Prepared in cooperation with the
Puerto Rico Department of Health and the
Puerto Rico Aqueduct and Sewer Authority

RECONNAISSANCE OF VOLATILE SYNTHETIC ORGANIC CHEMICALS AT PUBLIC WATER SUPPLY WELLS THROUGHOUT PUERTO RICO, NOVEMBER 1984 - MAY 1985

UNITED STATES GEOLOGICAL SURVEY
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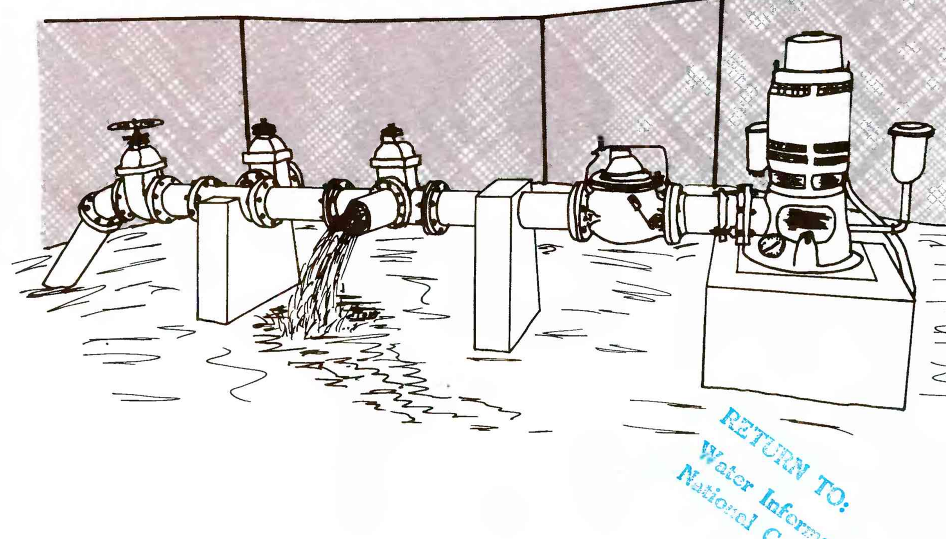

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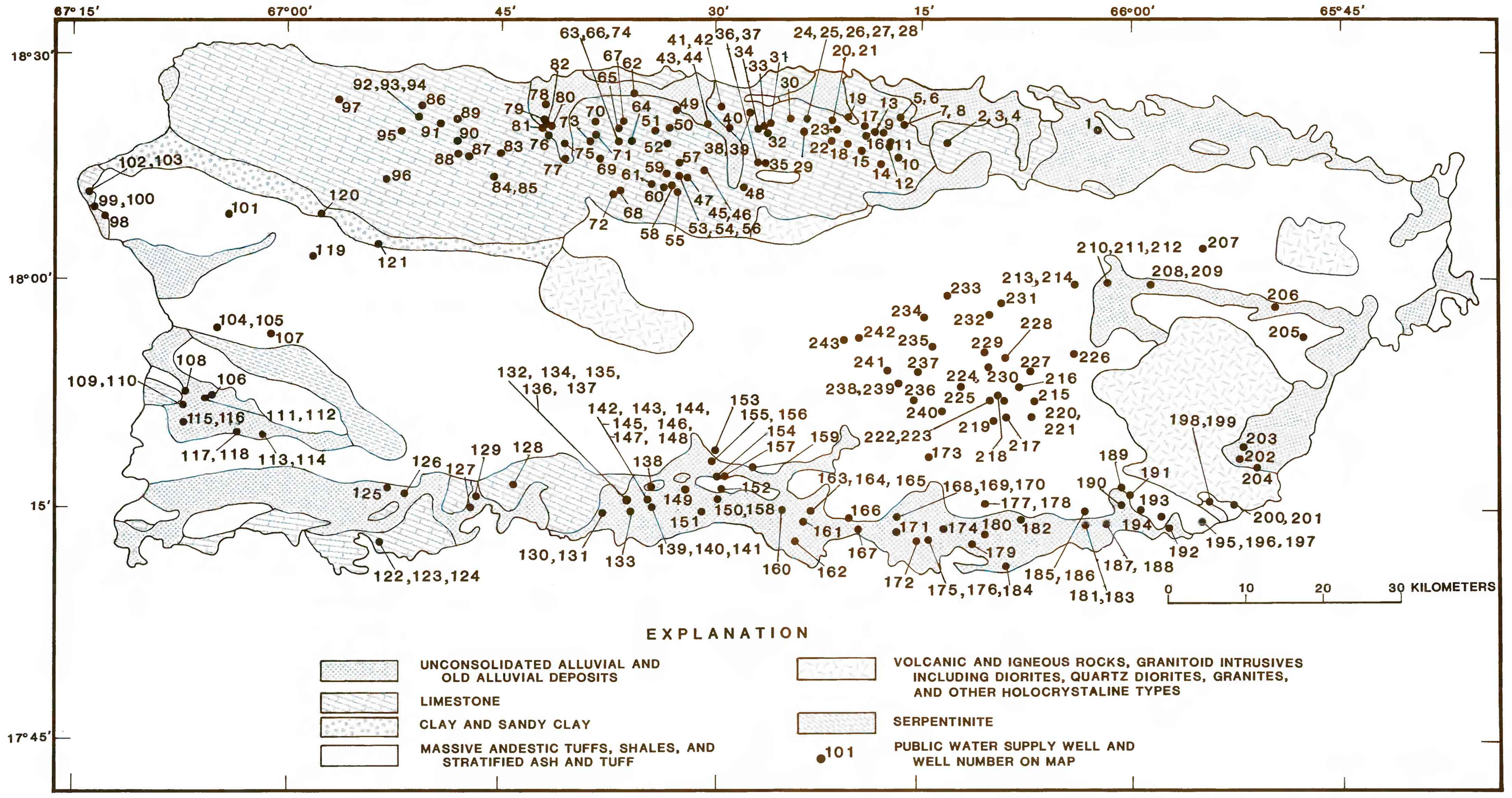


Figure 1.--Location of public supply wells operated by PRASA throughout Puerto Rico and sampled for VOC's during November 1984 — May 1985. (Map numbers refer to tables 2 & 3.)

RECONNAISSANCE OF VOLATILE SYNTHETIC ORGANIC CHEMICALS AT PUBLIC WATER SUPPLY WELLS THROUGHOUT PUERTO RICO, NOVEMBER 1984 - MAY 1985

By
Senén Guzmán-Ríos, René García, and Ada Avilés

INTRODUCTION

Ground water is the principal source of drinking water for about 850,000 people in Puerto Rico (National Water Summary, 1985). Ground-water withdrawals for public supply, agricultural, and industrial water uses in Puerto Rico are about 250 million gallons per day (Mgal/d) (Torres-Sierra and Avilés, 1985). The development of the most accessible surface water supplies will result in an increasing demand for ground water.

Recent investigations conducted by the U.S. Geological Survey, WRD (USGS) have shown the presence of toxic synthetic organic chemicals in ground water throughout Puerto Rico (Gómez-Gómez and Guzmán-Ríos, 1982). Volatile synthetic organic chemicals (VOC's) have been detected in water from public water supply wells in concentrations ranging from 1 to 500 micrograms per liter (Guzmán-Ríos and Quiñones-Marquez, 1984 and Guzmán-Ríos and Quiñones-Marquez, 1985). As result of these findings, pumpage was discontinued at 6 wells operated by the Puerto Rico Aqueduct and Sewer Authority (PRASA), the Commonwealth of Puerto Rico agency responsible for public-water supply. Monitoring of 10 additional wells in the vicinity of those wells is being conducted by the USGS in cooperation with PRASA.

In 1985, the USGS began a comprehensive islandwide study of VOC's in drinking water. The study was conducted in cooperation with the Puerto Rico Department of Health (PRDOH) and PRASA. Samples were collected from 243 public-water supply wells operated by PRASA (figure 1).

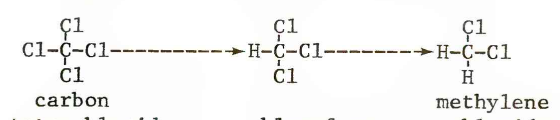
The authors wish to acknowledge the support, assistance and cooperation of the PRASA staff throughout Puerto Rico in the sample collection effort. The authors are especially grateful to Engineer Carlos García-Troche from the PRASA main office in San Juan.

VOLATILE ORGANIC CHEMICALS AND WATER CONTAMINATION

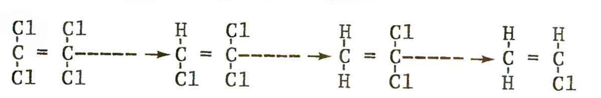
Volatile synthetic organic chemicals (VOC's) are among the most important groups of industrial chemicals. They are used extensively in the manufacture of degreasing agents, cleaning fluids, and industrial chemicals. Among the most important compounds of the VOC's group are trichloroethylene (TCE), tetrachloroethylene (PCE), carbon tetrachloride (CCl_4), chloroform ($CHCl_3$), methylene chloride (MCl), and vinyl chloride (VCl). Most of these compounds are toxic and/ or carcinogenic (table 1).

The use of VOC's for industrial and domestic purposes has resulted in the release to the environment of significant quantities of some of these compounds. Although VOC's are readily adsorbed by most soils, contamination of ground water with VOC's is one of the principal ground water quality problems in the Nation (USEPA, 1985). Several nationwide investigations to determine the extent of contamination of aquifers with VOC's have revealed widespread contamination with TCE and PCE (USEPA, 1980).

VOC's can bio-degrade or react chemically to form harmless or other organic compounds that may be more toxic than the original compounds (Wood and others, 1981). Methylene chloride, for example, can result from the degradation of carbon tetrachoride, once a common dry cleaner:



Similarly, vinyl chloride can be produced from tetrachloroethylene, a common degreaser agent:



Compounds like chloroform and bromoform can also be produced during disinfection by chlorination processes. The free chlorine reacts chemically with humic substances in water to produce chloroform and other halogenated compounds.

METHODS AND PROCEDURES

Sampling Procedures

Ground-water samples were collected as close as possible to the well discharge at 243 public water supply wells following techniques described by Brown and others (1970), Goerlitz and others (1972) and Wood and others (1976). The sampling was conducted from November 1984 to May 1985. Field determinations were made of the specific conductance and temperature. Physical characteristics of the well (latitude, longitude, code, name, depth of penetration, depth to water and pumping rate) were obtained from USGS and PRASA files.

Two raw-water (before water enters in contact with chlorination process) samples were collected in 120-milliliters clear glass vials at each well for further laboratory determination of volatile organic compounds. The vials were equipped with open-top screw caps and teflon-faced silicone rubber septa. After collection, the samples were wrapped in aluminum foil to reduce exposure to ultraviolet light, which may cause photochemical changes of the compounds. The samples were chilled to 4 °C and immediately shipped to the USGS National Water Quality Laboratory in Doraville, Georgia for analyses.

Analytical Methods

Laboratory analyses using the Gas Chromatography/Mass Spectrometry Method were performed on the samples collected to determine the possible presence of the following volatile organic chemicals:

Benzene	Cis-1,3-Dichloro-propene
Bromoform	2-Chloroethyl vinyl ether
Carbon Tetra-chloride	1,4-Dichloro-benzene
Chlorobenzene	1,1-Dichloro-ethylene
Chlorodibromo-methane	1,1-Dichloro-ethane
Chloromethane	1,1,1-Trichloro-ethane
Chloroethane	1,1,2-Trichloro-ethane
Chloroform	1,1,2,2-Tetra-chloroethane
Dichlorobromo-methane	1,2-Dichloro-ethane
Ethylbenzene	1,2-Dichloro-propane
Bromomethane	Trans-1,2-dichloro-ethylene
Methylene Chloride	
Tetrachloro-ethylene	
Toluene	
Trichloroethylene	
Vinyl Chloride	
Trans-1,3-dichloro-propene	

All laboratory analyses were performed within a time of 14 days after collection to a detection level of 0.2 micrograms per liter (ug/L). The detection level is the minimum concentration of a substance that can be identified, measured, and reported with 99% confidence that the substance concentration is greater than zero and determined from analysis of a sample in a given matrix containing the substance (Feltz and Anthony, 1985).

Quality Assurance

Field sampling quality assurance procedures included the collection of duplicate samples at all wells sampled. About 25% of those samples were sent to the laboratory for analysis and the results were compared with those from the original samples. Additional details for the quality assurance procedures for the field sampling are described by Friedman and Erdmann (1982). Procedures for laboratory quality assurance are also included by Friedman and Erdmann.

Wells with VOC's concentrations higher than the standard values established by USEPA or PRDOH were resampled to verify the laboratory analytical values.

RESULTS

Analytical results of the field and laboratory determinations for the 243 sampled wells are summarized on figure 2, table 2, and table 3. VOC's included in the list and not shown in any of the tables were not detected during analysis.

Relatively high concentrations of halogenated organic chemicals were detected at 16 water-supply wells throughout the Island. Trichloroethylene (TCE) and/or tetrachloroethylene (PCE), two organic compounds commonly used as degreasing agents, were detected in concentrations above 5 micrograms per liter (ug/L) at wells nos. 1, 12, 13, 16, 17, 48, 154, 177, 178, 191, 219, 221 and 233 (table 2). Chloroform at concentrations higher than 5 ug/L was detected at nine wells (wells nos. 18, 92, 126, 187, 210, 212, 217, 219, and 239) (table 2). Wells nos. 16, 193 and 233 showed high concentrations of 1,1-dichloroethylene and 1,1,1-trichloroethane (table 3). Only two of the sampled wells showed concentrations of carbon tetrachloride above 2 ug/L (wells nos.193 and 217). A sample collected at well no. 193 had a concentration of 7 ug/L while three samples from the other well showed concentrations of 87, 95 and 94 ug/L respectively. Toluene was detected in concentrations above 1 ug/L in only one well (well no. 211 with 12 ug/L).

In general, the concentrations of chemicals detected at 16 wells (wells nos. 1, 12, 13, 16, 17, 48, 154, 177, 178, 184, 191, 193, 217, 219, 221, and 233) exceeded the proposed maximum contaminant levels (MCL's) promulgated by the USEPA (table 4) for drinking water (USEPA, 1985). Actual criteria established by PRDOH (PRDOH, 1983) for suitability of drinking water (50 ppb of TCE or PCE or 100 ppb of all combined VOC's) was exceeded only at 7 wells (wells nos. 1, 16, 193, 210, 217, 219, and 233).

Additional information about the sampling sites, laboratory techniques and results, wells characteristics or any other information in this report may be available from the U.S. Geological Survey/WRD, Caribbean District Office in San Juan, Puerto Rico (Building 652, GSA Center, Hwy 28, Km. 7.2, Pueblo Viejo, telephone no. (809) 753-4414).

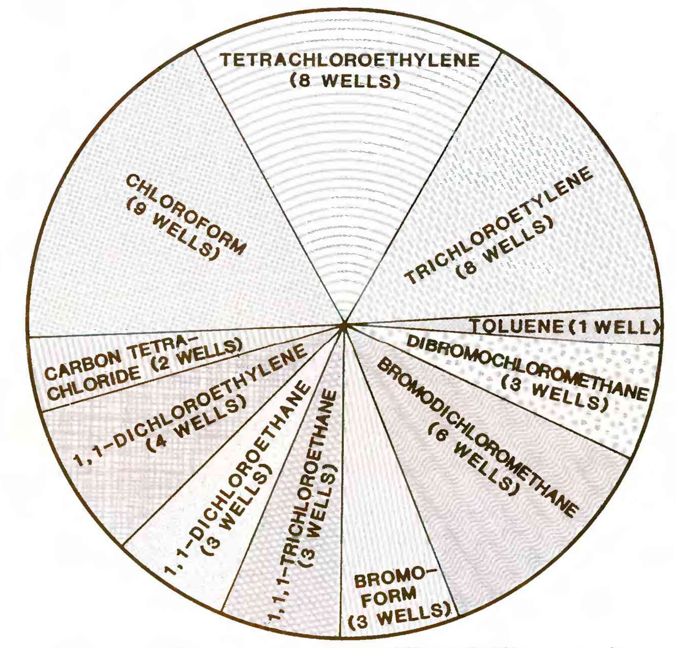


Figure 2.--Occurrence of specific volatile organic chemicals in concentrations larger than 5 µg/L at selected wells throughout Puerto Rico, November 1984 - May 1985.

Table 3. Other volatile synthetic organic chemicals detected at selected sampled wells throughout Puerto Rico, November 1984 - May 1985.

Well Number	Volatile organic chemical, in micrograms per liter (ug/L) or parts per billion (ppb)					
	A	B	C	D	E	F
16	<0.20	0.20	<0.20	58.00	24.00	18.00
32	4.0	<.20	<.20	<.20	<.20	<.20
	3.6	<.20	<.20	<.20	<.20	<.20
36	3.5	1.0	<.20	<.20	<.20	<.20
92	1.3	6.8	4.8	<.20	<.20	<.20
	1.4	8.9	4.9	<.20	<.20	<.20
114	8.1	1.5	2.6	<.20	<.20	<.20
	11	1.6	2.8	<.20	<.20	<.20
116	3.0	2.2	2.9	<.20	<.20	<.20
	5.1	<.20	<.20	<.20	<.20	<.20
119	4.3	<.20	<.20	<.20	<.20	<.20
120	1.4	<.20	<.20	<.20	<.20	<.20
121	2.6	<.20	<.20	<.20	<.20	<.20
126	<.20	9.4	1.0	<.20	<.20	<.20
172	4.6	1.2	1.7	<.20	<.20	<.20
178	3.4	1.9	1.9	<.20	<.20	<.20
184	<.20	<.20	<.20	10	<.20	<.20
187	7.9	13	5.3	<.20	<.20	<.20
188	1.3	<.20	<.20	<.20	<.20	<.20
	1.0	<.20	<.20	<.20	<.20	<.20
193	<.20	<.20	<.20	190	6.1	29
	<.20	<.20	<.20	356	8.9	30
210	2.2	13	3.8	<.20	<.20	<.20
	2.6	11	3.7	<.20	<.20	<.20
	2.6	57	8.9	<.20	<.20	<.20
211	<.20	1.2	<.20	<.20	<.20	<.20
212	<.20	46	7.3	<.20	<.20	<.20
	<.20	<.20	<.20	<.20	<.20	<.20
233	<.20	<.20	<.20	32	5.4	26
	<.20	<.20	<.20	31	4.7	24
	<.20	<.20	<.20	27	4.5	23
	<.20	.20	<.20	26	24	18
239	<.20	6.5	1.1	<.20	<.20	<.20
	<.20	5.5	1.4	<.20	<.20	<.20

Table 1. Physical characteristics of some volatile synthetic organic chemicals. (Sax, 1975.)

Chemical Name	Molecular Weight	Boiling Point °C	Chemical Formula	General Information
Methyl Chloride	50.49	-23.7	CH_3Cl	Colorless gas. Very slight irritant properties. Repeated exposure to low concentrations causes damages to the central nervous system and less frequently, to the liver, kidneys, bone marrow and cardiovascular system. High concentrations could cause dizziness, drowsiness, incordination, confusion, nausea and vomiting, abdominal pain, hiccoughs, diplopia and dimness of vision followed by delirium, convulsions and coma. Death may occur several days after exposure, resulting from degenerative changes in the heart, liver and kidneys.
Methylene Chloride	84.94	39.8	CH_2Cl_2	Colorless, volatile liquid. Very dangerous to the eyes. Except that induces narcosis, it has very few other toxic effects. It will not form explosive mixtures, however, it can be decomposed by contact with hot surfaces and open flame, yielding toxic fumes.
Chloroform	119.39	61.26	$CHCl_3$	Colorless liquid. Causes irritation of conjuctiva. An anesthetic. Prolonged inhalation will bring on paralysis accompanied by cardiac respiratory failure and finally death. Is a suspected carcinogen.
Carbon tetrachloride	153.84	76.8	CCl_4	Colorless liquid. Exposure to lower concentrations, insufficient to produce unconsciousness, usually results in severe gastrointestinal upset, and may progress to serious kidney and hepatic damage. High concentrations produce unconsciousness and death can follow from respiratory failure. Repeated contact may produce dermatitis. It is a suspected carcinogen.
Vivyl Chloride	62.50	-13.4	CH_2CHCl	Colorless liquid or gas (when inhibited). Acts as an anesthetic in high concentrations. Causes skin burns by rapid evaporation and consequent freezing. A recognized carcinogen. Dangerous when exposed to heat. Large fires of this material are practically inextinguishable.
1,1-Dichloroethylene	97.00	31.6	CH_2CCl_2	Colorless, volatile liquid. Details on toxicity are unknown. Is very dangerous when exposed to heat or flame. It can react with oxidizing materials.
Trichloroethylene	131.40	87.1	$CHClCCl_2$	Stable, colorless, heavy, mobile liquid. Inhalation of high concentrations causes narcosis and anesthesia. Prolonged inhalation of moderate concentrations causes headache and drowsiness. There is some questions as to damage to liver or other organs from chronic exposure. It's fire hazard is low when exposed to heat or flame.It is a common air contaminant. Suspected carcinogen.
Tetrachloroethylene	165.82	121.20	CCl_2CCl_2	Colorless liquid. Is extremely stable and resists hydrolysis. Not corrosive or dangerously reactive, but toxic by inhalation, by prolonged or repeated contact with the skin or mucous membrane or when ingested by mouth. Can cause dermatitis after repeated or prolonged contact with the skin. Upon ingestion it causes irritation of the gastrointestinal tract which in turn causes nausea, vomiting, diarrhea and bloody stools. Suspected carcinogen.
1,1-Dichloethane	99.0	57.3	CH_3CHCl_2	Colorless liquid. Aromatic. Liver injury has been reported in experimental animals. As fire hazard, it is dangerous when exposed to heat or flame.
1,1,1-Triethane	133.42	74.1	CH_3CCl_3	Colorless liquid. Narcotic in high concentrations. As other organic chlorides, when heated to decomposition, it may yield phosgene (carbonyl chloride), which is lethal in small doses.
Bromoform	252.77	149.5	$CHBr_3$	Colorless liquid or hexagonal crystals. Causes lachrymation. It can damage the liver to a serious degree and cause death. In addition to it's narcotic effects, it is a metabolic poison. When heated to decomposition, it emits highly toxic fumes.
Bromodichloromethane	163.8	90.6	$CHBrCl_2$	Colorless liquid. It's toxicity is unknown, but probably is narcotic in high concentrations. As other chlorides could be very dangerous during fires.
Dibromochloromethane	208.3	122	$CHClBr_2$	Colorless to pale yellow, heavy liquid. It's toxicity is unknown, but this kind of compound is irritant and narcotic. It emits toxic fumes when heated to decomposition.
Benzene	78.11	80.09	C_6H_6	Clear colorless liquid. Poisoning occurs most commonly through inhalation of the vapor, though benzene can penetrate the skin, and thus contribute to poisoning. Locally, benzene has a comparatively strong irritating effect producing erythema and burning. Exposure to high concentrations (3,000 ppm) may result in acute poisoning, characterized by the narcotic action of benzene on the central nervous system. Dangerous when exposed to heat or flame, can react vigorously with oxidizing material. Benzene is a common air contaminant and a suspected carcinogen.

Explanation for table 3.

A Bromoform ($CHBr_3$)
B Bromodichloromethane ($CHBrCl_2$)
C Dibromochloromethane ($CHClBr_2$)
D 1,1-Dichloroethylene or Vinylidene Chloride (CH_2CCl_2)
E 1,1-Dichloroethane or Ethylidene Chloride (CH_3CHCl_2)
F 1,1,1-Trichloroethane or Methyl Chloroform (CH_3CCl_3)
< Is less than

Table 4. Maximum contaminant levels (ug/L or ppb) proposed by U.S. Environmental Protection Agency for drinking water.

Chemical Name	Maximum Contaminant Level
Trichloroethylene	5
Carbon Tetrachloride	5
Vinyl Chloride	1
1,2-Dichloroethane	5
Benzene	5
1,1-Dichloroethylene	7
1,1,1-Trichloroethane	200
p-Dichlorobenzene	750

CONVERSION FACTORS

The following conversion table is included for the convenience of those who prefer to use the SI (International System of Units or metric units) rather than the inch-pound system of units. Concentrations of chemical parameters are given in milligrams per liter (mg/L) or micrograms per liter (µg/L), which are for the values presented numerically equal to parts per million (ppm) and parts per billion (ppb) respectively.

Multiply inch-pound units	By	To obtain metric units
	Length	
inch (in)	25.4	millimeters (mm)
feet (ft)	0.3048	meters (m)
	Volume	
gallons (gal)	3.785	liters (L)
million gallons (Mgal)	3,785	cubic meters (m^3)
	Volume Per Unit Time	
gallons per minute (gal/min)	0.06309	liters per second (L/s)
million gallons per day (Mgal/d)	.04381	cubic meters per second (m^3/s)
	Temperature	
degrees Farenheit	C = 0.55556 (F-32)	degrees Celsius
	Specific conductance	
micromhos per centimeter at 25 degrees Celsius (umhos/cm at 25°C)	1.0	microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C)

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