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# Chemical Contaminants of Water and Health Consequences

J. Anderson and  
O. Cumming

Scoping Review



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J. Anderson and O. Cumming

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# Chapter 1

## Background, Methods & Search Results

### Introduction

Under the Millennium Development Goals (MDGs), an international target was established to reduce by half the proportion of people without access to safe drinking water [1]. Safe drinking water was defined as having access to an ‘improved’ water source, spanning a number of categories of service deemed to serve as effective proxies for an adequate drinking water supply free from contamination [2]. Progress towards this target was assessed using representative household survey data whereby a household member was asked what type of water source was used by the household most of the time, although the extent to which the water consumed was free from microbial contamination was not directly measured [2]. However, multi-country analyses suggest that a significant proportion of “improved” water sources are faecally contaminated [3]. Whilst there has been no comparable multi-country study of chemical contamination of basic drinking water sources, there are examples of high levels of contamination of “improved” water sources with regard to priority chemicals in certain countries, such as is the case for arsenic in Bangladesh [4]. Whilst the MDG target for water was met in 2012, exposure to contaminated drinking water may remain high, especially in low and middle-income country (LMIC) settings leading some to argue that access to safe drinking water has been over-estimated in the MDG era [5,6].

Contamination of drinking water is addressed under the new water and sanitation Sustainable Development Goal (SDG). SDG 7 adopts a tiered approach with two ascending levels of target service: “basic water access” and “safely managed water access”. The higher tier of service, “safely managed” drinking water, is defined as, “drinking water from an improved water source that is located on premises, available when needed and free from faecal and priority chemical contamination” (Target 6.1; Indicator 6.1.1) [7]. As well as providing access to a source free from contamination, the new SDG includes a target addressing the causes of source pollution that is, “to improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials...” (Target 6.3) [7]. Whilst there is a large range of hazardous chemicals to which people are can be exposed through drinking water, the WHO/UNICEF Joint Monitoring Programme (JMP) has adopted only two - fluoride and arsenic - as “priority parameters for global monitoring”. Although the JMP has initiated direct measurement of microbial contamination through integrating water quality testing within nationally representative surveys [8] efforts to directly measure chemical contamination have been limited to arsenic and fluoride and to just one country in each case.

Although the new SDG addresses chemical contamination as an aspect of “safely managed” the priority parameters of arsenic and fluoride do not represent the wide range of potentially hazardous chemicals that may be found in drinking water. Relatively little is known about the scale of the problem, especially in low- and middle-income countries (LMIC) where both drinking water supply infrastructure

is limited and regulation of chemical pollution of drinking water may be weak. As countries industrialize, these problems are likely to worsen as industrial sectors expand, agriculture is intensified and water resources face increasing demand and stress. Some evidence exists already for the effects on human health of these trends [8] but the scale of the problem is poorly understood and priorities for monitoring and regulation, especially in LMIC with limited resources.

## Methods and Search Results

### Aim and Objectives of the Review

The purpose of the review is to review current literature on chemical contamination of drinking water to identify the main chemical contaminants, their sources and the associated health impacts.

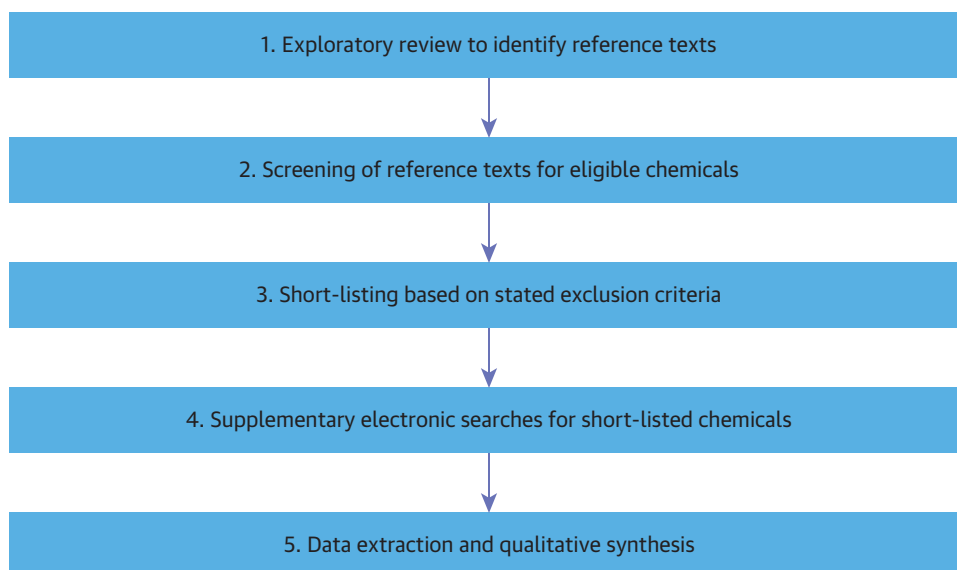
The specific objectives of the review are to:

1. Identify and categorise a list of key chemical contaminants of drinking water
2. Describe the properties and sources of these chemical contaminants
3. Describe health consequences of exposure through drinking water
4. Propose a priority list of chemicals with reference to regulatory norms

This exploratory review has been implemented in five stages (Figure 1.1).

For the review, we first performed scoping searches to identify key reference texts including global, regional and national guidelines for chemical contamination of drinking water, from which we established an initial list of chemicals for screening. A shortlist of chemical contaminants to be included in the review was then prepared using pre-formulated inclusion and exclusion criteria:

**FIGURE 1.1. The Process of the Exploratory Review**





**Inclusion:**

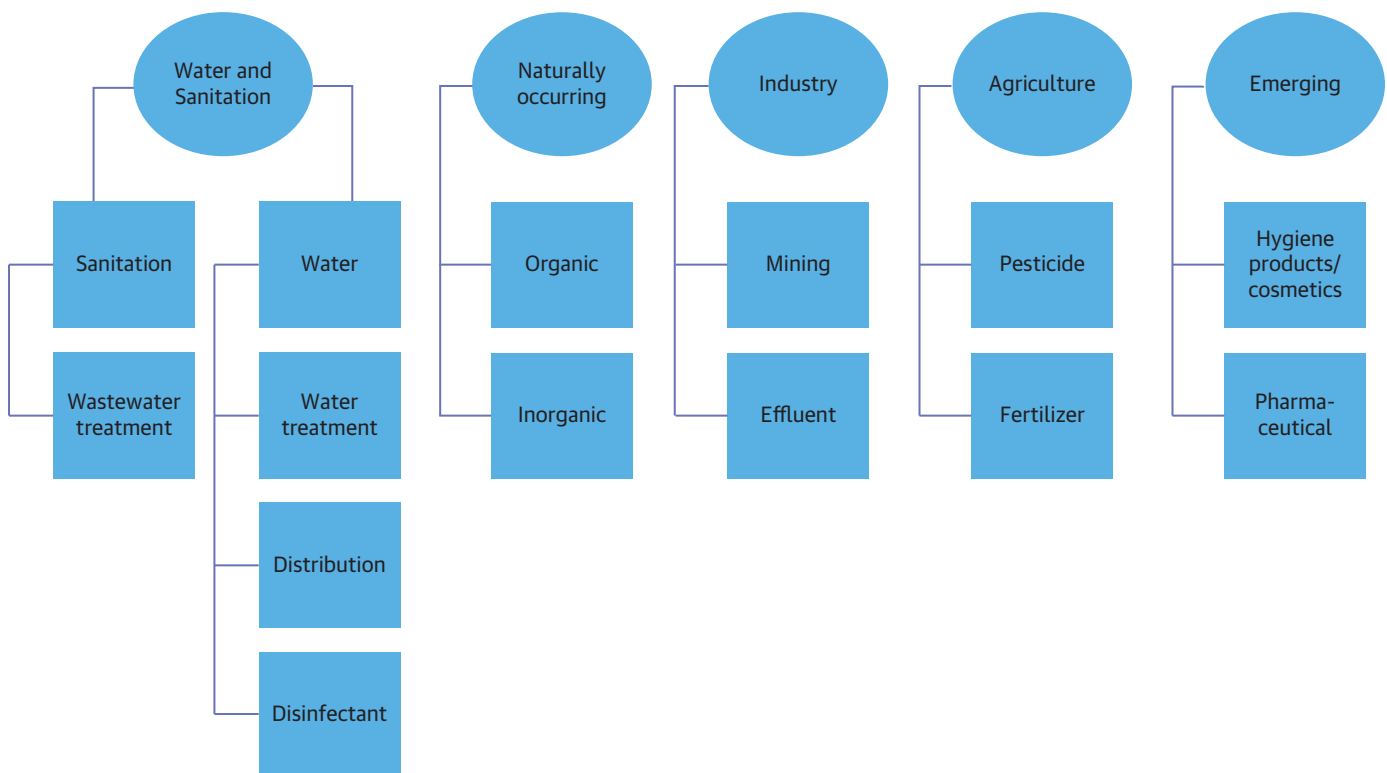
- Guideline value available from WHO
- AND/OR
- Guideline available from reference nation and regional regulatory bodies

**Exclusion:**

- Unlikely to appear in drinking water
- OR
- Unlikely to appear in sufficient concentration in drinking water
- OR
- No evidence of significant health impact

For the inclusion criteria, the reference for guideline values for WHO was the WHO Drinking Water Quality Guidelines [9] and specifically Chapter 8 concerning chemical aspects of drinking water quality. Three reference texts were used for the availability of guidelines values from a national or regional regulatory body: the European Union Water Directive [10]; the United States Environmental Protection Agency Drinking Water Requirements for States and Public Water Systems [11]; and the Canadian Drinking Water Quality Guidelines [12]. These guidelines differ somewhat in their approach

**FIGURE 1.2. Outline of the Report Structure**



to risk determination, identification and classification of individual chemicals, and regulatory provision but together provide a comprehensive list of eligible chemicals for this review to be subject to short-listing.

Following short-listing, all included chemicals were identified by Chemical Abstract Service (CAS) number and the list de-duplicated and then categorized by source and then further sub-categorized (Figure 2). We then identified key reference texts for each chemical, including synthetic references (policy guidelines and systematic reviews) and individual studies, using key word searches on two electronic databases (Google Scholar and PubMed). The main topics of interest with regard to each chemical were: (1) characteristics; (2) geographic distribution; (3) health consequences; and current regulatory guidelines and practice.

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## Chapter 2

# Water and Sanitation System Chemicals and By-products

### Introduction

Chemicals are used throughout the treatment process, summarized generally as 1) coagulation and flocculation, 2) sedimentation, 3) filtration, and 4) disinfection [1]. Disinfectants are also often applied to provide residual protection during water storage and distribution. They are also used to treat wastewater before discharging into surface and groundwater. Water treatment systems around the world vary in size and complexity, utilizing different combinations of physical and chemical processes. Flocculants and disinfectants can be used throughout treatment processes both in the primary disinfection stage but also in storage and distribution. Chemicals directly added to water supply can come in contact with organic matter, pipes, and tanks, forming indirect chemical compounds that can be dangerous to human health.

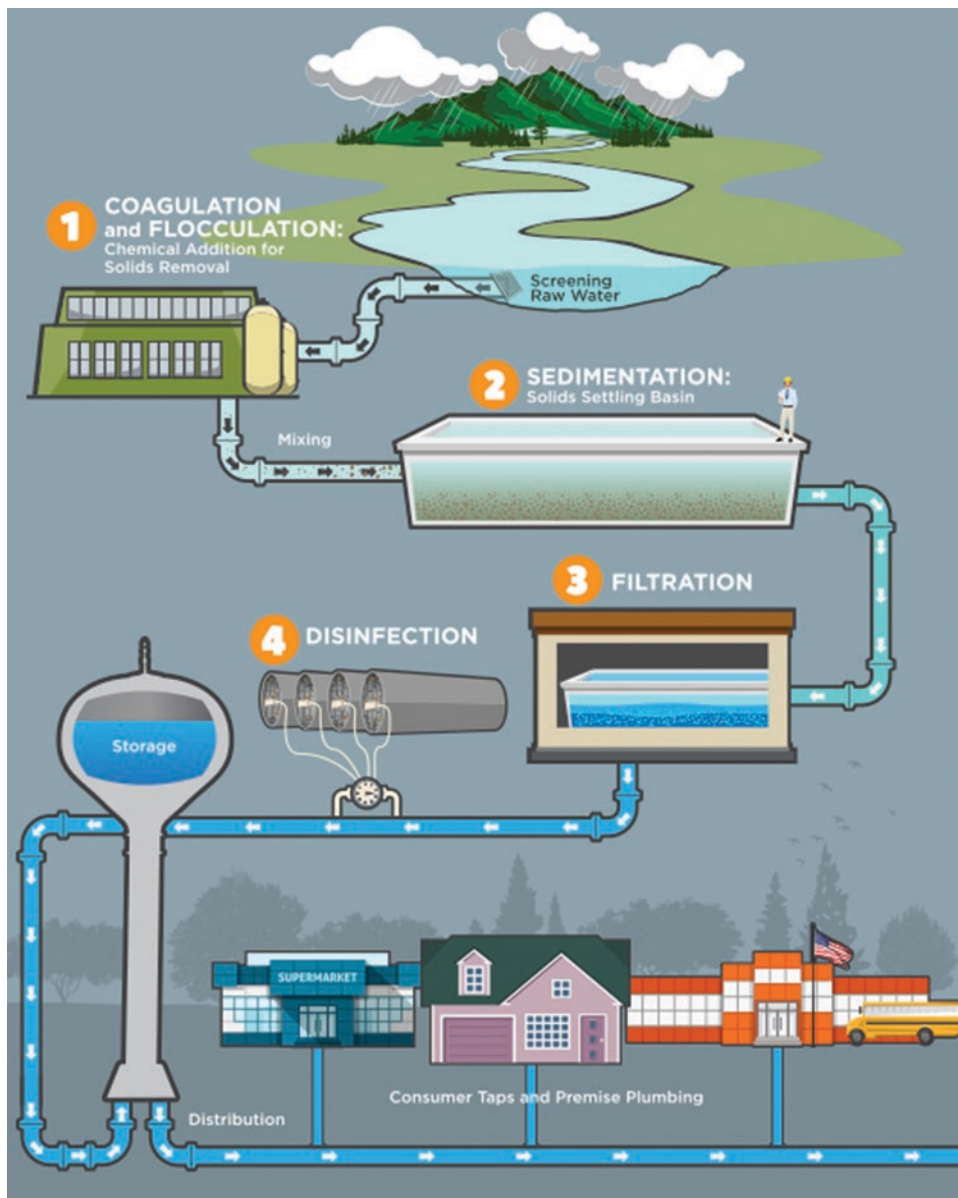
Conventional water treatment consists of coagulation and flocculation, sedimentation, filtration and disinfection steps (Figure 2.1). The addition of metal salts such as alum or iron is added to raw water to coagulate organic matter and other unwanted heavy metals that form larger masses (floc) that settle out of the water during the sedimentation stage. After sedimentation, water is filtered through a combination of materials or filters including sand, gravel, coal, activated carbons or membranes. After filtration disinfection chemicals, typically those that form free chlorine are added to the water to deactivate microorganisms. Conventional treatment is not or only partially effective against removal of many chemical contaminants (Table 2.4). Retrofitting current and building new treatment facilities with nanofiltration and other technologies needed to remove chemical contaminants from drinking water supplies are costly and prohibitive in many countries. Preventing contamination of drinking water and monitoring water quality to measure risk are increasingly important along with making changes and upgrades in treatment technologies.

### Water Treatment Chemicals

Chemical disinfectants and flocculants are critical to purifying water by reducing enteric pathogen loads and physical removal of potentially harmful particles from drinking water supplies and wastewaters. Flocculants and coagulants bind with metals and organic matter (OM), forming larger compounds that are precipitated out of water during filtration and sedimentation.

Treatment with chlorine or chlorinated compounds are the most commonly used chemicals in disinfection worldwide. Additional volumes of these compounds are added to sustain disinfection concentration levels throughout water distribution and storage. Most chemicals used in drinking water chlorination are mild irritants if levels are too high. The more serious health concerns are

**FIGURE 2.1.** Conceptual Diagram of Conventional Water Treatment from the American Chemistry Council's Publication On Drinking Water Chlorination [1]



caused by unintended and harmful disinfectant by-products (DBPs), leading to increased use of alternative treatments such as ultraviolet (UV) radiation and ozone. However, all treatment processes produce some form of harmful by-products that cause environmental and human health problems. Regulatory bodies have set guidelines for beneficial treatment chemicals, leachates from distribution systems, and harmful by-products to monitor and reduce drinking water and environmental contamination.

## Flocculants

Aluminum and iron are both found naturally in ground and surface waters worldwide. Aluminum and iron salts are added to water to coagulate and flocculate unwanted chemicals and OM that can be removed by filtration or sedimentation [2]. OM in source water is the key organic precursor to forming halogenated DBPs. Flocculants can also be used to remove both DBPs and their precursors. Recent lab research suggests that residuals from iron and aluminum coagulation and flocculation treatment may contribute to lead leachate from lead bearing pipes and solder during distribution [3].

Acrylamide is found in drinking water when intentionally added as polyacrylamide, a flocculent to reduce turbidity, and as a pollutant from industrial activities [4]. Acrylamide residuals are also a concern in surface and ground waters from use as a flocculent in wastewater treatment. Acrylamide has also been shown to form precursors to DBPs through chlorination during degradation [5]. The health risk associated with acrylamide has led to research exploring mixtures of polyacrylamides and starch-based alternatives [6].

Aluminum is generally considered to have low toxicity to humans in levels typically present in drinking water [7]. However, regulatory reviews cite concerns about research showing associations between aluminum levels found in drinking water and development of Alzheimer's disease [8,9]. WHO and Canada both reviewed this evidence and state that there is not enough evidence to consider aluminum as a critical neurotoxin in drinking water [10,11]. Canada has adopted an operational guideline based on WHO recommendations (Table 2.1), while the US EPA has established a non-enforceable secondary drinking water regulation of 0.05 to 0.2 mg/L maximum contaminant level [12].

Iron salts are considered as an alternative to alums because of concerns over chronic aluminum toxicity [13]. Iron is not considered to have acute toxicity concern at the levels found in drinking water, however, Canada has set aesthetic guideline because of its role in undesirable color and taste [14].

Residual acrylamide is a human neurotoxin and potential carcinogen [15-17]. WHO has set guidelines for drinking water while the US EPA has set treatment technique guidelines that provide legal processes for use (Table 2.1).

## Disinfectants

Compounds producing free chlorine are the most commonly and widely used to disinfect drinking water in both primary and secondary disinfection, first used in Europe in the 1890s and in the US in 1908 [1]. It is applied to drinking water as chlorine gas, sodium hypochlorite, calcium hypochlorite and sodium dichloroisocyanurate, forming a pH-dependent ratio of free chlorine, hypochlorous acid and hypochlorite in solution [21,22]. Chlorine is used for microbial disinfection mainly, but also acts as an oxidant, assisting in the removal or conversion of chemical contaminants [18].

Chlorine toxicity in drinking water is of minor concern. The most serious consequences of chlorine are its reactions with natural OM and other chemicals to form harmful DBPs [23]. As a result, chemical alternatives to free chlorine and other processes such as ozonation and UV disinfection are being used to reduce conventional chlorination, which produces the highest number of DBPs [24].

Chlorine dioxide and chloramines are chemical alternatives to using free chlorine that produce fewer halogenated DBPs than chlorination [25]. However, they all form some harmful DBPs [24] and can be

**TABLE 2.1. Regulatory Guidelines and Health Effects of Chemicals Used as Flocculants and Coagulants and Disinfectants in Drinking Water Treatment**

Regulation group	CAS ID number	WHO Guideline value	EU Parametric value	Health Canada Maximum Acceptable Concentrations	Health Canada Operational guidelines (mg/L)	Health Canada Aesthetic guidelines	US EPA Maximum Residual Disinfectant Level	US EPA Treatment technique	Health effects	Individual Chemical Names
<b>Flocculants</b>										
Aluminium	7429-90-5	-	0.2 mg/L	-	0.1 (conventional) & 0.2 (other treatment plants)	-	-	-	No consistent, convincing evidence that Al in drinking water causes adverse health effects in humans.	-
Iron	7439-89-6	-	0.2 mg/L	-	-	≤0.3 mg/L	-	-	None	-
Acrylamide	79-06-1	0.00005 mg/L	0.0001 mg/L	-	-	-	-	0.05% dosed at 1 mg/L	Nervous system or blood problems; increased risk of cancer	-
<b>Disinfectants</b>										
Chlorine	7782-50-5	5.0 mg/L	-	-	-	-	4.0 mg/L	-	Eye/nose irritation; stomach discomfortEPA	-
Chlorine dioxide	10049-04-4	-	-	-	-	-	0.8 mg/L	-	Anemia; infants and young children: nervous system effects EPA	-
Dichloramine	3400-09-7	-	-	3.0 mg/L	-	-	4.0 mg/L	-	Reduced body weight gain; Immunotoxicity effectsCA; Eye/nose irritation; stomach discomfort, anemia	-

*table continues next page*

TABLE 2.1. continued

Regulation group	CAS ID number	WHO Guideline value	EU Parametric value	Health Canada Maximum Acceptable Concentrations	Health Canada Operational guidelines (mg/L)	Health Canada Aesthetic guidelines	US EPA Maximum Residual Disinfectant Level	US EPA Treatment technique	Health effects	Individual Chemical Names
Dichloroisocyanuric acid	2893-78-9; 2782-57-2	50 mg/L <sup>a</sup> ; 40 mg/L <sup>b</sup>	-	-	-	-	-	-	Eye/nose irritation; stomach discomfort	<sup>a</sup> Sodium dichloroisocyanurate; <sup>b</sup> dichloroisocyanurate
Monochloramine	10599-90-3	3.0 mg/L	-	3.0 mg/L	-	-	4.0 mg/L	-	Reduced body weight gain; Immunotoxicity effects <sup>CA</sup> ; Eye/nose irritation; stomach discomfort, anemia	-
Trichloramine	10025-85-1	-	-	3.0 mg/L	-	-	4.0 mg/L	-	Reduced body weight gain; Immunotoxicity effects <sup>CA</sup> ; Eye/nose irritation; stomach discomfort, anemia	-

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada Guidelines [18-20]. Health Canada maximum acceptable concentration refer to maximum allowed concentration thresholds for finished drinking water. Health Canada operational guideline applies to treatment plants using aluminum-based coagulants. It does not apply to naturally occurring aluminum found in groundwater. Aesthetic quality guidelines address parameters which may affect consumer acceptance of drinking water, such as taste, odour and colour. US EPA maximum residual disinfectant level goal is the level of a drinking water disinfectant below which there is no known or expected risk to health. US EPA treatment technique is a required process intended to reduce the level of a contaminant in drinking water.

less efficient as microbial disinfectants or are costlier than chlorination alone. They are often used in combination with chlorination and other treatment methods.

Chlorine dioxide is a dissolved gas that is useful as a primary disinfectant, but is harder to maintain as a secondary disinfectant [1] than chlorination residuals. Chlorine dioxide treatment produces less halogenated DBPs than chlorination [26] and is a strong oxidant that is useful for controlling iron, manganese, taste and odor [25,27,28]. Chlorine dioxide is used in pre-oxidation and primary disinfection with free chlorine added to provide residual disinfection. This results in low levels of free chlorine (hypochlorous acid or hypochlorite ion) and chlorine dioxide, along with chlorite in the final water product.

Reactions between chlorine and chlorite can form chlorate at concentrations, depending on environmental conditions. Both chlorite and chlorate are harmful, commonly reported inorganic DBPs produced by chlorine dioxide treatment. Other DBPs, including carboxylic acids, ketones, aromatic compounds (e.g. naphthalene) and esters have also been found during experiments in treatment facilities [24]. At high levels, chlorite alters red blood cells and chlorate negatively impacts thyroid functions in laboratory animals [28,29].

Sodium dichloroisocyanurate produces free chlorine and is primarily used in emergencies or in household drinking water treatment [30] as well as in swimming pools and the food industry.

Monochloramine, dichloramine and trichloramine are formed by combining chlorine and ammonia [31]. The formation of each is dependent on pH, ammonia-chlorine ratios, temperature and contact time. Monochloramine is most commonly used in secondary disinfection due to its longer persistence than free chlorine residuals, while with dichloramine and trichloramine are undesirable by-products of chloramination of drinking water [18]. Chloramines have lower disinfectant power than free chlorine against resistant microorganisms (i.e. *Giardia* and *Cryptosporidium*) and are often not applied in primary disinfection.

Chloramine disinfection forms only trace amounts of trihalomethanes (THMs) and haloacetic acids (HAAs) compared to traditional chlorination [32]. The major drawback of monochloramine use is the formation of nitrogenous DBPs [33], some of which are dangerous to human health [34] and cause nitrification of drinking water [35].

Aside from occupational hazards associated with chlorine gas, chlorine in drinking water is only considered as an irritant. Residues of sodium dichloroisocyanurate are of little concern because, when in contact with saliva, they quickly form cyanuric acid which has low oral toxicity [36]. Chlorine dioxide is not considered to be dangerous to health as it quickly degrades to chlorite and chloride after ingested in drinking water [28].

### Disinfectant by-Products

The majority of risk of using free chlorine for drinking water disinfection is the formation of THMs and HAAs. In response, chemical alternatives such as chloramine has been promoted to reduce THMs and HAAs to acceptable levels. However, chloramines form halogenated acetonitriles and N-Nitrosodimethylamine (N-NDMA) by-products as well as producing nitrite and nitrate in finished drinking water. There is increasing concern with the number of unregulated emerging DBPs, with a



recent review identifying 110 species to include in their analysis. DBPs are also formed by alternatives to chlorination. Bromate is formed during ozonation with naturally occurring bromide in source waters [37].

Chlorine dioxide, another alternative to free chlorine treatment [25], degrades to form the inorganic ions chlorite and chlorate. Chlorite also combines with free chlorine, which can be added during secondary disinfection, to form chlorate [26,27]. Both are absorbed quickly into the blood plasma upon ingestion and are not considered to be dangerous to human health at levels typically present in drinking water. Neither are thought to persist long in the environment, though chlorate in groundwater in agricultural areas was associated with increased nitrate levels and may have originated from perchlorate originating in pesticides [38].

Trihalomethanes, including bromodichloromethane, bromoform, chloroform, dibromochloromethane, and HAAs including monochloroacetate, dichloroacetate, and trichloroacetate are formed when chlorine and organic matter are present together in water. THMs and HAAs were among the first regulated DBPs by the US EPA. TMH formation increases with chlorine concentration and residence times in the treatment facility or distribution system, while HAAs decrease with residence times [39]. TMHs concentration also increases with temperature, but the relationship between increasing temperature and HAAs is not as clearly associated, likely because of increased chemical and biological degradation rates as temperature increases [39].

In a review of Volatile Organic Compounds (VOCs) in drinking and environmental waters, the most common trihalomethanes detected in drinking water as disinfection by-products were trichloro- and tribromomethane, bromodichloromethane, and dibromochloromethane [40]. Trihalomethanes were the widely detected group of VOCs in US groundwaters as sampled through untreated drinking wells [41]. These may be entering groundwater as a result of DBPs, but they are also present in a wide range of industrial and household products (e.g. solvents, paints and glues).

Chronic exposure to TMH has been associated with bladder cancer [42], though identifying causative chlorination DBP agents of bladder cancer is still difficult from epidemiological studies [43]. The health consequences of THM in drinking water include those from oral ingestion and from skin absorption during bathing, in the case of chloroform [44]. Some of the HAAs are associated with tumor formation in animal models. For example, bromate was associated renal tumor formation also in rats and mice [43].

There is increased interest in nitrogenous disinfection by-products (N-DBPs) that have been studied and regulated less than other DBPs, because they demonstrate higher geno- and cytotoxicity than THMs and HAAs and are formed from increasing uses of chloramines as treatment chemicals to reduce formation of THMs and HAAs [33]. N-DBPs are formed when free chlorine or inorganic chloramine are added to water during treatment and react with organic dissolved nitrogen or organic dissolved carbon present in water. This group includes N-Nitrosodimethylamine and the halogenated acetonitriles (e.g dibromoacetonitrile and dichloroacetonitrile). The formation of N-DBPs will be determined also by the type and timing of disinfection chemicals.

**TABLE 2.2. Regulatory Guidelines and Health Effects of Disinfection By-Products Formed During Drinking Water Treatment**

Regulation group	CAS ID number	WHO Guideline value	EU Parametric value	Health Canada Maximum Acceptable Concentrations	US EPA Maximum Contaminant Level	Health effects	Individual Chemical Names
Bromate	15541-45-4	0.01 mg/L	0.01 mg/L	0.01 mg/L	0.01 mg/L	Renal cell tumours; Increased risk of cancer	-
Chlorate	14866-68-3	0.7 mg/L	-	1 mg/L		Thyroid gland effects (colloid depletion)	-
Chlorite	14998-27-7	0.7 mg/L	-	1 mg/L	1 mg/L	Neurobehavioural effects , decreased absolute brain weight, altered liver weights; Anemia; infants and young children: nervous system effects	-
Chlorophenols	87-86-5; 88-06-2; 120-83-2; 58-90-2	0.009 mg/L <sup>a</sup> ; 0.2 mg/L <sup>b</sup>	-	0.06 mg/L <sup>a</sup> ; 0.1 mg/L <sup>b</sup> ; 0.005 mg/L <sup>c</sup> ; 0.1 mg/L <sup>d</sup>	0.001 mg/L <sup>a</sup>	Reduced body weight, changes in clinical parameters, histological changes in kidney and liver, reproductive effects, Liver cancer , Liver effects, Developmental effects; Liver or kidney problems; increased cancer risk	<sup>a</sup> Pentachlorophenol; <sup>b</sup> 2,4,6-Trichlorophenol; 2,4-Dichlorophenol ; <sup>c</sup> 2,3,4,6-Tetrachlorophenol
Haloacetic acids	13425-80-4; 14526-03-5; 14357-05-2; Total haloacetic acids	0.05 mg/L <sup>a</sup> ; 0.02 mg/L <sup>b</sup> ; 0.2 mg/L <sup>c</sup>	-	0.08 mg/L (Total)	0.06 mg/L (Total)	Liver cancer (DCA); Other organ cancers (DCA, DBA, TCA); liver and other organ effects (MCA); Increased risk of cancer	Dichloroacetate; Monochloroacetate; Trichloroacetate
Halogenated acetonitriles	3252-43-5; 3018-12-0	0.07 mg/L <sup>a</sup> ; 0.02 mg/L <sup>b</sup>	-	-	-		<sup>a</sup> Dibromoacetonitrile; <sup>b</sup> Dichloroacetonitrile
N-Nitrosodimethylamine	62-75-9	0.0001 mg/L	-	0.00004 mg/L		Liver cancer (classified as probable carcinogen)	
Trihalomethanes	75-27-4; 75-25-2; 67-66-3; 124-48-1	0.06 mg/L <sup>a</sup> ; 0.1 mg/L <sup>b</sup> ; 0.005 mg/L <sup>c</sup> ; 0.1 mg/L <sup>d</sup>	0.1 mg/L (Total)	0.1 mg/L (Total)	0.08 mg/L (Total)	Liver effects (fatty cysts); Kidney and colorectal cancers; Liver, kidney or central nervous system problems; increased risk of cancer	<sup>a</sup> Bromodichloromethane; <sup>b</sup> Bromoform; <sup>c</sup> Chloroform; <sup>d</sup> Dibromochloromethane

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada maximum acceptable guidelines [18-20]. Chemical abstracts service numbers (CAS) are listed in the second column. Health Canada maximum acceptable concentration refer to maximum allowed concentration thresholds for finished drinking water. Health Canada operational guideline applies to treatment plants using aluminum-based coagulants. It does not apply to naturally occurring aluminum found in groundwater. Aesthetic quality guidelines address parameters which may affect consumer acceptance of drinking water, such as taste, odour and colour. US EPA maximum residual disinfectant level goal is the level of a drinking water disinfectant below which there is no known or expected risk to health. US EPA treatment technique is a required process intended to reduce the level of a contaminant in drinking water.

**TABLE 2.3. Regulatory Guidelines and Health Effects of Chemicals Formed During Drinking Water Distribution and Wastewater Treatment**

Regulation group	CAS ID number	WHO Guideline value	EU Parametric value	Health Canada Maximum Acceptable Concentrations	Health Canada Aesthetic guidelines	US EPA Maximum Contaminant Level (mg/L)	US EPA Treatment technique	Health effects	Individual Chemical Names
<b>Distribution</b>									
Cadmium	7440-43-9	0.003 mg/L	0.005 mg/L	0.005 mg/L	-	0.005 mg/L	-	Kidney damage and softening of bone	-
Lead	7439-92-1	0.01 mg/L	0.01 mg/L	0.01 mg/L	-	-	0.015 mg/L	Biochemical and neurobehavioural effects (intellectual development, behaviour) in infants and young children (under 6 years); Anaemia, central nervous system effects; in pregnant women, can affect the unborn child; in infants and children under 6 years, can affect intellectual development, behaviour, size and hearing; classified as probably carcinogenic to humans <sup>CA</sup> ; Adults: Kidney problems; high blood pressure	-
Nickel	7440-02-0		0.07	-	-	0.02	-	Dermatitis, carcinogenic	-
Polycyclic aromatic hydrocarbons	50-32-8; 206-44-0	0.0007 mg/L	0.0001 mg/L	0.00004 mg/L <sup>a</sup>	-	0.0002 mg/L <sup>a</sup>	-	Stomach tumours <sup>CA</sup> ; Reproductive difficulties; increased risk of cancer	<sup>a</sup> Benzo[a]pyrene; <sup>b</sup> Fluoranthene
Sulfide	18496-25-8	-	-	-	≤ 0.05 mg/L	-	-	None; Foul taste and odor	-
Vinyl chloride	75-01-4	0.0003 mg/L	0.0005 mg/L	0.002 mg/L	-	0.002 mg/L	-	Liver cancer; Raynaud's disease, effects on bone, circulatory system, thyroid, spleen, central nervous system <sup>CA</sup> ; Increased risk of cancer	-

*table continues next page*

TABLE 2.3. continued

Regulation group	CAS ID number	WHO Guideline value	EU Parametric value	Health Canada Maximum Acceptable Concentrations	Health Canada Aesthetic guidelines	US EPA Maximum Contaminant Level (mg/L)	US EPA Treatment technique	Health effects	Individual Chemical Names
Zinc	7440-66-6	-	-	-	≤ 5.0 mg/L	-	-	-	-
Copper	7440-50-8	2 mg/L	0.002 mg/L	-	≤ 1.0 mg/L	1.3 mg/L	1.3 mg/L	Short term exposure: Gastrointestinal distress; Long term exposure: Liver or kidney damage; People with Wilson's Disease should consult their personal doctor if the amount of copper in their water exceeds the action level	-
<b>Wastewater treatment</b>									
Nitritotriacetic acid	139-13-9	0.2 mg/L	-	0.4 mg/L	-	-	-	Kidney effects (nephritis and nephrosis); Classified as possible carcinogen	-
Nitrogen anions	14797-55-8; 14797-65-0	50 mg/L <sup>a</sup> ; 3 mg/L <sup>b</sup>	50 mg/L <sup>a</sup> ; 0.5 mg/L <sup>b</sup>	10 mg/L <sup>c</sup> ; 1 mg/L <sup>d</sup>	-	10 mg/L <sup>c</sup> ; 1 mg/L <sup>d</sup>	-	Methaemoglobinaemia (blue baby syndrome) and effects on thyroid gland function in bottle-fed infants; Classified as possible carcinogen under conditions that result in endogenous nitrosation	<sup>a</sup> Nitrate; <sup>b</sup> Nitrite; <sup>c</sup> N in Nitrate ; <sup>d</sup> N in Nitrite
Sodium	7440-23-5	-	200 mg/L	-	≤ 200 mg/L	-	-	-	-

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada maximum acceptable guidelines [18-20]. Chemical abstracts service numbers (CAS) are listed in the second column. Health Canada maximum acceptable concentration refer to maximum allowed concentration thresholds for finished drinking water. Health Canada operational guideline applies to treatment plants using aluminum-based coagulants. It does not apply to naturally occurring aluminum found in groundwater. Aesthetic quality guidelines address parameters which may affect consumer acceptance of drinking water, such as taste, odour and colour. US EPA maximum residual disinfectant level goal is the level of a drinking water disinfectant below which there is no known or expected risk to health. US EPA treatment technique is a required process intended to reduce the level of a contaminant in drinking water.

N-Nitrosodimethylamine can be formed from nitrogen contributed during chloramine treatment or from dissolved organic nitrogen. Increased nitrate and nitrogen are both sources of dissolved organic nitrogen in drinking water sources. If not removed before treatment with free chlorine or chloramine, dissolved organic nitrogen increase the probably of N-Nitrosodimethylamine formation [45].

### Distribution

Materials used for piping and connections must be regularly monitored as they can become sources of contamination as they age. Additionally, primary and secondary treatment chemicals reach levels that can corrode distribution materials and cause chemicals to dissolve into water supplies. The impact of treatment and pre-distribution DBP chemicals on corrosion depends upon the type and residence time of those chemicals and will vary widely depending on piping and solder used in the distribution system.

Corrosion in pipes can create scales that adsorb heavy metals, such as aluminum, lead, copper, cadmium, arsenic and zinc [46]. Aging pipes and pipe fittings can also corrode and potentially release lead, cadmium and nickel into drinking water supplies [47-49]. Polyvinyl chloride (PVC) pipes can also leach lead, as well as vinyl chloride into the drinking water supply [47,50]. A large EPA study to identify and quantify contaminants in lead pipe scale in several sites throughout the US found lead in the largest amounts, followed by zinc, copper, nickel, mercury, chromium, cadmium and arsenic [51]. Higher levels of arsenic have been found adsorbed to iron pipes in sites in Ohio and Michigan [52].

Polycyclic Aromatic Hydrocarbons (PAHs) exposures typically occur through inhalation rather than oral ingestion. Their presence in drinking water is likely due to the use of coal tar-based lined pipes in the water distribution system [53]. WHO has recommended the removal and discontinued uses of coal tar-based pipe lining. Benzo[a]pyrene is the most carcinogenic PAH, while Fluoranthene is the most detected in water distribution systems [53].

### Wastewater Treatment Chemicals

Several classes of emerging chemicals, including bromoform, a trihalomethane, were found in drinking water treatment plant (WTP) source streams and in raw water intakes [54]. Both source streams had significant effluent from sewage treatment plants upstream of the WTP and could be interpreted as bromoform entering the environment through sewage treatment processes or through industrial effluent. The authors did not specifically discuss bromoform at length as it was just one of 106 chemicals tested in the study.

The result of these studies indicate that many anthropogenic sources of chemical contaminants are enter drinking water sources during sewage treatment. Notably, conventional plants are only designed to eliminate contaminants that can be oxidized or other inorganic contaminants such as phosphorus, not trihalomethanes. Many of these contaminants are discussed further in the emerging chemicals chapter.

**TABLE 2.4. List of Chemicals Adapted from the United States Environmental Protection Agency Drinking Water Treatment Database [55] and the Effectiveness of Conventional Water Treatment At Removing Them from Drinking Water Based On Literature Review Up To 2009**

Chemical	Chemical Abstracts Service number (CAS)	Removal by Conventional Treatment	Description
1,4-dioxane	123-91-1	Ineffective	diethylene dioxide, diethylene ether, dioxane, glycol ethylene ether, p-dioxane
17a-ethynyl estradiol	57-63-6	Ineffective	EE2
4-Nonylphenol	104-40-5	Ineffective	4-Nonylphenol, 4-n-Nonylphenol, NP, Nonylphenol, p-Nonylphenol, para-Nonylphenol
Acetochlor	34256-82-1	Ineffective	Acenit, Harness, Surpass, Top Hand, Trophy
Acetochlor Degradates		Ineffective	acetochlor ethanesulfonic acid (ESA), acetochlor oxanilic acid (OXA), acetochlor sulfinylacetic acid
Alachlor	15972-60-8	Not very effective	Alanex, Alochlor, Lasso, Lazo, Metachlor, Pillarzo
Alachlor Degradates		Ineffective	alachlor oxanilic acid (OA), alachlor ethanesulfonic acid (ESA)
Aldicarb	116-06-3	No data	Ambush, OMS 771, Temic, Temik, UC 21149 , Unioin Carbide 21149
Arsenic	7440-38-2	Very effective	Arsenate, Arsenite, As(3), As(5)
Carbofuran	1563-66-2	No data	Curaterr, Furadan, Yaltox
Chlortetracycline	57-62-5	Not very effective	7-chlorotetracycline, Aureomycin, CLTC, CTC, Chlorotetracycline, Chlortetracyclin
Chromium	7440-47-3	Very effective	Chromium (III), Chromium (VI), Cr (III), Cr (VI), Hexavalent Chromium, Trivalent Chromium
Diuron	330-54-1	Not very effective	Crisuron, Diater, Direx, Karmex, N-(3,4-dichlorophenyl)-N,N-dimethyl urea, Unidron
Fluoride	7664-39-3	Moderately effective	fluorhydric acid, fluoric acid, hydrofluoric acid, hydrofluoride
Glyphosate	1071-83-6	Ineffective	Pondmaster, Rodeo, Rondo, Roundup
Ibuprofen	15687-27-1	Ineffective	Advil, Brufen, Hydratropic acid, Ibufen, Motrin
Mercury	7439-97-6	Very effective	Hg(0), Hg(2), hydrargyrum, quicksilver
Metolachlor	51218-45-2	Ineffective	Bicep, Codal, Dual, Milocep
Metolachlor Degradates		Ineffective	Metolachlor ESA, Metolachlor OA, Metolachlor ethane sulfonic acid, Metolachlor oxanilic acid
Microcystins		Little to moderately effective	Microcystin-LR
Natural Organic Matter		Effective	AOC, BDOC, DOC, DOM, NOM, SUVA, TOC, assimilable organic carbon, biodegradable dissolved organic carbon, dissolved organic carbon, dissolved organic matter, fulvic acid, humic acid, specific ultraviolet absorbance, total organic carbon

*table continues next page*

TABLE 2.4. continued

Chemical	Chemical Abstracts Service number (CAS)	Removal by Conventional Treatment	Description
Perfluorooctane Sulfonate	1763-23-1 (PFOS acid)	Ineffective	1-Octanesulfonic acid, 1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-, 1-Octanesulfonic acid, heptadecafluoro-, 1-Perfluorooctanesulfonic acid, Hepatadecafluoro-1-octanesulfonic acid, Perfluoro-n-octanesulfonic acid, Perfluorooctane Sulfonate, Perfluorooctane Sulphonate, Perfluorooctanesulfonic acid, Perfluorooctyl Sulfonate, Perfluorooctylsulfonic acid
Perfluorooctanoic Acid	335-67-1	Ineffective	C8, PFOA, perfluorooctanoate
Simazine and Simazine Degradates	122-34-9	Ineffective	Aquazine, Framed, Gesatop, Premazine, Primatol, Princep, Simadex
Trichloroethylene	79-01-6	Moderately effective	TCE, Trichloroethene

*Note:* Although removal categories in the removal by conventional treatment column are not explicitly defined in the US EPA database, a review of the descriptions roughly correspond to the following removal percentages: ineffective (0%-35% removal), not very effective (35%-50% removal), moderately effective (40%-70% removal), effective (70%-98% removal), very effective (99%-100% removal).

## Conclusions

Chemical contaminants originating from water treatment processes are of particular concern because of how directly that can impact human populations relying on piped water sources. DBP contaminants from wastewater treatment threaten sources of drinking water after being released into surface waters. Controlling DBP exposure and release into the environment requires monitoring at treatment, storage and distribution stages.

While very effective at removing biological contaminants, with the exception of microcystin, there is increasing concern that conventional water treatment does not remove many types of chemical contaminants. The EPA has reviewed literature on lab and field tests of contaminant removal efficiencies during different drinking water treatment facilities [55]. While conventional treatment is effective at removing fecal coliforms and some heavy metals, there are many industrial contaminants and pesticides that were not removed from conventional water treatment (Table 2.4).

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## Chapter 3

# Agricultural Chemicals

### Introduction

Chemical contaminants from agricultural activities enter surface water as runoff from pesticide and fertilizer applications to fields and crops, but also during improper storage or accidental spills during handling. Most contaminants in this category enter drinking water sources through non-point sources, or pollutants that are diffuse across the landscape. As precipitation accumulates as runoff, contaminants in runoff flow into surface and ground water. With the exception of spills or leaks, fertilizers and pesticides used in agriculture are considered nonpoint source pollutants. Most of the chemical contaminants in this group are used in agricultural production but are also commonly for landscaping industrial and residential properties and aquatic weed control in clearing waterways.

Definitions: Pre-emergence herbicides prevent the germination or establishment of weeds and are applied before weed seeds germinate.

### Fertilizers

Inorganic fertilizers are widely used and essential to agricultural productivity worldwide. Over-enrichment of soils with inorganic fertilizers has led to large amounts of nitrogen and phosphorus entering surface and ground waters and aquatic ecosystems across the world [1]. Though essential building blocks for plants and ecosystem nutrient cycles, excessive nitrogen and phosphorus are leading pollutants of drinking water. Nitrates and nitrites can be toxic and, along with phosphorus, can degrade water quality through eutrophication of water bodies [2,3].

Nitrogen and phosphorus are two limiting factors to plant growth. When these nutrients are released into aquatic ecosystems in excess, populations of photosynthetic primary producers including phytoplankton, cyanobacteria, algae and macrophyte plants grow rapidly [4]. The most common symptom of eutrophication in a water body occurs when excessive growth of primary producers significantly reduces oxygen necessary for supporting biota in aquatic ecosystems. If high populations of primary producers includes cyanobacteria, the result can be production of toxins such as microcystins.

### Nitrogen Ions

As a result of abundant use in modern, conventional agriculture, nitrate ( $\text{NO}_3^-$ ) and nitrite ( $\text{NO}_2^-$ ) ions are frequently found in ground and surface waters, especially in proximity to large or high concentrations of agricultural operations. In a 28 year study of nitrogen fertilizer fate in plant uptake and soil retention, 61 to 65% was taken up by plants, 12 to 15% remained in soil organic matter and 8 to 12% entered the hydrosphere [5]. Release from the soil to hydrosphere is predicted to continue for up to 50 years. Appropriate applications to growing biomass and managing soils for organic matter content are key to reducing excess nitrogen. Preventing nitrate and nitrite exposure in drinking water is best

managed by reducing concentrations in source waters due to difficulties in later removing them from drinking water [6].

In addition to fertilizer sources, nitrate, nitrite and other excess nutrients can also enter drinking water supplies through other nonpoint and point sources of untreated animal and human waste. Nitrates have been widely detected in numerous studies of domestic wells at concentrations exceeding recommended drinking water guidelines [7,8] and are often associated with mixtures of other volatile organic compounds and pesticides [9,10].

Nitrates and nitrites ingested through drinking water can induce methemoglobinemia in adults and is particularly dangerous for bottle-fed infants between the ages of 3-6 [11]. Methemoglobin forms when nitrite oxidizes ferrous iron of hemoglobin and prevents oxygen transport [12]. Some nitrate is converted into nitrite through endogenous bacteria in the saliva and intestinal tract. When methemoglobin levels reach 10% of circulating hemoglobin, the skin starts to show bluish or brownish gray coloring, called blue baby syndrome in infants. At above 60%, there is a high risk of mortality [12]. Treating water oxidizes nitrite to nitrate, the less toxic form, and reduce gastroenteritis which is a risk factor for methemoglobinemia in infants.

Subchronic exposures to nitrate and nitrite have been linked to problems with thyroid function and thyroid hormone concentration through nitrate inhibition of iodine uptake. Chronic exposures to nitrate and nitrite have been linked to cancer, but evidence is inadequate to conclude a causal mechanism. Nitrite can form N-DBPs, such as N-Nitrosodimethylamine, some of which have been shown to be carcinogenic to humans [13]. As a result of the potentially health impacts from nitrite and nitrate exposure, guidelines and regulations have been set by the WHO and regulatory bodies reviewed in this chapter (Table 3.1).

### Cyanobacterial Toxins

Eutrophication in a water body occurs when excessive growth of phytoplankton reaches levels that significantly reduces total dissolved oxygen necessary for supporting biota in aquatic ecosystems. In lakes and reservoirs cyanobacterial (blue-green algae) blooms are caused by *Microcystis* and *Anabaena* spp. in temperate areas and *Cylindrospermopsis* spp originating in tropical areas [14,15]. Polluted agricultural runoff, seasonal patterns of rainfall, and regional distribution of cyanobacterial species contribute to the types of blooms and whether or not these blooms will produce toxins [2,16,17].

Cyanotoxins produced by cyanobacteria include cyclic peptides, alkaloids, and lipopolysaccharides [18]. Of these, only microcystin-LR has a suggested WHO guideline [15]. Microcystins are acute hepatotoxins that impact the liver by inhibiting phosphatases and may be carcinogenic with chronic exposure at low doses [17]. Microcystin-LR is the most common isoform and only WHO has based guidelines for Microcystin-LR based on available health information (Table 3.1).

### Pesticides

Widespread use of chemical pesticides began in the 1940s and 50s. In 2012, worldwide consumption of pesticides was estimated at 2.6 million metric tons, which is likely an underestimate because of little market data on small acreage crops [22]. Herbicides make up nearly 50% of pesticides used, followed by

**TABLE 3.1. Regulatory Guidelines and Health Impacts of Fertilizers**

Chemical	CAS ID	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	EU Parameter (mg/L)	Health impacts
<b>Fertilizers</b>						
Nitrate	14797-55-8	50 (as NO <sub>3</sub> <sup>-</sup> )	10 as nitrate-nitrogen	45 as nitrate; 10 as nitrate-nitrogen	50 (as NO <sub>3</sub> <sup>-</sup> )	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome; Effects on thyroid gland function in bottle-fed infants; Classified as possible carcinogen under conditions that result in endogenous nitrosation
Nitrite	14797-65-0	3 (as NO <sub>2</sub> <sup>-</sup> )	1 as nitrite-nitrogen	3 as nitrite; 1 as nitrite-nitrogen	0.5 (as NO <sub>2</sub> <sup>-</sup> )	Infants below the age of six months who drink water containing nitrite in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome; Classified as possible carcinogen under conditions that result in endogenous nitrosation
<b>Cyanobacterial toxin</b>						
Microcystin-LR	101043-37-2	0.001 (P)	-	-	-	Liver toxicity

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada Guidelines [6,20,21].

WHO Guideline key: A, provisional guideline value because calculated guideline value is below the achievable quantification level; P, provisional guideline value because of uncertainties in the health database;

T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

insecticides, fumigants and fungicides. Pesticides are one of the most common chemicals from human activity detected in surface waters. A recent joint study that sampled 38 streams (32 by impacted by urban/agriculture developed and 4 undeveloped sites) from across the United States found that 8 of the top 10 chemicals detected were pesticides [23].

Globally, overall pesticide use is increasing along with population and global crop production [24]. The proportion of insecticides used is expected to decline, while herbicide use is expected to continue increasing [24,25]. Some of the decline in the proportion of insecticides used is due to genetic engineering of crops such as corn genetically modified with *Bacillus thuringiensis* (Bt) genes and pesticide resistance. Herbicide usage has increased dramatically since 2005 due largely to genetic engineering of crops to be resistant to herbicides, particularly glyphosate. Overall, estimates of the human and ecological impacts of increased overall use of pesticides on human health lag far behind the amounts and types of pesticides being introduced to food and water supplies and the environment [26].

Throughout the chapter, we refer to the WHO recommended pesticide hazard classifications as a quick reference for toxicity [27]. WHO classifications are based on estimated acute toxicity of humans handling each pesticide derived from a series of criteria around acute oral and dermal toxicity in rats. WHO Classes are Extremely (Ia), Highly (Ib), Moderately (II), and Slightly (III) hazardous, with two additional categories of Unlikely to present acute hazard (U) and Obsolete chemicals unlikely to be in use, currently (O). While acute toxicity during handling is different than exposure through drinking water, these categories provide a useful guide to the underlying toxicity of pesticide contaminants.

European Union pesticide guidelines are universal for all pesticides in drinking water. The maximum for any individual pesticide is 0.1 mg/L. Total pesticides detected in drinking water should not exceed 0.5 mg/L [19].

## Herbicides and Fungicides

### Chloroacetanilide herbicides

Two common chloroacetanilide herbicides that are subject to regulation or guidelines are alachlor and metolachlor. These are pre-emergence herbicides applied to a variety of agricultural crops to prevent germination of many grasses and some broadleaf weeds [28]. There is increasing concern about environmental degradates of chloroacetanilide herbicides being detected in surface waters [29]. Metolachlor is one of the top 10 organic anthropogenic chemicals detected in streams across the United States [23] and was found to be one of the most common elements in combination with Atrazine in a nationwide study of pesticides in wells across the US [30]. Alachlor was also consistently detected in mixtures with other compounds included in the study. In a study of 12 water treatment plants in the Midwestern US, alachlor and metolachlor were detected in upstream river intakes and in finished drinking water samples, though alachlor concentrations were below US EPA MCL guidelines and metolachlor is not regulated by the US EPA [31].

Existing regulations and guidelines (Table 3.2) have been established for alachlor based on toxicity to the liver, kidney, spleen and eyes in animal models [32] and is carcinogenic in rats [6]. Metolachlor has been shown to cause liver lesions and cause tumors in nasal cavities of rats [33].

### Chlorotriazine herbicides

As with chloroacetanilide herbicides, there are concerns over chlorotriazine herbicides and also for degradates formed in the environment and detected in surface waters [29].

Atrazine, simazine and propazine are often collectively referred to as triazines.

Atrazine was the 2<sup>nd</sup> most widely used pesticide, behind glyphosate in a study of 21 crops in 2008 [25]. A study of chloroacetanilide herbicides in 12 water treatment plants in the Midwestern US found atrazine near or above US EPA MCL levels seasonally [31]. This indicates that conventional water treatment is not completely effective at removing atrazine and other pesticides in drinking water in the US.

Regulations and guidelines have been set for atrazine and simazine by all agencies and the WHO (Table 3.2). Atrazine has been shown to decrease body weights of offspring and impact the reproductive system of adults in animal models [34]. Simazine increased tumors in rats but not in mice, and is considered not classifiable as carcinogenic in humans by IARC [35].

### Phenoxy herbicides

The selective control of broadleaf plants in monocotyledon grass crops such as wheat or corn has enormous value for conventional agricultural systems. This appeal has led to the widespread use of phenoxy herbicide compounds in food production, forestry, pasture and turf grass management, and aquatic weed control worldwide. [36]. Phenoxy herbicides have been in use for about 60 years and were often contaminated with dioxins in early years of their use [37]. The most infamous member of this group was Agent Orange, a chemical mixture of 2,4-Dichlorophenoxyacetic acid (2,4-D) and 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T), which was used by the United States military as a defoliant during the Vietnam war. Phenoxy herbicides are increasingly used in lawn care in North America [38].

Phenoxy herbicides are weak acids that are slightly water soluble and often converted to more soluble amines before mixing with other agents for easier application [36]. They can persist in soils with half-lives ranging from days to up to months [37] and are not thought to regularly contaminate ground water [39]. Phenoxy herbicides are also detected and persist in surface waters for days up to months [37,40,41] and can persist in drinking waters after treatment at lower levels, though permissible levels in the Canadian Great Plains [42]. The compounds 2,4-D and MCPA are of the most widely known phenoxy herbicides worldwide along with 2,4,5-T, which has been banned in many countries and in international trade [27]. 2,4-D is used to control aquatic plants as well and persists much longer with a half-life of 186 days in aquatic sediments [43].

Toxicity of phenoxy herbicides caused a range effects on body weight, and kidney, liver, blood and adrenal functions in animal studies and a smaller number of human epidemiological studies (Table 3.2) Many phenoxy herbicides had been considered to be potentially carcinogenic to humans based mainly on associations between occupational exposures and cancer rates. However, reviews of studies linking phenoxy herbicides have revealed inconsistent evidence of a causal relationship between phenoxy herbicides and cancer [44,45], some specific to 2,4-D [46] and MCPA [47].

Critical limitations to some of this research is the difficulty of controlling for combined usage of other pesticides and contamination with dioxins.

### **Organophosphorus herbicides**

Glyphosate is the only regulated herbicide in this group, but is one of the most popular and most produced (by volume) and used herbicides in the world [48]. Several major crops have been genetically engineered with glyphosate resistance. This has led to increased applications and has contributed to increased glyphosate resistance in weeds [49]. In addition to extensive agricultural use, glyphosate is also used in lawn maintenance and landscaping in residential and commercial properties [38]. Glyphosate is bound tightly in the soil and not considered a threat to entering groundwater, with some limited leaching in sandy soils, and is only likely to contaminant surface waters when used next to water bodies [50].

Glyphosate was not considered by WHO to occur in large enough quantities to cause health risks in drinking water [51]. Health Canada and the US EPA both set guidelines for drinking water based on negative impacts on kidney function, reproductive systems and body weight changes in animal models [52].

### **Phenylurea herbicides**

The Phenylurea herbicides typically interrupt photosynthesis by inhibition of photosystem II. Diuron is the most commonly used pesticides in this group and is one of the most widely used pesticides in the United States. Health Canada has recommended the maximum acceptable concentration of diuron based on evidence of weight loss, increased liver weight and blood effects [53]. Chemically, phenylurea is a urea molecule that has hydrogens substituted for methyl groups and a 3,4-dichlorophenyl group. Diuron has been linked to potential formation of *N*-nitrosodimethylamine (NDMA, a disinfection by-product) during water treatment disinfection, reacting with chloramine and chlorine [54].

Chlorotoluron is a pre- or early post-emergence herbicide and Isoproturon is a selective herbicide used to control grasses and broad-leafed weeds in grain crops. Chlorotoluron biodegrades slowly more slowly than isoproturon, which persists for days up to weeks and both are highly mobile in soils [6]. Both have been detected in drinking water and Isoproturon has been detected in both surface and ground water [6]. The WHO guideline for chlorotoluron is set based on evidence of its carcinogenic potential [55]. The WHO guideline for isoproturon is set based on evidence of toxic effects on the liver and as a tumor promotor [56].

### **Quaternary ammonium herbicides**

Diquat and Paraquat are the two main regulated herbicides in this group and both cause acute and chronic toxicity in humans. Paraquat is considered one of the most toxic widely used pesticides. Diquat is less toxic than paraquat. Both are thought to degrade rapidly in the environment, despite high toxicity, resulting in WHO deciding not to set a recommended guideline because they are unlikely to occur at levels presenting significant health risk in drinking water or drinking water sources [6,57].

Paraquat is one of the most acutely toxic of chemicals used as herbicides and is of interest because of evidence supporting neurological toxicity. Paraquat has high cytotoxicity, causing cell damage the lungs and kidneys, where it accumulates upon exposure and other organs. Paraquat is one of the few herbicides suspected as a neurotoxin. It is hypothesized to cause Parkinson's disease or similar symptoms



because its chemical structure is similar to a toxic metabolite of MPTP (1-methyl-4-phenyl-1,2,3,6-tetrahydropyridine), which has been shown to cause neurological damage producing symptoms similar to those of Parkinson's disease [58].

Paraquat usage has been banned in many countries and several companies have voluntarily discontinued its use over concerns of health and environmental risks, particularly for associations with Parkinson's Disease [59]. Based on historic usage and high acute toxicity, Health Canada has set regulatory guidelines (Table 3.2), though the report states that it is unlikely to end up in finished drinking water when applied in terrestrial contexts, it is likely to persist when used in aquatic applications [60]. The US EPA and Health Canada have both set regulatory guidelines for diquat due to development of cataracts.

#### **Thiocarbamate herbicides**

Herbicides known as thiocarbamates are primarily used as pre-emergence weed control, preventing the establishment of germinated weeds and similar to chloroacetanilide herbicides [28]. Molinate is used to control weeds in rice crops. Limited environmental data suggests that groundwater contamination from molinate may be concentrated in rice growing regions, though does not persist long in water or soil with a half-life of 5 days [6]. WHO has set the guideline for molinate based on toxicity to the male reproductive system (Table 3.2).

#### **Algicides**

Endothall has both terrestrial and aquatic applications and is listed as in Toxicity Category I (highly toxic and severely irritation) for oral and ocular routes [61]. However, the EPA did not consider it a threat to drinking water under normal application rates. Though highly mobile in soil, endothall is not thought to be a threat to groundwater because of rapid degradation [61,62]. A study of pesticides in wells in Michigan, USA did not find Endothall in 200 samples collected across 34 counties [43].

### **Insecticides, Acaricides and Nematicides**

#### **Carbamate insecticides**

Carbamate insecticides are widely used insecticides that have similar modes of toxicity to organophosphorus insecticides but are generally less severe. Carbamate insecticides are toxic to the nervous systems of humans and other mammals by inactivating acetylcholinesterase, an enzyme that helps form neurotransmitters [63]. Aldicarb and Carbaryl are two of the top insecticides used in the United States [25] and are popular globally.

Aldicarb has an established WHO guideline due to its high acute neurotoxicity (WHO hazard class 1a) and high toxicity in mammals that are likely to occur in humans [64,65]. It is likely that US EPA and Health Canada have not established guidelines for drinking water due to findings that indicate it is unlikely to be present drinking water at levels high enough to cause health concern [66]. Carbaryl has established guidelines by Health Canada due to reduced kidney function that is reversible and FAO/WHO daily food intake guidelines [67]. Carbofuran has guidelines set by all agencies and the WHO [6] because of evidence of cholinesterase inhibition and high toxicity hazard (WHO hazard class 1b, Table 3.3).

**TABLE 3.2. Regulatory Guidelines and Health Impacts of Insecticides, Acaricides and Nematicides Grouped by Pesticide Classification Group**

Chemical	CAS ID	WHO hazard classification	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	Health impacts
<b>Algicides</b>						
Endothall	145-73-3	II	-	0.1	-	Stomach and intestinal problems
<b>Aromatic acid herbicides</b>						
Dicamba	1918-00-9	II	-	-	0.12	Liver effects
Picloram	1918-02-1	U	-	0.5	0.19	Changes in body and liver weights and clinical chemistry parameters; Kidney effects (liver to body weight ratios and histopathology)
<b>Chloroacetanilide herbicides</b>						
Alachlor	15972-60-8	II	0.02a	0.002	-	Eye, liver, kidney or spleen problems; anemia; increased risk of cancer
Metolachlor	51218-45-2	III	0.01	-	0.05	Liver lesions and nasal cavity tumours
<b>Chlorotriazine herbicides</b>						
Atrazine	1912-24-9	III	0.1	0.003	0.005	Developmental effects (reduced body weight of offspring); Potential increased risk of ovarian cancer or lymphomas (classified as possible carcinogen); Cardiovascular system or reproductive problems
Cyanazine	21725-46-2	II	0.1	-	-	Hyperactivity and developmental malformations
Hydroxyatrazine	2163-68-0	-	0.1	-	-	Kidney toxicity
Simazine	122-34-9	U	0.002	0.004	0.01	Body weight changes and effects on serum and thyroid gland; Problems with blood
Terbutylazine	5915-41-3	III	0.007	-	-	Non-neoplastic lesions in the liver, lung, thyroid and testis and a slight decrease in body weight gain during toxicity study
<b>Dinitroaniline herbicides</b>						
Pendimethalin	40487-42-1	II	0.02	-	-	Liver toxicity
<b>Dinitrophenol herbicides</b>						
Dinoseb	88-85-7	O	-	0.007	-	Reproductive difficulties
<b>Halogenated aliphatic herbicides</b>						
Dalapon	75-99-0	U	-	0.2	-	Minor kidney changes
<b>Nitrile herbicides</b>						
Bromoxynil	1689-84-5	II	-	-	0.005	Reduced liver to body weight ratios
<b>Organophosphorus herbicides</b>						
Glyphosate	1071-83-6	III	-	0.7	0.28	Reduced body weight gain; Kidney problems; reproductive difficulties

*table continues next page*

TABLE 3.2. continued

Chemical	CAS ID	WHO hazard classification	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	Health impacts
<b>Phenoxy herbicides</b>						
2,4-D	94-75-7	II	0.03	0.07	0.01	Kidney effects (tubular cell pigmentation); Liver or adrenal gland problems
2,4-DB	94-82-6	II	0.09	-	-	Effects on body and organ weights, blood chemistry and haematological parameters
2,4,5-T	93-76-5	O	0.009	-	-	Reduced body weight gain, increased liver and kidney weights and renal toxicity; Suggested association with soft tissue sarcoma and non-Hodgkin lymphoma in epidemiological studies
Dichlorprop	120-36-5	II	0.1	-	-	Renal toxicity
Diclofop-methyl	51338-27-3	II	-	-	-	Liver effects (enlargement and enzyme changes)
Fenoprop	93-72-1	O	0.009	0.05	-	Liver problems
MCPA	94-74-6	II	-	-	0.009	Kidney effects (increased absolute and relative weights, urinary bilirubin, crystals and pH); Systemic, liver, testicular, reproductive/developmental and nervous system effects
Mecoprop	93-65-2	II	0.01	-	-	Effects on kidney weight
<b>Phenylurea herbicides</b>						
Chlorotoluron	15545-48-9	U	0.03	-	-	Carcinogenic potential
Diuron	330-54-1	III	-	-	0.15	Weight loss, increased liver weight and blood effects
Isoproturon	34123-59-6	II	0.009	-	-	Liver toxicity and tumour promoter
<b>Quaternary ammonium herbicides</b>						
Diquat	2764-72-9	II	-	0.02	0.07	Cataract formation
Paraquat	4685-14-7	II	-	-	0.01 as paraquat dichloride; 0.007 as paraquat ion	Various effects on body weight, spleen, testes, liver, lungs, kidney, thyroid, heart and adrenal gland
<b>Thiocarbamate herbicides</b>						
Molinate	2212-67-1	II	0.006	-	-	Male reproductive toxicity
<b>Triazinone herbicides</b>						
Metribuzin	21087-64-9	II	-	-	0.08	Liver effects (increased incidence and severity of mucopolysaccharide droplets)
<b>Aromatic fungicides</b>						
Hexachlorobenzene	118-74-1	Ia	-	0.001	-	Liver or kidney problems; reproductive difficulties; increased risk of cancer
<b>Unclassified fungicides</b>						
Hexachlorobutadiene	87-68-3	-	0.0006	-	-	Kidney toxicity; limited evidence for carcinogenicity and genotoxicity

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada Guidelines [6,20,21].

WHO classification: extremely (Ia), highly (Ib), moderately (I), and slightly (III) hazardous, unlikely to present acute hazard (U) and obsolete chemicals unlikely to be in use (O).

**TABLE 3.3. Regulatory Guidelines and Health Impacts of Insecticides, Acaricides and Nematicides Grouped by Pesticide Classification Group**

Chemical	CAS ID	WHO hazard classification	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	Health impacts
<b>Carbamate insecticides</b>						
Aldicarb	116-06-3	Ia	0.01	-	-	Nervous system effects including acetylcholinesterase inhibition
Carbaryl	63-25-2	II	-	-	0.09	Decreased kidney function (may be rapidly reversible after exposure ceases)
Carbofuran	1563-66-2	Ib	0.007	0.04	0.09	Nervous system effects (cholinesterase inhibition) and growth suppression; Problems with blood or reproductive system
Oxamyl	97502-85-7	Ib	-	0.2	-	Slight nervous system effects
<b>Cyclodiene insecticides</b>						
Aldrin	309-00-2	O	0.00003 (combined with Dieldrin)	-	-	Nervous system and liver toxicity
Chlordane	12789-03-6	II	0.0002	0.002	-	Liver or nervous system problems; increased risk of cancer
Dieldrin	60-57-1	O	0.00003 (combined with Aldrin)	-	-	Nervous system and liver toxicity
Endrin	72-20-8	O	0.0006	0.002	-	Liver problems
Heptachlor; Heptachlor epoxide	76-44-8; 1024-57-3	O	-	0.0002	-	Liver damage; increased risk of cancer
<b>Fumigant insecticides</b>						
1,2-Dichloropropane	78-87-5	O	0.04 (P)	0.005	-	Increased risk of cancer
Carbon tetrachloride	56-23-5	-	0.004	0.005	0.002	Liver toxicity; Kidney damage; liver tumours (classified as probable carcinogen)
1,2-Dichlorobenzene	95-50-1	II	1 (C)	0.6	0.2	Increased blood cholesterol, protein and glucose levels; Liver, kidney, or circulatory system problems
1,4-Dichlorobenzene	106-46-7	II	0.3 (C)	0.075	0.005	Benign liver tumours and adrenal gland tumours (classified as probable carcinogen); Anemia; liver, kidney or spleen damage; changes in blood

*table continues next page*

TABLE 3.3. continued

Chemical	CAS ID	WHO hazard classification	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	Health impacts
<b>Fumigant nematocides</b>						
1,2-Dibromo-3-chloropropane	96-12-8	O	0.001a	0.0002	-	Reproductive difficulties; increased risk of cancer
1,3-Dichloropropene	542-75-6	-	0.02a	-	-	Promotes lung and bladder tumours
<b>Organochlorine insecticides</b>						
Pentachlorophenol	87-86-5	Ib	0.009a(P)			Reduced body weight, changes in clinical parameters, histological changes in kidney and liver, reproductive effects (decreased neonatal survival and growth); Increased cancer risk
DDT and metabolites	DDT total	II	0.001	-	-	Developmental toxicity
Lindane	58-89-9	II	0.002	0.0002	-	Liver or kidney problems
Methoxychlor	72-43-5	U	0.02	0.04	-	Reproductive difficulties
Toxaphene	8001-35-2	O	-	0.003	-	Kidney, liver, or thyroid problems; increased risk of cancer
<b>Organophosphorus acaricides/insecticides</b>						
Azinphos-methyl	86-50-0	Ib	-	-	0.02	Neurological effects (plasma cholinesterase)
Chlorpyrifos	2921-88-2	II	0.03	-	0.09	Nervous system effects (cholinesterase inhibition)
Diazinon	333-41-5	II	-	-	0.02	Nervous system effects (cholinesterase inhibition)
Dimethoate	60-51-5	II	0.006	-	0.02	Nervous system effects (cholinesterase inhibition)
Malathion	121-75-5	III	-	-	0.19	Nervous system effects (cholinesterase inhibition)
Phorate	298-02-2	Ia	-	-	0.002	Nervous system effects (cholinesterase inhibition)
Terbufos	13071-79-9	Ia	-	-	0.001	Nervous system effects (cholinesterase inhibition)

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada Guidelines [6,20,21].

WHO classification: extremely (Ia), highly (Ib), moderately (II), and slightly (III) hazardous, unlikely to present acute hazard (U) and obsolete chemicals unlikely to be in use (O). WHO Guideline key: C, concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints; P, provisional guideline value because of uncertainties in the health database; T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

### Cyclodiene and Organochlorine insecticides

Organochlorine insecticides are persistent organic pollutants (POPs) that have been shown bioaccumulate and have been banned in many countries, but remain legal in some developing countries [68]. Despite the bans, organochlorine insecticides are still a public health concern and have been detected at trace levels nearly every river system in the world [69]. DDT is the most well-known insecticide in this group and has been banned in many countries for decades, including countries in North America, Europe and also China, but is still recommended for use in control of malaria vectors.

Organochlorine insecticides have a range of health effects including causing abnormal thyroid hormone levels and increased risk DDT, Lindane and Toxaphene are considered carcinogenic and tumor promoters in animals, although evidence for humans is considered insufficient [44]. Each of the four organochlorine insecticides (Table 3.3) with drinking water guidelines have been found to function as endocrine disruptors by interacting with estrogen and androgen hormones and receptors [70].

Cyclodiene insecticides are highly persistent organochlorine insecticides, initially introduced as alternatives to DDT. These pesticides have been banned in most developed countries because of high persistence in the environment, some are still used in lower income countries and remain present in soils where cyclodiene insecticide applied historically. Average times to reduce to a 5% residual can take up to 10 years for DDT, 8 years for Dieldrin and 6.5 years for Lindane [24]. Guidelines are still established because of international uses and potential for historic residues to be present in drinking water sources. These chemicals have been mostly banned and are regulated based on liver and neurotoxicity and increased risk of cancer [6,20,21].

### Fumigant insecticides and nematicides

Fumigants refer to highly volatile pesticide gas or vapor that is designed to reach pests by filling the air. This can include spraying for flying insects, termites in wood or filling airspaces between soil, or reach soil water to kill pests residing in soil, such as nematodes. The most immediate health risks from fumigants are caused by inhalation exposure. However, because many nematicides are injected into the soil there is a risk to entering drinking water sources via agricultural runoff and leaching of soil. A good illustration of this risk is from the use of a mixture of 1,2-Dichloropropane and 1,3-Dichloropropene known as D-D. The mixture was banned because 1,2-Dichloropropane displayed little nematicidal activity and was shown to be a groundwater contaminant [71] and increased risk of cancer (Table 3.3). It was banned in mixtures in 1984.

All of the chemical fumigants with guidelines are chlorocarbons or aromatic organic compounds. The Dichlorobenzenes range from acute toxicity at high doses, effecting the liver and kidneys in the case of 1,2-Dichlorobenzene to 1,4-Dichlorobenzene classification as a possible carcinogen in humans (IARC Group 2B, Table 3.3) [6,20,21].

1,2-Dibromo-3-chloropropane (DBCP) has a high residency in soil of up to 2 years or more and is mobile in soil with detection in drinking wells with nearby usage sites [72]. Health effects include reversible reductions in spermatogenesis and it is listed as a possible carcinogen. As a result, this substance was banned by the EPA in 1979 and in many other countries. 1,3-Dichloropropene is listed as a probable

carcinogen and is widely used in the US and around the world, though is being phased out as a pesticide in the EU.

### Organophosphorus acaricides/insecticides

Organophosphorus insecticides are a widely used group of pesticides, many of which have been discontinued for some uses and in agriculture. Chlorpyrifos is one of the most applied insecticide by weight on 21 crops in the United States and Phorate is in the top 6 [25]. Risk of organophosphorus insecticide contamination of surface waters is increasing with low environmental regulation quality and expanding population and agricultural production, including in low to low middle and middle income countries [73].

Organophosphorus insecticides are toxic to the nervous systems of humans and other mammals by inactivating acetylcholinesterase, an enzyme that helps form neurotransmitters and is similar to the inhibition in carbamate insecticides [63]. Health Canada has established guidelines for each organophosphorus insecticide in Table 3.3. Chlorination of chlorpyrifos produces chlorpyrifos oxon and is much more potent inhibitor of acetylcholinesterase. The substance is responsible for acute toxicity in humans and its widespread application to agricultural crops has concerning implications for drinking water treatment [74].

## Conclusions

The WHO has listed other chemicals as unlikely to have be in drinking water but have been frequently detected in tube wells pyrethroid insecticides in India [75] and are increasing in usage as they replace banned organophosphorus and organochlorine insecticides. The known human health impacts of pesticides are outnumbered by the number of pesticides in use and increasing amounts of new pesticides applied in agricultural, commercial and residential settings.

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## Chapter 4

# Industrial Chemicals

### Introduction

The use of chemicals is widespread and increasing in modern industries. The chemical industry is one of the largest sectors in the global economy and one of the main sources of industrial contaminants in water. Industrial chemical contaminants enter surface and ground waters directly as point sources of pollution, with effluents from manufacturing, chemical plants or refineries originating from pipes or contaminating water sources accidentally through from leaking storage tanks or pipelines. Extractive industries cause more diffuse contamination by disrupting hydrology over mining or drilling areas, releasing chemicals used in mining or accelerating erosion of naturally occurring chemical contaminants. Industrial chemical contaminants are frequently found in industrial waste sites and municipal landfills and then enter surface and groundwaters as leachate.

Industrial chemical contaminants that have established regulations or WHO guidelines are grouped by their chemical classification. A large number of contaminants in this chapter are considered volatile organic compounds (VOCs), including halogenated hydrocarbons and benzene derivatives. VOCs are released during combustion of fossil fuels or wood. They are major components of common industrial and household chemicals including many solvents such as paint and lacquer thinners, aerosol sprays, degreasers, wood preservatives, glues, paints and automotive products. Common examples of VOCs are gasoline, benzene, formaldehyde, toluene, xylene and styrene.

VOCs are commonly detected in aquifers including untreated domestic and public drinking water wells in the United States [1]. The number and diversity of VOCs entering environmental and drinking water sources requires a range of detection technologies [2].

### Halogenated Hydrocarbons

#### Polychloromethanes

Carbon tetrachloride (CT) and dichloromethane are commonly and widely used solvents that are mostly released into the atmosphere, but can contaminant soil and water during storage, as part of waste effluent and leachate from hazardous waste sites (Table 4.1) [3]. In studies of aquifers in the US dichloromethane was one of the most commonly detected in samples [1,4] and CT was found at levels within a factor of 10 but less than maximum contaminant levels (MCL) [1].

CT is a ubiquitous chemical in groundwater and the atmosphere, despite being banned for consumer use in 1970 in the US and world production declining since the 1970s [3]. Production has declined due to its role in chlorofluorocarbon (CFC) production. CFCs have been banned from aerosols since 1978, and heavily regulated through the Montreal Protocol, an international agreement to reduce chemicals that deplete atmospheric ozone [5]. CT was used widely in chemical production of refrigerants, aerosol propellants, fire extinguishers, household cleaners and industrial degreasers. However, due to its past and continued use in some countries, is still a common leachate from hazardous and landfill waste sites [6].

Production of dichloromethane has also declined due to increased regulation, with peak production in the US in the 1980s. The health consequences of CT and dichloromethane include liver toxicity and classifications as probably carcinogens [7,8]. Higher acute exposures by oral ingestion is generally considered to be less common than inhalation. Oral exposure from dichloromethane in humans are limited to case studies and report liver and kidney effects as well as neurological effects [9]. An epidemiological study of exposures to chemicals including CT showed significant odds ratios with low birthweights and low gestation weights-for-age, but participants were also exposed to a large number of other contaminants in drinking water [6,10].

### **Polychloroethanes**

1,2-Dichloroethane (1,2-DCA), 1,1,1-Trichloroethane (1,1,1-TCA), and 1,1,2-Trichloroethane (1,1,2-TCA) are commonly used as industrial solvents, degreasers, and intermediate chemicals during the production of plastics, textiles and a range of other industrial chemicals (Table 4.1) [3]. Globally, these chemicals are produced at large scales because they have a wide range of industrial usages. Industrial water effluents and accidental spills are the main ways that polychloroethanes enter environmental waters.

1,2-DCA is a very important bulk chemical with production among the highest of all halogenated chemicals, worldwide and released into the environment as a gas, but some entering rivers and lakes [3]. 1,2-DCA is not likely to be a threat in surface waters because they volatilize easily [11], though some research has shown presence in surface water near industrial sites [12]. 1,2-DCA can persist in groundwater sources. There is possibility of dermal and inhalation exposure during bathing and showering if present in drinking water [11].

Acute toxicity of 1,2-DCA can lead to fatalities due to circulatory and respiratory failure. Chronic and sub chronic occupational exposures can cause neurological disorders and dysfunction of the liver and kidneys [11,12]. 1,2-DCA is listed as a probable carcinogen based on tumor formation in animals, but little evidence in human studies.

1,1,1-TCA production has been on the decline and its usage phased out by the Montreal Protocol because of harmful effects on ozone after entering the atmosphere [5]. It has a wide range of uses including in aerosols, water repellents, adhesives, cosmetics, and degreasers. Despite declines in usages and being phased out in many parts of the world, it remains persistent in the troposphere for about 6 years and has low biodegradability. As a result and due to its common presence at hazardous waste sites, it is still a common groundwater contaminant [3]. 1,1,2-TCA is an isomer of 1,1,1-TCA and is used as an adhesive, a solvent for fats and oils, in lacquers, and in production of Teflon tubing. It enters groundwater as a contaminant from wastewater discharges, as spills and from improper disposal.

1,1,1-TCA is readily absorbed by the skin and gastrointestinal tract. Though less toxic than other halogenated compounds, oral ingestion of large doses of 1,1,1-TCA and its isomer, 1,1,2-TCA, can cause nausea, diarrhea and vomiting as well as neurological effects [13]. 1,1,1-TCA and 1,1,2-TCA are not considered carcinogens in humans [3].

### **Polychloroethenes**

Trichloroethene and tetrachloroethene are common groundwater contaminants due to their historic widespread use as industrial solvents for waxes, resins, rubbers, oils and extensive use as degreasers

and dry cleaning. Trichloroethene and tetrachloroethene were two of the top 5 most detected contaminants of U.S. aquifers [1]. Vinyl chloride can be found in drinking water as trichloroethene or tetrachloroethene degrade. 1,1-Dichloroethene and *cis*- and *trans*-1,2-Dichloroethene are all highly volatile and not expected to persist in surface waters.

There is substantial evidence that trichloroethene and tetrachloroethene cause cancer in animals and have a wide range of non-cancer toxic effects that target the central nervous system (Table 4.1) [14,15]. There is a substantial body of evidence that supports trichloroethene as carcinogen in humans when ingested orally, causing kidney cancer and may also cause liver cancer and non-Hodgkin lymphoma [16]. Trichloroethene toxicity also effects the liver, kidney, immune system, male reproductive system, and embryo/fetal development in humans [14,16]. Trichloroethene is classified as carcinogenic (Group 1) while tetrachloroethene is classified as probably carcinogenic (Group 2A) by IARC [17].

Vinyl chloride is common as a necessary substance in the production of polyvinyl chloride (PVC). Most vinyl chloride enters the environment as a gas that is heavier than air and enters drinking water through the ground, persisting for months or years, despite volatilizing from surface waters with a half-life of 1-40 hrs [18]. Vinyl chloride has also been shown to accumulate in PVC pipes used to distribute municipal chlorinated water [19]. Vinyl chloride is released into the environment from improper disposal and storage and industrial discharges from plastic factories [3].

Vinyl chloride is classified as carcinogenic in humans (Group 1) by IARC [17] with occupational exposure associated with rare forms of liver cancer leading to early evidence of causation in humans [20]. Vinyl chloride exposure may also be linked to brain and hepatocellular cancer and it is mutagenic with metabolites interact directly with DNA [18].

## Benzene Derivatives

### Contaminants from Petroleum Products

The organic compounds benzene, toluene, ethylbenzene and xylene (BTEX) contaminate ground and surface water through spills and leaks of petroleum derivatives [25] and spills associated with hydraulic fracturing operations [26,27]. Benzene is estimated to be a widespread contaminant. It has been discovered in drinking water treatment facilities and ground water across Canada [28] and suspected to be in 1.3% of all groundwater systems in the US at levels higher than drinking water standards [29]. In a study of volatile organic compounds in shallow groundwater in new residential and commercial areas across the US, toluene was one of the three most detected compounds, though rarely exceeding EPA drinking water standards [30].

In a Health risks from BTEX range from benzene which alters bone marrow, blood and immune responses and is a human carcinogen [29] causing it to be regulated by the WHO and the three regulatory bodies (Table 4.2). Ethylbenzene, toluene, and xylene are also widely regulated with exposures ranging from impacting liver and pituitary function and tumor formation in animal models [31], and nervous system damage [21]. Though for these three compounds, the main exposure is likely to be through inhalation.

### Other benzene derivatives

Dichlorobenzenes are used as fumigant insecticides but also enter the environment through industrial spills and leaks. The Dichlorobenzenes range from acute toxicity at high doses, effecting the liver and

**TABLE 4.1. Regulatory Guidelines and Health Effects of Halogenated Hydrocarbon Contaminants in Drinking Water**

Chemical	CAS ID	Source	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada		Health impacts
					Maximum Acceptable Concentrations (mg/L)	European Union (mg/L)	
<b>Polychloromethanes</b>							
Carbon tetrachloride	56-23-5	Industrial and chemical plant discharge	0.004	0.005	0.002	-	Liver toxicity; Kidney damage; liver tumours (classified as probable carcinogen)
Dichloromethane	75-09-2	Industrial and chemical plant discharge	0.02	0.005	0.05	-	Liver effects (liver foci and areas of cellular alteration); Classified as probable carcinogen
<b>Polychloroethanes</b>							
1,2-Dichloroethane	107-06-2	Industrial and chemical plant discharge	0.03a	0.005	0.005	0.003	Cancer of the mammary gland (classified as probable carcinogen)
1,1,1-Trichloroethane	71-55-6	Factory discharge	-	0.2	-	-	Liver, nervous system, or circulatory problems
1,1,2-Trichloroethane	79-00-5	Chemical factory discharge	-	0.005	-	-	Liver, kidney, or immune system problems
<b>Polychloroethenes</b>							
Vinyl chloride	75-01-4	Industrial discharge; plastic factory discharge	0.0003a	0.002	0.002 ALARA	0.0005	Liver cancer (classified as human carcinogen); Raynaud's disease, effects on bone, circulatory system, thyroid, spleen, central nervous system
1,1-Dichloroethene	75-35-4	Industrial spills; factory discharge	-	0.007	0.014	-	Liver effects (fatty changes)
cis-1,2-Dichloroethene; trans-1,2-Dichloroethene	156-59-2; 156-60-5	Chemical factory discharge	0.05	0.07; 0.1	-	-	Liver problems
Tetrachloroethene	127-18-4	Industrial spills; factory discharge	0.04	0.005	0.01	0.01	Neurological effects (colour confusion) in humans; Liver problems; Classified as probably carcinogenic to humans, based on sufficient evidence in experimental animals and limited evidence in humans
Trichloroethene	79-01-6	Industrial spills; factory discharge	0.02 (P)	0.005	0.005	0.01	Developmental effects (heart malformations); liver problems; Classified as probable carcinogen
<b>Other halogenated hydrocarbons</b>							
1,2-Dibromoethane	106-93-4	Petroleum refineries discharge	0.0004a(P)	0.00005	-	-	Problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer
1,2-Dichloropropane*	78-87-5	Chemical factories discharge	0.04 (P)	0.005	-	-	Increased risk of cancer
Hexachlorocyclopentadiene	77-47-4	Chemical factory discharge	-	0.05	-	-	Kidney or stomach problems

Note: Health effects summaries are adapted from WHO, European Union, US EPA and Health Canada guidelines [21-24].

WHO Guideline key: C, concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints; P, provisional guideline value because of uncertainties in the health database; T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

**TABLE 4.2. Regulatory Guidelines and Health Effects of Contamination of Drinking Water by Benzene Derivatives**

Chemical	CAS ID	Source	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	European Union (mg/L)	Health impacts
Benzene	71-43-2	Industrial waste; factory discharge	0.01a	0.005	0.005	0.001	Bone marrow (red and white blood cell) changes and cancer (classified as human carcinogen); Blood system and immunological responses
1,2-Dichlorobenzene	95-50-1	Industrial and chemical plant discharge	1 C	0.6	0.2	-	Increased blood cholesterol, protein and glucose levels; liver and kidney problems
1,4-Dichlorobenzene	106-46-7	Industrial and chemical plant discharge	0.3 C	0.075	0.005	-	Benign liver tumours and adrenal gland tumours (classified as probable carcinogen); Anemia; liver, kidney or spleen damage; changes in blood
Ethylbenzene	100-41-4	Chemical factories and petroleum refineries discharge	0.3 C	0.7	0.14	-	Effects on the liver and pituitary gland.; Tumour formation at various sites in animals, including kidney, lung, liver and testes.
Hexachlorobenzene	118-74-1	Metal refineries discharge; chemical factories discharge	-	0.001	-	-	Liver or kidney problems; reproductive difficulties; increased risk of cancer
Monochlorobenzene	108-90-7	Industrial spills; factory discharge	-	0.1	0.08	-	Reduced survival and body weight gain; Liver or kidney problems
Styrene	100-42-5	Rubber and chemical factories discharge	0.02 C	0.1	-	-	Liver, kidney, or circulatory system problems
Trichlorobenzenes	120-82-1	Textile factory discharge	-	0.07	-	-	Changes in adrenal glands
Toluene	108-88-3	Petroleum and chemical industries discharge	0.7 C	1	0.06	-	Adverse neurological effects, including vibration thresholds, colour discrimination, auditory thresholds, attention, memory and psychomotor functions; kidney or liver problems
Xylenes	xylenes	Petroleum and chemical industries discharge	0.5 C	10 (total)	0.09 (total)	-	Adverse neuromuscular effects; nervous system damage

Note: Health effects summaries are adapted from WHO, European Union, US EPA and Health Canada guidelines [21-24].

WHO Guideline key: C, concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints; P, provisional guideline value because of uncertainties in the health database; T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

kidneys in the case of 1,2-Dichlorobenzene to 1,4-Dichlorobenzene classification as a possible carcinogen in humans (IARC Group 2B, Table 4.2) [21-23].

Styrene is used in latex, rubber, resins and plastics production. Inhalation is the most common exposure. Styrene is mutagenic in animal models [32] and also causes liver, kidney and circulatory system problems in long term exposure in rats [33].

#### **Dioxins and dioxin-like contaminants**

Dioxins and polychlorinated biphenyls (PCBs) have many industrial uses because they are heat-stable and persistent, qualities that also make them unfavorable when they enter the environment and can bioaccumulate [34]. They are common in a wide range of uses including adhesives, flame retardants and electronic waste [35]. They are found in air, soil, sediment and water. Di(2-ethylhexyl) phthalate (DEHP) and Di(2-ethylhexyl)adipate (DEHA) are both plasticizers that add flexibility to resins. DEHP is a key component in adding flexibility to PVC. Studies of DEHP concentration in surface water and sediment and sewage effluent and sludge in levels higher than EPA guidelines throughout Europe [36]. 1,4-Dioxane is a common additive to chlorinated solvents, paints, strippers, waxes.

The compound 1,4-Dioxane is classified as a likely human carcinogen by the EPA and US Department of Health and Human Services [37]. Dioxins and dioxin-like compounds alter hormone levels in females during puberty and menstrual cycles [38]. PCBs impact the male reproductive system, altering sex steroid systems and are carcinogenic [39] (Table 4.3). DEHP also negatively impacts the male reproductive system [40]. Perchlorate and cyanide both impact thyroid functions [41,42].

#### **Elements**

Industrial waste and processes are a significant source of element contamination in drinking water sources. Beryllium metal is used in aerospace and nuclear industries. Chromium has wide uses in industry, wood preservation, tanning, and in the production of several alloys, including stainless steel. Chromium enters water sources through accidental spills, improper disposal of ore, as a component of car exhaust, in effluent from cooling towers, and also through oxidation of naturally occurring Chromium [43]. Thallium is likely to enter surface waters through atmospheric depositions of thallium ash from coal combustion and enter groundwaters through leakages and spills of thallium salts or from natural deposits [44].

Beryllium and Chromium are both considered Group 1 carcinogens by IARC [45,46]. Alopecia is characteristic of exposure to thallium salts along with kidney damage [47].

## **Conclusions**

Industrial development in countries around the world, the scope and scale of drinking water contamination by industrial chemicals is on the rise. Rapid urbanization in the world has led to higher concentrations of both chemical contaminants and the industries that produce them. In recent years, as governments in high-income countries have banned or outlawed some types of chemical waste, industries in these countries ship and dump hazardous waste in lower income countries [48].



**TABLE 4.3. Regulatory Guidelines and Health Effects of Industrial Contaminants in Drinking Water**

Chemical	CAS ID	Source	WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	European Union (mg/L)	Health impacts
1,4-Dioxane	123-91-1		0.05a	-	-	-	Induces tumors in animal models
Dioxin	1746-01-6	Chemical factory discharge	-	0.00000003	-	-	Reproductive difficulties; increased risk of cancer
Polychlorinated biphenyls	polychlorinated biphenyls	Waste chemicals discharge; landfill runoff	-	0.0005	-	-	Skin changes; thymus gland problems; immune deficiencies; reproductive or nervous system difficulties; increased risk of cancer
Di(2-ethylhexyl) adipate	103-23-1	Chemical factories discharge	-	0.4	-	-	Weight loss, liver problems, or possible reproductive difficulties.
Di(2-ethylhexyl) phthalate	117-81-7	Rubber and chemical factories discharge	0.008	0.006	-	-	Reproductive difficulties; liver problems; increased risk of cancer
Epichlorohydrin	106-89-8	Chemical factories discharge	0.0004 (P)	TT	-	0.0001	Increased cancer risk, and over a long period of time, stomach problems
Hexachlorobutadiene	87-68-3	Rubber and chemical factories discharge	0.0006	-	-	-	Kidney tumors in animal models
Perchlorate	14797-73-0	Oxidizer for solid rocket fuels, automotive airbags, fireworks and road flares	0.07	-	-	-	Inhibits synthesis of thyroid hormone
Cyanide	57-12-5	Factory discharge; mining effluent	-	0.2	0.2	-	Nerve damage or thyroid problems

Note: Health effects summaries are adapted from WHO, European Union, US EPA and Health Canada guidelines [21–24].

WHO Guideline key: C, concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints; P, provisional guideline value because of uncertainties in the health database; T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

EPA Guideline key: TT, 0.01% dosed at 20 mg/L (or equivalent) when used in water treatment

**TABLE 4.4. Regulatory Guidelines and Health Effects of Industrial Element Contaminants in Drinking Water**

Chemical	CAS ID	Source	WHO	US EPA	Health Canada		Health impacts
			guideline value (mg/L)	Maximum Contaminant Level (mg/L)	Maximum Acceptable Concentrations (mg/L)	European Union (mg/L)	
Beryllium	7440-41-7	Metal refineries discharge; fossil fuel combustion emissions	-	0.004	-	-	Intestinal lesions
Chromium	7440-47-3	Industrial spills; factory discharge	0.05 (P)	0.1 (total)	0.05	0.05	Enlarged liver, irritation of the skin, respiratory and gastrointestinal tracts from chromium (VI)
Thallium	7440-28-0	Ore processing discharge; factory discharge	-	0.002	-	-	Hair loss; changes in blood; kidney, intestine, or liver problems

Note: Health effects summaries are adapted from WHO, European Union, US EPA and Health Canada guidelines [21-24].

WHO Guideline key: C, concentrations of the substance at or below the health-based guideline value may affect the appearance, taste or odour of the water, leading to consumer complaints; P, provisional guideline value because of uncertainties in the health database; T, provisional guideline value because calculated guideline value is below the level that can be achieved through practical treatment methods, source protection, etc.

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## Chapter 5

# Naturally Occurring Chemicals

### Introduction

Chemical contaminants occurring naturally in the environment enter ground and surface water through a wide range of physical, chemical and biological processes.

Most naturally occurring chemical contaminants are inorganic elements bound during the formation of bedrock. Naturally occurring contaminants include a variety of elements such as metals, minerals and primordial and secondary radioisotopes. A biologically produced toxin, microcystin, are produced by cyanobacteria in surface waters. Cyanobacteria are discussed along with nitrate and nitrite at length in the Agricultural contaminants chapter because blooms and toxin release are often caused by excess fertilizer runoff into surface waters.

Chemical contaminants from the Earth are formed and deposited as igneous, metamorphic and sedimentary rock. Igneous rock is formed from magma activity and can be deposited during volcanic activity. Metamorphic rock is formed from mineralization under high temperatures and high pressure deep in the Earth's crust. Sedimentary rock is formed as bedrock erodes into smaller pieces and then transported and redeposited as sediment by wind, water or ice. Over time, sediments of loose, gravel, sand, silt, and clay may compress into conglomerates of loose and solid rock. Other forms of sedimentary rocks such as ironstone and limestone are formed by chemical and biological processes.

Over long periods of time, geochemical and biological processes erode and release contaminants into ground and surface waters. The rate of erosion and concentration of contaminants from bedrock in water sources are determined by climate, hydrology and biological factors and are also key to soil formation. Biogeochemical processes acting on parent materials (bedrock) during stages of soil formation release contaminants that leach into ground waters or are carried by water, wind or ice into surface waters.

Chemical contamination of water by natural processes can be accelerated by anthropogenic activities such as extractive mining, agricultural activity, and sewage effluent. Deep and surface mines alter hydrology, disturb soil, and increase surface area of rocks resulting in acidification and deposition of heavy metals into surface and ground waters near mines. Agricultural practices can accelerate erosion of soils, releasing contaminants into surface and irrigation waters. Nitrate, a natural product of nitrogen fixing plants and present in human and animal excrement, increases in water sources from high concentrations of livestock and direct inputs of sewage sludge from human settlements.

The concentration of naturally occurring chemicals in ground and surface waters is dependent on reduction-oxidation reactions (redox) that occur in all water. Reduction occurs as a species gains an electron from an electron donor while oxidation refers to the simultaneous loss of an electron by the electron donor. This process is dependent on the chemical species present in water and microbiological fauna that facilitate reactions. Redox potential in water can be heterogeneous even within the same aquifer, but can be assessed and monitored to predict surface or groundwater contamination risk [1]. Redox potential is also important in determining the rate of biodegradation of all chemical contaminants that enter water sources and finished drinking water.

## Elements

Arsenic (As), fluoride (F) and selenium (Se) are widely distributed and contaminant drinking water across a range of geologic contexts [2].

### Arsenic

Arsenic has been found in a limited number of geological contexts across continents in concentrations ranging from 0.5 µg/L to more than 5000 µg/L, but more commonly less than 10 µg/L [3]. Arsenic is often locally present in geothermal springs associated with black shales and more widespread in closed arid and semi-arid basins, often in volcanogenic areas, and highly reducing aquifers in alluvial sedimentary rock [4]. In both cases, high concentrations end up in groundwater because of historically low amounts of flushing and slow moving aquifers [3].

High arsenic concentrations in groundwater are particularly common throughout southern Asia often distributed along with high population densities that rely on groundwater as a drinking water source [5-7]. The highest region of exposure risk is in the Bengal basin because of the combination of arsenic in the groundwater and high population densities. Approximately 2.5 million people in Chile and Argentina and a total of 4 million people throughout Latin America [8] are at risk of arsenic exposure due to volcanic rock and volcanogenic sediments, high pH, in semi-arid to arid climates [4]. In both contexts, local mining activity exacerbates the release of natural arsenic into the drinking water.

In Bangladesh and west Bengal, India, increased access to drinking water free of enteric diseases has been accomplished in large part by increasing borehole wells. However, health gains in diarrheal prevention have been complicated by increased, chronic arsenic exposure, with total estimates of 77-85 million people impacted by arsenic poisoning in Bangladesh [9,10]. In addition to exposure from groundwater, release of arsenic from alluvial sediments can be further concentrated by flooding and drying cycles during wet rice agriculture. Arsenic poisoning in this region the largest incidence of chemical contamination in human history.

The elevated health risk of cancers is the main health risk of chronic exposure of high concentrations of arsenic (Table 5.1). Arsenic is one of the first chemicals in history to be considered as a cause for cancer [11]. Acute toxicity produces symptoms of nausea, flushing of skin, numbness and tingling of extremities, muscle cramping and skin rash. Chronic consumption of high levels of arsenic in drinking water produces skin lesions, peripheral nervous system damage, bladder, lung and skin cancers [12-14]. Lower birth weights have been reported in multiple studies at both low and high exposures from drinking water consumption [12].

### Fluorine

Fluorine, typically found in nature as fluoride, is another widespread chemical that has significant health impacts when found at high levels in drinking water and can co-occur with other contaminants, including arsenic. Fluoride occurs in natural water sourced worldwide, but is found at higher concentrations in groundwater in mountainous regions where bedrock has been formed from extensive marine deposits, regions with volcanic, granitic and gneiss rock [15,16].

Statistical models of high levels of fluoride in ground water show high concentrations throughout Central Asia, the Middle East, and North, East and Southern Africa, with significant high concentrations

in Argentina, western United States and Mexico, Russia and Australia [17]. As with arsenic, exposure to fluoride is significant in populations relying on groundwater as their main source of drinking water, estimated to impact 200 million people in 25 countries, with 66 million in India alone [18].

Chronic consumption of high levels of fluoride causes chronic dental and skeletal fluorosis in humans. The majority of morbidity is due to skeletal fluorosis, a condition causing osteosclerosis, calcification of ligaments and tendons and deformed bone structure [15]. Advanced stages of fluorosis cause chronic pain to bones and joints and brittle bones are more likely to fracture. Increased water consumption in hot tropical climates as compared to consumption levels in cooler climates is a significant factor contributing to fluorosis [15,16].

### Selenium

Selenium is an essential mineral to humans but ingestion at concentrations above 0.4 mg/day has negative health effects [19]. Selenium is widely distributed, but rarely occurs in Most selenium exposure occurs through consumption of foods rather than drinking water. When selenium occurs in high concentrations in surface waters, it is usually due to anthropogenic activities such as mining or irrigating with water in contact with selenium containing black shales, carbonaceous limestones, cherts and mudstone, or seleniferous coal [20]. High selenium levels due to anthropogenic activity have been reported in California, India and China.

Chronic exposure to subacute concentrations of selenium leads to brittle hair and nails, skin lesions and neurotoxicity [21,22]. Acute exposure to selenium produces dizziness, local or generalized tremors and convulsions [22].

### Barium

Naturally, barium is found in low to moderate concentrations in the environment. Barium is present in nearly all surface waters but reaches levels above recommended guidelines in surface and groundwater through water rock interactions that depend on the mineral matrix and physiochemical conditions. Water rock interactions with black shales, volcanic rock and deep wells associated with bedrock containing high concentration of barium have led to high levels of barium in ground and surface waters [23]. Industrial and medical uses of barium have more than doubled over the last 40 years [24], increasing concentrations in industrial effluent and toxic waste sites. Industrial uses of barium in manufacturing of petroleum and plastics have increased point sources of barium.

Acute exposure to barium is the basis for much of the guidelines in drinking water as human chronic exposure has not been well studied [23]. Acute toxicity, primarily from occupational exposure, has led to serious effects on heart rhythm, elevated blood pressure, gastrointestinal disturbances, and partial or total paralysis [21,24].

### Boron

Boron concentrations in groundwater range widely from less than 0.3 to greater than 100 mg/L and are found in many continents where there are highly mineralized, carbonated waters [25]. In fresh surface waters, boron concentrations vary from less than 0.001 to 360 mg/L near boron-rich deposits in North America [25]. Boron levels above recommended standards are typically associate with higher salinity

groundwater [26], which is particularly problematic in coastal aquifers experiencing seawater encroachment [27]. Other natural sources of boron include fossil brines and geothermal fluids [28].

Human studies of boron toxicity have focused on oral intake of borax and boric acid, both common household products. Infants appear more sensitive to boron than adults. Acute toxicity causes generalized or alternating focal seizure disorders, gastrointestinal disturbances and irritability, with documented potential lethal doses at 3-6 g boric acid for infants and 5-20 g for adults [29]. Guidelines have been developed based on animal studies showing toxicity attacking the male reproductive tract, causing testicular lesions and developmental malformations in fetuses [25].

### Mercury

Natural mercury is widely distributed due to atmospheric deposition of mercury through precipitation, but is one of the least abundant elements in crustal rocks [30]. A recent review estimated that 170 to 300 mg/acre from river discharge of naturally occurring mercury in soils and post-industrial atmospheric deposition in 'pristine' ecosystems, with 50% estimated to be natural mercury [31]. Sources of atmospheric mercury gas include volcanic eruptions, coal burning power plants, and reemission of terrestrial and aquatic mercury. Atmospheric deposits are typically confined to surface water, with only two studies tracing atmospheric mercury deposition to ground water through deep groundwater discharge and another study suggested mercury mobility in coastal plain soils [30]. Anthropogenic sources of mercury from burning of coal and petroleum products distribute mercury worldwide and increase terrestrial and aquatic reemissions.

Most mercury exposure from oral ingestion of fish where high levels of methylmercury from bioaccumulation [32]. Acute ingestion of inorganic or organic forms of mercury results in shock, cardiovascular system collapse, renal failure and gastrointestinal damage [32] and is also a neurotoxin [33]. Inorganic forms of mercury accumulate in the kidneys.

### Uranium

Most uranium in drinking water comes from natural sources and is found in groundwater supplies in a wide range of countries including Sweden, Finland, Norway, USA, Canada, India, and Brazil. Uranium exists as  $^{238}\text{U}$ ,  $^{235}\text{U}$  and  $^{234}\text{U}$  isotopes, but is a health risk due to toxicity more than its radioactivity [34]. Nephritis is one of the main human health effects from exposure to uranium [35] and is listed as a cause for cancer in humans and animals by Health Canada [36]. In animal models other health effects including, developmental defects, genotoxicity, and reduced bone growth have been reported [37].

### Radionuclides

Radioactive substances enter drinking water naturally through interactions with bedrock and artificially through radiation used for medical and industrial purposes as well as nuclear weapons testing and nuclear disasters [38]. Radiation doses from naturally occurring radionuclides are often higher than artificial radionuclides [38]. Most natural radionuclides come from the decay series of three primordial radioisotopes:  $^{232}\text{Thorium}$ ,  $^{235}\text{Uranium}$  and  $^{238}\text{Uranium}$  [42].



**TABLE 5.1. Regulatory Guidelines and Health Effects of Naturally Occurring Chemical Contaminants of Drinking Water**

<b>Chemical</b>	<b>CAS ID</b>	<b>WHO guideline value (mg/L)</b>	<b>US EPA Maximum Contaminant Level (mg/L)</b>	<b>Health Canada Maximum Acceptable Concentrations (mg/L)</b>	<b>European Union (mg/L)</b>	<b>Health impacts</b>
Antimony	7440-36-0	0.02	0.006	0.006	0.005	Microscopic changes in organs and tissues (thymus, kidney, liver, spleen, thyroid); Increase in blood cholesterol; decrease in blood sugar
Arsenic	7440-38-2	0.01 (A, T)	0.01	0.01	0.01	Cancer (lung, bladder, liver, skin) (classified as human carcinogen); Skin, vascular and neurological effects (numbness and tingling of extremities); Problems with circulatory systems
Barium	7440-39-3	1.3	2	1	-	Increases in blood pressure, cardiovascular disease
Boron	7440-42-8	2.4	-	5	1	Reproductive effects (testicular atrophy, spermatogenesis); Limited evidence of reduced sexual function in men
Mercury	7439-97-6	0.006	0.002	0.001	0.001	Irreversible neurological symptoms; Kidney damage
Selenium	7782-49-2	0.04 (P)	0.05	0.03	0.01	Chronic selenosis symptoms in humans following exposure to high levels; Hair or fingernail loss, tooth decay, weakened nails and nervous system disturbances at extremely high levels of exposure; numbness in fingers or toes; circulatory problems
Uranium	7440-61-1	0.03 (P)	0.03	0.02	-	Kidney effects (various lesions); Increased risk of cancer

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada guidelines [38–40].

**TABLE 5.2. Regulatory Guidelines and Health Effects of Naturally Occurring Radionuclide Contaminants of Drinking Water**

Chemical	CAS ID	WHO guideline value (Bq/L)	US EPA Maximum Contaminant Level	Health Canada Maximum Acceptable Concentrations (Bq/L)
Alpha particles	alpha particles	0.5	15 picocuries per Liter (pCi/L)	-
Beta particles and photon emitters	beta particles	1	4 millirems per year	-
Radium 226	13982-63-3	1	5 pCi/L	0.5 Bq/L
Radium 228	15262-20-1	-	5 pCi/L	-
Lead 210	-	0.1	-	0.2 Bq/L
Uranium-238	-	1	-	-
Uranium-234	-	1	-	-
Thorium-230	-	1	-	-
Polonium-210	-	0.1	-	-
Thorium-232	-	1	-	-
Thorium-228	-	1	-	-

Note: Health effects summaries are adapted from WHO, US EPA and Health Canada guidelines [38–40].

## Conclusions

Contamination of drinking water sources by naturally occurring chemicals are tied closely to their water-bedrock interactions and the composition of reduction-oxidation (redox) species present in the water source. Anthropogenic activities often increase concentrations of contaminants found in nature, either directly through industrial and wastewater effluents or agricultural runoff, or indirectly by increasing redox species that increase potential for release or availability of toxic contaminants occurring in ground and surface waters.

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## Chapter 6

# Emerging Chemical Contaminants in Drinking Water

The number of chemicals produced by humans has increased exponentially over the last few decades and the possible combinations and arrangements for new unique chemical formulations are nearly infinite. Regulations and guidelines for contaminants in drinking water set by WHO and country regulatory bodies cover a wide range of chemicals numbering in the hundreds. The American Chemical Society's Chemical Abstract Service has registered 142 million unique organic and inorganic chemicals. The number of chemicals monitored and regulated are only a fraction of the chemicals present in surface and ground waters. The number and amounts of those chemicals in drinking water remain unknown and are constrained by the ability of regulatory bodies and scientists to detect and monitor the vast number of potential contaminants. Generally, there is a lack of policy requiring new chemical additives to be tested for safety before approval for commercial use. Companies that produce chemicals affecting humans through the environment have far lower requirements than drug, vaccine, or medical device manufacturers, even though the consequences of exposure may be equally dangerous.

The body of literature around emerging pollutants or micropollutants captures compounds that are present at relatively low concentrations and are difficult to remove during drinking and wastewater treatment [1]. Emerging chemicals include micropollutants that originate from both natural and anthropogenic sources. The major groups of anthropogenic chemicals including pharmaceuticals, personal care products (PCPs), surfactants, pesticides and industrial chemicals such as flame retardants and plasticizers. More recently microplastics or plastic particles <5mm are of rising concern in fresh and marine water bodies [2] and present in drinking water, food, and air [3].

Since wastewater treatment plants are not typically equipped to remove micropollutants, their presence is widespread, though at low levels in many cases, in water bodies receiving effluent from wastewater treatment plants [1,4]. Pharmaceuticals, surfactants, PCPs, and various industrial chemicals enter the wastewater treatment plants through sewage and gray water and are discharged into surface waters without being metabolized or removed from effluent [5]. Though they may be diluted and present in low concentrations, some will end up entering drinking water treatment plants which are not equipped to remove micropollutants and are not required to monitor them before distribution to end point users.

Though there is much concern over the fact that emerging chemicals are ubiquitous in surface water and groundwater [6], the health impacts of exposure to human populations is largely unknown. Generating proof of chemical safety or risk for human health is economically and logistically prohibitive due to the requirement for large, lengthy cohort studies to capture potential later life outcomes. There is a lack of political will in investing in these studies since connecting exposure to health effects is more complex and dependent on environmental factors. Endocrine disruptors are the most likely to be connected to immune deficiency, neurological disorders, child development, high rates of infertility, low sperm count and ovarian, prostate, testicular and breast cancers [7]. Anti-inflammatory drugs, analgesics, antibiotics, lipid regulators, hormones, beta-blockers and cancer therapeutics are the most frequently detected pharmaceuticals in environmental waters [8].

## Future Monitoring and Regulation Strategies

The formation of regulations are often centered on ‘legacy chemicals’ that have been banned or their usage is in decline but they still persist in the environment. The chemicals covered in this report represents some of those legacy chemicals, but also many relevant new priority chemicals. Regulations and guidelines based on legacy and priority chemicals without updates that keep pace with the roughly 2,000 new chemicals that are introduced for use each year, prevent adaptive regulation to new and emerging contaminants [9].

In response to the rapid introduction and increased use of chemicals with potential to contaminate drinking water sources, new regulations have been introduced to accelerate the number of chemicals that are reviewed by the US EPA [10]. The European Union-funded SOLUTIONS project is charged with more comprehensive monitoring of individual chemicals and improving sampling and analytical chemistry methods to detect lower concentrations of emerging and priority pollutants [9].

Recommendations from SOLUTIONS include expanding monitoring and risk assessment from a focus on individual chemicals to mixtures of chemicals occurring in freshwater [9]. A sample of freshwater from a water body may contain tens of thousands of chemicals, including unknown chemicals. Testing for chemical mixtures and grouping them by concentration levels or by toxicological groups in combination with site specific characteristics could provide chemical “fingerprints” assigned to anthropogenic activities (e.g. cultivation of specific crops, specific industries, urban wastewater effluents) in a basin or catchment area [9].

Studies that sample a wider range of chemical pollutants beyond priority or regulated chemicals and studies that test chemical mixtures often result in different risk assessments than tests for individual chemicals alone and allow for consideration of combined toxicological effects of exposure to multiple chemicals. In a study of ecotoxicity in of several anti-inflammatory drugs against algae species, toxicity was higher for the chemical mixtures than for the individual drugs at the same concentrations [11].

Another recommendation from the SOLUTIONS research group is the use of batteries of bioassays on molecular, cellular and whole organism levels to test chemical mixtures, a method know as effect-directed analysis. Traditionally, animal models such as rats and mice are used as bioassays to form many of the established guidelines and regulations. In effect-directed analysis a set of bioassays testing for a range of toxicity measures including mortality, cytotoxicity, effects on metabolism, genotoxicity, endocrine disruption and enzyme inhibition [12]. Chemical mixtures are tested by fractionation, or dividing the samples into portions by chemical gradients, allowing for testing the effects of more than one chemical in the mixture at a time. This process adds more flexibility in monitoring and identifying a more realistic picture of ecotoxicity and human health risks that is potentially cost-effective [9].

While these methods are very promising in providing a more accurate picture of the health risk from exposure to chemical contaminants to drinking water sources, they are fairly novel in their application to governmental monitoring and regulations. Advances in analytical chemistry and bioassays will need to be developed and tailored to the diversity of freshwater systems worldwide. Methods will also need to be cost-effective and affordable in order to be available to and implemented by lower income countries.

A comprehensive assessment of all chemical contaminants is beyond the scope of global studies of water quality, though promising new methods allowing for measuring chemical mixtures and using new

bioassays are promising for expanding the scope of risk assessment and monitoring of freshwater. Consideration of contexts and the types of comparisons that can be made within and between individual freshwater systems and regions will be important in selecting the correct number and composition of indicators of chemical contamination. Contextual information about potential sources of contamination in freshwater systems is essential to an accurate understanding of human health risks and appropriate policy responses to mitigating these risks, regardless of the composition of chemical contaminant sampling.

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## Chapter 7

# Indicators of Water Quality

### Introduction

Freshwater lakes and rivers are essential sources of drinking water as well as water necessary for power generation, manufacturing and irrigation for crops. Maintaining safe water sources is beneficial to humans as well as the biota that maintain ecosystem services that support improved water quality. The cleaner the source of water for drinking or other activities, the less resources and energy are needed for removing contaminants and the less risk there is to human health [1]. Using surface waters as a source of drinking water requires quality monitoring to prevent exposure to contaminants during consumption and to ensure that treatment facilities have the capacity to remove contaminants.

Water quality is determined by the natural geology of bedrock and soils, and human activities within the lake catchment, including rivers and streams. Freshwater quality is a function both of the natural state of water body, which in some cases may not be suitable for human consumption because of high levels of naturally occurring heavy metals, such as arsenic or fluoride, or salinity, and a function of various human activities that add chemical contaminants directly or accelerate naturally occurring contaminants to levels that are dangerous to human health. Even when present, wastewater treatment facilities can still be a source of human pollution. Based on model estimates from 108 low and low-middle income countries, a hypothetical scenario where global access to piped sewage or septic was assumed, current capacity for wastewater treatment would only remove 58% of phosphorus, 58% of nitrogen, reduce biochemical oxygen demand (BOD) by 68% and fecal coliforms by 80% [2].

Under international, national and local regulations, lake and river water quality is monitored to assess risks to human health. Physical and chemical indicators of water quality are widely used to monitor and assess the health of freshwater lakes and rivers. The United Nations Environment Program Global Environment Monitoring System (GEMS)/Water Programme [3] is a global database of approximately 3,000 monitoring stations of rivers, lakes, reservoirs and wetlands from 75 countries [4]. The database contains data for about 250 parameters including many of those proposed for this World Bank led analysis. The database is composed of data voluntarily contributed by official national agencies and availability of consistent data for all parameters is limited.

A key example of a comprehensive national assessment of freshwater quality is that undertaken by the United States Environmental Protection Agency (USEPA). USEPA completed two rounds of lake water quality sampling across 1,038 lakes in the United States of America (USA) in 2007 and 2012 [5]. The lakes were sampled for 12 indicators including biological indicators (benthic macroinvertebrates and zooplankton), chemical indicators (acidification, nitrogen, dissolved oxygen, and phosphorus), and human use indicators (atrazine, mercury, chlorophyll-a, cyanobacteria, and microcystin).

The objective of this work is to summarize and assess a list of water quality parameters and what level of information about health risks from specific contaminants can be gleaned from them. With a few

exceptions, these water quality measures rarely have health guidelines associated with them because they measure conditions that may have a range of underlying causes that could be natural or caused by human activities. In general, the threats to human health as indicated by measures of water quality are associated with 1) identification of sources of pollution, 2) treatability of water, specifically regarding the formation of disinfection by-products, and 3) direct health risks from fecal contamination and nitrates.

## Water Quality Parameters

Water quality parameters used in monitoring and assessment measure biological and physiochemical aspects of water. Nine parameters are under consideration for monitoring freshwater quality (Table 7.1). These parameters are commonly used to assess aquatic ecosystem health and potential human health risks associated with contact or consumption of water from a body of water. Parameters can be used to identify and monitor sources of contamination within a body of water and also for general comparisons to other bodies of water when standardized to account for expected local levels of chemicals and biological life under natural circumstances.

### Physiochemical Parameters

#### Temperature

The water temperature of lakes influences the rate of chemical reactions, growth of microbial populations, the rate of photosynthesis of algae and macrophytes, and disease transmission within aquatic biota. Temperature also determines the amount of dissolved oxygen and other chemicals that are present in solution and available for biological life and chemical reactions. Temperature will vary along the depth of the water column and across seasons. Though temperature of lakes does not have direct impacts on human health from the standpoint of consuming hotter or colder drinking water (Table 7.1), it is an important factor for understanding and predicting the natural presence of biological and chemical contaminants, influencing oxidation reactions and degradation of parent contaminants.

Rising temperatures of surface waters due to human industrial activity and climate change may increase the likelihood that disinfection by-products, such as bromate, trihalomethanes (THMs), haloacetic acids (HAAs), halogenated acetonitriles and N-Nitrosodimethylamine (N-NDMA), formed during and distributed after drinking water treatment [6,7]. Temperature increases of a few degrees have been shown to increase formation and variability of disinfection by-products in water distribution systems [8].

#### pH

The level of acidity in water is commonly measured by pH values. Low pH can decrease productivity and is typical naturally in peat bogs and some wetlands. The alkalinity of water bodies refers to its ability to buffer against acids, including natural and anthropogenic acidity in precipitation. Though there are now well-established health-based guidelines waters between 6.5 and 8.5 are considered of good water quality (Table 7.1).

**TABLE 7.1. Physiochemical Water Quality Measures and Related Health and Aesthetic Guidelines for Drinking Water from WHO, US EPA, Health Canada and the EU**

Indicator	Global Lakes Data	Brazil	Mexico	India	Mekong	WHO guideline value (mg/L)	US EPA	Health Canada	EU	Quality of human health risk	Health impacts
							Maximum Contaminant Level (mg/L)	Maximum Acceptable Concentrations (mg/L)	Parameter (mg/L)	evidence	
<b>General physiochemistry</b>											
Temperature	X			X	X					plausible	Increasing temperature of source waters can contribute to formation of disinfection by-products during drinking water treatment
pH		X		X	X			7.0-10.5 (No units)		plausible	The control of pH is important to maximize treatment effectiveness, control corrosion and reduce leaching from distribution system and plumbing components.
Alkalinity/ acidity					X					plausible	The control of acidity and alkalinity is important to maximize treatment effectiveness, control corrosion and reduce leaching from distribution system and plumbing components.
<b>Water clarity and color</b>											
Coloured dissolved organic matter	X									plausible	Increasing organic matter in source waters can contribute to formation of disinfection by-products during drinking water treatment
Dissolved solids in water			X			Aesthetic recommendation: ≤ 600; greater than 1000 considered unpalatable		Aesthetic guideline: ≤ 500		plausible	Naturally occurring; sewage, urban and agricultural runoff, industrial wastewater; Based on taste; TDS above 500 mg/L results in excessive scaling in water pipes, water heaters, boilers and appliances; TDS is composed of calcium, magnesium, sodium, potassium, carbonate, bicarbonate, chloride, sulphate and nitrate.
Optical Water Type Class	X									plausible	Increasing organic matter in source waters can contribute to formation of disinfection by-products during drinking water treatment
Total suspended matter concentration	X				X					plausible	Increasing organic matter in source waters can contribute to formation of disinfection by-products during drinking water treatment
Turbidity	X	X								plausible	Increasing organic matter in source waters can contribute to formation of disinfection by-products during drinking water treatment

### **Water clarity and color**

Measures of water clarity do not have health-based guidelines for drinking water (Table 7.1). However, aesthetics on color of drinking water are discussed in WHO Drinking Water Quality Guidelines (DWQG) [9]. Measures of turbidity, total dissolved solids and total suspended matter are consistently collected to assess water quality worldwide. These measures represent levels of organic matter present in water which can be critical to decisions about the suitability of a water source for treatment. Optical water type classification approaches offer potential in monitoring these parameters and others such as cyanobacteria concentrations using analyses of remotely sensed reflectance data. Initially used primarily for marine systems, analytic techniques are being adapted to inland freshwater systems [10].

Monitoring solids and organic matter can be used to identify pollution from sewage and municipal wastewater, runoff from agricultural and mining activities, oil extraction and refining, pulp and paper mills, metallurgy, machine production and textile manufacturing [11]. Pathogens and chemicals can attach to suspended solids through sorption and can be partially protected from disinfection and oxidation during drinking water treatment [12]. Thus, high organic matter can also indicate high pathogen and fecal contamination loads and protect some pathogens against chlorination. Measuring solid concentrations in water can also indicate the presence of metals in suspension or solution from natural or human activity.

High levels of organic matter are a challenge to drinking water treatment. If not removed completely before disinfection stages, they interact with disinfection chemicals and processes and can form disinfection by-products that are hazardous to human health, including THMs, HAAs when free chlorine is the main disinfectant and halogenated acetonitriles and N-NDMA when chloramines are used as disinfectants [7]. In addition to human activities, extreme rain events can increase soil erosion and threaten human drinking water by increasing solids and organic matter content of source waters [6].

### **Conductivity and Major ions**

The ability of a water body to conduct electricity is measured as conductivity and corresponds to ion levels present in water. Major cation and anion levels determine the conductivity of water and determine overall salinity. Levels of conductivity and salinity can indicate contamination from wastewater and industrial effluents and agricultural runoff, especially when compared against benchmark or references for expected natural concentrations of cations and anions. Effluents and runoff could increase conductivity by contributing chloride, phosphate and nitrate ions while oils or some organic compounds may decrease conductivity, despite increases in total dissolved solids. Addition of contextual data and temporal monitoring of conductivity can help detect influxes of effluents harmful to human health.

Four major cations are commonly used in water quality assessments including calcium, magnesium, sodium and potassium. Calcium and magnesium levels are collectively or individually measures of hardness. Though there are no health-based guidelines, there are several aesthetic guidelines established for water hardness as measured by calcium and magnesium (Table 7.2). Major anions including chloride and sulfate also lack health-based guidelines but have suggested aesthetic guidelines due to odor and taste preferences of users.

## Nitrogen and Phosphorus

Of the chemical measures proposed, only nitrate has well established health-based guidelines for drinking water. Excess nitrates in water are of major concern for direct human ingestion and have wide ranging negative impacts on ecosystem health, drinking water treatment systems, and wastewater treatment. Preventing nitrate and nitrite exposure in drinking water is best managed by reducing concentrations in source waters due to difficulties in removing them from drinking water [9].

In addition to fertilizer sources, nitrate, nitrite and other access nutrients can also enter drinking water supplies through other nonpoint and point sources of untreated animal and human waste. Nitrates have been widely detected in numerous studies of domestic wells in concentrations exceeding recommended drinking water guidelines [13,14] and are often associated with mixtures of other volatile organic compounds and pesticides [15,16].

Nitrates and nitrites ingested through drinking water can induce methemoglobinemia in adults and is particularly dangerous for bottle-fed infants between the ages of 3-6 [17]. Methemoglobin forms when nitrite oxidizes ferrous iron of hemoglobin and prevents oxygen transport [18]. Some nitrate is converted into nitrite through endogenous bacteria in the saliva and intestinal tract. At above 60%, there is a high risk of mortality [18]. Treating water oxidizes nitrite to nitrate, the less toxic form, and reduce gastroenteritis which is a risk factor for methemoglobinaemia in infants. Subchronic exposures to nitrate and nitrite have been linked to problems with thyroid function and thyroid hormone concentration through nitrate inhibition of iodine uptake. Chronic exposures to nitrate and nitrite have been linked to cancer but are inadequate to conclude a causal mechanism. Nitrite can form N-nitroso compounds, some of which have been shown to be carcinogenic to humans. As a result, most regulatory bodies have set health-based guidelines for nitrite and nitrate (Table 7.2).

Nitrogen-fixing bacteria and some cyanobacteria can convert dissolved nitrogen ( $N_2$ ) into ammonium. Although there are no health-based guidelines for ammonium, there are recommended aesthetic guidelines because of taste and odor issues for users.

High levels of phosphorus in waters can cause increased productivity and is commonly present around areas of intensive fertilizer use in agricultural systems. Like nitrogen, phosphorus is a key nutrient and can limit or increase primary productivity through growth and large populations of algae, macrophytes and cyanobacteria. There are no health or aesthetic guidelines for phosphorus, but it can indicate high levels of agricultural and wastewater discharge into water sources.

Nitrogen or phosphorus are two limiting factors that when released into aquatic ecosystems in excess can cause increased primary productivity, typically photosynthetic organisms including phytoplankton, cyanobacteria, algae and macrophyte plants [19]. The most common symptom of eutrophication in a water body occurs when excessive growth of primary producers reaches levels that significantly reduces oxygen necessary for supporting biota in aquatic ecosystems. The biological indicators discussed below

## Oxygen

Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) are measures of the amount of oxygen needed to decompose the amount of organic matter in water. COD also includes oxygen required

**TABLE 7.2. Chemical Water Quality Measures and Related Health and Aesthetic Guidelines for Drinking Water from WHO, US EPA, Health Canada and the EU**

Indicator	Global Lakes Data	Brazil	Mexico	India	Mekong	WHO	US EPA	Health Canada	EU	Quality	Health impacts
						guideline value (mg/L)	Maximum Contaminant Level (mg/L)	Maximum Acceptable Concentrations (mg/L)	Parameter (mg/L)	of human health risk evidence	
<b>Conductivity and Major ions</b>											
Calcium					X	Aesthetic guideline: 100-300				plausible	High levels can increase corrosion of pipes resulting in release of heavy metals that have associated health risk.
Chloride					X	Aesthetic guideline: ≤ 250	Aesthetic guideline: ≤ 250	Aesthetic guideline: 250		suggestive	Chloride in surface and groundwater from both natural and anthropogenic sources, such as run-off containing road de-icing salts, the use of inorganic fertilizers, landfill leachates, septic tank effluents, animal feeds, industrial effluents, irrigation drainage, and seawater intrusion in coastal areas
Conductivity				X	X					plausible	A general indicator of human pollution, as human disturbance tends to increase dissolved solids and conductivity of water. High levels can increase corrosion of pipes resulting in release of heavy metals that have associated health risk.
Magnesium					X					plausible	High levels can increase corrosion of pipes resulting in release of heavy metals that have associated health risk.
Potassium					X					plausible	
Sodium					X					plausible	High levels are used to indicate pollution from urban runoff, industrial effluent, leachate from landfills, private and municipal septic system effluent and some agricultural chemicals.
Sulphate					X		Aesthetic guideline: ≤ 500			plausible	High levels (above 500 mg/L) can cause physiological effects such as diarrhoea or dehydration
<b>Nitrogen and phosphorus</b>											
Ammonium				X		Aesthetic guideline: 35			Aesthetic guideline: 0.3	suggestive	Ammonia is toxic to fish, but does not pose a direct risk to human health in concentrations found in surface waters. High levels of ammonia in source water can contribute to the formation of nitrogenous disinfection by-products during treatment.

*table continues next page*

TABLE 7.2. continued

Indicator	Global Lakes Data				WHO guideline value (mg/L)	US EPA Maximum Contaminant Level (mg/L)	Health Canada Maximum Acceptable Concentrations (mg/L)	EU Parameter (mg/L)	Quality of human health risk evidence	Health impacts
	Brazil	Mexico	India	Mekong						
Nitrate	X		X	X	50 (as NO <sub>3</sub> <sup>-</sup> )	10 as nitrate-nitrogen	45 as nitrate; 10 as nitrate-nitrogen	50 (as NO <sub>3</sub> <sup>-</sup> )	strong	Infants below the age of six months who drink water containing nitrate in excess of the MCL could become seriously ill and, if untreated, may die. Symptoms include shortness of breath and blue-baby syndrome; Effects on thyroid gland function in bottle-fed infants; Classified as possible carcinogen under conditions that result in endogenous nitrosation
Nitrogen				X					suggestive	Nitrates and nitrites are toxic to human health, elemental nitrogen is not dangerous at natural levels.
Phosphorus	X			X					plausible	A major driver of eutrophication which could indicate higher organic matter concentrations, leading to higher probability of formation of disinfection by-products as well as providing a substrate for sorption of pathogenic microbes and chemicals
<b>Oxygen</b>										
BOD	X		X	X					plausible	Biochemical Oxygen Demand (BOD) at high levels reflects high microbial growth. Higher levels are an indicator of influxes of nutrients such as wastewater or industrial effluents high in nutrients.
COD	X	X		X					plausible	Chemical Oxygen Demand (BOD) at high levels reflects high levels of oxidizable pollution which can be organic or inorganic. Includes BOD but includes non-biological chemical oxidation
Dissolved Oxygen			X	X					plausible	Indicator of eutrophication associated with high nutrient influxes. Eutrophication could indicate higher organic matter concentrations, leading to higher probability of formation of disinfection by-products as well as providing a substrate for sorption of pathogenic microbes and chemicals

Note: Each parameter is graded by the level of evidence supporting it has presented a health risk if indicating poor quality. Strong indicates a parameter that has a large body of evidence supporting a health guideline. Suggestive indicates the parameter is often associated with specific chemical contaminants or disinfection by-product of health concern. Plausible indicates that the parameter is less often associated with a specific chemical contaminant or group of contaminants.

to break down inorganic chemicals including nitrate, nitrite, or ammonium in addition to organic matter decomposition. Both are used to measure and monitor the amount of organic matter and inorganic pollutants present in waste water or contamination from wastewater and industrial effluents. It is often used to identify the points of wastewater and industrial effluents within the same body of water [20].

Oxygen availability is one of the most important measures of a healthy ecosystem as it is necessary for aerobic organisms as well as many inorganic chemical reactions. High levels of dissolved oxygen generally indicate good water quality. High levels of salinity and temperature decrease dissolved oxygen levels in water. High productivity due to algae, cyanobacteria or floating vegetation can decrease dissolved oxygen levels as plant material as cells die and are decomposed at the bottom of the lake, consuming oxygen.

## Biological Parameters

### Microbial indicators

Monitoring water for waterborne pathogens is most commonly done by detecting indicators of presence of fecal matter in water bodies. Total coliforms are a general indicator of contamination, but do not necessarily mean that the source is fecal matter as coliforms are also found in plants and soils and could indicate high levels of erosion. Fecal coliforms are a subgroup of coliforms that are commonly found in the feces and digestive systems of humans and animals. *Escherichia coli* (E. coli) is a taxonomic group of fecal coliforms, some of which can be pathogenic and is the most specific proxy indicator of fecal contamination in water.

Though generally not pathogenic, coliforms indicate potential presence of fecal pathogens that are responsible for high disease burden, particularly acute diarrheal mortality (2<sup>nd</sup> leading cause of death in children 1-59 months of age) [21], morbidity [22] and chronic stunting in children frequently exposed to enteric pathogens [23]. The recommended and regulatory guidelines are set at 0 / 100 mL for fecal coliforms and E. coli because of high burdens of disease and risk [9,17,24,25].

### Floating vegetation

Floating vegetation are a group macrophyte that are found naturally on the surface of aquatic environments. The distribution and abundance of floating vegetation is controlled by presence of nutrients in the water column, temperature, light and water flow. Monitoring abundance over time can show influxes of nutrient, sediment and toxins. There is no direct human health risk associated with floating vegetation, but its abundance, especially changes in abundance are a significant indicator of eutrophication and overall aquatic ecosystem health.

### Cyanobacteria

In lakes and rivers excess cyanobacterial (blue-green algae) blooms, including *Microcystis* and *Anabaena* spp. in temperate areas and *Cylindrospermopsis* spp. originating in tropical areas [26,27] are indicators of eutrophication and can also produce cyanotoxins. Cyanotoxins include cyclic peptides, alkaloids, and lipopolysaccharides [28]. Of these, only microcystin-LR has a suggested WHO guideline (Table 7.3) [27]. Microcystins are acute hepatotoxins that impact the liver by inhibiting phosphatases and may be carcinogenic with chronic exposure at low doses [29]. Microcystin-LR is the most common isoform.



**TABLE 7.3. Biological Water Quality Measures and Related Health and Aesthetic Guidelines for Drinking Water from WHO, US EPA, Health Canada and the EU**

Indicator	Global Lakes Data	Brazil	Mexico	India	Mekong	WHO	US EPA	Health Canada	EU	Quality	Health impacts
						guideline value (mg/L)	Maximum Contaminant Level (mg/L)	Maximum Acceptable Concentrations (mg/L)	Parameter (mg/L)	of human health risk evidence	
Chlorophyll- <i>a</i> (mean for the lake + maximum peak height)	X									plausible	Indicator of eutrophication
Coli		X				0 number /100 ml	0 number /100 ml	0 number /100 ml	0 number /100 ml	strong	Indicator of enteropathogens
Fecal coliform				X	X	0 number /100 ml	0 number /100 ml	0 number /100 ml	0 number /100 ml	strong	Indicator of enteropathogens
Floating cyanobacteria	X									plausible	Certain species can produce cyanotoxins
Floating vegetation	X									plausible	High levels are an indicatory of eutrophication which could include high nitrites, nitrates, or ammonium concentrations
Immersed Cyanobacteria	x									plausible	Certain species can produce cyanotoxins
Total coliform	X			X		0 number /100 ml	0 number /100 ml	0 number /100 ml	0 number /100 ml	strong	Indicator of enteropathogens

Note: Each parameter is graded by the level of evidence supporting it has presented a health risk if indicating poor quality. Strong indicates a parameter that has a large body of evidence supporting a health guideline. Suggestive indicates the parameter is often associated with specific chemical contaminants or disinfection by-product of health concern. Plausible indicates that the parameter is less often associated with a specific chemical contaminant or group of contaminants.

Polluted agricultural runoff, seasonal patterns of rainfall, and regional distribution of cyanobacterial species contribute to the types of blooms and whether or not these blooms will produce toxins [29-31]. Increases in cyanobacteria concentrations can pose problems with water treatment facilities that must increase filtration capacity to ensure that cells are removed and also monitor that cyanotoxins are removed after cell lysis. Most conventional treatment facilities remove most major cyanotoxins including microcystins, but removal efficiency is not known for less studied cyanotoxins [32].

## Recommendations

The set of water quality indicators (Tables 7.1-7.3) provide a general overview of water quality as related to *ecosystem health*, especially from agricultural runoff and wastewater pollution. However, of the proposed indicators only nitrates and fecal indicators are a direct indicator of risk to *human health* with specific health-based guidelines that permit an estimation of risk based on exposure levels. Faecal indicator bacteria - such as *E. coli* - offer well-established proxy indicators for faecal contamination of water with global guideline safe drinking water values of 0/100ML [9] based on observed dose-related increases in health risks for drinking water [33-35] and recreational waters [36]. One type of microcystin cyanobacteria also has a health-based guideline should it produce toxins. Other water quality parameters that measure the presence of organic matter, temperature and pH are all important in assessing risk of disinfection by-products that are hazardous to human health and that form during water treatment [6,7].

Specific information on the distribution, number and abundance of contaminants a river or lake drainage basins is the most effective way to optimize human health assessment and facilitate the most effective policy recommendations. However, tests for specific contaminants can be expensive and presents logistical challenges for consistent and frequent monitoring across large watershed areas. The set of water quality measures presented here are frequently used to locate the sources of pollution within a river or lake basin [20,37] and are used to measure seasonal and temporal variation in pollution inputs [38-40], but offer only a general, qualitative assessment of human health risk based on assumptions about quality changes associated with natural and human impacts. The addition of indicators appropriate for remote sensing detection offers the ability to show larger scale changes over individual monitoring stations while detailed data on human activity such as spatial information on the types and intensity of activities [41] can further guide testing for specific contaminants.

Measurement and determination of the impact of human activity on fresh surface water quality must account for underlying natural conditions which vary significantly by setting. Any measurement must be compared and standardized against the natural signature of indicators without influence from anthropogenic activities. Environmental factors such as climate, seasonality, composition of bedrock, groundwater flow, surface soil runoff, atmospheric deposition, wind erosion, and the composition of biological life all influence the natural water quality of a lake independent of human activity. Human inputs to surface waters from agriculture, industrial, and domestic activities should be considered in the context of the natural water quality conditions. The USEPA assessment benchmarks were established based on a set of reference lakes that represented water bodies in a state close to what would be expected naturally in each region of the US [5]. This allowed for water quality and lake condition indicators to be classified relative to a set of benchmarks that represented minimal human influences, permitting a meaningful assessment of changes associated with human activity.

Geospatial data on human activities relative to the geophysical and ecological characteristics of the watershed is critical to understanding the sources of contamination and can provide valuable insight into the types of contamination underlying water quality. In the US EPA National Lakes Assessment, characteristics of the lakeshore conditions including riparian vegetation cover, shallow water habitat, lakeshore disturbance, lake drawdown, and lake habitat were assessed in addition to biological and chemical indicators [5]. Seasonal changes in the water column of deeper rivers and lakes must also be considered as water movements between depths change during the season and could impact the detection of chemical contaminants.

In several studies in river and lake contexts, multivariate statistical and data reduction methods to group sampling sites into clusters based on water quality measures and relating the most important water quality measures to specific types of pollution inputs based on their pollution classification and qualitative information about human activities and pollution sources near each sampling point [20,37-40,42]. However, other than fecal contamination indicators, nitrate and some heavy metals, they do not test for or attempt to correlate measures to other specific guidelines on chemical contaminants.

### **Suggested Contaminants and Water Quality Parameters to Monitor**

The advantage of using water quality measures presented here is their wide use as a result of being cost-effective as compared to more lab or equipment intensive measures for specific chemical contaminants. As a result of sharp increases in chemical manufacturing over the last few decades, the number of chemical contaminants entering the environment from human activities has increased faster than our ability to monitor them in then environment. In addition to currently regulated contaminants, there is a literature around ‘emerging’ contaminants that represent potentially hazardous species that are not yet monitored or regulated in surface water supplies. Broadly, these include pharmaceuticals, personal care products, flame retardants and microplastics [43,44]. Currently, these are not included in these recommendations, but interested in monitoring them is growing and are becoming more relevant to policies aimed at protecting drinking water sources.

Addition of a select number of commonly used contaminants that represent industrial effluent and pesticide residues would expand assessment of contaminants relevant to human health risk and provide more specific information on industrial and agricultural contamination risk not captured by the current candidate list. In the USEPA National Lakes Assessment, atrazine, nitrate, mercury and microcystin have enforced and recommended guidelines set by the EPA, WHO and other regulators. Conditions and indicators were compared to 2007 results and by major geographic regions, and categorized as least, moderately and most disturbed condition classifications based on reference lake benchmarks. The pesticide atrazine was monitored due to its popular and widespread use in US agricultural systems [5].

In the GEMS/Water Programme, organic contaminants such as polychlorinated biphenyls and oil and grease were selected to monitor contamination from industrial activity [3]. Heavy metals such as arsenic, mercury, fluoride, lead and selenium are also often measured as part of water quality assessments that can be present naturally, but could also be linked to mining activities in the lake catchment area [45-48]. The selection contaminants to be monitored directly could be tailored to the specific and relevant industrial activities present around the lake or in the lake catchment area.

Polycyclic aromatic hydrocarbons (PAHs) are a useful group to consider adding to country monitoring agendas. PAHs are ubiquitous in the environment because most are considered pyrogenic, formed during the incomplete combustion of coal, wood and oil [49]. Others are considered petrogenic or released from crude oil or during the refining of oil. Some PAHs are also released biologically, during natural fires or from volcanic activity. An advantage of monitoring PAHs is that there is an extensive literature on using the PAH ratios to identify the sources of PAHs (pyrogenic or petrogenic) as water contaminants [49,50].

A common measure for assessing water quality in river systems is discharge and could be an important addition to the measures discussed in this chapter. Discharge is included in studies of river systems because the concentration and duration of contaminants in rivers is determined by the volume and speed of water flow. In most river systems discharge will vary with season and in all rivers with heavy rainfall events. Pejman et al. found that the contributions of different water quality measures varied according to season in their multivariate analysis of seasonality and spatial distribution of water quality parameters [39]. Discharge was an important variable in determining seasonal water quality in their study.

### Global Water Quality Index

Comparing water quality between, and within, water bodies has been a challenge to large-scale studies attempting to draw conclusions about ecosystem and human health of water sources. Through the history of water quality assessment, several aggregate indices composed of multiple water quality parameters have been proposed to assess and compare the health aspects of water bodies [51,52]. One of the more versatile indices is the Canadian Water Quality Index (CCME-WQI) because health and aesthetic guidelines or background benchmarks of natural conditions can be used instead of weights established by expert panel, as had been used in some earlier indices [51]. After selecting the water quality measures to be included in the index (WQI), three factors based on comparisons to benchmarks or guidelines are included for each: 1) the percentage of measures that exceed benchmarks or guidelines (scope,  $F_1$ ) over a period of time, 2) the percentage of records in a dataset that exceeded benchmarks (frequency,  $F_2$ ), and 3) the amount that the measure exceeded a benchmark or guideline amplitude,  $F_3$ ) [53].

$$WQI = 100 - \left( \frac{\sqrt{F_1^2 + F_2^2 + F_3^2}}{1.732} \right)$$

The CCME-WQI was adapted for use across 75 countries under the GEMS/Water Programme with three different versions of the index adapted with WHO guidelines [53]. Two indices contained separate water quality measures: 1) the Health Water Quality Index (HWQI), based on health guidelines and 2) the Acceptability Water Quality Index (AWQI) based on acceptability or aesthetic guidelines. The third index, the Drinking Water Quality Index (DWQI) included all of the water quality measures included in the HWQI and AWQI together. In developing the indices, the indicators for fecal contamination were left out because levels almost always exceed 0 / 100 mL in most lakes and rivers [53]. The lack of health-related guidelines in Table 7.2 will not allow for calculation of a HWQI if indicators of fecal contamination are adjusted based on evidence-based criteria. Thus, use of a DWQI that includes both types of measures would be the most suitable for this group of measures.

## Conclusion

A comprehensive assessment of all chemical contaminants is beyond the scope of global scale studies of water quality. Consideration of contexts and the types of comparisons that can be made within and between lakes and regions will be important in selecting the correct number and composition of indicators of water quality. With few exceptions, broad indicators of ecosystem health are suitable for the assessment of lakes as sources of water for human consumption before treatment and distribution. However, contextual information about potential sources of contamination in lakes is essential to an accurate understanding of human health risks and appropriate policy responses to mitigating these risks.

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