAGNOLIA 4 TOWER, 30 JUNE 1981

Compound ^a	Concentration in Inlet Air ($\mu\text{g}/\text{m}^3$)	Concentration in Exhaust ($\mu\text{g}/\text{m}^3$)
1,2-Dichloroethane	ND ^b	≥ 23 ^c
Pentane	ND	≥ 3
Trichloroethylene	≥ 5	≥ 14
Benzene	ND	19
Hexane	≥ 11	≥ 12
Tetrachloroethylene	20	≥ 34
Toluene	41	56
Ethylbenzene	ND	17
m-xylene	12	ND
o-xylene and p-xylene	9	39

^aMany unidentified peaks were observed in each chromatogram.

^bND = Significantly below limit of detection.

^cConcentrations expressed as " \geq " the stated value are for compounds detected in backup Tenax traps.

benzene, toluene and hexane in the ambient air near either tower may be due to the handling and storage of power plant fuel oil in a facility about 50 m due west of the Magnolia 4 tower.

Four of the components of the cooling tower exhaust air (1,2-dichloroethane, pentane, benzene, and ethylbenzene) were not detected in the inlet air. In all cases in which a compound was detected in both types of air samples, its concentration was higher in the exhaust. The greatest difference in concentration was that for the combination of o-xylene and p-xylene; $39 \mu\text{g}/\text{m}^3$ in the exhaust versus $9 \mu\text{g}/\text{m}^3$ in the ambient air. Whether these differences are meaningful is unknown. The import of our findings is discussed in Chapter 8.

Indicator Bacteria and Virus

Makeup and Recirculating Water. Results of our analyses of the composited makeup and recirculating water samples are presented in Table 7.4-3. Concentrations of all organisms in both the makeup water and the hot water basin were lower than during the Task 3 sampling. No relation of concentration to hour of sampling is apparent.

Stack Emission Sample. Indicator organisms were detected in neither the glass vial sample (approximately 5 ml) nor the washings from the sampler interior (approximately 150 ml). We believe that the main reasons for this result were low concentrations of bacteria and virus in the hot water basin and our limitation of sample collection to the afternoon and morning hours, times of low humidity and high exposure of aerosolized microorganisms to ultraviolet radiation. On the basis of this experience, we decided to use the stack sampler thenceforth at night, and did so in our tests on Municipal Tower No. 1.

7.5 TASK 4 SAMPLING AT INDUSTRIAL TOWER NO. 1

7.5.1 Site Description and Sampling Conditions

Task 4 sampling was conducted on 22 January 1981 at the same cooling tower as in Task 3. The day was cold and overcast. During the first three hours of sampling, the tower was enveloped in a dense fog, a major portion of which was due to emissions from a steam vent in a pipe to the southeast of the tower.

Table 7.4-3

INDICATOR MICROORGANISMS IN COMPOSITE SAMPLES
FROM BURBANK/MAGNOLIA 4 TOWER, 3-4 FEBRUARY 1981 SAMPLING

Organism	Units	Makeup Water			Hot Water Basin		
		1200	2000	+2200	1200	2000	+2200
Total coliforms	MPN/100 ml	3	7	23	43	43	23
Fecal coliforms	MPN/100 ml	3	3	3	3	3	3
Fecal streptococcus	MPN/100 ml	4	23	14	9	4	4
E. coli phage	Plaques/ml ^b	0	8.0	0	0.8	0.9	0.2

^a4 February

^bValues reported as (plaques/5ml + plaques/1 ml + plaques/0.5 ml)/6.5

7.5.2 Procedures

Neither the SAI microbiological sampler nor the support rail was necessary for these tests. The vane of the air velocity meter was affixed to a wooden pole, which was extended to various known distances from the fanstack edge. The fanstacks were about 1.5 m (5 ft) high, so scaffolding was not needed. After a velocity traverse was made on two perpendicular diameters, a Tenax sampling assembly was affixed to the south edge of the fanstack, so that the inlet of the front trap was 51 cm (20 in) inside the rim. The cooling tower inlet air sampling point was a horizontal wooden platform above the cold water basin, in the indentation between the first and second cells on the north end of the tower. Air sampling times and rates were as follows:

Run	Type	Start Time	Sampling Time (min)	Flow Rate (ml/min)	Volume Sampled (L)
1	Stack	1004	113	16.2	1.83
2	Inlet	1029	123	21.4	1.64
3	Stack	1255	124	20.7	2.56
4	Inlet	1305	111	30.0	3.33

Water samples for volatile organic analysis were taken at 1000 and 1400 hours from the points described in Section 6.6.2. Temperature readings were made hourly from 0800 to 1500 hours and pH was measured from 1100 to 1500 hours.

7.5.3 Results and Discussion

General Observations

Because of the cold, humid weather, the cooling tower plumes were heavy with fog, and the upper deck was quite wet. However, drift from the tower was, as during our 5 August 1980 sampling, rather minimal. A slight sulfur odor was present around the tower throughout the day.

Temperature and pH

Results of our temperature and pH measurements are presented in Table 7.5-1. Neither temperature nor pH varied much during the day. One difference between the measurements on this occasion and those made during our Task 3 sampling at this tower was noted. The differential between hot and

Table 7.5-1

TEMPERATURE AND pH MEASUREMENTS AT
INDUSTRIAL COOLING TOWER NO. 1, 22 JANUARY 1981 SAMPLING

Hour	Temperature (° c)			pH		
	Hot Water Basin	Cold Water Basin	Makeup	Hot Water Basin	Cold Water Basin	Makeup
0815	30.4	17.0	20.8	6.4	7.1	6.95
0900	30.8	17.8	21.2	6.8	7.2	7.05
1000	31.0	18.2	20.5	6.85	7.05	7.0
1100	31.4	18.5	20.5	6.8	7.25	7.05
1200	31.6	18.5	21.0	6.8	7.15	7.25
1300	31.0	18.0	20.8	6.8		
1405	31.0	18.2	20.9	6.8		
1500	30.6	18.2	20.3	6.8		

cold water basin temperatures averaged 8.4 °C in August 1980 and 12.9 °C during the January 1981 tests. The greater differential implies greater water losses to evaporation and therefore the need for a greater rate of makeup water supply.

Fanstack Exhaust Air Flow Rate

Velocity profiles for the east-west and north-south traverses are shown in Figure 7.5-1. Positive air flow was slightly lower on the side of the stack where our Tenax traps were placed. The calculated air flow rate for the tower is 443 m³/s, and the average upward velocity is 8.3 m/s.

Volatile Organics

Water Samples. Figure 7.5-2 shows the GC/FID traces corresponding to the morning samples of makeup and hot water basin water, while Figure 7.5-3 is a mass spectrum of the makeup sample. Standards were available for identifying and quantifying only about half the peaks in the GC/FID traces of the makeup water.

Makeup water composition is similar to that determined in our August 1980 sampling. (See Table 6.6-2 for comparison.) In both cases concentrations of benzene, toluene and xylene are over 100 ppb. It is not surprising that a particular compound would be present on one occasion and absent on another, since the reclaimed wastewater is derived in this case from a number of industrial processes, not all of which may be in operation at a given time. It is interesting to note that the makeup water contained almost 400 ppb of bromodichloromethane at our January 1981 sampling. As will be discussed in Chapter 8, this compound is commonly associated with chlorination of water, yet it was absent in the tower's circulating water.

Except for hexane, which was present at about the same concentration as in the makeup, and xylene, which was detectable but not quantifiable, the hot water basin did not have detectable concentrations of the makeup water constituents. This result is consistent with the idea that volatile organic compounds in the makeup are effectively released to the atmosphere.

Ambient and Stack Samples. Figures 7.5-4 and 7.5-5 are GC/FID traces for the front and back Tenax samples collected from the fanstack and the ambient air, respectively. Because there was considerable breakthrough of certain components, some of the estimated concentrations, which are presented

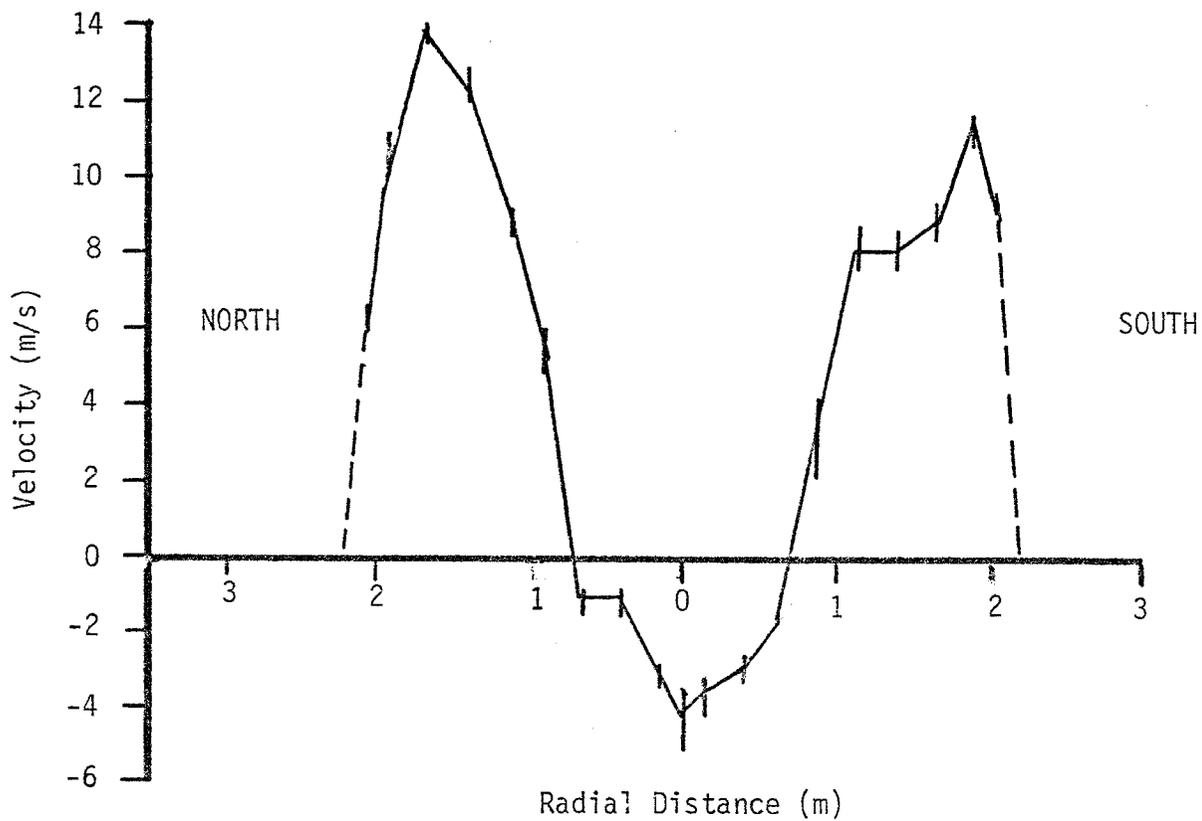
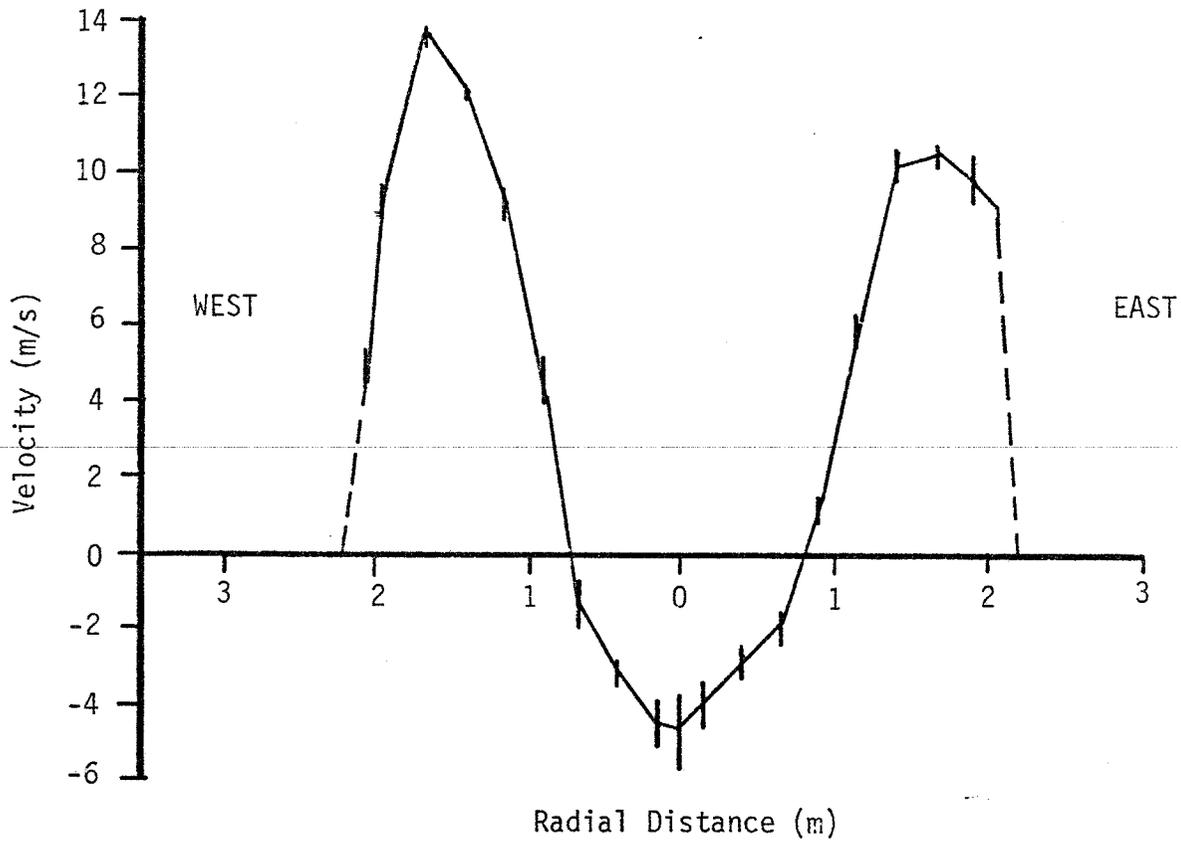
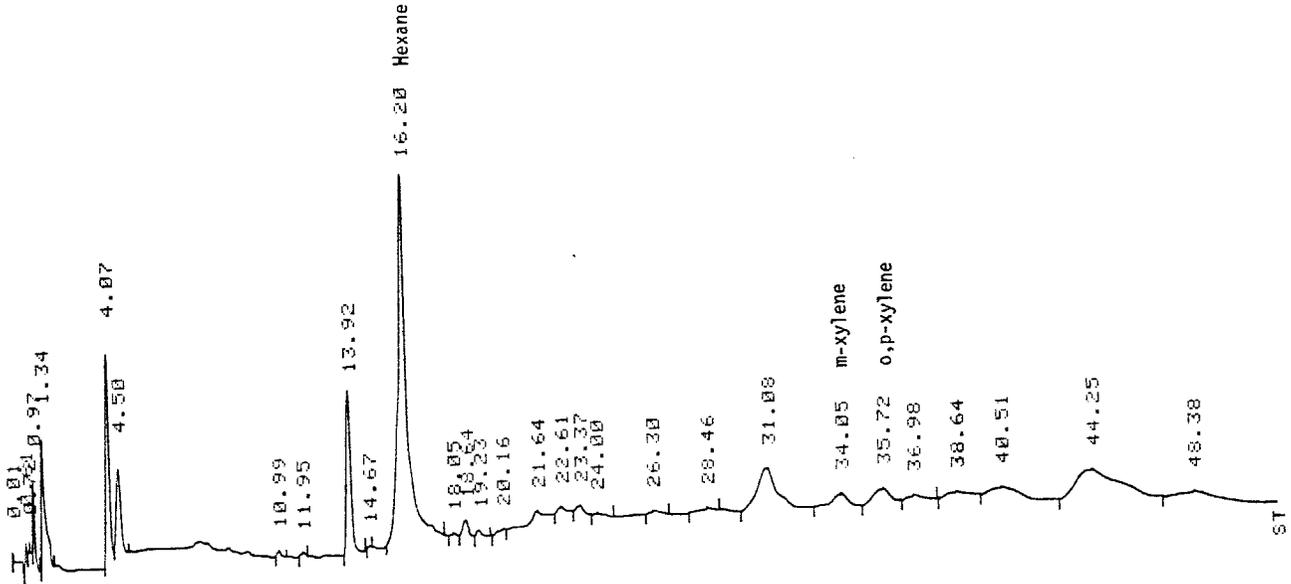
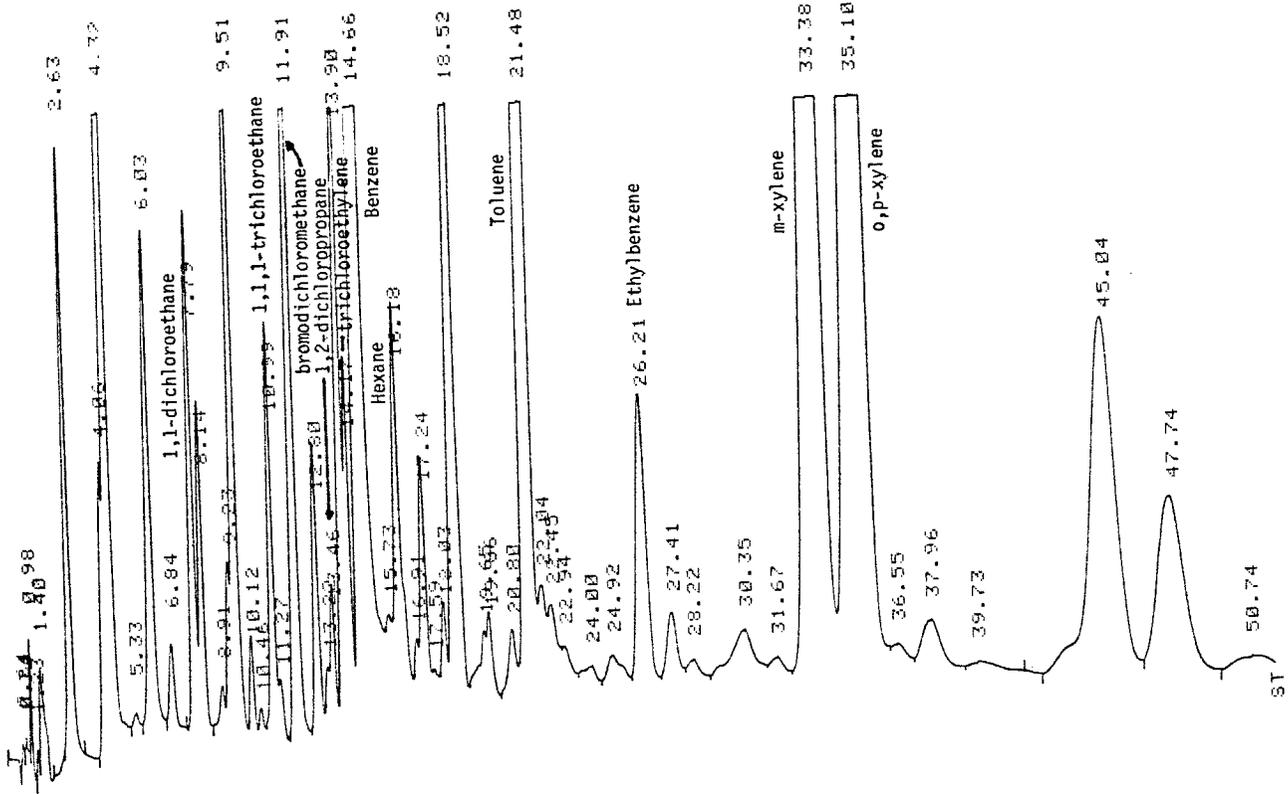


Figure 7.5-1. Velocity Profiles for West-East and North-South Traverses, Industrial Tower No. 1.



Hot Water Basin



Makeup

Figure 7.5-2. Gas Chromatograms of Morning Makeup and Hot Water Basin Samples, Industrial Cooling Tower No. 1, 22 January 1981.

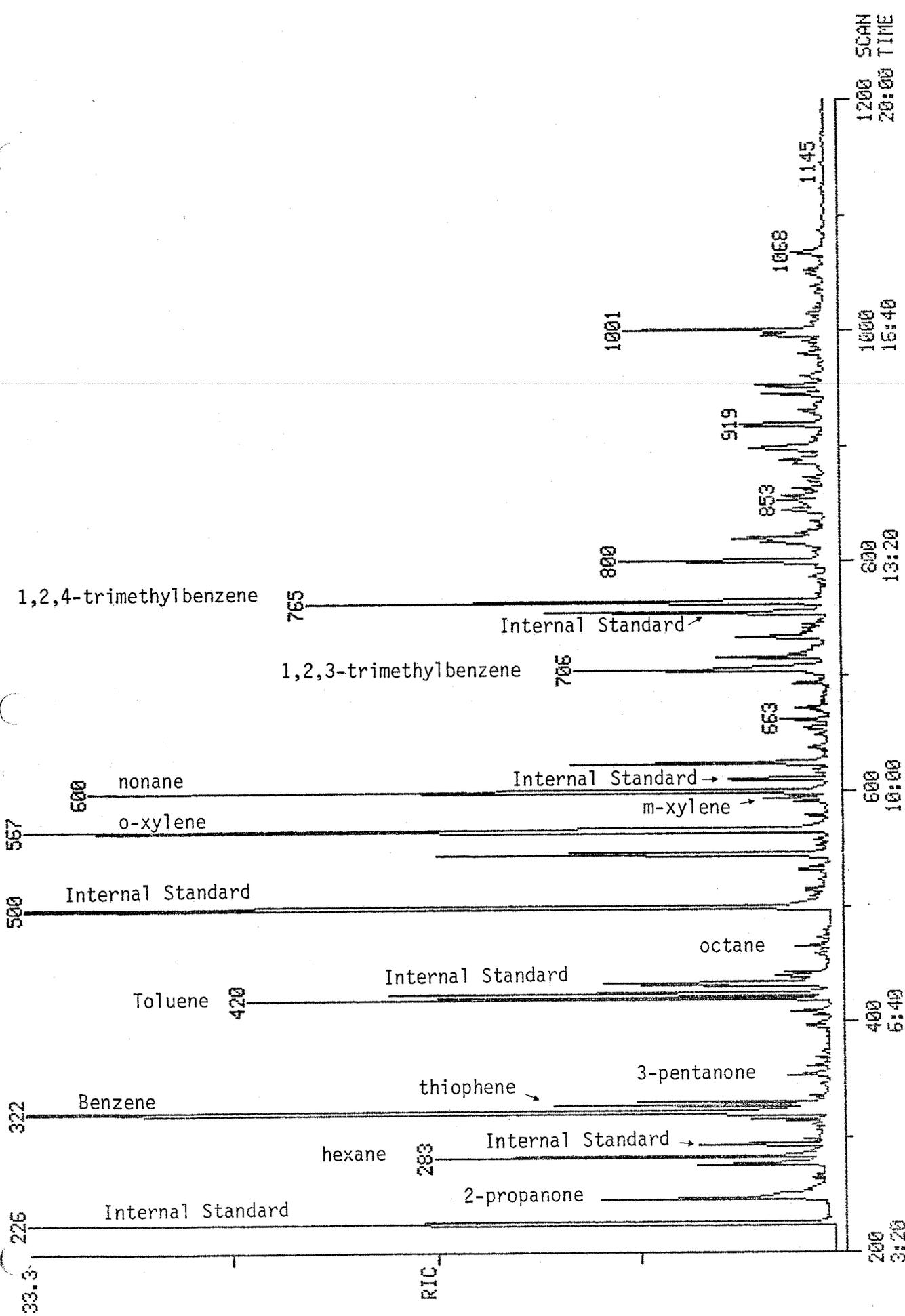


Figure 7.5-3. Mass Spectrum of Makeup Water Sample, Industrial Cooling Tower No. 1, 22 January 1981.

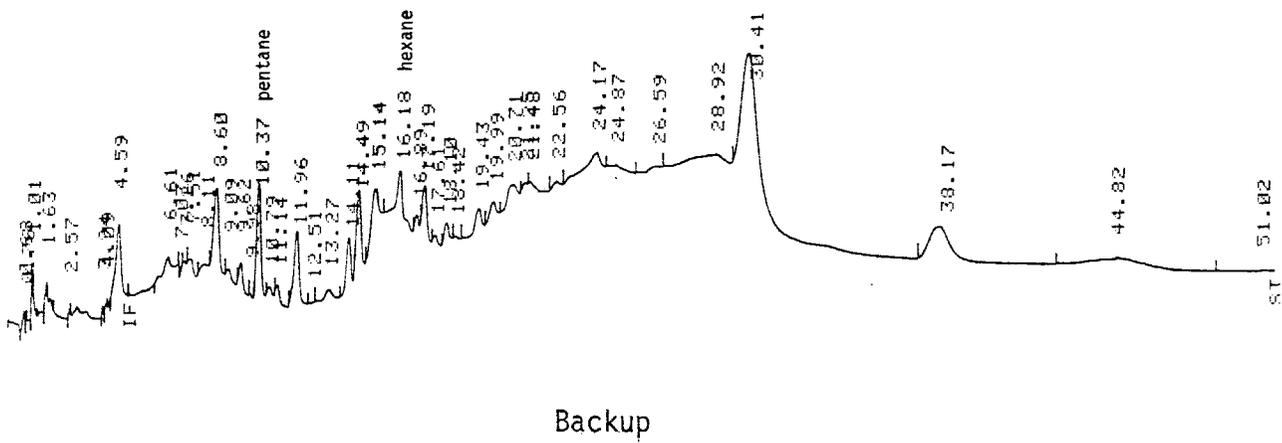
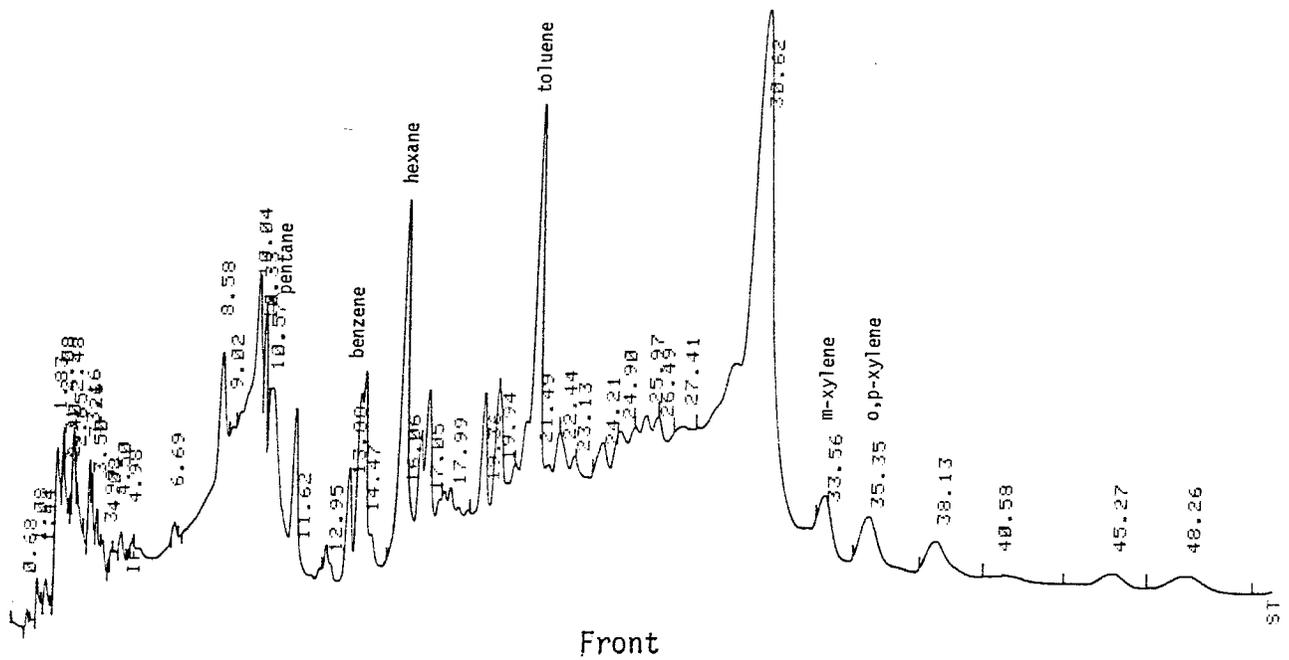


Figure 7.5-4. Gas Chromatograms of Samples of Exhaust Air (Front and Backup Tenax Traps), Industrial Cooling Tower No. 1, 22 January 1981.

in Table 7.5-2, had to be stated as minima. Another difficulty in quantifying concentrations was that the peaks for pentane, benzene and hexane in the stack sample co-eluted with other compounds. Finally, the stack sample's GC/FID trace has a relatively large unresolved area. It is believed that the Tenax adsorbent reacted chemically with sulfur compounds present in the stack exhaust.

All of the components identified in the stack sample were also present in the inlet air, while four of the inlet air components (dichloromethane; 1,2-dichloroethane; 1,1,1-trichloroethane; and trichloroethylene) were in the inlet air but not the exhaust. We find it remarkable that the inlet air contained 2.7 mg/m^3 of dichloromethane (methylene chloride), yet none was observed in the stack sample. While methylene chloride commonly shows up as a contaminant of GC/FID traces, in this case it was absent from sample blanks. Some implications of this and other findings from these tests are discussed in Chapter 8.

7.6 GEOTHERMAL TOWER

7.6.1 Site Description and Sampling Conditions

On 9 July 1981, SAI staff conducted stack testing on, and collected water samples from, the same geothermal tower sampled in Task 3. The day was sunny and hot, with scattered high clouds. Winds were very light. In the afternoon, a slight southwest wind arose.

According to the tower operator, the power plant was operating at about one third of its capacity of 60 MWe during our sampling. A major difference between Task 3 and 4 sampling conditions was that the Stretford process for H_2S removal, which was down in January 1980, was now functioning. Greater abatement of H_2S was thus anticipated.

7.6.2 Procedures

Stack Sampling Points

Stack sampling was conducted on the second cell from the northwest end of the tower. All five fiberglass fanstacks are roughly hyperboloid in shape. The fanstack we sampled was perforated with numerous holes for insertion of probes. Figure 7.6-1 shows the locations and approximate spacing of the test holes we used; angles between sampling radii are accurate

Table 7.5-2

VOLATILE ORGANIC COMPOUNDS IN MAKEUP WATER, HOT WATER BASIN, INLET AIR,
AND COOLING TOWER EXHAUST, INDUSTRIAL TOWER NO. 1, 22 JANUARY 1981

Compound	Water Concentrations (ppb)		Concentrations in ₃ Air Samples ($\mu\text{g}/\text{m}^3$)	
	Makeup ^a	Hot Water	Inlet Air	Exhaust
Dichloromethane	ND ^a	ND	≥ 2700	ND
1,1-Dichloroethane	70	ND	ND	ND
1,2-Dichloroethane	ND	ND	47	ND
Pentane	ND	ND	≥ 29	NQ
1,1,1-Trichloroethane	116	ND	21	ND
Bromodichloromethane	389	ND	ND	ND
1,2-Dichloropropane	18	ND	ND	ND
Trichloroethylene	68	ND	≥ 42	ND
Benzene	636	ND	NQ ^c	NQ
Hexane	6	5	≥ 36	NQ
Toluene	422	ND	73	70
Ethylbenzene	42	ND	ND	ND
m-Xylene	230	<4	33	10
o-Xylene and p-Xylene	253	<4	20	20

^a Many unidentified peaks

^b ND = significantly below limit of detection.

^c Detected but quantification prevented by peak overlap.

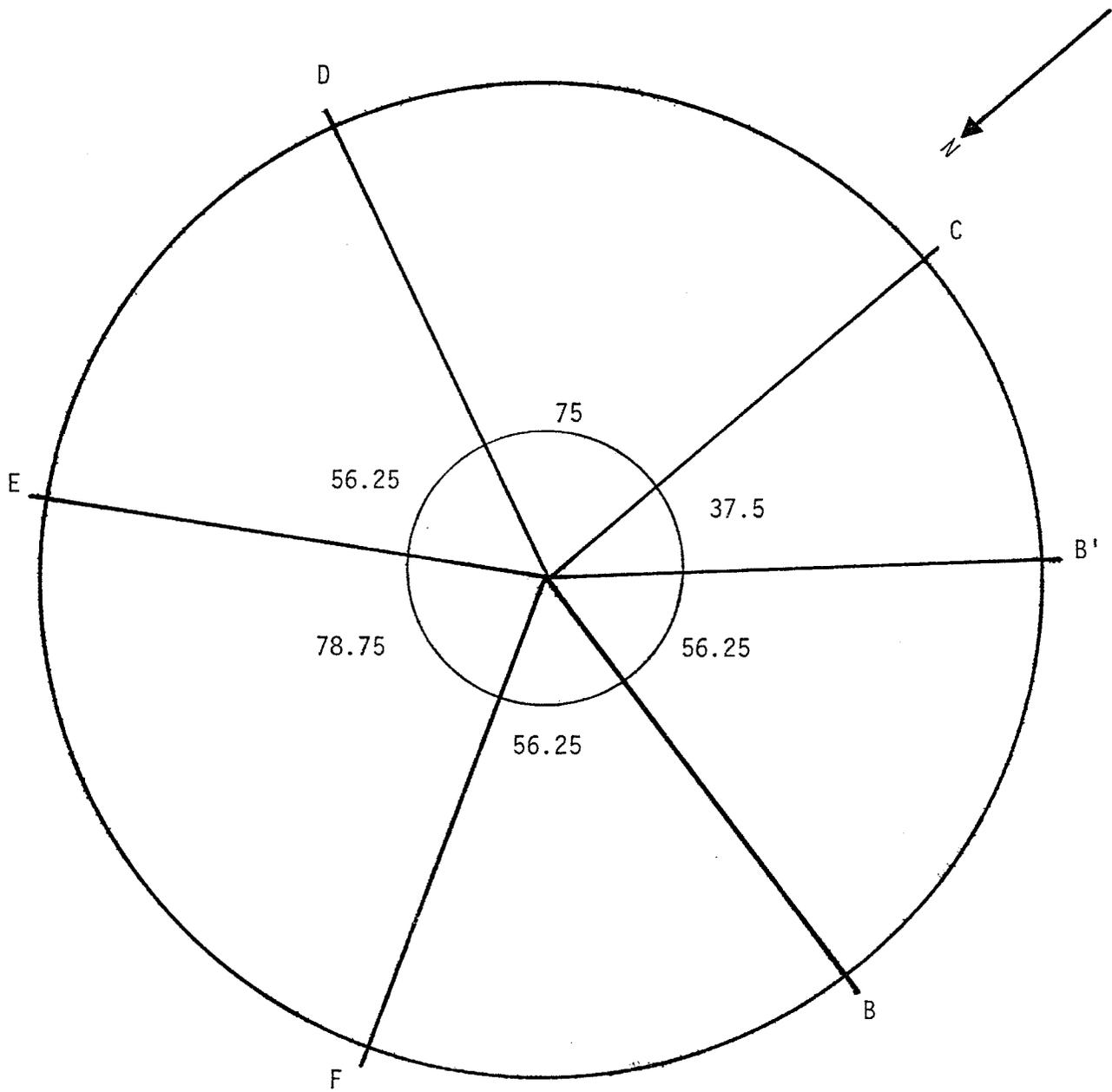


Figure 7.6-1. Positions of Test Holes on Geothermal Tower Fanstack.

to about ± 4 degrees of arc. The tower diameter in the plane of our sampling points was about 9.58 m (31.4 ft), and the points were approximately 2.1 m (7 ft) above the fan blades. It should be noted that a set of eight equally-spaced sampling holes had been drilled in the fanstacks by previous investigators. These holes were, however, too small to accommodate even the smaller of our two probes.

Sampling Train

Figure 7.6-2 shows the various configurations of our sampling train. The probe assembly consisted of two 1.83-m (6-ft) sections of 1.9-cm (0.75-in) O.D. stainless steel tubing connected with Swagelok fittings. Swagelok fittings at the downstream end of the pipe reduced the diameter for connection to 0.63-cm (0.25-in) Teflon tubing. For all three sampling train configurations, the length of Teflon tubing between the stainless steel probe and the first impinger was 6.1 m (20 ft).

Hydrogen Sulfide. For H_2S measurement, the Teflon tubing was connected to a 250-ml all glass impinger. The purpose of the impinger, which sat vertically in a plastic bag filled with ice, was to prevent drift and condensed fog from reaching the H_2S meter. The meter was an Interscan portable H_2S analyzer which had been calibrated in the 0-10 ppm range by Interscan Corporation (Chatsworth, California) three days before use. A 0-1 ppm measurement range is also available. An internal pump draws air at a nominal 0.8 - 1.2 L/min through an electrochemical sensor. The meter was connected to a Soltec VP-6723S dual-channel chart recorder so that a continuous trace of the day's H_2S readings could be made.

Mercury. For the mercury sampling, the same ice-bath impinger arrangement was left in place. Downstream from the impinger, an in-line filter case holding a pre-weighed Gelman 0.3 - μm glass fiber filter was used to trap particulate mercury. Next in series were two traps (front and backup) containing gold-coated glass beads. Before going to the field, the traps had been heat desorbed at 550 $^{\circ}C$ and purged with nitrogen gas which itself had been pre-filtered by passage through a gold trap. Air samples were drawn with a Thomas Model 107CA18-485-1 vacuum pump, whose flow rate was monitored with a rotameter. Just prior to the testing, the rotameter was calibrated by the falling soap film method.

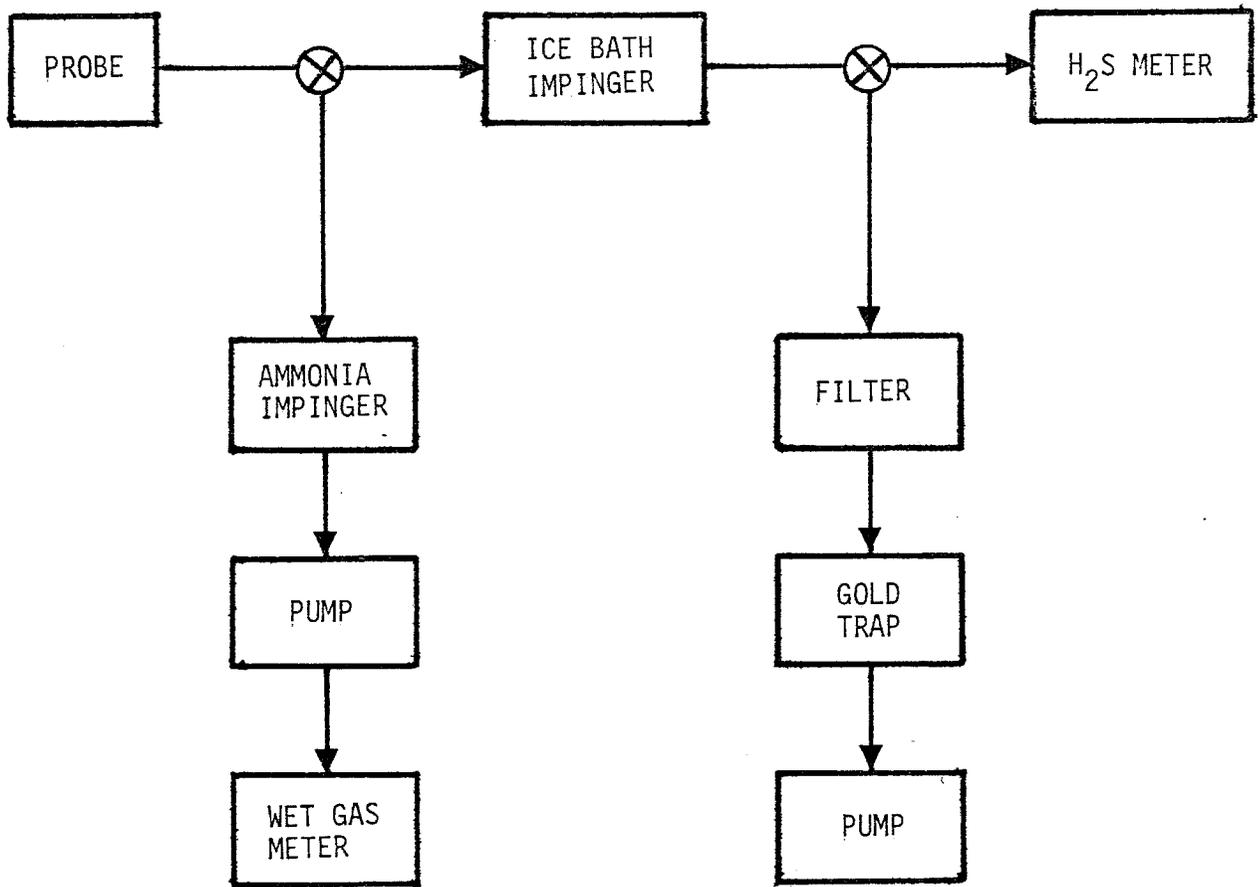


Figure 7.6-2. Schematic of Geothermal Tower Sampling Train.

Ammonia. For NH_3 measurement, the Teflon line was disconnected from the ice-bath impinger and connected to a 250-ml polypropylene impinger containing a scrubbing solution composed of 0.02M H_2SO_4 and 2M KCl. The same pump as in the mercury sampling train was used. Air flow was measured with a GCA Precision Scientific Model 63126 wet gas meter accurate to 0.05 L.

Stack Sampling Procedure.

The Interscan H_2S analyzer was allowed to run throughout the testing period so that ambient levels of hydrogen sulfide could be monitored for safety reasons. Radial traverses for H_2S measurements were made at points B, C, D, and F on the fanstack (see Figure 7.6-1). Clearance between fanstacks was too small to permit insertion of the probe into the other sampling holes. Measurements were made at 1, 2, 3, 4, 5, 6, 6.75, and 7.75 feet from the inner surface of the fanstack. With the probe at each radial point, the analyzer was allowed to operate for at least one minute so that the "dead volume" from the previous point's sampling could clear the system. The measured run lasted from one to five minutes, depending upon the variability in concentrations. During three runs it was occasionally necessary to switch the analyzer scale from 0 - 1 ppm to 0 - 10 ppm or vice versa.

Mercury measurements were conducted at sampling holes D and F. A radial distance of 2.83 m (6 ft) from the fanstack wall was chosen since H_2S measurements at that point appeared to be about average for each radial traverse. Our objective was to pass approximately 3 L of air through the sampling train.

Ammonia samples were taken at the same points as were those for mercury. Consideration of probable concentrations of ammonia in the cooling tower exhaust led us to require a minimum of 50 L of air sample.

After the H_2S traverses and NH_3 and mercury sampling runs were completed, the probe and sampling line were washed down into the impinger with distilled, deionized water. The impinger contents were then transferred to a glass bottle. The purpose of saving probe wash and the drift and condensate collected by the impinger was to analyze the resulting solution for mercury; since the total volume of air passing through the probe during the day could be determined from our records of the traverses and the NH_3 and Hg measurement, we could then obtain a rough estimate of the amount of mercury emissions not collected by the filter and gold traps.

Water Sampling Procedure

Water samples for analysis of H_2S , NH_3 and several trace metals were collected from the hot and cold water basins at 1300, 1340, 1615 and 1705 hours. Collection methods were as described in Section 6.2.1. Water temperature measurements were also made. The hot water basin sample was obtained from the distribution trough associated with the cell on the northwest end of the tower. The cold water basin sample was taken from the center of that cell.

Analytical Procedures

Water samples were analyzed by the same techniques described for the Task 3 sampling. Recorder traces of the H_2S stack tests were measured by eye and by a polar compensating planimeter to determine the average concentration over each run at each sampling point. Mercury was desorbed from the gold traps at $550^\circ C$ and measured by cold vapor atomic absorption spectrophotometry, using a Laboratory Data Control Model 1230 mercury monitor with 30-cm quartz cells. The light source used was at 254 nm. Finally, the ammonia collected in the impingers was measured with an Orion Model 95-10 ammonia electrode connected to an Orion Model 901 microprocessor. Details of the procedure are presented in Appendix B.

7.6.3 Results and Discussions

General Observations

Before noon, the cooling tower's plumes were barely visible. At approximately 1430 hours, denser plumes were emitted, and large-sized drift droplets were in greater evidence.

Temperature

During our January 1980 sampling, hot and cold water basin temperatures ranged from 38.5 to $40.5^\circ C$ and 25.7 to $27.7^\circ C$, respectively. (See Table 6.8-1) In July 1981, the hot water temperatures were 33.6 and $37.7^\circ C$ at the two sampling times (1300 and 1615 hours), and the cold water temperatures were 22.0 and $24.5^\circ C$. The lower operating temperatures probably reflect the lower heat load on the tower during the second visit.

Inorganic Constituents of the Circulating Water

Table 7.6-1 presents the results of our analyses of the hot and cold water basin samples for metals (except mercury), ammonia, hydrogen sulfide, total suspended solids (TSS) and total dissolved solids (TDS). Mercury is discussed below. All metals concentrations reported are for filtrates of the water samples. Several differences between these concentrations and those determined for samples taken on our first visit may be seen by comparing Tables 7.6-1 and 6.8-2. The average TDS concentration for the two basins in July 1981 was over five times that measured in 1980. Total suspended solids concentrations were an order of magnitude higher on the second visit. Copper had increased slightly, and zinc levels were above 50 ppb, versus 2 to 7 ppb in 1980. On the other hand, dissolved arsenic concentrations were markedly lower (an average of 13.9 ppb for the two basins in 1981, as opposed to 476 ppb in 1980). Because details of this tower's operation are unknown, the reasons for these differences are a matter of speculation.

Hydrogen Sulfide

Figure 7.6-3 shows the values of H_2S measured at each of our sampling points along the four radii traversed. The highest reading of the day was 3.8 ppm, near the fanstack wall at sampling hole B. Traverses from holes B and D found the highest H_2S values to be near the stack walls. Both these locations are near the hot water trays, from which the H_2S evaporation is expected to be greatest. Hydrogen sulfide concentrations along the traverses from holes C and F are more uniform. Concentrations profiles, except for the traverse originating at hole B, converge to about 0.15 ppm near the center of the fanstack. That H_2S levels are relatively low there is not surprising, since the net air flow is negative, i.e. downward near the fan.

Hydrogen sulfide concentrations in the hot and cold water basins were considerably lower than those measured at the same points in January 1980. This result was to be expected since on the second visit the Stretford process for H_2S removal was operating, whereas during our first visit it was not. The exhaust gases from the Stretford process are injected into the cooling tower, but their H_2S concentration is lower than that of the noncondensable gas stream injected in January 1980. Furthermore, air iron catalyzt system is now used in this tower to treat residual H_2S .

Table 7.6-1

INORGANIC CONSTITUENTS OF GEOTHERMAL COOLING
TOWER CIRCULATING WATER, 9 JULY 1981 SAMPLING

Constituents	Units of Concentration	Hot Water Basin	Cold Water Basin
Arsenic	ppb	10.4	17.4
Cadmium	ppb	0.1	0.1
Chromium	ppb	<0.5	<0.5
Copper	ppb	6.6	7.3
Lead	ppb	<0.5	<0.5
Selenium	ppb	<20	<20
Zinc	ppb	49.2	50.4
Ammonia	ppm	44.8 ^a	46.2 ^a
Hydrogen Sulfide ^b	ppm	<0.2	<0.2
Total Susp. Sol	ppm	17.2	22.4
Total Diss. Sol	ppm	2745	2770
Conductivity	μmho/cm	3300	3350

^a Mean of two values.

^b As sulfide.

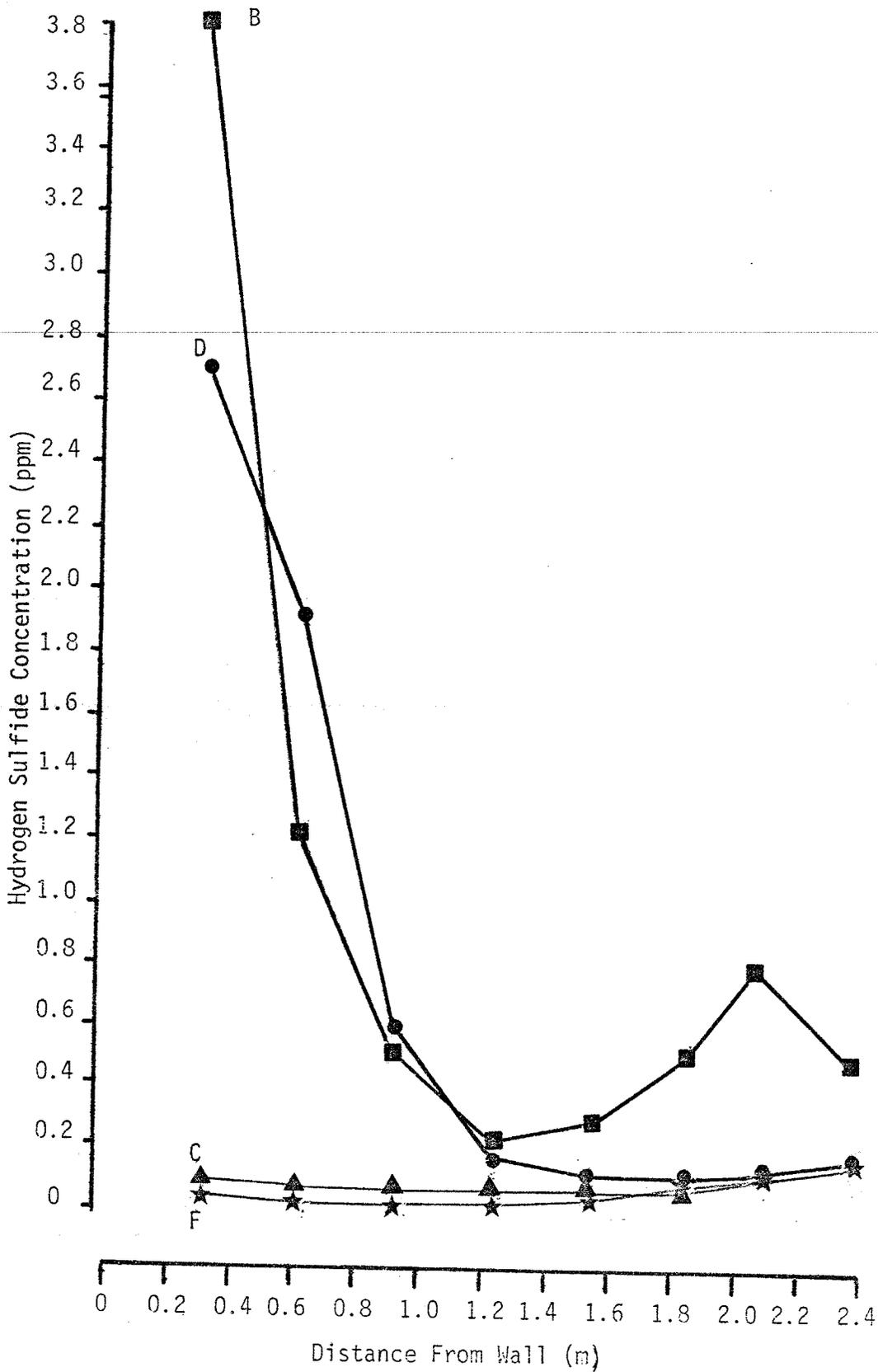


Figure 7.6-3. Hydrogen Sulfide Concentrations Along Traverses From Sampling Holes B, C, D, and F, Geothermal Cooling Tower, 9 July 1981.

Ammonia

Ammonia concentrations in the circulating water were also lower than during our first visit (an average of 45.3 ppm in 1981 versus 61.0 ppm in 1980), although the reduction was not as great as for the hydrogen sulfide. The mass-to-volume concentrations of ammonia in the exhaust air at the points sampled were 1.76 and 3.84 mg/m³, respectively. To express these concentrations as parts per million by volume requires information about the exhaust air temperature. In tests performed by the tower operator, air temperatures at various points in the fanstack cross section ranged from 32 to 43 °C. Using these values as a reasonable range, we estimate that the NH₃ concentration at our two measurement points would be 2.6 to 2.7 ppm and 5.6 to 5.8 ppm, respectively.

Mercury

As with the samples from our first visit, analyses of both dissolved and particulate mercury from the circulating water were made. Again, the great majority of the mercury was found to be in particulate form. In the hot water basin, the dissolved and particulate mercury concentrations were 0.052 and 15.3 ppb, respectively. As may be seen by comparing these results with the values shown in Table 6.8-2, the total mercury in the hot water basin sample was about three times that measured on our first visit. The dissolved mercury in the cold water basin was 0.042 ppb in 1981 (versus <0.03 ppb in 1981). Particulate mercury in the cold water basin cannot be compared because such an analysis was not performed for the 1980 sample. In addition, the spectrophotometer reading for the 1981 sample was beyond the linear range of the standard calibration curve; all that can be stated with certainty is that the particulate mercury concentration in that case was above 7 ppb.

Table 7.6-2 summarizes the results of our stack sampling for total mercury at two points. If only the mercury caught on the filters and in the gold traps is taken into account, then the fanstack exhaust concentrations were 2.1 and 0.38 µg/m³ for the samples taken through fanstack holes F and D, respectively. In addition to that collected by the filters and gold traps, a total of 275 ng was measured in the combined solution from the knockout impinger and probe and line wash. The total volume of air passing through the probe during the day was estimated to be from 232 to 285 L; the uncertainty is due to the fact that only a nominal range of H₂S meter flow rates is known.

Table 7.6-2

RESULTS OF MERCURY EMISSIONS MEASUREMENTS
AT GEOTHERMAL TOWER, 9 JULY 1981 SAMPLING

Run	Collected by Filter (ng)	Collected by Gold Trap (ng)	Total Hg (ng)	Volume Air Samples (L)	Concentration in Exhaust (µg/m ³)
1	7.89	0.46 - 0.51	8.35 - 8.40	3.94	2.1
2	0.919	> 0.33 ^a	> 1.25	3.29	0.38
Impinger and Probe			275	232 ^c - 285 ^c	1.0 ^d - 1.2 ^d

^a Sample lost due to blockage of sample tube.

^b Includes impinger and probe wash.

^c Based on nominal range of air flow rates for H₂S meter.

^d Based on filter + gold trap + impinger + probe wash.

If all the mercury (filter, gold trap, impinger, probe wash) is taken into account, then the average concentration in the exhaust air would have been 1.0 to 1.2 g/m³. All our results are quite consistent with those reported by Robertson et al. (1977 and 1981) for mercury measured in geothermal cooling tower exhaust. (See Section 8.2.3 for details.) We therefore believe that they are at least of the right order of magnitude.

7.7 REFERENCES

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COOLING TOWER EMISSIONS AND THEIR IMPLICATIONS

Interest in measuring pollutant emissions from cooling towers, as chronicled by Shofner (1978), dates back only to the early 1970's, when a proposal to use saline water as makeup to a large power plant cooling tower generated fears of environmental damage from emissions of salt. Since then, several studies of emission rates, plume trajectories, and pollutant deposition have been made. For example, a natural-draft tower at the Potomac Electric Power Company's Chalk Point, Maryland power plant has been investigated for a number of years, since its use of brackish water for makeup was believed to pose a potential air pollution problem (Meyer and Stanbro, 1977). While the Chalk Point investigation has been quite thorough, field tests of cooling tower emissions in the U.S. have been limited to only a handful of towers. As Laulainen (1978) and others have pointed out, lack of real emissions data has handicapped the development of models to predict dispersion and deposition of cooling tower pollutants. Furthermore as will be described below, only a few of the potential pollutants of concern have been the subject of previous emissions tests. In this chapter, we review previous studies of cooling tower emissions, estimate emissions from the towers we sampled, and derive emission factors for pollutants of concern.

8.1 ANALYTICAL FRAMEWORK

8.1.1 Mechanisms of Cooling Tower Emissions

A major goal of our field testing program was to determine whether cooling towers using reclaimed wastewater as makeup are net emitters of air pollutants which are potentially harmful to human health and welfare. The following discussion of emission mechanisms is based upon our observations and findings.

Inorganic Salts

The main source of inorganic salt input to a cooling tower is the makeup water. Reclaimed water usually (and brackish water always) has higher concentrations of many chemical species of interest than do conventional sources such as rivers, lakes and high quality ground water. In addition, geothermal condensate may contain species which are not commonly found in either wastewater or conventional sources. Because a significant percentage

of the circulating water evaporates, the cooling tower acts as a concentrator for most of the inorganic constituents. Inorganic salts which are added to cooling towers for corrosion control and other maintenance purposes are not properly within the scope of the present study, unless the use of treated wastewater necessitates more than the normal amount of chemical treatment. Similarly, metals which enter the cooling tower through corrosion of heat exchangers are not of interest.

Inorganic salts are emitted chiefly as constituents of tiny water droplets, called "drift," which are entrained in the exhaust air. (Drift is discussed in detail in Section 8.1.2) They are also emitted through the splashing of water from the open spaces between the louvers on the air intake sides of the tower, especially if the tower is in poor repair. It should be noted that cooling towers may also serve as sinks for salts which become insoluble under certain physical and chemical conditions. These salts contribute to scale in heat exchangers and precipitate out as sludge at the bottom of the cold water basin and hot water trough.

Organic Vapors

Volatile organic compounds probably enter cooling towers both as dissolved components of the makeup (especially if certain industrial wastewaters are used) and from the atmosphere. Makeup water constituents are likely to be emitted rapidly; indeed, if the makeup water inlet is open to the atmosphere and the water is highly turbulent, a good percentage of the volatile organics may not even be incorporated in the circulating water. Those constituents entering and remaining in the circulating water may be emitted in part as drift from the stacks or as splashing from the louvers, but it is more likely that they volatilize from the cold water basin, which is often partially exposed to the outside air, or from the hot water trough, where high temperatures decrease their solubilities. An even more probable emission site is the tower interior, where contact of falling water with fill creates an enormous surface for gas-liquid interchange. Thus the cooling tower transforms water pollutants into air pollutants and may be properly considered to be an emission source.

Potential organic air pollutants may also enter the tower as precursors to halogenated compounds which form when the circulating water is chlorinated. Again, the tower is a net emission source.

The atmosphere around a cooling tower can contain many organic pollutants of concern, especially if the tower is associated with a refinery or a chemical plant or is in a heavily polluted urban area. Air pollutants of concern may be drawn into the tower and passed out the stacks unchanged and undiminished. Alternatively, the tower may act as a "scrubber," transferring the compounds to the circulating water. In the latter case, however, it is the same as if the volatile organics entered the system via the makeup; eventually they are re-emitted to the atmosphere. Therefore, when the atmosphere is both the source and the sink for volatile organics, the tower cannot be considered to be a source of these pollutants.

Finally, relatively nonvolatile organics enter the cooling system both through the makeup and from the atmosphere. These compounds are probably emitted to some extent in the drift. It is possible that the tower may also serve as a sink, at least in the short run, as the heavier constituents migrate to the cold water basin sludge.

Bacteria and Virus

The two most important sources of bacteria and virus input to a cooling tower are the surrounding atmosphere and the makeup water. Because even treated wastewater has been shown to have appreciable concentrations of microorganisms, including many pathogens, it is likely that, for the cooling towers sampled in this project, the latter source predominates. Whatever the source of organisms, cooling towers generally provide an hospitable environmental for their growth and therefore act as amplifiers. In principle, at least, cooling towers may be considered to be net emitters of microorganisms. The chief emission routes are the stack exhaust and splashing from the louvers. In either case, organism may be emitted in water droplets, attached to particulate matter, or as free-floating particles.

8.1.2 The Nature of Cooling Tower Drift

Cooling tower drift has been traditionally defined as "mechanically entrained water droplets which are generated inside the cooling tower and carried along with the air flowing through the tower and exhausted to the environment" (Wistrom and Ovard, 1973). It is necessary to distinguish between drift and the other major form of aerosolized water, "fog." Cooling tower fog consists of very fine droplets of water which have condensed to the liquid

phase from water vapor in the exhaust air. The mass of water emitted as fog exceeds that of drift by three orders of magnitude in most cases. Fog emissions are responsible for most of the visible emissions from cooling towers, as the smaller fog particles scatter light more efficiently than do the larger drift droplets. On the other hand, the drift is assumed to contain virtually all of the inorganic salts emitted by the tower.

Measurements of Drift

Before the abovementioned awakening of interest in cooling tower emissions, drift release rates were not measured directly. Rather, water balance calculations led to the widespread "rule of thumb" that drift constituted 0.2 percent of a tower's recirculating water rate. Subsequent measurement work has shown this estimate to be high by one or two orders of magnitude in most cases (Shofner, 1978). Researchers have concentrated on measuring both drift droplet size distributions and overall mass emission rates.

The most common methods for measuring droplet size distribution are the sensitive paper technique and the Particulate Instrumentation by Laser Light Scattering (PILLS) system (Shofner et al., 1975). In the first of these a specially treated strip of paper is exposed to the cooling tower exhaust. Drift droplets striking the paper are absorbed, and the size of the captured impression can be correlated with actual droplet size through laboratory calibration with known aerosol size distributions (Cheng, 1977). Glass slides coated with an organic solvent can also be used, although the method is unreliable for droplets larger than about 200 μm . In the PILLS system, which was developed by Environmental Systems Corporation (ESC), an electro-optical device measures the size of drift droplets as they pass through a laser beam. This method is most reliable in the range of 80 to 900 μm (Park and Vance, 1978). Thus a combination of methods would appear to be necessary if all droplet sizes are to be accounted for.

The most accurate way to measure drift mass emissions is by isokinetic sampling of the exhaust at strategically defined points in a plane of the fanstack. This type of sampling is discussed in detail in Appendix C, as a prelude to the design of the SAI microbiological stack sampler. To date, the principal methods of collecting drift for quantification are by cyclone separation and by the hot glass bead method. In the first of these, which has

been developed by Ecodyne Cooling Products Division (Wistrom and Ovard, 1973), air is drawn at a known rate through a cyclone, which captures roughly 95 percent of the water mass. By comparing the concentrations of a nonvolatile, conservative constituent (e.g. sodium) in the collected drift and the hot or cold water basin, one can estimate the mass of drift lost to evaporation. Unfortunately, the device is highly efficient for fog collection, so that dilution of the drift is possible.

The other method, which was developed by ESC, consists of collecting drift in a tube packed with heated glass beads. The drift water evaporates, leaving behind a deposit of inorganic salts. By assuming that the cold water basin and the drift have the same concentrations of a tracer ion, the volume of drift can be estimated from the mass of that ion remaining on the beads. The glass bead method is reported to have an efficiency of at least 90 percent for droplets larger than $0.3 \mu\text{m}$ (Park and Vance, 1978).

According to Shofner (1978), drift measurement technology has advanced relatively little since the abovedescribed techniques were implemented. A comprehensive study by Chen (1977), and more recent work by Policastro et al. (1980) have demonstrated considerable variability in the ability of mathematical models to predict cooling tower plume behavior from the same input data set; in about 90 percent of the cases, these models are accurate to a factor of 1.5 to 2. For comparison consider the consequence of estimating emissions from a tower having a circulating water flow rate of $100\text{m}^3/\text{min} \pm 20$ percent, a drift rate of 0.002 percent ± 15 percent, and a pollutant concentration of $10 \text{ mg/L} \pm 15$ percent. The maximum overall error of estimate would be about 60 percent. Thus there is no immediate benefit, at least as far as use in modelling is concerned, in obtaining more accurate drift emission values.

Drift Size Distribution

Knowledge of the size distribution of drift droplets is important for accurate estimation of pollutant emissions and transport. Distributions vary from tower to tower, and depend upon several factors, including tower geometry; shape, density, height and composition of fill; air temperature; humidity; updraft air velocity; and efficiency of drift elimination devices. It is generally believed that, despite the fact that the air within the cooling tower is highly saturated with water vapor, drift droplets do not grow

during the brief time in which they are carried aloft by the exhaust air (Holmberg and Kinney, 1973). Larger droplets may form, however, when drift particles are caught temporarily on internal structural elements, coalesce with fog, and are re-entrained (Wistrom and Ovard, 1973).

Figure 8.1-1 shows the results of drift particle size and mass emission measurements on four industrial cooling towers. Curves A through D show the cumulative mass (as a percentage of the total) emitted in the form of droplets smaller than the stated diameter. Curve E represents the cumulative distribution of droplet numbers by size of droplet for the same tower as in curve A. It is immediately apparent that the median droplet size, at least for the case shown, is considerably lower than the mass median diameter. In other words, drift consists of a relatively large number of small particles, yet most of the water mass is in the larger particles. Mass median diameters (MMD) for towers B through D range from 70 to 290 μm . These values are consistent with a statement by Shofner (1978) that 100 μm was a "typical" value for several towers in the U.S. and Europe. Tower A, for which no descriptive information is available, has the highest MMD of all the towers encountered in our literature review.

The findings illustrated in Figure 8.1-1 have important consequences for the fate of drift emissions. Although, as noted above, dispersion and deposition models show widely varying results, it is generally true that the larger particles will settle out relatively near the tower, while the small particles will be transported with the cooling tower plume. Since the larger particles contain most of the drift water mass and--by assumption--most of the dissolved inorganic pollutant mass, most of the inorganic pollutant emissions will not be subject to long-range transport.

As Schrecker and Henderson have observed, no instrumentation is available to measure simultaneously drift particle size, number and salt concentrations. It is generally assumed that all drift droplets contain salts at the same concentrations as in the circulating water, yet experimental data may be interpreted to show otherwise. According to Schrecker and Henderson nearly all drift tests since 1971 have found higher mass emissions of a tracer salt (e.g. sodium) than would be predicted by multiplying water mass emission rates by salt concentrations in basin water. After considering the accuracies of all components of their measurement system, Schrecker and Henderson

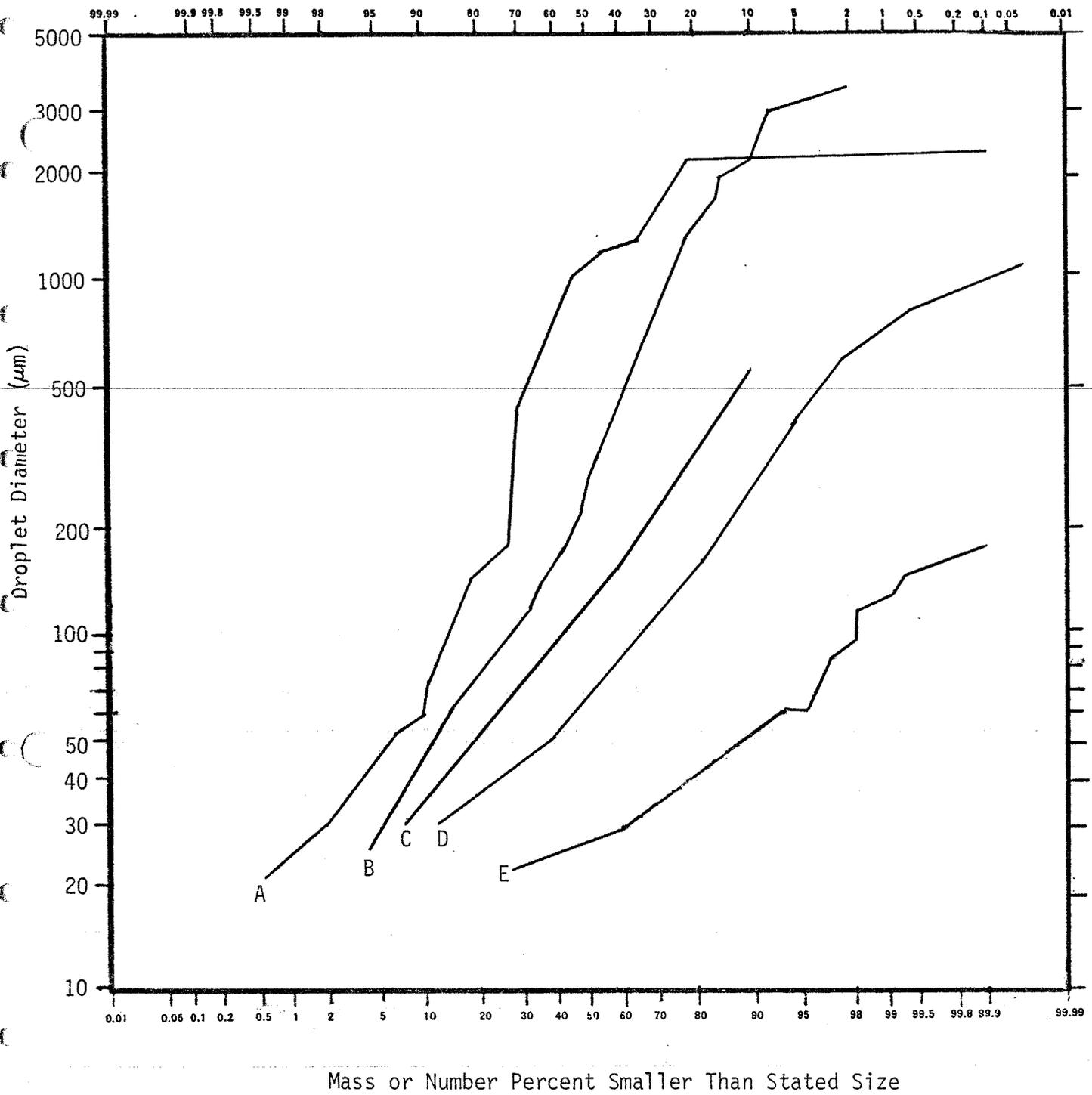


Figure 8.1-1. Cumulative Mass and Number Distributions of Cooling Tower Drift Droplets, By Droplet Size. A = Industrial, Mechanical Draft, Cross-Flow Tower (Wistrom and Ovard, 1973); B = Industrial, Mechanical Draft, Cross-Flow Tower (identity confidential); C = Turkey Point Mechanical Draft, Cross-Flow Tower (Schrecker and Henderson, 1976); D = Chalk Point Natural Draft Tower (Margetts, 1977); E = Number Distribution for Same Tower as A.

conclude that droplets larger than about 50 μm will remain at salt concentrations essentially the same as that of the basin water. Salt concentrations in the smaller droplets could increase if sufficient net evaporation takes place before they are emitted. However, since these small particles account for such a small percentage of drift mass emissions, even large changes in their salt concentrations would have a minor effect upon total salt mass emissions. We have therefore assumed for the remainder of this report that salt concentrations in drift and basin water are essentially the same.

8.1.3 Definition of Emission Factors

One of the principal objectives of this study was to develop "emission factors" for pollutants of potential concern for human health and general environmental quality. In the case of cooling towers, it is necessary to define very carefully what is meant by an emission factor. To be of value in estimating or predicting emissions from a process or device, an emission factor must relate emissions to some readily available or easily measurable characteristic. To date, the most common type of cooling tower emission factor is the measure of drift loss as a percentage of circulating water rate. While circulating water rates are rarely measured or monitored, they can be estimated reasonably well from tower manufacturer specifications or circulating water pump ratings.

This approach has two deficiencies, however. First, it cannot be used to estimate emissions of volatile compounds, since gases may be released to the atmosphere by means other than evaporation of emitted drift droplets. In addition, the correlation between circulating water rate and drift rate is not as close as is commonly assumed. After conducting laboratory tests on crossflow test cells, Holmberg and Kinney (1973) concluded that a more meaningful basis upon which to estimate emissions is in terms of mass per unit mass of air exhaust flow. Meanwhile, Schrecker and Henderson (1976) have proposed the use of a "salt mass emission fraction," which relates measured mass emissions of a particular species to the total mass of that species in the recirculating water system.

As will be seen below, we were able to calculate air flow-based emission factors for microorganisms and volatile organic compounds emitted from the towers we sampled. We could not do this for inorganic substances,

however, since we were unable to collect a sufficient amount of drift to analyze for the species of interest. Instead, we had to fall back upon the conventional method of basing drift losses upon recirculating water rate. Thus we developed two types of emission factors: air-based factors for microorganisms and organic vapors, and water-based factors for metals.

In order to apply these types of emission factors to towers not tested or to existing towers which may one day use wastewater, it is necessary to derive a relationship between air flow and circulating water rates. Fortunately, such a measure is commonly used in the cooling tower industry. It is the liquid-gas ratio (L/G), which is defined as the mass of water circulation per unit time divided by the mass flow rate of air (Cooling Tower Institute, 1977). Most cooling towers are operated so that the L/G ratio is between 1 and 2, and a large percentage of the towers associated with power plants have L/G ratios between 1.3 and 1.7 (Holmberg and Kinney, 1973). Calculated L/G ratios for the towers we sampled were:

Municipal Tower No. 1:	1.73
Municipal Tower No. 2:	1.55
Industrial Tower No. 1:	0.49
Geothermal Tower:	1.66

For towers about which we have no other information, we shall assume that $L/G = 1.5$. If Q_w and Q_a are the volumetric flow rates of water and air, respectively, and ρ_w and ρ_a are the respective densities of the two media, then

$$L/G = \frac{\rho_w Q_w}{\rho_a Q_a} \quad (8-1)$$

Therefore, if either Q_a or Q_w is known, then the other can be determined. For the purpose of making emissions estimates for towers not actually measured, we assume that the towers operate at sea level, that exhaust air temperature is 310°K (100°F), and that the vapor pressure of the exhaust air is at its saturation value for these conditions. From psychrometric tables and formulas

presented by Linsley et al. (1975), the density of the exhaust air is estimated to be 1.1 kg/m^3 (0.069 lbm/ft^3). The density of the recirculating water is assumed to be 1000 kg/m^3 . By substituting these values into Equation 8-1, we find that, given Q_a or Q_w in units of m^3/s ,

$$Q_a \text{ (m}^3/\text{s)} = 606 Q_w \quad (8-2)$$

and

$$Q_w \text{ (m}^3/\text{s)} = 0.00165 Q_a \quad (8-3)$$

Note that ranges of values of all the variables in Equation 8-1 can be used for evaluating a panoply of possible cases.

In Section 8.5 we will use our field test results to estimate emission factors for the constituents of concern. Let $F_{a,i}$ and $F_{w,i}$ be the air- and water-based emission factors, respectively, for pollutant i . In both cases, the units of the emission factor are kg/m^3 . Then for any tower,

$$E_i = \begin{cases} F_{a,i} Q_a \\ F_{a,i} Q_a + F_{w,i} Q_w \\ F_{w,i} Q_w \end{cases} \quad (8-4)$$

where E_i is the emission rate for pollutant i in kg/s . In cases for which there is only one emission mode (e.g. salt emissions in drift particles), only one emission factor is used.

8.2 PREVIOUS MEASUREMENT OF POLLUTANTS OF CONCERN

While a moderate amount of research into cooling tower emissions has been conducted, scant attention has been paid to characterizing emissions chemically or biologically. The purpose of this section is to review the few available data on species-specific emissions tests, with an emphasis upon those performed on California cooling towers. Note that only three towers studied by previous researchers use reclaimed wastewater or brackish water as makeup.

8.2.1 Inorganic Particulate Emissions

Our literature review and discussions with other researchers found no attempts to estimate toxic inorganic chemical species emissions directly by collecting and analyzing drift. The emphasis of most research to date has been upon collecting ambient air samples around cooling towers and/or measuring drift deposition. For example, a series of studies have been made to assess the effects of chromium emissions from a complex of cooling towers at the Oak Ridge Gaseous Diffusion Plant in Tennessee (Hanna, 1974; Alkezweeny et al., 1975). Emissions from the tower have been estimated by multiplying basin concentrations of chromium-based corrosion inhibitor by the measured drift flux rate. The calculated emissions of 0.04 g/s (from three towers) are rather high, and are probably due to the fact the towers have a drift rate (0.1 percent of circulating water flow) from 10 to 100 times those of modern towers. Alkezweeny et al. report ambient atmospheric chromium concentrations of 50 ng/m³ about 200 m downwind from one of the towers. Chromium in vegetation exceeds background levels for distances of up to 1.8 km (1 mile) from the complex (Taylor et al., 1975).

A similar study of chromium transport and distribution was made by Taylor et al. (1979) at the Paducah, Kentucky Gaseous Diffusion Plant. Chromium of cooling tower origin was observed to concentrate in vegetation and surface waters downwind from the plant. One interesting finding of the Kentucky study was that the full spectrum of elements detected in the tower's recirculating water was not present in the vegetation samples; whether this was due to selective emission of certain elements, differential dropout around the tower, or to different rates of retention on the vegetation is unknown.

The one California study of which we are aware was conducted at the Pacific Gas and Electric Company's Pittsburg power plant by Battelle Pacific Northwest Laboratories and Environmental Systems Corporation (Laulainen, 1979). This plant uses brackish water for cooling tower makeup during part of the year. (See Sections 4.3.4 and 5.5.1.) Concentrations of Na⁺, K⁺, NH₄⁺, Ca⁺⁺, Mg⁺⁺, Cl⁻, NO₃⁻, and SO₄⁼ were measured in drift droplets caught in deposition pans around the tower. Na⁺ and Mg⁺⁺ were measured in the recirculating water and in the particulate mass caught in ESC's hot glass bead isokinetic stack sampler, so that mass emissions of drift could be calculated. Unfortunately, none of the pollutants of concern in our study was measured.

8.2.2 Organic Vapor Emissions

To the best of our knowledge, only two measurements of organic vapor emissions from cooling tower stacks were made before the present study. An extensive indirect oil refinery cooling tower emissions test program was conducted over 20 years ago in Los Angeles County by a consortium of federal, state and local governmental agencies and the Western Oil and Gas Association (Bonamassa and Yee, 1957). Bubble-free samples of water were collected from the hot water inlet line and from a funnel poised to catch flow from the hot water trough to the cold water basin. Samples were then stripped with hydrocarbon-free nitrogen and analyzed by infrared spectrophotometry at 3450 nm. Concentrations were expressed as n-hexane. Emissions from the tower were estimated by multiplying the difference in makeup and recirculating water concentrations times the recirculating water flow rate. Using this methodology, Bonamassa and Yee estimated that 17 cooling towers associated with oil refineries emitted a combined 1028 metric tons/yr (1131 tons/yr) of hydrocarbons.

Several aspects of this study make it difficult, if not impossible, to compare its results with ours. First, the problem addressed was the potential contamination of recirculating water by leaks in heat exchanger systems, rather than the deliberate use of treated industrial wastewater as makeup. In addition, cooling tower technology has changed since these tests were made, so that emissions characteristics could be quite different. Finally, no attempt was made to identify hydrocarbon species. Some of the lower molecular weight species of interest, such as chloroform, cannot be measured quantitatively by the method used (Bonamassa and Yee, 1957).

The Electric Power Research Institute (EPRI) is currently sponsoring emissions tests at power plant cooling towers to determine the relationship between chloroform and nonvolatile organic compounds and chlorination practices (Kawaratani, 1981). Although three towers were measured, the results of the EPRI study (RP 1744-1) were unavailable as of this writing.

The deliberate use of cooling towers to transfer volatile pollutants from wastewater to the atmosphere has been explored by Thibodeaux (1974), who set up a laboratory apparatus to simulate a counterflow cooling tower. Desorption experiments were performed on single pure components in water, simulated wastewater, and actual samples of wastewater from poultry, metal,

oil-field, canning, pharmaceutical, paper, food, fiber, petroleum refining and petrochemical industries. The volatile organic constituents of these wastewaters had relative volatilization rates from 4.4 to 41.6 times that of water. Thibodeaux's conclusion was that a significant portion of the volatile organics in industrial wastewater can be emitted to the air in counterflow cooling towers.

Finally, under another California Air Resources Board Contract, SAI measured benzene emissions from the fanstack of a one-cell mechanical forced-draft cooling tower associated with a coke byproduct recovery plant. The results of that study will be available in mid-1982.

8.2.3 Geothermal Pollutants

While numerous analyses of geothermal steam, steam condensate and cooling tower recirculating water have been made, direct measurements of stack emissions have been limited. To our knowledge, only hydrogen sulfide, ammonia and mercury have been measured in stack emissions from The Geysers, the only operating geothermal power plant complex in the state.

Hydrogen Sulfide

Pacific Gas and Electric Company (PG&E) performed H₂S emissions tests between 26 August and 1 September 1976 on the Unit 11 cooling tower (Semprini, 1977). The tower is a nine-cell, mechanical induced-draft, crossflow unit. Hydrogen sulfide enters the tower in two ways. First, from 60 to 70 percent of the H₂S in the incoming steam is absorbed by cooling water in the direct-contact condensers and thus enters the tower via the return flow. The remaining H₂S is injected into the air inlet for each cell of the tower, where some of it is absorbed by the falling water and some is released to the atmosphere. Treatment chemicals comprising the iron catalyst abatement system circulate with the tower water and act upon any H₂S dissolved therein.

Velocity, temperature and H₂S sampling traverses were made on each fanstack, along three diameters spaced 60 degrees from each other. Hydrogen sulfide concentrations were measured by the same type of continuous analyzer used in our test program (see Section 7.6.2).

H₂S distribution in the cooling tower exhaust was found to be decidedly nonuniform. Concentrations were generally higher at measurement

points near the hot water trays, from which some H_2S is stripped out of the water phase, and near the noncondensable gas injection points. Concentrations were generally lower towards the centers of the stacks, where airflows are negative. The fact that H_2S concentrations were nonzero in these areas of net downward flow implies that considerable diffusion of the gas throughout the cell may occur. Finally, local winds had some effect upon the distribution of gases in the exhaust. Mass emissions from the individual cells ranged from 0.00258 kg/s (20.5 lb/hr) to 0.00436 kg/s (34.6 lb/hr) of H_2S . The iron catalyst system abated 57 to 66 percent of the incoming hydrogen sulfide. Similar tests on the tower which we later measured were conducted by Robertson et al. (1981), who estimated combined emissions of 0.00542 kg/s (43.0 lb/hr) from all the tower's cells.

Mercury

Battelle Pacific Northwest Laboratories researchers have conducted mercury emissions tests at several cooling towers associated with The Geysers and the Cerro Prieto, Mexico geothermal power plants (Robertson et al., 1977). At both plants, samples of incoming steam, ejector off-gases, cooling tower exhaust and ambient air were collected on gold-coated glass beads, following the methods of Braman and Johnson (1974). The mercury was then analyzed by volatilization and flameless atomic absorption spectrophotometry. Table 8.2-1 shows the mercury concentrations in the various gaseous samples. Concentrations in cooling tower exhaust air ranged from 0.20 to $1.3 \mu\text{g}/\text{m}^3$. Robertson et al. point out, however, that contamination of their sampling equipment may have resulted in the two highest readings shown in the table. Elemental mercury constituted 84 to 87 percent of the total mercury in the cooling tower exhaust from Geysers Unit 3 and the Cerro Prieto plant, respectively. The remaining mercury was assumed to be in the Hg^{2+} state, but species were not absolutely identified. Robertson et al. believe that the high temperatures and reducing environment, together with the high vapor pressure of Hg^0 , prevent reaction of the elemental mercury with H_2S in the incoming steam and in the ejector off-gases.

Attempts were made to calculate mass balances for all the towers except Geysers Units 4 and 11. Although the cooling towers were identified as the dominant pathways for release of mercury to the atmosphere, only 40 to 60 percent of the incoming mercury of The Geysers could be accounted for;

Table 8.2-1

MERCURY CONCENTRATIONS IN AIR SAMPLES COLLECTED
AT THE GEYSERS AND AT CERRO PRIETO
(Concentrations in $\mu\text{g}/\text{m}^3$)

Sample Source	Cerro Prieto	The Geysers				
		Unit 3	Unit 4	Unit 7	Unit 8	Unit 11
Incoming steam	300	5800	>4000	2500	1800	1800
Ejector off-gas	190	<10	>400	65	50	83
Cooling tower exhaust	0.56	0.59	1.3 ^a	0.18	0.20	0.93 ^a
Ambient air ^b	0.068	0.001	0.001	0.001	0.001	0.001

Source: Robertson et al. 1977.

^aHigh values believed to be due to contamination of sampling and analytical equipment.

^bRange was <0.001 to 0.018 $\mu\text{g}/\text{m}^3$. Most measurements were near the detection limit of 0.001 $\mu\text{g}/\text{m}^3$.

Robertson et al. believe that the sludge that accumulates in the cold water basin of the towers could be an important sink for the mercury. Estimated mass emission rates for The Geysers towers ranged from 0.63 to 1.6 grams per MWe per day.

Battelle teams have also conducted mercury emissions tests on the tower we sampled (Robertson et al., 1981). The concentration of mercury in the exhaust ranged from 0.16 to 1.13 $\mu\text{g}/\text{m}^3$, compared to our range of 1.0 to 1.2 $\mu\text{g}/\text{m}^3$.

8.2.4 Microbiological Testing

Our literature review found only one report of attempts to measure the microbial emissions from cooling towers. Adams et al. (1978, 1979, and 1980), examined four electrical generating facilities. Two of these used sewage effluent for cooling tower makeup and two used polluted river water. Bacterial assays were made of cooling tower basin water, the particles exiting the cooling tower fan vents, and aerosolized bacteria-containing particles downwind of the towers. Downwind aerosols were collected with a Litton high volume sampler, the Reyniers time-sequence sampler, and the Anderson six stage particle impactor sampler. The number of bacteria-laden particles exiting each tower vent was determined by inverting a 150-mm petri plate over the vent for 15 seconds. Exiting aerosol particles were impinged on the agar. By assuming 95-percent impingement, measuring the area of the vent opening and the exit velocity, the number of bacteria particles per cubic meter of exhaust air was calculated.

One of the towers studied was the Burbank/Olive 1 tower, which was "Municipal Tower No. 1" in our field sampling. Adams et al. sampled the tower twice. On the first visit the total bacteria count (TBC) in the cold water basin was 1.7×10^5 bacteria/ml. The number of impinged bacteria particles on the inverted petri plate indicated that 2.8×10^3 bacteria per cubic meter of air were exiting the vent. The circulating water on the second visit was found to contain only 180 bacteria/ml, and only 50 particles/ m^3 were estimated to be exiting the vent. It was thus concluded that a change in biocidal treatment from the use of gaseous chlorine to chlorine dioxide resulted in a thousand-fold reduction of viable particles in the circulating water between the two visits.

In general, more bacteria were found in the circulating water than in the makeup. Because water counts were low in relation to the relatively high counts measured exiting the vents, Adams et al. (1978) concluded that the airborne bacterial particles leaving the vent may have originated from the ambient air rather than from the basin water. Consideration of our air flow test data and data furnished by the plant operator calls this conclusion into question, however. Given the circulating water bacterial concentrations on Adams et al.'s first visit and assuming a drift rate of 0.02 to 0.002 percent of circulating water rate, one estimates a potential bacterial concentration of 6.7×10^5 to 6.7×10^6 particles/m³ in the tower exhaust. Adams et al. measured 2.8×10^3 particles/m³. For the second visit, calculated exhaust concentrations would be 6.9×10^2 to 6.9×10^3 particles/m³; Adams et al. measured 50 particles/m³. Therefore fewer, rather than more, particles were collected than would be expected.

The impingement method of measuring the bacteria in vented air may have resulted in undercollection. Because this technique does not sample isokinetically, a significant number of particles may ride air currents around the petri dish and escape capture.

Bacteria identified in the Burbank/Olive 1 tower are listed in Table 8.2-2. Only about one percent of the bacteria collected were of the family Enterobacteriaceae.

The second electrical generating plant studied was located in the Southwest. The makeup water source for its cooling towers was a municipal sewage treatment plant which used trickling filters for secondary treatment. The TBC in the cooling tower basin water varied from 4.2×10^4 to 1.4×10^6 particles/ml, and the number of bacterial particles found exiting the vent varied from 241 to 984 per m³. Sixty percent of the colonies isolated from vent samples were gram negative rods. (See Table 8.2-2.)

The third plant was located in the Midwest on the bank of a heavily polluted river. Downwind aerosols, cooling tower basin water and exhaust from vents were sampled for bacteria. The cooling tower had a TBC of 10^5 /ml. As the result of a heavy rainfall, the makeup water at the time of sampling was taken from a shock-loaded water source (bypassing the sewage treatment facility). The resultant concentration of fecal coliforms collected from the cooling tower had increased from a normal value of less than 2/ml to more than

Table 8.2-2

BASIN WATER BACTERIA IDENTIFIED IN PREVIOUS STUDIES OF COOLING TOWERS
USING RECLAIMED MUNICIPAL WASTEWATER AS MAKEUP

Burbank/Olive 1	"Southwest" Power Plant
<u>Enterobacter agglomerans</u>	<u>Pseudomonas</u> genera
<u>Citrobacter freundii</u>	<u>Enterobacter agglomerans</u>
<u>Citrobacter diuicis</u>	* <u>Serratia sp.</u>
* <u>Yersinia enterocolitica</u>	* <u>Pseudotuberculosis sp.</u>
<u>Escherichia coli</u>	* <u>Shigella flexneri</u>
* <u>Proteus mirabilis</u>	(Other Enterobacteriaceae)
* <u>Serratia liquifaciens</u>	<u>Acinetobacter sp.</u>
* <u>Serratia marcescens</u>	<u>Alcaligenes sp.</u>
* <u>Klebsiella pneumonia</u>	<u>Achromobacter sp.</u>
<u>Providencia stuartii</u>	("Pseudomonas-like" genera)
* <u>Klebsiella ozaenae</u>	* <u>Bordetella sp.</u>
	* <u>Proteus vulgaris</u>
	<u>Proteus mirabilis</u>

Source: Adams et al., 1978; Adams et al., 1979; Adams et al., 1980.

* Human Pathogen.

2×10^4 /ml. TBC exhaust emissions were measured at 25,190 particles/m³. Aerosol recoveries at 100 to 150 m downwind were 200 to 600 bacteria/m³.

Adams et al. (1979) have done subsequent work on the determination of the particle size, source strength, and downwind travel of emitted aerosols from cooling tower vents. In one study Bacillus subtilis was added to the cooling tower water as a tracer, and fluorescent particles were added above the vent fan. Over 75 percent of the particles collected downwind were in the 1.0 to 5.0 μm range, and were thus respirable. Furthermore, particles in this size range have a negligible settling velocity and thus could travel long distances from the source, depending upon meteorological conditions. In addition, Spendlove et al. (1979) have used source strength and downwind travel data obtained from Adams et al.'s study to generate models of plume rise and downwind dosages.

8.3 EMISSIONS FROM TOWERS USING MUNICIPAL AND INDUSTRIAL WASTEWATER

8.3.1 Emissions of Inorganic Salts

No drift mass flux measurements were made under this research program. Measured drift rates are unavailable for all the towers except the one associated with the geothermal power plant. In estimating inorganic salt emissions from the municipal and industrial cooling towers it was therefore necessary to assume a range of values for the drift rate. After considering the results of all the major studies reported in the literature, we have assumed that the drift losses from modern mechanical draft cooling towers are likely to range between 0.001 and 0.01 percent of the circulating water flow rate. (The geothermal tower's drift rate was measured at 0.00162 percent.) We believe that the 0.01-percent value represents a realistic "worst case."

Inorganic constituent emissions were estimated for each municipal and industrial cooling tower by the following formulas:

$$E_{i,l} = D_l Q_w C_{i,l} \quad (8-5)$$

$$E_{i,u} = D_u Q_w C_{i,u} \quad (8-6)$$

where $E_{i,l}$ and $E_{i,u}$ are the lower and upper bounds, respectively, of emissions

of constituent i (mass/time); Q_w is the circulating water flow rate (volume/time); $C_{i,l}$ and $C_{i,u}$ are lower and upper measured values of concentration of constituent i (mass/volume); and D_l and D_u are the lower and upper assumed drift fractions (0.00001 and 0.0001, respectively).

Table 8.3-1 presents our estimates of annual emissions of total dissolved and suspended solids (TDS and TSS), major minerals and trace metals from the five municipal and industrial cooling towers sampled in this study. The three towers using municipal wastewater for makeup appear to be the largest sources of total salt and major mineral emissions. The largest of these sources would be Municipal Tower No. 3 (Glendale), whose total salt emissions are estimated to be between 2.22 and 22 metric tons (2.4 to 24 tons) per year. Sodium, chloride and sulfate emissions could exceed one metric ton/year for these towers. The highest estimated sulfate emissions would be 1.2 and 12 tons (1.3 to 13 tons) per year from the Glendale Tower. It should be noted that the emission rates for the Burbank towers are likely to be toward the lower end of the stated ranges, since their drift elimination systems are fairly modern. As the Glendale tower is over 20 years old, its emissions may be closer to the upper end of the range.

Emissions of all toxic trace metals except chromium, copper and zinc are estimated to be below 1 kg/yr (0.45 lb/yr) per tower. Chromium emissions would exceed this level only at Industrial Tower No. 1. Although our estimate of 10 to 110 kg/yr (22 to 240 lb/yr) shows a need for further attention to this tower as a toxic metals source, the chromium emissions are due to the use of the element as a corrosion inhibitor, rather than to its presence in the industrial wastewater used as makeup. Chromium emissions from the other industrial tower and the municipal towers are estimated to be about three orders of magnitude lower. Similarly the relatively high zinc emissions from all the towers (maximum of 1.3 to 29 kg/yr from Municipal Tower No. 1) are probably due to use of zinc-based treatment chemicals. Finally, the relatively high copper emissions (maximum of 1.3 to 13 kg/yr) from most of the towers are likely the result of corrosion of condenser elements, rather than to use of wastewater for makeup.

In conclusion, toxic trace metal emissions resulting from the use of treated wastewater for makeup do not appear to be significant. The high salt emissions, particularly those of sulfate, would warrant further attention if

Table 8.3-1

ESTIMATED ANNUAL INORGANIC SALT EMISSIONS FROM MUNICIPAL AND INDUSTRIAL
COOLING TOWERS SAMPLED
(All emissions in kg/yr)

<u>Total Dissolved Solids (TDS)</u>			<u>Total Suspended Solids (TDS)</u>		
MT 1	1,300	- 13,000	MT 1	12	- 140
MT 2	770	- 8,400	MT 2	11	- 120
MT 3	2,200	- 22,000	MT 3	17	- 180
*IT 1	1,700	- 18,000	*IT 1	11	- 110
IT 2	110	- 1,200	IT 2	5.6	- 70
<u>Sodium as Na⁺</u>			<u>Magnesium as Mg⁺⁺</u>		
MT 1	250	2,500	MT 1	42	420
MT 2	Not analyzed		MT 2	Not analyzed	
MT 3	360	3,700	MT 3	70	710
*IT 1	39	390	*IT 1	5.1	52
IT 2	19	19	IT 2	3.2	32
<u>Chloride as Cl⁻</u>			<u>Sulfate as SO₄⁻⁻</u>		
MT 1	240	3,000	MT 1	500	5,000
MT 2	Not analyzed		MT 2	Not analyzed	
MT 3	450	4,500	MT 3	1,200	12,000
*IT 1	Not analyzed		*IT 1	110	1,200
IT 2	14	170	IT 2	16	160
<u>Cadmium</u>			<u>Chromium</u>		
MT 1	0.01	0.11	MT 1	0.01	0.1
MT 2	0.007	0.07	MT 2	0.023	0.25
MT 3	0.007	0.13	MT 3	0.015	0.15
*IT 1	0.0005	0.005	*IT 1	10	110
IT 2	Not analyzed		IT 2	0.0008	0.008
<u>Copper</u>			<u>Iron</u>		
MT 1	1.3	13	MT 1	Not analyzed	
MT 2	0.64	6.7	MT 2	Not analyzed	
MT 3	0.64	6.6	MT 3	Not analyzed	
*IT 1	0.011	0.13	*IT 1	Not analyzed	
IT 2	Not analyzed		IT 2	0.042	0.43

* Emission based upon a highly uncertain estimate of circulating water flow; see text.

Table 8.3-1
(Cont.)

<u>Lead</u>			<u>Mercury</u>				
MT 1	0.027	-	0.3	MT 1	0.00011	-	0.0012
MT 2	0.00052	-	0.01	MT 2	0.000021	-	0.00022
MT 3	0.002	-	0.027	MT 3	0.000023	-	0.00041
*IT 1	0.00066	-	0.013	*IT 1	0.0000012	-	0.000012
IT 2	Not analyzed			IT 2	Not analyzed		

<u>Zinc</u>			
MT 1	1.3	-	29
MT 2	0.32	-	3.3
MT 3	0.13	-	2.4
*IT 1	1.4	-	15
IT 2	Not analyzed		

* Emission based upon a highly uncertain estimate of circulating water flow; see text.

wastewater were used for cooling in agricultural areas. Finally, the problem of chromium emissions from use of hexavalent chromate salts for corrosion inhibition in all sorts of towers (whatever the makeup water source) needs to be explored further.

8.3.2 Organic Vapor Emissions

Nonvolatile Organics

Nonvolatile organic compound emissions were estimated by assuming that all such material present in the circulating water was emitted through the drift. Equations 8-5 and 8-6 were used to calculate the results presented in Table 8.3-2. Because negligible levels of nonvolatile organics were detected in Municipal Tower No. 2 and Industrial Tower No. 2, no emission estimates were made for those cases. Nonvolatile organic emissions from the remaining cooling towers which use municipal wastewater as makeup would be on the order of one kg/yr. Emissions from Industrial Tower No. 1 would range from 23 to 250 kg/yr (50 to 550 lb/yr). It is difficult to judge which end of the range is more realistic. On the one hand, the tower is relatively old, and does not have modern drift eliminators. On the other, visible drift emissions were observed to be very small.

Volatile Organic Compounds

Earlier in this chapter, we discussed possible mechanisms by which cooling tower systems using reclaimed wastewater may serve as net emission sources of volatile organic compounds. Before attempting to estimate volatile organic emissions, let us see whether the postulated mechanisms are consistent with the results of our field tests. First let us examine the relationship between makeup water and circulating water concentrations of the chemical species of interest. Except for the cases of chloroform at Municipal Tower No. 1 during the first visit and hexane in Industrial Tower No. 1 on the second visit, makeup water concentrations of volatile organic compounds greatly exceeded those in the hot and cold water basins; indeed, these constituents were generally found to be below detectable limits in almost all the circulating water samples examined. The only cases of detectable circulating water concentrations of volatile organics were:

Table 8.3-2

ESTIMATED EMISSIONS OF NONVOLATILE ORGANIC COMPOUNDS
FROM COOLING TOWERS USING MUNICIPAL AND INDUSTRIAL WASTEWATER

Tower	Nonvolatile Organic concentration (µg/L)	Circulating Water Flow Rate (m ³ /s)	Estimated Emissions (kg/yr)	
			Low	High
Municipal Tower No. 1	3.31 - 3.72	2.15	0.22	2.5
Municipal Tower No. 2	Negligible	1.64	Negligible	14
Municipal Tower No. 3	5.12 - 21.94	2.11	0.34	250
Industrial Tower No. 1	2985 - 3340	0.241	23	Negligible
Industrial Tower No. 2	Negligible	1.26	Negligible	250

<u>Compound</u>	<u>Tower</u>	<u>Visit</u>	<u>Makeup Water Conc. (ppb)</u>	<u>Circ. Water Conc. (ppb)</u>
Chloroform	MT1	1	22	14 - 20
Chloroform	IT1	1	16	2.3
Benzene	IT1	1	196	2.3
Toluene	IT1	1	354	2.4 - 2.7
Hexane	IT1	2	6	5

As will be discussed below, a considerable part of the chloroform in the circulating waters of both Municipal Tower No. 1 and Industrial Tower No. 1 may have been due to generation of halomethanes in the towers themselves, while the three hydrocarbons (benzene, toluene and hexane) probably entered the industrial tower from the outside air. It is therefore consistent with our field data to assume that most or all of the volatile organic complement of the makeup water entered the atmosphere either immediately upon discharge of the water to the cooling towers' cold water basins, or shortly thereafter.

Another result which must be explained by some emissions mechanism is the presence of 11 compounds, including one straight-chain hydrocarbon, five aromatic hydrocarbons, one halomethane and four chlorinated two-carbon species, in the inlet air of Municipal Towers No. 1 and 2. Three explanations are plausible. First, the hydrocarbons may have been emitted as a result of the storage and handling of fuel oil in a facility about 50 m west of the cooling tower complex at the Burbank power plant. Second, as seen in Table 8.3-3, nine of the eleven compounds have been detected in ambient urban air at concentrations comparable to those we measured in the inlet air. (No measurement data could be found for bromodichloromethane and 1,1,2,2-tetrachloroethane.) Thus our inlet air samples could have been "typical" of urban air in the Los Angeles Basin. A final alternative explanation for the presence of the 11 volatile organics in the inlet air samples would be that the samples were contaminated by emissions from the tower. Although the general direction of air flow was decidedly toward the cooling tower louvers, the Tenax sampler intake orifice may have been in a counterdirectional eddy. Alternatively, low molecular weight organic compounds may have been diffusing away from the tower, toward the sampler.

Table 8.3-3

COMPARISON OF VOLATILE ORGANIC COMPOUND CONCENTRATIONS IN
COOLING TOWER INLET SAMPLES AND URBAN AMBIENT AIR
(Concentrations in $\mu\text{g}/\text{m}^3$)

Compound	Range Detected in Task 4 Sampling at Municipal Towers No. 1 and 2	Literature Values for Urban and Suburban Ambient Air	References
1,2-Dichloroethane (EDC)	≥ 31	< 0.02 Rural Wash. State 16 near EDC plant	Verschueren, 1977 Barber, 1977
Bromodichloromethane	24	No Data Available	
Trichloroethylene	5	1-6 Tuscaloosa, AL 0.6-48 Urban U.S.	Holzer et al., 1977 Lillian et al., 1975
Benzene	19	13-240 Los Angeles, CA	Margler et al., 1979
Hexane	≥ 11	29 Suburban Italy	Ciccioli et al., 1976
1,1,2,2-tetrachloroethane	20 - 70	No Data Available	
Tetrachloroethylene (perc)	20 - 70	0-29 Los Angeles, CA 5-14 Los Angeles, CA	Simmonds et al., 1974 Singh et al., 1977
Toluene	36 - 41	38-190 Los Angeles, CA	Verschueren, 1977
m-Xylene	12	18-93 Los Angeles, CA	Verschueren, 1977
o-Xylene	7 - 9	9-48 Los Angeles, CA	Verschueren, 1977
p-Xylene	7 - 9	9-44 Los Angeles, CA	Verschueren, 1977

Finally, it would be desirable to explain the presence of 32 and 24 $\mu\text{g}/\text{m}^3$ of bromodichloromethane in the exhaust and inlet air, respectively, of Municipal Tower No. 1 and its absence in makeup and circulating water samples taken concurrently. By using our air flow measurement data and makeup flow data provided by the plant operator, we estimate that, if all bromodichloromethane in the exhaust had originated in the makeup, then its concentration in this medium would have had to have been about 0.6 mg/L. Since the limit of detection of bromodichloromethane by our analytical techniques was 0.024 mg/L, it would have been detected had it been present. There is thus reason to postulate that this halomethane was generated by the haloform reaction (See Section 5.6.2) in the circulating water during the round of chlorination which took place shortly before our air samples were taken, and was effectively emitted. But, it may be asked, what about the 24 $\mu\text{g}/\text{m}^3$ of bromodichloromethane measured in the inlet air. Unfortunately, no data on "typical" concentrations of this compound in urban ambient air are available, so we cannot rule out the possibility that it was merely passed through by the cooling tower. However, bromodichloromethane, which is used as an industrial solvent, is far less common than the other chlorinated hydrocarbons, such as ethylene dichloride and tetrachloroethylene, detected in our inlet air samples. It would therefore be expected to be at lower concentrations in ambient air. The possibility thus arises that the inlet air sample contained bromodichloromethane which was in the process of being emitted from the cold water basin.

In summary, we believe that the following "scenario" is consistent with the observed data (although cannot be shown to be the only one possible):

- (1) Most or all of the volatile organic compounds present in the makeup are emitted to the atmosphere;
- (2) Most or all chemical species, other than halomethanes, present in the exhaust originate in the ambient air, and should not be considered to be cooling tower emissions; and
- (3) Most or all of the halomethane emissions detected in the cooling tower exhaust originate in the tower itself.

Emissions due to the presence of volatile organic compounds in the makeup are, by the terms of this study, a result of the use of wastewater for cooling. Whether halomethane emissions can be ascribed to the use of wastewater is more problematic. Wastewater generally has higher concentra-

tions of some of the believed precursors of halomethanes, namely complex humic acids, than do many freshwater sources, and both makeup and circulating water are chlorinated. Both our data and those available from previous studies are insufficient, however, to draw any conclusion.

Emissions due to the presence of volatile organic compounds (including halomethanes) in the makeup were estimated by the following equation:

$$E_i = C_{i,m} Q_m \quad (8-7)$$

in which E_i is the emission of constituent i (mass/time); $C_{i,m}$ is the concentration of constituent i in the makeup (mass/volume); and Q_m is the makeup water flow rate (volume/time). Emissions due to generation of halomethanes in the tower were estimated from:

$$E_i = C_{i,e} Q_a \quad (8-8)$$

Where E_i is the emission of constituent i (mass/time); $C_{i,e}$ is the measured concentration of constituent in the exhaust air (mass/volume); and Q_a is the total exhaust air flow rate for the tower (volume/time).

Table 8.3-4 presents our estimates of annual emissions of individual organic compounds from the three towers having detectable volatile organic compound concentrations in their makeup water. It should be clearly understood that these estimates are based upon the unrealistic assumption that makeup water concentrations measured in one or two grab samples continue at the same levels 24 hours per day, 365 days per year. We do not know how representative the observed values really are. Our estimates do serve, however, as an order-of-magnitude estimate of the maximum emissions from the three towers. Thus, volatile organic emissions are probably at most a couple of hundred kg/yr from the municipal towers and 500 to 1000 kg/yr from the industrial tower measured.

8.3.3 Emissions of Bacteria and Virus

Estimates Based Upon Stack Test Data

Viable indicator bacteria and bacterial virus particles were collected only from the stack of Municipal Tower No. 1; organisms collected

Table 8.3-4

ESTIMATED ANNUAL VOLATILE ORGANIC EMISSIONS FROM MUNICIPAL
AND INDUSTRIAL COOLING TOWERS, ASSUMING THAT ALL VOLATILE
COMPONENTS OF WASTEWATER MAKEUP ARE EMITTED
(Emissions in kg/yr)

Compound	Municipal Tower No. 1	Municipal Tower No. 3	Industrial Tower No. 1
Hexane	-	-	1
Benzene	-	0.7	24 - 78
Toluene	-	-	43 - 52
m-xylene	-	-	20 - 28
o-xylene and p-xylene	-	-	19 - 31
Ethylbenzene	-	-	2 - 5
Ethylmethylbenzene	-	-	10
2-Propanone	-	-	11
2-Butanone	-	-	6
Chloroform	43	4	2
Bromodichloromethane	-	3	48
Dibromochloromethane	-	3	-
1,1-Dichloromethane	-	-	9
Trichloroethane	35	-	-
Trichloroethene	16	-	7
1,1,2,2-Tetrachloroethane	-	-	-
Tetrachloroethylene	31 - 59 ^a	-	14
1,2-Dichloropropane	-	-	2
"Others"	NQ ^b	NQ	139

^a 1,1,2,2-tetrachloroethane and tetrachloroethylene co-eluted, and were quantified as a combination.

^b NQ = Not quantified.

from the stack of Municipal Tower No. 2 were at below detectable concentrations in the sampling media, and Municipal Tower No. 3 was not tested under Task 4. We can only estimate a lower bound for total coliform emissions from Municipal Tower No. 1, since the number of organisms captured was higher than the upper confidence limit for the dilution examined in the laboratory. (It could only be reported as greater than or equal to 2400 organisms per 100 ml.) As estimated in Section 7.3, the concentration of total coliforms in the exhaust air was at least 1.6 particles per cubic meter. Given the tower's total exhaust air flow rate of 1125 m³/s, total coliform emissions would be at least 1800 particles per second. Using the same air flow rate and the results presented previously in Table 7.3-8, we estimate that fecal coliform and fecal streptococcus emissions were each less than 18 particles per second, that E. coliform and fecal streptococcus emissions were each less than 18 particles per second, and that E. coliphage emissions were about 80 particles per second.

Estimates Based Upon Water Sampling Data

Microbial emissions may also be estimated by assuming that bacteria and virus particles are present in the drift in the same concentrations as in the circulating water. Ranges of indicator bacteria and virus emissions were computed with Equations 8-5 and 8-6, using microorganism concentrations instead of inorganic salt concentrations. Results are presented in Table 8.3-5. Table 8.3-6 shows our estimates of indicator organism concentrations in the exhaust air. For Municipal Towers No. 1 and 2, measured air flow rates were used. For Municipal Tower No. 3, the air flow rate was calculated from Equation 8-2.

With only a few exceptions, estimated emissions vary by only one order of magnitude from one tower to another, and between visits to the same tower. Emissions from the two Burbank towers appear to have been slightly greater than those from the one sampled in Glendale. One very interesting finding is that the cooling tower exhaust air concentrations of all indicator bacteria and virus measured directly at Burbank/Olive 1 fall within the ranges of concentrations and assumed drift rates. For example, as seen in Table 8.3-6, E. coliphage concentrations in the tower exhaust are estimated to be between 0.055 and 0.86 particles/m³. The measured concentration was 0.07 particles/m³.

ESTIMATED EMISSIONS OF INDICATOR ORGANISMS FROM COOLING
TOWERS USING RECLAIMED MUNICIPAL WASTEWATER
(All emissions in particles/second)

Organism	Range ^a	Burbank/Olive 1		Burbank/Mag. 4		Glendale ^b	
		Task 3	Task 4	Task 3	Task 4	Task 3	Task 4
Total Coliforms	Low	≥520	≥5	39	3.8	1.5	
	High	≥5200	≥51	754	71	19	
Fecal Coliforms	Low	3.2	4.9	0.66	0.49	0.84	
	High	49	320	71	4.9	8.4	
Fecal Streptococcus	Low	1.5	4.9	2.5	0.66	0.84	
	High	19	320	46	5.5	32	
E. Coliphage	Low	34	62	30	3.3	0	
	High	1520	965	800	150	0	

^aLow and high estimates based upon assumption of drift rates of 0.001 and 0.01 percent of circulating water rate, respectively.

^bNo Task 4 sampling done at this tower.

Table 8.3-6

ESTIMATED EXHAUST AIR CONCENTRATIONS OF INDICATOR ORGANISMS
 IN COOLING TOWERS USING RECLAIMED MUNICIPAL WASTEWATER
 (All concentrations in particles/m³)

Organism	Range ^a	Burbank/Olive 1		Burbank/Mag. 4		Glendale ^{b,c} Task 3
		Task 3	Task 4	Task 3	Task 4	
Total Coliforms	Low	≥0.46	≥0.46	0.041	0.0039	0.0012
	High	≥4.6	4.6	0.79	0.073	0.015
Fecal Coliforms	Low	0.0029	0.0044	0.0007	0.0005	0.0007
	High	0.044	0.29	0.073	0.0051	0.0066
Fecal Streptococcus	Low	0.0013	0.0044	0.0026	0.0007	0.0007
	High	0.017	0.29	0.048	0.0057	0.025
E. Coliphage	Low	0.031	0.055	0.031	0.0034	0
	High	1.35	0.86	0.837	0.15	0

^aLow and high estimates based upon assumption of drift rates of 0.001 and 0.01 percent of circulating water rates, respectively.

^bNo Task 4 sampling done at this tower.

^cAir flow estimates; see text.

8.4 EMISSIONS FROM THE GEOTHERMAL TOWER

8.4.1 Hydrogen Sulfide Emissions

Hydrogen sulfide emissions were estimated by the following procedure. Velocity measurement data for north-south and east-west traverses of the tower we sampled were obtained from the tower operator. Since our sampling radii were coincident with only one of the radii for which velocity data were available, angular and radial interpolations were used to estimate the velocities at our 32 sampling points. Annular flows were then estimated and multiplied by the average measured H_2S concentration within each annulus. Concentrations in ppm were converted to units of mass per volume by assuming a "typical" stack exhaust temperature of $37^{\circ}C$ and atmospheric pressure. Our calculations are summarized in Table 8.4-1. Mass flow is seen to be highly non-uniform.

Hydrogen sulfide emissions from the cell we measured are estimated to be 0.97 kg/hr (2.1 lb/hr). Since the tower has five cells, the total emissions for the tower would be 4.8 kg/hr (11 lb/hr). That this value is about one fourth that measured by Robertson et al. (1981) in January 1980 is not surprising, since the Stretford Process was not operating at the earlier date. The great reduction in circulating water concentrations of H_2S between our two visits (0.87 to 1.62 ppm in 1980 versus <0.2 ppm in 1981) is further corroboration of the effective operation of the Stretford Process.

8.4.2 Ammonia Emissions

Ammonia emissions were calculated by assuming that ammonia vapors were distributed in the fanstack in proportion to hydrogen sulfide concentrations. On the basis of our measurements, we estimate ammonia emissions of 7.6×10^{-3} kg/s (60 lb/hr). According to the plant operator, this estimate is probably too high, since approximately 36 lb/hr of ammonia typically enters the plant. The most probable reason for the overestimate is that NH_3 was not distributed in the same manner as was hydrogen sulfide, and our probe sampled high local concentrations.

8.4.3 Mercury Emissions

Although most of the mercury emitted from this tower is believed to be in the form of elemental mercury vapor, it is probably even less realistic to assume co-distribution with hydrogen sulfide as it was in the case of

TABLE 8.4-1
 CALCULATION OF HYDROGEN SULFIDE EMISSIONS
 FROM GEOTHERMAL TOWER

Point	Velocity m/s	Flow (m ³ /s)	H ₂ S Conc. (ppm)	Mass Flow (mg/s)
B1	8.7	9.5	3.8	48.3
B2	11.4	21.2	1.2	34.0
B3	11.3	21.6	0.5	14.5
B4	10.8	11.1	0.22	3.3
B5	10.4	17.1	0.28	6.4
B6	8.7	14.5	0.49	9.5
B7	6.1	7.6	0.76	7.7
B8	1.7	9.0	0.49	5.9
C1	9.6	10.5	0.09	1.3
C2	11.2	22.0	0.07	2.1
C3	11.2	21.3	0.06	1.7
C4	10.7	19.9	0.06	1.6
C5	9.6	16.4	0.06	1.3
C6	8.0	10.8	0.06	0.9
C7	6.3	7.3	0.08	0.8
C8	2.4	10.1	0.13	1.8
D1	9.3	10.2	2.7	36.8
D2	10.7	21.1	1.9	53.6
D3	11.2	20.8	0.6	16.7
D4	11.4	10.5	0.17	4.7
D5	10.7	17.8	0.11	2.6
D6	9.2	15.1	0.10	2.0
D7	7.3	8.5	0.11	1.3
D8	3.2	12.2	0.14	2.3
F1	8.1	8.9	0.04	0.5
F2	10.5	19.6	0.02	0.5
F3	10.9	20.3	0.02	0.5
F4	10.9	19.7	0.02	0.5
F5	10.5	17.2	0.03	0.7
F6	9.4	15.1	0.08	1.6
F7	8.0	8.9	0.09	1.1
F8	4.2	14.2	0.13	2.5

ammonia. We have estimated total emissions by multiplying the measured concentration of 1.0 to 1.2 g/m³ by the total exhaust air flow rate for the tower, 2705 m³/s (data provided by the plant operator). The resulting emission rate is 2.7 to 3.2 x 10⁻³ g/s (0.026 to 0.031 lb/hr).

8.4.4 Other Inorganic Emissions

According to the cooling tower operator, drift emissions (as water) were found to be 80.25 g/s in a recent test. Using this value, along with our measured values of trace metal concentrations in the circulating water, we estimated the emission rates shown in Table 8.4-2. Only concentrations measured on our second visit were used, since samples were taken when the Stretford Process was operating, and are thus more representative of current operations than were our January 1980 measurements. Low and high emission rates correspond to low and high concentration values measured in either the cold or hot water basin. It is clear that emissions of any one trace metal except zinc are lower than a few tens of grams per year. The zinc emission rate is estimated to be about 0.1 kg/yr.

8.5 MODELING OF EXPOSURES TO METALS FROM COOLING TOWERS

Although the focus of this study was on cooling tower emissions, we were requested by the California Energy Resources Conservation and Development Commission (CERCDC) to estimate ambient metals concentrations around a typical tower using municipal wastewater as makeup. Before describing the approach it is necessary to mention that our goal was to predict the order of magnitude of the concentrations; more precise calculations require extensive site-specific meteorological data and more sophisticated modeling techniques.

8.5.1 Modeling Approach

In order to estimate population exposures around a cooling tower, a simple Gaussian dispersion model was used. Use of a more sophisticated model was inappropriate given the uncertainty in our emission rate estimates. It is questionable whether any real gain in accuracy would have resulted.

The well-known Gaussian dispersion formula is (Porter, 1976):

$$C = \frac{10^6 Q}{\pi u \sigma_z \sigma_y} \exp \left[-\frac{1}{2} \left(\frac{H}{\sigma_z} \right)^2 \right] \exp \left[-\frac{1}{2} \left(\frac{y}{\sigma_y} \right)^2 \right] \quad (8-9)$$

TABLE 8.4-2
 ESTIMATED TRACE METAL EMISSIONS FROM
 THE GEOTHERMAL POWER PLANT

Element	Estimated Emissions (kg/yr)	
	Low	High
Arsenic	0.026	0.044
Cadmium	0.00025	0.00025
Chromium	<0.0013	<0.0013
Copper	0.017	0.018
Lead	<0.0013	<0.0013
Mercury	0.039	0.039
Selenium	<0.05	<0.05
Zinc	0.12	0.13

where

- c = ground level concentration ($\mu\text{g}/\text{m}^3$)
- Q = emission rate (g/s)
- u = average wind speed at the physical stack height (m/s)
- σ_z = standard deviation of the vertical concentration distribution
- σ_y = standard deviation of the horizontal concentration distribution.
- H = effective stack height (m) and
- y = crosswind distance from the plume centerline to the receptor point (m).

the values for the standard deviations σ_y and σ_z are functions of the downwind distance, x:

$$\sigma_z = ax^b \quad (8-10)$$

$$\sigma_y = cx^d \quad (8-11)$$

where a, b, c, and d are constants that fit the function to the empirical curves presented in Turner (1970). The wind speed at physical stack height is given by the equation:

$$u = u_0 \left(\frac{h_s}{h_0} \right)^p \quad (8-12)$$

where

- u = wind speed at physical stack height (m/s)
- u_0 = measured wind speed (m/s)
- h_s = physical stack height (m)
- h_0 = the height at which the known wind speed was measured (m) and
- p = an empirical constant which varies with stability class

Lacking data on the heights at which all the known wind speeds were measured, we followed common practice and assumed a value of 10 m for h_0 . Plume rise formulas developed by Christiansen (1975) and cited by Porter (1976) were used; the rise was assumed to be momentum-dominated. Table 8.5-1 shows the parameters used in plume rise calculations. Wind direction and speed data, meanwhile, were obtained from the South Coast Air Quality Management District for each of the 16 major compass points.

A 21 by 21 km Cartesian grid was then defined, such that the cooling tower was at point (0,0). Calculations were performed for each point on the grid except for the origin. The first step was to determine the compass

Table 8.5-1

VALUES OF PARAMETERS USED TO CALCULATE PLUME RISE

Parameter	Value	Unit
Stack height	15	m
Gravitational constant	9.8	m/sec ²
Ambient temperature	294.25	°K
Source Temperature	299.85	°K
Exhaust velocity	11	m/sec
Stack radius	3.81	m

directions between which each point lay. The concentration at the point was then calculated as the sum of the concentrations resulting from plumes having the bounding compass directions as centerlines. If the ray to the point was congruent with a compass direction, then only one set of calculations was necessary. Ambient concentrations were computed. The calculation was performed once for every hour of the day since annually averaged values of hourly wind speed were available. The following typical California pattern of hourly stability class (suggested by D. Chang of UC Davis) was assumed to be valid for the entire year:

<u>Hour</u>	<u>Class</u>	<u>Hour</u>	<u>Class</u>
0	E	13	C
1	E	14	B
2	E	15	B
3	E	16	C
4	E	17	C
5	DN	18	DD
6	DN	19	DD
7	DN	20	DN
8	DD	21	DN
9	DD	22	E
10	DD	23	E
11	C		
12	C		

Concentrations derived from Equation 8-9 are for 10-minute averaging times. To adjust to other averaging times, one must multiply the calculated concentration by a factor $(t_0/t)^a$ where $t_0 = 10$ minutes, $t =$ the desired averaging time (min), and a is a constant which varies with stability class. Values for a were taken from Porter (1976). Since it was desired to know the average concentration at each hour of the day, t was set to 60 minutes.

Let $C(\theta_1, t_i)$ and $C(\theta_2, t_i)$ be the concentrations calculated at hour i for compass directions θ_1 and θ_2 , respectively. Our meteorological data included the frequency of wind direction for each hour of the day. Let $f(\theta_1, t_i)$ and $f(\theta_2, t_i)$ be the probabilities of occurrence of wind in the directions θ_1 and θ_2 , respectively at hour i . Then the expected value of the concentration at the point in question at hour i is:

$$C(t_i) = f(\theta_1, t_i)C(\theta_1, t_i) + f(\theta_2, t_i)C(\theta_2, t_i) \quad (8-13)$$

The average annual exposure was then calculated as the average exposure on this composite day:

$$C = (1/24) \sum_{i=0}^{23} C(t_i) \quad (8-14)$$

The model was programmed in Applesoft BASIC on an Apple II microcomputer having 48 K bytes of random access memory and a disk storage capability. The program was compiled with an On-Line Systems, Inc. Expediter II BASIC compiler, in order to decrease running time.

The final variable to be considered was the emission rate Q. Since the discrete emission sources (the fanstacks) on each tower are so close together, emitted fog and drift often form a single plume. Rather than apportioning emissions among fanstacks and modeling each one separately, we assumed that all emissions would be from a single stack. An upper bound on emissions was set by assuming the higher emission rates presented previously in Table 8.3-1. (A drift rate of 0.01 percent of recirculating water flow, which is probably high by a factor of about 10, was assumed.) Emission rates used were:

<u>Element</u>	<u>Emission Rate (g/s)</u>
Cd	0.0002
Cr	0.0002
Cu	0.025
Pb	0.0006
Hg	0.0000023
Zn	0.055

8.5.2 Results of the Modeling Exercise

Figure 8.5-1 is a graphical representation of concentrations resulting from a unit (e.g. 1 g/s) emission rate, for any pollutant. The graph was generated on the Apple II by means of the "Topographic Mapping Programs" software package produced by Apple Computer Inc. (Cupertino, California). Each side of the figure represents 21 km. The view is towards the northwest, at a viewing angle of 30 degrees above the horizontal. Concentrations are lowest southwest of the plant and highest in the north-northeast and east-southeast direction.

At the request of the California Energy Resources Conservation and Development Commission (Gaumon, 1981), model results were compared with suggested governmental standards for ambient air concentrations of the six

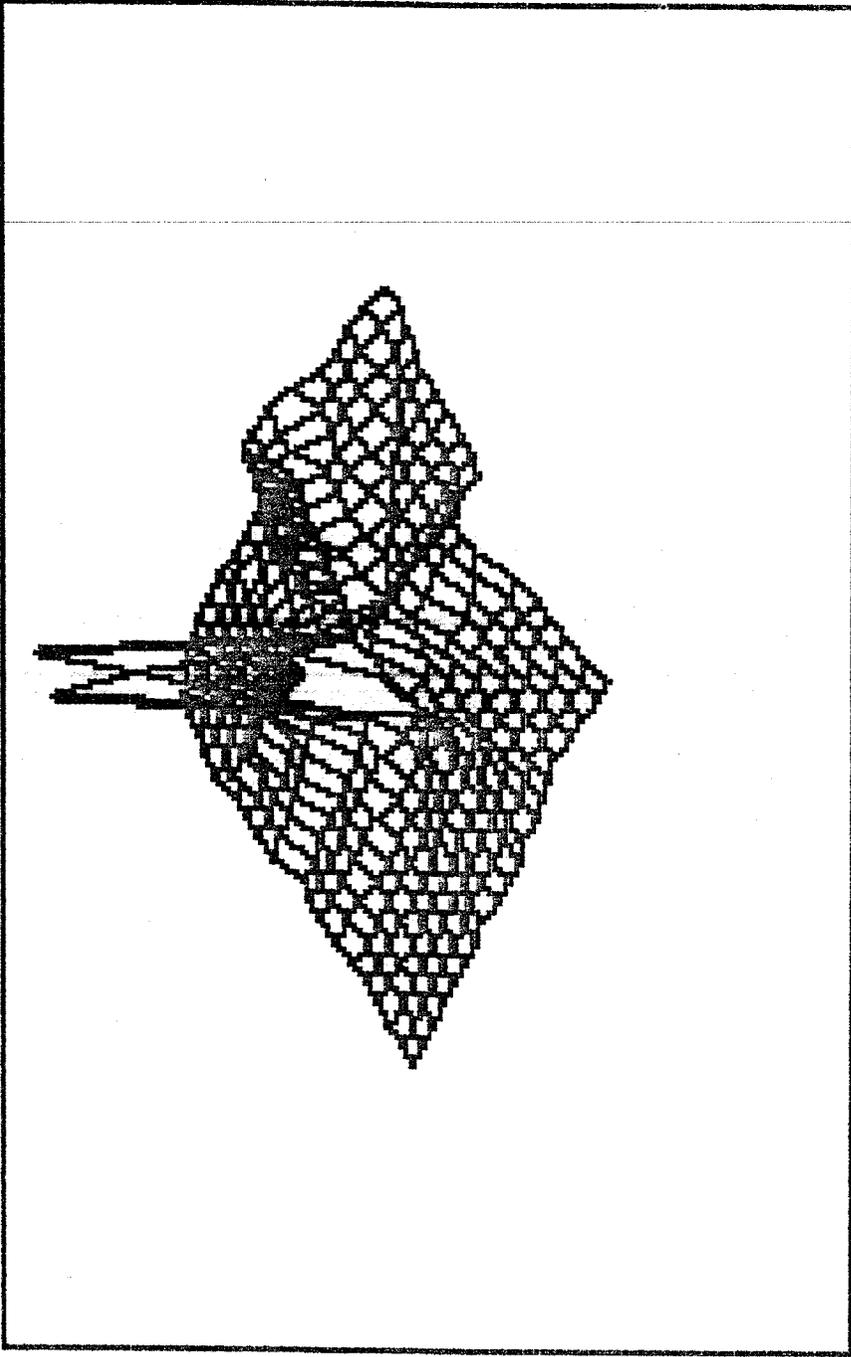


Figure 8.5-1-1. Modeled Ambient Concentrations of Metals Around Municipal Tower No. 1. (Area Depicted is 21 km by 21, Scale Factor is 0.01, "Elevations" Are in ng/m^3 , View is Toward the Northwest.)

metals. Since the cooling towers operate continually, standards based upon annual average concentrations were used. USEPA maximum exposure guidelines (MEG) are:

Metal	Annual Average (ng/m ³)	
	Toxicity Base	Carcinogenicity Base
Cd	120	20
Cr	120	2
Cu	500	-
Pb	360	1000
Hg	100	10
Zn	9500	-

Table 8.5-2 shows the estimated concentrations of these metals at one kilometer due east of the power plant. Chromium approaches 7.5 percent of the recommended maximum set to protect against carcinogenic exposure. It is not that chromium concentrations are very high; rather the guideline is the lowest of all those considered here. This result points to the need to carefully assess the potential for chromium exposure in cases, such as Industrial Tower No. 1, where chromium emissions are higher than those assumed for this exercise. Figure 8.5-2 shows isopleths (lines of equal concentration) for ambient chromium concentrations representing 1, 2, 3, 4, and 5 percent of the carcinogenicity based guideline.

Actual metal concentrations at more than 1 km from the tower are likely to be lower than those estimated here. First, as was noted above, maximum emission rates were assumed. Modern cooling towers have drift rates lower than the assumed 0.01 percent. Finally, as was noted in Section 8.1.2, a considerable amount of deposition--as much as 70 percent, according to one model (Wistrom and Ovard, 1973) occurs in the vicinity of the tower. Thus emissions, and resulting ambient concentrations, could be lower by a factor of 10 than those reported here.

8.6 ESTIMATION OF EMISSION FACTORS

Using the method outlined in Section 8.1.3, we estimated circulating water flow- and exhaust air flow-based emission factors for inorganic salts, volatile and nonvolatile organics, indicator microorganisms and geothermal pollutants. Our results are shown in Tables 8.6-1 through 8.6-4. In order to

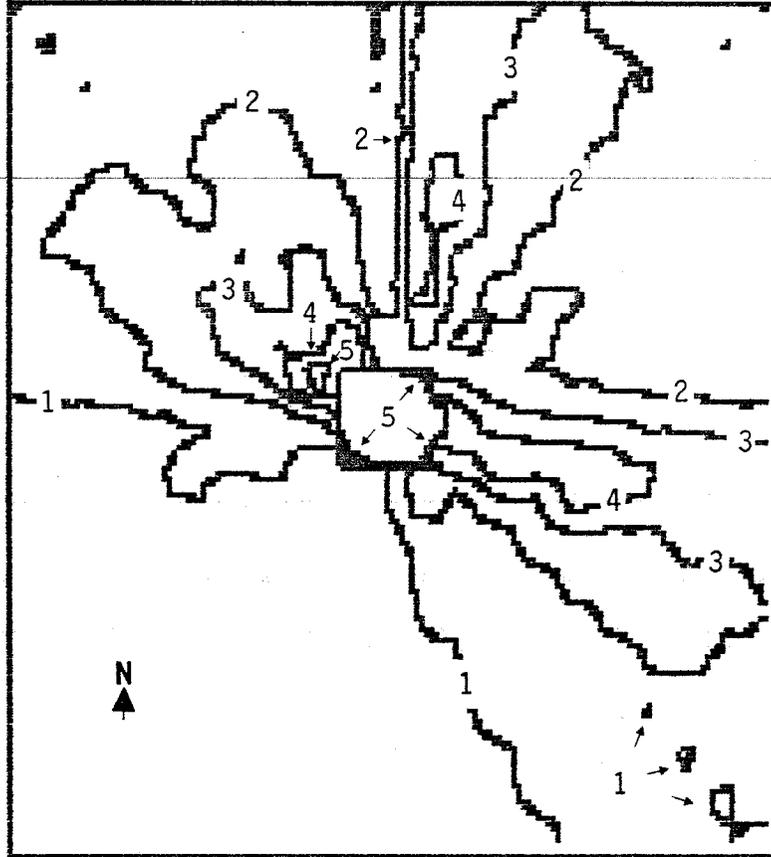


Figure 8.5-2. Isopleths Representing Modeled Percentages of Recommended Limits for Exposure to Chromium Around Municipal Tower No. 1. (Grid is 21 km by 21 km.)

Table 8.5-2
 COMPARISON OF MODELLED MAXIMUM AMBIENT METAL CONCENTRATIONS
 1 KM FROM BURBANK TOWER WITH EPA MAXIMUM EXPOSURE GUIDELINES
 (All concentrations in ng/m³, annual average)

Element	Maximum Concentration	Concentration/ Toxicity Std.	Concentration/ Carc. Std.
Cadmium	0.15	0.00125	0.0075
Chromium	0.15	0.00125	0.075
Copper	18	0.036	NA ^a
Lead	0.44	0.00122	0.00044
Mercury	0.0017	0.000017	0.00017
Zinc	40	0.0042	NA

^aNA = No carcinogenicity reference standard available.

Table 8.6-1

EMISSION FACTORS FOR INORGANIC SALTS

Pollutant	Emission Factors ^a		
	Water-Based		Air-Based
<u>Major Minerals</u>			
Total Dissolved Solids	9.0 x 10 ²	- 1.1 x 10 ⁴	1.4 x 10 ⁻¹ - 1.7 x 10 ²
Total Suspended Solids	4.0 x 10 ⁰	- 8.5 x 10 ²	7.3 x 10 ⁻³ - 1.4 x 10 ⁻¹
Sodium	6.0 x 10 ²	- 1.8 x 10 ³	2.4 x 10 ⁻² - 2.9 x 10 ⁰
Magnesium	3.0 x 10 ⁰	- 3.4 x 10 ²	4.2 x 10 ⁻³ - 5.6 x 10 ⁻¹
Chloride	1.1 x 10 ¹	- 2.1 x 10 ³	1.8 x 10 ⁻² - 3.5 x 10 ⁰
Sulfate	1.3 x 10 ¹	- 5.7 x 10 ³	2.1 x 10 ⁻² - 9.4 x 10 ⁰
<u>Trace Metals</u>			
Cadmium	3.3 x 10 ⁻³	- 6.2 x 10 ⁻²	5.5 x 10 ⁻⁶ - 1.0 x 10 ⁻⁴
Chromium	7.0 x 10 ⁻³	- 1.5 x 10 ⁻¹	1.0 x 10 ⁻⁶ - 2.6 x 10 ⁻⁴
Copper	3.0 x 10 ⁻¹	- 6.0 x 10 ⁰	5.0 x 10 ⁻⁴ - 1.2 x 10 ⁻²
Iron	3.3 x 10 ⁻²	- 3.4 x 10 ⁻¹	5.5 x 10 ⁻⁵ - 5.6 x 10 ⁻⁴
Lead	3.2 x 10 ⁻⁴	- 1.4 x 10 ⁻¹	5.4 x 10 ⁻⁷ - 2.7 x 10 ⁻⁴
Mercury	1.1 x 10 ⁻⁵	- 5.6 x 10 ⁻⁴	1.8 x 10 ⁻⁷ - 1.1 x 10 ⁻⁶
Zinc	6.2 x 10 ⁻²	- 1.3 x 10 ²	1.0 x 10 ⁻⁴ - 2.6 x 10 ⁻²

^aAll emission factors are in units of kg/yr per m³/s (air or water)

Table 8.6-2

EMISSION FACTORS FOR VOLATILE ORGANIC COMPOUNDS

Compound	Emission Factors ^a	
	Water-Based ^b	Air-Based
Hexane	0 - 1.3 x 10 ⁰ (b)	0 - 2.3 x 10 ⁻³
Benzene	0 - 1.1 x 10 ² (b)	0 - 1.8 x 10 ⁻¹
Toluene	0 - 7.3 x 10 ¹ (b)	0 - 1.2 x 10 ⁻¹
m-xylene	0 - 4.0 x 10 ¹ (b)	0 - 6.3 x 10 ⁻²
o-xylene and p-xylene	0 - 4.3 x 10 ¹ (b)	0 - 7.0 x 10 ⁻²
Ethylbenzene	0 - 6.9 x 10 ⁰ (b)	0 - 1.1 x 10 ⁻²
Ethylmethylbenzene	0 - 1.4 x 10 ¹ (b)	0 - 2.3 x 10 ⁻²
2-Propanone	0 - 1.5 x 10 ¹ (b)	0 - 2.5 x 10 ⁻²
2-Butanone	0 - 8.2 x 10 ⁰ (b)	0 - 1.4 x 10 ⁻²
Chloroform	8.3 x 10 ⁰ (b) - 2.0 x 10 ¹	3.1 x 10 ⁻³ - 3.8 x 10 ⁻²
Bromodichloromethane	0 - 6.6 x 10 ¹ (b)	0 - 1.1 x 10 ⁻¹
Dibromochloromethane	0 - 1.4 x 10 ⁰	0 - 2.3 x 10 ⁻³
1,1-Dichloromethane	0 - 1.2 x 10 ¹ (b)	0 - 2.0 x 10 ⁻²
Trichloroethane	0 - 1.6 x 10 ¹	0 - 3.1 x 10 ⁻²
Trichloroethene	0 - 7.4 x 10 ⁰	0 - 1.6 x 10 ⁻²
1,1,2,2-Tetrachloroethane	0 - 2.7 x 10 ¹	0 - 5.2 x 10 ⁻²
Tetrachloroethylene	0 - 2.7 x 10 ¹	0 - 5.2 x 10 ⁻²
1,2-Dichloropropane	0 - 8.3 x 10 ⁰	0 - 4.5 x 10 ⁻³
"Others"	NQ ^c - 1.9 x 10 ² (b)	0 - 3.1 x 10 ⁻¹

^aEmission factors are in units of kg/yr per m³/s (air or water)

^bThese values are based upon a highly uncertain estimate of circulating water flow for one cooling tower; see text.

^cU identified compound emissions were quantified for only one tower.

Table 8.6-3

EMISSION FACTORS FOR INDICATOR BACTERIA AND VIRUS

Organism	Emission Factors ^a	
	Water-Based	Air-Based
Total Coliforms	7.1 x 10 ⁻¹ - >2.4 x 10 ³	1.2 x 10 ⁻³ - >4.6 x 10 ⁰
Fecal Coliforms	4.0 x 10 ⁻¹ - 1.5 x 10 ²	5 x 10 ⁻⁴ - 2.9 x 10 ⁻¹
Fecal Streptococcus	4.0 x 10 ⁻¹ - 1.5 x 10 ²	7 x 10 ⁻⁴ - 2.9 x 10 ⁻¹
E. Coliphage	0 - 7.1 x 10 ²	0 - 1.4 x 10 ⁰

^aEmission factors are in units of particles/second per m³/s (air or water)

Table 8.6-4

EMISSION FACTORS FOR THE GEOTHERMAL TOWER

Pollutant	Emission Factors ^a	
	Water-Based	Air-Based
Arsenic	$5.3 \times 10^{-3} - 8.9 \times 10^{-3}$	$9.6 \times 10^{-6} - 1.6 \times 10^{-5}$
Cadmium	5.1×10^{-5}	9.2×10^{-8}
Chromium	$<2.6 \times 10^{-4}$	$<4.8 \times 10^{-7}$
Copper	$3.4 \times 10^{-3} - 3.6 \times 10^{-3}$	$6.3 \times 10^{-6} - 6.7 \times 10^{-6}$
Lead	$<2.6 \times 10^{-4}$	$<2.6 \times 10^{-4}$
Mercury	$1.7 \times 10^1 - 2.0 \times 10^1$	$3.7 \times 10^{-2} - 3.7 \times 10^{-2}$
Selenium	$<1.0 \times 10^{-2}$	$<1.8 \times 10^{-5}$
Zinc	$2.4 \times 10^{-2} - 2.6 \times 10^{-2}$	$4.4 \times 10^{-5} - 4.8 \times 10^{-5}$
Hydrogen Sulfide	8.5×10^3	1.6×10^1
Ammonia ^b	4.9×10^4	8.9×10^1

^aEmission factors are in units of kg/yr per m³/s (air or water).

^bThese estimates may be high by at least a factor of two.

be able to apply these factors to towers for which only the circulating water flow rates or the exhaust air flow rates are known, we have used units of kg/yr per m^3/s of either water or air flow ($\text{kg}\cdot\text{s}/\text{m}^3\text{-yr}$). Using Equation 8-4, which was presented in Section 8.1.3, one would multiply the appropriate factor times the air or the water flow rate to estimate total emissions. For example, if new tower having a circulating water flow rate of $5 \text{ m}^3/\text{s}$ was to be built, then cadmium emissions would be estimated as $E_{\text{Cd}} = (5)(3.3 \times 10^{-3})$ to $(5)(6.2 \times 10^{-2}) = 0.017$ to 0.31 kg/yr .

Nonvolatile organic emission factors, which are not shown in the tables, are 0.1 to $340 \text{ kg}\cdot\text{s}/\text{m}^3\text{-yr}$ for circulating water flows and 0.0002 to $0.56 \text{ kg}\cdot\text{s}/\text{m}^3\text{-yr}$ for air flows. It should be noted that several of the organic emission factors are based upon a highly uncertain estimate of circulating water flows for Municipal Tower No. 1; in addition, as was mentioned previously, we do not know whether the makeup water concentrations we measured were typical of the long term.

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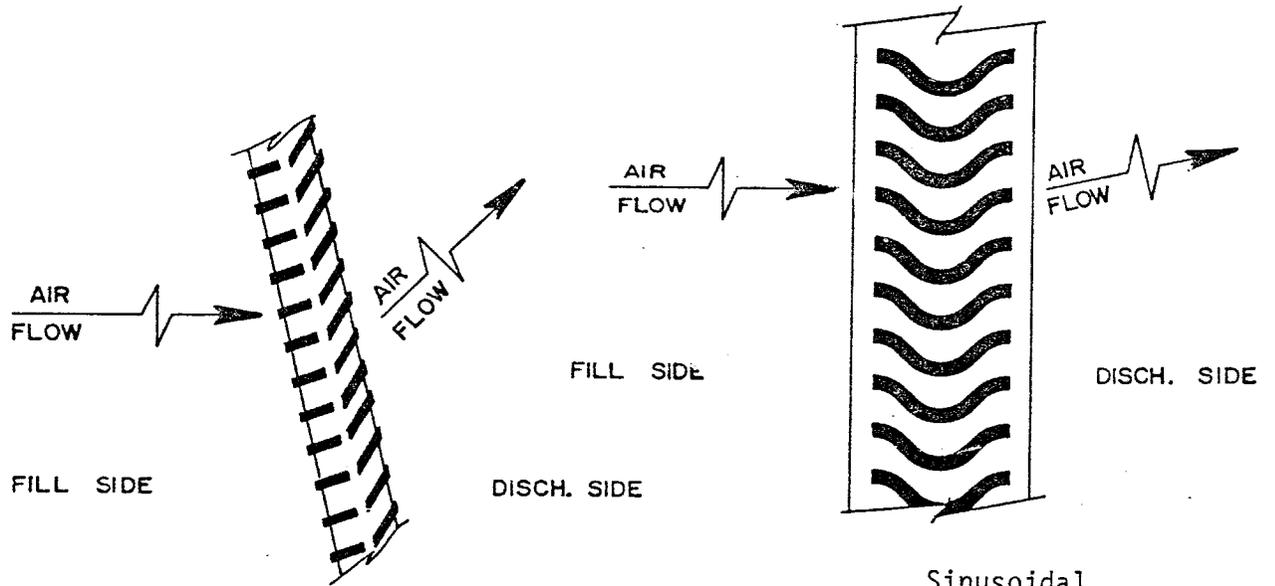
REVIEW OF COOLING TOWER EMISSION CONTROL TECHNOLOGY

Under Task 5 of this project, we were to review existing and developing methods of controlling emissions of pollutants of concern from cooling towers. Certain emissions, such as those of salts and bacteria, can be reduced as a consequence of controlling cooling tower drift. We therefore reviewed drift elimination technology. (See Section 9.1) Other emissions may be reduced by specially pretreating wastewater before it is recycled as cooling tower makeup, or by treating the circulating water. Thus, as is discussed in Sections 9.2 and 9.4, wastewater treatment technology was reviewed. Finally, a special review was made of methods to abate hydrogen sulfide emissions from geothermal cooling towers. Our findings are presented in Section 9.3.

9.1 DRIFT ELIMINATION TECHNOLOGY

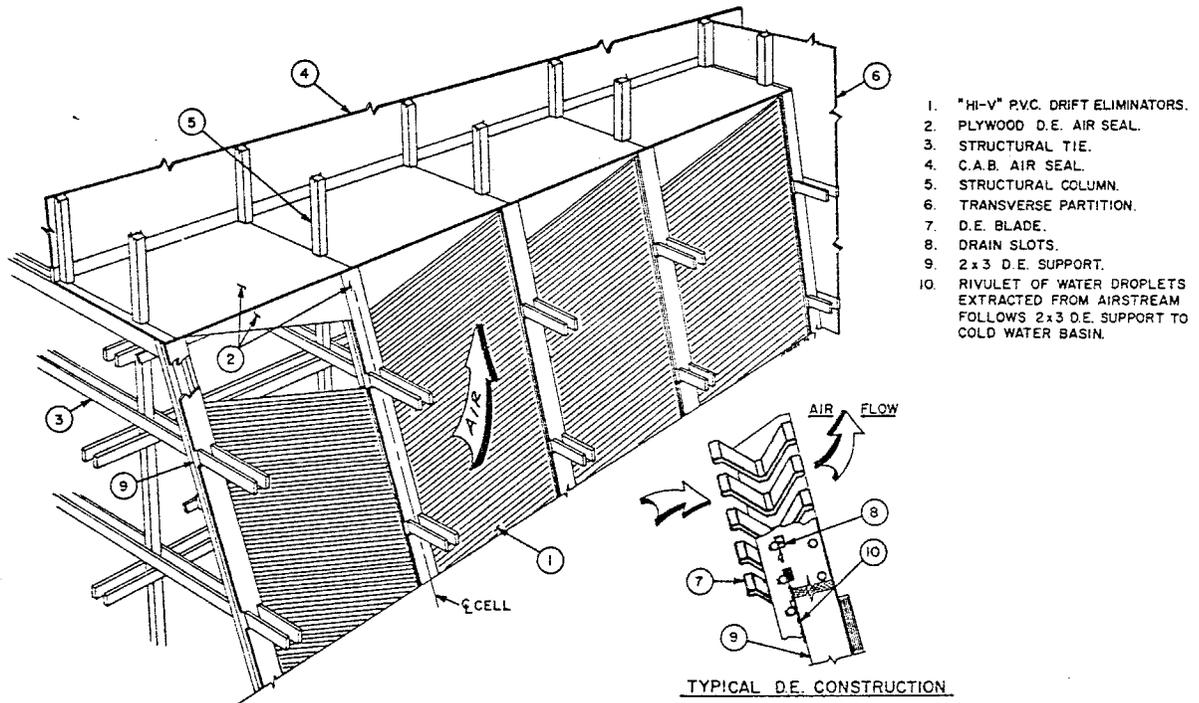
The design and operation of drift eliminators has been discussed at length by Holmberg and Kinney (1973) and Wistrom and Ovard (1973). The following brief discussion is based upon these works, except where otherwise noted. The purpose of drift eliminators is to remove water droplets from cooling tower exhaust air. While designs vary, all drift elimination systems operate on the same basic principle. The two-phase flow (i.e. air and water droplets) is directed into many narrow passageways, most of which are at an angle to the initial flow. The change in flow direction causes the water droplets to strike the drift eliminator surfaces and lose momentum, while the air continues on relatively unimpeded.

The basic components of a drift eliminator system are the "blades," the most common types of which are shown in Figure 9.1-1. The herringbone configuration is the oldest and is less efficient than newer designs. In both the sinusoidal wave eliminator and the "hi-v" configurations, the exhaust air is made to flow through many curved pathways. Experiments and mathematical modelling studies by Chan and Golay (1978) have shown that the efficiency of sinusoidal drift eliminator blades is highly sensitive to the amplitude of the wave. The greater the amplitude, the higher the percentage of water removal. However, as with most drift eliminator types, an increase in droplet removal efficiency is accompanied by an increased system pressure drop, which is not



Herringbone
(Holmberg and Kinney, 1973)

Sinusoidal
(Holmberg and Kinney, 1973)



"Hi-V" (Ecodeyne)

Figure 9.1-1. Examples of Drift Eliminator Blade Designs.

desirable from the point of view of cooling tower performance.

A third blade configuration, not shown in the figure, is the honeycomb, whose main advantage is a relatively large surface area, which supports a boundary layer in which localized turbulence and reduced air velocity cause drift droplets to be stripped from the air stream. Holmberg (1975) reports that placing a honeycomb unit downstream of a sinusoidal or herringbone unit results in a 10-fold reduction in drift emissions.

Another combination of blade systems is the two-pass herringbone drift eliminator shown in Figure 9.1-2. The purpose of this design is to provide a tortuous path for the exhaust and yet minimize pressure drop at high velocities.

According to Wistrom and Ovard (1973) the installation of the drift eliminator system can be as important as the design of the blades themselves in determining drift elimination efficiency. One phenomenon to be avoided is the accumulation of water at points where the blades are connected to the tower supports; droplets from these areas can be reentrained by the exhaust flow and emitted as drift. According to Holmberg and Kinney (1973), good performance requires sufficient vertical spacing between cooling tower fill and the drift eliminators, so that the water droplets are flowing at the same uniform rate as the exhaust air. Problems occur when, in the case of crossflow towers, large upward-travelling water droplets reflect off the fill and strike the drift eliminators, flooding them and reducing their effectiveness.

As was mentioned in Chapter 8, field verification of drift eliminator performance dates back only to the early 1970's. It was previously believed that drift volume emissions were 0.2 percent of tower circulating water rate. Measurements on towers equipped with modern properly functioning drift eliminators have resulted in a lowering of this estimate. Our review of the literature, as well as discussions with researchers (Gavin, 1979; Schrecker, 1980) leads us to believe that a likely range of emission rates is 0.001 to 0.01 percent.

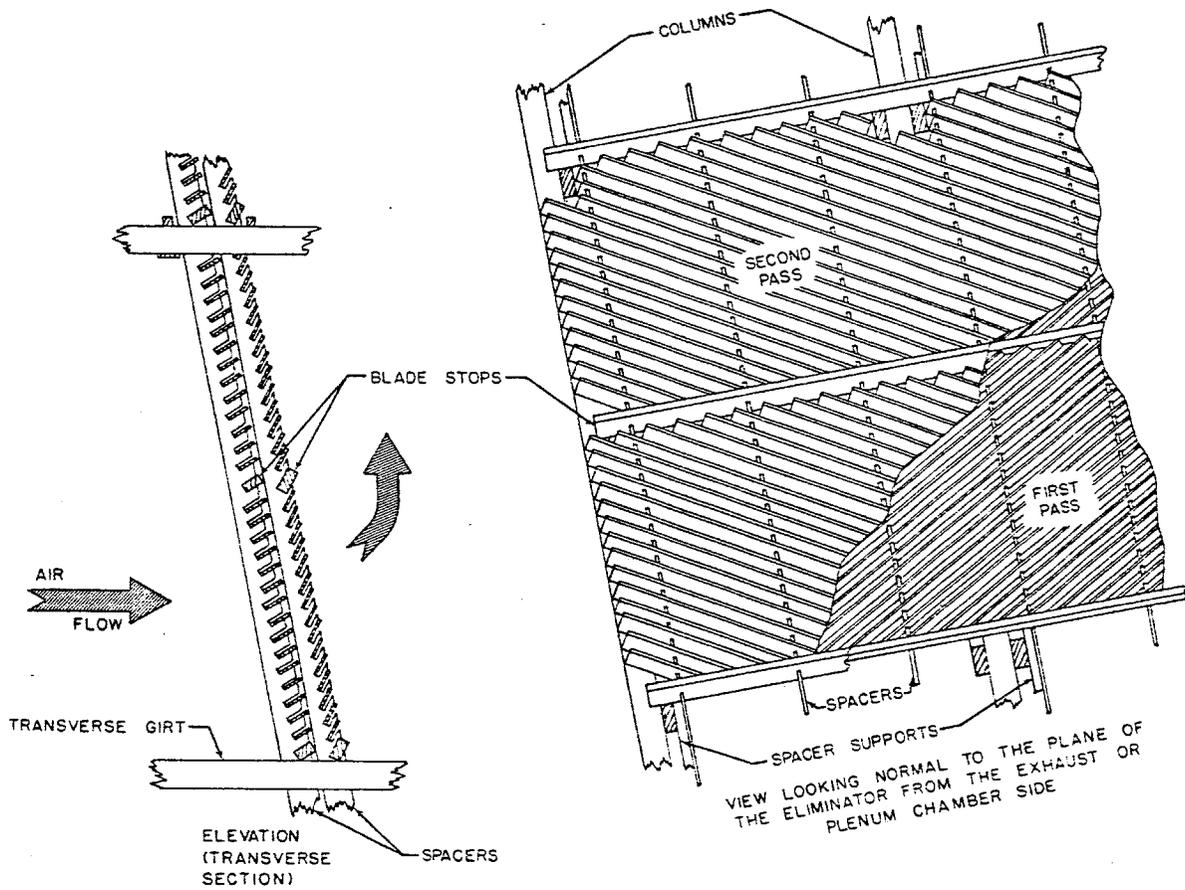


Figure 9.1-2. Example of Two-Pass Drift Eliminator System (Marley).

9.2 MICROBIOLOGICAL CONTROL OF COOLING TOWERS

Because a cooling tower is essentially a dynamic ecosystem, microbiological control must take into account many different interactive variables. A partial list would include pH of the water, ambient air and water temperatures, residence time, and the concentration and growth rate of the bacteria. A review of the literature reveals that current practices are directed more towards the general control of biofouling as opposed to interventions against specific pathogens. Because of this we include a summary of a paper by Carter and McGraw (1979) which reviews the major microbicides and their application in cooling towers. We will also discuss some examples of control of individual species.

Many different types of chemical agents are employed for microbiological control in cooling water systems. The bacteriocidal or bacteriostatic effects of a given chemical is often a function of concentration. If a microbicide is present in a sufficient quantity, or is highly toxic, bacteria will be killed. At levels below its killing concentration, the chemical used will only inhibit growth. At extremely dilute concentrations, the chemical agent may actually stimulate the growth of microorganisms (Shair and Dorrington, 1976). Microbicides fall into two major classes: oxidizing and non-oxidizing.

9.2.1 Oxidizing Microbicides

Chlorine

Chlorine is the most widely used oxidizing microbicide. It is fed either as chlorine gas or in one of several forms of chlorine such as sodium or calcium hypochlorite, chlorinated lime, or chlorinated cyanurates. Chlorine gas is fed either continuously or intermittently to maintain a residual chlorine level of a few tenths of a ppm. The feed is usually based on the recirculating rate of the cooling system. Because a chlorine demand has to be satisfied before a free chlorine residual is achieved, an excessive feed is required in many systems. (For a detailed discussion of chlorination chemistry, see Section 5.6.1.)

Chlorine and chlorine-releasing microbicides should be avoided in systems with a high chlorine demand or when the water characteristics, in combination with chlorine, may lead to damage of cooling tower lumber (Shair and Dorrington, 1976).

In a study examining the interrelationship of bacterial counts with other water quality parameters, Reilly and Kippin (1981) found an inverse relationship between free chlorine residual and turbidity. However, of the chemical and physical parameters measured (temperature, turbidity and free chlorine), the free chlorine residual was found to have the greatest influence on the microbial population. Nevertheless encapsulated Klebsiella pneumoniae, Enterobacter agglomerans, Enterobacter aerogenes and Enterobacter cloacae exhibited the ability to survive a free chlorine residual of 0.2 ppm or more. Current government regulations restrict chlorine in discharges to less than 0.2 ppm. However, Adams and Lewis (1980) suggest that the potential health hazard is greater for the opportunistic bacteria than from these enteric organisms.

Although chlorine is an effective low-cost microbicide, it has several limitations. First, chlorine becomes much less effective at a pH greater than 7.5. Second, best results are produced in conjunction with a non-oxidizing microbicide. Other disadvantages are its short activity (which requires frequent feed), its lack of effectiveness on some species of fungi and algae, and its inability to penetrate slime masses.

Chlorine Dioxide

Chlorine dioxide has been widely used as a disinfectant. Among its advantages over gaseous chlorine are that (1) it is more independent of pH and is a stronger oxidizing agent; (2) it does not react with ammonia to form chloramines, which have less bacteriocidal effect; and (3) it does not form chlorophenols with phenolic compounds in the water, thus minimizing subsequent ecological consequences. However, chlorine dioxide does react with other contaminants, which can result in a chlorine dioxide demand for the system. Scarpino et al. (1979) found the disinfecting ability of chlorine dioxide to be superior to chlorine against fecal coliform, E. coli and several enteroviruses, although the viruses were significantly more resistant. Adams et al. (1978) also found a greatly decreased total bacteria count in cooling tower water that had been treated with chlorine dioxide.

Peroxyulfates

Salts of Caro's acid (H_2SO_5), such as potassium peroxymonosulfate, are strong, odorless microbicides which are particularly effective against

bacteria and fungi. Their breakdown product, sulfate, is non-toxic and can be considered environmentally safe.

9.2.2 Non-Oxidizing Microbicides

Brominated Propionamides

Dibromonitrilopropionamide is considered to be a particularly attractive microbicide because it is easily hydrolyzed into essentially harmless degradation products, and is effective at low dosages. Carter and McGraw (1979) found that only 5 ppm over a four-hour period were required for a 95-percent kill in an electric utility cooling tower. Brominated propionamides are limited, however, to systems operating at a pH of 7.5 or less because they decompose rapidly at higher pH.

Chlorinated Phenols

2,4,5-trichlorophenol and pentachlorophenol are particularly effective against fungi and algae. Chlorinated phenols can be fed intermittently, or used to spray cooling tower wood fill to protect against fungal attack.

Organosulfur Compounds

Thiocyanates. Methylene(bis)thiocyanate (MBT) is an effective agent against slime forming bacteria. Although MBT is active over a broad spectrum of pH, it tends to hydrolyze at higher levels. The hydrolysis products are significantly less toxic than the parent compound, which makes MBT environmentally attractive.

Sulfones and Thiones. Bis(trichloromethyl)sulfone is only effective in a pH 6.5 - 8.5 range, while the thiones are most effective in the alkaline pH range.

Thiocarbamates. This group of compounds are excellent microbicides against slime forming bacteria, cellulytic fungi and sulfate reducers. At low dosages, they are not effective algaecides.

Organotin Compounds

Organotin compounds are used to control fungi and algae. They adsorb on wooden surfaces, giving the wood longer protection. The tin compounds are not particularly effective against slime forming bacteria, and

are usually blended with other microbicides such as quaternary ammonia for broad spectrum activity.

Cationic Compounds

Quaternary Ammonium Salts are effective over a wide pH range against bacteria and algae. Because they are surfactants, they have dispersant activity and tend to foam excessively when overfed. In heavily fouled systems they may lose some of their activity because of competing adsorption reactions.

Amines and diamines have broad spectrum activity over a wide range of pH. However, they also can foam excessively if overfed.

Cationic Polymers have properties similar to those of the amines, but they present less of a foaming problem.

Copper Salts

Although copper salts are effective algacides and bacteriocides, they are limited in use because they cause severe galvanic corrosion problems.

9.2.3 Application of Microbicides

Microbicides are often applied in combinations blended specifically to enhance the activity of individual compounds. For example, the fungicidal properties of organotin compounds are often combined with quaternary ammonium in a synergistic formulation to provide broad spectrum activity. In addition, alternating chemical groups can provide better control because of the ability of some microorganisms to acquire resistance to a specific chemical.

Most non-oxidizing biocides are fed on a slug basis. Slug feeding has proven to be a rapid and effective method of reducing microbiological populations from which recovery is difficult. However, some research suggests that although chlorination achieves satisfactory short-term disinfection, it may have questionable long-term effects. Kinney et al. (1978) have found an increase in the number of coliform groups five to seven days after chlorination of wastewater effluent. They suggest that the mechanism causing the increasing bacterial numbers is recovery of damaged cells rather than growth of surviving cells.

The rate of microbicide application depends on the severity of the problem and the retention time. In order to obtain a maximum retention time

within a given system it is desirable to bleed-off heavily prior to addition, then to add the microbicide with no bleed-off, and after a period of 24 hours to then return to the normal operating control limits. An antifoulant is often necessary to break open slime masses, thus allowing the microbicide to reach the organisms and do a more effective job.

Antifoulants fall into two basic categories: those that function by dispersion and those that function by flocculation. Both types are effective in continuous treatment to prevent deposition and act as cleaning agents. The use of antifoulants should be considered not only for cleaning up or preventing deposits in cooling water systems, but also as materials which enhance the biological activity of biocides, especially the non-oxidizing types (Shair and Dorrington, 1976).

Adams et al. (1980) discuss using precipitation and coagulation to treat wastewater effluent before it is re-used in cooling towers. Coagulation has been found to decrease the number of bacteria and viruses found in the effluent by 99 percent. Treatment consists of mixing the influent with lime and a flocculating agent such as aluminum sulfate, ferrous sulfate or organic polyelectrolytes. The treated influent is recirculated through a flocculation zone, where sediments settle out, and the supernatant is drawn into a collection trough. Some plants may further purify liquid by passing the water through beds of activated charcoal. However, Adams et al. (1980) found that while the coagulation treatment reduces the amount of phosphate and bacteria in wastewater effluent, it apparently has little effect on removing dissolved nutrients, as evidenced by a substantial regrowth of the genus Pseudomonas in the circulating water of the cooling towers they investigated.

9.2.4 Control of Specific Pathogens

As stated above, current practices in the control of microbial growth have emphasized general defouling without particular attention to specific pathogens. In order to attain optimal conditions of environmental safety, attention to specific pathogens and their eradication must be considered. The control of some selected species is now discussed. More effective control of these pathogens, however, depends on a further understanding and control of ecological factors.

Legionnaires Disease Bacterium (LDB)

Cooling towers associated with outbreaks of Legionnaires' Disease in Memphis, Tennessee and Bloomington, Indiana had been treated two to four times with high levels of free chlorine (Tyndall, 1980). Several hundred ppm of chlorine were added to these towers while they were in operation to maintain a bacterial exposure level of 3 to 5 ppm. The towers were drained after each treatment to facilitate bacterial elimination. This treatment, although uncontrolled, proved successful.

Results from laboratory tests suggest that LDB and E. coli appear to have comparable susceptibility to 0.65 ppm of hypochlorite (Wang, 1979). Nevertheless, the residual amount of chlorine recommended for standard water purification is not sufficient for killing LDB when the organism is present in high concentrations. Wang also observed survival of organisms after exposure for 30 minutes in HCl at pH 2.0. A pH of 1.7 was required for complete inhibition at one minute. Other test results with various biocides have also shown that while chlorine inhibited LDB, the quaternary ammonium compounds were more effective (Anon., 1979).

One possible complication of biocidal treatment of cooling towers is suggested by Flierman (1979), who found that growth of LDB may be greatly enhanced by algae products, and that the damage or destruction of algae could result in a massive release of these growth factors and a stimulation of LDB growth. Conversely, prevention of algae growth could impede the propagation of LDB. Finally, bacteria and algae may survive chlorination merely by living in crevices in towers and wooden slats of wet deck surfaces (Miller, 1979).

Amoebae

The pathogenic amoebae Naegleria and Acanthamoeba are more sensitive to chlorine than are their non-pathogenic counterparts. Acanthamoeba, however, is more resistant to chlorine than is Naegleria and would be more difficult to control with this biocide. In laboratory tests, 2 ppm of free chlorine killed both trophozoites and cysts of Naegleria (De Jonckheere and Van de Voorde, 1976). In spite of this finding, Tyndall et al. (1980) have repeatedly isolated Naegleria from discharge canals of electric power plants in which water was exposed 3 times a day to 0.5 ppm chlorine for 30 to 60 minutes. As an alternative to extensive chlorination, Tyndall (1980) has

suggested encouragement of the growth of thermophilic nonpathogenic amoebae in competition with the pathogens.

Fungi

Most studies on growth and control of fungi in cooling towers have been concerned with the destructive action of these organisms. Fungi in general are much more resistant to chlorinated phenols and quaternary ammonium compounds than are bacteria and amoebae. In fact, 90 ppm of pentachlorophenols are required to inhibit Aspergillus species (Tyndall, 1980). Candida albicans has been found to be sensitive to a combination of high levels of chlorine, long exposure time, and a low pH (Buck, 1980).

9.3 CONTROL OF GEOTHERMAL POLLUTANTS

Because virtually all of the hydrogen sulfide present in geothermal steam would be emitted to the atmosphere if no controls were available, considerable effort has gone into H₂S abatement. The following discussion is based upon a thorough review of geothermal pollution control technology by Sung et al. (1979), the proceedings of the recent Workshop on Environmental Control Technology for the Geysers-Calistoga Known Geothermal Resource Area (Hill, 1980), and other sources as noted. The major strategies in H₂S control are downstream and upstream abatement.

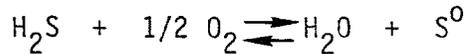
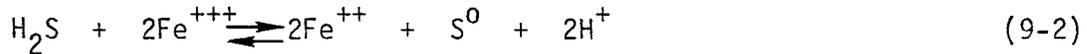
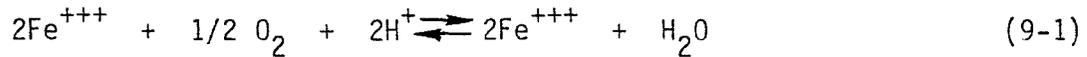
9.3.1 Downstream Abatement Strategies

Downstream abatement strategies attempt to remove hydrogen sulfide after the geothermal steam has passed through the power plant turbines. The only techniques in commercial use today are the iron catalyst system and the Stretford Process.

Iron Catalyst System

The iron catalyst system, which was developed by Pacific Gas and Electric Company (PG&E), is used to control H₂S emissions from Units 3 through 6, 11, and 12 at The Geysers. These units have direct-contact condensers, in which geothermal steam comes into contact with cooling water downstream from the turbine. About two-thirds of the hydrogen sulfide in the steam is dissolved in the cooling water. The rest is injected into the inlet air stream of the cooling tower associated with the plant. Soluble iron compounds (mainly ferrous sulfate) are added to the circulating water. The iron is

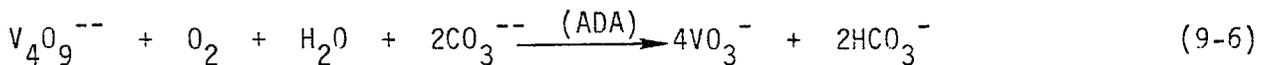
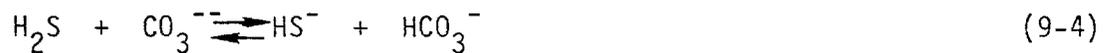
oxidized to Fe(III) by atmospheric oxygen; the Fe(III) then oxidizes the H₂S to elemental sulfur. Reactions for the process are:



Variations on the process include using small amounts of nickel (as nickel sulfate) to improve catalysis and use of hydrogen peroxide (H₂O₂) as an auxiliary oxidizing agent. In recent tests, caustic soda (NaOH) has been added to the noncondensable vent gas line to raise the pH and thus increase the solubility of H₂S in the cooling tower water. Use of the iron catalyst abatement system adds iron and nickel to the water, as well as S⁰ and SO₄²⁻ (Altshuler, 178).

Stretford Process

The Stretford Process has been used for quite some time to control hydrogen sulfide in gas streams in refineries and chemical plants, and has recently been applied to emissions abatement at Unit 15 of The Geysers. In the process, which is shown in Figure 9.3-1, H₂S in a gas stream is absorbed in an aqueous solution of Na₂CO₃ and is then oxidized to elemental sulfur with sodium vanadate. The vanadate is regenerated by oxidation with air, using 2,7-anthraquinone disulfonic acid (ADA) as a catalyst. Equations for the processes are:



In order to optimize system performance, NaOH is added to keep the pH between 8.5 and 9.5. Air blown into the oxidizer brings the suspended elemental

sulfur to the surface. After filtration and other treatment, a high quality sulfur is produced.

Since the Stretford Process can remove over 99 percent of the H_2S from the condenser off-gases, it is desirable to partition as much hydrogen sulfide as possible into the gas stream to be treated. For this reason, new units at The Geysers will be equipped with surface condensers, which are designed to divert 80 to 98 percent of the H_2S to the abatement process (PGE, 1978). Use of this abatement system is expected to introduce small amounts of ADA and vanadium into the circulating water. It should be noted that the Stretford process itself requires an evaporative cooling tower. Also, while the process can effectively remove hydrogen sulfide with no detrimental effect on the power cycle, it may be very costly to retrofit existing towers.

Other Downstream Processes

Two H_2S abatement processes developed in Japan are potentially applicable to geothermal operations, although they are not under active consideration. The Fumaks process, which has been used to treat coal gas, oxidizes H_2S to elemental sulfur in the presence of a catalyst such as picric acid. The Takahax process uses wet oxidation to convert H_2S to sulfate; the catalyst here is naphthoquinone sulfonate.

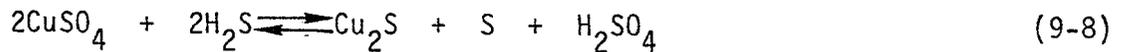
9.3.2 Upstream Abatement Strategies

Upstream abatement processes, which remove hydrogen sulfide from the geothermal fluid before it reaches the turbines, have several advantages (Hill, 1980). First, the abatement system can operate even when the power plant is off line. If one steam source serves several facilities, then one abatement system can handle emissions control for all of them. Upstream removal of H_2S reduces corrosion of downstream hardware, such as turbine blades. Finally, if the system includes a scrubber, then ammonia, suspended solids, and various toxic trace elements can be removed along with the H_2S . The major disadvantages of upstream treatment are that it may degrade the steam and that chemicals or reaction products from the abatement process may be introduced into the power plant system.

The EIC System

The major upstream treatment under active consideration at The Geysers is one developed by EIC Corporation (Dagani, 1979). In this

process, the steam is scrubbed with an acidic solution of copper sulfate, resulting in precipitation of copper sulfide. Reactions for the process are (Hill, 1980):



Both CuS and Cu₂S are insoluble solids. They can be roasted in air or leached with pressurized oxygen to regenerate the copper sulfate. Excess sulfuric acid produced through Reaction 9-8 must be neutralized with calcium carbonate, ammonia, sodium hydroxide, or sodium carbonate. The main advantages of the system are that it can be installed on-site and uses regenerable reagents. A potential disadvantage is that Cu⁺⁺ and elemental sulfur could become entrained in the air stream and find their way onto the turbine blades.

Other Systems

Battelle Pacific Northwest Laboratories have been doing research on an activated carbon adsorption process, in which the collected H₂S is desorbed with carbon disulfide, ammonium sulfate, or dichloromethane. The process does not work well when free water is present, but could be used when steam is "stacked" during power plant outages. Finally, the use of an iron oxide "sponge" to oxidize H₂S is being investigated. The "sponge" is not regenerable, so the process could only be used for steam stacking.

9.4 REMOVAL OF VOLATILE ORGANICS FROM WASTEWATER

If it is desired to reduce potential emissions of volatile organic compounds present in the makeup water, then additional pretreatment of the wastewater source will be necessary. The following review is based upon a previous study performed by the Principal Investigator for the U.S. Department of Energy (Rogozen et al., 1978). The findings of that study have been updated, with special attention to removal of the low-molecular weight organics and halogenated hydrocarbon compounds found in the makeup water of the towers we tested.

The three most practical methods for removing organic compounds from wastewater are adsorption, oxidation and membrane retention.

9.4.1 Adsorption

Activated Carbon

Adsorption is most commonly performed with activated carbon. Van Vliet et al. (1980) conducted a series of phenol adsorption tests of various adsorbents and found that activated charcoals generally performed best, followed by carbonaceous adsorbents, and finally by the polymeric and resinous adsorbents. Powdered carbon technology is less advanced than that for granular carbon largely for lack of an efficient carbon regeneration system (Culp and Shuckrow, 1977), though regeneration in a fluidized bed furnace now appears feasible (Culp and Shuckrow, 1977; Hernandez and Hariott, 1976). Because powdered carbon was found to reach equilibrium several weeks before granular carbon, Van Vliet et al (1980) recommended the powdered carbon for use over granular carbon whenever possible.

Carbon adsorption can be used successfully for treating many kinds of organic containing wastewaters, including chemical manufacturing wastes (Minor, 1974), domestic wastewater (Garrison and Miele, 1977; State of California, 1975) and petroleum refinery wastes (DeJohn and Adams, 1975). Carbon adsorption can also be employed prior to biological treatment both to prevent upsets and to remove refractory organics (Wiseman and Bawden, 1977). Although the technique has been applied mainly to waters containing a few hundred to several thousand ppm of organic matter, it has also been used on wastes containing relatively low concentrations of chlorinated hydrocarbons and phenol (Hager, 1976). For example, an 8-hour contact time resulted in a decrease in chlorinated hydrocarbons from 4 to 0.05 ppm in a 1000-gallon per day waste stream. Whether adsorption would be effective for the much lower adsorbate concentrations found in the makeup water (0.005 to 0.5 ppm) is unknown.

General statements have been made about the relationship between chemical properties of the adsorbate and adsorption efficiency. Hager and Rizzo (1974) stated that chemical properties of the adsorbate favoring adsorption to active carbon include high molecular weight, non-polarity, and limited solubility. Al-Bahrani and Martin (1976) confirmed that, in synthetic

aqueous solution, the adsorption capacity of carbon increased with molecular weight, but they also failed to detect greater adsorption with lower solubility and polarity. In studies of sewage treatment utilizing carbon adsorption, Chow and David (1977) and Guirguis et al. (1978) found that higher molecular weight components were more resistant to adsorption than were lower molecular weight components. It appears that generalities derived from one system do not always hold in others.

Stopka (1978) studied the ability of a combined ozonation/activated charcoal system to remove chloroform and other trihalomethanes (THM's). When activated charcoal was used by itself, the removal percentage decreased from 29 percent 7 weeks after installation to essentially zero after 16 weeks of operation. However, 90-percent removal of chloroform and other THM's was found within 2 minutes contact time of ozone followed by activated carbon adsorption. Of interest to the present study was the finding that this system proved especially effective in the adsorption of benzene, toluene, o-xylene, ethylbenzene and cyclohexane, all of which were detected in cooling tower makeup water.

Polymeric Adsorption

Adsorbent technology has been advanced significantly with the development of organic polymeric adsorbents with macroreticular pore structures. Unlike classical adsorbents such as activated carbon, polymers having a wide range of pore structures can be constructed, offering the possibility that adsorbents can be custom made for specific applications (Kunin, 1977; Kim et al., 1976). For example, Amberlite XAD-2 and XAD-7 (Rohm and Haas, Philadelphia, Pa.) remove phenol, chlorophenols and naphthalene (Kunin, 1977).

Fox (1979) summarized the commercial use of polymeric adsorption to remove and recover four classes of toxic organic materials from wastewater: chlorinated pesticides, phenols, aliphatic chlorinated hydrocarbons, and benzene, toluene and xylene. Fox also estimated the costs of various adsorbent systems. These varied from \$0.28/m³ for the recovery of benzene, toluene, and xylene from a flow of 0.016 m³/s at a concentration of 300 mg/L to \$4.50/m³ for phenol recovery. While an extensive cost analysis is beyond the scope of this review it is of interest to estimate roughly the cost of treating makeup for Industrial Tower No. 1. This tower uses approximately

0.004 m³/s of makeup water containing benzene, toluene and xylene at about one-thousandth the concentrations studied by Fox (1979). At \$0.28/m³, the annual cost would be only about \$600. However, whether the treatment system is effective for such low influent concentration is unknown.

Higosaki et al. (1980) demonstrated that crosslinked polystyrene adsorbed more trichloroethylene than did activated charcoal. Cross-linked poly (2-ethyl-hexylacrylate) proved effective in removing ethylene dichloride. The apparent rate of adsorption was a function of pH.

9.4.2 Oxidation of Organics

Biological Oxidation

Phenol (Capestany and McDaniels, 1977), aromatic amines (Tabak and Barth, 1978; Baird et al., 1977) naphthalene, and other resistant organics can be degraded by activated sludge after sufficient acclimation.

Takiguchi (1980) reviewed the biodegradabilities of heterocyclic, condensed ring, and polycyclic compounds. The biodegradabilities of 32 halogenated diphenylmethanes in activated sludge were also studied. The rate of degradation was found to decrease with the degree of substitution. Activated sludge was also found capable of degrading dichloromethane in both suspended growth and continuous flow systems (Rittman and McCarty 1980).

The use of bacteria for the oxidation of specific chemicals has also been suggested. In fact, a bacterium of the strain Alcaligenes was found to be capable of degrading mono-, di-, and trichlorobiphenyls. In addition, claims have been made that blends of adapted, mutant microbes applied to refinery activated sludge systems markedly improved effluent quality and stability (Tracy and Zitrides, 1979; McDowell and Zitrides, 1980; Thibault and Tracy, 1980). Kerelin et al. (1980) studied the cultivation and use of single-cell microalgae for treatment of refinery wastewater under laboratory conditions.

Ozonation

Ozone is a powerful oxidizing agent, and it can be used to degrade organic compounds in aqueous effluents. Destruction of phenols, humic acids, and many other compounds by ozone has been reported (Gabovich and Kurennoy, 1966; Gould and Weber, 1976; Neufeld and Spinola, 1978). However, complete

removal of organics may not be achieved at economical ozone doses. For example, chemical oxygen demand (COD) and chloroform levels in flocculated and filtered secondary effluent were reduced by only 31 percent and 10 to 30 percent, respectively, by an ozone dose of 10 mg/L (18-minute contact time). The total cost of ozonation was about \$0.02/m³ at an 0.44 m³/s hydraulic flow (Garrison and Miele, 1977).

Arisman et al. (1980) found that UV-ozone treatment could economically and selectively destroy PCB's at levels of 30 to 50 ppb to less than 1 ppb. Capital and operating costs would be \$300,000 to \$350,000 and \$0.45 to \$0.50 per cubic meter (\$1.71 to \$1.91 per 1000 gal), respectively.

Oxidation by Ferrate

Ferrate (FeO₄²⁻) contains iron in its +6 oxidation state and is a powerful oxidizing agent. It is currently being tested for its usefulness in destroying organics in wastewaters. Phenol and alkylbenzene in synthetic aqueous solution are removed to a high degree, while benzene, chlorobenzene, and 1-hexane-4-ol were only 50 percent oxidized, though their oxidation is enhanced in mixed solution (Waite and Gilbert, 1978).

Thermal Catalytic Wet Oxidation

Thermal catalytic wet oxidation includes processes which have also been termed wet air oxidation (Adams and Cunningham, 1976) and aqueous phase catalytic oxidation (Katzer et al., 1976). In this process, an organic-laden aqueous waste is subjected to elevated temperature (130 °C to 350 °C) and pressure (about 1700 psig or less) in the presence of oxygen and a metallic catalyst, resulting in complete or partial oxidation of the organics. Phenol and cresol have been treated quite effectively (Adams and Cunningham, 1976; Katzer et al., 1976).

Batch wet oxidation of phenol, orthochlorophenol, toluene, diphenylhydrazine, cyanides, and 1,2-dichloroethane has been studied by Baillo.

Randall and Knopp (1980) found that wet oxidation of acenaphthene, acrolein, acrylonitrile, 2-phenylhydrazine, 4-nitrophenol, pentachlorophenol, and phenol provided destruction greater than or equal to 99 percent when carried out for 1 hour from 275 °C to 320 °C.

9.4.3 Membrane Retention

Reverse osmosis, ultrafiltration, and hyperfiltration are pressure-driven membrane-mediated techniques for separating dissolved matter from water. Though it is not their main purpose to do so, membrane techniques also remove suspended matter. The precise meaning of these terms is often clouded in the literature, for they are not always synonymous. For this discussion, we shall adopt the following definitions:

- Reverse Osmosis (RO): a process in which water is passed through a semi-permeable membrane under high pressure (500-1500 psi) against a solute concentration gradient. Many inorganic and organic constituents will not pass through the membrane along with the water, allowing for the separation of the two. The purified water is referred to as the RO permeate.
- Ultrafiltration and Hyperfiltration: a processes in which water is passed through a porous membrane under low pressure (atmospheric to 150 psi), leaving behind mid-size molecules which are too large to pass through the holes in the membrane.

Reverse osmosis is better suited than ultrafiltration for achieving a high degree of organics (and inorganics) removal in the lower, as well as higher, molecular-size ranges. Ultrafiltration is appropriate when high rejection of inorganics and low-molecular weight organics is not required, though moderate rejections of inorganics by membranes containing charged groups has been achieved (Bhattacharyya et al., 1978). However, Wahl et al. (1980) indicated that a survey of tubular ultrafiltration systems revealed successful treatment of refinery wastewaters to regulatory effluent limitations. The average permeate oil concentration was 60 mg/L and the direct costs ranged from \$0.50/m³ to \$20/m³.

While some RO membranes generally permit greater removal of organics than others, no membrane demonstrates a uniformly high retention of all compounds. In viewing the data of Chian et al. (1975) and Fang and Chian (1976), who tested 13 single-compound solutions against 12 membranes, one can see that a specific membrane may retain nearly 100 percent of one compound but only 50 percent or less of another. Similarly, one membrane can retain nearly all of a particular compound, while a different membrane will retain none of it. Kosarek (1979) has also used reverse osmosis to increase water recovery and reuse from cooling tower blowdown. It was estimated that 80 percent water recovery was possible.

9.4.4 BATEA For Organics

As a result of the U.S. Environmental Protection Agency's program to develop the "best available technology economically achievable" (BATEA) several studies of toxic pollutants and their relative treatabilities have emerged. For example, McCarty (1980) examined several treatment steps including steam stripping, carbon adsorption, biological treatment, synthetic resins and reverse osmosis in the control of aromatics. Percent removals of trihalomethanes, chlorinated solvents, chlorobenzenes and aromatic hydrocarbons were reported across the treatment system.

A pilot process demonstration to test the potential of an organic chemical manufacturing plant wastewater being upgraded to cooling water makeup was reported by Scherm et al. (1980). Sedimentation/filtration, carbon adsorption, pressure filtration and reverse osmosis were evaluated.

Meiner and Mazewski (1980) discussed the operation of the wastewater treatment plant at the Santa Maria Refinery of Union Oil Company in California. The overall treatment system included API oil-water separation, biological trickling filter and activated sludge processes.

Although many organic removal methods are under intensive study, and specific applications to the problem may rapidly improve, it is clear that a comprehensive approach using a succession of techniques is presently required.

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RECOMMENDED PROTOCOLS FOR FUTURE TESTING

The final task (Task 6) of this project was to recommend protocols to be used in future cooling tower field tests. We believe that the analytical procedures described in Appendix B are adequate for the types of future tests to be discussed in this chapter.

10.1 DESIGN OF FUTURE TESTING PROGRAMS

As the objective of this study was to determine whether there was a potential air pollution problem connected with the use of reclaimed wastewater for cooling tower makeup, it was necessary to conduct field tests at several towers. While this approach served the stated purpose, it had some drawbacks. First, given time and resource limitations, it was not possible to sample each tower under a sufficient variety of conditions to determine whether our results were truly representative. Second, the need to sample for so many potential pollutants at the same time prevented us from studying any one pollutant class (e.g. volatile organics) in depth. Finally, the SAI microbiological stack sampler was of necessity originally designed to simultaneously quantify drift volume, collect and keep alive microorganisms, and provide moisture-free air for organic vapor sampling; only the second two of these functions were served by the final design. As is discussed in Appendix C, the multipurpose requirement resulted in a design which was suboptimum for any of the single purposes.

We recommend, therefore, that future cooling tower field testing programs be either (1) in-depth, long-term studies of one or two towers; or (2) multi-tower surveys focussing upon a single pollutant class. The design of either type of program will depend upon which of the following objectives are pursued by the ARB:

- To verify that wastewater-based pollutants are indeed emitted from cooling towers;
- To quantify with a high degree of accuracy mass emissions of chemical pollutants and/or number emissions of pathogenic microorganisms;

- To develop data which can be used in modelling of pollutant deposition and long-range transport; or
- To study potential human health effects and environmental degradation around cooling towers.

The first of these objectives has been substantially accomplished by the present research. Certain types of emissions have also been quantified, although the certainty of our estimates was subject to the limitations enumerated above. More comprehensive emissions data development will require a considerably more ambitious field testing program, alternatives for which are discussed in the remainder of this chapter.

If it is desired to obtain accurate field data to be used as input to a mathematical model of cooling tower emissions, deposition and transport, then the ARB must measure both mass emission rates and the size distribution of drift particles. As was pointed out in Chapter 8, no one has to date been able to obtain field data which accurately apportion mass emissions among droplet sizes.

Finally, the fourth objective could be accomplished through epidemiological surveys, deposition measurements, and vegetation studies. The prospects for success in an epidemiological study are quite limited, since the types of health effects to be hypothesized are so common that it would be difficult to prove excess morbidity or mortality among the relatively small population exposed to the highest concentrations or airborne pathogens from the tower. The fact that all the cooling towers presently using reclaimed wastewater in California, (except the geothermal towers) are in moderately or heavily polluted urban areas would make it even more difficult to correlate health outcomes with cooling tower emissions. Deposition measurements could provide useful information for assessing the potential effects of future use of wastewater for cooling in agricultural areas, where vegetative damage is of concern.

In the remainder of this chapter, we present suggestions for improving field sampling of various types of emissions from cooling towers using reclaimed wastewater.

10.2 MEASURING INORGANIC SALT EMISSIONS

In the following discussion, it is assumed that one is interested in a limited number of inorganic constituents of the makeup and circulating water. The first approach, mass balance, is relatively inexpensive and convenient but of undetermined accuracy; to our knowledge it has never been attempted. The second approach, isokinetic sampling, is certainly feasible, but may be quite expensive.

10.2.1 Approach No. 1--Mass Balance

In this approach one attempts to account for changes in mass of a given pollutant in all parts of the cooling tower system; that which cannot be accounted for is assumed to be emitted to the atmosphere. It is assumed that the following may be measured:

$$\begin{aligned} \text{Mass Input} = & (\text{makeup flow rate}) \times (\text{concentration in makeup}) \\ & + (\text{treatment solution addition rate}) \times (\text{conc. in} \\ & \text{solution}) + (\text{corrosion from heat exchanger}) \end{aligned}$$

$$\begin{aligned} \text{Mass Output} = & (\text{blowdown rate}) \times (\text{concentration in blowdown}) \\ & + (\text{rate of deposition to cold water basin sludge}) \end{aligned}$$

$$\begin{aligned} \text{System Change} = & (\text{circulating water volume at end of test}) \times \\ & (\text{concentration in circ. water at end of test}) \\ & - (\text{circulating water volume at start of test}) \times \\ & (\text{concentration in circ. water at start of test}) \end{aligned}$$

The estimated pollutant mass emission rate is then:

$$\text{Emission} = \text{Mass Input} - \text{Mass Output} - \text{System Change}$$

This approach would require installation of accurate flow measurement devices to monitor makeup and blowdown rates over several days or weeks. Water samples would be taken periodically during each measurement interval so that pollutant concentrations could be measured. Measurement of corrosion from heat exchanger surfaces and/or treatment solution addition rates would not be necessary if the pollutant of interest did not enter the tower system by these means. The most problematic sorts of measurements would be those for the

sludge deposition rate and the circulating water volume. Sedimentation rate measurement could be accomplished by placing sampling trays in the hot and cold water basins. Changes in circulating water volume could be determined by measuring basin depth levels over time, although some initial system volume would still have to be estimated (with questionable accuracy).

The advantages of this approach are that it is relatively inexpensive and, once the flow measurement devices have been set up, relatively convenient. Also, the method will account for mass emissions from all parts of the tower, including the louvers. The fact that pollutant mass emission rates are very likely only a tiny fraction of the mass in the system, however, means that the accuracy of the emission estimate depends heavily upon the term which may be quantified with the least accuracy, the system change.

10.2.2 Approach No. 2--Stack Measurement

Because one would be interested in the mass emissions of one or two chemical species, rather than of drift water per se, it would not be necessary to measure, or even collect, drift water. The most promising approaches would be isokinetic sampling using some variation of Environmental Systems Corporation's hot bead sampler, which was described in Chapter 8, or an impinger train. The sensitivity of the analytical methods described in Appendix B is such that either of these forms of sampling would provide enough material for analysis of expected mass emissions.

Most isokinetic drift sampling projects to date have focussed on one or two cells of a multi-cell tower, and have included one or two traverses on one or two days. To more accurately characterize emissions of chemical species of concern, it would be necessary to conduct a large number of tests, under many different tower operating regimes and weather conditions. Thus, this approach, while yielding a good deal of valuable information, could be quite expensive, and should be undertaken only where there is a potential for significant environmental damage from operation of the tower.

10.3 MEASURING ORGANIC VAPOR EMISSIONS

Our testing program showed that there is a strong possibility that volatile organic compounds present in reclaimed wastewater are emitted to the atmosphere (perhaps before becoming incorporated in the circulating water), and that some halogenated methanes may form in the circulating water of towers

which use chlorinated municipal wastewater. It is also likely that most of the volatile organic compounds detected in the fanstack exhaust originate in the inlet air and are thus not properly to be considered as cooling tower emissions. Although the foregoing statements are consistent with our field measurement results, they could not be proven conclusively. The following sampling approaches would provide much of the missing information.

10.3.1 Cases in Which Pollutants are in the Makeup

The testing program in these cases should be conducted in three steps: ~~compound identification, determination of pathways, and quantification of emissions.~~

Compound Identification

The same protocols used in our Task 4 tests on Municipal Towers No. 1 and 2 and on Industrial Tower No. 2 should be used, except that the "ambient" air sample should be taken at least 50 m from the tower to avoid contamination from emissions from the cold water basin. In addition, where sulfur compounds are likely to be present in ambient air and/or stack emissions, Tenax adsorbent should not be used unless the sulfur compounds can be scrubbed from the sample air. The compound identification step provides a first-cut picture of what chemical species are present in the makeup, circulating water, stack exhaust and ambient air.

Determination of Pathways

The purpose of the second step should be to verify that the tower is indeed a net emitter of pollutants of concern. Because the chemical species of interest may also be present in the inlet air, it is necessary to isolate the contribution of the makeup water. This may be done by injecting a relatively volatile tracer which is normally not present in cooling tower waters and ambient air. One possibility is sulfur hexafluoride (SF_6), which is detectable at extremely low concentrations. The tracer would be injected continuously into the makeup water supply far upstream from the point of discharge to the tower's cold water basin. The system would be judged to have come to equilibrium after tracer concentrations at several points in the circulating water had reached steady levels; this process could take as long as 24 hours. A portable laboratory for purging water samples would be necessary so that the tracer could be analyzed by GC immediately after sample

collection. Once the system was in equilibrium, continuous measurements of tracer emissions from the fanstacks could be made. By comparing mass emissions to mass injections into the makeup water supply, one could determine the percentage of the gas which is emitted by the tower and the percentage which is stripped from the makeup water before it reaches the cold water basin.

Quantification of Emissions

If it is determined that specific volatile organic compounds of concern are emitted through the makeup, then makeup water composition should be monitored regularly over a period of several months. As was pointed out in Section 8.3.2 the annual emissions estimates we calculated were based upon the untested assumption that measured concentrations were typical of year-round operation. Monitoring would have to be performed frequently enough so that frequency distributions of component concentrations could be established. These distributions, in combination with makeup water flow patterns, could then be used to estimate emissions.

10.3.2 Cases in Which Pollutants are Generated in the Tower

While halocarbons may indeed be generated in cooling tower basins and subsequently emitted to the atmosphere, emission levels are probably minor compared to those from chemical plants and other industrial sources. The sort of major field testing program necessary to explore this potential problem in depth would probably be too expensive. An alternative approach, if the ARB continues to be interested in the problem, would be a series of laboratory experiments, in which a cooling tower environment is simulated. Treated municipal wastewater would be circulated in a closed loop and put through cycles of temperature and chlorine concentrations similar to those in one of the municipal cooling towers sampled in our program. Halomethane concentrations in the circulating water could then be monitored.

10.4 MEASURING MICROORGANISMS

While the SAI microbiological stack sampler served its purpose, we believe that future sampling of cooling tower emissions for bacteria, viruses, and other microorganisms of interest should be conducted in a different manner. One alternative means of collection which merits attention is the use of impingers. In the early stage of our sampler design process (see Appendix

C), we planned to use an impinger train. The approach was abandoned, however, when it was learned that the air flows necessary to maintain isokinetic sampling would essentially flush out the impinger solutions. We believe that this potential problem can be overcome through use of a carefully designed manifold system.

One advantage of the impinger approach is that media which support different types of microorganisms can be apportioned among the impingers. In addition, the effects of chlorination can be counteracted more effectively through the use of media designed to enhance bacterial recovery.

As in the case of other pollutants of interest, microbiological sampling should be conducted over many days, under a variety of tower operating conditions and weather types. Careful monitoring of chlorine levels in all parts of the tower system would make it possible to determine the effects of disinfection practices on microbial emissions.

APPENDIX A

INDUSTRIAL COOLING TOWER SURVEY

- COVER LETTER
- QUESTIONNAIRE



Gentlemen:

Science Applications, Inc. (SAI) is currently under contract to the California State Air Resources Board (CARB) to evaluate the potential for airborne pollutant emissions from cooling towers using reclaimed wastewater. One of the initial tasks in this study is to make the first detailed inventory of all industrial cooling towers in California, whether or not they use reclaimed wastewater. Among the parameters of interest are circulating water rate, drift rate, use of corrosion inhibitors, and the likelihood of use of reclaimed wastewater in the future.

We have identified your firm as one falling under one of the four Standard Industrial Classifications using over 85 percent of the cooling water in California. We would greatly appreciate your taking a few minutes to complete the enclosed questionnaire. If your firm does not use industrial water cooling towers in California, please so indicate and return the questionnaire anyway. A self addressed, stamped envelope is included for your convenience.

Information obtained through this survey will be provided to the CARB in a statistical summary form only. Your firm's identity will remain confidential.

If you have any questions, please contact the Principal Investigator, Dr. Michael B. Rogozen, at (213) 553-2705.

Thank you for your cooperation in this important study.

Sincerely,

SCIENCE APPLICATIONS, INC.

Michael B. Rogozen, D.Env.
Principal Investigator
ARB Cooling Tower Study

Enclosure

MBR/r

SURVEY OF INDUSTRIAL COOLING TOWER USERS IN CALIFORNIA

PLEASE ANSWER THE FOLLOWING QUESTIONS (IF UNABLE TO ANSWER, PLEASE INDICATE WHY: E.G., DO NOT KNOW THE ANSWER, PROPRIETARY INFORMATION, ETC.):

1. Name and address of Company _____

2. Name of person to contact about questionnaire _____

_____ Title _____

Telephone Number _____

3. Principal activities of company by Standard Industrial Classification Code (four-digit where possible) _____

4. Does your firm utilize industrial water cooling towers in California?
 Yes _____ No _____. If no, please sign and return questionnaire anyway.

5. If yes, please list the number of towers and their location by California county and the combined circulating rate of cooling water in each county (use back for additional space).

Number of Towers

County

Combined Circulating Rate
 (e.g., gal/min)

<u>Number of Towers</u>	<u>County</u>	<u>Combined Circulating Rate</u> (e.g., gal/min)
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____
_____	_____	_____

6. Is municipal wastewater, industrial process wastewater, agricultural wastewater, geothermal water, natural brackish or saline water, or other recycled water used as makeup in any of your firms cooling towers?

7. If so, what kind of water is recycled as cooling water makeup and what is its rate of use (e.g., gallons/year)? _____

8. If not, does your firm have plans to recycle water as cooling water makeup in the next 5, 10, or 15 years? _____

9. Is chromate used for corrosion control in any of your firm's cooling towers?

10. Do any of your industrial cooling towers have components, such as packing (fill), drift eliminators, sides, pipes, or louvers, which are composed of asbestos? _____

11. What is the approximate drift rate (as a percent of circulating rate) of your firms cooling towers? _____

12. On what is this drift rate(s) based (e.g., measurement, manufacturer's guarantee, rule of thumb)? _____

13. What is the condenser fluid at your firm's facilities (e.g., petroleum fractions, clean water, chemical process water, etc.)? _____

14. How is blowdown disposed of? _____

15. Who is the manufacturer of your firm's industrial cooling towers? _____

Signature _____

Thank you for taking the time to assist us in our survey. If you have any questions, please contact Dr. Michael Rogozen at (213) 553-2705.

Please return the completed questionnaire to:

Science Applications, Inc.
Attention: Dr. Michael Rogozen
1801 Avenue of the Stars
Suite 1205
Los Angeles, California 90067

APPENDIX B

SUPPLEMENTARY INFORMATION ON ANALYTICAL TECHNIQUES

Appendix B

ANALYTICAL PROCEDURES

B.1 PROCEDURES FOR DETERMINATION OF ORGANISMS

B.1.1 Water Samples

Water samples collected from the makeup water supply and the hot and cold water basins of the municipal and industrial cooling towers were analyzed for volatile and nonvolatile organic compounds. Figure B.1-1 is a schematic of our analytical procedures.

Volatile Organic Compounds

Both chlorinated and reactive volatile hydrocarbons were analyzed by flame ionization detection gas chromatography (GC/FID). Gas chromatography/mass spectrometry (GC/MS) was used in certain cases to confirm compound identities. A 5-ml sample of water was stripped of its volatiles with an inert gas (nitrogen for GC/FID, helium for GC/MS) using the USEPA-approved technique of Bellar and Lichtenberg (1974 and 1978). The volatiles were then transferred to Tenax adsorbent traps, thermally desorbed onto a GC column, and analyzed by flame ionization detection or mass spectrometry. The purge and trap device used was a Tekmar LSC-2 directly interfaced with a Hewlett-Packard 5730A gas chromatograph or a Finnegan 4000 quadrupole mass spectrometer, depending upon the type of detection. Compounds found in samples run by GC/FID were identified and quantified by direct comparison with standards analyzed in the same manner. Standard chromatograms are shown in Figures B.1-2 through B.1-4, while limits of detection of individual chemical species are listed in Table B.1-1. The spectrum of each peak acquired through GC/MS analysis was recorded and identified using the instrument's library system. All data acquired on the mass spectrometer were archived on magnetic tape for subsequent retrieval and interpretation.

Semi- and non-volatile organics were analyzed for by electron capture detection (ECD) and flame ionization detection (FID) gas chromatography. Each two-liter pooled sample was extracted using pH-controlled methylene chloride into a base-neutral and an acid fraction. After sodium sulfate drying, the base-neutral fraction was split, with half being analyzed by GC/ECD (2-m glass column with 0.5-percent SP-2250/1.95-percent SP-2401) or a 30-m SE-54 fused silica capillary column for the

WATER SAMPLE

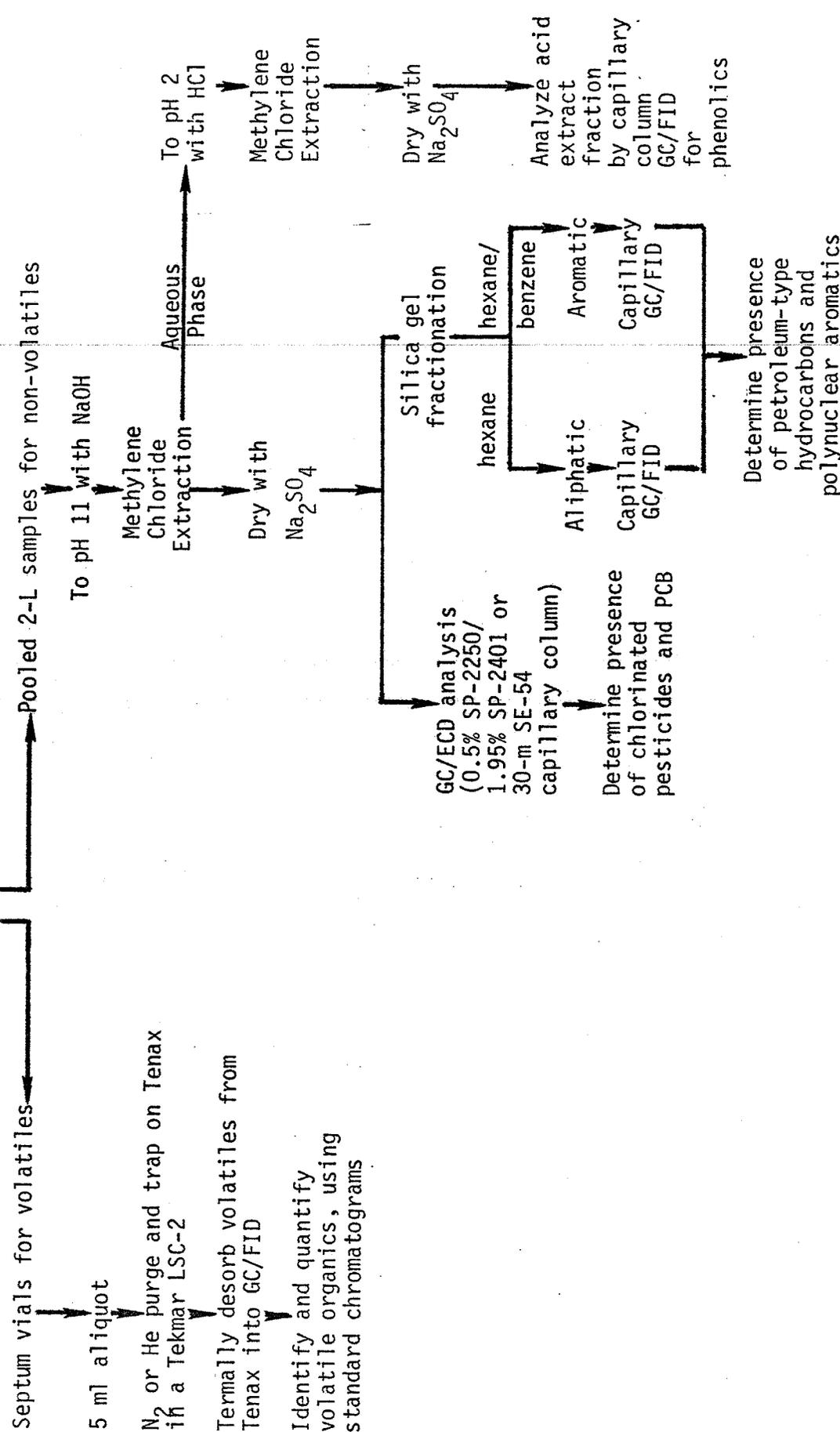


Figure B.1-1 Flow Chart For Analyses of Cooling Tower Water Samples

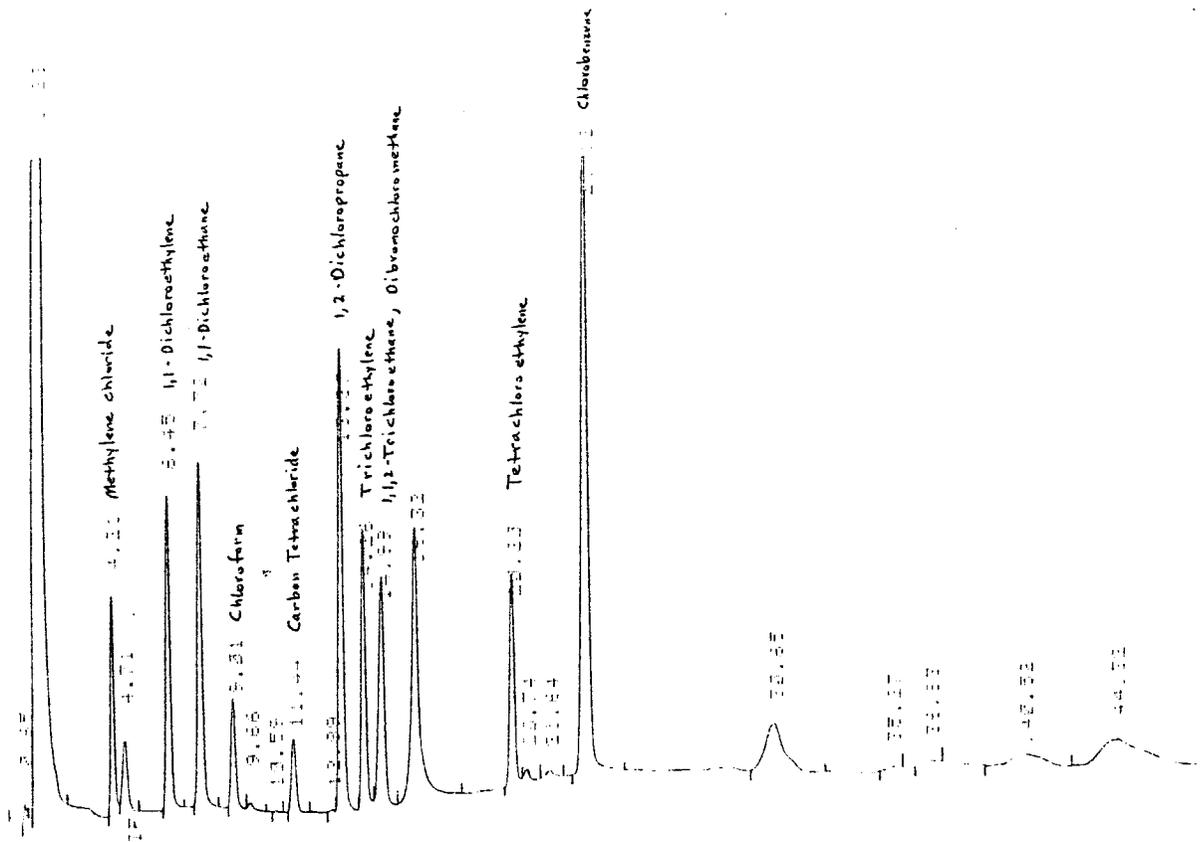


Figure B.1-2. Standard Gas Chromatographic Trace For 5- μ L Injection of Volatile Organic Compound Group A

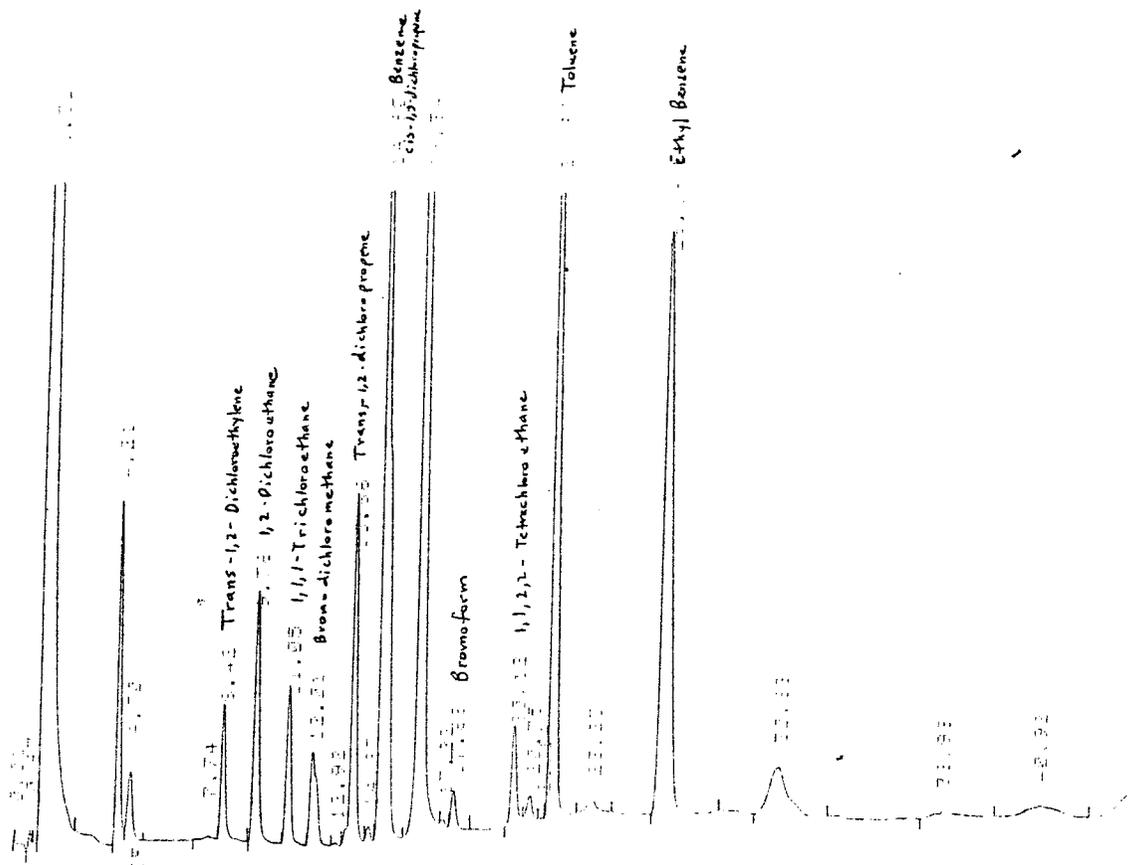


Figure B.1-3. Standard Gas Chromatographic Trace for 5- μ L Injection of Volatile Organic Compound Group B

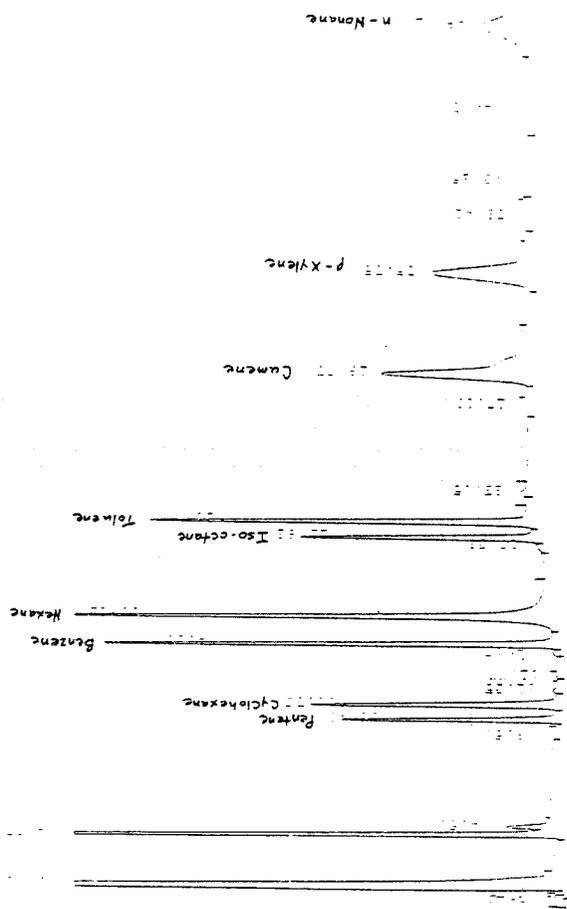


Figure B.1-4. Standard Gas Chromatographic Trace for 2.5- μ L injection of Volatile Organic Compound Group C.

Table B.1-1

DETECTION LIMITS FOR VOLATILE ORGANICS
ANALYZED BY FID GAS CHROMATOGRAPHY

Compound	Instrument Detection Limit (ng)	Water Sample Detection Limit (µg/L) ^a	Tenax Trap Detection Limit (µg/m ³) ^b
Pentane	20	4	20
Cyclohexane	20	4	20
Benzene	20	4	20
Hexane	20	4	20
Iso-octane	20	4	20
Toluene	20	4	20
Cumene	20	4	20
p-xylene	20	4	20
n-Nonane	20	4	20
Dichloromethane	100	20	100
1,1-Dichloroethylene	50	10	50
1,1-Dichloroethane	45	9	50
Chloroform	150	30	150
Carbon Tetrachloride	175	35	180
1,2-Dichloropropane	40	8	40
Trichloroethylene	75	15	80
1,1,2-Trichloroethane	c	c	c
Dibromochloromethane	c	c	c
Tetrachloroethylene	80	16	80
Chlorobenzene	20	4	20
Trans-1,2-dichloroethylene	120	24	120
1,2-Dichloroethene	60	12	60
1,1,1-Trichloroethane	90	18	90
Bromodichloromethane	120	24	120
Trans-1,3-dichloropropene	50	10	50
Cis-1,3-dichloropropene	c	c	c
Bromoform	250	50	250
1,1,2,2-Tetrachloroethane	175	35	180
Ethylbenzene	20	4	20

^aPurgeable Detection Limit based on a sample size of 5 ml of water.

^bTenax Detection Limit based on a sample size of 1 liter of air.

^cThese compounds co-elute with others, so detection limits were not determined.

measurement of PCBs and chlorinated organics (pesticides) and the other half analyzed by capillary (30-m WCOT SP-2100 column) GC/FID for petroleum-type and polynuclear aromatic hydrocarbons. The GC/FID split of the base-neutral fraction was further fractionated, prior to analysis, into an aliphatic fraction and an aromatic fraction using silica gel chromatography and selective elution. The acidic fraction obtained from the initial extraction/fractionation was also analyzed by capillary GC/FID for the measurement of phenols and other polar materials.

Selected fractions obtained in this scheme were also analyzed by capillary GC/MS for higher certainty identification of suggested components found in GC analysis.

B.1.2 Air Samples

Tenax adsorbent traps used for collecting samples of cooling tower inlet air and fanstack exhaust were thermally desorbed into a GC/FID with a 2.7-m packed column (SP 1000 on 60/80 Carbopak B). Procedures for compound identification and quantification were the same as reported above for the water sample analysis.

B.2 PROCEDURES FOR MEASURING INORGANICS

B.2.1 Water Samples

Except for samples from Municipal Tower No. 1, water to be analyzed for metals was pressure filtered through 0.4- μm , 47-mm diameter, Nuclepore membranes. Filtrates were acidified with HNO_3 in polypropylene bottles and particulates were preserved for analysis in individual containers. Both sample types were refrigerated. Municipal Tower No. 1 samples were not filtered but were digested in hot nitric acid and hydrogen peroxide.

Metals

Acidified filtrates were directly analyzed by flameless (graphite furnace) atomic absorption, using a Perkin-Elmer Model 603 spectrophotometer, for the metals of interest. Table B.2-1 lists the operating condition and detection limits for the metals analyzed. Particulates were tare weighed on the filters to determine total suspended loads of each sample.

Mercury was analyzed for in the filtrates by direct gas stripping of the elemental form into the 30-cm quartz cell of a Laboratory Data Control

Table B.2-1

INSTRUMENT OPERATING CONDITIONS, PARAMETERS AND DETECTION LIMITS (GRAPHITE FURNACE)

Element or Compound	Wavelength (nm)	Lamp Current (mA)	Slit	Volume (μ l)	Gas	Furnace Conditions	Minimum Detection Limit
As	193	10	4	50	Ar (3 sec, normal flow, 20)	Dry: 110 ^o C, 30 sec Char: 700 ^o C, 25 sec Atomize: 2700 ^o C, 7 sec	5 ppb
Cd	228.8	8	4	10	Ar (3 sec, normal flow, 20)	Dry: 110 ^o C, 22 sec Char: 350 ^o C, 22 sec Atomize: 2100 ^o C, 7 sec	0.1 ppb
Cr	357.9	8	3	20	Ar (3 sec, normal flow, 30)	Dry: 110 ^o C, 20 sec Char: 1100 ^o C, 20 sec Atomize: 2700 ^o C, 8 sec	0.5 ppb
Cu	324.7	10	4	20	Ar (3 sec, normal flow, 40)	Dry: 110 ^o C, 24 sec Char: 900 ^o C, 24 sec Atomize: 2700 ^o C, 7 sec	0.5 ppb
Fe	248.3	30	4	20	Ar (3 sec, normal flow, 30)	Dry: 110 ^o C, 24 sec Char: 1100 ^o C, 24 sec Atomize: 2700 ^o C, 7 sec	0.5 ppb
Pb	283.3	8	4	20	Ar (3 sec, normal flow, 20)	Dry: 110 ^o C, 24 sec Char: 750 ^o C, 30 sec Atomize: 2300 ^o C, 7 sec	0.5 ppb
Se	196	8	9	50	Ar (3 sec, normal flow, 20)	Dry: 110 ^o C, 30 sec Char: 700 ^o C, 30 sec Atomize: 2700 ^o C, 8.5 sec	10 ppb

Table B.2-1
(Cont.)

Element or Compound	Wavelength (nm)	Lamp Current (mA)	Slit	Volume (μ l)	Gas	Furnace Conditions	Minimum Detection Limit
Zn	213.9	15	4	20	Ar (3 sec, normal Flow, 20)	Dry: 110 ^o C, 22 sec Char: 500 ^o C, 22 sec Atomize: 2500 ^o C, 7 sec	0.1 ppb
Hg	254	---	---	---	---	---	0.6 ng
NH ₃	640	---	---	---	---	---	0.8 ppm
H ₂ S	---	---	---	---	---	---	1.0 ppm

Model 1234 cold vapor, 254-nm absorption photometer. Particulate matter was analyzed for mercury by strong acid (H_2SO_4 , HNO_3 and KMnO_4) digestion of all mercury species followed by reduction with hydroxylamine hydrochloride and stannous chloride to elemental form and purging into the photometer.

Ammonia and Hydrogen Sulfide

Ammonia and hydrogen sulfide were measured in water samples from the geothermal cooling tower. Ammonia was determined by the phenate technique (APA, 1976, Standard Method 418C) at 640 nm. Hydrogen sulfide was determined as sulfide by using the standard titrimetric (iodine) method (APHA, 1976, Standard Method 428 D).

Chlorine

Chlorine concentrations were in general determined in the field with a Fischer-Porter Model 17T1010 amperometric titrator at the time of sample collection. Samples from Municipal Tower No. 1 were analyzed for chlorine in the laboratory using the colorimetric leuco crystal violet technique (APHA, 1976, Standard Method 409 G).

B.2.2 Air Samples

Ammonia

Impinger solutions from the geothermal tower stack sampling were analyzed by Orion Research, Inc.'s Procedure No. 502 (Orion, 1980), which is based upon the method of Booth and Thomas (1973). Samples were treated with 10N NaOH and then analyzed with a selective ion electrode (Orion Model 195-10). Electrode current was related to NH_3 concentration by use of 10^{-2} , 10^{-3} and 10^{-4} molar standards. Each sample was analyzed in triplicate, and the resulting molar concentrations were averaged.

Mercury

Glass Fiber filter samples collected from the geothermal tower exhaust were digested with a hot solution of HNO_3 , H_2SO_4 , $\text{K}_2\text{S}_2\text{O}_8$, and KMnO_4 , and then reduced with hydroxylamine hydrochloride and stannous chloride. Elemental mercury (Hg^0) vapor was quantified by the method described above.

Gold traps used in the tower exhaust tests were thermally desorbed at 550°C . Elemental mercury was then measured by the photometric method described above.

B.3 REFERENCES

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APPENDIX C

DESIGN AND TESTING OF THE SAI MICROBIOLOGICAL STACK SAMPLER

The device used to sample cooling tower exhaust air for bacteria, virus particles and organic vapors was described in detail in Section 7.2. The purpose of this appendix is to chronicle the design and construction of the sampler and to report on bacterial recovery and survival tests performed before we used the device in the field.

C.1 BACKGROUND

C.1.1 Sample Requirements

In Task 4 we were required to collect cooling tower exhaust air samples and analyze them for bacteria and virus, organic vapors and, if possible, inorganic metal constituents of the drift. The following criteria were used to consider existing sampling devices and, ultimately, to design our own sampler:

- Exhaust air must be sampled isokinetically; i.e. air must enter the sampler at the same velocity as it exits the cooling tower fanstack.
- In order not to contaminate adsorbent materials with water vapor, air collected for subsequent organic vapor analysis must be water-free.
- Bacteria and virus particles must not only be collected efficiently, but they must be able to survive for sampling periods of up to several hours.
- The device must be readily autoclavable.
- The apparatus must be easily assembled and disassembled, light-weight, and compact.
- Enough water must be collected within a reasonable amount of time for all necessary analyses.

C.1.2 Rejection of Other Samplers

To the best of our knowledge, only Environmental Systems Corporation (ESC) and Ecodyne had isokinetic drift samplers at the time of our proposal effort. ESC's device was deemed inappropriate because (1) it could not be

used to collect volatile substances and (2) bacteria collected would very likely be destroyed by the system's heating mechanism. We believed, however, that the Ecodyne device could be modified to suit the purposes of this project. A tentative agreement was reached for Ecodyne to perform the Task 4 sampling.

After the project was underway, some drawbacks to the original plan to use Ecodyne's sampler became apparent. First, the Ecodyne device would have to be modified to suit the purposes of our project. According to Dr. Gunther Schrecker of SAI, who evaluated the Ecodyne design and under another contract, the collection efficiency of the cyclone declines rapidly for particles below 1.2 μ m. Thus free floating bacteria may pass right through the device. Since so little drift water is likely to be collected, additional media are necessary to trap bacteria. In addition, the Ecodyne device must be modified to permit sampling of volatile organics.

Another problem with using Ecodyne was that its services are generally unavailable during the spring and summer, when we had planned to do the stack sampling. It is during those seasons that their crew is fully engaged in using the sampler for its original purpose, assuring cooling tower buyers that actual drift rates correspond to those guaranteed. Thus our testing program would be conducted at Ecodyne's convenience.

Finally, we believed that the cost to the ARB of sampler construction, laboratory testing and field use would be significantly low. In addition, the ARB would end up owning the device and could use it for a variety of future studies.

C.1.3. Development of the SAI Microbiological Stack Sampler

On 18 January 1980, the SAI project team met in La Jolla to begin design of the sampler. Agreement was reached on a preliminary design concept, which consisted of an elbow inlet, a series of glass fiber filters and a sidestream sampling port for collection of organic vapors. The dimensions of the sampler and the air flow rate through the device were determined from consideration of likely exhaust air velocities and volumetric drift rates for the towers to be sampled. Table C.1-1 shows our estimates of ranges of water volumes collected by various combinations of sampler inlet diameter and exhaust air velocity. In order to permit isokinetic sampling at Municipal

Table C.1-1
 QUANTITY OF COLLECTED DRIFT AS A FUNCTION
 OF UPDRAFT AIR VELOCITY AND SAMPLING TUBE
 INLET DIAMETER
 (Collection rates are in ml/hr)

Air Velocity (m/s)	Sampler Inlet Diameter (inches)		
	1	2	3
5.3	0.59 - 5.9	2.36 - 23.6	5.3 - 53
9.0	0.93 - 9.3	3.7 - 37.0	8.4 - 84
12.0	1.3 - 13.0	5.2 - 52.0	11.7 - 117

Tower No.1, which had the highest average exhaust in velocity (11 m/s), and to avoid the enormous pumping requirements of a larger system, we decided to use a 2-inch diameter inlet.

Several alternatives for the microbiological collection media were considered. Thought was given to using an impinger train. One advantage of the impinger approach is that media which support different types of microorganisms can be apportioned among the impingers. In addition, the effects of chlorination can be counteracted more effectively through the use of media designed to enhance bacterial recovery. However, as pointed out by Fannin (1980), impinger are most effect for low air sampling rates and short sampling times. For example, all-glass impingers are commonly designed for an air flow of $0.0125 \text{ m}^3/\text{min}$. In contrast, the flow rate through our sampler was on the order of $1.3 \text{ m}^3/\text{min}$. At the suggestion of Dr. Daniel Chang of the University of California at Davis, we ended up using the polypropylene and polyvinylidene filter pads described in Section 7.2.1.

The sampler was constructed in SAI's La Jolla laboratories during March and early April 1980. The pump did not arrive until May. In late May and early June, the device was given physical tests (flow rate, etc.) in the laboratory. On 4 June 1980, SAI staff showed the ARB and CEC drawings and photographs of the device. Preliminary microbial and volatile organics recovery tests were performed in July 1980. Sampler development was then delayed until October. We had ordered support beam materials in July and after a series of excuses for non-delivery, we were forced to cancel our order and find another supplier. The railing and beam system was finally ready on 10 October 1980.

On 20 November 1980 we used the sampler at the Burbank Power Plant's Olive 1 cooling tower. According to the plant operators, the heat load on the tower was normal. However, both drift and visible fog emissions were negligible. The sampler collected only 1.08 ml of water in over two hours. After the sampler was taken down from the tower, the filter material was washed twice with approximately 100 ml of sterile nonisotonic water. The collected drift and the two washings were analyzed by Morning Star Laboratories of Vernon, California by the standard methods described in

Section 6.2.3. Results are summarized as follows:

	MPN/100ml				
<u>Sample</u>	<u>TC</u>	<u>FC</u>	<u>FS</u>	<u>Coliphage</u>	
Drift	43	<3	<3	None	
Washing No. 1	<3	<3	4	None	
Washing No. 2	<3	<3	9	None	

These results demonstrated that at least some organisms were emitted and furthermore, that SAI's sampler could collect them. Particularly significant was the fact that fecal streptococci were collected on the filter material. That led us to believe that a carefully designed washing procedure could yield useful emissions data, even though little or no drift water is collected. We therefore consulted with Dr. Lawrence Margler, formerly of SAI, who recommended the filter washing protocol described in Section 7.2.2. Further bacterial tests using the new washing protocol were conducted at SAI's La Jolla laboratory on 28-29 January 1981.

C.2 BACTERIAL RECOVERY AND SURVIVABILITY TESTS

C.2.1 Objectives

The objectives of this series of laboratory tests were (1) to quantify the ability of the sampler to trap aerosolized microorganisms and (2) to determine whether the indicator organisms of interest could survive for long periods of time in the sampler. The latter objective was considered quite important since sampling times of several hours duration would be necessary to collect enough drift water for microbiological analysis.

C.2.2 Methods

In order to make the experiments as realistic as possible, water was collected from the hot water basin of Municipal Tower No. 1 on the morning of the first test day. A carboy containing this sample was maintained at room temperature in the laboratory throughout the testing. From here on, we shall refer to this medium as the "wastewater." As a control, we used sterile phosphate buffer solution prepared by Standard Method 905 C (APHA et al., 1976).

Test Procedures

Figure C.2-1 is a schematic of the flow of water and wastewater through the laboratory system. Before each run, the sampler (including filter pads) and all glassware were autoclaved. Graduated cylinders were used as reservoirs for the wastewater and control solutions. At the start of each run, the sterile buffer was pumped from the reservoir through a spray nozzle directly in the sampler inlet. (Isokinetic sampling was not necessary in this case, since the water flow rate could be determined from changes in reservoir levels, and virtually all the water removed from the reservoir entered the sampler.) The sampler blower was set to simulate air flow at 11 m/s, corresponding to Municipal tower No. 1.

At a predetermined time, the system was shut off, and water was recovered from the sample bottles attached to the sampler. The sampler was then opened and the filter pads were removed and washed by the procedure described in Section 7.2.2. The whole test procedure was then repeated, without intermediate autoclaving, with the wastewater.

Vial samples, filter washings, and samples from the wastewater reservoir were analyzed for total coliforms (TC), fecal coliforms (FC) and fecal streptococcus (FS) by Environmental Engineering Laboratory of San Diego. Analyses for E. coliphage were performed by Morning Star Laboratories of Vernon. Standard methods were used for all analyses.

Table C.2-1 summarizes the conditions under which each run took place. The purpose of Runs 1A and 1B was to test the sampler's ability to collect microorganisms, irrespective of the organisms' ability to survive over long test periods or not. In order to assure that enough organisms were introduced into the sampler inlet, the volumetric flow rate had to be quite high. Runs 2A and 3B were intended to simulate likely sampling times. Because sampling times could (and indeed did) exceed two hours, one seven-hour run (4A) was made to determine bacterial and viral survivability inside the sampler.

C.2.3 Results

Table C.2-2 shows the amount of water (sterile control or wastewater) collected in the sampler's vials and interior during each test run. Although the trend is not monotonic, the recovery percentage appears to

Table C.2-1
SAMPLER TEST CONDITIONS

Run	Medium Injected	Volume Injected (ml)	Test Time
1A	Control	129.5	34.7 sec
1B	Wastewater	133.7	35.8 sec
2A	Control	ND ^a	62 min
2B	Wastewater	344	62 min
3A	Control	322.5	117 min
3B	Wastewater	472	124 min
4A	Wastewater	618	420 min

^aND = Not determined for this run.

Table C.2-2
VOLUMETRIC RECOVERY RATES

Run	Flow Rate (ml/min)	Volume Recovered (ml)	Recovery Percent
1A	223.9	109	84.2
1B	224.1	107	80.0
2B	5.6	196.5	57.1
3A	2.8	129	40.0
3B	3.8	35	7.4
4A	1.5	60	9.7

decrease with decreasing flow rates. It should be noted that no attempt was made to characterize the size distribution of the droplets produced by the spray nozzle. Thus no statement regarding the efficiency of the sampler for collecting drift droplets can be made.

Results of the microbiological analyses are shown in Tables C.2-3 through C.2-6. At the time that Environmental Engineering Laboratory (EEL) received its first batch of samples, concentrations of indicator bacteria were believed to be considerably lower than they turned out to be; as a result, samples were insufficiently diluted to permit precise quantification. For example, total coliform concentrations could in many cases be expressed only as ">2400 MPN/100 ml." By the time the second batch arrived at EEL, concentrations could be predicted more accurately, and it was possible to obtain absolute values for the fecal streptococci. Unfortunately, the methods used were not sensitive enough to detect the rather lower concentrations of fecal coliforms. The sensitivity of the E. Coliphage assay was 0.2 plaques/ml.

With some exceptions, the concentrations of the indicator microorganisms in the wastewater solution increased with time. This is understandable, inasmuch as the wastewater "reservoir" was sitting for 24 hours at room temperature. At one point, fecal streptococcus plate counts reached 1×10^6 per 100 ml.

The data show that the sampler was capable of collecting significant numbers of total coliform fecal streptococcus and E. coliphage particles. Measurable numbers of fecal coliforms were collected in the sampler vials in Run 1B and in the composite vial and filter sample in Run 2B, but on other runs it is difficult to judge whether these organisms were indeed collected.

The filter pads do not appear to be able to trap and/or support E. coliphage particles; plaque counts were zero for the filters samples in all cases. In Run 2B, 91 particles were detected in the composite vial and filter sample. We cannot say for sure whether these particles were trapped in the vials or on the filters. Total coliforms evidently can survive better in the sampler vials than on the filter material. This trend becomes more marked with longer sampling times. In the 35-second and 2-hour runs, the filters appeared to support growth of fecal streptococci better than the fluid in the sampler vials. During the 7-hour run, the opposite pattern was observed.

Table C.2-3
RECOVERY OF TOTAL COLIFORMS BY THE SAMPLER

Run	Time	Medium ^a	Organisms Introduced (MPN)	Vials	Organisms Recovered (MPN) Filters	V+F ^b	Total Recovery Percentage
1A	35 sec	C	0	<2	<2	-	NA ^c
1B	35 sec	WW	>3209	372	41	-	<12.9
2A	1 hr	C	0	-	-	<3	NA
2B	1 hr	WW	>8256	-	-	3162	<38.3
3A	2 hr	C	0	30	<2	-	NA
3B	2 hr	WW	>11328	5632	>7104	-	<100
4A	7 hr	WW	>14832	14400	302	-	<99

^aC = Control, WW = Wastewater.

^bV+F = Samples from vials and filter washings were combined.

^cNA = Not applicable.

Table C.2-4
RECOVERY OF FECAL COLIFORMS BY THE SAMPLER

Run	Time	Medium ^a	Organisms Introduced (MPN)	Organisms Recovered (MPN)	Vials	Filters	V+F ^b	Total Recovery Percentage
1A	35 sec	C	0	<2	<2	<2	-	NA ^c
1B	35 sec	WW	<3	5	<2	<2	-	<100
2A	1 hr	C	0	-	-	-	<3	NA
2B	1 hr	WW	<7	-	-	-	10	<100
3A	2 hr	C	0	,3	<2	<2	-	NA
3B	2 hr	WW	<9	<7	<6	<6	-	<100
4A	7 hr	WW	<12	<12	<6	<6	-	100

^aC = Control, WW = Wastewater.

^bV+F = Samples from vials and filter washings were combined.

^cNA = Not applicable.

Table C.2-5
RECOVERY OF FECAL STEPTOCOCCI BY THE SAMPLER

Run	Time	Medium ^a	Organisms Introduced (Plate Count)	Vials	Organisms Recovered (Plate Count) Filters	V+F ^b	Total Recovery Percentage
1A	35 sec	C	0	<44	<44	-	NA ^c
1B	35 sec	WW	<53	<43	<50	-	ND ^d
2A	1 hr	C	0	-	-	>60	NA
2B	1 hr	WW	<138	-	-	<79	57
3A	2 hr	C	0	<52	<40	-	NA
3B	2 hr	WW	1.79×10^6	2.42×10^5	1.69×10^6	-	>100
4A	7 hr	WW	4.33×10^6	2.19×10^6	1.41×10^6	-	83

^aC = Control, WW = Wastewater.

^bV+F = Samples from vials and filter washings were combined.

^cNA = Not applicable.

^dND = Cannot determine from available data.

Table C.2-6
RECOVERY OF E. COLIPHAGE BY THE SAMPLER

Run	Time	Medium ^a	Organisms Introduced (Plaque Count)	Vials	Organisms Recovered (Plaque Count) Filters	V+F ^b	Total Recovery Percentage
1A	35 sec	C	0	0	0	-	NA ^c
1B	35 sec	WW	41	99	0	-	>100
2A	1 hr	C	0	-	-	0	NA
2B	1 hr	WW	291	-	-	91	31
3A	2 hr	C	0	0	0	-	NA
3B	2 hr	WW	1.8	0.3	0	-	17
4A	7 hr	WW	333	128	0	-	38

^aC = Control, WW = Wastewater.

^bV+F = Samples from vials and filter washings were combined.

^cNA = Not applicable.

The most encouraging result of these tests was that TC, FS and E. coliphage can survive in the sampler for long enough times to permit lengthy sampling of cooling tower fanstacks.

C.3 REFERENCES

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