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Chloroform in the Hydrologic System—Sources, Transport, Fate, Occurrence, and Effects on Human Health and Aquatic Organisms

Scientific Investigations Report 2004-5137

U.S. Department of the Interior
U.S. Geological Survey

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By Tamara Ivahnenko and Jack E. Barbash

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U.S. Department of the Interior
Gale A. Norton, Secretary

U.S. Geological Survey
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Foreword

The U.S. Geological Survey (USGS) is committed to serve the Nation with accurate and timely scientific information that helps enhance and protect the overall quality of life, and facilitates effective management of water, biological, energy, and mineral resources. Information on the quality of the Nation's water resources is of critical interest to the USGS because it is so integrally linked to the long-term availability of water that is clean and safe for drinking and recreation and that is suitable for industry, irrigation, and habitat for fish and wildlife. Escalating population growth and increasing demands for the multiple water uses make water availability, now measured in terms of quantity *and* quality, even more critical to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program to support national, regional, and local information needs and decisions related to water-quality management and policy. Shaped by and coordinated with ongoing efforts of other Federal, State, and local agencies, the NAWQA Program is designed to answer: What is the condition of our Nation's streams and ground water? How are the conditions changing over time? How do natural features and human activities affect the quality of streams and ground water, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. Collectively, these Study Units account for more than 60 percent of the overall water use and population served by public water supply, and are representative of the Nation's major hydrologic landscapes, priority ecological resources, and agricultural, urban, and natural sources of contamination.

Each assessment is guided by a nationally consistent study design and methods of sampling and analysis. The assessments thereby build local know-ledge about water-quality issues and trends in a particular stream or aquifer while providing an understanding of how and why water quality varies regionally and nationally. The consistent, multi-scale approach helps to determine if certain types of water-quality issues are isolated or pervasive, and allows direct comparisons of how human activities and natural processes affect water quality and ecological health in the Nation's diverse geographic and environmental settings. Comprehensive assessments on pesticides, nutrients, volatile organic compounds, trace metals, and aquatic ecology are developed at the national scale through comparative analysis of the Study-Unit findings.

The USGS places high value on the communication and dissemination of credible, timely, and relevant science so that the most recent and available knowledge about water resources can be applied in management and policy decisions. We hope this NAWQA publication will provide you the needed insights and information to meet your needs, and thereby foster increased awareness and involvement in the protection and restoration of our Nation's waters.

The NAWQA Program recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for a fully integrated understanding of watersheds and for cost-effective management, regulation, and conservation of our Nation's water resources. The Program, therefore, depends extensively on the advice, cooperation, and information from other Federal, State, interstate, Tribal, and local agencies, non-government organizations, industry, academia, and other stakeholder groups. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch
Associate Director for Water

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Acronyms and Abbreviations Used in This Report

AQUIRE	AQUatic Information REtrieval system
BCF	Bioconcentration factor
CAS	Chemical Abstract Service
CCl_2F_2	Dichlorodifluoromethane
CCl_3COOH	Trichloroacetic acid
CCl_4	Tetrachloromethane
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CFCs	Chlorofluorocarbons
$CHBr_2Cl$	Dibromochloromethane
$CHBr_3$	Tribromomethane (bromoform)
$CHBrCl_2$	Bromodichloromethane
$CHCl_2Br$	Dichlorobromomethane
$CHCl_3$	Trichloromethane (chloroform)
$CHClBr_2$	Chlorodibromomethane
$CHClF_2$	Chlorodifluoromethane
CI	Confidence interval
Cl	Chloride
Cl_2	Chlorine gas
CPO	Chloroperoxidase enzyme
DBPs	Disinfection by-products
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
f_{oc}	Fraction of organic carbon
HCFCs	Hydrochlorofluorocarbons
HCl	Hydrochloric acid
HOCl	Hypochlorous acid
IGR	intrauterine growth retardation
K_H	Henry's Law constant
K_{oc}	Organic-water sorption partition coefficient
K_{ow}	Octanol-water partition coefficient
LOELs	Lowest-observed-effect-levels
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
NAWQA	National Water-Quality Assessment Program
NIOSH	National Institute for Occupational Safety and Health
NOM	Natural organic matter
OCl	Hypochlorite ion
OSHA	Occupational Safety and Health Administration
RCRA	Resource Conservation and Recovery Act
SUVA	Specific ultraviolet absorbance
THMs	Trihalomethanes
TRI	Toxic Release Inventory

TTHMs	Total trihalomethanes
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOCs	Volatile organic compounds

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Abstract

Chloroform is one of the volatile organic compounds (VOCs) detected most frequently in both ground and surface water. Because it is also one of the four trihalomethanes (THMs) produced in the highest concentrations during the chlorination of drinking water and wastewater, the frequent detection of this compound in ground and surface water of the United States is presumed to be caused primarily by the input of chlorinated water to the hydrologic system. Although anthropogenic sources of the compound are substantial, they are currently estimated to constitute only 10 percent of the total global input to the hydrologic system. Natural sources of the compound include volcanic gases, biomass burning, marine algae, and soil microorganisms. Under most conditions (except in the presence of unusually high bromide concentrations), chloroform is the THM produced in the highest concentrations during chlorination. Furthermore, in most cases where more than one THM is produced from chlorination, the relative concentrations among the different compounds usually decrease with increasing bromination (chloroform > dichlorobromomethane $\geq$ chlorodibromomethane $\geq$ bromoform). This phenomenon is presumed to be responsible for the common observation that when more than one THM is detected during investigations of the occurrence of these compounds in the hydrologic system, this same trend is typically observed among their relative concentrations or, for a uniform reporting limit, their relative frequencies of detection. This pattern could provide a valuable means for distinguishing between chlorinated water and other potential sources of chloroform in the environment.

Chloroform has been widely detected in national, regional, and local studies of VOCs in ground, surface, source, and drinking waters. Total THM (TTHM) concentrations of the compound, however, were typically less than the Maximum Contaminant Level (MCL) of 80 µg/L (micrograms per liter) established by the U.S. Environmental Protection Agency (USEPA) for TTHMs. In the studies that compared land-use settings, frequencies of detection of chloroform were higher beneath urban and residential areas than beneath agricultural or undeveloped areas. Because chloroform is a suspected human carcinogen, its presence in drinking water is a potential human health concern. Liver damage, however, is known to occur at chloroform exposures lower than those required to cause cancer, an observation that has been considered by the USEPA as the basis for setting a new, non-zero Maximum Contaminant Level Goal of 70 µg/L for the compound.

As part of its National Water-Quality Assessment Program, the U.S. Geological Survey has been assembling and analyzing data on the occurrence of VOCs (including chloroform) in ground and surface water on a national scale from studies conducted between 1991 and the present. This report presents a summary of current (2004) information on the uses, sources, formation, transport, fate, and occurrence of chloroform, as well as its effects on human health and aquatic organisms.

Introduction

Chloroform—known more formally as trichloromethane ($CHCl_3$)—has been one of the volatile organic compounds (VOCs) detected most frequently in the Nation's ground water by the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program (Squillace, Moran, and others, 1999). Grady (2003) also reported chloroform to be the most frequently detected VOC in a national study of both ground- and surface-water sources of drinking water.

Most of these detections are presumed to have been a consequence of contamination by chlorinated water and wastewater because chloroform and the three other most frequently detected trihalomethanes (THMs)—bromodichloromethane ($CHBrCl_2$), dibromochloromethane ($CHBr_2Cl$), and bromoform ($CHBr_3$)—are commonly produced during the chlorination of water and wastewater. Although the word trihalomethanes applies to trihalogenated methanes containing any of the halogen atoms (chlorine, bromine, iodine, or fluorine), this term will be used in this report to refer only to those containing

either chlorine or bromine because these are the ones most commonly detected, or analyzed for, in chlorinated water.

The presence of chloroform in drinking water is a potential human-health concern. In 1986, the U.S. Environmental Protection Agency (USEPA) classified chloroform as a probable human carcinogen ("Group B2" carcinogen), based on evidence of its carcinogenicity in animals (U.S. Environmental Protection Agency, 2000a). In 1998, the USEPA revised the carcinogenicity risk assessment for chloroform, stating that the compound is likely to be carcinogenic to humans by all routes of exposure at concentrations high enough to cause cytotoxicity or the formation of regenerative nodules in susceptible tissues (U.S. Environmental Protection Agency, 2002a). More recently, the USEPA revised the Maximum Contaminant Level Goal (MCLG) for chloroform to 70 μg/L (micrograms per liter) based on non-cancer effects (U.S. Environmental Protection Agency, 2004a). Other Federal legislation that has listed chloroform as a potential health concern includes the Occupational and Safety Health Act, the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or "Superfund"), the Clean Air Act, the Resource Conservation and Recovery Act (RCRA), the Safe Drinking Water Act, Clean Water Act, the Toxic Release Inventory (TRI), and the Chemical, Food, Drug and Cosmetic Act (Environmental Defense Fund, 1999).

Purpose and Scope

Information on chloroform in the hydrologic system was compiled by the VOC National Synthesis team of the U.S. Geological Survey (USGS) NAWQA Program. A major component of the NAWQA Program, the National Synthesis Investigations use NAWQA and other water-quality data to examine and describe the sources, transport, distribution, and fate of specific contaminant groups on a national scale. This report provides a summary of current knowledge regarding the uses, nonpoint sources, formation, transport and fate of chloroform in the hydrologic system; its occurrence in ground water, surface water, and drinking water; and its effects on human-health and aquatic organisms. As such, it is intended to provide a current (2004) information resource for the managers of water systems where elevated chloroform concentrations may be a source of concern. This summary includes data collected by the NAWQA program from 1991 to 2002. Because the focus of the discussion is on ambient ground and surface waters, rather than on specific contamination incidents, data on the occurrence of chloroform in water affected by known point sources are not included. The report also focuses primarily on chloroform—rather than on all four of the THMs produced in the highest concentrations during chlorination—both because chloroform is the most frequently detected THM, and because far less information is currently available on the sources, transport, fate, and biological effects of the other three compounds.

Production and Use of Chloroform

The major industrial use of chloroform is for the production of hydrochlorofluorocarbon-22 or HCFC-22 (known more formally as chlorodifluoromethane ($CHClF_2$)). A refrigerant in home air conditioners and large commercial freezers, HCFC-22 also has been proposed as a potential replacement for chlorofluorocarbons (CFCs), which are known to deplete stratospheric ozone. In 1987, concerns over the potential damage to the Earth's ozone layer caused by CFCs led to the "Montreal Protocol on Substances that Deplete the Ozone Layer," which called for restrictions on the production of CFCs (Alternative Fluorocarbon Environmental Acceptability Study, 2002). While CFCs are fully halogenated compounds, in HCFCs, one or more of the halogens are replaced by hydrogen atoms, resulting in a reduced potential to react with ozone. HCFC-22 was therefore proposed as a substitute for the highly ozone-depleting CFC-12 (dichlorodifluoromethane (CCl_2F_2)) (Mannsville Chemical Products Corporation, 1999).

To accommodate the higher demand for HCFC-22 resulting from its use as a substitute for CFC-12, an estimated 98 percent of the total chloroform production in the United States has been used in the manufacture of HCFC-22 since 1990 (Mannsville Chemical Products Corporation, 1999). HCFC-22 itself, however, is expected to be phased out of production in the United States by the year 2020 (U.S. Environmental Protection Agency, 2002b). The remaining 2 percent of chloroform manufactured in the United States since 1990 has been used for a variety of commercial purposes, including its use as a reagent and extraction solvent for fats, oils, grease, resins, lacquers, rubber, alkaloids, gums, and waxes (Budavari,

1989; Mannsville Chemical Products Corporation, 1999). Chloroform also has been used as a fumigant, as an insecticide, as a fire extinguishing agent, as a precursor for dyes and pesticides, and for the manufacture and processing of pharmaceuticals (Lucius and others, 1992; Agency for Toxic Substances and Disease Registry, 1997).

Figure 1 displays the history of the industrial production of chloroform in the United States from 1970 to 1999. Although the importation of chloroform peaked at 33 million pounds in 1985, no chloroform was imported to the United States from 1996 to 1998. Exports, however, increased from 48 to 240 million pounds per year between 1990 and 1997 (Mannsville Chemical Products Corporation, 1999).

Sources of Chloroform

Chloroform may enter the hydrologic system from direct releases, intentional or inadvertent inputs of chlorinated water, dehalogenation of tetrachloromethane, and a variety of natural sources. All of these sources are examined in greater detail below, with a discussion of anthropogenic fluxes of the compound in relation to global emissions.

Direct Releases

The USEPA's TRI documents industrial releases of a broad range of anthropogenic compounds to the environment on a nationwide basis. In the United States, these releases are reported annually and include air emissions (fig. 2), discharges to surface water (fig. 3), underground injections, and releases to land (fig. 4). According to the TRI, a total of approximately 1.6 million pounds of chloroform was released by these routes across the Nation in 2001 (U.S. Environmental Protection Agency, 2003a). The TRI, however, excludes data on direct releases of chloroform to the atmosphere from hazardous waste-disposal sites and sanitary landfills, as well as from municipal and hazardous waste incinerators that either burn waste containing chloroform or produce chloroform during combustion (Travis and others, 1986; Green and Wagner, 1993).
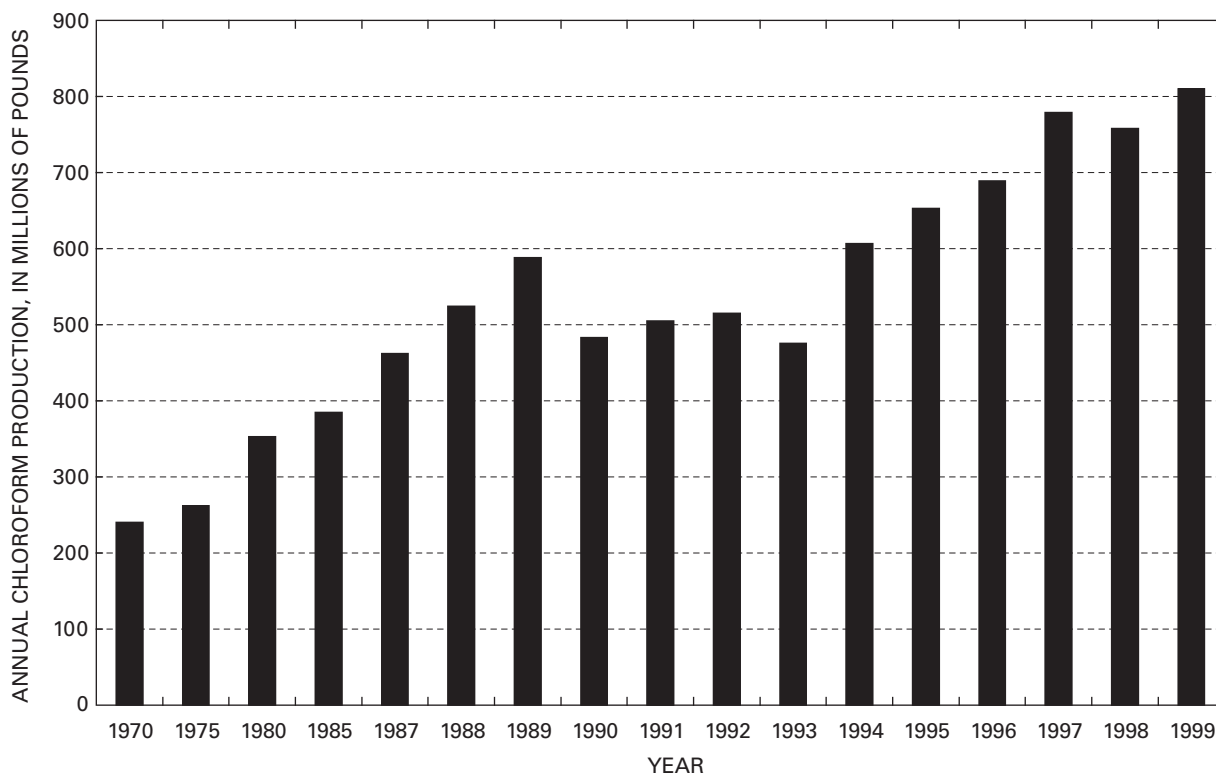
Figure 1.   Industrial production of chloroform in the United States from 1970 through 1999. (Data for years 1970, 1975, 1980, 1985, 1990, and 1994-98 were obtained from Mannsville Chemical Products Corporation (2002); those for 1987-89 and 1991-93 were obtained from the Chemical Manufacturers Association (1998).)

Emissions of anthropogenic chloroform to the atmosphere, as reported by the TRI (fig. 2), have decreased steadily since 1989, perhaps as a consequence of improved air pollution control measures. In 2001, air emissions represented about 89 percent of the total releases of chloroform to the hydrologic system from reporting industries. The largest air emissions of chloroform that year were from the paper (56 percent), chemical (18.8 percent), and food (5.1 percent) industries.

Unintentional releases of chloroform to the atmosphere may occur during the manufacture of HCFC-22, fluoropolymers, pharmaceuticals, dyes, or fumigants (Hazardous Substances Databank, 1996). Other unintentional chloroform releases to the atmosphere result from its formation in, and subsequent volatilization from, chlorinated water. Chloroform stripping efficiencies from water to air, based on computer simulations, were estimated by Moya and others (1999) to be as high as 55 percent and by Corsi and others (1992) to be as high as 65 percent. These predictions indicate that airborne chloroform concentrations could be significant in a confined space, such as a shower stall. Other local sources of airborne chloroform from chlorinated waters include washing machines, dishwashers, and sinks, where heat and aeration can be expected to increase volatilization rates (Shah and Singh, 1988; Corsi and others, 1992; Howard and Corsi, 1996; Agency for Toxic Substances and Disease Registry, 1997; Howard and Corsi, 1998; Howard-Reed and others, 1999; Levesque and others, 2002).

Discharges and releases of chloroform to surface water and land, as reported by the TRI, decreased from 1988 to 2001 (figs. 3 and 4, respectively). Releases to land, as defined by the USEPA, include disposal or burial of chemicals in landfills, application farming (in which the chemical is incorporated into the soil, a practice also known as land treatment), spills, leaks, and leaching from surface impoundments and waste piles (U.S. Environmental Protection Agency, 1999). In 2001, the paper industry contributed about 34 percent of the anthropogenic chloroform releases to surface water and 92 percent of the releases to land. Releases of chloroform through industrial practices to surface water and land, however, represent approximately 1.2 and 0.5 percent, respectively, of the total releases of anthropogenic chloroform to the environment; as noted earlier, most of the chloroform released to the hydrologic system by human activities is through air emissions. According to the RCRA solvent recovery program (Standard Industrial Classification Code 4953—Refuse Systems), which is responsible for 75 percent of the chloroform injected into the subsurface (that is, the vadose and/or saturated zones), underground injections

Figure 2.   Industrial emissions of chloroform to the air in the United States from 1988 through 2001. (Data from U.S. Environmental Protection Agency, 2003a).

of chloroform increased from 25,000 to 227,000 pounds between 1997 and 2000 (fig. 4) and decreased to 147,000 pounds in 2001 (U.S. Environmental Protection Agency, 2003a).

Formation of Chloroform and Other Trihalomethanes as Disinfection By-Products

In 1902, Belgium was the first country to implement the continuous use of chlorine to disinfect drinking water (Drinking Water and Wastewater, 2002). Chlorination of public water supplies in the United States first began in 1908, when the community of Jersey City, New Jersey, began adding hypochlorite to water drawn from the Boonton Reservoir. This led to a celebrated court case in which the right of the city to chlorinate the water supply was upheld in the best interest of public health (Sawyer and McCarty, 1978). As a result, the practice of chlorinating public water supplies soon became a nearly routine method of water treatment in the United States. The disinfection of drinking water in the United States by chlorination, which includes the use of chlorine gas, sodium hypochlorite, calcium hypochlorite, and/or chloramines (collectively referred to as reactive chlorine), is now a common practice (table 1).

Table 1.   Percentage of large and small drinking-water systems using chlorine and non-chlorine disinfection methods, in 1998.

[Source: Chlorine Chemistry Council, 2002; <, less than; --, not used]

Disinfection method	Proportion of systems employing method, in percent	
	Large systems (serving more than 10,000 people)[a]	Small systems (serving 10,000 or fewer people)
Chlorine gas	84	61
Sodium hypochlorite	20	34
Calcium hypochlorite	<1	5
Chloramines	29	--
Ozone	6	--
Ultraviolet	--	--
Chlorine dioxide	8	--

[a]Column does not sum to 100 percent because many larger systems employ more than one disinfection method, whereas some employ no disinfection at all.
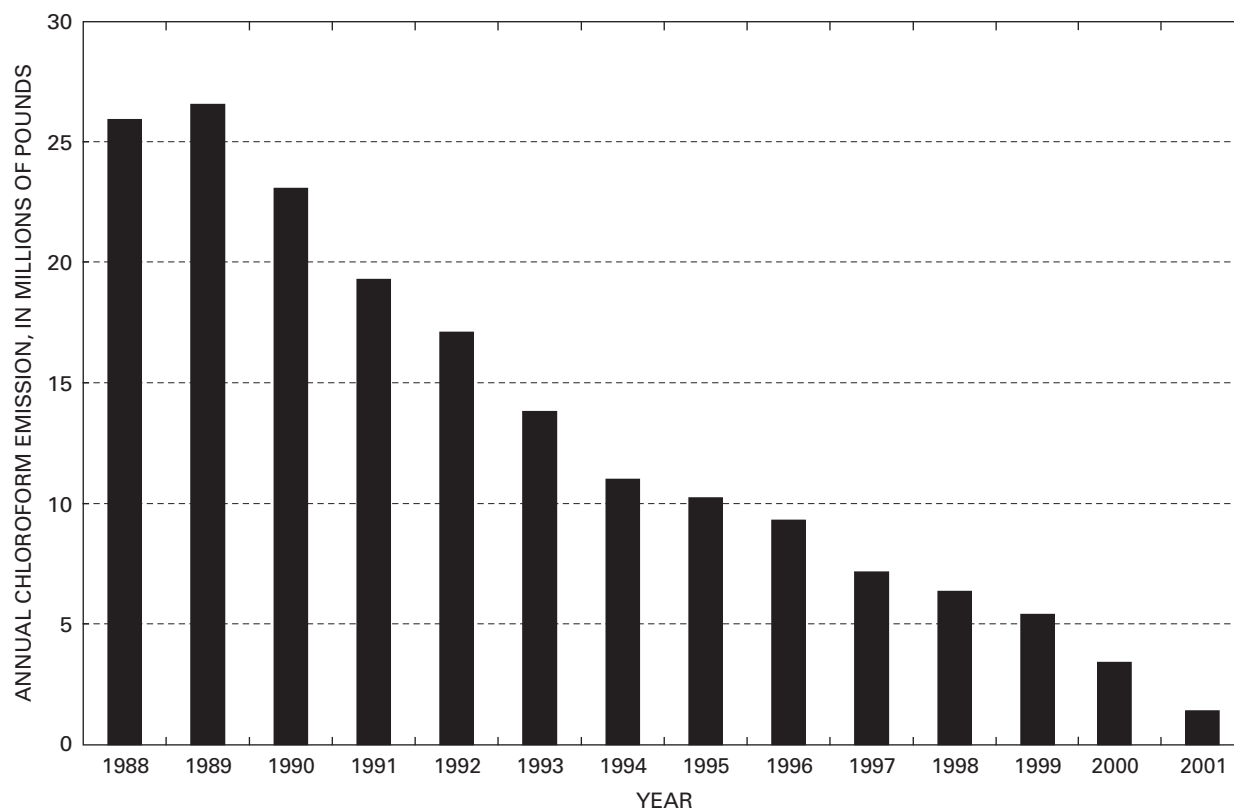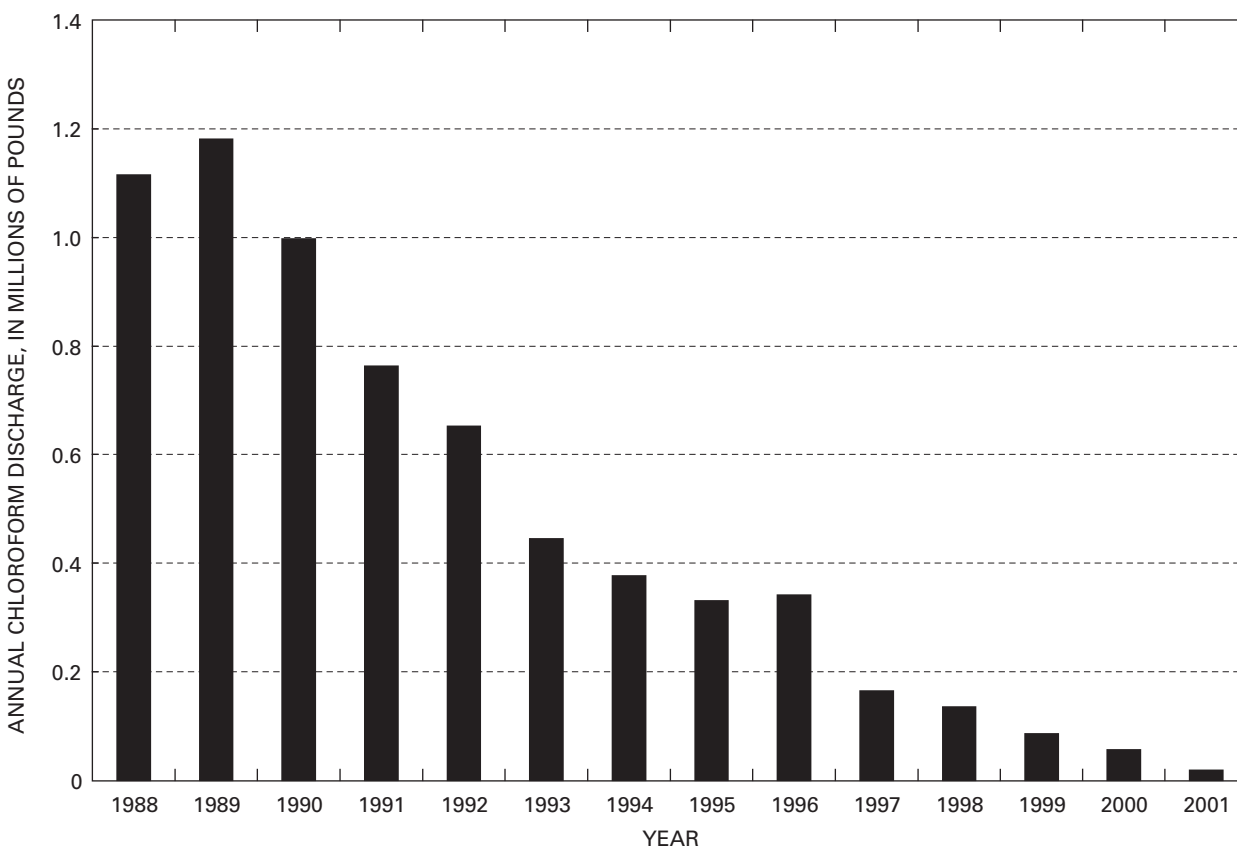

Figure 3.   Industrial discharges of chloroform to surface water in the United States from 1988 through 2001. (Data from U.S. Environmental Protection Agency, 2003a.)
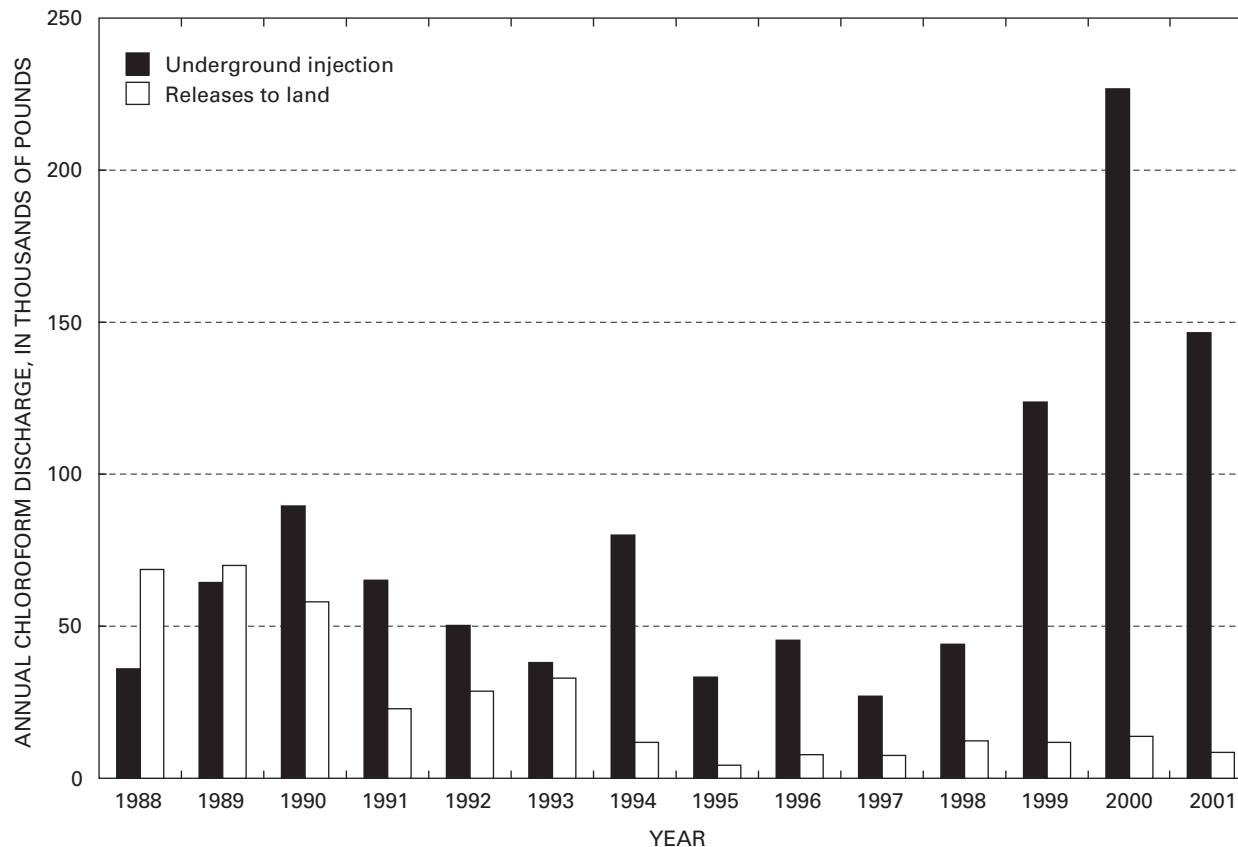
Figure 4. Industrial discharges of chloroform by underground injection and releases to land in the United States from 1988 through 2001. (Data from U.S. Environmental Protection Agency, 2003a.)

One of the principal advantages of chlorination over other disinfection methods is that, in addition to the destruction of microorganisms that takes place on initial contact (as discussed below), the maintenance of a minimum concentration of reactive chlorine in the treated water (commonly referred to as a chlorine residual) provides ongoing disinfection within the distribution system (Weber, 1972). Some systems use ozone, ultraviolet light, or potassium permanganate rather than chlorination for initial disinfection, but none of these other methods provide residual protection within the distribution system. Because of the use of these other initial methods of drinking water disinfection, the USEPA now requires (through the Stage 1 Disinfectants and Disinfection By-Products Rule) that each community water system maintain an adequate chlorine residual to control microorganisms in the distribution system, regardless of the initial disinfection method used (U.S. Environmental Protection Agency, 2002c).

The initial step in the chlorination of water or wastewater commonly involves the dissolution of chlorine gas (Cl_2) in the medium of interest. When dissolved in water, the Cl_2 molecule—in which both atoms possess an oxidation state of

zero—readily undergoes a disproportionation reaction, in which one of the chlorine atoms is reduced to chloride (Cl^-), and the other is oxidized to Cl^+, a highly reactive species that rapidly displaces a proton from water to form hypochlorous acid (HOCl). The overall result is the hydrolysis of the Cl_2 molecule according to the following equilibrium:

$$Cl_2 + 2H_2O \leftrightarrow H_3O^+ + Cl^- + HOCl \qquad (1)$$
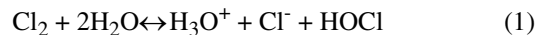
Hypochlorous acid dissociates at alkaline pH to form hypochlorite ion (OCl^-) according to the following equilibrium:

$$HOCl + H_2O \leftrightarrow H_3O^+ + OCl^- \qquad (2)$$
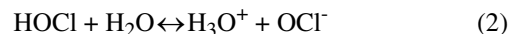
At 20°C, the pK_a (dissociation constant) value for equilibrium (eq. 2) is 7.6, indicating that the concentration of OCl^- will be higher than that of HOCl at pH values greater than 7.6, while the opposite will occur at pH values less than 7.6. Disinfection occurs primarily through the oxidation of biological tissues by HOCl and OCl^-, as well as by other reactants containing chlorine (or other halogens) with an oxidation state higher than that

of Cl⁻. The term "free available chlorine" (or, for the purposes of this report, simply free chlorine) refers collectively to the reactants HOCl, OCl⁻, and Cl_2. While the term "combined available chlorine" refers to reactive chlorine species such as chloramines that include elements other than oxygen or hydrogen. Because HOCl is a much stronger disinfectant than OCl⁻, the effectiveness of disinfection by chlorinated water increases with decreasing pH (Weber, 1972). The bromide ion, if present, is rapidly oxidized by the free chlorine to form a variety of reactive bromine species such as HOBr, OBr⁻, Br_2 and BrCl (Trussell and Umphres, 1978). The oxidation of bromide by HOCl, for example, can produce hypobromous acid (HOBr) which, like HOCl, is a powerful disinfectant (Boyce and Hornig, 1983):

$$HOCl + Br^- \rightarrow HOBr + Cl^- \qquad (3)$$
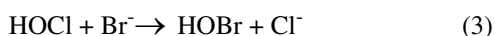
The presence of THMs and other halogenated compounds in water disinfected through chlorination was first reported in the mid 1970s by Rook (1974) who, in a subsequent publication (Rook, 1975), attributed this association to the reaction of free chlorine with dissolved organic matter (DOM). (DOM is commonly defined as the fraction of natural organic matter (NOM) that passes through a 0.45-micron filter (Thurman, 1985).) The reactions of free chlorine with DOM and other precursor compounds in chlorinated waters generate chloroform and a variety of "disinfection by-products" or DBPs (Weinberg and others, 2002), as a result of the haloform reaction. If bromide is present, products from the haloform reaction usually include brominated compounds, including one or more of the three brominated THMs. Similarly, iodinated THMs form if iodide is present.

Because ammonia, ferrous iron, and sulfide are all reduced species, if any of them are present, they will provide an additional inorganic demand for the chlorine immediately following chlorination, competing with the DOM for reaction with the free chlorine. As a result, in the presence of sufficiently high concentrations of one or more of these reduced species, only traces of THMs will form during the initial stages of the reaction. Once most of the inorganic demand is satisfied, reaction of the remaining free chlorine with DOM produces higher yields of THMs (Trussell and Umphres, 1978).

A variety of mechanisms have been proposed for the haloform reaction. For aromatic substrates (including humic and fulvic acids that contain an aromatic ring), this reaction (shown in fig. 5, using a generic 1,3-hydroxyaromatic compound as model substrate) is presumed to take place through an initial, rapid halogenation by HOCl (although, as noted above, in the presence of dissolved bromide or iodide, the attacking species also might be HOBr or HOI) of one or more aromatic carbon atoms activated by ortho hydroxyl (-OH) or (at pH values above the pK_a of the phenol), phenoxy (-O⁻) substituents (reaction 1 in fig. 5). The initial halogenation is then presumed to be followed by the hydrolytic cleavage of the ring at a site adjacent to a halogenated carbon (reaction 2); further halogenation of the aliphatic products of ring scission (reaction 3); and release of the THM following alkaline hydrolysis (reaction 4)

(Rook, 1977; Boyce and Hornig, 1983). The reactions shown in figure 5 also include separate pathways that account for the frequent detection of dichloromethane (methylene chloride) (reaction 5) and polyhaloacetic acids (reactions 6 and 7) in chlorinated water.

An extensive amount of research has helped to elucidate the factors that affect the production rates and yields of chloroform and other DBPs during chlorination. Of principal importance among these factors are the structure and concentrations of the DOM and other precursor compounds that may be present, the concentration (or dose) of free chlorine, pH, bromide ion concentration, and temperature.

Several studies have shown that the rate of DBP formation is directly related to DOM concentration and to chlorine dose. Alawi and others (1994) observed the rate of chloroform appearance to be linearly related to the concentrations of both free chlorine and DOM. Trussell and Umphres (1978) reported similar results, but observed this relation only after the inorganic demand was satisfied. Fujii and others (1998) observed a linear correlation between the dissolved organic carbon (DOC) concentrations in agricultural drainage waters from the Sacramento-San Joaquin Delta, California, and the THM formation potential (that is, the total yield of THMs over a fixed reaction time under standardized conditions) in samples of these waters. The reaction of chlorine with DOM, however, is relatively slow. Under conditions typical of water treatment, significant rates of formation of chloroform and other THMs may still be observed after 24 hours (Babcock and Singer, 1979).

Many different characteristics of NOM have been examined as potential predictors of the yields of THMs and other DBPs during chlorination. The precursors that have been found to produce DBPs in highest yields include several aliphatic ketones, such as 2-butanone (methyl ethyl ketone) and acetone (Reckhow and others, 1990). In most cases, however, DBP precursors possess aromatic structures, usually with a variety of different functional groups, including hydroxyl, aldehyde, ketone, carboxyl, and methoxyl moieties. Evidence that most of these precursors possess some aromatic character is provided by the observation that the DBP formation potential of NOM has been found to be correlated with its specific ultraviolet absorbance (SUVA), a property that provides an indirect measure of aromatic content. The SUVA is defined as the absorbance of ultraviolet light at 254 nanometers by the material of interest, in aqueous solution, normalized by the concentration of DOC (Fujii and others, 1998; Liang and Singer, 2003).

DOM is often classified operationally into two types of compounds—humic and fulvic acids—based on their solubility at low pH. Humic acids precipitate from aqueous solutions at pH values less than 1, whereas fulvic acids do not (Thurman, 1985). Although the relative proportions of the two fractions vary considerably among different source materials, climates, ecosystems, and locations, fulvic acids generally constitute approximately 90 percent of DOM by weight, whereas humic acids constitute about 2 to 3 percent (Babcock and Singer, 1979).
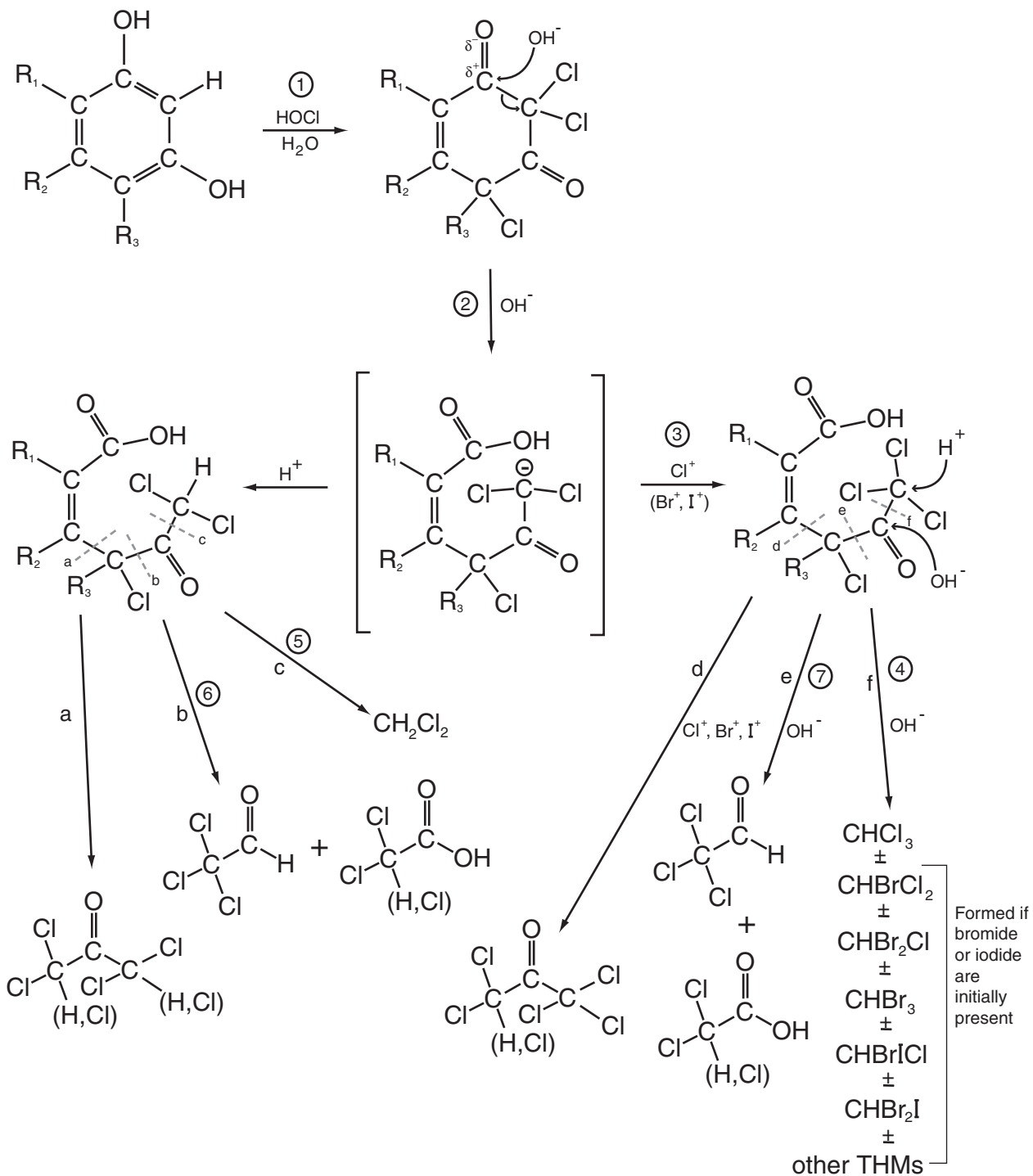
Figure 5. Hypothesized mechanisms by which a generic 1,3-hydroxyaromatic compound (a model for a humic or fulvic acid molecule containing an aromatic ring) is transformed during chlorination. (Cl^+, Br^+, and I^+ represent any halogenating electrophiles of the form XOH_2^+, X_2, HOX, X_2O, etc., where X = Cl, Br or I.) Numbers in circles refer to reaction steps listed in text. Bonds broken during reactions a-f are indicated by dashed lines, and resulting compounds are labeled a-f, respectively. Curved arrows denote movement of electron pairs. Adapted and redrawn from Rook (1977).

Both humic and fulvic acids may react during chlorination to form chloroform and other THMs (Trussell and Umphres, 1978; Reckhow and others, 1990; Adin and others, 1991; Alawi and others, 1994). Although humic acids usually constitute a small percentage of the total DOM, Babcock and Singer (1979) observed them to react with free chlorine more readily than fulvic acids, producing more than three times as much chloroform per gram of DOC as that produced by fulvic acids, and consuming 75 percent of the free chlorine under the conditions examined. Given the fact that humic acids generally are more hydrophobic than fulvic acids (Thurman, 1985), the results reported by Babcock and Singer (1979) were corroborated during a more recent study by Liang and Singer (2003), who observed that the hydrophobic fractions of DOC taken from a variety of different sources usually generated higher THM yields than did the hydrophilic fractions (at both pH 6 and 8).

The rates of production of chloroform and other THMs during the haloform reaction have a complex dependence on pH that may vary among different precursor compounds. For a series of chlorination experiments conducted between pH 2 and 12, Boyce and Hornig (1983) observed that a variety of 1,3-dihydroxyaromatic precursors had similar patterns of chloroform yield as a function of pH—provided the aromatic carbon atom between the two hydroxyl groups was either unsubstituted or possessed a carboxyl group—with maximum yields occurring between pH 8 and 10 (fig. 6). The authors suggested that the lower rate of chloroform production at pH values greater than 10 is most likely a result of the diminished rate at which OCl^- engages in the haloform reaction, relative to $HOCl$ (eqs. 1 and 2). Results from more recent experiments involving the chlorination of water from a Florida reservoir also showed higher rates of THM formation at pH 8 than at pH 6 (Liang and Singer, 2003), consistent with the pattern observed for 1,3-dihydroxybenzene within this pH range (fig. 6).

The substantial rates at which the 1,3-dihydroxyaromatic compounds undergo the haloform reaction appear to result from the presence of an unsubstituted carbon atom at the ortho position shared by the two hydroxyl-bound carbons in these
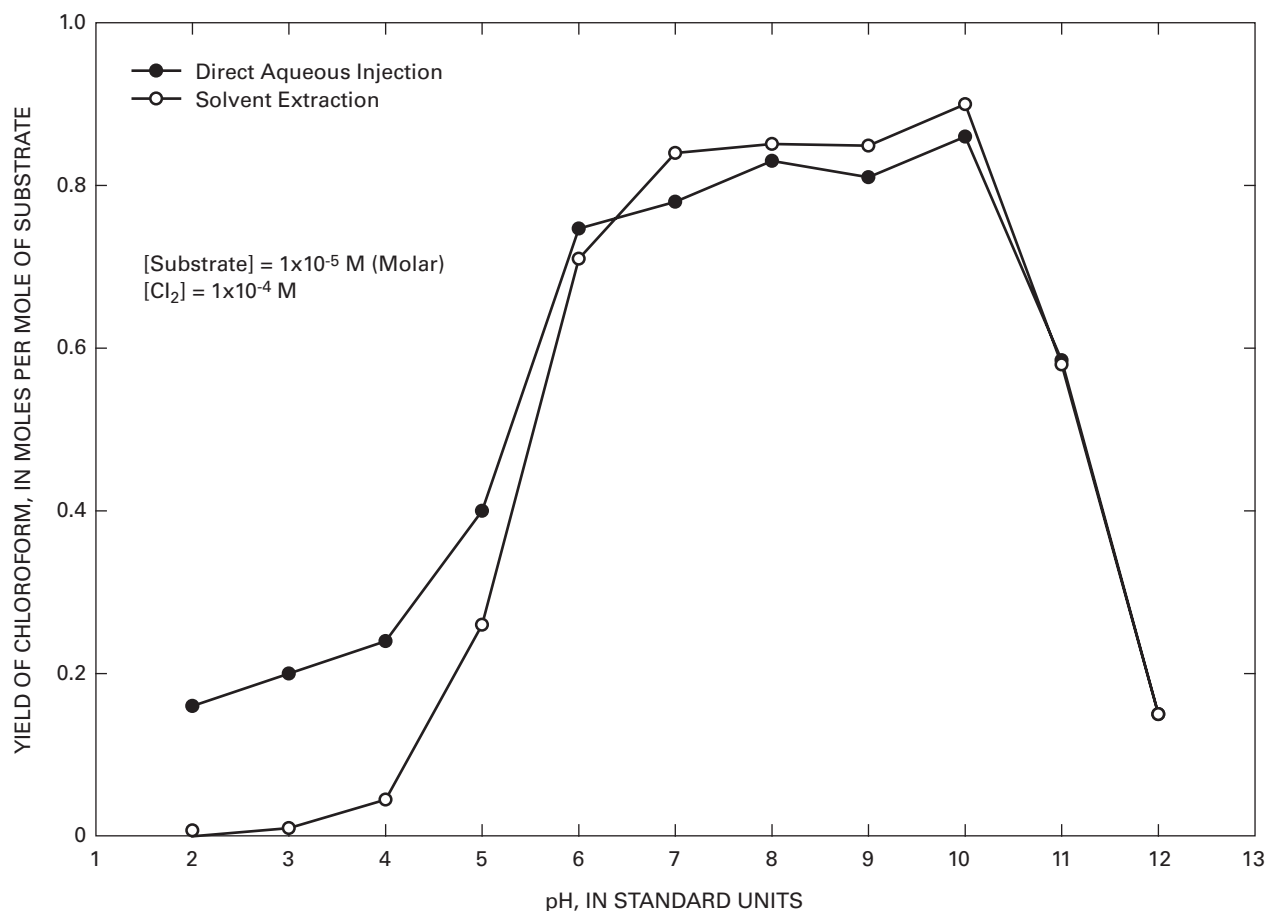
Figure 6. Effect of pH on the yield of chloroform from the chlorination of the substrate 1,3-dihydroxybenzene (resorcinol), based on measurements of chloroform concentrations using either direct aqueous injection or solvent extraction. (Modified from Boyce and Hornig, 1983.)

molecules (Boyce and Hornig, 1983), since hydroxyl groups, like alkoxy groups, are known to be ortho and para directing with respect to electrophilic aromatic substitution (Rook, 1977). (According to Boyce and Hornig (1983), the elevated reactivity of 2,6-dihydroxybenzoic acid appears to be facilitated by the decarboxylation of the molecule. While the authors do not state this explicitly, structural constraints appear to require that the halogenation of the molecule be preceded, rather than followed by, the decarboxylation step.) Other studies also have reported high yields of chloroform (greater than 85 percent) from the chlorination of 1,3-dihydroxybenzenes at pH 7, 10, and 11 (Rook, 1977; Johnson and Jensen, 1986). In contrast, 1,2- and 1,4-dihydroxybenzenes produce chloroform yields greater than 10 percent at pH 10, but not at pH 7 (Stevens and others, 1976; Boyce and Hornig, 1983).

As noted previously, when bromide ion is present during chlorination, the haloform reaction commonly produces one or more of the brominated THMs, in addition to chloroform (for example, Boyce and Hornig, 1983). This occurs even if bromide concentrations are several orders of magnitude lower than chlorine concentrations on a molar basis (Luong and others, 1982). Formation of brominated THMs occurs under such conditions because (1) free chlorine oxidizes bromide to free bromine (reaction 3) much more rapidly than it reacts with DOM (Luong and others, 1982), and (2) free bromine is a more powerful halogenating agent than free chlorine (Rook, 1974).

At low molar ratios of bromide ion to free chlorine (that is, 0.03 or less), the yields of the four principal THMs, generated during chlorination, decrease with increasing bromination of the product, that is, in the following order: $CHCl_3 > CHBrCl_2 \geq CHBr_2Cl \geq CHBr_3$ (Luong and others, 1982; Summers and others, 1993). This trend also was evident among the concentrations of the THMs formed during the study by Fujii and others (1998) of the THM formation potential of agricultural drainage waters from the Sacramento-San Joaquin Delta, California. Results from studies where more than one THM has been detected in the hydrologic system commonly indicate the same trend among the detection frequencies for these compounds (Rook, 1974; Westrick and others, 1984; Voelker, 1989; Kolpin and Thurman, 1995; Stackelberg and others, 1997; Reiser and O'Brien, 1998; Lundgren and Lopes, 1999; Squillace, Moran, and others, 1999; Inkpen and others, 2000; Thiros, 2000; Grady and Casey, 2001; Moran and others, 2002). Such observations indicate that the presence of brominated THMs might be used as a valuable criterion for distinguishing chlorinated waters from other potential sources of chloroform in the hydrologic system—especially if the concentrations among the four principal THMs (or detection frequencies, if based on the same detection limit for all four compounds) have the trend noted above.

In water chlorinated in the presence of sufficiently high concentrations of bromide, bromoform may be the predominant THM formed. The bromide concentration threshold above which this occurs has been found to range between 0.1 and 2 mg/L (milligrams per liter) and depends upon several factors, including DOM concentration and chlorine dose. For a given chlorine dose, the presence of bromide has been found to

increase both the total yield of THMs and the rate of THM formation (Trussell and Umphres, 1978; Luong and others, 1982).

As is the case for other thermal (that is, non-photochemical) reactions, rates of THM formation increase with temperature according to the Arrhenius relation (see Moore and Pearson (1981) for a description of this equation). Estimated activation energies, however, show considerable variation among studies. While Urano and others (1983) reported an activation energy of 37 kJ (kilojoules) per mole for the haloform reaction, the value estimated by Kavanaugh and others (1980) was 9.6 kJ per mole.

The effect of temperature on the rate of the haloform reaction is probably responsible for the common observation of higher chloroform concentrations in chlorinated water during the summer, relative to winter. Stevens and others (1976), for example, suggested that seasonal variations in water temperature could account for the differences observed in the concentrations of chloroform in finished Cincinnati tap water between winter (30 μg/L or less) and summer (as much as 200 μg/L). Similarly, in a year-long comparison of raw and treated water from three drinking-water treatment plants in Canada, LeBel and others (1997) reported lower chloroform concentrations during the period from December to April (raw water temperatures less than 5°C) than during the period from June to September (raw water temperatures between 15 and 23°C). For all three treatment plants, mean chloroform concentrations were significantly higher ($p \leq 0.02$) in the summer than in the winter. (A significance level [alpha] of 0.05 will be used for all statistical tests described in this report.) These observations also indicate that as temperatures increase, the effects of higher haloform reaction rates on THM concentrations are generally large enough to overwhelm the effect of the enhanced volatilization of these compounds that also is likely to occur as a result of the increase in their Henry's Law constants (Nicholson and others, 1984).

Chlorinated Water as a Source of THMs in the Hydrologic System

A major source of anthropogenic chloroform detected in ground and surface water appears to be chlorinated drinking water and wastewater that is discharged intentionally into the hydrologic system. This includes wastewater from the bleaching processes in pulp and paper mills, wastewater generated from the manufacturing and processing of chloroform-containing chemicals and materials, effluent from hazardous waste-disposal sites, and rinse water from domestic and industrial cleaning and laundry operations. Other such sources include regulated discharges of chlorinated water from wastewater treatment plants, cooling tower blowdown from electric power generating plants, and combined sewer overflows (California Department of Health, 1990; Agency for Toxic Substances and Disease Registry, 1997). These intentional discharges, however, are expected to represent only minor contributions to the total chloroform releases of anthropogenic chloroform to the

hydrologic system, relative to the amount of the compound contributed by inadvertent releases of chlorinated drinking water and wastewater (Agency for Toxic Substances and Disease Registry, 1997). Chlorinated drinking water from public water-supply systems may enter ground and surface water through the irrigation of lawns, gardens, golf courses, athletic fields, and parks, as well as leaking swimming pools, spas, or distribution lines for treated wastewater. In addition, because the maintenance of a chlorine residual is now required in community water supplies and distribution systems, this measure increases the likelihood that leakage from these systems also will discharge chloroform and other DBPs to ground and surface water. Solley and others (1998) have estimated that the loss of treated drinking water through leaking distribution pipes and other unknown routes may be as high as 15 percent in some systems. Overall, McCulloch (2003) reported that an estimated 2 gigagrams (Gg, where 1 Gg = 1×10^9 g), or 4.41 million pounds of chloroform are generated per year through the chlorination of drinking water in the United States.

Chloroform has been detected in rainwater (Kawamura and Kaplan, 1983; Adachi and Kobayashi, 1994). Precipitation therefore represents a potential source of the compound to the hydrologic system. However, in studies of chloroform contamination of the shallow ground water in Indianapolis, Indiana (Fenelon and Moore, 1996), and Glassboro, New Jersey (Baehr and others, 1999), the maximum concentrations of chloroform estimated (through equilibrium partitioning calculations) to be present in rainwater at the two locations (0.1 and 0.0025 µg/L, respectively) were lower than those measured in the ground water at those locations. This indicates that precipitation was unlikely to have been the sole source of the compound detected at either study site. Fenelon and Moore (1996) suggested that the chloroform detected in ground water during their study may have been derived from chlorinated water from irrigation of turfgrass, septic systems or industrial settling ponds, or leakage of treated water and wastewater from distribution lines.

Baehr and others (1999) hypothesized that the chloroform detected in ground water at the study site in Glassboro, New Jersey, was likely to have emanated from a nearby point source. However, the fact that $CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ were all detected in ground water within the study area—and in the order of decreasing detection frequency above (Stackelberg and others, 1997; Baehr and others, 1999)—indicates that the ultimate source of the chloroform detected during this investigation may have been chlorinated water, regardless of its spatial configuration (that is, point or nonpoint).

Concentrated hydrochloric acid (HCl) is commonly added as a preservative to inhibit biological activity (by lowering the pH) in water samples collected for VOC analysis. Because concentrated HCl may contain trace levels of free chlorine, it is possible that residual free chlorine in the HCl may react with DOM to produce chloroform in such samples. An investigation by Squillace, Pankow, and others (1999), however, indicated that the preservation of ground-water samples by the addition of HCl did not form significant concentrations of THMs when samples were stored at 4°C and analyzed within 14 days.

Formation of Chloroform from the Dehalogenation of Tetrachloromethane

Tetrachloromethane (CCl_4, also known as carbon tetrachloride) has been widely used for several decades as an industrial solvent, degreaser, and grain fumigant. This compound also is one of the most common contaminants present in the chlorine gas used for chlorination (Christman, 1980), perhaps because it is frequently used to rinse out the cylinders in which chlorine gas is supplied (Krasner and others, 2001). Several studies have demonstrated that chloroform may be produced from the transformation of tetrachloromethane by microorganisms under iron- or sulfate-reducing conditions (Criddle and others, 1990; Assaf-Anid and others, 1994; Curtis and Reinhard, 1994; Matheson and Tratnyek, 1994). The replacement of a chlorine atom with hydrogen in this manner is an example of a type of reaction known as hydrogenolysis (fig. 7), and occurs in this example by way of a trichloromethyl radical intermediate (•CCl_3). Although this transformation, which is an example of a broader class of reactions known as reductive dechlorination, has been shown to occur abiotically in the laboratory (Klečka and Gonsior, 1984), it is unlikely to occur to any appreciable extent in the hydrologic system without either direct or indirect microbial assistance.

Natural Sources

Chloroform and other chlorinated compounds are often considered to be of solely anthropogenic origin. However, many studies have indicated that some of these compounds, including chloroform, also may be produced by natural processes (fig. 7). For chloroform, marine and terrestrial sources appear to contribute in roughly equal amounts to natural global production (Laturnus and others, 2002). A source that is common to both marine and terrestrial settings is volcanic gas, especially that derived from solfataric volcanoes, which produce high concentrations of sulfur compounds (Isidorov and others, 1990).

Khalil and others (1983) indicated that the tropical oceans may be a major source of chloroform, with an estimated production rate of approximately 350 Gg of chloroform per year. Marine micro and macroalgae have been found to be a significant source of chloroform in the oceans, contributing about 7 percent of the total annual emission of the compound from marine sources (Laturnus and others, 2002). Gribble (1994) has suggested that marine algae produce chloroform as a defense against predation. Other possible, but undocumented marine sources include other organisms, cold vents, marine volcanoes, and other geologic phenomena associated with tectonic activity (Laturnus and others, 2002).

Figure 7.   Reactions that may either produce chloroform or transform it into other compounds in the hydrologic system.
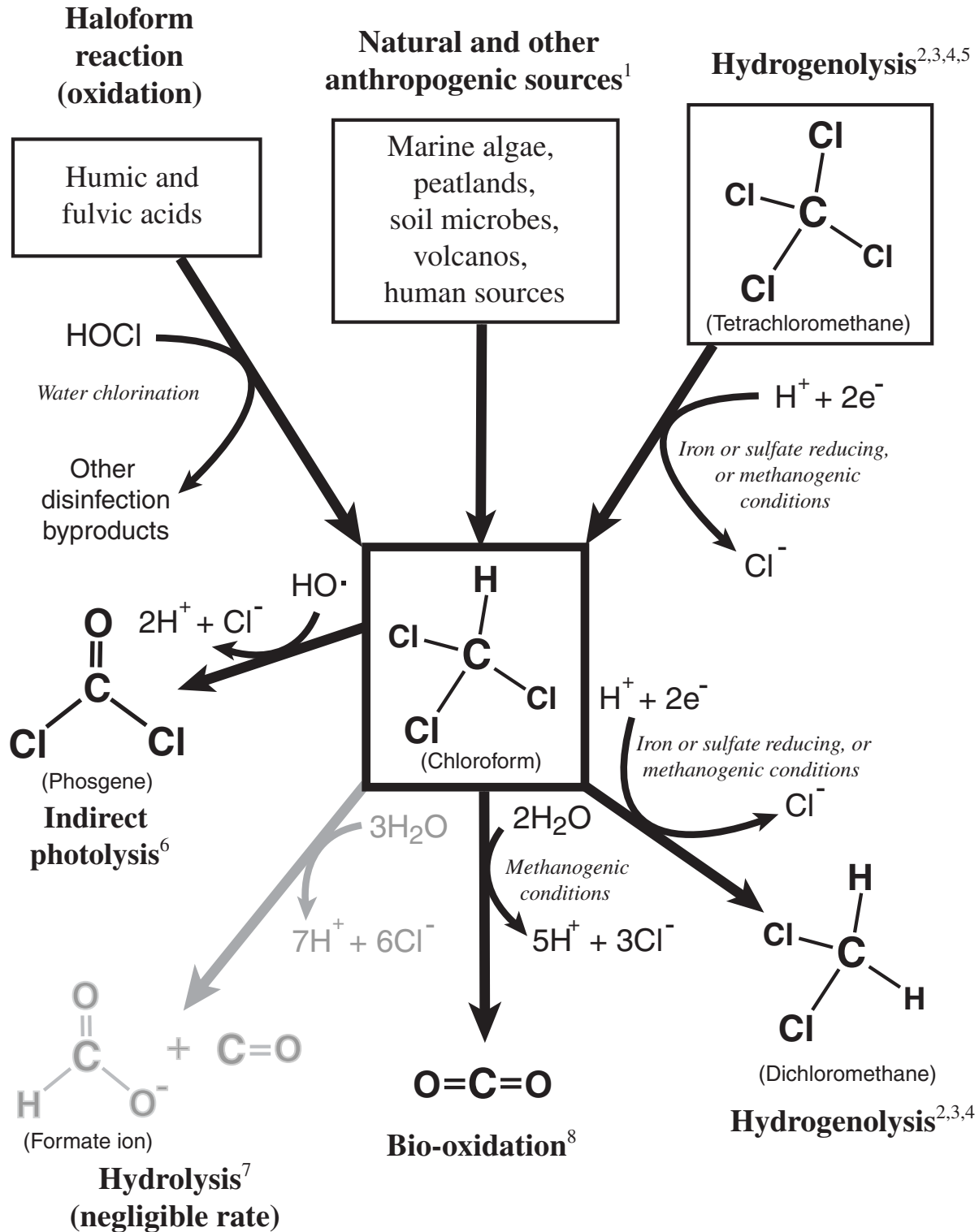
[[1]McCulloch, 2003; [2]Klečka and Gonsior, 1984; [3]Egli and others, 1988; [4] Gälli and McCarty, 1989; [5]Picardal and others, 1995; [6]Howard, 1991; [7]Fells and Moelwyn-Hughes, 1959; [8]Bouwer and McCarty, 1983]

While paper manufacturing and water treatment are the largest sources of anthropogenic chloroform (Laturnus and others, 2002), soils, termite mounds, and rice fields are estimated to be the largest natural terrestrial sources of the compound. In soils, the production of chloroform, and chlorinated soil acids such as trichloroacetic acid (CCl_3COOH) has been found to be a result of the chlorination of NOM by naturally produced HOCl—a transformation analogous to the haloform reaction discussed previously (fig. 5). In soils, HOCl is produced by the oxidation of chloride ion by hydrogen peroxide under acidic conditions. This reaction is catalyzed by the chloroperoxidase enzyme (CPO), which is commonly detected in soils, and most likely derived from soil fungi (McCulloch, 2003):

$$H_2O_2 + H_3O^+ + Cl^- \xrightarrow{CPO} HOCl + 2H_2O$$

$$NOM + HOCl \rightarrow \text{ chlorinated NOM} + CHCl_3$$

$$+ CCl_3COOH + \text{other chlorinated products} \qquad (4)$$
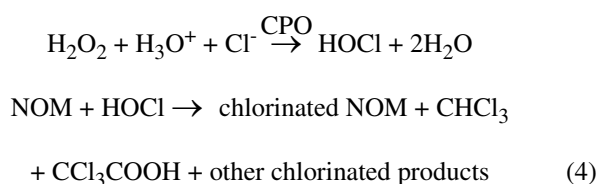
Rates of chloroform production by natural soils show considerable variability, depending upon soil characteristics. Consistent with the mechanism described above, higher rates are observed in soils containing larger amounts of NOM. The highest rates of chloroform production (1 microgram per square meter per hour ($\mu g/m^2/hr$)) have been measured in Douglas fir forest soils, in soils covered with decaying wood chips, and in soils with large amounts of humic material. In spruce forest soils, chloroform production rates have been estimated to be as high as 0.5 $\mu g/m^2/hr$ (Haselmann and others, 2000). Substantially lower rates have been observed in less organic rich soils, such as those encountered in dry swamps, grasslands, sandy areas, and pine forests (Hoekstra and others, 2001).

Anthropogenic Fluxes in Relation to Global Emissions

Laturnus and others (2002) reported that of the estimated 700 Gg of chloroform released annually across the planet, 9.5 percent is attributable to anthropogenic sources. Similarly, McCulloch (2003) reported a global chloroform emission rate of 660 Gg per year, with 10 percent derived from anthropogenic sources. Khalil and others (1983), however, estimated a global anthropogenic chloroform production rate of 250 Gg per year, considerably higher than the estimates provided by Laturnus and others (2002) and McCulloch (2003). The burning of biomass, of which about 90 percent is induced by humans (Laturnus and others, 2002), releases approximately 2 Gg of chloroform annually worldwide, representing less than 1 percent of total global production of the compound (Lobert and others, 1999). The chloroform emission rate from the Northern Hemisphere is considerably higher than that from the Southern Hemisphere (Laturnus and others, 2002; McCulloch,

2003), perhaps as a consequence of the higher levels of industrial activity and development in the north.

Physical and Chemical Properties Controlling the Transport and Fate of Chloroform

Based on its large Henry's Law constant compared to other VOCs (table 2), chloroform is expected to be present mostly in the vapor phase following its release to the atmosphere (Howard, 1993). However, because the compound also is relatively water soluble, some removal of atmospheric chloroform is expected to occur during rainfall events, as demonstrated by the fact (noted previously, p. 12) that it has been detected in precipitation (Kawamura and Kaplan, 1983; Adachi and Kobayashi, 1994). The relatively large Henry's Law constant for this compound also implies that much of the chloroform in surface waters is likely to volatilize soon after its release. As might be anticipated from fundamental principles of mass transfer (for example, Weber, 1972), the rate of chloroform volatilization from streams increases with increasing water velocity, as well as with decreasing stream depth. Also in accord with theory is the observation noted previously that chloroform volatilization rates, like the Henry's Law constant, increase with increasing temperature (O'Connor and Dobbins, 1958; Churchhill and others, 1962; Owens and others, 1964).

The relatively low organic carbon-water partition coefficients (K_{oc}) values for chloroform and the other THMs (table 2) indicate that these compounds have relatively low affinities for soil organic carbon. As discussed further below, chloroform also is quite persistent under oxic conditions (that is, in the presence of detectable concentrations of dissolved oxygen) in the hydrologic system. As a result, chloroform that is not volatilized in near-surface soils or taken up by plants following its release is expected to migrate substantial distances through the subsurface, particularly in aquifers containing materials with a low mass fraction of organic carbon, or f_{oc} (that is, $f_{oc} \leq 0.001$ (McCarty and others, 1981)).

Similarly, field experiments involving the injection of chloroform below the water table have demonstrated that the migration of the compound through the saturated zone is only moderately retarded by low-carbon aquifer materials. Roberts and others (1982) observed retardation factors varying between 2.5 and 3.8 for the migration of chloroform through a relatively carbon-poor aquifer (f_{oc} about 0.01) beneath Palo Alto, California. (A retardation factor (R) represents the ratio between the rate of migration of a conservative solute (that is, a non-sorbing, non-reactive species such as chloride under oxic conditions) through ground water and that of the compound of interest (Freeze and Cherry, 1979). The R values given above, for example, imply a rate of chloroform migration through the subsurface that is between 25 and 38 percent of the speed of a conservative solute.)

Table 2. Chemical and physical properties that influence the transport and fate of the four trihalomethanes discussed in this report.

[BCF, bioconcentration factor; CAS, Chemical Abstract Service; °C, degrees Celsius; g/cm^3, grams per cubic centimeter; g/mol, grams per mole; K_H, Henry's Law constant; K_{oc}, organic carbon-water partition coefficient; K_{ow}, octanol-water partition coefficient; mg/L, milligrams per liter; mL/g, milliliters per gram; mm Hg, millimeters of mercury; NL, not listed; Pa m^3/mol, Pascal meter cubed per mole]

Property	Chloroform	Bromodichloromethane	Dibromochloromethane	Bromoform
CAS number	67-66-3	75-27-4	124-48-1	75-25-2
Molecular weight	119.39[a]	163.83[a]	208.28[a]	252.73[b]
Density (g/cm^3 at 20°C)[c]	1.4799	1.980	2.451	2.890
Boiling temperature (°C)	61.7 (at 760 mm Hg)[a]	90 (at 760 mm Hg)[a]	119-120 (at 748 mm Hg)[a]	149.5 (at 15 mm Hg)[b]
Water solubility (mg/L)[d]	7,950[a]	4,700 at 22°C[a]	4,000[c]	3,100[b]
Vapor pressure (Pa)[d]	26,241[c]	6,665 at 20°C[c]	1,014[c]	719.9[b]
Henry's Law constant (H) (Pa m^3/mol)[c]	314.1	162.0	88.2	62.0
K_{ow}	93.3[a]	125.9[c]	173.8[a]	234.4[b]
K_{oc} (mL/g soil organic carbon)[c]	43.7	61.0	NL	117.5
BCF (mL/g tissue)[c]	2.88 - 691.8	5.25 - 34.7	NL	63.1

[a]From Howard (1991).

[b]From Howard (1993).

[c]From Mackay and others (1993).

[d]At 25° Celsius, unless otherwise noted.

The relatively low affinity of chloroform and other THMs for organic carbon also is responsible for the limited tendency of these compounds to build up in the tissues of living organisms, as indicated by their low bioconcentration factor (BCF) values (table 2). (The BCF represents the predicted ratio between the concentration of a given compound in the tissues of an organism and the concentration of that compound in the surrounding water (Nowell and others, 1999).)

Transformation of chloroform and the other THMs in the hydrologic system takes place primarily through photolysis or, under hypoxic conditions (that is, in the absence of detectable levels of dissolved oxygen), reductive dehalogenation. THMs also are subject to hydrolysis, but at rates that are effectively negligible under most environmental conditions.

Phototransformations in the hydrologic system occur through one of two principal mechanisms—direct photolysis, in which the compound undergoes transformation as a result of its absorption of solar energy of the appropriate wavelength and sufficient intensity, and indirect photolysis, in which the compound reacts with another chemical species that have been energized, either directly or indirectly, in this manner. Direct photolysis of chloroform is not considered a significant transformation process in the atmosphere because chloroform does not show significant light absorbance within the solar spectrum, that is, at wavelengths greater than 290 nanometers (Harris, 1990; Agency for Toxic Substances and Disease Registry, 1997). Thus, when chloroform undergoes phototransformation

in the atmosphere, it does so primarily through indirect, rather than direct photolysis (fig. 7).

One of the most significant mechanisms by which chloroform undergoes indirect photolysis is its reaction with hydroxyl radical (•OH), which occurs with a half-life of 26 to 260 days (Howard, 1991; Mackay and others, 1993). This reaction occurs through a trichloromethyl radical intermediate to form products that include phosgene ($Cl_2C=0$) and •OCl (Hanst, 1978):

$$CHCl_3 + \bullet OH \rightarrow H_2O + \bullet CCl_3$$

$$\bullet CCl_3 + O_2 \rightarrow Cl_2C=0 + \bullet OCl \qquad (5)$$
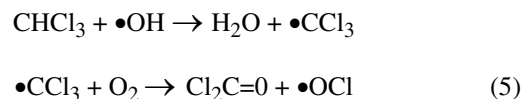
The potential importance of this process is suggested by the observation that the reactivity of airborne chloroform increases in the presence of photochemical smog, which often contains substantial concentrations of hydroxyl radical (Baulch and others, 1980). During irradiation experiments conducted under artificial light in the presence of 0.2 parts per million of NO_x, Dimitriades and Joshi (1977) observed an average chloroform transformation rate of 0.8 percent per hour, or a half-life of about 11 days. Given its large Henry's Law constant and generally low photochemical reactivity in the absence of smog, chloroform is likely to be transported relatively long distances in the atmosphere before undergoing transformation or being removed by precipitation. Although photodegradation may lead to some removal of chloroform from the atmosphere, it appears

to be too slow in water to represent a significant transformation process in most aquatic systems (Howard and others, 1991).

Under most conditions, hydrolysis (fig. 7) also is not considered to be a significant degradation process for chloroform in the hydrologic system. Half-lives estimated at 25°C and pH 7 for this reaction range from 1,760 to 31,600 years (Rathbun, 1998). Chloroform hydrolyzes more slowly than the other three THMs, reflecting the greater ease with which bromide is displaced from halogenated organic compounds, relative to chloride (March, 1985). At 25°C and pH 7, half-lives for the hydrolysis of $CHBrCl_2$, $CHBr_2Cl$, and $CHBr_3$ have been estimated to be approximately 128, 274, and 686 years, respectively (Washington, 1995).

Because they are highly oxidized compounds, THMs undergo more rapid transformation under hypoxic conditions than under oxic conditions. Thus, in contrast to the relatively slow transformation rates described previously, half-lives for the biotransformation of chloroform in water under hypoxic (sulfate reducing) conditions have been observed to range from 3 to 21 days at 15°C between pH 6 and 8. At pH values less than 6, half-lives increase to between 28 and 173 days (at the same temperature) (Saunders and others, 1996). As might be expected from the higher oxidation potential of chlorine relative to bromine (March, 1985), chloroform undergoes microbial transformation in hypoxic aqueous solution more rapidly than either $CHBr_2Cl$ or $CHBr_3$, the rates decreasing with increasing bromination ($CHCl_3 > CHBr_2Cl > CHBr_3$) (Howard and others, 1991). (No data appear to be available for $CHBrCl_2$.) Few data are reported for chloroform biotransformation under oxic conditions; however, using an initial chloroform concentration of 500 µg/L under oxic conditions, Tabak and others (1981) reported chloroform biotransformation to occur in the laboratory with half-lives ranging from 5 to 7 days at 25°C.

Chloroform Occurrence in the Hydrologic System

The detection of chloroform in the hydrologic system has been documented in several national, regional, and local studies. Most of these studies have found chloroform to be the most frequently detected VOC examined, although its concentrations in water are usually low enough that the USEPA's current (2004) Maximum Contaminant Level (MCL) of 80 µg/L for the sum of all THM concentrations (also referred to as the total trihalomethanes or TTHM concentration) is not often exceeded.

Atmosphere

In a study of VOCs in ambient air in 13 rural and urban locations in the United States, chloroform concentrations were found to increase with the degree of urbanization; however, chloroform was one of the few compounds that did not appear to have seasonal trends in concentration (Pankow and others, 2003). By contrast, in the Arctic region of Norway, average concentrations of chloroform in air were found to be lower in July 1982 (16.5 parts per trillion by volume (pptv)) than in the spring of 1983 (26.6 pptv) (Howard, 1991). Data on chloroform concentrations in precipitation appear to be scarce, but concentrations as high as 125 µg/L in rainfall have been reported (Kawamura and Kaplan, 1983; Adachi and Kobayashi, 1994).

Ground Water

Table 3 summarizes data on chloroform detections in untreated ground water from a variety of studies ranging in scale from individual urban areas (for example, Mullaney and Grady, 1997) to the entire United States (Squillace, Moran, and others, 1999; Moran and others, 2002; Grady, 2003). For all of the studies listed, chloroform was the VOC detected most frequently in ground water. However, with the exception of the investigation by Squillace, Moran, and others (1999), all of the sampled ground water contained TTHM concentrations that were less than the USEPA MCL of 80 µg/L for TTHMs. Figure 8 presents data on THM detections in ground and surface water from the national study by Grady (2003).

Chloroform was detected in ground water beneath a broad range of land-use settings during these studies, including not only urban, residential, and industrial locations, but also agricultural, forested, and other undeveloped areas. As might have been expected, among those studies that compared different land-use settings, frequencies of detection of the compound were higher beneath urban and residential areas than beneath agricultural or undeveloped areas (Grady and Mullaney, 1998; Squillace, Moran, and others, 1999; E.A. Frick, U.S. Geological Survey, written commun., 2003). During the study of VOC occurrence in shallow ground water by Grady and Mullaney (1998), the differences in chloroform detection frequencies among urban, agricultural, and undeveloped areas (table 3) were found to be statistically significant (p=0.0110).

As noted previously, the widespread detections of chloroform in many of the urban and suburban areas are likely to have been a result of contamination from a variety of sources, including chlorinated public-supply water used to irrigate lawns and gardens, leakage from distribution systems for treated water and wastewater, spas, pools, and leachate from septic-system drainfields (Thiros, 2000). In addition, results from a study of public-supply wells in the Coastal Los Angeles and Santa Ana Basins indicate that the detection of chloroform and other VOCs in ground water downgradient from artificial recharge facilities might be a result of contamination from such facilities. Observations from this study also attest to the comparatively high mobility of chloroform in the subsurface, because the compound was detected at or greater than 0.024 µg/L more frequently and at greater distances from the recharge facilities than any of the other VOCs analyzed (Shelton and others, 2001). Similarly, in ground water downgradient from an artificial recharge facility receiving chlorinated wastewater in Palo Alto, California, Roberts and others (1982) observed chloroform to show the highest mobility among all of the VOCs examined (including $CHBr_2Cl$ and $CHBr_3$).

Table 3.   Studies of chloroform and other trihalomethane occurrence in ground water in the United States.

[Ag, Agricultural; Com, Commercial; Dom, Domestic; Dp, Deep; Irr, Irrigation; LV, Las Vegas; MCL, Maximum Contaminant Level; Mon, Monitoring; Mul, Multi-level; Mx, Mixed; PS, Public-Supply; Res, Residential; Ru, Rural (less than 386 persons per square kilometer); Sh, Shallow; SP, Spring; TTHM, total trihalomethanes; Un, Undeveloped; Urb, Urban; USGS, U.S. Geological Survey; µg/L, micrograms per liter; <, less than; --, data not available]

Study location, by State	Land-use setting	Reference	Number of sites sampled	Site type	Frequency of chloroform detection at or greater than 0.2 µg/L (percent)	Maximum chloroform concentration (µg/L)	Frequency of exceedance of MCL of 80 µg/L for TTHMs (percent)	Maximum TTHM concentration (µg/L)
National study	Ru	Moran and others (2002)	1,926	Dom	4.3	74	0	76.1
National study	Ru	Squillace, Moran, and others (1999)	2,538	Mon, PS, Dom	5.1	210	0.04	210
National study	Urb	Squillace, Moran, and others (1999)	405	Mon, PS, Dom	26	400	0.25	400
National study	--	Grady (2003)	579	PS	12	22.4	0	70.6
Conn., Mass., N.H., Vt.	Ag	Grady and Mullaney (1998)	24	Mon	8.3	0.4	0	0.4
Ala., Fla., Ga.	Ag	Frick, E.A. (USGS, written commun., 2003)	30	Mon	0	<0.2	0	<0.2
Conn., Mass., N.H., Vt.	Un	Grady and Mullaney (1998)	22	Mon	4.5	2.6	0	2.8
N.J.	Un	Stackelberg and others (1997)	13	Mon, Sh	7.7	1.3	0	1.3
Conn., Mass., N.H., Vt.	Urb	Grady and Mullaney (1998)	40	Mon	33	3.1	0	3.1
Fla., Ga.	Urb, Ag, Un	Berndt and others (1998)	32	Mon, Sh, Dp	12.5	2.2	0	2.2
Ariz.	Ag	Cordy and others (2000)	9	Mon, Sh	33	0.5	0	0.5
Ind.	Ag	Fenelon and Moore (1996)	72	Mon, Sh, Dp	3	1.7	0	1.7
Tenn.	Ag	Johnson and Connell (2001)	30	Mon	3.3	0.4	0	0.4
N.J.	Ag	Stackelberg and others (1997)	15	Mon, Sh	13	0.3	0	0.3
Ariz.	Mx	Cordy and others (2000)	77	PS, Dom, Irr, Com	16	9.9	0	10.2
Tenn.	Mx	Johnson (2002)	35	Sp	11	1.3	0	1.4
Utah	Res, Com	Thiros (2000)	30	Mon	60	2.4	0	2.7
Calif.	Urb	Domagalski and others (2000)	19	Mon, Sh	11	5.1	0	5.2

Table 3.   Studies of chloroform and other trihalomethane occurrence in ground water in the United States.—Continued

[Ag, Agricultural; Com, Commercial; Dom, Domestic; Dp, Deep; Irr, Irrigation; LV, Las Vegas; MCL, Maximum Contaminant Level; Mon, Monitoring; Mul, Multi-level; Mx, Mixed; PS, Public-Supply; Res, Residential; Ru, Rural (less than 386 persons per square kilometer); Sh, Shallow; SP, Spring; TTHM, total trihalomethanes; Un, Undeveloped; Urb, Urban; USGS, U.S. Geological Survey; μg/L, micrograms per liter; <, less than; --, data not available]

Study location, by State	Land-use setting	Reference	Number of sites sampled	Site type	Frequency of chloroform detection at or greater than 0.2 μg/L (percent)	Maximum chloroform concentration (μg/L)	Frequency of exceedance of MCL of 80 μg/L for TTHMs (percent)	Maximum TTHM concentration (μg/L)
Ind.	Urb	Fenelon and Moore (1996)	28	Mon, Sh, Dp	40	21	0	21
Ga.	Urb	Frick, E.A. (USGS, written commun., 2003)	40	Mon, Sp	35	4	0	4
Tex.	Urb, Mx	Bush and others (2000)	119	Mon, PS	4.2	1.3	0	1.5
Conn.	Urb	Mullaney and Grady (1997)	10	Mon, Mul, Sh	71	13	0	13.8
N.J.	Urb	Stackelberg and others (1997)	50	Mon, Sh	30	5.6	0	5.7
Conn.	--	Grady (1997)	103	Mon, PS	23	13	0	13.8
Nev.	--	Bevans and others (1998)	57	PS	50 LV/ 28 Reno	23	0	70.5
Del.	--	Ferrari (2002)	30	PS	40	3.9	0	4.2
Calif.	--	Shelton and others (2001)	178	PS	10	11	0	17
N.J.	--	Stackelberg and others (2000)	30	PS	40	2.5	0	2.53
Utah	--	Thiros (2003)	31	PS	26	19.7	0	26.1

The likely reasons for the detection of chloroform in shallow ground water beneath agricultural areas, however, are more elusive. In some locations, such as the West Salt River Valley of Arizona (Cordy and others, 2000), the occurrence of chloroform in shallow ground water may be attributable to the use of treated effluent from wastewater treatment plants for irrigation. Other agricultural areas, such as those in Connecticut (Grady and Mullaney, 1998) or New Jersey (Stackelberg and others, 1997), may have frequent chloroform detections because of the proximity of residential or commercial development. Support for the latter hypothesis is provided by the frequent detection of predominantly agricultural pesticides in the shallow ground water beneath the urban areas examined during the Connecticut and New Jersey studies. Alternatively, the detection of chloroform in ground water beneath agricultural areas may be a consequence of its use either as an adjuvant compound in commercial pesticide formulations (Bishop, 1987) or as a fumigant (Meister, 2000).

Surface Water

As in ground water, chloroform often is the most frequently detected VOC in surface water (Lundgren and Lopes, 1999). Table 4 summarizes results from several studies of chloroform occurrence in rivers and streams across a broad range of spatial scales in the Nation. The highest concentrations of chloroform in surface water are most commonly detected downstream from discharges of chlorinated urban wastewater. Locations where this observation has been documented include sites along the Raritan and Passaic Rivers in New Jersey (Reiser and O'Brien, 1998), Rowlett Creek in Texas (Buszka and others, 1994), the San Antonio River near Elmendorf, Texas (Bush and others, 2000), and the Las Vegas Wash in Nevada (Bevans and others, 1998). Lundgren and Lopes (1999) also reported higher frequencies of chloroform detection in the Ohio River among samples collected from stations downstream from large cities relative to sites sampled upstream from major metropolitan areas.
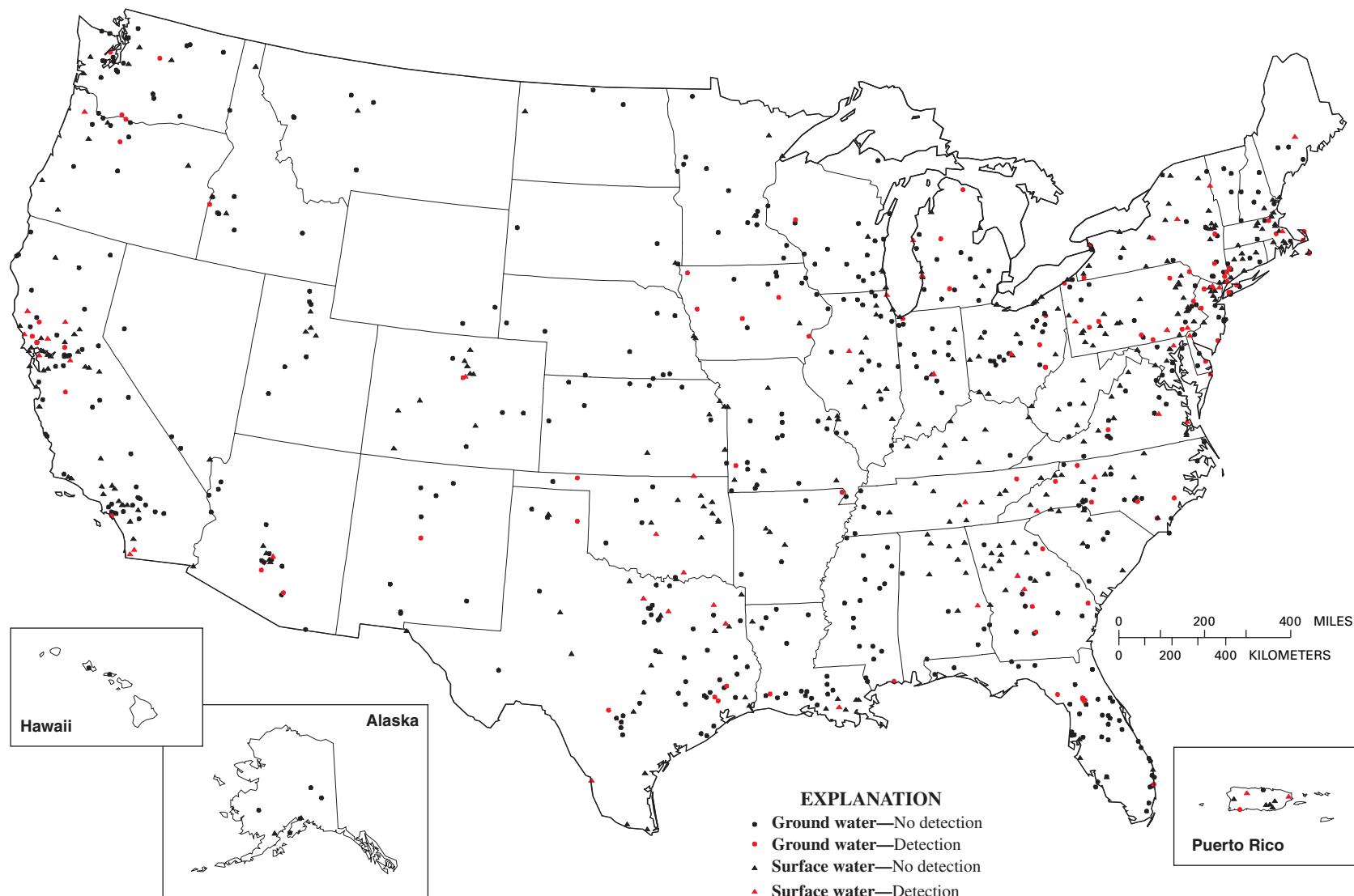
Figure 8.   Detections of total trihalomethanes at or greater than 0.2 micrograms per liter in ground and surface waters sampled for the American Water Works Research Foundation national study (modified from Grady, 2003).

Table 4. Studies of chloroform occurrence in surface waters in the United States.

[MCL, Maximum Contaminant Level; TTHMs, total trihalomethanes; μg/L, micrograms per liter; <, less than; --, data not available]

Study location, by State	Reference	River or stream	Reporting limit for chloroform (μg/L)	Number of samples	Frequency of chloroform detection in samples (percent)	Chloroform concentration range (μg/L)	Frequency of exceedance of MCL of 80 μg/L for TTHMs (percent)	Maximum TTHM concentration (μg/L)
National study	Grady (2003)	163 River Sites	0.2	375	14	<0.2 to 84.7	0.27	102
Ill., Ind., Ohio, Pa., Tenn., Va., W. Va.,	Lundgren and Lopes (1999)	Ohio River	.1	44,837	26	<0.1 to 125	3.8	137
N.J., N.Y.	Ayers and others (2000)	42 stream sites	.05	112	63	<0.05 to 1.5	0	3.1
Calif.	Shelton and others (2001)	Santa Ana River	0.024; 0.05	40	100; 100	0.13 to 0.86	0	1
Nev.	Bevans and others (1998)	Las Vegas Wash	.05	4	100	0.6 to 1.4	0	1.9
N.J.	Reiser and O'Brien (1998)	Passaic River	.05	9	100	0.13 to 1.5	0	3.1
N.J.	Reiser and O'Brien (1998)	Raritan River	.05	11	100	0.1 to 4	0	5.6
Tex.	Buszka and others (1994)	Rowlett Creek	.2	4	75	1.9 to 3.8	0	4.8
Tex.	Bush and others (2000)	San Antonio River	.1	13	100	0.4 to 4.6	0	6.5

Drinking Water

The term drinking water refers to water at its point of use for human consumption. Table 5 summarizes data on the occurrence of chloroform in treated drinking water from a regional study by Grady and Casey (2001), who reported that chloroform was more frequently detected at or greater than 1.0 μg/L in randomly selected community water systems than any other VOC examined. As might be expected, drinking water provided by a water utility is more likely to have been chlorinated than water drawn from a surface-water body, spring, or domestic well by a private homeowner. Thus, high concentrations of chloroform measured in some surface waters (table 5) were likely to have been a consequence of some of the utilities having used chlorination to treat the water.

Although most homeowners who obtain their water from private wells do not chlorinate their water prior to use, chloroform was found to be the most frequently detected VOC in domestic well water in 20 States across the Nation (Moran and others, 2000) (table 3). Concentrations of chloroform reported in well water were generally low (with a median of 0.5 μg/L), with no exceedances of the USEPA MCL for TTHMs (80 μg/L). One potential source of chloroform to domestic wells is shock chlorination, a disinfection process in which a dilute solution of bleach is added directly to a well to eliminate bacterial contamination. Septic systems also may be a significant source of chloroform in ground water. Previous studies have documented the presence of chloroform in septic-system effluent (DeWalle and others, 1985; Ayers Associates, 1993), and several States have identified septic systems as a major source of ground-water contamination, second only to underground storage tanks (U.S. Environmental Protection Agency, 2000b). In addition, the U.S. Environmental Protection Agency (2000b) has noted that improperly designed, maintained, or operated septic systems can result in ground-water contamination in the vicinity of the system, especially if the degradation of the organic matter within the system is incomplete. Chloroform also may be present in septic systems as a result of the reaction between organic matter and bleach used for laundering operations.

Table 5.   Summary of chloroform and other trihalomethane detections in drinking water in eleven States[a] of the Northeastern and Mid-Atlantic regions of the United States.

[Data from Grady and Casey, 2001; S.J. Grady, U.S. Geological Survey, written commun., 2003. GW, ground water; MCL, Maximum Contaminant Level; SW, surface water; TTHM, total trihalomethanes; μg/L, micrograms per liter; --, data not available]

Number and type of public-supply systems sampled	Frequency of chloroform detection at or greater than 1.0 μg/L (percent)	Maximum chloroform concentration (μg/L)	Frequency of exceedance of MCL of 80 μg/L for TTHMs (percent)	Maximum TTHM concentration (μg/L)
1,190 GW-derived systems (public supply wells)	19.4	200	0.06	208
199 SW-derived systems	87.4	410	10.9	425
112 combined systems (GW + SW)	82.1	200	5.2	215

[a]Connecticut, Delaware, Maryland, Maine, New Hampshire, Massachusetts, New Jesey, New York, Rhode Island, Virginia, and Vermont.

Human-Health Effects and Drinking-Water Criteria

Human exposure to chloroform occurs primarily through two routes—ingestion and inhalation. Most of these exposures appear to occur through the ingestion of chlorinated drinking water, consumption of foods processed with chlorinated water, or inhalation of the compound while showering or washing dishes with treated water (Agency for Toxic Substances and Disease Registry, 1997). Dermal absorption represents another potential route of exposure, especially in the shower (Jo and others, 1990; Gordon and others, 1998; Miles and others, 2002) and in chlorinated swimming pools (Levesque and others, 1994; Lindstrom and others, 1997). Current (2004) drinking-water-quality criteria, however, focus on ingestion as the sole route of exposure.

Inhalation Exposure and its Effects

Dating back as far as the 1840s, chloroform was commonly administered as an anaesthetic. This practice was discontinued at the beginning of the twentieth century when it was discovered that many patients anesthetized with chloroform developed complications of the liver and kidneys (BBC Education, 2003). Although no increases in mortality occurred when patients undergoing surgery were exposed to vapor-phase chloroform concentrations less than 22,500 parts per million by volume (ppmv), concentrations of 40,000 ppmv or greater were considered an overdose (Agency for Toxic Substances and Disease Registry, 1997).

During inhalation studies involving laboratory animals, rats and mice exposed to concentrations of chloroform ranging from 2 to 300 ppmv for as many as 90 days (6 hours per day, 5 to 7 days per week) developed lesions in the liver, kidney, and nasal passages. Histological effects in the liver and kidneys were only observed at exposure levels greater than 30 ppmv, although atrophy of the nasal tissues was observed in rats at 2 ppmv (U.S. Environmental Protection Agency, 2001).

The long-term health effects upon workers exposed to chloroform for 3 to 10 years at vapor-phase concentrations as high as 237 ppmv have included nausea, vomiting, dry mouth, dizziness, and headaches (Agency for Toxic Substances and Disease Registry, 1997). The National Institute for Occupational Safety and Health (NIOSH) has recommended a short-term (15-minute) exposure limit of 2 ppmv for the compound, whereas the Occupational Safety and Health Administration (OSHA) has set a maximum ceiling value of 50 ppmv for an 8-hour workday (U.S. Department of Health and Human Services, 1997). Twenty-four-hour limits for exposure to chloroform in ambient air vary among the States that have established such standards, with values (in ppmv) of 0.003 in Arizona, 0.005 in Florida, 0.027 in Massachusetts, 0.020 in Oklahoma, 0.051 in South Carolina, and 0.10 in Virginia (Sittig, 1994).

Table 6 summarizes data on the vapor-phase concentrations of chloroform in equilibrium with chlorinated water. The values listed in the table represent either measurements or model predictions in air in residences, shower stalls, or indoor swimming pool facilities; in air vented from washing machines and dishwashers; and in air near a kitchen sink. None of the concentrations listed in table 6 exceed the NIOSH short-term exposure limit of 2 ppmv or the OSHA ceiling limit of 50 ppmv. However, the chloroform concentrations measured in the air above indoor swimming pools and within shower stalls exceeded the 24-hour exposure limits set by some of the States listed previously. (Note that the aqueous concentrations of chloroform measured or predicted during several of the investigations exceeded the MCL of 80 μg/L for TTHMs.) Studies by Jo and others (1990), Weisel and Jo (1996), and Gordon and others (1998) also have documented the vapor-phase concentrations to which people are exposed while showering or bathing with chlorinated water.

Table 6. Concentrations of chloroform in air (either measured directly or predicted from models) in shower stalls, near washing machines, dishwashers, above kitchen sinks, and in indoor swimming pool facilities.

[μg/L, micrograms per liter; --, not applicable]

Location of measurement	Concentrations measured [M] or predicted [P]	Concentration of chloroform in air, in parts per million, by volume	Assumptions or relevant experimental conditions (where applicable)	Reference
Residence	M	0.00002 to 0.004	Aqueous concentration, 100 μg/L	Howard and Corsi (1996)
Residence	M	0.002	--	Levesque and others (2002)
Shower stall	M	0.030	--	Levesque and others (2002)
Washing machine	M	0.006	--	Corsi and others (1992)
Washing machine	P	0.001	Aqueous concentration, 100 μg/L	Howard and Corsi (1998)
Kitchen sink	P	0.002	Aqueous concentration, 100 μg/L	Howard and Corsi (1996)
Dishwasher	P	0.002	20-cubic-meter room; aqueous concentration, 10 μg/L	Howard-Reed and others (1999)
Indoor swimming pool	M	0.6 to 1.63	Aqueous concentration, 159–533 μg/L	Levesque and others (1994)
Indoor swimming pool	M	0.054	--	Mannschott and others (1995)
Indoor swimming pool	M	0.0297	Aqueous concentration, 68-73 μg/L	Lindstrom and others (1997)

Ingestion Exposure and its Effects

Ingestion of chloroform may be through several routes. Of principal importance in this regard is the direct consumption of chlorinated water, but some foods—many of which are processed with chlorinated water—also contain chloroform. For example, chloroform has been found to be a contaminant in fish, butter, cheddar cheese, cereals, and margarine (California Department of Health, 1990; Agency for Toxic Substances and Disease Registry, 1997). It also has been detected in fresh vegetables, tea leaves, and frozen vegetables at average concentrations of 30.9, 62.9, and 15.7 micrograms per kilogram of biomass, respectively (Adachi and others, 2001). Little information on mortality in humans following ingestion of pure chloroform is available, but fatal doses as low as 212 milligrams per kilogram (mg/kg) of body mass have been reported (Agency for Toxic Substances and Disease Registry, 1997).

In most laboratory studies of animal mortality from chloroform ingestion, males had lower survival rates than females, although higher female mortality was observed in pregnant animals. Consistent with the acute effects of chloroform exposure by inhalation, the liver and kidney also are the primary target organs in humans, rats, and mice following ingestion (Agency for Toxic Substances and Disease Registry, 1997).

Available evidence indicates that chloroform (as well as tetrachloromethane) undergoes reductive dehalogenation by mixed-function oxidases in the liver, resulting in the formation of toxic metabolites that cause damage by binding covalently to hepatic and renal tissues (Hook and Hewitt, 1986).

Recent studies have explored some of the ways in which oral exposure to THMs in drinking water may affect human reproduction, although many of these investigations did not report separate results for chloroform alone. Results from some of these studies are summarized in table 7. Many of these results are discussed in terms of an odds ratio (OR), which is a parameter used to compare the probabilities of a certain event occurring in each of two different study groups. For two hypothetical groups A and B, an odds ratio of unity (A/B=1) implies that the event is equally likely in both groups, whereas odds ratios greater or less than unity imply that the event is more likely in group A or B, respectively (Ott and Longnecker, 2001). For the studies listed in table 7, the numerator in the OR (group A from the example above) is the frequency with which the targeted outcome is encountered in the group exposed to the chloroform or THM concentration range given, while the demoninator (group B) is the frequency of occurrence of the same outcome in either the reference (for pregnancy studies) or the control group (for cancer studies) group.

Table 7. Summary of the effects of chloroform and total trihalomethanes on pregnancy outcomes and the incidence of cancer.

[CHCl$_3$, chloroform; CI, confidence interval; IGR, intrauterine growth retardation; IGR5, live birth weights (adjusted for race, sex, and gestational week) at or below the fifth percentile; IGR10, live birth weights (adjusted for race, sex, and gestational week) at or below the tenth percentile; Low birth weight, infants born with weights less than 2.5 kilograms; Low term birth weight, infants born after 37 or more weeks of gestation and weighing less than 2.5 kilograms; M, male; NR, not reported; OR, odds ratio; SW, surface water; TTHMs, total trihalomethanes; µg/L, micrograms per liter; %, percent; <, less than; >, greater than; ≥, greater than or equal to]

Target outcome	Study location	Number of target subjects	Number of reference or control subjects	Chloroform or TTHM threshold concentration examined		OR	Reference
				Target population	Reference or control population		
Pregnancy Studies							
Low birth weight	Iowa	187	935	≥10 µg/L CHCl$_3$	<10 µg/L CHCl$_3$	1.3; 95% CI 0.8-2.2	Kramer and others, 1992
Low birth weight	North Carolina	74	118	63.4-82.7 µg/L TTHMs	40.8-63.3 µg/L TTHMs	1.5 95% CI 1.0-2.3	Savitz and others, 1995
Low birth weight	Nova Scotia	440	693	>100 µg/L TTHMs	<50 µg/L TTHMs	1.04 95% CI 0.92-1.2	Dodds and others, 1999
Low birth weight	Massachusetts	195,506	91,227	>20 µg/L CHCl$_3$	≤20 µg/L CHCl$_3$	1.05; 95% CI 1.02-1.09	Wright and others, 2004
Low term birth weight	Northern New Jersey	37,053	22,098	>100 µg/L TTHMs	≤20 µg/L TTHMs	1.4; 90% CI 1.0-2.0	Bove and others, 1995
Low term birth weight	Colorado	6	11	>50 µg/L TTHMs	≤20 µg/L TTHMs	5.9; 95% CI 2.0-17.0	Gallagher and others, 1998
Low term birth weight	Massachusetts	1,325	NR	>80 µg/L TTHMs	<60 µg/L TTHMs	1.05; 95% CI 0.85-1.3	Wright and others, 2003
IGR5	Iowa	187	935	≥10 µg/L CHCl$_3$	<10 µg/L CHCl$_3$	1.8; 95% CI 1.1-2.9	Kramer and others, 1992
IGR5	Northern New Jersey	2,727	1,355	>100 µg/L TTHMs	≤20 µg/L TTHMs	1.5; 90% CI 1.2-1.9	Bove and others, 1995
IGR10	Massachusetts	5,310	NR	>80 µg/L TTHMs	<60 µg/L TTHMs	1.13; 95% CI 1.03-1.24	Wright and others, 2003
IGR10 (genetically susceptible newborns)	Montreal, Canada	45	37	≥29.4 µg/L TTHMs	<29.4 µg/L TTHMs	13.2; 95% CI 1.2-146.7	Infante-Rivard, 2004
Stillbirth	Nova Scotia	44	43	>100 µg/L TTHMs	<50 µg/L TTHMs	1.66; 95% CI 1.09-2.25	Dodds and others, 1999
Spontaneous abortion	California	121	565	≥75 µg/L TTHMs and ≥5 glasses of water per day for first trimester of pregnancy	<75 µg/L TTHMs and ≥5 glasses of water per day for first trimester of pregnancy	2.0; 95% CI 1.1-3.6	Waller and others, 1998

Table 7. Summary of the effects of chloroform and total trihalomethanes on pregnancy outcomes and the incidence of cancer.—Continued

Target outcome	Study location	Number of target subjects	Number of reference or control subjects	Chloroform or TTHM threshold concentration examined		OR	Reference
				Target population	Reference or control population		
Pregnancy Studies—Continued							
Neural tube defects	New Jersey	112	248	≥40 µg/L TTHMs	<40 µg/L TTHMs	2.1; 95% CI 1.1-4.0	Klotz and Pyrch, 1999
Central nervous system defects	Northern New Jersey	82	36	>80 µg/L TTHMs	≤20 µg/L TTHMs	2.6; 90% CI 1.5-4.3	Bove and others, 1995
Cancer Studies							
Bladder	Finland	M 79	M 89	NR (Non-smokers; >30 years exposure)	NR (Non-smokers; <30 years exposure)	2.59; 95% CI 1.13-5.94	Koivusalo and others, 1998
Rectal	Iowa	13	40	NR (Ingested chlorinated SW for ≥60 years)	NR (Ingested chlorinated SW for <60 years)	2.50; 95% CI 1.3-4.9	Hildesheim and others, 1998

Nieuwenhuijsen and others (2000) and Bove and others (2002) recently reviewed pregnancy outcome studies (including some of the investigations listed in table 7) that evaluated the effect of THMs on adverse birth outcomes such as low birth weight, preterm births, birth defects, spontaneous abortions, and fetal deaths. These studies provided evidence for associations between the consumption of drinking water containing elevated concentrations of THMs (>10 µg/L) and intrauterine growth retardation, neural tube defects, and spontaneous abortions (Bove and others, 2002). However, because Bove and others (1995) reported the results from their study as 90-percent confidence intervals for their OR values—rather than 95-percent confidence intervals—the statistical significance of the conclusions from their investigation cannot be compared directly with those from the other studies discussed in this report (for which, as noted earlier, a significance level of 0.05 has been used).

Many of the studies that examined associations between the ingestion of THMs and adverse birth outcomes, however, were inconclusive. In particular, one of the most substantial limitations to the pregnancy outcome studies conducted to date is the considerable uncertainty associated with the assessment of exposure (Nieuwenhuijsen and others, 2000). Accurate assessments of THM exposure often are difficult to obtain because THM concentrations vary among different locations within the water distribution system, seasonally, and with variations in subjects' behavior at home and in the workplace. Another limitation is that many of the studies did not include inhalation or dermal contact as routes of exposure during showering or swimming. Ideally, large studies that focus on well-defined endpoints and include a more complete characterization of exposure—including exposure to mixtures of THMs, and all routes of exposure—are needed to either confirm or refute the findings of previous investigations (Nieuwenhuijsen and others, 2000).

Although few conclusive studies are available, epidemiological investigations to date have reported more frequent occurrences of colon, rectal, and bladder cancer with regular consumption of chlorinated drinking water (Agency for Toxic Substances and Disease Registry, 1997). Complicating factors such as the presence of other THMs (which also appear to be carcinogenic) and other chemicals in drinking water make definitive conclusions elusive, but the consumption of chlorinated drinking water appears to be most strongly associated with bladder and rectal cancers (table 7). However, the USEPA has concluded that the available data are currently insufficient to establish a causal relation between exposure to chloroform and an increased risk of cancer (U.S. Environmental Protection Agency, 2002a). Furthermore, recent summaries of the genotoxicity of chloroform indicate that chloroform has a negligible tendency to cause genetic mutations or directly damage DNA (Fawell, 2000; U.S. Environmental Protection Agency, 2002a).

According to a summary by the USEPA (2002a), several animal bioassay studies have reported significant increases in the incidence of liver tumors in male and female mice, as well as increases in the incidence of kidney tumors in male rats and mice, following the ingestion of chloroform at or greater than 60 mg/kg per day of body mass per day. In other studies, tumors were only observed at chloroform concentrations high enough to cause cytotoxicity and regenerative cell proliferation in the target organs. Tumor production, however, also was found to be dependent upon the species, strain, and gender examined. For example, in many studies summarized by the USEPA (2002a), the incidence of tumors in female laboratory animals did not significantly increase upon exposure to chloroform (Roe and others, 1979; Jorgenson and others, 1985; Matsushima, 1994). This observation appears to be consistent with the lower overall mortality rate for females relative to males following chloroform ingestion.

Current (2004) evidence indicates that chloroform is likely to be carcinogenic to humans by all routes of exposure (inhalation, ingestion, and dermal absorption) at high concentrations, but is unlikely to be carcinogenic to humans by any route of exposure at low concentrations (U.S. Environmental Protection Agency, 2002a). According to the USEPA—and consistent with the results from the laboratory animal studies—chloroform appears to be carcinogenic to humans at aqueous concentrations that lead to cytotoxicity and cell regeneration in susceptible tissues. However, chloroform is not deemed likely to be carcinogenic to humans at concentrations less than those that cause cell regeneration, although cytotoxicity may still be evident at concentrations less than those that are apparently required to cause cancer (U.S. Environmental Protection Agency, 2001). Based on the available evidence, chloroform has been classified by the USEPA as a Group B2 compound—a probable human carcinogen for which there is sufficient evidence of carcinogenicity in animals, but for which data on carcinogenicity in humans are either absent or inadequate.

As noted earlier, the current (2004) MCL for TTHMs is 80 µg/L. A considerably more stringent water-quality guideline is the USEPA's MCLG, which is not a regulatory standard, but is defined by the USEPA as the highest concentration at which a compound is deemed to pose a negligible health hazard in drinking water. The USEPA has historically established an MCLG value of zero for all carcinogens—including chloroform—based on the presumption that any exposure to carcinogens represents a non-negligible health risk. In addition, it has traditionally been assumed that the risk of contracting cancer from a particular carcinogen increases linearly with exposure to that compound (Hogue, 2001). However, given the assumption (noted previously) that chloroform is not likely to be carcinogenic to humans at concentrations less than those that cause cell regeneration, the USEPA decided to remove the zero MCLG for chloroform from its National Primary Drinking Water Regulations in May 2000 (U.S. Environmental Protection Agency, 2000a). More recently, the USEPA revised the MCLG for the compound to 70 µg/L (U.S. Environmental Protection Agency, 2004a). Thus, despite the usual assumption that cancer risk

increases linearly with exposure, such a change has involved the adoption of a non-linear approach for the extrapolation of health risk to low doses for chloroform. Such an approach is used by the USEPA for compounds that have adverse non-cancer effects at concentrations lower than those required to cause cancer (U.S. Environmental Protection Agency, 2001).

Dermal Absorption

Several studies have indicated that dermal absorption may be another significant route of chloroform uptake, either through showering or bathing in treated water or from swimming in chlorinated swimming pools. Studies by Jo and others (1990), Weisel and Jo (1996), and Gordon and others (1998) have indicated that humans absorb chloroform by both dermal absorption and inhalation while showering with chlorinated water, and that the mean internal chloroform dose resulting from dermal contact is approximately equal to that from inhalation. Furthermore, the amounts of chloroform and other THMs that the body absorbs increase with increasing temperature; concentrations of chloroform measured by Gordon and others (1998) in the exhaled breath of subjects taking showers increased from 0.00004 ppmv at 28 to 32°C to 0.0014 ppmv at 38 to 41°C. However, breath concentrations of chloroform from all exposure temperatures—and in all subjects—were observed to decrease to about one-half of their peak value within 10 minutes after showering (Gordon and others, 1998). Using a physiologically based, pharmacokinetic model, Corley and others (2000) concluded that the contribution of dermal uptake of chloroform to the total body burden after bathing in chlorinated water for 30 minutes and drinking 2 liters (L) of chlorinated water (tested through exhaled breath) is likely to range from 1 to 28 percent, depending on the temperature (30–40°C) of the bath. The model used by Corley and others (2000), however, did not account for contributions from inhalation exposure.

Levesque and others (1994) and Lindstrom and others (1997) observed an increase in chloroform levels in the body following immersion in treated water in chlorinated public swimming pools. The results from these two studies indicate that the proportion of the total body burden of chloroform contributed by dermal uptake under such circumstances may range from approximately 24 percent (Levesque and others, 1994) to approximately 80 percent (Lindstrom and others, 1997). Table 6 lists the aqueous concentrations of chloroform and resulting chloroform concentrations in air to which subjects were exposed during these two investigations.

Other studies have attempted to compare body burdens of chloroform from all three principal routes of exposure to chlorinated water—inhalation, ingestion, and dermal contact. Weisel and Jo (1996) measured the body burdens of chloroform that developed in 11 subjects as a consequence of showering and bathing in 40°C water, and drinking 0.5 L of tap water (20 µg/L chloroform in both shower and drinking water). The authors observed approximately equivalent amounts of chloroform entering the body by inhalation, ingestion, and dermal

contact. Their experiments also revealed that the route of exposure to chloroform may affect the persistence of the compound in the body. Ingested chloroform was not detected in the exhaled breath of the test subjects, presumably because it had been metabolized in the liver. Chloroform was detected in breath, however, for more than 3 hours following either dermal contact or inhalation during 10-minute showers, reflecting the more widespread dispersion of the compound throughout the body following these routes of exposure. Thus, chloroform may persist longer in the body following inhalation or dermal uptake than following ingestion (Weisel and Jo, 1996).

Toxicity to Aquatic Organisms and Aquatic Water-Quality Criteria

Like other VOCs, chloroform and other THMs have relatively low bioconcentration factor (BCF) values (table 2) compared to those for most other organic contaminants in the hydrologic system. Consequently, the bioaccumulation of THMs in aquatic organisms is anticipated to be relatively small. Results from several investigations of THM bioaccumulation in aquatic organisms are consistent with this expectation. A summary of studies of chloroform concentrations in the tissues of marine organisms by McCulloch (2003) reported ranges of 0.02 to 5 nanograms of chloroform per gram of tissue (ng/g) chloroform in plankton, 15 to 180 ng/g in crabs, and 7.6 to 22 ng/g in grey seal blubber. No significant correlation was observed between chloroform concentrations in animal tissue and the trophic levels of the animals examined. During a study by Toussaint and others (2001), the livers of Medaka fish exposed to aqueous chloroform concentrations of 1,463 µg/L for 9 months contained between 23 to 219 milligrams of chloroform per gram of tissue—substantially less than those that would have been expected from the aqueous concentrations to which the fish had been exposed based on the BCF for the compound.

These results indicate that chloroform did not bioaccumulate in the livers of the fish examined during the study. (Although it is possible that the fish may have detoxified the chloroform *in vivo* by reductive dechlorination to form phosgene—a known chloroform metabolite in mammals—that latter compound was not detected in their hepatic tissues during the study.)

Several studies have examined a variety of non-lethal effects of chloroform on aquatic organisms, most commonly in terms of the EC_{50}—that is, the median effective concentration required to produce a targeted effect in 50 percent of the test organisms. The principal features of some of these studies are summarized in table 8. With respect to lethal effects, Rowe and others (1997) provided a summary of published values of the median lethal concentration (LC_{50}) for chloroform (the concentration resulting in the death of 50 percent of the test organisms), based on results abstracted from the USEPA's AQUatic toxicity Information REtrieval (AQUIRE) system. The authors also summarized data from the AQUIRE system on water-quality criteria for several species of aquatic animals and plants.

In 1980, the USEPA issued an acute freshwater criterion of 28,900 µg/L and a chronic freshwater criterion of 1,240 µg/L for chloroform (U.S. Environmental Protection Agency, 1980); however, these values are no longer published (U S. Environmental Protection Agency, 1998). According to the USEPA, the development of formal criteria for the protection of aquatic life is hindered by a paucity of adequate data; the values of 28,900 and 1,240 µg/L for freshwater acute and chronic exposures, respectively, are the lowest-observed-effect-levels (LOELs) for the compound (U S. Environmental Protection Agency, 1986). The Canadian interim guideline for the protection of freshwater aquatic life is currently 1.8 µg/L for chloroform (Canadian Council of Ministers of the Environment, 2002), nearly three orders of magnitude lower than the USEPA's LOEL for the compound. According to the Canadian Council of Ministers of the Environment (2002), however, insufficient data exist for establishing a corresponding guideline for the protection of marine life.

Table 8.   Selected studies of the non-lethal effects of chloroform exposure on aquatic organisms.

[From Rowe and others (1997). EC_{50}, Median Effective Concentration—Concentration at which a specific non-lethal effect is observed in 50 percent of the organisms tested; >, greater than]

Species	Chloroform EC_{50} concentration (micrograms per liter)	Duration of exposure (hours)	Observed effect	Reference
Spring peeper (*Hyla crucifer*)	270	168	Birth defects	Birge and others (1980)
Fowler's toad (*Bufo woodhousei fowleri*)	>40,000	72	Birth defects	Birge and others (1980)
Water flea (*Daphnia magna*)	51,000	48	Immobilization	Abernathy and others (1986)
Water flea (*Ceriodaphnia dubia*)	340,000	240	Impaired reproduction	Cowgill and Milazzo (1991)
Green algae (*Scenedesmus subspicatus*)	560,000	48	Inhibited growth	Kuhn and Pattard (1990)

The aquatic criteria that currently (2004) are recommended by the USEPA for the protection of human health from the potentially carcinogenic effects of ingesting chloroform in contaminated water and aquatic organisms (particularly fish) is 5.7 µg/L in water for people who consume both organisms and water, and 470 µg/L in water for those who consume organisms only (U.S. Environmental Protection Agency, 2003b). Both of these values incorporate the use of the BCF to estimate the concentrations of the compound that are likely to accumulate in the tissues of aquatic organisms as a function of the trophic levels that they occupy (U.S. Environmental Protection Agency, 2003b). In 2003, the USEPA proposed revised values for these criteria—68 µg/L for the consumption of water and organisms and 2,400 µg/L for the consumption of aquatic organisms only. These values incorporate more recent information, including a nationwide fish consumption rate of 17.5 grams per person per day, the USEPA Integrated Risk Information System reference dose of 0.01 mg/kg of body mass per day, and the BCF (U.S. Environmental Protection Agency, 2004b).

Implications for Future Research

Several topics related to the sources, transport, fate, and biological effects of chloroform and other THMs in the hydrologic system merit additional investigation. More detailed information is needed regarding the spatial distributions and temporal variability of anthropogenic sources of the compound, especially chlorinated drinking water and wastewater derived from leaking distribution lines, as well as chlorinated water used to irrigate lawns, golf courses, gardens, and other urban and residential settings. Assumptions regarding fluxes of the compound from natural sources should also be tested using field observations in order to more precisely determine their contributions to the global production of chloroform, relative to anthropogenic sources.

In addition, more data on the rates and mechanisms of transformation of chloroform and other THMs under varying redox conditions might help to improve the accuracy of predictions regarding the persistence of the compound in major aquifers and its concentrations in drinking-water wells. Finally, systematic epidemiological data on the incidence of cancers, reproductive anomalies, and other health effects associated with chronic exposure to chlorinated drinking water would help regulatory agencies charged with the protection of public health and aquatic ecosystems make more informed decisions regarding maximum acceptable levels of chloroform and other THMs in the hydrologic system.

Summary

Chloroform ($CHCl_3$) is one of the most frequently detected volatile organic compounds (VOCs) in both ground and surface water in the United States. Although anthropogenic sources of

the compound are substantial, they are currently estimated to constitute only 10 percent of the total global input to the hydrologic system. Natural sources of the compound include volcanic gases, biomass burning, marine algae, and soil microorganisms.

In the United States, known industrial releases of chloroform to the atmosphere, surface water, ground water (through underground injections), and the land surface (through spills, leaks, disposal in landfills, or incorporation into soil) totaled approximately 1.6 million pounds in 2001. In chemical manufacturing, chloroform is used primarily for the production of hydrochlorofluorocarbon-22 (HCFC-22), a refrigerant used in air conditioners and freezers, and a proposed substitute for the more highly ozone-depleting CFC-12. However, the largest documented releases of industrial chloroform to the environment in 2001—56 percent of the total—were reported by the paper industry. Chloroform also may be produced from the *in situ* dehalogenation (under iron- or sulfate-reducing conditions) of another anthropogenic contaminant, tetrachloromethane (carbon tetrachloride). Although this transformation has been observed to occur by both biotic and abiotic pathways, the former is likely to be the predominant mechanism in most environments where this reaction takes place.

The widespread detections of chloroform contamination in the hydrologic system, however, appear to be largely a consequence of the use of chlorination for the disinfection of drinking water and wastewater. Although chlorination has been used to treat drinking water since the beginning of the twentieth century (having first begun in Europe in 1902 and in the United States 6 years later), it was only in the mid-1970s that chloroform and other trihalomethanes (THMs)—primarily dichlorobromomethane ($CHCl_2Br$), chlorodibromomethane ($CHClBr_2$), and bromoform ($CHBr_3$)—were first found to be produced by the process. The discharge of chlorinated drinking water and wastewater may be either intentional (through such mechanisms as the use of municipally supplied chlorinated water to irrigate lawns, golf courses, gardens, and other areas, the use of septic systems, or the regulated discharge of chlorinated wastewater to surface waters or ground-water recharge facilities) or inadvertent (through leakage of chlorinated water from swimming pools, spas, or distribution systems for drinking water or wastewater).

The production of chloroform and other disinfection by-products (DBPs) during chlorination occurs by the haloform reaction, which involves the reaction of free chlorine (that is, dissolved chlorine as HOCl, OCl⁻, and Cl_2) with dissolved organic carbon (DOC). Factors that affect the rate and amount of chloroform production during the haloform reaction include pH, bromide concentration, the concentration and composition of the DOC, and temperature. Although the overall effectiveness of disinfection during chlorination increases with decreasing pH, the rate of chloroform production during the haloform reaction has a complex dependence on pH that varies with the structure of the precursor molecules. Increasing bromide concentrations may reduce the concentration of chloroform in treated waters by forming higher proportions of brominated

THMs ($CHCl_2Br$, $CHClBr_2$, $CHBr_3$) and other brominated DBPs. Except in the presence of unusually high bromide concentrations, chloroform is the THM produced in the highest concentrations during chlorination. Furthermore, when more than one THM is produced from chlorination, the relative concentrations among the different compounds usually decrease with increasing bromination ($CHCl_3 > CHCl_2Br \geq CHClBr_2 \geq CHBr_3$). This phenomenon is presumed to be primarily responsible for the common observation that when more than one THM is detected during investigations of the occurrence of these compounds in the hydrologic system, this same trend is typically observed among their relative concentrations or, for a uniform detection limit, their relative frequencies of occurrence. This pattern could provide a valuable means for distinguishing between chlorinated water and other potential sources of chloroform in the environment.

Because of its higher Henry's Law constant, most chloroform is expected to exist primarily in the vapor phase following its release to the atmosphere, or to volatilize when released to surface water or soil. The compound is relatively non-reactive with respect to phototransformation, however, so it is likely to persist long enough to undergo long-range transport in the atmosphere. Furthermore, because of its relatively low affinity for soil organic carbon (that is, its low K_{oc} value) and considerable persistence under oxic conditions, chloroform that reaches ground water has been observed to migrate substantial distances in the subsurface as well.

Chloroform has been widely detected in national, regional, and local studies of VOCs in ground, surface, and drinking water. In many of these studies, chloroform was the most frequently detected VOC examined. Total THM (TTHM) concentrations of the compound, however, were typically below the Maximum Contaminant Level (MCL) of 80 µg/L (micrograms per liter) established by the U.S. Environmental Protection Agency (USEPA) for TTHMs. In the studies that compared land-use settings, frequencies of detection of chloroform were higher beneath urban and residential areas than beneath agricultural or undeveloped areas.

Human health may be affected by chloroform primarily through two routes of exposure—inhalation and ingestion. Inhalation of chloroform occurs most commonly while showering or washing dishes with chlorinated water. However, ingestion of chlorinated drinking water—or foods processed with chlorinated water—is the most common route of exposure. Studies of birth outcomes for pregnant women consuming chlorinated drinking water with elevated TTHM concentrations have shown an increased risk of low birth weight, central nervous system defects, and first trimester miscarriages and stillbirths relative to reference populations consuming water with lower TTHM concentrations. The value of many pregnancy outcome studies, however, has been limited by complications with the methods used to assess exposure. Epidemiological investigations indicate an increase in the incidence of cancer with consumption of chlorinated drinking water, although complicating factors, such as the presence of other carcinogenic DBPs in the drinking water, often produce inconclusive results from such studies.

Despite these uncertainties, chloroform has been classified as a probable human carcinogen (Group B2 compound) based on what is considered to be sufficient evidence of carcinogenicity in animals. The USEPA has determined that the compound is likely to be carcinogenic to humans by all routes of exposure at concentrations high enough to cause cytotoxicity and lead to cell regeneration in susceptible tissues. Liver damage, however, is known to occur at chloroform exposures lower than those required to cause cancer, an observation that has been considered by the USEPA as the basis for setting a new, non-zero Maximum Contaminant Level Goal of 70 µg/L for the compound.

In 1980, the USEPA issued acute and chronic water-quality criteria of 28,900 and 1,240 µg/L, respectively, to protect aquatic organisms from exposure to chloroform in freshwater. These criteria were no longer published after 1998, however, owing to what was considered by the USEPA to be insufficient data to support them. Currently (2004), values of 28,900 and 1,240 µg/L represent the acute and chronic lowest-observed-effect-levels (LOELs) respectively, for aquatic organisms. In Canada, the interim water-quality guideline for the protection of freshwater aquatic life from chloroform contamination currently (2004) is 1.8 µg/L, nearly three orders of magnitude lower than the USEPA's chronic freshwater LOEL. According to the Canadian Council of Ministers of the Environment, however, the available data are currently insufficient to establish a corresponding guideline for marine biota. The USEPA's aquatic criteria for the protection of human health from ingestion of chloroform-contaminated aquatic organisms and water are 5.7 µg/L for people consuming both organisms and water, and 470 µg/L for those consuming aquatic organisms only.

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