SOURCES, PATHWAYS, AND RELATIVE RISKS OF CONTAMINANTS IN SURFACE WATER AND GROUNDWATER: A PERSPECTIVE PREPARED FOR THE WALKERTON INQUIRY

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On a global scale, pathogenic contamination of drinking water poses the most significant health risk to humans, and there have been countless numbers of disease outbreaks and poisonings throughout history resulting from exposure to untreated or poorly treated drinking water. However, significant risks to human health may also result from exposure to nonpathogenic, toxic contaminants that are often globally ubiquitous in waters from which drinking water is derived. With this latter point in mind, the objective of this commission paper is to discuss the primary sources of toxic contaminants in surface waters and groundwater, the pathways through which they move in aquatic environments, factors that affect their concentration and structure along the many transport flow paths, and the relative risks that these contaminants pose to human and environmental health.

In assessing the relative risk of toxic contaminants in drinking water to humans, we have organized our discussion to follow the classical risk assessment paradigm, with emphasis placed on risk characterization (see Figure 1). In doing so, we have focused predominantly on toxic contaminants that have had a demonstrated or potential effect on human health via exposure through drinking water. In the risk assessment process, understanding the sources and pathways for contaminants in the environment is a crucial step in addressing (and reducing) uncertainty associated with estimating the likelihood of exposure to contaminants in drinking water. More importantly, understanding the sources and pathways of contaminants strengthens our ability to quantify effects through accurate measurement and testing, or to predict the likelihood of effects based on empirical models. Understanding the sources, fate, and concentrations of chemicals in water, in conjunction with assessment of effects, not only forms the basis of risk characterization, but also provides critical information required to render decisions regarding regulatory initiatives, remediation, monitoring, and management.

Our discussion is divided into two primary themes. First we discuss the major sources of contaminants from anthropogenic activities to aquatic surface and groundwater and the pathways along which these contaminants move to become incorporated into drinking water supplies. Second, we assess the health significance of the contaminants reported and identify uncertainties associated with exposures and potential effects.

Loading of contaminants to surface waters, groundwater, sediments, and drinking water occurs via two primary routes: (1) point-source pollution and (2) non-point-source pollution. Point-source pollution originates from discrete sources whose inputs into aquatic systems can often be defined in a spatially explicit manner. Examples of point-source pollution include industrial effluents (pulp and paper mills, steel plants, food processing plants), municipal sewage treatment plants and combined sewage–storm-water overflows, resource extraction (mining), and land disposal sites (landfill sites, industrial impoundments). Non-point-source pollution, in contrast, originates from poorly defined, diffuse sources that typically occur over broad geographical scales. Examples of non-point-source pollution include agricultural runoff (pesticides, pathogens, and fertilizers), storm-water and urban runoff, and atmospheric deposition (wet and dry deposition of persistent organic pollutants such as polychlorinated biphenyls [PCBs] and mercury).

Within each source, we identify the most important contaminants that have either been demonstrated to pose significant risks to human health and/or aquatic ecosystem integrity, or which are suspected of posing such risks. Examples include nutrients, metals, pesticides, persistent organic pollutants (POPs), chlorination by-products, and pharmaceuticals. Due to the significant number of toxic contaminants in the environment, we have necessarily restricted our discussion to those chemicals that pose risks to human health via exposure through drinking water. A comprehensive and judicious consideration of the full range of contaminants that occur in surface waters, sediments, and drinking water would be a large undertaking and clearly beyond the scope of this article. However, where available, we have provided references to relevant literature to assist the reader in undertaking a detailed investigation of their own.

The information collected on specific chemicals within major contaminant classes was used to determine their relative risk using the hazard quotient (HQ) approach. Hazard quotients are the most widely used method of assessing risk in which the exposure concentration of a stressor, either measured or estimated, is compared to an effect concentration (e.g., no-observed-effect concentration or NOEC). A key goal of this assessment was to develop a perspective on the relative risks associated with toxic contaminants that occur in drinking water. Data used in this assessment were collected from literature sources and from the Drinking Water Surveillance Program (DWSP) of Ontario. For many common contaminants, there was insufficient environmental exposure (concentration) information in Ontario drinking water and groundwater. Hence, our assessment was limited to specific compounds within major contaminant classes including metals, disinfection by-products, pesticides, and nitrates. For each contaminant, the HQ was estimated by expressing the maximum concentration recorded in drinking water as a function of the water quality guideline for that compound.

There are limitations to using the hazard quotient approach of risk characterization. For example, HQs frequently make use of worst-case data and are thus designed to be protective of almost all possible situations that may occur. However, reduction of the probability of a type II error (false negative) through the use of very conservative application factors and assumptions can lead to the implementation of expensive measures of mitigation for stressors that may pose little threat to humans or the environment. It is important to realize that our goal was not to conduct a comprehensive, in-depth assessment of risk for each chemical; more comprehensive assessments of managing risks associated with drinking water are addressed in a separate issue paper by Krewski et al. (2001a). Rather, our goal was to provide the reader with an indication of the relative risk of major contaminant classes as a basis for understanding the risks associated with the myriad forms of toxic pollutants in aquatic systems and drinking water.

> For most compounds, the estimated HQs were <1. This indicates that there is little risk associated with exposure from drinking water to the compounds tested. There were some exceptions. For example, nitrates were found to commonly yield HQ values well above 1 in many rural areas. Further, lead, total trihalomethanes, and trichloroacetic acid yielded HQs >1 in some treated distribution waters (water distributed to households). These latter compounds were further assessed using a probabilistic approach; these assessments indicated that the maximum allowable concentrations (MAC) or interim MACs for the respective compounds were exceeded <5% of the time. In other words, the probability of finding these compounds in drinking water at levels that pose risk to humans through ingestion of drinking water is low.
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> Our review has been carried out in accordance with the conventional principles of risk assessment. Application of the risk assessment paradigm requires rigorous data on both exposure and toxicity in order to adequately characterize potential risks of contaminants to human health and ecological integrity. Weakness rendered by poor data, or lack of data, in either the exposure or effects stages of the risk assessment process significantly reduces the confidence that can be placed in the overall risk assessment.
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> Overall, while our review suggested selected instances of potential risks to human health from exposure to contaminants in drinking water, we also noted a distinct paucity of information on exposure levels for many contaminants in this matrix. We suggest that this represents a significant limitation to conducting sound risk assessments and introduces considerable uncertainty with respect to the management of water quality. In this context, future research must place greater emphasis on targeted monitoring and assessment of specific contaminants (e.g., pharmaceuticals) in drinking water for which there is currently little information. This could be conducted using a tiered risk approach, beginning with, for example, a hazard quotient assessment. Potentially problematic compounds identified in these preliminary assessments would then be subjected to more comprehensive risk assessments using probabilistic methods, if sufficient data exist to do so. On this latter point, adequate assessment of potential risks for many contaminants in drinking water is currently limited by a paucity of toxicological information. Generating this important information is a critical research need and would reduce the uncertainty associated with conducting risk assessments.

When contamination of water supplies leads to tragic events as it did in Walkerton, Ontario, we are reminded of the complacency with which we view and treat our water. Of all the natural resources necessary to ensure human health and civilization, water is one of the most important (Gibbons, 1986). Yet astonishingly, in North America we have a remarkable history of taking both the supply and quality of water for granted. For example, with the exception of trihalomethanes and important pathogenic organisms such as *Escherichia coli*, the monitoring of chemicals in drinking water supplies in Ontario and Canada varies considerably from municipality to municipality, and many chemicals, such as pesticides are monitored very infrequently, often as little as once per year (Government of Canada, 1991). At present, there is no coordinated monitoring program for private wells in Ontario; monitoring of private wells for pollutants is left entirely up to the homeowner.

The importance and seriousness of our present situation with respect to issues surrounding the management of both water quality and quantity were recently emphasized in the publication of the agenda-setting book *The Freshwater Imperative* (Naiman et al., 1995):

Changes in the distribution, abundance, and quality of water and fresh-water resources in this century represent a strategic threat to the quality of human life, the environmental sustainability of the biosphere, and the viability of human cultures. The United States is facing, in a real sense, a freshwater imperative. (p. 1)

Although this quote makes reference to state of water resources in the United States, its disposition, sense of urgency, and implications for the future research and management of water resources are equally applicable for Canada and other countries of the world. Indeed, it is probably fair to suggest that jurisdictional and economic issues pertaining to water quantity and quality will demand global attention in the 21st century in a manner and intensity greater than those induced by petroleum products in the 20th century.

Most Canadians perceive Canada as a land with an abundant supply of fresh water, and this perception is reflected in our daily use patterns. In terms of total water use, the average Canadian drew approximately 4500 L per person per day; in terms of personal use, we drew 340 L per person per day (Government of Canada, 1996). On a global basis, we rank second only to the United States in our per capita use of water for all purposes. In comparison, per capita water use by Europeans is approximately half that of Canadians. Approximately three-quarters of water used for drinking purposes in Canada and Ontario originates from surface waters. With a few notable exceptions (e.g., Kitchener–Waterloo, Ontario), drinking water in urban and suburban centers originates almost exclusively from treated surface water. Groundwater serves as the primary source of drinking water for approximately 7.9 million people (about 26%) of Canadians, with approximately two-thirds (5 million) living in rural areas (Environment Canada, 2000a). In Ontario, close to 30% of residents rely on groundwater as a source of drinking water (Goss et al., 1998). Groundwater not only serves as the primary source of drinking water in rural areas but is also used extensively for important agricultural practices such as irrigation and livestock watering.

We have been charged with the task of identifying and describing the sources and pathways of toxic contaminants in surface water and groundwater and providing perspective on the relative risks that these compounds pose to human health and ecosystem integrity. This is a significant undertaking in light of the large number of toxic contaminants known to occur in surface water and groundwater.

Why examine issues of water contamination by toxic chemicals when the tragic events of Walkerton occurred as a result of pathogenic contamination? Pathogenic contamination of water arguably represents the most significant risk to human health on a global scale, and there have been countless numbers of poisonings and disease outbreaks throughout history resulting from poorly treated or untreated water. Issues surrounding the his-

tory of disease outbreaks in Ontario are discussed in a separate issue paper by Krewski et al. (2001b).* However, significant risks to human health may also result from exposure to nonpathogenic, toxic contaminants in drinking water. Indeed, many chemicals have been identified from surface and groundwater resources that serve as the primary source of drinking water throughout North America and Canada (Larson et al., 1997; Nowell et al., 1999; Allen et al., 1993; Gustafson, 1993). Many of these chemicals occur at low levels and do not pose significant risks to human health. However, others are known or suspected carcinogens and some have been implicated as causative agents of endocrine disruption, potentially causing developmental and reproductive problems in humans and aquatic organisms (National Research Council [NRC], 1999). Aquatic ecosystem integrity may also be significantly compromised by the occurrence of toxic pollutants in surface waters and sediments. Viewed in this context, the scientific and philosophical implications of the Walkerton Inquiry for water quality issues in Ontario and other jurisdictions extend far beyond the catalyst issue of pathogenic contamination and its associated risks to human health. In short, the Walkerton Inquiry provides an excellent opportunity to discuss all issues pertaining to water quality in Ontario and, in doing so, to provide a more holistic perspective on this critical subject.

An important theme throughout the ensuing discussion is our consideration of both human and environmental health issues; these must be treated in full recognition of their intimate connectivity, not as separate entities. For example, many of the sources and pathways of chemicals that have the potential to compromise human health are the same as, or shared with, those that compromise the health of aquatic ecosystems. In fact, many parallels have been drawn between human and ecosystem health with respect to diagnosis and risk assessment (Schaeffer et al., 1988; Rapport, 1989), even though the merits of doing so have been debated at length (Suter, 1993; Lancaster, 2000). If nothing else, the debate has brought much needed attention to the intimate relationship that exists between the state of our environment and the relative health of humans and ecosystems, to the extent that we must concede that a stressed environment is much more likely to be manifest in the poor condition of its inhabitants than a healthy one.

The list of substances that have been identified from surface waters, groundwater, and sediments of North America is long. For many chemicals (e.g., DDT, polychlorinated biphenyls [PCBs]), the sources, environmental chemodynamics, and toxicological implications for human and aquatic ecological health have been well studied, although not necessarily well understood. Through numerous pathways, many of these chemicals find

*Commissioned issue papers for the Walkerton Inquiry can be viewed and downloaded from the official Walkerton Inquiry web site at www.walkertoninquiry.com.

there way into drinking water. A list of the toxic chemicals identified in Canadian drinking water is presented in Table A1 (Appendix), along with descriptions of their uses, sources, and toxicity. This list is not complete. Information for many chemicals is lacking, and old chemicals may be "rediscovered" when they are found to pose risks in new ways. This is illustrated by the emergence of the endocrine disruption hypothesis, in which it has been hypothesized that many well-studied chemicals, under appropriate conditions of exposure, can cause developmental and reproductive problems in wildlife and humans (Colborn et al., 1996). Moreover, new contaminants continue to appear, presenting new problems for which data must be collected. For example, pharmaceuticals have been discharged to aquatic environments in sewage effluents for many years, but only recently have their environmental fate, distribution, and potential risks to humans and ecosystems begun to receive scientific scrutiny (Daughton & Ternes, 1999). A similar scenario exists for fluorinated surfactants, a large class of compounds that are common constituents of many consumer products. Like pharmaceuticals, these compounds have existed for many years, but only recently, following the discovery that some members of this class are highly persistent, have they attracted the attention of environmental scientists with respect to distribution and environmental toxicity. Compounds in these novel classes are not currently monitored in drinking water, so potential human exposure from this route is unknown.

Gaining an adequate understanding of the risks to human health and ecosystem integrity associated with impaired water quality requires a thorough consideration of the spectrum of pollutants that contaminate water, including pathogens. Bringing light to this fact is one of the goals of this article. However, it must also be kept in mind that the number of chemicals that have been identified from aquatic environments and drinking water is large, such that a detailed consideration of the sources, pathways, and potential risks for each is not possible. Thus, to facilitate a focused review, we restrict our discussion primarily to toxic contaminants that have had a demonstrated or potential effect on humans through drinking water. Some of these are listed in Table A1. In doing so, we only briefly consider sources and pathways and relative risks of pathogens originating in water, as these are addressed in greater detail in separate papers submitted to the commission (Goss et al., 2001; Reilly, 2001). In addition, apart from some examples for selected contaminant classes, we do not address issues of contaminant remediation and management. While we recognize that this is a critical aspect of the risk assessment process, it is a substantive subject that itself could form the basis of a commission paper. Interested readers can obtain information on remediation and management technologies from U.S. Environmental Protection Agency (EPA) (2000b).

In assessing the sources, pathways, and relative risks of the various toxic contaminants that occur in drinking water, we follow the classical risk

assessment framework outlined in Figure 1. This model is widely accepted internationally as the basis for the expression of risk and informed decision making on a wide array of chemicals such as pesticides, metals, therapeutic drugs, and other environmental contaminants (National Academy of Sciences, 1983). The key components of this risk-assessment framework are hazard identification, dose-response (effects) evaluation, exposure (sources/pathways) evaluation, and risk characterization. The last step is important as it brings together information from the three preceding steps to determine the probability of an adverse effect under defined exposure conditions.
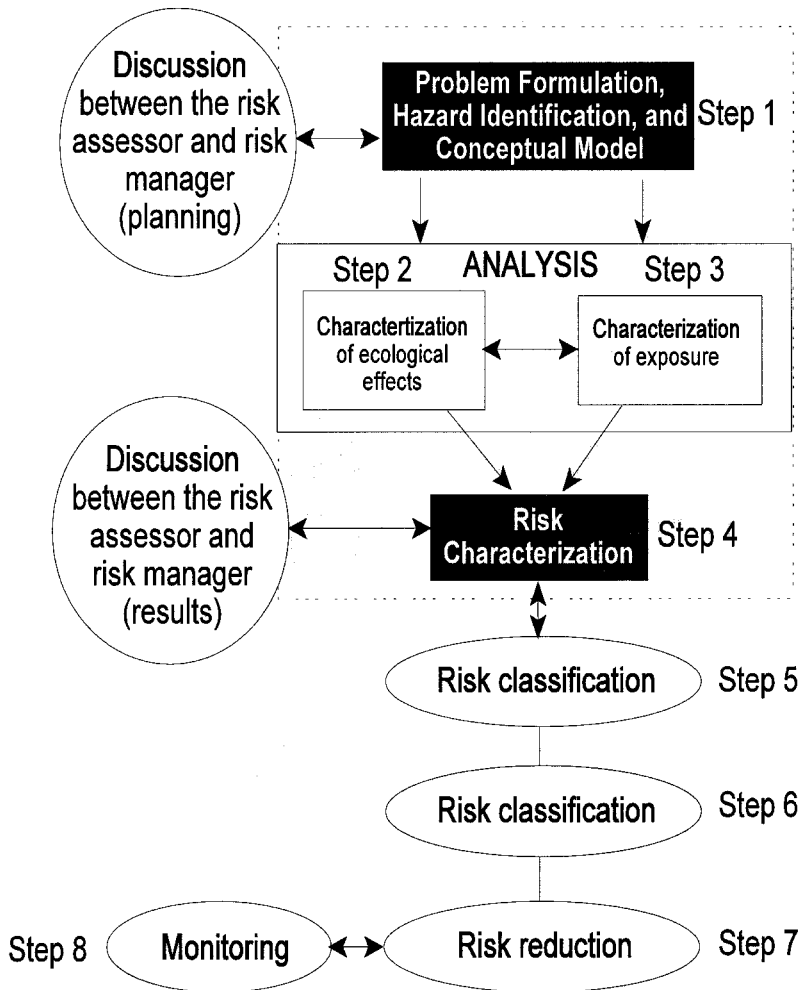
FIGURE 1. Risk assessment framework developed by National Academy of Sciences (1983).

TABLE 1. Major Point Sources and Nonpoint-Sources of Contaminants to Surface Waters, Ground-water, and Sediments

Source	Explanation	Types of contaminants
	Point sources	
Industrial	Process effluents from pulp and paper mills, chemical manufacturers, steel and metal product manufacturers, textile manufacturers, food processing plants	Organochlorines, metals, dyes, BOD
Municipal (sewage treatment plants)	Publicly owned sewage treatment plants that may receive indirect discharges from industrial facilities or businesses	Metals, pharmaceuticals, antimicrobials, nutrients
Combined sewer overflows	Sewage treatment facilities or single facilities that treat both storm water and sanitary sewage, which may become overloaded during storm events and discharge untreated wastes into surface waters	Pathogens, metals, polycyclic aromatic hydrocarbons (PAHs), sediment
Resource extraction	Mining, petroleum drilling, runoff from mine tailing sites	Metals, PAHs, acidity
Land disposal	Leachate or discharge from septic tanks, landfills, industrial impoundments, and hazardous waste sites	Pathogens, nitrates, hazardous chemicals
	Nonpoint sources	
Agricultural	Crop production, pastures, rangeland, feedlots, animal operations	Pesticides, nutrients, pathogens, sediment
Storm sewers/urban runoff	Runoff from impervious surfaces including streets, parking lots, buildings, roof, and other paved areas	PAHs, sediments, pesticides, pathogens, metals
Silvicultural/forestry	Forest, crop, and pest management, tree harvesting, logging, road construction	Pesticides, sedimentation
Atmospheric deposition	Emissions from industrial stacks and municipal incinerators, pesticide applications	Persistent organic (lipophilic) and polar pollutants (POPs and PPOPs), metals
	Other sources	
Construction	Land development, road construction	Export of sediment/soils and nutrients

TABLE 1. Major Point Sources and Nonpoint-Sources of Contaminants to Surface Waters, Groundwater, and Sediments (*Continued*)

Source	Explanation	Types of contaminants
	Other sources (*continued*)	
Habitat modification	Removal of riparian vegetation, stream-bank modification, drainage/filling of wetlands	Export of sediment/soils and nutrients, loss of habitat diversity
Hydrologic modification	Channelization, dredging, dam construction, flow regulation	Sedimentation, temperature changes, flow restriction
Cooling-water effluent	Discharges intended to remove heat (e.g., power generating stations)	Temperature

Note. Adapted from U.S. EPA (1998a).

OBJECTIVES

With this background and associated caveats in mind, the objectives of our issue paper are:

1. To identify and describe key point and nonpoint sources (environmental loading) of contaminants to surface waters, the environmental pathways through which contaminants move in aquatic environments (surface water and groundwater), and the mechanisms that act to modify their concentration or chemical structure as they are transported along these flow paths. A key goal in this discussion is to identify the types of toxic contaminants in drinking water and to describe how they came to be present in this matrix.
2. To assess the probability of exposure to the various contaminant classes by humans and aquatic biota in relation to the sources/pathways.
3. To assess the relative risk of selected contaminants that have had a demonstrated or potential effect on human health via drinking water using the hazard quotient approach.
4. To identify important information gaps and research needs and provide prioritized recommendations for future research and management of toxic contaminants in Canada's water resources.

SOURCES AND PATHWAYS OF CONTAMINANTS IN AQUATIC SYSTEMS AND DRINKING WATER

Anthropogenic and natural contaminants that occur in surface waters, groundwater, sediments, and ultimately in drinking water originate from two primary source categories: (1) point-source pollution and (2) non-point-source pollution (Table 1). Point-source contributions of contaminants originate from discrete sources whose inputs into aquatic systems and can often

be defined in a spatially explicit manner through measurement of chemical residues (in water, sediments, or affected species) and/or epidemiological factors associated with varying incidences of morbidity, mortality, or community disruption (Kleinow & Goodrich, 1994). Examples of point-source pollution include industrial effluents (pulp and paper mills, steel plants, food processing plants), municipal sewage treatment plants and combined sewage–storm-water overflows, resource extraction (mining), and land disposal sites (landfill sites, industrial impoundments).

Non-point-source pollution, in contrast, is diffuse by nature, occurring over broad geographical scales. Because of its diffuse nature, non-point-source pollution typically yields relatively uniform environmental concentrations of contaminants in surface waters, sediments, and groundwater. From a risk assessment perspective, non-point-source pollution often cannot readily be delineated in a spatially or temporally explicit manner. This leads to significant difficulty in the management of non-point-source pollution using conventional regulatory approaches. Examples of non-point-source pollution include agricultural runoff (pesticides, pathogens, and fertilizers), storm-water and urban runoff, and atmospheric deposition (wet and dry throughput of persistent organic pollutants).

It must be kept in mind that the distinction between point and non-point sources of contamination for some contaminant classes can be difficult to establish. For example, the discharge of metals to surface waters from mining operations may represent a significant point source of contamination, but many of these same metals may occur ubiquitously in the environment as a result of natural geological processes.

In addition to the traditional point and nonpoint sources listed in Table 1, there are a number of other sources of water contamination. Examples include construction (land development, roads), habitat modification (removal, addition of riparian buffer zones), hydrologic modification (dams, channelization), and cooling-water effluents. These sources generally do not directly contribute toxic chemicals per se to water, but their associated stressors may be just as significant in terms of their effects on in-stream ecological integrity. For example, siltation as a result of habitat or hydrologic

TABLE 2. Five Leading Pollutants Causing Water Quality Impairment in Various Surface Waters of the United States

Rank	Rivers	%	Lakes	%	Estuaries	%
1	Siltation	51	Nutrients	51	Nutrients	57
2	Nutrients	40	Metals	51	Pathogens	42
3	Pathogens	32	Siltation	25	Toxic organic chemicals	40
4	Oxygen-depleting substances	29	Oxygen-depleting substances	21	Oxygen-depleting substances	33
5	Pesticides	21	Noxious aquatic plants	16	Oil and Grease	20

Note. Percent impairment attributed to each pollutant is shown in parentheses. For example, siltation is listed as a cause of impairment in 51% of impaired river miles. Adapted from U.S. EPA (1998a).

modification can result in significantly increased sediment loading in streams, with a corresponding loss of benthic productivity and fish habitat (Waters, 1995). In fact, siltation was identified by the U.S. EPA (1998a) as the most significant pollutant causing degradation of U.S. streams (Table 2). Indirectly, however, changes in the physicochemical characteristics of receiving water or sedimentary environments resulting from habitat and hydrologic modification can significantly influence the transport and loading of contaminants contributed from other sources. For example, the primary route for phosphorus loading to surface waters is via runoff of sediment particles to which the phosphorus is bound (Ritter, 1988). Increased phosphorus loading may therefore occur in agricultural areas that do not incorporate management strategies aimed at mitigating the loss of soils due to surface runoff.

Following release to the environment from any of the point and non-point sources identified in Table 1, a contaminant may move or partition into several different environmental matrices, whereupon it may be subjected to a myriad of factors that act to modify its concentration and chemical characteristics. For example, toxic contaminants may be converted to nontoxic forms by microbial, chemical, and photolytic degradation in both surface waters and sediments. Some contaminants, particularly lipophilic (lipid-loving) forms, adsorb to suspended particles, soils, or sediments, which reduces their ambient water concentrations and biological availability (bioavailability). Occasionally, degradation of contaminants leads to the formation of toxic or bioaccumulative metabolites. For example, the insecticide DDT can be metabolized to the biologically active environmental metabolite DDE; it is the latter that has been implicated in eggshell thinning and possible endocrine disruption.

The mobility and extent to which a chemical undergoes transformation in the environment, and hence the pathways and degree to which aquatic biota and humans may be exposed to it, depend largely on the physicochemical characteristics of the contaminant. For example, polar (water-loving) contaminants will generally remain dissolved in water and are often highly mobile in the environment. A notable example is the herbicide atrazine, which is commonly detected in both surface water and groundwater (atrazine and other pesticides are discussed in greater detail under nonpoint sources of contamination). Polar compounds generally do not bioaccumulate (but see atmospheric transport section for an exception) and therefore are rarely found at elevated concentrations in biotic tissues unless exposure is constant. In areas in which specific polar compounds occur, they may be common constituents of influent water in water treatment plants. In contrast, nonpolar (water-hating) or lipophilic compounds are more likely to be associated with suspended particles or to become entrained in aquatic sediments. Notable examples are polychlorinated biphenyls (PCBs) and DDT. These sparingly soluble compounds are rarely detected in treated drinking water. The primary route for exposure to lipophilic compounds for humans and aquatic biota is through the diet.

To facilitate discussion of the pathways through which contaminants move in the environment, it is instructive to identify the two matrices that serve as the primary conduits for contaminants to drinking water: surface water and groundwater. Surface water includes all water that occurs on the landscape, including streams, ponds, lakes, and oceans. In Canada, surface waters have long been used as a sink for many forms of anthropogenic waste; however, they also serve as the primary source of drinking water. Approximately three quarters of water used for drinking purposes in Canada and Ontario, particularly in urban centers, originates from surface waters. Groundwater, as the name implies, is water that occurs in the pores and crevices of soil and rock beneath the ground. Although groundwater exists virtually everywhere underground, some areas naturally contain more water than others. Such areas are referred to as aquifers and they range in size from only a few hectares in area to thousands of square kilometers, and in depth from only a few meters to several hundreds of meters (Environment Canada, 2000a).

In Canada, groundwater serves as the primary source of drinking water for approximately 7.9 million people or about 26% of the population (Government of Canada, 1996). In some provinces, this proportion is much higher. For example, in Prince Edward Island and New Brunswick, 100% and 60% of drinking water originates from the ground, respectively (Health Canada, 1997). In Ontario, approximately 23% of residents rely on groundwater as a source of drinking water, extracted via both community and privately owned wells; the majority of these residents live in rural communities.

As with surface water, there are many sources of contamination to groundwater (Table 3). The spatial extent and intensity of groundwater contamination depends upon many factors that collectively make detection, treatment, and management of this resource unique from that of surface water when it becomes contaminated. For example, groundwater moves at variable rates, depending upon the nature of the geological formation in which it occurs. The rate at which contaminants move in groundwater will depend upon the comparative density and natural flow pattern of the water already contained within an aquifer (Miller, 1980). In general, groundwater contamination moves as a plume. Where the hydrogeology of an area has been well defined, it may be possible to track the movement of the plume or determine the spatial extent of contamination. However, in some soils plume movement is so slow that by the time groundwater contamination has been detected, it is often too late to prevent contamination of drinking-water sources, and impacts on aquatic ecosystems have already occurred. Further, it is often too expensive to initiate practical remedial action. Thus, for groundwater contamination, attention must be focused on source protection such as ensuring safely and properly constructed wells, the use of secure landfill sites (if these must be used), and appropriate disposal of waste materials. Some of these aspects of waste management are considered

TABLE 3. Sources of Groundwater Contaminants

Category 1: Sources designed to discharge
  substances

1 Sub-surface percolation from septic tanks/
  cesspools

2 Injection wells
  Hazardous waste
  Nonhazardous waste (e.g., brine disposal)
  Nonwaste (e.g., solution mining)

3 Land application
  Wastewater (spray irrigation)
  Wastewater by-products (biosolids)
  Hazardous waste
  Nonhazardous waste

Category 2: Sources designed to store, treat, and/
  or dispose of substances; discharge through
  unplanned release

1 Landfills
  Industrial hazardous waste
  Industrial nonhazardous waste
  Municipal sanitary

2 Open dumps, including illegal dumping

3 Residential disposal

4 Surface impoundments
  Hazardous waste
  Nonhazardous waste

5 Materials stockpiles (nonwaste)

6 Graveyards

7 Animal burial

8 Above-ground storage tanks
  Hazardous waste
  Nonhazardous waste
  Nonwaste

9 Underground storage tanks
  Hazardous waste
  Nonhazardous waste
  Nonwaste

10 Containers
  Hazardous waste
  Nonhazardous waste
  Nonwaste

11 Open burning and detonation sites

12 Radioactive disposal sites

Category 3: Sources designed to retain
  substances during transport or
  transmission

1 Pipelines
  Hazardous waste
  Nonhazardous waste
  Nonwaste

2 Materials transport and transfer operations
  Hazardous waste
  Nonhazardous waste
  Nonwaste

Category 4: Sources discharging substances as
  a result of other planned activities

1 Irrigation practices

2 Pesticide applications

3 Fertilizer applications

4 Animal feeding applications

5 De-icing salt applications

6 Urban run-off

7 Percolation of atmospheric pollutants

8 Mining and mine drainage
  Surface mine related
  Underground mine related

Category 5: Sources providing conduit or
  inducing discharge through altered flow
  patterns

1 Production wells
  Oil and gas wells
  Geothermal and heat recovery wells
  Water supply wells

2 Other wells
  Monitoring wells
  Exploration wells

3 Construction excavation

Category 6: Naturally occurring sources
  whose discharge is created and/or
  exacerbated by human activity

1 Groundwater–surface-water interactions

2 Natural leaching

3 Salt water intrusion

Note. Adapted from Barcelona et al. (1990); based on a survey conducted by the U.S. Office of Technology Assessment (1984).

in greater detail later in relation to the various point and nonpoint sources of pollution.

Finally, it is important to bring attention to the fact that historical approaches and philosophies regarding the governance and management of groundwater/surface-water research has been to treat these two water systems as separate entities (Naiman et al., 1995; Duncan, 1999). However, the intimate chemical and biological connections between groundwater and surface waters and their important relationship to the hydrological cycle have gained wide acceptance by scientists and greater appreciation by environmental managers. Understanding the nature of groundwater–surface-water relationships is a crucial step to understanding the pathways through which contaminants may be exchanged between these two systems. Thus, it is imperative that future assessment and management of these systems be conducted in a manner that recognizes this intimate connection.

POINT SOURCES OF WATER CONTAMINATION

In this section, we identify and describe key point sources of contaminants to aquatic environments. The discussion is organized according to the type of source, within which we identify the major contaminants that have had demonstrated or potential risks to human health via drinking water. In doing so, we describe the major transport pathways along which contaminants from each source move in surface water, groundwater, sediments, and the atmosphere, with the goal of identifying the main pathways by which contaminants enter into drinking-water supplies. Where possible, emphasis is placed on contaminant distribution and loading in Ontario waters; however, these data were not always available for some contaminants so we have augmented our discussion with examples drawn from elsewhere in Canada and the United States.

Industrial and Resource Extraction

Industrial applications constitute a significant source of toxic contaminants to surface waters, sediments, and groundwater in Canada, and many contaminants of industrial origin have been detected in drinking water. In Canada, there are three primary industries that are based on the extraction or removal of resources from within or on the land: mining (predominantly metals), petrochemical, and pulp and paper. Collectively, these industries account for approximately 10% of Canada's gross domestic product (GDP) and directly employ over one million people (Government of Canada, 1991). Chemical manufacturers, steel and metal processing plants, textile manufacturers, and food processing plants are also important industries in Canada. Most contaminants from industry are discharged directly to surface waters in effluent or to the atmosphere via stack emissions. However, leaching of chemicals from waste disposal dumps and hazardous waste

wells may be significant direct sources of industrial contaminants to ground-water. In either case, industrial-borne contaminants have had broad impacts on aquatic ecosystems, and many pose risks to human health (Government of Canada, 1996).

Keith (1979) reviewed the occurrence and frequency of detection of organic contaminants and metals in industrial waste waters in a 1979 survey conducted by the U.S. EPA. Although not inclusive, this review listed 129 chemicals, many of which have been designated priority pollutants (contaminants that are given high priority for risk assessment and management). Many of these chemicals have been detected in drinking water extracted from both surface-water and groundwater sources. Indeed, there are numerous classic examples of contaminated drinking-water supplies resulting from the inappropriate or poor disposal of industrial wastes across North America (Jorgenson, 1989; Gustafsson, 1993).

Industrial wastes can lead to the contamination of drinking water by one of three primary routes. The most common pathway is through direct discharge of effluents into surface waters from which drinking water supplies are extracted. Industries that use large amounts of water for processing (e.g., the pulp and paper industry) have high potential to pollute waterways and sediments through the discharge of their effluent into streams and rivers. Industrial contaminants may also enter drinking water supplies through leakage, leaching, runoff, or seepage of contaminants from waste water impoundments and hazardous waste wells into nearby groundwater aquifers. Industrial contaminants may also enter aquatic environments via atmospheric transport of smokestack emissions that are deposited either directly to surface waters via wet and dry deposition or indirectly in runoff and leachates following deposition on land. Atmospheric transport of pollutants is treated separately later under non-point-source pollution. In each case, contamination of drinking water supplies from industrial sources will depend upon the various types of industrial processes, the types of contaminants contributed by the different industries, and the disposal practices of the industry.

In the following text, we consider the types of contaminants originating from three primary industrial point sources: mining, pulp and paper, and petroleum. Although other industrial point sources exist (e.g., food processing industry), these are relatively minor compared to the industries just named in terms of both their economic importance and potential for contributing contaminants to surface waters and groundwater in Canada and Ontario. Of the contaminants contributed by these three industries, we have devoted considerable text to metals. Metals are one of the most common yet toxicologically significant contaminants found in water. When examining natural inorganic substances in the context of contaminants, the metals, metalloids, their parent minerals, and derivative compounds must be considered differently than other classes of contaminants for two important reasons. First, metals, unlike synthesized organic compounds, occur naturally

and persist indefinitely in nature, cycling through the environment without breaking down. Second, some of these elements are required as macro- and micronutrients and are essential at specific concentration ranges for health of biological organisms. Owing to their natural and anthropogenic origins, and ubiquitous occurrence in surface and groundwater, we have purposefully departed from the general organizational structure of the document to consider both point and nonpoint sources of metals together.

Mining and Other Sources of Metals and Metalloids in the Environment

Metals are solid substances in their elemental state at room temperature, with the exception of mercury, which is a liquid. They are elements that are naturally present in the earth's crust and in water. Metals can occur as dissolved or particle constituents and are significantly influenced by physical and chemical processes in the environment. Of the multiple forms of metals present in the environment, not all of these are biologically available for uptake by organisms. The particular physical or chemical form in which an element exists, referred to as the *speciation* of an element, is a unique quality of metals that can influence whether the element will have positive or negative impacts on the natural environment. It is essential to recognize that the speciation of the metal along with the total metal contaminant concentration is important in the evaluation of human health and environmental risk and determining the contaminant's behavior. Indeed, the degree of trace metal toxicity depends largely on the form of the metal and on water quality of the receiving environment. Metals can be categorized in general terms according to their potential to be toxic to organisms, as outlined in Table 4.

Sources of trace metals are either natural or influenced by human activities. Natural sources of metals are largely the result of chemical weathering of rock or volcanic activity, both of which can have considerable spatial variability. Regional and vertical variations in metal concentrations in mineral deposits in Canada must be considered in evaluation of trace metal contamination. In some cases, naturally occurring concentrations of trace metals in some regions exceed safe-limit criteria established in particular jurisdictions (Klassen, 1998). Burning of fossil fuels, mining operations, and the industrial use of metals and mineral compounds are prime human-influ-

TABLE 4. Classification of Trace Elements in Water Supplies According to Water Quality Significance

Significance	Trace element
Aesthetic significance—taste and discoloration problems	Cu, Fe, Mn, Zn
Toxic at levels found in some water	As, Ba, Cd, Cr, Hg, Pb
Toxic but present levels in water are probably unimportant	Ag, Al, Be, Bi, Ni, Sb, U
Probably not toxic up to ppm levels, current levels are ppb or less	Ga, Ge, Sn, Sr, Ti, V, Zr
Nutrient metals (at ppb levels), some may be toxic at higher levels	B, Co, Cu, Fe, Mn, Mo, Se, Zn

Note. From Brezonik (1976).

TABLE 5. Concentrations (ppb) of Trace Metals in Municipal Wastewater

Metal	St. Paul, MN	Los Angeles	New York influent	New York effluent	Ontario influent	Ontario effluent
Al					3800	470
As		5	1	0.5	5	1
Cd	36	1	1	0.3	20	<0.01
Cr	470	5–15	20	2	970	90
Cu	280	25–36	76	8	300	60
Hg	2.8	<0.1	<1	0.5	1	0.07
Ni		13–37	8	7	110	50
Pb	69	3	17	2	170	20
Se		1–14			3	2
Zn		49–80	110	32	1120	290

Note. St. Paul from Costner and Thorton (1989). Los Angeles from http://www.sccwrp.org/pubs/annrpt/92-93/ar-01.htm, 1992. New York from http://www.cooper.edu/~ahmed/mtpc.html, 1994. Ontario from Atkins and Hawley (1978).

enced sources of trace metals in the environment. Sources of trace metals in the environment can be described by five general categories: (1) natural geological weathering, (2) industrial processing of minerals and ores, (3) industrial use of metals and metal complexes, (4) leaching of trace metals from waste disposal and urban surface runoff, and (5) human and animal wastes that contain trace metals.

Common point sources of trace metal contaminants are disposal of effluents from mining industries, refining, smelting and manufacturing industries, cement plants, sewage treatment plants that serve domestic and industrial wastewater sources, combined sewer outfalls, incinerators, power plants, landfills, leaking underground storage tanks, spills, and contaminated sites (Williams et al., 1976). Mining is one of the most important point sources of metals to surface waters. In Ontario in 1995, there were 24 metal-producing mines, from which gold, silver, lead, copper, nickel, zinc, molybdenum, and iron represented 68.8% of total value of the nonfuel mineral production in Canada for that year (Alloway, 1995). Of the four mining stages, only mining and milling and postoperational waste management contributed to contamination of surface water and groundwater resources (Alloway, 1995). Another important source of elevated metal concentrations in receiving environments is domestic wastewater (Table 5), since many household and personal products contain metals (Atkins & Hawley, 1978). Corrosion of plumbing pipes and fixtures also contributes metals to wastewater (Millette & Mavinic, 1988). Hazardous material dumps and injection wells for radioactive materials also serve as point sources of trace metal contaminants. Deliberate illegal dumping of metallic residues and wastes must also be included when considering point sources of trace metal contamination.

Nonpoint sources of trace metal contamination include the burning of fossil fuels, agricultural practices, and atmospheric deposition (Williams et

al., 1976). Deliberate application of trace metals in fertilizers, manure, sewage sludge, and pesticides makes agricultural runoff a key nonpoint source in rural areas. In addition to this, soil erosion in agricultural regions contributes to greater mobilization of trace metals. In urbanized areas, trace metal contamination due to stormwater runoff can be a significant nonpoint source of pollution. Common sources of trace metals in urban runoff originate from automobile fuel exhaust and wear and corrosion of automobile components such as tires, brake linings, and exhaust systems (Bannerman et al., 1993). Corrosion from ship traffic on the Great Lakes is also important as a mobile nonpoint source of trace metal contaminants.

Contaminated sediments can also be sources of metal pollution (Smith & Hamilton, 1992). These sediments are usually found downstream of pollution discharges and in highly industrialized and urbanized areas due to discharges from industry and sewage treatment plants. In Ontario, such sediments are found in the Niagara, St. Clair, and St. Mary's rivers, along with the Toronto and Hamilton harbors. Disturbing or dredging these sediments, however, has the potential to release contaminants into the water.

Soil ingestion, both purposeful and inadvertent, by wild animals, livestock, and humans is a pathway of trace metal exposure, especially in the case of dust adhering to plants, that is sometimes overlooked when assessing the environmental fate and transport of metals (Sheppard, 1998).

Factors That Affect Metal Concentrations in the Environment

Although trace metals can enter natural water systems by normal weathering of minerals, localized inputs as a result of human activities can make significant contributions to trace metal contaminant loads. Several phenomena unique to trace metals govern the extent to which they become contaminants in natural water systems (Leckie & James, 1976; Parametrix, Inc., 1995). Many of these phenomena depend on interactions between organic and inorganic species present in solution and physical effects at the solid–solution interface. Chemical and physical properties of trace metals influence their availability for uptake by biological organisms and their potential to be toxic to organisms, as well as transport mechanisms in natural waters. For example, fish take up dissolved metals relatively easily, so these metals are more bioavailable than those that are complexed to large organic molecules such as humic acids.

Within aquatic systems, there are many pathways and transport mechanisms by which trace metals partition between the different components of the environment (Harrison, 1990). In both water and sediments, metals are subject to complex chemical and biochemical reactions that affect their chemical behavior and partitioning between different phases (Honeyman & Santschi, 1988; Elder, 1988). Some of these are illustrated in Figure 2. Interactions of these trace metal ions involve many processes, including exchange reactions, adsorption/desorption processes and oxidation–reduction
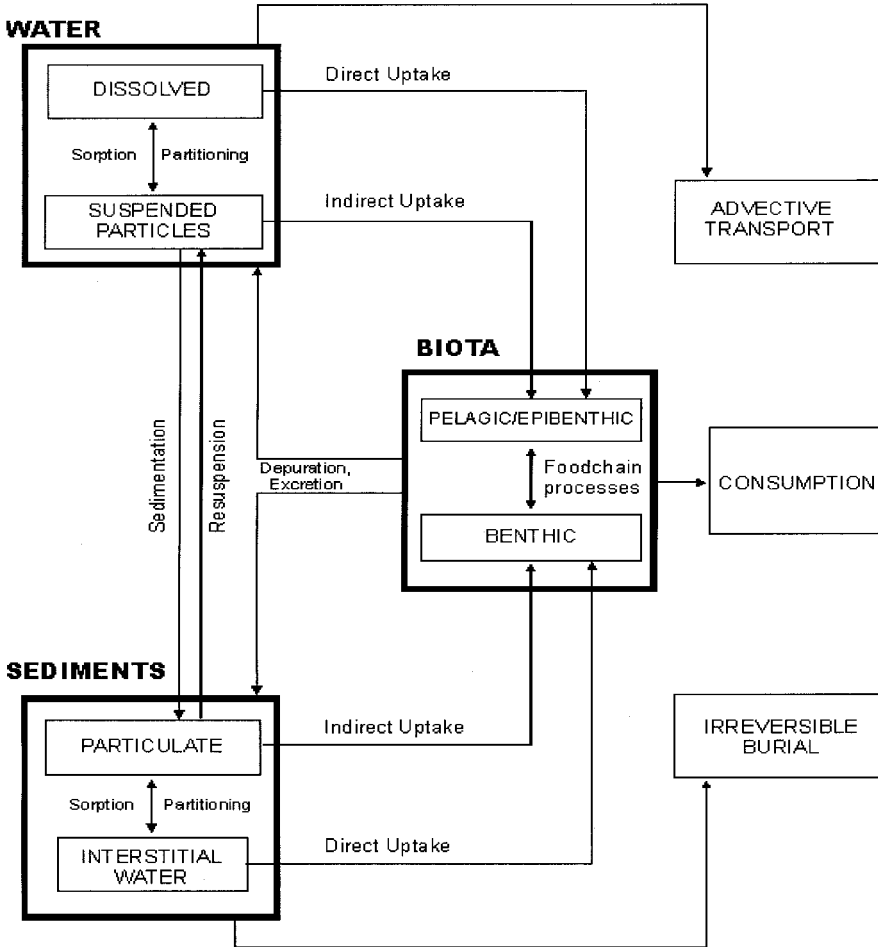
INTERNAL DISTRIBUTION   **EXTERNAL LOSS**

FIGURE 2. Schematic diagram illustrating the complex, heterogeneous environment of a natural water system, which contains a multitude of organic and inorganic matter and is composed of a number of different phases. These include the air above the water, the water column, suspended matter, biota, and the sediment column.

reactions, burial, volatility, and physical advection (Leckie & James, 1976; Demayo et al., 1978). Collectively, these transformation processes are the key factors affecting the distribution, environmental fate, bioavailability, and effects of trace metals in aquatic systems. Importantly, the transport and pathways of trace metal contaminants in water and sediments are strongly influenced by the form of the metal in solution. Many trace metal complexes can exist in the environment for long periods of time in nonbioavailable forms, and thus competing fate processes in receiving environments control the form and species of bioavailable contaminants. For trace metals, many

of these fate mechanisms can transform, bind, or transport compounds such that the bioavailable portion of the total contaminant concentration is reduced. Other important chemical reactions of trace metals such as redox reactions have the potential to change the bioavailable concentrations in the water system. It is now generally accepted that trace metal concentrations in large water bodies are strongly influenced by those removal processes that encourage transformation and transportation of metals into sediment. The complex interactions of these different processes and how they affect the distribution of metals in different components of the aquatic ecosystems are presented in Figure 3. We next briefly review some of the primary factors that control the fate, transport, and bioavailability of trace metals in the aquatic environment.

Hydrogen Ion Activity and pH Of the factors that influence metal partitioning in the aquatic environment, hydrogen ion activity has an overwhelming impact on trace metal chemistry (Elder, 1988). Small changes in pH can have dramatic effects on the speciation of trace metals. The narrow pH ranges in which these changes can occur are common in natural waters. Natural waters have a pH range of 4 to 9 due to carbonate buffering and local geological conditions. Many of the major pathways of trace metal partitioning, including complexation, adsorption/desorption, precipitation, biological uptake, and their respective reverse processes, are highly dependent on pH (Leckie & James, 1976; Black et al., 1973). The critical role of pH on trace metal speciation has a direct influence on the bioavailability and potential for toxicity of metal contaminants.
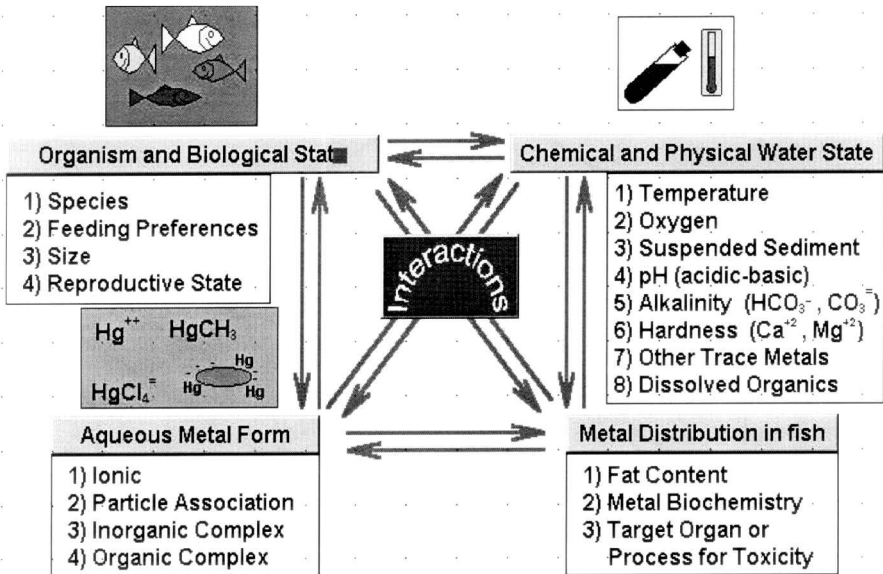

FIGURE 3. Effects of hardness, alkalinity, and pH on the toxicity of copper to rainbow trout (*Oncorhynchus mykiss*). Adapted from Miller and Mackay (1980).

Precipitation, Complexation, and Sorption Many metals form insoluble hydroxide precipitates, especially under basic conditions. These precipitates are often insoluble under natural water pH conditions. Since pH is intimately linked to hydroxide ion activity, the solubility of hydroxide precipitates increases significantly as pH decreases (Pankow, 1991a).

Bonding between charged metal ions and oppositely charged coordinate sites often leads to formation of coordination complexes. Since the hydrogen ion can be a competitor for metals in these metal–ligand complexes, pH can be as important in the degree to which these complexes will form as the concentrations of the metals and complexing molecules themselves. Organic matter in natural water can chelate trace metals and significantly influence mobilization of trace metals by changing their behavior (Singer, 1974). A good example of this is complexation with natural organics such as humic and fulvic acids. Metals can also complex with inorganic anions such as chloride and sulfate. This complexation can alter availability to organisms.

Physical and chemical properties of metals affect surface interactions and the tendency for metals to adsorb to particle surfaces or absorb into the particle. Trace metals ions tend to adsorb onto clay minerals due to negative charges present on the surface of the clay particles. Metal ions of one element can replace other ions of another element via ion exchange, depending on the properties of the element and environmental conditions. Coatings of Fe or Mn oxides and/or organic matter can act as scavengers of trace metals and sorb them onto particle surfaces (Allard et al., 1987; Bendell-Young & Harvey, 1992).

Hardness Water hardness is a measure of the amount of dissolved salts in water [especially calcium, magnesium, and iron(II)]. Usually expressed as equivalents of $CaCO_3$, it has been shown that increasing hardness decreases toxicity of some metals in natural waters to many biological organisms by providing competition for the metal ions for binding sites in organisms. Bioavailability and toxicity of some trace metals can be influenced by the formation insoluble metal carbonate precipitates or by direct adsorption of metals onto calcium carbonate surfaces. The safe concentration of trace metals in solution is closely linked to water hardness, and some water-quality criteria (lead, nickel, and zinc) are expressed in terms of separate values for different levels of hardness of receiving water. An example of the effect of alkalinity and hardness on the toxicity of copper to rainbow trout is provided in Figure 4.

Carbonates Dissolved carbon dioxide (CO_2) in water can equilibrate as three carbonate species (H_2CO_3, HCO_3^-, and CO_3^{2-}), depending on the pH of the water. These carbonate species form the main buffering system in natural waters. Metals can bond or become coordinated with species in solution such as carbonates (Pankow, 1991b).

Since trace metal toxicity depends on its form or speciation, equilibrium concentrations of the carbonate anions influence solution pH, and the
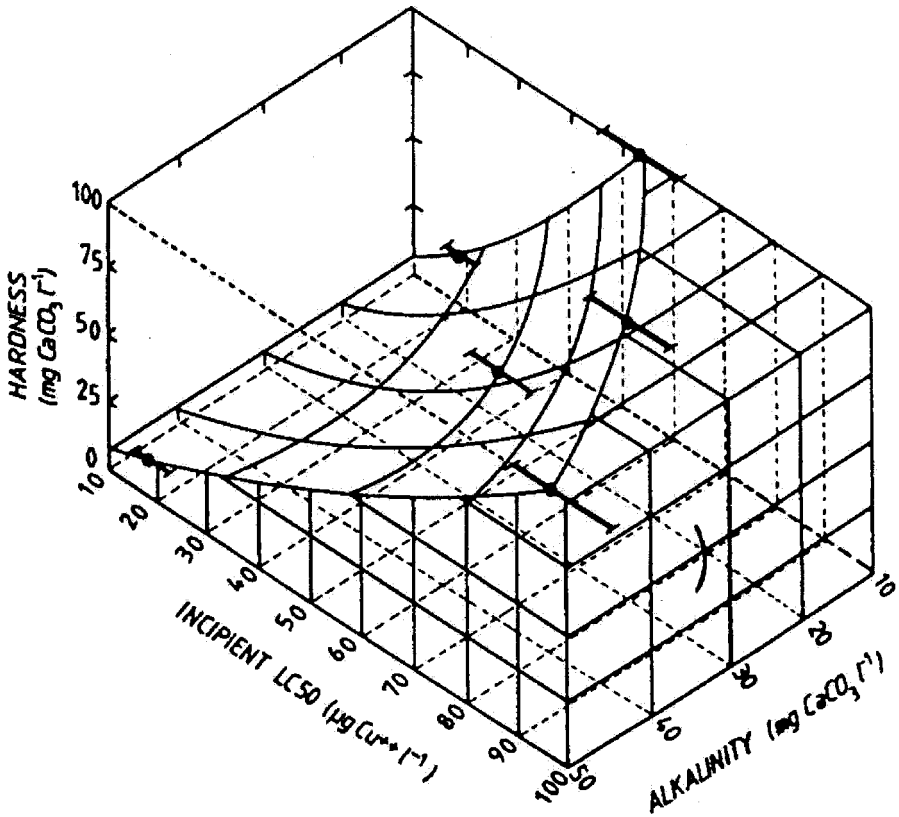
FIGURE 4. Complex interactions between many different parameters and processes affect the distribution of trace metals in the different phases of aquatic ecosystems.

pH, in turn, has a direct influence on the speciation of the metal. Thus, carbonates help determine the behavior of metals in water.

Oxidation–Reduction   In natural waters, oxidation–reduction (redox) processes influence the environmental chemistry of trace metals. Dissolved oxygen is important in establishing the redox conditions in water. Since photosynthesis, respiration, and decomposition processes help regulate the dissolved oxygen concentrations in water, they can indirectly influence the behavior of trace metals.

Changing redox conditions can affect trace metal concentrations in natural waters in two ways. First, direct changes in the oxidation state of the metal ion influences the speciation of the metal. Second, redox conditions in solution influence the competition between complexing species and can alter the bioavailability of a particular trace metal ion (Snoeyink & Jenkins, 1980). The redox conditions and pH become very important in trace metal mobilization and bioavailability in aquatic sediments where a vertical gradient of oxygen is usually present (Campbell et al., 1988).

Biological Factors   Microorganisms, especially bacteria and fungi, can mediate transformation processes of trace metals. Transformations can change the speciation of trace metals and considerably alter the intrinsic behavior of elements. Most heterotrophic organisms depend on oxygen for respiration; therefore, insufficient dissolved oxygen concentrations in natural waters that compromise the health of those microorganisms involved in metal transformations will have impacts on trace metal form and transport. Those contaminants that compete with biological organisms for oxygen can also have an effect on trace metal contaminant concentrations in natural water systems. For example, oxygen-saturated waters are preferred for drinking water, since the oxygen helps precipitate out Fe and Mn.

Trace metals such as Hg, Pb, Se, Sn, and As can form very labile organic complexes, which significantly changes their toxicity (Fergusson, 1990). One such reaction is the methylation of Hg to methylmercury (CH_3Hg) or dimethylmercury ($(CH_3)_2Hg$) (Jernelöv, 1974). Microorganisms in anaerobic environments can mediate these reactions. The alkylated compounds can be many orders of magnitude more toxic than the initial metal species due to their ability to penetrate the blood-brain barrier. For example, the methylated forms of mercury and lead are much more toxic than the elemental forms. However, the opposite can also occur, as shown by the methylation of arsenic which reduces its toxicity. These methylated compounds more readily bioaccumulate in the lipids of organisms. Less toxic forms of these metals can also be transformed to the more toxic forms in the bodies of organisms, including humans.

Pathways and Transport of Metals into Waterways

The hydrologic cycle and the related geophysical conditions within watersheds determine the chemistry of trace metals in human drinking water. In natural water systems, water quality, discharge, and biological productivity are especially important in the transport of trace metals. Water storage and discharge influences dispersion of water constituents, and this in turn has impacts on dissolved trace metal concentration and the tendency for trace metals to undergo sorption processes. Unlike evaluation of transport pathways of synthetic contaminants, trace metal contamination requires an understanding of natural loadings from atmospheric and aqueous pathways (Rasmussen, 1998).

Moving water can dissolve and mobilize metals in its path. These can include contaminants on the surface or in the subsurface of the earth. They can subsequently flow into bodies of water that are used as sources of drinking water. In the urban environment, storm water is usually collected through storm sewers, due to the creation of impervious surfaces. This can accumulate significant metal pollution from the streets, which can then flow into bodies of water that may be used as drinking-water supplies. Creation of impervious surfaces exacerbates the contamination,

since covering soil reduces its ability to filter contaminants (Marsalek & Schroeter, 1988).

Storage of some waste material or tailings from mine operations in regions where high concentrations of sulfide and microorganisms may be present can result in formation of a highly acidic leachate, known as acid rock drainage. This type of mining effluent generates high concentrations of sulfuric acid that can solubilize metals and potentially compromise the quality of drinking water drawn from surface water or groundwater (Gray, 1988).

Facilitated transport is another mechanism that can move trace metals that might otherwise be relatively immobile in the aquatic environment. Trace metals can bind to colloids, natural complexing agents (humic and fulvic acids), and anthropogenic complexing agents such as nitrilotri-acetic acid (NTA), which can "protect" the metal from some precipitation and adsorption reactions (Grout et al., 1999; Gadh et al., 1991).

The amount of trace metal contamination in water is often difficult to quantify because the pollution may be transient and may flow in variable patterns. For this reason, sediments are good long-term indicators of contamination (Smith & Hamilton, 1992; Wilber & Hunter, 1979). Many contaminants including trace metals preferentially partition to sediments from the water column. Trace metals partition to the sediments based on their physical properties. Sediments are composed of many different materials of many different particle sizes. They are composed of materials that have been weathered, washed downstream, and deposited. The heterogeneous nature of sediments is the resulting combination of silt, sand, clays, minerals, organic matter, living organisms, water, and dissolved gases.

Depending on the stream gradient and flow, large amounts of sediments containing metal contaminants may be scoured and transported by the stream during storm events and flooding. Water entering lakes from streams slows and deposits suspended sediments, making lakes sinks for contaminants. The water in the Great Lakes has a long residence time; therefore, contaminants that enter the lakes get trapped within the lakes and concentrate over time. Lakes can become stratified due to temperature gradients, resulting in layers with different physiochemical properties. This process has important implications for contaminant mobility and transport. During certain times of the year, lakes may become sources of contaminants due to the release of contaminants from the bottom sediments. For example, Hg may flow from Lake St. Clair into Lake Erie.

Sediments can exist as deposited bed sediments or as suspended sediments in the water column. Sediment particles usually have coatings of Mn and Fe oxides and organic matter. These coatings provide strong binding sites for contaminants, including trace metals (Bendell-Young & Harvey, 1992). Some of the binding sites hold the contaminants very strongly, while

others only hold the contaminants weakly. This illustrates the concept of bioavailability. Those contaminants that are weakly held are easily available to organisms and the environment, while those that are strongly bound are not as bioavailable. Therefore, the total concentration of a contaminant in sediment is not indicative of its bioavailability, and therefore of its potential to cause harmful or toxic effects on humans or aquatic organisms.

Sediments are composed of many geochemical phases or fractions, such as ion-exchangeable, easily reducible, Mn oxide-bound, organic-bound, and residual components (Bendell-Young et al., 1992; Tessier et al., 1979). Each of these phases holds contaminants with different affinities. Contaminants in the easily reducible phase may be available to the water column with only a small change in the environmental conditions, where-as, in order for the trace metals sequestered in the residual phase to become available for uptake by organisms, the water would have to be-come very acidic.

Transport of contaminants can be augmented as storms, high water flows, and turbulence from boating activities physically disrupt sediment layers. This is one mechanism by which pollution can be transported while still sediment associated. Sediments can release some of their contaminant load when environmental conditions change (Tessier et al., 1994). These events can include aerobic sediments becoming anoxic by burial, changes in redox potential or pH, burrowing by benthic organisms, etc. As more sediments are deposited, layers accumulate and the conditions change, resulting in physical and chemical reactions occurring in the sediments. The water in sediments, often referred to as interstitial water or porewater, also plays an important role in determining contaminant fluxes between the water column and the sediment column and cycling of contaminants within the sediment column (Carigan et al., 1985). Complex processes occur at the sediment–water interface that result in fluxes of contaminants between the sediment and water. Dredging or removal of contaminated sediments may also release large amounts of pollution. One remediation method is to cover the sediments with a layer of material that isolates the sediments, thereby protecting the sediment surface from physical disruption by natural or anthropogenic means.

Concentrations of Trace Metals and Effects in the Environment

Several trace metals are both essential to the overall health of organ-isms at low concentrations and have the potential to become toxic to the organism when tolerable concentrations are exceeded. Figure 5a illus-trates this unique quality of some trace metals. In contrast, some trace metals are nonessential but do not demonstrate toxic effects below a criti-cal threshold concentration (Figure 5b). The tolerable concentration range between thresholds that satisfy fundamental nutritional requirements and levels above which the element becomes toxic to organisms varies among trace metals.
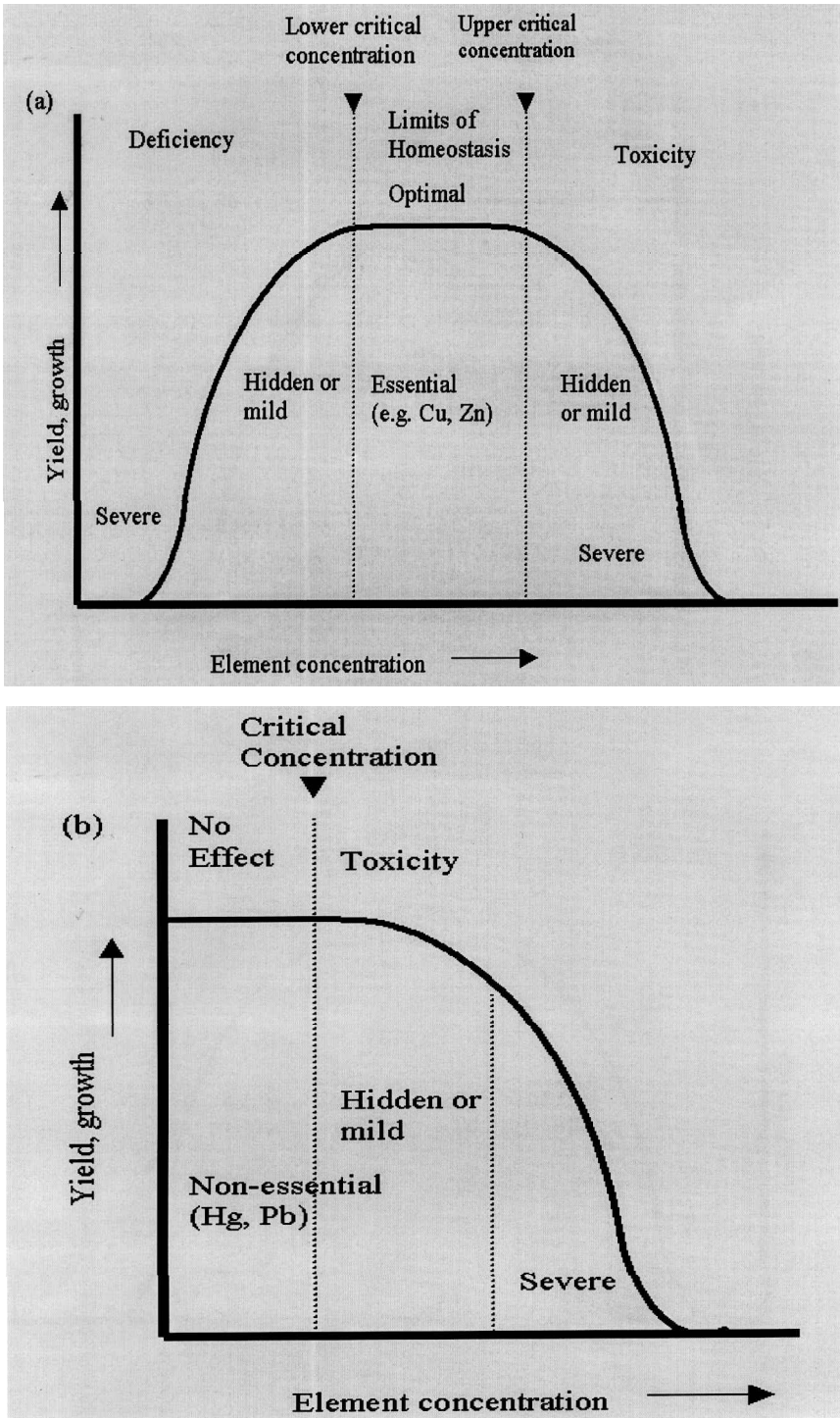
FIGURE 5. Typical dose-response curve for (a) essential and (b) nonessential metals.

Essential elements such as copper, zinc, nickel, and selenium have played a critical role in the evolutionary development of life. Nature became conditioned to the natural levels of metals present in the environment, but this delicate balance can be disturbed by human input of metals. These essential elements can be toxic at concentrations that are too high, and a deficiency of these metals can also be harmful to the health of humans, plants, and aquatic organisms. This is very important in children, as they are growing and do not have fully evolved detoxification systems. Humans can tolerate a range of concentrations of these metals due to excretion and detoxification processes that exist in our bodies. All individuals have small amounts of all metals in their bodies, often referred to as a body burden. This amount usually increases with age. Nonessential metals can substitute for essential metals in individuals, resulting in toxic effects. For example, a Cd ion is approximately the same size as a Zn ion and can replace Zn in various molecules in our bodies. Scientific investigations form the basis for establishing tolerable levels of contamination that provide minimal risk to human and ecosystem health. Understanding the nature of trace metal chemistry in the receiving environment is critical to maintaining suitable water quality for all water uses. There are multiple definitions used to describe the contaminant levels that current science indicates are suitable targets for overall health of organisms within an ecosystem. Water quality criteria, guidelines, and objectives differ from water quality standards, and these descriptors cannot be used interchangeably (Strachan, 1987). A water quality standard is an objective or limit that is recognized in enforceable environmental control laws of a level of government. A water quality objective is a numerical concentration or narrative statement that has been negotiated to support and protect the designated use of water at a specific site. Water quality guidelines are numerical concentration limits or narrative statements recommended to support and maintain a designated water use. Criteria are the scientific data evaluated to derive the recommended limits (either guidelines or objectives) for water uses. The distinction between these terms is important in assessing risk and acting to ensure suitable water quality for all ecosystem members. A federal–provincial committee of the Council of Canadian Ministers of the Environment (CCME) has developed the Guidelines for Canadian Drinking Water Quality (GCDWQ). Various provincial guidelines such as the Ontario provincial water quality objectives also exist. These are shown in Table 6. Sediment quality guidelines have recently been developed by CCME and are shown in Table 7, along with the probable effects level (PEL). The PEL is the concentration at which toxic effects can be expected to occur in aquatic organisms.

An examination of data from the 1998 and 1999 Ontario Drinking Water Surveillance Program (www.ene.gov.on.ca/envision/dwsp9899/dwsp.htm) indicated that metal concentrations in Ontario's drinking-water supply were within guideline values in most of the samples. The program reported results from 162 waterworks that supply water to over 88% of the population served by municipal water supplies. Some water

TABLE 6. Various Drinking Water Guidelines and Objectives for Trace Metals (μg/L)

Metal	GCDWQ	CCME aquatic life	PWQO
Ag		0.1	0.1
Al			15–75[d]
As	25[a]	5	5
Cd	5	0.017	0.1–0.5[c]
Cr	50		100
Cu	1000[b]	2–4[c]	1–5[c]
Fe	300[b]	300	300
Hg	1	0.1	0.2
Mn	50[b]		
Ni		25–150[c]	25
Pb	10	1–7[c]	1–5[c]
Se	10	1	100
U	20[a]		
Zn	5000[b]	30	20

Note. GCDWQ, Guidelines for Canadian Drinking Water Quality (Federal–Provincial Subcommittee on Drinking Water, 1996). CCME, Canadian Council of Ministers of the Environment guidelines for the protection of aquatic life, same as Ontario drinking water standards. PWQO, Ontario provincial water quality objectives.
[a]Interim maximum acceptable concentration (IMAC).
[b]Aesthetic objective.
[c]Depends on hardness.
[d]pH dependent.

supplies that were obtained from groundwater had naturally high levels of salts and minerals; however, these present only an aesthetic concern. No samples had any significant mercury concentrations. A few drinking-water supplies had elevated aluminum levels due to the treatment process. Selenium levels were slightly above guideline values in 4 samples out of approximately 1000. A few water supplies had high copper and lead con-

TABLE 7. Canadian Council of Ministers of the Environment (CCME) Sediment Quality Guidelines (mg/kg)

Metal	ISQG	PEL
As	5.9	17
Cd	0.6	3.5
Cr	37.3	90
Cu	35.7	197
Pb	35.0	91.3
Hg	0.170	0.486
Zn	12.3	315

Note. ISQG, interim sediment quality guidelines; PEL, probable effects level.

centrations due to leaching of these metals from pipes. Flushing the pipes before obtaining drinking water reduces the concentrations of these metals to acceptable levels. The treatment plants that obtain their water from the Great Lakes had influent water-borne metal concentrations that did not exceed the drinking water guidelines.

There are a number of areas of the Great Lakes that contain severely contaminated sediments. These are the largest source of contaminants into the food chain. Forty-three sites have been identified and are awaiting remediation. These include Port Hope, the Toronto and Hamilton harbors, St. Mary's River, Niagara River, and many others. A list is maintained by the U.S. EPA at www.epa.gov/glnpo/sediment/gpra/index.htm.

The following information about the characteristics, sources, environmental concentrations, toxicology, routes of exposure, and effects of the individual metals was derived from the supporting documents for the Guidelines for Canadian Drinking Water Quality (GCDWQ) developed by Health Canada. They can be found on the web at http://www.hc-sc.gc.ca/ehp/ehd/bch/water_quality.htm along with other valuable water quality information. A good discussion of many of these individual metals can also be found in the work by Moore and Ramamoorthy (1984).

Aluminum   Aluminum (Al) is a natural constituent of many minerals and is the most abundant metal in the earth's crust. It is also found extensively in clays. Al is also used in many drinking-water treatment plants to improve water quality. In some treatment plants, incomplete removal of Al can result in elevated Al concentrations in treated water. Health Canada recommends that treatment plants attempt to reduce Al levels in treated water to 0.1 to 0.2 ppm (parts per million), as long as proper disinfection is not compromised.

Current research suggests low level exposure to aluminum in water does not have any significant adverse effects on humans. In 1987, levels of Al in Ontario drinking water ranged from 0.0003 to 4.6 ppm, with a average of 0.16 ppm. At these levels, individuals would have to consume over a 100 L of water every day to experience toxic effects. Ninety-seven percent of Al intake occurs through food. There is some evidence to suggest that ingestion of high levels of Al may play a role in neurodegenerative diseases such as amyotropic lateral sclerosis (ALS), Parkinson's disease, and Alzheimer's disease. However, this has neither been proven nor disproven at the current time and further research is ongoing.

Arsenic   The average arsenic (As) concentration in the earth's crust is 2 ppm, but it can be much more concentrated in arsenic-containing ores such as arsenopyrite (FeAsS). Arsenic can also be a contaminant of other minerals such as pyrite (FeS_2). Arsenic is the 20th most common element in the earth and the 12th most common element in the human body. Sources of As include natural weathering of geologic material, especially those found near gold- and other metal-rich areas, pesticides, wood preservatives,

and smelting. Arsenic is used in semiconductor manufacturing, in pigments, in glass production, and in many other minor uses (Nriagu, 1994).

Arsenic can occur in different forms in the environment, although in groundwater it is usually found as As(III) or As(V). Arsenic in groundwater is usually assumed to be in the As(III) form due to the anoxic conditions present in the aquifer. In surface water, the As(V) form is more common, along with organoarsenic compounds. The aqueous chemistry of arsenic is discussed in depth by Cullen and Reimer (1989).

Elevated levels of As have been found in groundwater in many parts of Canada, including British Columbia, Nova Scotia, Manitoba, and Ontario, as well as in New Hampshire and Michigan. In one area of Nova Scotia, 10% of samples of well water from areas with natural arsenic sources contained more than 500 ppb arsenic. The U.S. Environmental Protection Agency (EPA) recently concluded an extensive study on As in water and recommended lowering the MAC to 10 ppb, in line with the World Health Organization (WHO) and many European countries. Consumption of water containing arsenic concentrations above drinking-water guidelines over long periods of time can cause a variety of health effects. Arsenic is one of the few metals recognized as a carcinogen, and as such is on the drinking water Priority Substance List 1. Arsenic has been implicated to cause a type of skin cancer that is very common, along with cancers of other internal organs.

Different forms of arsenic have varying degrees of toxicity. The trivalent form, As(III), is the most toxic, followed by the pentavalent form, As(V), and then by the organic forms. The average person consumes about 10 µg/d of As through water and food. Most of the exposure comes from eating seafood and meat; however, As in food is usually found in the less toxic organic forms. Smoking also exposes humans to arsenic.

Cadmium Cadmium (Cd) is usually found associated with zinc ores and is therefore released into the environment during the production of zinc and other ores. Cadmium may also be present as an impurity in other metals. The natural average of Cd in the earth's crust is 0.1–0.2 mg/kg. It is most commonly found in the environment in the Cd(II) form and is usually present in water as an inorganic complex. At pH values above 7, most of the Cd is bound to sediments. Canada produced 890 tonnes of Cd in 1982, with most of it being exported. It is used in metal plating, alloys, pigments, Ni–Cd batteries, as a plastic stabilizer, and in a number of other smaller applications. The use of Cd has been increasing over time. The major sources of Cd contamination in the environment are municipal and industrial wastes.

The major source of Cd for humans is food. Cd is not an essential element. It may be released from sediments or dissolved into solution by a decrease in pH. Unpolluted water contains less than 1 ppb Cd. Levels found in Lake Erie and Lake Ontario were below 1 ppb in most cases

(Nriagu et al., 1996), with a few samples as high as 2 ppb. Cd has been found in Ontario sewage sludge at concentrations between 4 and 9 ppm (National Research Council of Canada [NRCC], 1979). Rain in Ontario was found to have an average Cd concentration of 0.8 ppb. Another source of Cd may be impurities in pipes and other plumbing equipment. Flushing pipes before drawing water for consumption can reduce this exposure. Long-term consumption of high levels of Cd may cause accumulation of Cd in the kidneys and may cause itai-itai disease, which leads to weakening of bones.

Chromium   Chromium (Cr) is mostly found in the nontoxic Cr(III) form; however, it can be oxidized to the toxic Cr(VI) form by chlorination in drinking water treatment plants. Cr(III) forms stable complexes with negatively charged organic or inorganic species in water. Cr is naturally found in soils at concentrations up to 120 ppm. Cr is widely used in the metallurgy industry. It is not usually found in the dissolved form in waters above pH 5.

Cr(III) is essential for humans, while Cr(VI) is toxic to humans in high doses and is not essential. Chromium is found in the Great Lakes at concentrations between 0.0002 to 0.019 ppm, with an average of 0.001 ppm. The concentrations of Cr in raw and treated water are predominantly below maximum acceptable concentrations. The major route of exposure to humans is via food consumption. Smoking is also suggested to make significant contributions to Cr exposure in humans (NRCC, 1976).

Copper   Copper (Cu) is a common metal that is found in the environment most frequently as Cu(II), but also as Cu(I). The Cu(II) ion is usually found complexed with organic species such as humic and fulvic acids, or particle or colloid associated. It is often used for plumbing pipes, wire, wood preservatives, pesticides, animal feed, water disinfection, etc. In 1981 over 150,000 tonnes of Cu was produced in Ontario. Mine tailings containing copper and other metals have been disposed of in Lake Superior in the past and may contribute some Cu to the aquatic environment. Copper is often widely distributed in water.

Copper is an essential micronutrient for plants, as well as for animals and humans. Significant health effects do not occur until concentrations of Cu are much higher than the aesthetic guideline (1000 μg/L), which is set to prevent staining of plumbing fixtures. Much of the Cu found in tapwater is due to leaching from Cu pipes that are used to distribute water in homes. Studies of tapwater from across Canada indicate that Cu is present at safe levels. Almost 90% of the average Canadian's intake of Cu is through food.

Iron and Manganese   Iron (Fe) is the fourth most common element in the earth's crust. Iron ore deposits are found in Ontario and are used mainly for the production of steel. Iron and manganese (Mn) are very common in drinking water.

Iron and Mn are essential nutrients for human life. The majority of Fe and Mn exposure comes from food. Concentrations of Fe and Mn in most waters do not present any significant hazards to human life. The aesthetic water quality guidelines (300 and 50 µg/L for Fe and Mn, respectively) are set to prevent precipitates from forming in pipes and to prevent undesirable tastes and color.

Lead   The average lead (Pb) concentration in the earth's crust is 10 ppm. Lead has many commercial uses. Over a quarter million tonnes of Pb was produced in Canada in 1984. It is used in batteries, solder, paints, ammunition, and pipes, and was extensively used as a gasoline additive. Lead additives were banned in most forms of gasoline in 1990. However, vast amounts of Pb that were released into the environment from the combustion of leaded gasoline are still present in the environment and may be available to cycle. In many cases the Pb is held in soils or sediments. Pb is also found in the air; however, these levels have begun to decrease since the elimination of Pb from gasoline in the 1970s. In aquatic ecosystems, Pb is usually found in sediments.

Lead affects the central nervous system of humans, especially children. It is a nonessential element and a cumulative poison if chronically ingested. Most of the Pb found in treated water is introduced from pipes and solder. Flushing of pipes for 3–5 min before drinking should significantly decrease exposure to Pb. Soil, dust, and paint are the major sources of Pb exposure for children. Lead exposure for young children is of concern due to the high percentage of Pb that is absorbed into the body; absorption is thought to impair mental function. The majority of Pb exposure to humans is through food (NRCC, 1978).

Mercury   Mercury (Hg) is a natural and anthropogenic contaminant. It is released naturally from volcanoes and from weathering of soils. In its elemental state it has a high vapor pressure, meaning it can be easily volatilized. In natural waters it can be found in three ionic forms, depending on the pH, redox conditions, and other environmental parameters. When sufficient chloride ion is present in water, the most common form is $HgCl_2$, with sulfide forms present in sediments. Human sources of Hg include fossil fuels, municipal waste incinerators, pulp mills, dental amalgams, electrical equipment, fungicides, seed coatings, and industrial wastes. Chloralkali plants near rivers and lakes in Ontario have dumped massive amounts of Hg into the waters, resulting in contaminated fish and sediments that will continue to be a cause of concern for many years to come. Up to 1960, a plant near Sarnia released up to 90 kg Hg/d into adjacent waterways. Creation of hydroelectric reservoirs also results in high Hg concentrations in the water and fish in the reservoir. This is attributable to mercury release from the decomposing vegetation and soils in the flooded zone (Mierle & Ingram, 1991). Sang and Lourie (1995) reported that 5138 kg Hg is released by humans into Ontario's environment each year. Approximately half of this is released into the air and the other half

into water bodies. The amount released from natural sources may be much greater. However, it is important to remember that these are estimates and there is continuing debate over the numbers. Nriagu (1997) estimated that 39 tonnes of Hg was released into the Canadian environment in 1990, with half of this from nonferrous metal production.

Mercury as a contaminant is known for its toxicity, its tendency to bioaccumulate, and its persistence. Hg can readily transform into the more toxic methylmercury form in the environment and can accumulate in fish. This methylated Hg in fish is the largest source of Hg exposure to humans, primarily through ingestion of contaminated fish and wildlife. Advisories have been issued for the consumption of fish from the Great Lakes due to high levels of Hg in fish. It is a candidate to be banned in the Great Lakes (Sang & Lourie, 1995). Hg is not an essential element and causes neurological and renal problems in humans. The alkylated forms are teratogenic, meaning they cause harm to fetal tissues. Concentrations of Hg are low in most raw and treated water, except near areas of severe contamination. With tighter regulation on the use of Hg, the amounts present in water have begun to decline. Concentrations of Hg in the Great Lakes range from 13 to 18 ppb.

Selenium   The average concentration of selenium (Se) in the crust is 0.09 mg/kg. Like most metals, it is not distributed evenly over the earth's surface. Selenium is found in a variety of oxidation states and is easily taken up by plants. It is a by-product in the production of other ores. Canada is a major exporter of Se, which has a variety of uses, including the production of pigmented glass, microelectronics, stainless steel, and explosives. In some parts of California's agricultural regions, irrigation runoff has been found to contain extremely high levels of Se.

Se is an essential element for humans; however, it is unclear if excessive amounts may cause cancer. Most water sources that were tested had Se levels that were considered safe. Higher concentrations were found in proximity to urban areas, indicating anthropogenic origins. Ingestion of food is the major source of Se for humans.

Uranium   Uranium (U) is a radioactive element that may be found in water in areas with high levels of U mineralization, including areas in Ontario. It may also be found in mine tailings, and from human activities using U such as the nuclear industry. Nuclear power plants are the main end users of U. It is also released from the combustion of fuels such as coal. Canada produced 11,000 tonnes of U in 1984. Most of the human exposure to U is through food.

Zinc   Zinc (Zn) is a common element and its average concentration in Canadian soils is 90 ppm. Zn is usually associated with ores of other common metals such as Pb, Cu, Cd, and Fe. It is used in steel, as an industrial metal, and in galvanizing, along with numerous other uses. Smelters release significant quantities of Zn into the air. Over a million tonnes of Zn was produced in Canada in 1984. A 1980 estimate shows

that over 750,000 tonnes of natural Zn and over 400,000 tonnes of anthropogenic Zn were released into the Canadian environment.

Zn is an essential element that has a recommended daily intake of at least 8 mg/d for adults. Unpolluted freshwater usually has less than 15 ppb Zn. The concentrations of Zn in air are higher in southern Ontario than in northern Ontario. Higher concentrations of Zn were found in precipitation near smelting operations, such as those found near Sudbury. Concentrations of Zn in some lakes used for drinking water in Ontario were found to be below 10 ppb. Water in pipes and plumbing fixtures can be enriched in Zn due to leaching of galvanized pipes and other plumbing fixtures. Food accounts for over 99% of a typical Canadian's Zn intake. The Zn water quality guideline of 5 ppm is an aesthetic objective, set because of the potential for objectionable tastes at higher levels.

Other Metals   The major metals of concern have just been discussed. There are other metals that may be significant in localized areas, such as near geological formations or near mining or smelting operations. The largest nickel (Ni) and copper mining, smelting, and refining complex in the world is located near Sudbury. Higher environmental contamination with Ni is possible in regions such as Sudbury (Nriagu et al., 1998). Silver is another industrial metal that may be of concern in some areas, it is often found in wastewaters associated with photographic processing. Both Ag and Ni are found in sewage. Tin compounds such as tributyltin (TBT) are used as antifouling paints to protect the hulls of ships from attracting barnacles and algae. They are toxic to aquatic organisms and are found in water bodies that are frequented by boats (Randall et al., 1986).

Exposure to Metals From Sources Other Than Water

Primary nonaqueous pathways of trace metals to humans are through consumption of food, occupational exposure, smoking, and air. Many pharmaceutical and therapeutic products (described later) also contain metals and may be a significant route of exposure for some individuals. It is important to realize that these sources of exposure are intimately linked with those from drinking water and should therefore be considered collectively in the risk assessment process.

Risk Assessment and Management of Metals

Risk assessment of trace metals and metal compounds requires an understanding of the fundamental differences between inorganic metal compounds and organic compounds. There are unique attributes of trace metals that must be considered in all steps of the risk assessment process. As naturally occurring substances that persist over time in altered forms, risk associated with the toxicity of the various trace metal elements must be carefully examined in the context of its species, form, and bioavailability. Many metals are essential for health of organisms, and contamina-

tion of waters with nonmetallic contaminants that reduce essential trace metal bioavailability is as much of concern as excessive loading of trace metal contaminants.

Identification of trace metal exposure hazards relies on information about toxicity, persistence, and potential to bioaccumulate in an ecosystem food chain. Although toxicity is the universal measure of potential of hazard applied to all substances, not all substances demonstrate a toxic response. In the case of metals, this is important because some relatively nontoxic metal species can be transformed into potentially very toxic compounds depending on the biological, chemical, and physical characteristics of the receiving environment. Short-term, or acute, toxicity drives the hazard identification process, whereas chronic toxicity endpoints such as reproductive success and growth impairment are secondary measures of hazard identification. An additional important consideration is that metal exposure is cumulative. Unlike exposures to microorganisms, which can be traced back to the source, metal exposure is continuous over a lifetime, so it is difficult to determine the time or route of exposure that may lead to toxic effects.

Petroleum

In Ontario, there are currently seven petroleum refineries. Wastewater discharged from these industries may contain a wide range of organic and metallic pollutants, including phenols, oil and grease, sulfides, ammonia nitrogen, and polycyclic aromatic hydrocarbons (PAHs) (Government of Canada, 1996). Some of these are used or produced during the process of refining, but many are already contained in the crude oil itself (Government of Canada, 1996). Of these contaminants, PAHs have attracted the greatest attention because they are ubiquitous in the environment and some are highly toxic. PAHs may have significant impacts on aquatic ecosystems where they become entrained in sediments and are accumulated by aquatic biota (Huggett et al., 1992). From a human risk perspective, PAHs constitute a significant health concern because some, such as benzo-[a]pyrene, have been shown to be carcinogenic. Importantly, PAHs have been detected in groundwater due to leaching of oils or creosote from spills, untreated discharges, or poor waste management practices (Mueller et al., 1989). For example, one of the common waste disposal methods in the petrochemical industry is the use of deep wells (described later). In general, this is a safe disposal practice, but it can lead to significant contamination of groundwater, as was the case in western Ontario (Lambton County) in the early 1970s. Goss et al. (1998) found no evidence of petroleum derivatives in well water from wells that were located within 60 m of a fuel storage tank on 160 farms. This suggests that there were few incidences of pertoleum spills, leakages, or seepage to the groundwater, or that the relatively lipophilic PAHs were sequestered by soil particles and hence rendered immobile.

Because hydrocarbon processing is a water-intensive practice, the petroleum industry uses and discharges large volumes of wastewater to surface waters. Petroleum-associated contaminants in the wastewater may arise from six separate wastewater streams that flow out of the refinery subsystem. Oil and its associated PAHs are the most common contaminants in refinery effluent, but much of this is typically treated and recovered for reuse in the refinery using separators before entering into the final mill effluent. Sludge produced during this process is treated in the sludge disposal system to produce inert solids for land disposal (Finelt & Crump, 1980).

Most of the refinery effluent undergoes extensive treatment, but some is lost to evaporation and cooling tower blowdown. The effluent is treated using secondary treatment in an activated sludge unit. The treated wastewater resulting from these processes flows into a mixing and surge pond, where further treatment can upgrade the quality for reuse in cooling tower makeup. The biological oxygen demand of the wastewater can be reduced to less than half its original value by using a secondary treatment process. Notably, the dissolved organics that occur in some effluents are not amenable to biological degradation and require tertiary treatment using activated carbon adsorption or reverse osmosis for removal (Beychok, 1980). A final holding basin downstream of the treatment system allows for dilution of effluent and reprocessing of effluent in the case of a plant malfunction. Chlorination may also be added to this last step of the treatment process if there is any pathogenic (coliform) contamination present in the total wastewater (Beychok, 1980).

With a strong effort in reducing environmental impact to meet regulations, the petroleum refining industry has undergone important technological advances in all areas of pollution management, including wastewater. At present, the petroleum industry is subject to a number of environmental regulations under the Petroleum Refinery Effluent Regulations of the Fisheries Act (Government of Canada, 1997). These regulations limit the amount of oil and grease, phenols, sulfide, ammonia nitrogen, and total suspended matter that can be discharged by a refinery in a 24-hour or month-long period (Government of Canada, 2000a). The 1996 Compliance Inspection Summary Report gave a 99% compliance rate for the 84 company reports received (Government of Canada, 1997). With more efficient treatment processes including filters and reverse osmosis units, effluent discharges have been reduced by up to 90% over the last two decades (Government of Canada, 1996). Overall, there does not appear to be any substantial environmental or human health risks associated with petroleum refining based on present-day practices. However, despite significant reductions in the volume of wastewater and associated contaminants over the past 20 years, concerns still persist over discharges of carcinogenic substances and other potentially toxic metal and organic contaminants to surface waters (Government of Canada, 1996). Moreover, localized areas of sediment contamination, particularly in some Great Lakes Areas of Concern (e.g., Hamilton

Harbor in Ontario and the St. Louis River system in Duluth, MN), continue to store and release hydrocarbon compounds, such as PAHs, contributed historically by the petroleum industry (Sibley et al., 1999).

Pulp and Paper

The process of converting wood to fiber produces hundreds of individual compounds that are discharged to surface waters in pulping effluents (Owens, 1991). Pulping effluents represent a significant point source for so-called traditional pollutants such as biological oxygen demand (BOD) and suspended solids to enter into aquatic systems. However, where chlorine is used to bleach pulp, significant quantities of chlorinated substances have also been discharged to surface waters (Suntio, 1988). In general, the majority of chlorinated compounds are high-molecular-weight chlorolignins, which are not thought to cause significant environmental harm because they cannot cross biological membranes (Bonsor et al., 1988). However, a significant contaminant discovered in effluents from plants that used chlorine to bleach pulp was dioxin. The discovery of dioxins and furans, and corresponding concerns about effects on human and ecological health, precipitated a massive research effort to investigate the environmental practices of the pulp and paper industry in Sweden, Canada, and the United States (U.S. EPA, 1988; Svanberg & Bengtsson, 1996; Travis & Nixon, 1996).

The ensuing research showed that the discharge of untreated pulp mill effluents to receiving waters caused significant environmental degradation. Much of this degradation was attributed to factors associated with severe organic enrichment due to heavy loadings of the traditional pollutants (Owens, 1991). Areas affected in this manner were typically characterized by complete loss of benthic habitat and associated benthic communities (Environment Canada, 1987; Scrimgeour, 1989; Owens, 1991; Sibley et al., 2000). However, considerable research on fish populations in both Sweden and Canada also clearly demonstrated significant biochemical and physiological impacts (McMaster et al., 1991; Adams et al., 1992; Munkittrick et al., 1992, 1994; Tana et al., 1994; Forlin et al., 1995; Svanberg & Bengtsson, 1996). The most common abnormalities reported include elevated levels of detoxification enzymes, higher than expected condition factors, reduced gonad size, lower fecundity, and alterations in secondary sex characteristics. More recently, research has been directed toward examination of alterations of sex steroids, stimulated by emerging evidence that these may be causally related to the physiological and morphological impairments observed in wild populations (McMaster et al., 1996). These effects were originally assumed to be present only at mills having a bleaching process and hence linked to exposure to chlorinated organic contaminants, particularly dioxins and furans, discharged in the effluent. However, these effects have recently been shown to occur in fish collected adjacent to mills that do not employ bleaching and/or that have

secondary treatment of effluent (Personen & Andersson, 1992; Munkittrick et al., 1994).

In response to both scientific and public pressure, the pulp and paper industry has undergone extensive changes over the past two decades aimed at reducing pollutants loadings to aquatic environments. At the mills themselves, internal (e.g., changes to in-mill processes such as substituting or eliminating the use of chlorine to bleach pulp) and external (e.g., installation of secondary treatment facilities) changes have led to significant reductions in the loadings of both traditional and chlorinated contaminants to aquatic environments. For example, between 1988 and 1994, loadings of total suspended solids were reduced by 68%, BOD fell by 65%, and the release of dioxins was reduced by 99.4% (Government of Canada, 1996). At present, most pulp mill effluents in Canada are no longer toxic based on toxicity tests with fish and invertebrates. In addition, the pulp and paper industry is currently in the second iteration of the Environmental Effects Monitoring Program, which is designed to track changes in the environmental effects of effluents in relation to changing mill practices and to ensure compliance with existing legislation under the Fisheries Act.

Sewage Treatment and Combined Storm Water Overflows

The collection, treatment, and disposal of wastewater and solids from municipal wastewater treatment plants (WWTPs) may contribute significant loadings of contaminants to surface waters and groundwater via several direct and indirect routes: (1) discharge of effluent to surface waters, (2) leakage from old or improperly maintained collecting sewers, (3) leakage from the treatment plant during waste processing, (4) land disposal of treatment plant effluent and solids, and (5) leaching and runoff of sludge following land disposal. The most significant route in terms of volume is discharge to surface waters, although spills and overflows may also be significant. The latter two routes may lead to contamination of groundwater, especially if the surface water into which the effluent is discharged recharges local aquifers or material is leached through the soil. Where WWTPs are combined with storm-sewer overflows, flow volume may be an important factor determining the quantity of pollutants discharged to surface waters. For example, a recent survey comparing the relative contribution of flow volume, and hence contaminant loading, to surface waters from storm-water runoff, combined sewer overflows, and WWTP effluent discharge in 47 urban centers in Ontario showed that flow volume varied considerably among jurisdictions in relation to precipitation events (Schroeter, 1997). For example, in dry weather conditions, flow volumes varied at 17–65% for storm water, 1–6% for combined sewer overflows, and 35–80% for WWTP effluents. However, in wet weather conditions, the flow volume proportions changed to approximately 80%, 7%, and 13% for these sources, respectively.

Effluents from WWTPs are derived predominantly from household and industrial sources. (Chambers et al., 1997). The effluent may contain solids, suspended and dissolved substances that may incur a biological oxygen demand in receiving waters, nutrients, pathogens, organic chemicals, metals, and oil and grease (Ontario Ministry of the Environment, 1988; Chambers et al., 1997; Li & McAteer, 2000). From a human health perspective, potential impacts of sewage treatment and combined sewer overflows on drinking water quality have focused predominantly on pathogenic pollution and nutrient contamination. However, up to 200 chemicals have been identified from effluents of WWTPs and combined sewer overflows. Interestingly, sewage treatment effluents have recently been shown to contain a variety of hormonally active agents (chemicals that are capable of disrupting the endocrine system), such as alkylphenol ethoxylate surfactants (Bennie, 1999; Servos, 1999). There is also emerging evidence that WWTP effluents contain numerous pharmaceuticals, the environmental fate and effects of which are virtually unknown (Halling-Sorensen, 1998; Koenig et al., 2000). Next, we briefly discuss the sources and pathways of four contaminant classes discharged to surface water and groundwater from WWTP and combined sewer overflow effluents: pathogens, nutrients, hormonally active agents, and pharmaceuticals. Note that contaminant loading issues related to urban and storm water runoff are treated separately under non-point-source pollution.

Pathogens   The most significant from of pollution from sewage treatment and combined storm-water overflows is pathogenic. Sewage treatment plants contribute numerous species of potentially infectious agents including *Salmonella,* coliforms, viruses, and protozoans to surface waters (Table 8). These pathogens are commonly detected in treated waste water treatment effluents, often long distances below the point of discharge (Geldreich, 1996). Drinking water intake pipes of municipalities located downstream of such effluent discharge points may then draw high numbers of pathogenic organisms.

Separate and combined sewer systems that bypass treatment during intense storms are major sources of coliforms to surface waters. For example, the U.S. EPA (1998a) found that approximately 32% of degraded river miles in United States rivers in a nationwide survey could be attributed to pathogenic pollution. This compares to 51% by siltation and 40% by nutrient enrichment (see Table 2). In the Great Lakes region, many miles of shoreline are routinely impaired by pathogenic contamination and many beaches close during the summer months due to human health concerns (U.S. EPA, 1998a). Although much of this contamination results from the discharge of sewage treatment effluents and combined storm sewer overflows, pathogens from agricultural activity and urban runoff also contribute significantly to degradation of water quality (these latter two sources are discussed in greater detail later; see also commission paper by Goss et al., 2001).

TABLE 8. Major Infectious Agents Found Globally in Contaminated Drinking Waters

Organism	Disease	Primary sources
Bacteria		
Campylobacter	Gastroenteritis	Human feces
Enteropathogenic *E. coli*	Gastroenteritis	Human feces
Salmonella (1700 spp.)	Typhoid fever/salmonellosis	Human/animal feces
Shigella (4 spp.)	Bacillary dysentery	Human feces
Vibrio cholerae	Cholera	Human feces
Yersinia enterocolitica	Gastroenteritis	Human/animal feces
Legionella pneumonophila	Acute respiratory illness	Thermally enriched waters
Viruses		
Adenovirus	Upper respiratory and gastrointestinal illness	Human feces
Enteroviruses (71 types)	Aseptic meningitis poliomyeltis	Human feces
Hepatitis A	Infectious hepatitis	Human feces
Norwalk virus	Gastroenteritis	Human feces
Reovirus	Mild upper respiratory and gastrointestinal illness	Human/animal feces
Rotavirus	Gastroenteritis	Human feces
Coxsackie virus	Aseptic meningitis	Human feces
Protozoans		
Balantidium coli	Balantidiasis (dysentery)	Human feces
Cryptosporidium entamoeba histolytica	Amoebic dysentery	Human feces
Giardia lamblia	Giardiasis (gastroenteritis)	Human feces

Note. Adapted from Olivieri (1986) and Geldreich (1990).

Nutrients   Household sewage represents the largest point-source discharge of nitrogen and phosphorus to the Canadian environment (Chambers et al., 2001) (Table 9). However, relative to nonpoint discharges such as agriculture and atmospheric deposition, the contribution of these nutrients from sewage treatment plants and combined storm sewer overflows is comparatively low (<20%). Based on a comprehensive review of all sources of nutrients to Canadian surface waters, Chambers et al. (1997) concluded that N and P loading has increased risks to human health by increasing the frequency and spatial extent to which drinking water guidelines for nitrate are exceeded in groundwater. Indeed, as discussed later, it is not uncommon to observe a relatively high proportion of exceedences of nitrate water quality criteria in rural well waters (Briggins & Moerman, 1995; Frank et al., 1990). Further, they have led to an increase in blooms of blue green algae, which are capable of producing natural toxins that pose risks to human health (see natural toxins, later). They may also impart undesirable tastes and ordors in drinking water. From an ecosystem perspective, increased N and P loadings have accelerated eutrophication (nutrient enrichment) in some rivers, lakes, and wetlands, with a concomitant decline in diversity and habitat quality.

TABLE 9. Comparison of Nitrogen and Phosphorus Loading (10^3 tonnes/yr) to Canadian Surface Water and Groundwater from Various Sources

Nutrient source	Nitrogen	Phosphorus
Municipal wastewater treatment plants	80.3	5.6
Sewers	11.8	2.3
Septic systems	15.4	1.9
Industry[a]	11.8	2.0
Agriculture[b]	293	55
Aquaculture	2.3	0.5
Atmospheric deposition to water	182	N/A

Note. From Chambers et al. (2001).

[a]Industrial N loads are based on $NO_3 + NH_3$ and are thus dissolved inorganic nitrogen and not total nitrogen.

[b]Determined as the difference between the amount of N or P available to the growing crop and that removed in harvest (data are not available regarding the proportion of this residual that moves to surface or groundwater).

Hormonally Active Agents   In recent years, there has been increasing concern regarding potential adverse human and environmental health effects of various contaminants that act on the endocrine system (Colborn et al., 1993, 1996; NRC, 1999). These compounds, designated as hormonally active agents, or endocrine disruptors, have been alleged to include many well-studied compounds such as organochlorine pesticides (e.g., DDT, toxaphene, dieldrin), phenolics (e.g., alkylphenol ethoxylates), PCBs, and dioxins and furans. A comprehensive list of known or suspected hormonally active agents was compiled by Keith (1997); a listing of major

TABLE 10. Estrogenic Potencies of Some Common Xenoestrogens, Relative to 17-β-Estradiol (E2)

Compound	Vitellogenin induction		
	LOEC[a] (μM)	Maximum % of max E2	Potency relative to E2
17-β-Estradiol	0.002	100	1
Diethylstilbestrol (DES)	0.006	135	0.5
Methoxychlor	5	48	1×10^{-3}
o,p-DDT	25	19	2×10^{-4}
Chlordecone	20	3.2	1×10^{-4}
Bisphenol A	50	10	1×10^{-4}
4-t-Pentylphenol	50	10	1×10^{-4}
o,p-DDE	ND[b]	ND	ND
Toxaphene	ND	ND	ND
β-Endosulfan	ND	ND	ND
Dieldrin	ND	ND	ND

Note. Adapted from Smeet et al. (1999).

[a]Lowest-observed-effect concentration; see glossary for definition.

[b]Not detected.

classes of hormonally active agents in the Canadian environment is provided by Hewitt and Servos (2001), selected examples of which are listed in Table 10. Toxicological concerns have arisen from evidence that these compounds may, under conditions of high exposure, mimic the action of the female sex hormone, causing developmental and reproductive effects in wildlife. Strong evidence for such action has been observed among bird populations that feed on contaminated fish (Fox, 1992; Giesy et al., 1994), but several studies have also demonstrated the potential for endocrine disruption in a wide variety of organisms, ranging from invertebrates to mammals (NRC, 1999). Recently, a series of papers was published in which evidence for endocrine disruption in humans and wildlife in the Canadian environment are reviewed (McMaster, 2001; Fox, 2001; Foster, 2001; Munkittrick, 2001). These studies suggest that there is strong evidence for endocrine disruption (e.g., reproductive and developmental impairment) in certain populations, but there has been little progress in linking these effects with specific contaminants. Importantly, some scientists have hypothesized that exposure of humans to hormonally active agents may produce effects on reproduction and development similar to that observed in wildlife and may be involved, for example, in the increasing incidence of breast cancer in human populations (Davis et al., 1993). Further, dietary exposure to PCBs has been correlated with intellectual deficits in children who have been breast-fed in some Great Lakes areas (Colborn et al., 1996).

Hormonally active agents enter the environment from a wide variety of sources, both natural and anthropogenic. Exposure of humans and wildlife to naturally occurring phytoestrogens from plants and vegetables is common. There is little scientific consensus as to the potential risks that these natural estrogen mimics pose to humans; however, whatever risks exist, they probably do not result from exposure via drinking water since exposure to phytoestrogens is predominantly via dietary sources. This is also true of exposure of humans and wildlife to many anthropogenic hormonally active agents, because most are highly lipophilic (James & Kleinow, 1994). However, sparingly soluble, endocrine-active compounds like PCBs, DDT, and alkylphenol ethoxylates are routinely detected in surface water samples from the Great Lakes, albeit at extremely low concentrations (Pearson et al., 1996; Bennie et al., 1997). These compounds could be taken up in the influent water by water treatment plants, although most would not pass through the treatment process and into the final distribution water. Nonetheless, a number of hormonally active agents have been detected at various times in drinking water. Surprisingly, few hormonally active agents are routinely monitored in water treatment plants in Ontario. Although exposure via drinking water is a comparatively minor exposure route for humans, exposure could occur if contaminated water is ingested from an untreated source.

Pharmaceuticals   Despite widespread use in numerous sectors of society, until recently, pharmaceuticals (or medical substances) received

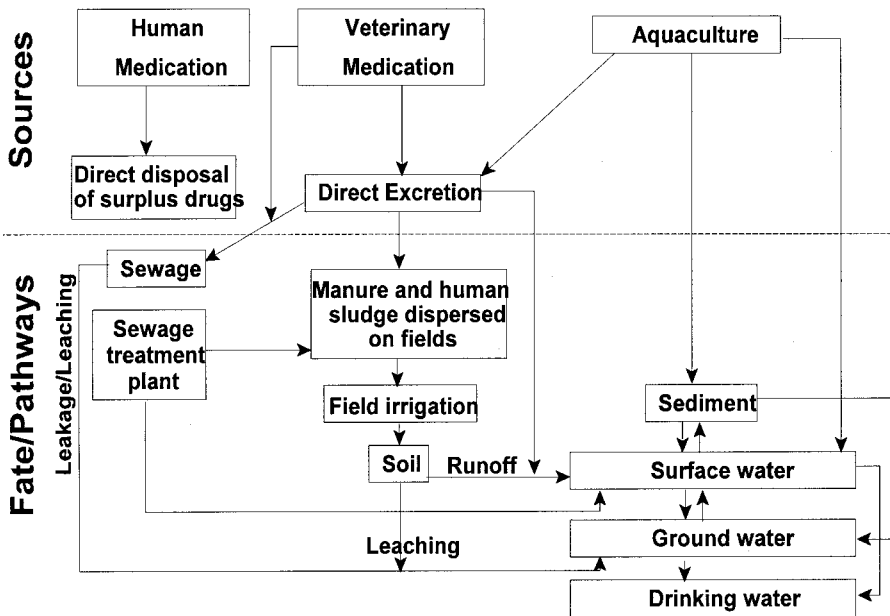## Sources and Fate of Pharmaceuticals in the Environment

FIGURE 6. Sources and pathways of pharmaceutical compounds in aquatic environments. Modified from Halling-Sorensen et al. (1998).

little attention as potential contaminants in drinking water. However, there is considerable emerging evidence that pharmaceutical compounds are relatively widespread in the surface waters of many countries, especially in water bodies receiving effluent from sewage treatment facilities (Halling-Sorensen et al., 1998; Buser, 1999; Daughton & Ternes 1999; Stumpf et al., 1999). In most cases, the concentrations of pharmaceuticals in surface waters occur in the nanograms to micrograms per liter range, with the highest concentrations generally found in waters receiving effluent from sewage treatment plants. However, some pharmaceuticals have also been detected in surface waters that are remote from points of sewage discharge (Daughton & Ternes, 1999), suggesting that some may be at least moderately persistent in the environment.

The various sources and routes of pharmaceuticals in the environment are provided in Figure 6. In Ontario, sewage treatment plants are probably the primary source of pharmaceuticals in surface waters and many have been detected in sewage discharges (Koenig et al., 2000). However, it is likely that pharmaceuticals will also be detected in other aquatic matrices in Ontario as they have in other countries. For example, pharmaceuticals have been detected in groundwater via leachates from landfill sites (Eckel et al., 1993; Holm et al., 1995) and in sediments in conjunction with aqua-

cultural practices (Jacobsen & Berglind, 1988; Kerry et al., 1995). In the latter source, antibiotics administered to fish that are not consumed fall to the bottom to be accumulated in the sediments or discharged after treatment. Veterinary pharmaceuticals used as growth additives in livestock operations (eliminated in urine) could occur in surface waters as runoff from fields that have been subjected to spreading of manure. The same situation may exist in relation to land application of human sludge. Similarly, contamination of groundwater may occur due to mineralization of compounds in the manure or sludge as it lies on the field (Halling-Sorensen et al., 1998). Interestingly, Hirsch et al. (1999) found little evidence of groundwater contamination by pharmaceuticals in areas influenced by agriculture or when sewage was applied to fields.

While numerous pharmaceuticals have been identified in a number of environmental matrices, the extent to which pharmaceuticals occur in drinking water in Ontario and other jurisdictions is virtually unknown. Interestingly, clofibric acid, a common pharmaceutical, was routinely detected in drinking water in Germany, where it was thought to have originated from various medical applications (Stan et al., 1994). Unfortunately, there is no concerted effort to monitor pharmaceuticals in drinking water in Canada, so the potential effects of these compounds on human health are essentially unknown. Similarly, despite routine detection in surface waters, there is nothing known of the potential effects of pharmaceuticals on aquatic biota. It must be kept in mind that pharmaceuticals are designed with the intention of eliciting biological effects, often at very low concentrations. One area of concern is the potential for many antibiotic pharmaceuticals to induce resistance among natural bacterial populations, a phenomenon that has already been demonstrated in aquacultural applications (Kerry et al., 1995; Kummerer, 2000). In light of recent experiences with hormonally active agents, which may impair development and reproduction in humans and wildlife at low concentrations, it is essential to investigate this class of compounds in order to provide a strong basis upon which to assess their potential risk to humans and aquatic biota.

Water Treatment and Disinfection By-Products

Most surface water in North America would be unpotable without some form of treatment to remove pathogens and contaminants (Naiman et al., 1995). Water may be disinfected using a number of treatment methods (WHO, 1996): (1) chlorination, in which water is treated with elemental chlorine; (2) chloramination, in which water is treated with monochloramine; (3) chlorine dioxide; (4) iodination (generally only used for short-term disinfection); (5) ozonation, in which water is injected with ozone to destroy organic compounds that impart taste or odor to drinking water; and (6) irradiation with ultraviolet (UV) light. Of these disinfection procedures, the most common method of treatment on a global basis is chlorination; in Ontario, chlorination is also the disinfection method used

by the vast majority of water treatment plants. Although chlorination is most often used independently to treat water, it may also be used in concert with other treatment processes such as ozonation or UV radiation. These latter methods to control pathogens are often perceived to be too expensive to operate in many treatment systems, so there is often a reluctance to incorporate them as the sole treatment method in many municipalities. Although issues associated with the treatment and disinfection of water are considered extensively in separate issue papers by Doyle (2001a, 2001b), we briefly discuss this source of contaminants here to provide perspective relative to other toxic contaminants and because of the risks to human health associated with certain cancers resulting from exposure to disinfection by-products.

The production of chlorinated contaminants as a result of disinfecting drinking water by chlorination was first discovered in the early 1970s following a nationwide survey in the United States (Crosby, 1998). This was the first evidence that the process of disinfecting drinking water itself could serve as a source of contaminants that posed risks to human health. These chemicals, termed disinfection by-products (DBPs), are formed through the interaction of the chlorine molecules with naturally occurring residual organic compounds, such as humic and fulvic acids, that are ubiquitous in most source waters. Because higher concentrations of residual organic matter generally occur in surface waters compared to groundwater, the formation of DPBs is typically greater when the former is used as a source of drinking water. In addition to the precursor concentration of organic compounds, the formation and quantity of DPBs also depends upon the chlorine dose, pH, temperature, contact time, and bromide ion concentration (Stevens et al., 1989). A list of the DBPs identified from a national survey conducted in Canada in 1993 is provided (Health Canada, 1995) in Table 11.

There are three main classes of DBPs in drinking water that represent potential risks to human health (Table 5 and Table A2): (1) chlorophenols, (2) trihalomethanes (THMs), and (3) haloacetic acids (HAAs). Chlorophenols occur in drinking water as a result of the chlorination of phenols, interaction between hypochlorite and phenolic acids, or as degradation products of phenoxy herbicides (e.g., 2,4-D) (WHO, 1996). Of the several phenolic DBPs produced during chlorination, 2,4,6-trichlorophenol has been reported to induce lymphomas, leukemia, and hepatic tumors in rats. The concentration of 2,4,6-trichlorophenol in drinking water associated with a 10^{-5} excess lifetime cancer risk is 200 µg/L.

From a human health risk perspective, trihalomethanes (THMs) constitute the most important group of DBPs in drinking water. The THMs include four important compounds: bromoform, chlorodibromomethane, bromodichloromethane, and chloroform (the latter is most common). THMs have been closely linked to increased incidences of bladder cancer and possible increases in rectal and colon cancer in humans (Mills et al., 1999). However, the evidence in support of the association between

TABLE 11. Identity and Ranges of Concentrations for Disinfection By-Products Analyzed in Treated Water (Immediately Prior to Distribution) in a 1993 National Survey Conducted by Health Canada, with Corresponding Water Quality Values, Where Available

Disinfection by-product	MAC[a] or IMAC (Canada)	WHO[b] guideline (µg/L)	IARC designation[c]	Concentration range (µg/L)[d]	
				Summer	Winter
Trihalomethanes (THMs)	0.1 mg/L	—	2B	0.2–342.4	0.2–221.1
Chloroform (trichloromethane)	NA	200	2B	0.2–335.9	0.2–216.2
Bromodichloromethane	NA	60	2B	<0.1–29.8	<0.1–16.7
Chlorodibromomethane	NA	100	3	<0.1–19.8	<0.1–9.0
Bromoform	NA	100	3	<0.1–4.2	<0.1–3.3
Haloacetic acids (HAAs)					
Monochloroacetic acid	NA	—	3	0.21–12.1	0.17–7.5
Dichloroacetic acid	NA	50	NA	0.25–163.3	0.11–45.4
Trichloroacetic acid	NA	100	NA	<0.01–296.1	<0.01–473.1
Monobromoacetic acid	NA	NA	NA	<0.01–2.3	<0.01–9.22
Dibromoacetic acid	NA	NA	NA	<0.01–1.9	<0.01–1.98
Other DPBs					
Dichloroacetonitrile	NA	90	3	<0.1–15.0	<0.1–16.3
Trichloroacetonitrile	NA	1	3	<0.1–0.2	<0.1–0.5
Bromochloroacetonitrile	NA	—	3	<0.1–3.7	<0.1–2.4
Dibromoacetonitrile	NA	100	3	<0.01–1.9	<0.01–1.9
1,1-Dichloro-2-propanone	NA	NA	NA	<0.1–2.6	<0.1–3.7
1,1,1-Trichloro-2-propanone	NA	NA	NA	<0.1–9.3	<0.1–10.1
Chloral hydrate	NA	10	NA	<0.1–18.6	<0.1–22.5
Chloropicrin	NA	NA	NA	<0.1–2.5	<0.1–1.6
Bromide ion	0.01 mg/L	NA	NA	10–500	2–500

[a]MAC, maximum allowable concentration; IMAC, interim MAC.

[b]From WHO (1996). Level determined as the concentration of drinking water associated with a lifetime cancer risk of 10^{-5}.

[c]International Agency for Research on Cancer: Group 1A, chemical is carcinogenic to humans; Group 2A, chemical is probably carcinogenic to humans; Group 2B, chemical is possibly carcinogenic to humans; Group 3, chemical is not classifiable as to its carcinogenicity to humans; Group 4, chemical is probably not carcinogenic to humans.

[d]Represents minimum and maximum values measured in distribution water at the treatment plants ($n = 53$) assessed across Canada.

bladder cancer and DBPs is considered to be inadequate by the International Agency for Research on Cancer (WHO, 1996). The levels of these compounds associated with a 10^{-5} excess lifetime cancer risk are 200, 60, 100, and 100 µg/L for chloroform, bromodichloromethane, chlorodibromomethane, and bromoform, respectively.

Chlorinated acetic acids (haloacetic acids) formed during disinfection include mono-, di-, and trichloroacetic acid. Of these, the latter two occur most frequently in treated water and also represent the greatest risks to human health. Dichloroacetic acid has been used pharmaceutically and has been shown to induce hepatic tumors in mice; however, evidence in support of cancer in humans is considered to be insufficient

(WHO, 1996). Trichloracetic acid has been used as a herbicide and the acetate form has been found to induce hepatic tumors and is mutagenic in in vitro assays. The levels of these two compounds associated with a 10^{-5} excess lifetime cancer risk are 50 and 100 µg/L, respectively.

Debates surrounding the merits and potential risks associated with the practice of chlorination versus other forms of disinfection have been prevalent in the scientific and trade journal literature and public fora for many years. The recent declination by the people of Erickson, British Columbia, to chlorinate their water supply is testimony to the intensity and passion invoked by the issue of water chlorination. The issues surrounding DBPs provides us with an excellent opportunity to remind ourselves of the relative nature of risk. That is, while both chlorination and nonchlorination possess inherent risks to human health, the risks associated with failing to treat water are generally deemed to substantially outweigh those associated with the practice of disinfecting water. Indeed, in most jurisdictions, the failure to treat water in some manner is associated with well-recognized and significant human health risks, most notably those associated with the transmission of pathogenic disease and infection. Increased exposure to many of the chemicals discussed in this document may also occur. An overall assessment of the impact of disinfection on pubic health must consider both the microbiological quality of the treated water and the toxicity of the disinfectants and their reaction products (WHO, 1996). However, where local circumstances require that a choice must be made between meeting either microbiological quality or guidelines for disinfectants or disinfectant by-products, microbiological quality must always take precedence (WHO, 1996). In the absence of new, risk-free technologies for water disinfection, the challenge that we are faced with at present, therefore, is how to best manage water disinfection in a manner that maximizes the reduction of risk without compromising disinfection efficiency (Health Canada, 1996a).

Although not a disinfection by-product per se, fluoride is another commonly encountered halogen in drinking water. Like chlorine, the addition of fluorine to water has been enveloped in public controversy. Fluoride is a widespread, naturally occurring element that accounts for approximately 0.3 g/kg of the earth's crust and occurs widely in surface waters (WHO, 1996). Although fluoride can be obtained through the diet, supplemental fluoridation of drinking water is routinely conducted because it has been shown to significantly reduce dental caries (bacterial decay of teeth), particularly among children (Health Canada, 1996a; WHO, 1996). However, inorganic fluorides are also toxic, with forms such as sodium fluoride, sodium fluorophosphate, and cryolite (sodium aluminum fluoride) historically being used as insecticides and rodenticides (Crosby, 1998). Chronic exposure to fluoride may cause mottled teeth and eventually bone defects, the latter resulting from the replacement of hydoxy (OH^-) groups with F^- in the structural mineral apatite of bones (WHO, 1984).

Land Disposal and Leachates

Leachates associated with land disposal of industrial and human waste can represent a significant point source of contaminants to both surface water and groundwater (Miller, 1980; Jorgensen, 1989). Numerous historical examples of how waste disposal practices have lead to significant contamination of groundwater resources have been documented throughout North America. The most significant environmental problem associated with waste disposal is leaching of contaminants into groundwater (Figure 7). These leachates are typically comprised of complex mixtures containing, for example, metals and chlorinated organics. Groundwater contamination often results from historical problems related to inadequate management of wastes and industrial chemicals (Government of Canada, 1996). In the 1980s, a Canadian study of groundwater contamination showed that 60% of contaminated sites resulted from landfills, industrial waste sites, septic systems, and deep-well injection of wastes; over 20% resulted from underground leaking storage tanks, spills, above-ground material storage, and other industrial operations (Statistics Canada, 1994). Cherry and Harmon (1994) examined 92 groundwater sites reputed to be contaminated by organic chemicals; this represented only a small fraction of the estimated
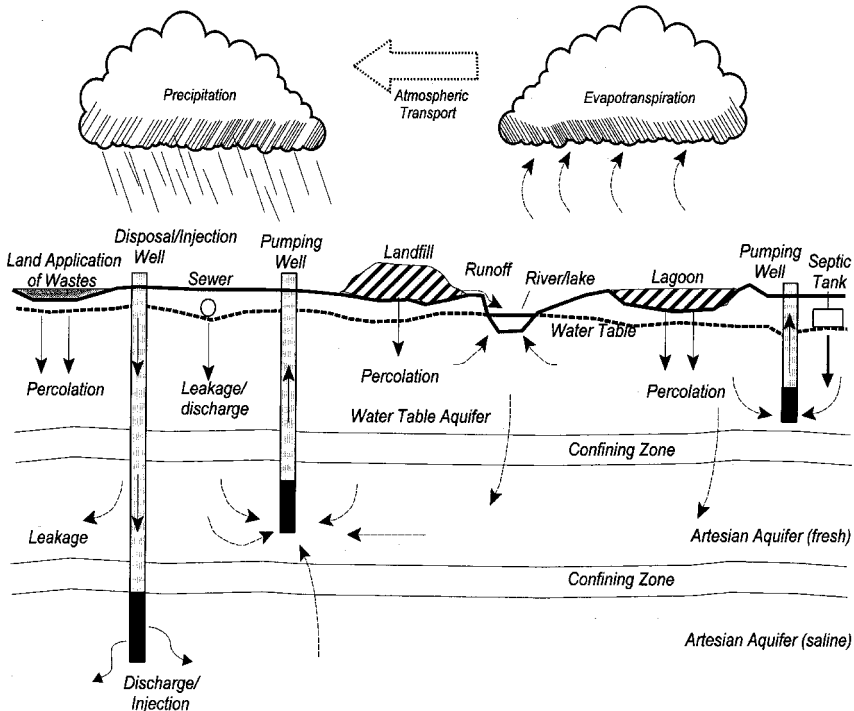

FIGURE 7. Sources of contaminants to groundwater and surface water via landfills, leachates, and disposal wells. Adapted from Miller (1980).

number of existing sites. Although more recent containment systems are generally constructed using elaborate leak prevention systems, there are still significant problems associated with contamination from historical containment practices, many of which often consisted of nothing more than a hole in the ground that was covered with dirt (Jorgensen, 1989). These problems have been exacerbated by poor management practices in the past and a corresponding lack of detailed records pertaining to the location and the nature of the material stored within the landfill.

There are numerous types of land disposal systems, each with its own potential to contribute anthropogenic contaminants to surface waters and groundwater (Miller, 1980; Devinny, 1990; Qasim & Chang, 1994; Shah, 2000). Sources and pathways of contaminants from landfills, leachates, and containment systems are considered briefly next; other aspects are also discussed in detail elsewhere in this article.

Industrial Wastewater Impoundments   Industrial wastewater impoundments are storage facilities designed to store liquid waste or liquid–solid waste mixtures, usually for the purpose of waste treatment (Miller, 1980). Surface impoundments are most common and are used to store organic wastes from municipal wastewater and sewage treatment facilities and animal feedlots and farms, and hazardous wastes from numerous industries, including oil and gas, mining, pulp and paper, and chemical operations (Jorgensen, 1989; Shah, 2000).

Once treated, the liquid waste is primarily discharged to local surface waters; residual waste solids resulting from the waste treatment process are either incinerated, applied to land (this is common for solid waste material from municipal, agricultural, and some pulp and paper waste treatment), or sent to a land fill site. Treated waste material discharged as effluent from wastewater impoundments can represent a significant point source of contaminants to surface waters. The type of contaminants discharged will, of course, depend upon the industry in question, and some of these were discussed in greater detail earlier.

Leakage or seepage of contaminants from wastewater impoundments into surrounding shallow aquifers can also lead to localized contamination of groundwater. Leakage can occur as a result of flawed design or poor construction, system failure, or accident. In view of the diversity of municipal and industrial applications, wastewater impoundments can contribute a wide variety of contaminants to groundwater.

Leaking Underground Storage Tanks   Underground storage tanks (USTs) have long been used to store toxic chemicals, particularly petroleum products such as gasoline, diesel and heating oil, waste oil, and aviation fuel (Devinny & Lu, 1990; Swaigen, 1995). When leaks occur in these tanks (whereupon they are referred to as LUSTs) due to age, neglect, or improper maintenance, there is significant potential for widespread groundwater contamination. For example, a single liter of gasoline leaked from a underground storage tank can contaminate up to 1 million liters of groundwater

(Environment Canada, 2000a). In 1986, Environment Canada estimated that as many as 200,000 USTs may be present in Canada and that between 10,000 and 20,000 of these may be leaking (Swaigen, 1995). Based on the assumption that Ontario has approximately 17% of the gas stations in Canada (Swaigen, 1995), there are potentially between 1700 and 3400 leaking tanks in the province of Ontario.

From both an environmental and human health perspective, the primary toxicological concern of underground storage tanks that are used to store petroleum products is the occurrence of BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). Benzene is the most significant of these because it is known to be a potent carcinogen (Group 1 classification by IARC). In Canada, the maximum allowable concentration of benzene in drinking water associated with an excess lifetime cancer risk of 10^{-5} is 5 µg/L (Health Canada, 1996b). The other three compounds are currently regulated on the basis of aesthetic objectives (taste and odor) and have no established maximum allowable concentrations in drinking water in Canada (Health Canada, 1996b) or Ontario (Phyper & Ibbotson, 1994).

Landfills and Dumps   Landfills and dumps are primarily used to dispose of solid wastes generated by human or animal activities. A dump is generally defined as an uncovered disposal site in which there is little or no regard for pollution control or aesthetics (Miller, 1980). A landfill is generally defined as a disposal site in which cover is provided and there is some concern for pollution control and aesthetics. There are two types of landfill sites, a sanitary landfill and a secured landfill. Only the latter is designed to ensure that there is no hydraulic connection with natural waters, but there are few examples of these in practice (Miller, 1980).

Land disposal of solid wastes can be a significant source of contaminants to groundwater via the generation of leachates, which are caused by the percolation of water through the refuse and waste materials. Leachates are highly mineralized fluids that may contain a toxic mixture of contaminants (Qisam & Chiang, 1994; Shah, 2000). Leachates from landfills in which industrial and manufacturing wastes have been dumped often contain hazardous chemicals such as heavy metals (e.g., cyanide, cadmium, lead) and chlorinated organics (e.g., PCBs, chlorinated hydrocarbons), which may pose concerns to human health should the leachate enter into aquifers that supply water for drinking. Untreated, private wells are most susceptible in this regard. Leachates may enter surface waters if there is hydraulic connection between the contaminated groundwater and local surface waters (e.g., a stream). In this case, lipophilic compounds associated with the leachate (e.g., PCBs) could be accumulated by aquatic biota and ultimately passed up the food chain. For example, organochlorines have been detected in the water and biota throughout the Niagara River system, and these have been traced to leachates from hazardous waste dump sites located adjacent to the river in New York (Government

of Canada, 1996). These compounds eventually find there way into Lake Ontario and undoubtedly into the influent water abstracted by water treatment facilities to supply municipalities with drinking water.

Septic Tanks and Cesspools In the United States, septic tanks and cesspools discharge or leak the highest quantity of wastewater of all sources directly to groundwater (Miller, 1980). For this reason, concerns regarding potential risks to human health from this source are predominantly associated with contamination of groundwater with pathogens originating in the discharged or leaked septic fluids. However, significant above-ground contamination may also occur if leaks or damaged tanks break through the soil surface. In addition to potential risks from exposure to pathogens from surface-associated sludge from leaking or broken tanks/cesspools, significant local odor problems may also prevail. Nitrates in groundwater may also constitute a significant problem (nutrients are discussed in greater detail later), although the extent to which these originate from septic systems relative to other sources is not well understood. Potential risks to human health are greatest in rural areas, where bacterial contamination of drinking water extracted from private wells may occur. For example, Goss and Barry (1995) reported that approximately one-third of wells on 1200 rural farms were contaminated with bacteria. However, in rural areas, it is often difficult to differentiate between contamination due to runoff and leaching of animal manure or to faulty septic systems (Conboy & Goss, 1999). If properly maintained, bacterial contamination of groundwater by septic systems can be negligible (Seyfried & Joy, 1995). Interestingly, Rudolph and Goss (1993) found no significant correlation between the proximity of a wellhead to the septic tank or weeping bed at distances up to 300 ft in rural areas.

Land Application of Sludges The land application of sludges (also referred to as residual waste materials and biosolids), usually over farm and forest land, is becoming increasingly common and can represent an environmentally responsible method of disposing of residual waste materials and recycling nutrients to the soil (OMAFRA, 1998). This subject is treated comprehensively in a separate issue paper (Reilly, 2001) and is considered here briefly to provide perspective.

Municipal (sewage treatment) and industrial sludge is the residual material that remains after treatment of wastewater. In the agriculture, application of residual waste materials from both municipal (human wastes) and farming (animal wastes) origins has been practiced by farmers for many years. When applied using one of several best management practices, the land application of residual waste materials can be conducted in a manner that minimizes losses via runoff and leaching, thereby ensuring maintenance of environmental quality (Miner et al., 2000). However, land application of residual waste material can lead to contamination of surface water via runoff or of groundwater via leaching. Common contaminants associated with farms sludges include pathogens and nutrients (nitrogen

and phosphorus), while contaminants associated with municipal or industrial sludges may include heavy metals, toxic chemicals, pharmaceuticals, pathogens, and nitrates.

Disposal Wells/Deep-Well Injection   Disposal or drainage wells are wells drilled into the ground for the express purpose of disposing of industrial waste, sewage effluent, spent cooling water, storm water, and agricultural drainage (Miller, 1980). The primary concern associated with disposal wells is contamination of groundwater aquifers. Drainage wells are particularly common in agriculture where they are used to remove surface and subsurface drainage and maintain favorable soil moisture levels (Tobin & Rajagopal, 1990). However, they may also channel agricultural contaminants, such as pathogens and nutrients, directly into underground aquifers (Baker et al., 1985; Tobin & Rajagopal, 1990), which supply water for drinking.

Disposal wells are also commonly used by the chemical, petroleum, metals, minerals, aerospace, and wood-preserving industries. In the United States, more than 8 billion gallons (approximately 32 billion liters) of industrial wastes is disposed of annually in deep injection wells (Wickstrom & Baranowski, 2001), a practice that has resulted in the contamination of groundwater supplies in a number of jurisdictions (Jorgensen, 1989). Comparable statistics for Ontario and Canada could not be located, although this technology for waste disposal is used on both a national and provincial basis.

A common form of disposal well is the deep injection well, which is principally used by industry to dispose of hazardous wastes. It is a popular disposal method within industry because of its relatively low cost (Jorgensen, 1989). As the name implies, deep disposal wells are drilled deep into the ground, often between 1000 and 6000 ft, to the point at which an appropriate geologic formation for holding the wastes can be located (Shah, 2000). Such a formation usually consists of permeable, brackish sandstone or limestone/dolomite deposits confined by layers of relatively impermeable geologic deposits (Jorgensen, 1989). The water associated with these deposits is characteristically saline and unpotable. In most situations, disposal of wastes using deep disposal wells can be practiced safely. However, chemicals contained in the waste material may enter into usable groundwater supplies through small cracks and fissures in the well casings or the geologic formation itself if the latter are not detected prior to construction of the well. Moreover, the chemicals themselves may corrode geological formations such as limestone, leading to the movement of contaminants into adjacent aquifers.

Brine Disposal from Petroleum Exploration and Development
Disposal of brine solutions from oil and gas production has been a historical problem in areas of intense petroleum exploration and development (Miller, 1980). In these areas, the principal problem has been contamination of surface waters via direct discharge of saline effluent waters, or of groundwater via leaching of the effluent from unlined pits. Occasionally,

metals may also be present in the brine solutions and these may also enter surface waters or leach to groundwater. As this practice has been prohibited for many years, this form of pollution is no longer considered to be a major point source of water contamination (Miller, 1980). However, in the United States deep disposal wells (described earlier) are currently used for the injection of brines resulting from oil and gas production or of fluids used for the enhanced recovery of oil or natural gas (Shah, 2000). In Ontario, due to the relatively small size of the oil and gas industry (restricted to southwestern regions of the province), brine disposal has generally not represented a significant source of groundwater contamination in the province. Further discussion of the petroleum industry, and its relationship to surface water and groundwater contamination, was provided earlier under industrial sources of contamination.

Disposal of Animal Feedlot Wastes   Issues related to the sources and pathways of contaminants associated with animal wastes are described in separate sections earlier and later in this article. For additional information on this subject, the reader is referred to the issue paper of Goss et al. (2001) and the book by Miner et al. (2000). With recent concerns over the construction of so-called factory farms and concerns over the disposal of the large volumes of animal waste generated from such farms, it is likely that pathogenic and nutrient contamination issues related to the management of feedlot wastes will continue well into the future.

Abandoned/Poorly Constructed Wells   An area of potentially significant, yet poorly understood, groundwater contamination is that originating from abandoned and poorly constructed wells. In Ontario, it is estimated that there may be up to 100,000 abandoned wells. These abandoned wells, along with existing, older wells, which may be poorly constructed and do not meet current standards, represent a direct conduit for contaminants to groundwater (Gustafsson, 1993). Indeed, in a study of Nebraska wells, Exner and Spaulding (1985) found a strong correlation between well construction quality and the likelihood of groundwater contamination. In most cases, greatest environmental and human health concerns center around the potential for pathogenic contamination of groundwater sources; however, other chemicals and nutrients associated with runoff may also enter into these wells.

In many cases, abandoned wells are difficult to locate due to poor historical records. Thus, plugging these wells as stipulated in current regulations (regulation 903 in Ontario; Ontario Ministry of the Environment, 1998) cannot be conducted (OMAFRA, 1998). Moreover, the cost of plugging and/or repairing poorly constructed wells may be high (up to $10,000 to properly plug a well), so there is often a lack of incentive for owners to report existing wells that are no longer in service or to repair those that require it.

According to Gustafsson (1993), a properly constructed drinking-water well (e.g., one in which groundwater contamination potential is minimized) should have the following features:

1. Optimal placement on the land surface. Avoid low spots and keep away from contaminant sources, such as pesticide storage areas or treated fields.
2. The hole should be drilled to a sufficient depth, avoiding surficial aquifers whenever possible. Deep wells are generally less susceptible to pesticide and pathogenic contamination.
3. The bore hole should be sealed and protected with a casing that extends at least 0.15 m above the land surface and higher in areas susceptible to flooding.

NONPOINT SOURCES OF CONTAMINATION

Agriculture

Agriculture constitutes the most important nonpoint source of certain contaminants to aquatic environments. There are four primary classes of pollutants associated with agricultural activities: pathogens, siltation, nutrients, and pesticides. The relative contribution of each type of pollutant to impairment of surface and groundwater quality will depend upon numerous factors including agricultural practices (tillage, erosion control, waste treatment, nutrient management plans), application rates, and soil type. Hence, the risks posed by each to human health and ecosystem integrity will vary accordingly. Historically, the most significant pollutant of agricultural origin affecting water quality and ecosystem integrity in streams has been siltation associated with surface runoff (Karr et al., 1985; Rabeni & Smale, 1995; Waters, 1995; see Table 2). However, pesticides and nutrients can also have significant impacts on ecosystem structure and function in regions of intense agriculture, where they may be either toxic to water and sediment-dwelling organisms or promote eutrophication and habitat degradation (Fenn et al., 1998; Schultz & Leiss, 1999). Recently, due to advances in the use and application of technologies such as geographical information systems (GIS) and remote sensing, increasing emphasis has been placed on the assessment of nonpoint agricultural impacts on aquatic ecological integrity at higher geographical scales, including catchment, watershed, and landscape perspectives (Richards et al., 1993; Allan et al., 1997; Johnson & Gage, 1997; Harding et al., 1999; Lammert & Allan, 1999; see also *Environmental Toxicology and Chemistry,* Vol. 19, Special Issue 4[2]). Approaches that incorporate higher levels of scale may be particularly useful in terms of assessing and managing risks to ecosystem integrity associated with nonpoint pollutants collectively, rather than single pollutants.

Pesticides, nutrients, and pathogens of agricultural origin may also present risks to human health when they enter into drinking water supplies. Each of these classes are considered in greater detail next.

Pathogens   The origin, transport, and management of pathogens associated with animals wastes and agriculture are reviewed by Goss et al. (2001) in a separate issue paper. Further information on pathogens in farm animal wastes may also be obtained from Miner et al. (2000), and information on

pathogens in drinking water in Ontario may be obtained from Geldreich (1996), Conboy and Goss (1997, 1999), Goss et al. (1998) and Rudolph et al. (1998). Thus, we provide only a brief contextual description of pathogenic pollution in relation to agricultural activities and potential human health risks.

Pathogenic pollution of drinking water from agricultural sources poses the most significant health risks to that segment of the population that draws its water from private wells located within areas of agricultural activity. A number of pathogens are commonly associated with animal wastes in agriculture, including the H7:0157 variant of *Escherichia coli.* Although this variant has been implicated as a significant pathogen associated with well-water contamination from agriculture, in fact normal variants of this bacteria (e.g., fecal coliforms) are a far more common source of contamination. These pathogens may enter private wells via surface runoff or groundwater. Wells positioned below grade or that are poorly sealed are particularly susceptible to contamination via surface runoff; wells that are old, have deteriorated, or are poorly constructed are most susceptible to contamination via groundwater.

From either source, contamination of drinking water supplies can be significant. A series of recent, comprehensive surveys of farm wells in Ontario have revealed relatively high levels of bacterial contamination. For example, Conboy and Goss (1999) found that 52.9% and 59.2% of wells tested ($n = 302$) exceeded the provincial water quality objective for total coliforms and fecal coliforms, respectively, on at least one occasion during the 12-month period in which they were sampled. In that study, it was shown that the bacterial contamination was associated with an increase in the proportion of individuals experiencing diarrhea; no other illnesses were noted and the increased incidences of diarrhea did not increase the number of visits to the hospital. Interestingly, these authors indicated that there has been a significant increase in the number of wells showing *E. coli* contamination between the early 1950s and the mid 1990s (Conboy & Goss, 1997).

Pesticides   Pesticides have been used widely to control pests in agriculture since the middle of the 20th century. Many of the early pesticides were chlorinated organics (e.g., DDT, chlordane, dieldrin), which, due to their propensity to bioaccumulate, were subsequently discovered to have serious environmental effects, including significant risks to human health (Colborn et al., 1996). These problems were brought to the attention of the public by Rachel Carson in the book *Silent Spring,* and with it came the birth of the environmental movement. Although most of the problem pesticides have long been banned in North America, their residues can still be found in many environmental matrices, particularly in the Arctic (see later section on atmospheric transport). Moreover, there are renewed concerns about potential risks that these persistent pesticides may pose to human health in light of recent evidence that some of these chemicals affect functioning of the endocrine system and may lead to developmental and reproductive problems in wildlife and humans (NRC, 1997).

Today, pesticides continue to constitute an integral component of crop protection and pest management. In both Canada and the United States, the vast majority (about 80%) of pesticide use occurs in agriculture (Figure 8). Other sources include forestry and household applications (these are discussed in greater detail later). From all sources, the quantity of pesticides applied annually in the United States is approximately 500,000 kg, a figure has been relatively stable since 1978 (Nowell et al., 1999). In Canada, 70% of pesticides applied in agriculture are herbicides, and these were applied to approximately 8.7 million hectares in 1990 (Government of Canada, 1996). In Ontario, Hunter and Magee (1994) found that pesticide use decreased from 7200 tonnes to 6200 tonnes of active ingredient between 1988 and 1993. Among major pesticide classes, herbicide use has increased significantly since the 1960s in both Canada and the United States (Government of Canada, 1996; Larsen et al., 1997). Over this same time period, insecticide use has declined slightly, with a major shift away from chlorinated organics to organophosphate and other insecticides. Fungicide use has increased slowly over the past 30 years, but currently constitutes only a small fraction of pesticide used in agriculture. However, fungicides may be the dominant pesticide in specific types of agriculture such as fruit production.
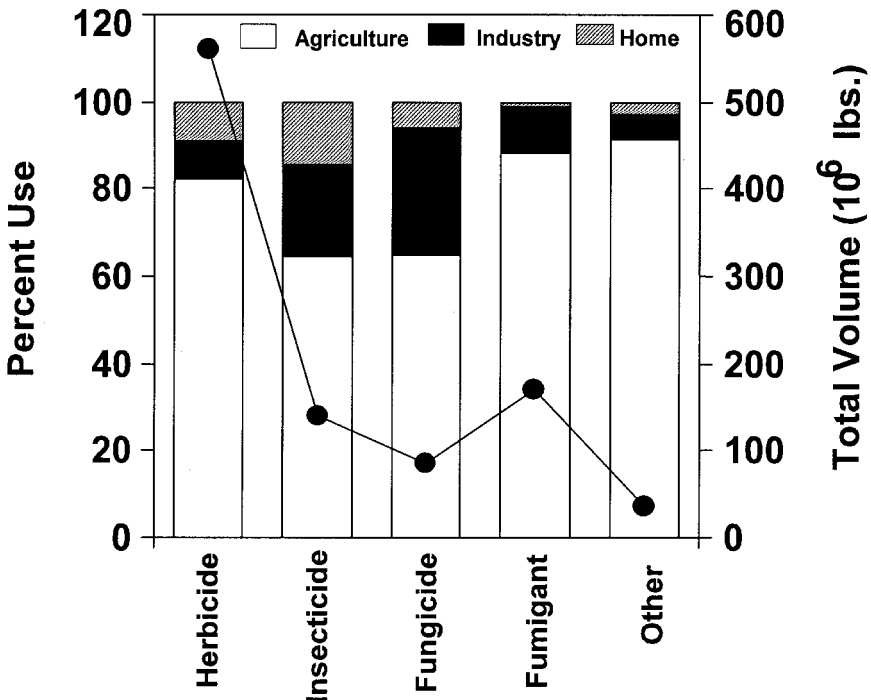

FIGURE 8. Relative proportion of pesticides by use in the United States. Adapted from Nowell et al. (1999).

Pesticides used in agriculture can enter surface waters, groundwater, and drinking water from several sources. Direct routes to surface waters include careless handling (e.g., disposal of pesticide containers), accidental spills, and overspray. Indirect routes include atmospheric transport by volatilization and subsequent deposition, spray drift during spraying of crops, runoff from fields, and leaching of soluble pesticides through soils into underground aquifers. Once in the environment, pesticides may be subjected to numerous transformation processes that can significantly alter their mobility, environmental fate, and toxicity (Figure 9). Some of the most common processes affecting environmental fate and toxicity include hydrolysis (reaction of parent molecule with water leading to cleavage and hence more water-soluble metabolites), biodegradation (breakdown of the molecule by living organisms, such as bacteria, using enzymatic reactions), and photolysis (breakdown of the molecule following addition of energy from sunlight). In most cases, these transformation processes yield less toxic and more water-soluble compounds; however, there are examples in which toxic metabolites may also be formed. Lipophilic pesticides (e.g., DDT, chlordane, dieldrin, endosulfan) generally partition rapidly into organic matrices such as bed sediments, where they may reside for many years. Owing to bans on their use in Canada, environmental levels of most persistent pesticides are significantly lower today than a couple of decades ago. However, these pesticides can still be found in the tissues of most organisms, particularly in Arctic regions, and continue to exert effects on aquatic biota and humans. It is important to realize that exposure to these pesticides is predominantly through food chain transfer due to their insolubility in water. Hence risks to human health from ingestion of drinking water, especially when the water is treated, are probably negligible. In this context, it is important to note that the Ontario Drinking Water Surveillance Program, which is designed to monitor toxic contaminants in drinking water, does not routinely measure lipophilic compounds.

In contrast to the historically problematic persistent pesticides, many of the current-use pesticides are water soluble and hence considerably more mobile in the environment. Consequently, these compounds are often widespread in aquatic matrices. Although the heaviest loading of these pesticides to aquatic environments generally occurs in areas of high agricultural activity, residues appear to be ubiquitous in surface waters. For example, Gilliom et al. (1999) reported that more than 95% of samples collected from streams and 50% of samples collected from wells across the United States contained at least one pesticide. In the vast majority of cases, concentrations did not exceed water quality criteria.

Atrazine offers perhaps the best example of high solubility and environmental mobility. Atrazine is one of the most widely applied herbicides in agriculture, is highly mobile in soil and water, and is commonly detected in surface waters and groundwater throughout North America (Halberg, 1989; Solomon et al., 1996). A survey of Midwestern streams in the United States detected atrazine in 98% ($n = 149$) of the streams sam-
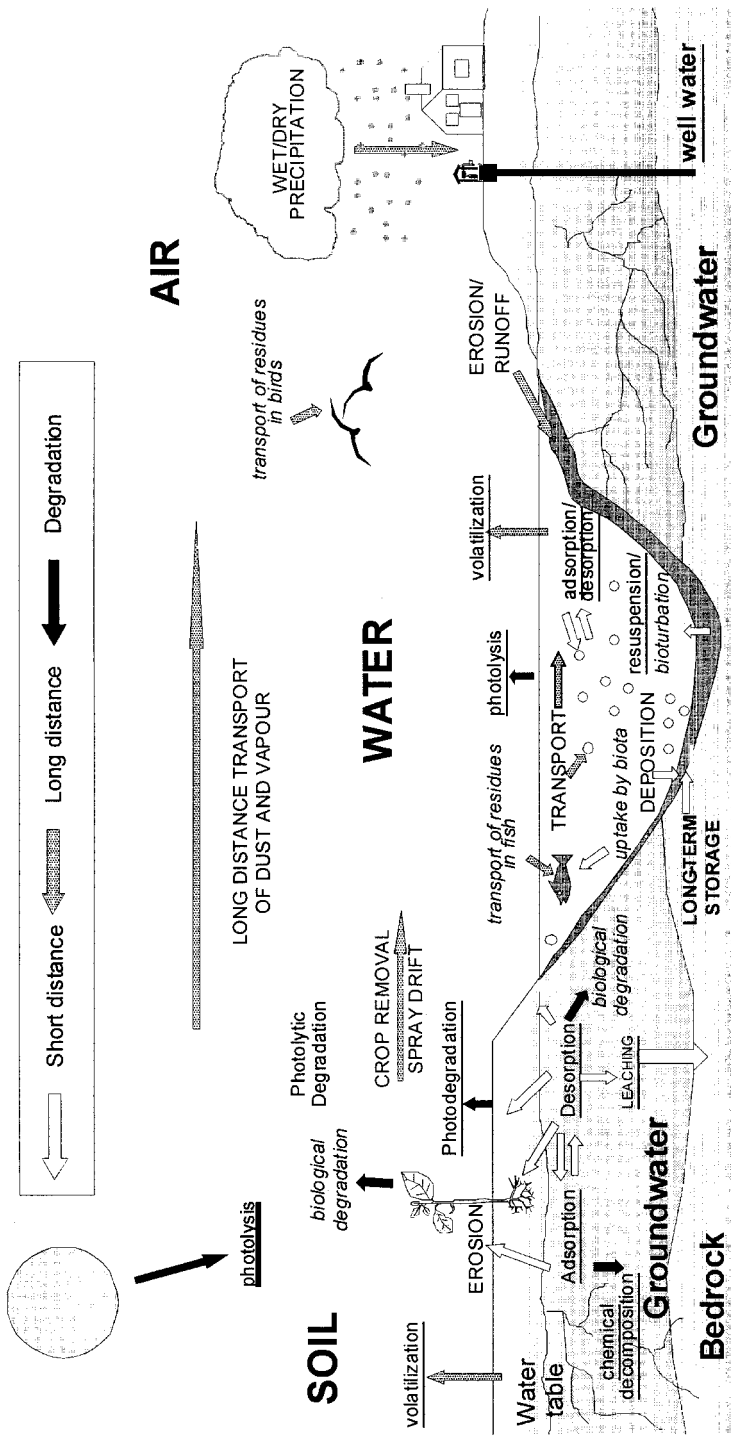
FIGURE 9. Sources, sinks, pathways, and movement of pesticides in terrestrial and aquatic environments.

pled (Thurman et al., 1991). In southern Ontario, atrazine was detected in most surface waters flowing into the Great Lakes (Frank et al., 1982). Solomon et al. (1996), in a comprehensive probabilistic environmental risk assessment of atrazine in North American surface waters, concluded that this compound does not pose a significant risk to the aquatic environment. However, it was noted that a subset of surface waters in areas of intense atrazine use may be at greater risk and should be subjected to independent, site-specific risk assessments.

Because of its solubility and mobility, atrazine is commonly detected in groundwater samples throughout many parts of North America and Canada in areas in which this herbicide is used (Gustafsson, 1993). In a recent survey of 7 high-use herbicides in groundwater of the United States, atrazine was detected in approximately 20% of shallow groundwater sites (Barbash et al., 1999). The widespread occurrence of atrazine in groundwater is not surprising, as this compound was ranked as having the highest leaching potential in a survey of 86 pesticides by the Canadian government (McRae, 1991). Atrazine is commonly detected in drinking-water supplies drawn from both surface-water and groundwater sources. For example, in our survey of drinking water from water treatment plants in Ontario, atrazine was the most frequently detected (and most frequently measured) pesticide (see Table 19, later in this article). Goss et al. (1998) detected atrazine in 6.6 and 10.5% of approximately 1300 domestic wells sampled in the winter and summer, respectively. Briggins and Moerman (1995) found atrazine in 32% of wells ($n = 102$) in Nova Scotia, although none were above the Canadian water quality criterion of 5 µg/L. Other pesticides detected in that study (<4% of wells) included simazine, metribuzin, alachlor, metolachlor, captan, chlorothalonil, dimethoate, and permethrin.

On the basis of the hazard assessment that we conducted, the estimated hazard quotients for atrazine based on the maximum concentrations found in both treated drinking water and well water were all well below 1, suggesting little risk to human health associated with its occurrence in this matrix. However, the widespread and persistent occurrence of this compound in water supply systems continues to raise concerns about potential effects on human health resulting from long-term, chronic exposures. In this context, it is interesting to note that exposure to low concentrations of atrazine was recently shown to increase the production of males in water fleas (*Daphnia pulicaria*), a species in which males are typically rare (Dobson et al., 1999). These authors suggested that this effect by atrazine could have been due to hormonal interference (endocrine disruption). However, in a similar study using comparable exposure conditions and atrazine concentrations, Hosmer et al. (2000) found no evidence to support a shift in sex ratio in this species.

In Ontario, a number of extensive surveys have been conducted to measure pesticide concentrations in surface water and groundwater. The earliest surveys were conducted on the occurrence of pesticides in drink-

ing water by the Ministry of the Environment during the mid 1980s in response to evidence that alachlor, a widely used herbicide, had been implicated as a possible carcinogen in animal studies (Ontario Ministry of the Environment, 1985). The first survey was targeted to agricultural areas and to a lesser extent areas that were hydrogeologically susceptible to contamination (Ontario Ministry of the Environment, 1987a). In total, nine pesticides, all herbicides, were detected in the wells. At least 1 pesticide was detected in 51% of the wells sampled, while 21% contained residues of at least 2 pesticides (Table 12). Of those wells that tested positive, 95% contained residues of atrazine. A similar survey was conducted in 1986, with site selection restricted to avoid well construction/placement problems (Ontario Ministry of the Environment, 1987b). The results of this more restricted survey were similar to those of the 1985 survey with respect to the percentage of detections, but the number of multiple detections and maximum concentrations was generally lower. A key finding of these surveys was that contamination of the wells was due approximately equally to surface-water and groundwater contamination.

In a series of studies on pesticide contamination of farm wells and groundwater in Ontario, Frank and colleagues found varying frequencies of contamination. For example, in surveys conducted between 1969 and 1978, 67% of wells ($n = 237$) suspected of being contaminated with herbicides contained residues (Frank et al., 1979). In surveys conducted between 1979 and 1984 on a broader range of pesticides, 71% of wells ($n = 359$) contained pesticide residues (Frank et al., 1987a). In a survey of

TABLE 12. Pesticides Detected in Wells Drawn from Groundwater During a Monitoring Program Conducted by the Ontario Ministry of the Environment

Pesticide	1985 Survey		1986 Survey	
	Number of detections (%)	Maximum concentration (µg/L)	Number of detections (%)	Maximum concentration (µg/L)
Alachor	15	20	5	2.3
Atrazine	—	—	43	4.2
Atrazine and deethyl atrazine	48	354	50	10.5
Deethyl atrazine[a]	—	—	31	7.5
Cyanazine	5	4	ND	
Dicamba	<1	2.3	ND	
Metolachlor	15	1800	7	3.2
Metribuzin	6	300	ND	
Prometryne	<1	0.8	ND	
Simazine and deethyl atrazine	3	23	ND	
2,4-D/2,4-DB	1	5800	ND	
Total detections	51		50	

Note. Adapted from Halberg (1989).
[a]Atrazine and deethyl atrazine combined in 1985 survey.

pesticide contamination of wells in different soil types, Frank et al. (1987b) found that <25% (*n* = 11) of wells in organic soils and 13% (*n* = 91) of wells in mineral soils were contaminated by at least one herbicide (mostly atrazine). Finally, in a series of surveys conducted in 1984, 1986, and 1987, Frank et al. (1990) found that 13% (*n* = 91), 9.7% (*n* = 103), and 5.3% (*n* = 76) of wells, respectively, contained pesticide residues from all classes of pesticides. In these studies, it was shown that a relatively high proportion of well-water contamination was due to accidental spills, back-siphoning, and use of the well as a supply of water for mixing pesticide formulations. For example, in a 1985 survey, it was shown that of the 18 out of 61 (about 30%) wells contaminated by pesticides 11 were due to direct spills, 3 from runoff immediately following an application event, and 4 from a combination of the two.

In one of the most comprehensive investigations of the potential risks of pesticide exposure of farm families to pesticides in well water, Ripley et al. (1998) found that pesticide application practices on the farms participating in the study resulted in little or no inadvertent exposure to farm families from drinking water. In that study, 20% of wells (*n* = 126) contained pesticide residues; atrazine was found in 15% of wells, MCPA (monochlorophenoxyacetic acid) in 3% of wells, and MCPP (mecaprop), dicamba, metolachlor, and simazine in 2% of wells each. In all cases, the levels were below respective drinking water guidelines, where these existed.

In Ontario, monitoring programs for the detection of pesticide residues in treated drinking water are virtually nonexistent. For example, in our review of water quality monitoring data for water treatment plants in southern Ontario, with the exception of atrazine, very few pesticide residues were measured. The overwhelming majority of measurements were conducted on disinfection by-products and metals. In contrast, there have been several recent comprehensive surveys of farm well water for pesticide residues. Well water used for drinking on farms is typically untreated and has a higher probability of experiencing contamination by pesticides due to their proximity to various agricultural practices. Goss et al. (1998) and Rudolph et al. (1998) conducted a survey of contaminants (pathogens, nutrients, and pesticides) in approximately 1300 domestic wells and multilevel monitoring well installations at 144 farms in northern and southern Ontario. This survey measured the pesticides alachlor, metolachlor, atrazine, metribuzin, and cyanazine and found that detection in wells and groundwater was relatively low—7% in winter samples and 11% in summer samples. Atrazine was the most common pesticide detected. Only six wells had residues that exceeded the provincial IMAC.

Nonagricultural Sources of Pesticides

Although agriculture accounts for 70–80% of pesticides found in surface water, groundwater, and drinking water in North America (Apselin, 1994), a number of other significant sources exist. Some of these may con-

stitute the dominant source of pesticides to surface waters or groundwater on a localized basis, depending upon the pesticides in question and their respective use patterns (Larson et al., 1997; Nowell et al., 1999). Some applications include (1) forestry, (2) transportation (to control weeds along road sides, railways, and right-of-ways), (3) urban and suburban areas (to control pests in homes, gardens, buildings, and ornamental and turf grasses), (4) commercial and industrial applications (e.g., control of wood rot in lumberyards), and (5) lakes and streams for control of aquatic weeds and nuisance organisms (e.g., pestifierous midges). The various sources of pesticides used in nonagricultural applications are provided in Figure 10. We next briefly discuss these nonagricultural sources of pesticides with respect to their loading to, and movement in, aquatic environments.

Forestry   The amount of pesticides applied in forestry, and the corresponding areal coverage, represents a small fraction of the amount and areal coverage used in agriculture (Government of Canada, 1996; Larson et al., 1997). In Canada the total area receiving herbicide treatments in 1993 was 235,000 ha, and most of the treatments were applied in British Columbia, Ontario, Quebec, and New Brunswick. Herbicides are the most commonly applied pesticide in the forest industry, where they are used for weed control in silvicultural applications. Historically, the herbicides with the highest use in forestry were 2,4-D, picloram, and hexazinone. More recently, however, the use of triclopyr and glyphosate has increased significantly. Insecticides, in contrast, are not routinely used as part of silvicultural practices and are more typically directed to controlling pest outbreaks (e.g., gypsy moth, spruce budworm) in localized areas. Here,
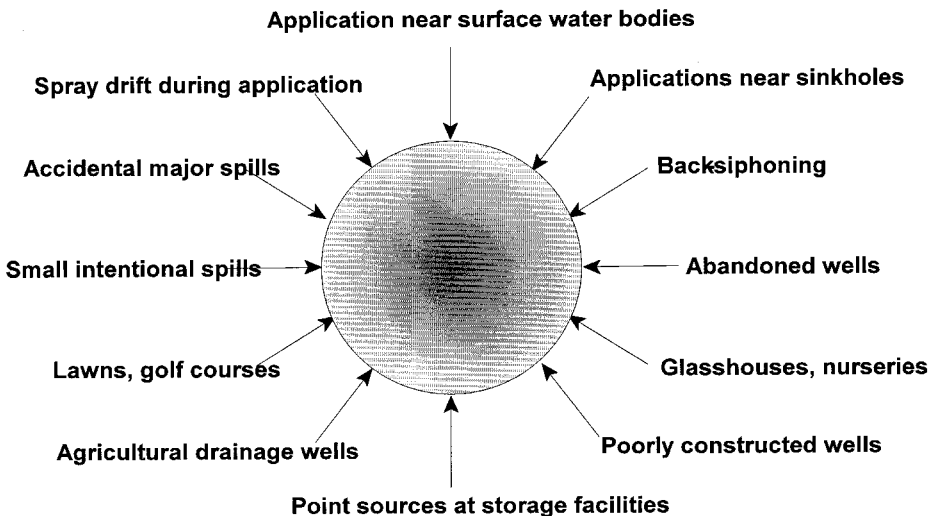

FIGURE 10. Potential sources of pesticides other than crop protection that can lead to drinking-water contamination. Adapted from Gustafsson (1993).

DDT and organochlorines were used extensively in the 1950s and 1960s. These were succeeded by organophosphates (malathion, azinphos-methyl, fenitrothion) and carbamates (carbofuran and carbaryl) in the 1970s and 1980s. Most recently, the bacterial agent *Bacillus thuringiensis* var. *kurstaki* (Bt) has become the primary insecticide to control forest pests. Between 1980 and 1993, the total amount of land with insecticides applied in forest operations declined significantly (from over 3 million ha to less than 270,000 ha coverage), reflecting a decline in spruce budworm populations (Government of Canada, 1996).

Depending upon the nature of the forest practice, forestry activities may significantly affect water quality of surface waters draining forests, and these are typically regulated as nonpoint sources of pollution (Binkley & Brown, 1993). The primary pollutants associated with forest practices are pesticides, sediments, nitrate-N, and phosphates. The former typically enters into aquatic surface waters or groundwater via direct overspray or spray drift during aerial applications for pest control, runoff, and leaching (Neary et al., 1993). In most cases, pesticides used in forestry are nonpersistent and degrade quickly under normal environmental conditions. However, impacts, when present, may be experienced by nontarget organisms. In this latter context, primary concern has focused on fish, and these have been investigated extensively in relation to historical applications of DDT, aminocarb, and fenitrothion used to control forest pests (Eidt et al., 1989). Overall, there are few documented accounts of forest pesticides in drinking water. Neary et al. (1993), in a review of over a decade of research on the use of pesticides in forestry operations, concluded that the low concentrations and short persistence of forestry pesticides in surface water and groundwater do not pose a significant risk to water quality, aquatic biota, or human health.

In addition to pesticides, forestry may contribute significant quantities of sediments, nitrate-N, and phosphorus; loadings of these compounds typically increase following harvesting and fertilization of forests. The environmental significance of siltation was discussed earlier in relation to general degradation of surface waters and fish habitat. Nitrate-N can be a significant problem from a human health perspective, but the overall contribution of nitrate from forestry operations is very small compared to agricultural and atmospheric sources, and it is rare that forestry practices contribute N at levels that exceed water quality criteria in the United States or Canada (Binkley & Brown, 1993). Phosphorus is not a significant concern in drinking water, but it may cause increased enrichment (eutrophication) of receiving-water environments, leading to an increase in productivity in lakes and streams and a corresponding reduction in water and habitat quality.

Urban/Suburban Pesticide Use   The home and garden sector uses relatively small amounts of pesticides compared to agriculture (see Figure 8). For example, in the United States, 8.9% (herbicides), 14.3% (insecticides), and 5.9% (fungicides) of all pesticide use was attributed to urban activities such as lawn and garden maintenance, golf course and cemetery applications,

and insect pest control of household plants and gardens. Among insecticides, chlorpyrifos and diazinon are most common where they are used in numerous household applications, such as dormant sprays on fruit trees, in professional landscape and maintenance uses, and structural pest control agents (Bailey et al., 2000). Both are regularly detected in urban runoff and occasionally in drinking water. For example, Bailey et al. (2000) measured these two insecticides in several urban streams in California. Both were detected in the majority of samples collected. More importantly, diazinon levels exceeded the California Fish and Game criterion for this pesticide in 85% of samples collected ($n = 231$); chlorpyrifos exceeded its respective criterion in 80% of samples collected ($n = 90$). Recently, the U.S. EPA initiated a ban on certain uses of chlorpyrifos because of potential increased risks to children, including exposure via drinking water (U.S. EPA, 2000a). Parker et al. (2000) found that organochlorines such as DDT, DDE, dieldrin, chlordane, and toxaphene were ubiquitous, although generally low in concentration, in urban runoff samples collected in Phoenix, AZ, despite the fact that these compounds have been banned for up to 30 years.

Many of the transport pathways along which pesticides move to surface water or groundwater are the same in urban areas as they are for agriculture; however, the greater frequency of impervious surfaces (concrete, asphalt) in urban areas increases the efficiency and rapidity with which pesticides (and other contaminants) are moved to surface waters by runoff during rain events or lawn watering. Moreover, the impermeable surfaces of urban areas have few adsorptive sites that might otherwise bind and retain the pesticides. Interestingly, studies have shown that well-maintained lawns, including those on golf courses, can prevent or greatly mitigate the loss of pesticides applied to them, thereby minimizing the amount reaching surface waters and groundwater (Harrison et al., 1993; Gustafsson, 1993).

Roadways and Rights-of-Way   Herbicides are often applied to roadways and rights-of way to control weeds and grasses for safety and aesthetic purposes, and occasionally as firebreaks (Larson et al., 1997). The most common herbicides used in this context include 2,4-D, triclopyr, and picloram. On rare occasions, insecticides such as fonofos may also be applied to control pests such as grasshoppers during periods of heavy infestation. Pesticides used along roadways and rights-of-ways may enter adjacent aquatic or groundwater environments via spray drift, volatilization, runoff, or leaching; however, the relative contribution from each source is poorly known (Larson et al., 1997). A study conducted in Ontario showed that 2,4-D applied to a right-of-way could be detected in soil samples taken up to 36 m from the original place of application and in water samples taken from a nearby lake (McKinley & Arron, 1987). However, residual concentrations of this herbicide were well below levels of toxicological concern. Watson et al. (1989) found little evidence of movement of the herbicide picloram applied to roadsides in a mountain valley. In contrast to these studies, Abke et al. (1993) found that 87% of groundwater control wells ($n =$

150) were contaminated with various herbicides used for weed control along railway tracks in Germany. The soils in that study were sandy, which likely aided the transport of the herbicides to the local groundwater aquifers.

In general, herbicide use to control weeds along roadways and right-of-ways is minor relative to many other pesticide uses. Hence, the contribution of pesticides from this application to surface waters and groundwater (and hence drinking water) in Ontario is probably quite minor and correspondingly poses little risk to human health.

Aquatic Plant Control   Pesticides may be applied directly to surface waters for control of insect pests (e.g., blackflies, mosquitoes, and nuisance midges), algae, and aquatic macrophytes. Herbicides (e.g., 2,4-D, glyphosate, copper sulfate) are the most commonly applied pesticides in aquatic environments, where they are used to control invasive weeds (e.g., water hyacinth and Eurasian watermilfoil) in reservoirs and canals, and algae in ponds (Larson et al., 1997). Insecticides are commonly applied directly to surface waters in areas prone to heavy infestations of nuisance aquatic insect pests. Historically, insecticides used in this capacity included DDT and a number of organophosphorus compounds (e.g., fenthion, malathion, fenitrothion); some of the latter are still used in some regions of Canada. However, in recent years, applications of bacterial agents such as *Bacillus thuringiensis* var. *isrealensis* (Bti), and of growth regulators such as methoprene, have been used increasingly to control aquatic pests such as mosquitoes (Larson et al., 1997). Pesticides applied to control aquatic weeds could enter into drinking water if it is drawn from the treated water bodies around or shortly after a spray program. However, most of the pesticides used in current pest control applications are quickly degraded under normal environmental conditions.

Greenhouses   Although pesticides are commonly used in greenhouses (or glasshouses), this industry probably represents only a minor source of pesticide loading to surface waters or groundwater (Gustafsson, 1993). Where contamination does occur, it is likely to be restricted in area (point source) and limited in magnitude. Contributions of pesticides to drinking water from greenhouse sources may occur when drainage water containing pesticides is released to surface waters that also serves as a source of drinking water (Gustafsson, 1993).

Nutrients   The two predominant sources of nutrients in agriculture are animal wastes and fertilizers applied to crops. The origin of nutrients from animal wastes, with their management, is the subject of a separate issue paper (Goss et al., 2001) and is not considered further here. However, fertilizers may also represent a significant source of nutrients to both surface waters and groundwater; these are considered in detail.

When fertilizers are applied to soil, the nutrients contained within them will either be taken up by the crop, remain in the soil, or be lost from the soil of the crop systems by one of several possible mechanisms (Marschner, 1986). The relative amounts of nutrient exported from soil to surface waters

and ground water varies widely between nutrients, soil type, and climatic and agricultural circumstances. The two most significant nutrients in terms of their potential impact to aquatic ecological integrity, and/or that pose a threat to human health, are nitrogen (N) and phosphorus (P). High levels of nitrate in drinking water is an important human health concern due to the potential for nitrate toxicosis or methemaglobinemia (oxygen starvation). Nitrates are less significant to aquatic biota from a direct toxicological perspective. However, nitrate, along with phosphorus, contributes to eutrophication and degradation of water quality. It is also important in the formation of ammonia, which is toxic to aquatic organisms, especially fish. Fertilizers can also contain trace amounts of a variety of metals such as arsenic, cadmium, and lead that may contribute to the contamination of surface water and groundwater. In most cases, however, contributions of metals from fertilizers are small relative to other sources, typically much less than 1% of total metal loading to aquatic environments.

Leaching, runoff, and atmospheric transport are the primary mechanisms by which nutrients enter aquatic environments. Nitrogen and phosphorus may enter surface waters from agricultural, atmospheric, and urban (sewage) sources. Total nitrogen concentrations found in Canadian rivers, lakes, and underground water bodies has been estimated to range between 1 and 10 mg/L, but may be considerably higher in localized areas, most notably in regions of high agricultural intensity. Nitrate is also produced naturally (for example, by blue-green algae) and is assimilated from water through uptake by aquatic plants or denitrification in bottom sediments. However, nitrogen in excess of that which can be assimilated by an aquatic system may, in conjunction with phosphorus loading, contribute to eutrophication (nutrient enrichment) and a concomitant decline in water quality and ecological diversity.

Phosphorus in the chemical form of phosphate is one of the principal nutrients for plants. Assimilation of fertilizer phosphorus by crops is generally poor, and that which is not taken up is effectively converted to water-insoluble forms or is strongly adsorbed on soil particles. Thus, loss of phosphorus to surface water or groundwater via leaching is relatively low, typically less than 1–2 kg phosphorus/yr/ha (International Potash Institute, 1983). Phosphorus loading to aquatic environments occurs primarily as runoff of soil particles to which the phosphorus is adsorbed (Bockman, 1990). The phosphorus content of streams in Canada ranges between 0.01 and 0.1 mg/L in forest watersheds and up to 0.5 mg/L in agricultural runoff (International Potash Institute, 1983). Phosphorus loading to streams may account for up to 80% of phosphorus present in these systems (Bockman, 1990).

From a human health perspective, phosphorus does not pose a significant risk when present in drinking water and there are currently no water quality standards for phosphorus in this matrix. However, phosphorus can have a significant effect on the ecological integrity of surface waters, where it is the primary cause of eutrophication. Indeed, phos-

phorus from agricultural fertilizers is the main source of nutrient loading to, and eutrophication of, the lower Great Lakes, particularly Lake Erie and the St. Lawrence River (Government of Canada, 1996). Fortunately, because phosphorus is quickly adsorbed by soil particles, best management practices directed at reducing nonpoint sources of pollution, such as erosion control, can greatly reduce phosphorus loading to aquatic environments.

Leaching is the most significant source of nitrates in groundwater. Nitrate in soil generally follows the main flow paths of water, but will also migrate by diffusion. Nitrogen leaching in soil depends on soil structure and porosity, water supply from precipitation and irrigation, evaporation from the soil surface, and the degree of drainage (Table 13). Groundwater in areas of high agricultural activity are most susceptible to contamination by nitrates. Consequently, it is frequently detected in drinking water derived from domestic wells in these areas, often at levels that exceed water quality criteria. Wells located in sandy soils are most susceptible to nitrate contamination. For example, Hill (1982) found high concentrations of nitrates in several wells located in sandy soils near Alliston, Ontario. Nitrate concentrations in well waters often exceed water quality criteria. For example, Briggins and Moerman (1995) found that 13% of wells sampled in an agricultural area of Nova Scotia exceeded provincial guidelines for nitrate. In Ontario, Frank et al. (1991) found that 15.5 and 6.6% of wells ($n = 180$) exceeded the provincial maximum allowable concentration (MAC) of 10 mg/L. A recent survey by Goss et al. (1998) found that 14% ($n = 1292$) of wells surveyed in rural areas of northern and southern Ontario contained nitrate concentrations above the MAC. Rudolph et al. (1998), as part of the same study, showed that 23% ($n = 144$) of multilevel monitoring wells contained concentrations of nitrate that exceeded the provincial drinking water standard (MAC). Our survey of southern Ontario drinking water treatment stations also showed that nitrate was a common contaminant in treated waters. However, there were few instances in which nitrate, nitrite, or ammonia exceeded provincial standards.

TABLE 13 Factors Affecting Nitrogen Leaching to Groundwater

Factor	Less leaching	More leaching
Crop	Vigorous crop Established crop	Poor crop Seedbed application
Soil	Heavy soil Poor drainage	Light soil Good drainage
Time of application	At the beginning of the main growing period or during active crop growth	At the end of the growing season or out of season
Climate	Low rainfall	High or irregularly distributed rainfall

Atmospheric Transport

The atmosphere is a principal recipient and global transporter of a wide range of pollutants. It also represents a significant source of contaminants to surface waters of streams and lakes. Most atmospheric pollutants occur in the troposphere, which extends from the earth's surface to an altitude of about 10 km. Uncontaminated air is comprised of a complex mixture of nitrogen (78.09%), oxygen (20.94%), rare gases (0.93%), carbon dioxide (0.03%), and a number of trace constituents (0.01%; Table 14). Contaminated air may contain a large number of both polar and lipophilic compounds. For example, Majewski and Capel (1995) identified 63 pesticides and pesticide transformation products in the atmosphere that were deposited in rain, snow, and fog. Atmospheric transport is also a significant route for persistent organic pollutants (POPs) to enter into aquatic environments (Table 15).

Pollutant emissions to the atmosphere are typically categorized as anthropogenic (released by human activities), natural (e.g., releases of geologically-bound pollutants by natural processes), or reemitted (e.g., mass transfer of previously deposited pollutants to the atmosphere by biologic/geologic processes). Anthropogenic emissions include those from industrial stacks, municipal waste incinerators, agricultural activities (e.g., pesticide applications), and vehicle exhaust. Natural emissions include

TABLE 14. Trace Constituents of the Normal Trophosphere

Constituent	Formula	Conc. (ppb)	Conc. ($\mu g/m^3$)
Carbon compounds			
Methane	CH_4	1400	900
Carbon monoxide	CO	60–200	70–230
Terpenes	$(C_5H_8)_n$	36,900	36,979
Formaldehyde	CH_2O	<10	<12
Halogenated compounds			
Methyl chloride	CH_3Cl	0.5	1
Carbon tetrachloride	CCl_4	0.1–0.25	0.6–1.6
Freon 12	CF_2Cl_2	0.21	
Freon 11	$CFCl_3$	0.1	0.7
Oxygen compounds			
Ozone	O_3	37,193	20–60
Nitrogen compounds			
Nitrous oxide	N_2O	330	600
Ammonia	NH_3	37,061	36,994
Nitric acid	HNO_3	3	7.5
Nitrogen oxides	NO/NO_2	1	~1.6
Sulfur compounds			
Sulfur dioxide	SO_2	36,894	36,960
Hydrogen sulfide	H_2S	<0.2	<0.3

Note. Adapted from Crosby (1998).

TABLE 15. Deposition of Selected Persistent Contaminants in Rain

Pollutant	Typical concentration in air (ng/m³)	Concentration in rain (ng/L)
PCBs, total	1	30
Chlorinated pesticides		
DDT, total	0.03	5
BHC, total	2.3	20
Dieldrin	0.05	2
HCB	0.2	2
Methoxychlor	1	8
Total PAH	20	100
Phthalate esters	4	12

Note. Adapted from Eisenreich et al. (1981).

those associated with volcanic eruptions, windblown gases and particles from forest fires, windblown dust and soil particles, and sea spray. In many cases, it is difficult to differentiate between natural and anthropogenic atmospheric pollutants. Depending on weather conditions and the chemical and physical properties of the contaminant, air pollutants can be transported varying distances and may undergo significant physical, chemical, and/or biological transformation during this transport (U.S. EPA, 1997a). Indeed, many atmospheric pollutants are transported over long distances, leading to deposition and accumulation in areas, such as the Arctic, in which they have never been used or released (discussed later).

Pollutant loading to water bodies from the atmosphere primarily occurs through wet or dry deposition. The process of wet deposition refers to the removal of air pollutants from the air by a precipitation event, such as rain or snow. The deposition of atmospheric vapor and dust by absorption and physical entrainment into raindrops is an important transport route over much of the world. All but the largest drops of water (possibly containing many pollutants) may remain airborne for many minutes, hours, or even days, depending on the chemical, physical characteristics of the pollutant, and the climatic conditions.

The process of dry deposition refers to the removal of aerosol pollutants through eddy diffusion and impaction, large particles through gravitational settling, and gaseous pollutants through direct transfer from the air to the water (i.e., gas exchange). Air pollutants can also enter surface waters indirectly, which occurs when an air pollutant is deposited on land and is subsequently carried into a receiving water body by other routes, such as storm-water runoff or inflow from tributaries. The tendency of a specific pollutant to enter a water body through wet or dry deposition, or gas exchange, is strongly influenced by the physical and chemical properties of the pollutant and the meteorological conditions to which it is subjected.

Although a potentially significant source of contaminants to surface waters, atmospheric deposition is generally only a minor direct source of contaminants to groundwater. However, contaminants of atmospheric origin may nonetheless eventually find their way into groundwater via indirect pathways, through exchange of previously deposited contaminants at sediment–water interfaces, movement of surface waters into fluvial aquifers, or upwelling/downwelling events in streams (discussed later).

Persistent Organic Pollutants (POPs) and Other Contaminants Transported in the Atmosphere   Persistent organic pollutants consist of a group of chemicals that are highly persistent in the environment, bioaccumulate in tissues, and exhibit significant toxicological properties (Crosby, 1998). These chemicals have no natural sources and are produced entirely through commercial and industrial activity (Hester & Harrison, 1994; Harrad, 1996; Edjulee & Cains, 1996). Many have been banned, phased out, or severely restricted in use for many years; however, only recently has the United Nations Environment Program (UNEP) agreed to completely abolish the worst offenders (Table 16) and set forth a process to determine the next chemicals to be proscribed (UNEP, 1999; Kaiser & Enserink, 2000). These chemicals are semivolatile, so they are capable of undergoing long-range atmospheric transport, a process that is characterized by the gradual movement of chemicals that are produced in midlatitude regions toward polar regions in a series of volatilization–distillation events (Figure 11). This process, also referred to as the global distillation hypothesis (Wania & Mackay, 1982) or the grasshopper effect, has led to high concentrations of these contaminants in Arctic environments and bioaccumulation in associated biota and humans. Indeed, many persistent organic pollutants (POPs) can be detected in virtually every environmental matrix around the world. Some of these chemicals (e.g., organochlorine pesticides, DDT dioxins/furans) have been implicated as potential endocrine-disrupting compounds, raising concerns about possible developmental, immunological, and reproductive effects in wildlife and humans (see also earlier discussion). Despite longtime bans on most, significant human health problems continue to be experienced in polar regions due to exposure of adults and children to these

TABLE 16. POPs Currently Listed Under the UNECE and UNEP Initiatives

Pesticides	By-products	Industrial chemicals
Aldrin/dieldrin	PCDDs	Hexabromobiphenyl
Endrin	PCDFs	PCBs
DDT/DDE	PAHs	
HCH/lindane	HCB	
Chlordane		
Heptachlor		
Chlordecone		
Mirex		
Toxaphene		

FIGURE 11. Illustration of the movement of persistent organic pollutants according to the global distillation hypothesis.

chemicals through dietary sources. Because exposure of humans and biota is overwhelmingly via food (it is estimated that less than 1% of the uptake of these compounds is accumulated via nondietary sources; Government of Canada, 1991), there is little risk of exposure to these compounds via drinking water. In fact, although many of the POPs listed in Table 16 have at one time or another been detected in drinking water (see Table A1), most are extremely rare in this matrix today. The primary reason for the absence of these compounds in drinking water is that they are sparingly soluble, preferring instead to be associated with lipophilic matrices such as sediments and lipids.

Among the most important POPs from a human health perspective are PCBs. In general, the number and magnitude of PCB sources have decreased significantly (20-fold) in the past 20 years. The largest national-level stationary air emission source of PCBs is incineration of hazardous waste materials and consumer products containing PCBs (Mojewski & Capell, 1995). The primary route for human health exposure is diet, and because PCBs are rarely found in water, there is presently little risk associated with ingestion of drinking water.

A number of persistent pesticides are also commonly encountered in the atmosphere (Majewski & Capell, 1995) and are subject to long-range atmospheric transport (Kurtz, 1990). Pesticides can enter the atmosphere as spray

drift generated as droplets or as particles of the pesticide formulation. Such particles or droplets may travel considerable distances. In a global monitoring survey of air and surface seawater from 1989 to 1990, Iwata et al. (1994) found hexachlorocyclohexane (HCH) to have the highest concentration among organic pollutants. Concentrations were greatest in tropical source regions and in cold water deposition areas near the Arctic. Other persistent organic pesticides, such as chlordane, showed a more uniform global distribution. Although long-range transport of persistent pesticides is of greatest interest due to human health concerns, it is important to recognize that polar pesticides may also be transported long distances in the atmosphere. For example, Thurman and Cromwell (2000) found residues of atrazine, a highly polar and widespread herbicide, in pristine areas of Ilse Royale National Park in Lake Superior. This area is well removed from the primary agricultural areas of the Midwestern United States where atrazine is applied.

Atmospheric deposition also represents a significant route for the entry of mercury into aquatic ecosystems. Anthropogenic mercury emissions are only one component of the global mercury cycle; the amount of mercury in the land, water, and air at any one location is comprised of mercury from the natural global cycle, the global cycle perturbed by human activities, and from regional anthropogenic sources. Other sources of mercury include direct discharges to water or the application of mercury in the form of fungicides to protect crops. In total, natural, industrial, and recycled anthropogenic mercury contribute about one-third of the current mercury burden in the global atmosphere (Pirrone et al., 1996). Estimates of the global contribution of mercury emissions to the atmosphere from anthropogenic sources are 2000 to 4000 tons per year (tpy) and from natural sources are 2200 to 4000 tpy, resulting in total mercury air emissions of 4200 to 8000 tpy (Pirrone et al., 1998). In comparison, U.S. mercury air emissions for 1994–1995 were 158 tpy (U.S. EPA, 1997b). Approximately 87% of anthropogenic mercury emissions in the United States is from combustion sources, including waste and fossil fuel combustion.

Interestingly, new measurement methods suggest that natural mercury emissions rates from mercury-rich soils and bedrocks may be larger than past estimates suggested. Also, a recently identified source of mercury to the atmosphere is emissions of elemental mercury gas (Hg°) from soils that have been amended with municipal sewage sludge (Carpi & Lindberg, 1997). These researchers estimated that land application of sewage sludge in the United States and European Union may account for approximately 5×10^6 g/yr (5 metric tons/yr) of Hg° released to the atmosphere based on the area of land amended each year and measured Hg° emission rates. It is important to understand the source of mercury and the amount of mercury contributed by each source type so that the most efficient control strategies can be devised.

The atmosphere also represents a significant source of nitrogen to surface waters (National Atmospheric Deposition Program, 1999). The predom-

inant natural source of nitrogen in the atmosphere is via microbial decomposition of organic matter in soil and water. Microorganisms release ammonia (NH_3) to the atmosphere during the breakdown of amino acids (Oke, 1978; Smith, 1980). Predominant anthropogenic atmospheric nitrogen sources include (1) emissions of nitrogen oxides from the combustion of fossil fuel, (2) ammonia (NH_3) and ammonium (NH_4^+) emissions from fertilizer and explosive factories, and (3) volatilization of ammonia-based fertilizer from agricultural fields (Oke, 1978; Lippman, 1989; Paerl, 1993).

As with many atmospheric contaminants, once emitted into the atmosphere, nitrogen may be deposited locally or may travel great distances before deposition. More than 3.2 million tons of atmospheric nitrogen is deposited on watersheds of the United States annually. In Canada, atmospheric deposition of nitrogen to surface waters amount to approximately 182,000 tonnes per year (Chambers et al., 2001). Wet deposition accounts for the majority of nitrogen removed from the atmosphere (Paerl et al., 1990). The degree to which a watershed retains nitrogen is a function of the soil characteristics, topography, underlying geology, amount and type of surface vegetation, and degree of impervious cover (Paerl, 1993). Inevitably, a significant amount of deposited nitrogen will be transported during a precipitation event, via overland or subsurface flow, into a freshwater system. Here it may contribute to processes such as eutrophication of aquatic systems or may enter into groundwater supplies through various exchange mechanisms with surface waters.

Recently, a number of persistent *polar* organic pollutants (PPOPs) have come to the attention of environmental scientists. Like POPs, this class of chemicals contains several highly persistent compounds, some with half-lives in the order of thousands of years. Examples include trifluoroacetic acid (TFA, an atmospheric breakdown product of some chlorofluorocarbon replacement compounds), chlorodifluoroacetic acid (CDFA), and perfluorooctane sulfonate (PFOS), a flourinated surfactant that is commonly used as a stain repellent in products such as ScotchGuard. Unlike the POPs, however, these compounds are highly water-soluble and therefore generally do not bioaccumulate in tissues. Further, most PPOPs also appear to exhibit low levels of toxicity to most organisms. However, a notable exception is PFOS. This compound has been detected in tissues of wildlife, mammals, and humans (Giesy & Kannan, 2001; Kannan et al., 2001; Gilliland & Mandel, 1996) and may be globally ubiquitous. Unfortunately, data on exposure of humans to PPOPs via diet or drinking water, and on potential risks to human or ecosystem health, are scarce. However, in view of their solubility and general recalcitrance to microbial and chemical breakdown, the occurrence of some of these compounds in drinking water would not be surprising.

It is important to point out that new POPs continue to be identified and detected in the tissues of Arctic biota. For example, polychlorinated paraffins and polybrominated diphenyl ethers (PBDEs, used as fire retar-

dants and are structurally similar to PCBs), and the pesticide endosulfan, which is still used in Canada, have recently been added to the UNEP list of potentially important POPs that are subject to long-range atmospheric transport. In some cases (e.g., PBDEs), these compounds appear to be undergoing significant increases in many aquatic environments, but information on potential effects on human health and ecosystem integrity is scarce. As with many of the classic POPs, the most significant route of exposure to these compounds for humans and aquatic biota will be dietary; exposure via treated drinking water is likely to be negligible.

Urban/Suburban Runoff

Urban runoff represents a significant source of contamination in surface waters. The impacts of urban runoff on the quality of surface waters have become a key issue in Canada in recent decades. Currently, approximately 80% of Canadians live in urban areas, but this proportion is expected to increase within the next 15 years as the Canadian population is projected to increase by 5 million people (Statistics Canada, 2000). Approximately 80–90% of this expansion will occur in urban areas. Intensified urbanization and the resultant increase in impervious surfaces (concrete, pavements, roofs, etc.) will alter the volume and quality of urban runoff (Ellis, 1986). There is already concern about storm-water pollution in the Great Lakes Basin, particularly in Hamilton Harbor and the Toronto Waterfront (Marsalek & Kok, 1997), where storm water is often contaminated with suspended solids, phosphorus, heavy metals, hydrocarbons, and fecal bacteria (Chambers et al., 1997).

Runoff from urban centers primarily occurs during or shortly after precipitation or snowmelt events. As the water contacts and subsequently moves over the many urban surfaces, a wide range of contaminants may become dissolved or suspended in the resulting runoff. Urban runoff is ultimately discharged into receiving waters, either before or after being passed through storm-water treatment facilities, if such technologies exist in the municipality (Chambers et al., 1997). Thus, coastal areas, large rivers, and the Great Lakes are the main recipients of urban runoff; however, small streams and metropolitan lakes often accept primary inflows (Waller & Hart, 1986).

Precipitation intensity and volume are important removal factors of surface contaminants in runoff (Ellis, 1986). In most cases, precipitation intensity is the most significant removal factor (Price & Mance, 1978), but water volume can be very important in transporting solids, particularly those of large diameter (Ellis, 1986). Runoff volume is dependent upon on the type (industrial, commercial, residential) and density of development, as well as the conditions and gradient of the developed area (Ellis, 1986). Precipitation of low pH can also affect the dislodgibility of pollutants, since acidic rain solubilizes some pollutants (e.g., metals) that are weakly bound to urban surfaces (Ellis, 1986). Typically, the first flush that accompanies

each storm or snowmelt event is the most concentrated and contaminated outflow (Ferguson, 1994), especially if there has been a protracted period between precipitation events.

Contaminants in runoff originate from a variety of nonpoint sources in the urban environment. Solids such as glass, asphalt, stone, rubber, rust, building materials, pavements, dust, and human litter accumulate on paved surfaces (highways and large parking lots) between storm events (Ferguson, 1994). Urban snowpacks also accumulate large quantities of solids and contaminants over the winter months. Schroeter (1997) assessed the wastewater contaminant discharges in 17 Ontario areas where waste water pollution is a concern. He reported that during wet weather events, storm water accounted for 77 to 100% of the solid loadings into receiving waters. Although solids are frequently found in surface waters, they rarely migrate into groundwater, due to the filtering and adsorptive properties of soil (Bianchi & Muckel, 1970). Hence, environmental problems associated with solids in runoff (e.g., sediment loading) are generally restricted to impacts on aquatic biota.

Canadian highways and parking lots also accumulate high levels of salts, which are widely used as deicing agents and, in lower quantities, as dust suppressants. Salts are highly water-soluble and their ions may be persistent in both surface waters and groundwaters (Mayer et al., 1999). All road salts are chloride based; thus, chloride is the principal contributing anion to salinity from road salt application. Salt use in urban Ontario has increased substantially over the past few decades, leading to an increase in chloride concentrations in receiving waters. For example, Bowen and Hinton (1998) reported that chloride concentrations in Highland Creek, a stream in the Greater Toronto Area (GTA), increased from 150 mg L^{-1} in 1972 to over 250 mg L^{-1} in 1995. Similarly, median chloride concentrations in Duffin Creek, also in the GTA, were 10 to 20 mg L^{-1} in the 1960s, but increased to between 30 to 40 mg L^{-1} in the early 1990s (Bowen & Hinton, 1998). Road-salt contamination of surface waters also exhibits significant seasonal variation, which are characterized by "salt pulses." For example, in the Don River, Toronto, the autumn baseline chloride concentration ranged from 100 to 150 mg L^{-1} (Scott, 1980), whereas in the winter months, concentrations were as high as 1000 mg L^{-1} after thaw periods (Scott, 1980; Schroeder & Solomon, 1998). Indeed, deicing compounds are a major contributor to snow-pack contamination (Oberts et al., 2000). These trends precipitated a joint assessment by Environment Canada and Health Canada on the environmental impacts from road salts (Environment Canada, 2000b). They concluded that road salts were entering aquatic habitats at concentrations that had, or were predicted to have, immediate or long-term harmful effects on the environment and its biological diversity (Environment Canada, 2000b). As a result, road salts are now considered to be toxic under Section 64 of CEPA.

Urban oil spills also represent a significant source of organic pollution in runoff in Ontario. Between 1988 and 1997, an estimated 6.84 million liters

of oil was spilled in the highly populated Golden Horseshoe area of south-western Ontario (Li & McAteer, 2000). Approximately 1.34 million liters of this oil passed through the urban drainage systems within the region and entered Lake Ontario (Li & McAteer, 2000), contributing to the con-tamination of surface water from which many municipalities draw drink-ing water.

Automobile emissions and the wear of automobile parts and road con-struction materials are the primary sources of lead, zinc, copper, and iron to roadways and parking lots (Marsalek, 1986; Ferguson, 1994). However, the banning of leaded gasoline in the 1970s greatly reduced lead residues found on and surrounding roadways (Marsalek, 1986).

Pesticides and fertilizers from intensively managed golf courses, parks, and lawns are common constituents in urban runoff. The most prevalent contaminants that originate from fertilizers are nitrogen and phosphorus; however, metals can also be leached out of some fertilizers (Ferguson, 1994). Nutrient enrichment problems exist in a number of harbors on the Canadian side of the Great Lakes (Waller & Novak, 1980), where eutrophi-cation, as well as elevated biological and chemical oxygen demands, has been evident (Ellis, 1986; Ferguson, 1994). Additionally, fecal bacteria from dog, cat, rodent, and bird wastes frequently contaminate urban runoff (Feldman, 1974; Ferguson, 1994).

Roofs are sources of numerous contaminants such as solids, metals, and bacteria. Solids are often deposited on rooftops via atmospheric sources in quantities large enough to deem roofs to be one of the key origins of solids in urban runoff (Ellis, 1986). Roofs are also a source of metal contamina-tion. Malmquist (1983) suggested that as much as 70 to 90% and 50 to 70% of the total mass discharges of copper and zinc, respectively, in urban runoff are derived from the corrosion of roofing materials. Copper, zinc, and lead are also components of exterior paints, which flake or are leached off walls and roofs (Marsalek, 1986; Ferguson, 1994). Roof runoff can also be high in bacterial pathogens, a problem that been associated with bird droppings (Ellis, 1986).

Other urban sources of runoff contaminants include construction sites where soil and metal particulates can originate, and urban garbage dis-posal sites, which are sources of bacterial pathogens, nitrogen, and phos-phorus (Ferguson, 1994).

Sediments

Sediment consists of a heterogeneous matrix of all detrital, inorganic, and organic particles that occur on the bottom of a body of water (Power & Chapman, 1992). From a pollution standpoint, sediments have the unique characteristic of acting as both a source and a sink for many natural and anthropogenic contaminants. As a sink, contaminants from many of the point and nonpoint sources outlined earlier become entrained in sediments, either by partitioning out of the water or via deposition of suspended solids

to which they are adsorbed. Many contaminants and organic wastes discharged to aquatic systems eventually accumulate in sediments, where they may adversely affect the benthic biota, and enter into pelagic and human food chains (Thomas, 1994). Particularly problematic in this regard are lipophilic chemicals (having a strong affinity for lipids), which preferentially partition into sediments and other (e.g., tissues) environmental matrices. Areas of significant sediment contamination exist in well-defined areas throughout North America as indicated by the numerous Area of Concerns in the Great Lakes and many of the Superfund sites in the United States. In these areas, sediment contamination could be considered as point sources for pollution of aquatic habitats. However, the majority of sediment contamination is relatively diffuse, characterized by low-level contamination spread over broad geographical ranges.

As a source, contaminated sediments may release chemicals to water via desorption from organic ligands into surrounding interstitial water. One of the theories used to describe this process is equilibrium partitioning (EqP), which is based on the assumption that organic chemicals and certain metals reach a thermodynamic equilibrium between benthic fauna, solid phases in the sediment (e.g., organic ligands), and interstitial water (Lee, 1992) (Figure 12). If the dissociated free chemical is lipophilic, it may be taken up and
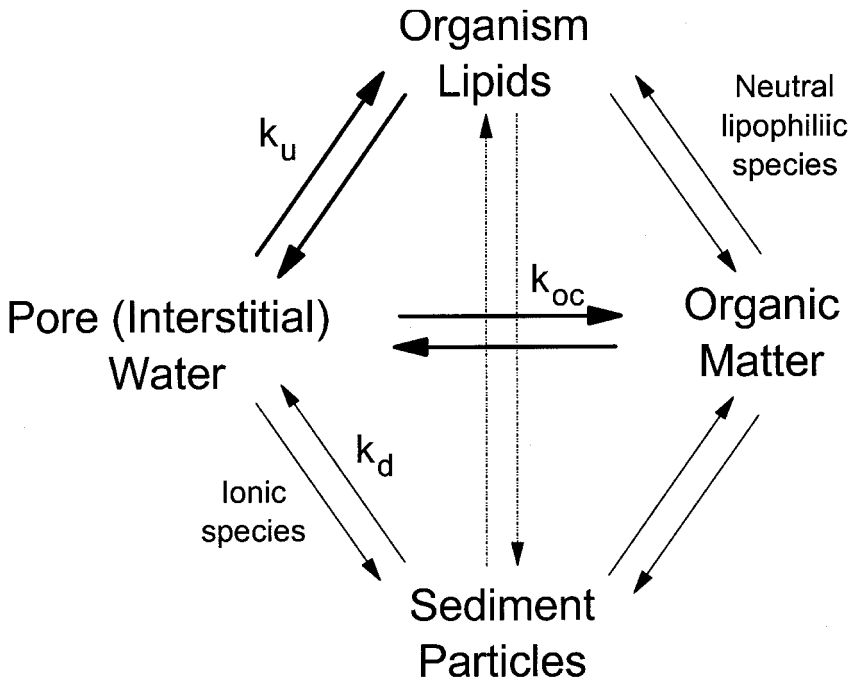

FIGURE 12. Partitioning relationships between sediment phases and biotic tissues as a basis for equilibrium partitioning. Partitioning is represented by a constant (K) between any two respective phases (e.g., K_{oc} between sediment organic carbon and interstitial water).

accumulated from the interstitial water by benthic aquatic organisms that come into contact with it. An equally important route for accumulation of contaminants by benthos is by ingestion of sediment particles and organic matter to which the contaminants are adsorbed; the contaminants desorb in the gut and pass across the intestinal wall into the tissues (Fisher, 1995). In either case, the compounds may subsequently be passed through the food chain as organisms at each trophic level are consumed by those at higher levels; the contaminants may become increasingly concentrated with each level, a process referred to as biomagnification. This route of exposure is typical for lipophilic compounds such as DDT, PCBs, and mercury, and it can lead to significant impacts on aquatic and terrestrial biota as illustrated by the decline of bald eagles in the Great Lakes region due to eggshell thinning and widespread fish consumption advisories due to mercury contamination. Metals may be accumulated in a similar fashion, but these are also subjected to natural biogeochemical cycling processes (see earlier metals section; see also Allen, 1995; Di Toro et al., 1991; Ankley et al., 1996).

The EqP approach has formed the cornerstone of the U.S. EPA program to establish sediment quality criteria for the protection of aquatic life; however, this approach has come under considerable scrutiny in recent years (e.g., see Chapman et al., 2001) because increasingly it is recognized that a true thermodynamic equilibrium between the sediment and interstitial water or between the interstitial water and organism is probably rarely achieved. For this and other reasons, there have been a number of alternative approaches proposed (Reynoldson et al., 1997; Long et al., 1998; Burton, 2001), although these are not without limitations. Regardless of the approach used, it is critical that sediment criteria be reassessed on a periodic basis to be certain that they are protective of both human health and ecosystem integrity; this will mean that they must be sufficiently flexible (Standley & Bott, 2001), particularly in terms of acceptance and application by key regulatory agencies, to accommodate new scientific understanding of sediment-associated processes and factors that affect the bioavailability of contaminants.

One of the most significant routes for contaminants in sediments to enter overlying water is dredging. Dredging is routinely conducted in harbors, ports, and other areas of high boat and water transportation activity (NRC, 1997). Because resuspension of contaminants and associated impacts due to dredging activities are usually restricted to a local scale (e.g., harbor), this essentially represents a point-source form of pollution. Due to the lipophilic nature of most sediment-associated contaminants, they tend to remain tightly bound to sediment particles during dredging activities (Digiano et al., 1993). Nonetheless, dredging can lead to the dissolution of certain contaminants, particularly metals, into the water column, and these may exert toxicological effects on surrounding biota. Recognition of the potential impacts of dredging activities on aquatic communities led to the development of some of the first sediment bioassays (Lee, 1992) and arguably marked the

beginning of sediment toxicology and the development of sediment quality criteria. Risks to humans from dredging are unknown but probably minor due to the localized nature of this activity. Plausibly, sediment-associated contaminants that are liberated during dredging could enter into drinking water if such water was extracted from the same area in which the dredging activity occurred.

While considerable effort has been directed toward understanding relationships between sediment and overlying (surface) water regarding the movement and bioavailability of contaminants in aquatic environments, much less effort has been directed toward understanding such relationships between surface water and groundwater. Potentially, contaminants that desorb from sediments, or that are adsorbed to suspended particles, could enter groundwater if the overlying surface water into which the contaminants partition enters into a fluvial aquifer (a stream that drains into a groundwater aquifer). Recent evidence has also shown that sediment-associated contaminants may also move to groundwater via downwelling of water, particularly in streams (Greenberg et al., 2000). These authors hypothesize that localized sediment contamination, and exchange of contaminants between surface water and groundwater, is strongly influenced by upwelling or downwelling events in streams. Areas of upwelling may facilitate entry of contaminants associated with groundwater into surface waters, where they may enter into drinking-water supplies extracted from the water body. Such exchanges have been demonstrated in groundwater-dominated streams in agricultural areas where nitrate loading to surface waters via groundwater have caused significant deterioration of drinking-water supplies (van Lanen & Dijksma, 1999). In addition to potential human health risks, the contribution of contaminants via upwelling may also impact benthic communities that live in the sediments and that serve as the basis of production in these systems (Duncan, 1999).

Downwelling, in contrast, can move contaminants associated with surface waters and sediments into subsurface systems where they may be incorporated into the groundwater. These contaminants may become incorporated into shallow aquifers that supply domestic wells, or may resurface at another location in a stream via upwelling.

Other Sources of Contaminants to Surface Waters and Groundwater

A number of sources of environmental stressors cannot be definitively categorized as either point or nonpoint sources of pollution, or may not constitute chemical contaminants per se, yet may significantly affect the quality of surface waters or groundwater and hence have effects on in-stream ecological integrity and risks to human health. These sources include construction (e.g., land development, roads), habitat modification (e.g., removal, addition of riparian buffer zones), hydrologic modification (e.g., dams, channelization), discharge of cooling-water effluents, and the occurrence of natural toxins. The most significant of these sources are

described briefly next. In the United States, sediment/siltation has long been recognized as the most significant "nontoxic" pollutant contributing to degradation of surface waters (Oschwald, 1972; U.S. EPA, 1990). Increased sedimentation in streams due to habitat or hydrologic modification can result in significantly increased sediment loading, with a corresponding loss of benthic productivity and fish habitat (Waters, 1995).

From the perspective of human exposure to contaminants in drinking water, these sources generally do not directly contribute toxic chemicals per se to aquatic environments. However, they can have a significant effect on the physicochemical characteristics of receiving water or sedimentary environments, which may in turn affect the environmental chemodynamics of naturally occurring contaminants (e.g., metals) or contaminants contributed from other anthropogenic sources. This could ultimately change the pathways along which many contaminants may eventually come to be present in drinking water. For example, increased runoff and transport of soil particles to which contaminants are adsorbed can lead to reductions in water quality and loss of habitat in developed watersheds, particularly in agricultural areas. Such events have been closely linked with the removal of riparian or wetland vegetative zones (Naiman et al., 1988; Petersen, 1992; Rabeni & Smale, 1995), which is a common practice in watersheds being developed from human use.

Hydrologic and Habitat Modification   Historically, hydrologic and habitat modification of streams and lakes has represented arguably the most significant disturbance of aquatic systems since the arrival of humans in North America. Hydrologic modification includes activities such as channelization, dredging (see earlier sediment section), dam construction, and flow regulation (U.S. EPA, 1998b). Habitat modification includes removal of riparian vegetation, stream-bank modification, and drainage and filling of wetlands. In general, hydrologic and habitat modification of aquatic environments poses far greater risks to aquatic biota and ecosystem health than it does to human health. However, such modifications can significantly affect the transport and chemodynamics of pollutants in the environment and hence on the exposure of humans to them. For example, the removal of forest, grass, or wetland riparian buffer zones along streams can lead to an increase in the quantity of sediments, nutrients, or other pollutants (e.g., pesticides) transported from terrestrial landscapes into aquatic environments. Humans could experience increased exposure to these pollutants if drinking water is extracted from the contaminated surface waters.

The most common forms of hydrologic modification are channelization/diversions and dam construction, and these are often found together in aquatic systems. In the United States, the extent of channelization is extensive, with 26,550 km of channelization having been completed by 1977 (Leopold, 1977). In Canada, Quinn (1987) documented 54 interbasin diversions, representing a mean annual flow rate of approximately 1 m/s. These are predominantly used in relation to hydroelectric development. Smaller

scale channelization is particularly common in urban areas to ensure ex-
peditious movement of water to wastewater treatment facilities or receiving
waters, and in agriculture where it is often used to divert stream water for
use in crop irrigation. From an ecosystem perspective, stream channeliza-
tion disrupts the riffle–pool habitat complexes required by many organisms
for the completion of life cycles and destroys spawning habitat for fish
(Allen, 1995). Although channelization may yield benefits in terms of flood
control, this is often offset by losses in habitat diversity and ecological con-
dition. The effects of dams on the physical and biotic integrity of stream
ecosystems have been well documented, perhaps most dramatically in rela-
tion to declines in migrating fish populations (e.g., salmon), which cannot
reach critical spawning grounds located above the dams (Nehlsen et al.,
1991). Damming and pooling of streams may also lead to significant in-
creases in water temperature downstream due to the increased residence
time and surface area of dammed water, which allow for greater solar heat-
ing. This may lead to substantial declines in, or loss of, sensitive species
such as trout, or shifts in fish community structure such as, for example, the
replacement of cold-water species with warm-water species.

Other forms of habitat modification can also significantly alter water
and habitat quality in water courses. Loss of riparian buffer zones along
streams and lakes and loss of wetlands through draining and filling can
have dramatic effects in this regard. The riparian zone consists of the area
of land adjacent to streams and rivers or surrounding lakes, and repre-
sents an important transition zone that regulates the flow of energy and
materials between the terrestrial landscape and the aquatic environment
(Naiman & Descamps, 1997; Naiman et al., 2000); this interface is often re-
ferred to as an ecotone. Because of its important function in regulating
the flow of materials, loss of riparian vegetation can lead to a significant
increase in non-point-source pollution and the export of toxic contaminants
to aquatic environments. Conversely, the presence of riparian buffer areas
has been shown to significantly reduce inputs of nutrients and suspended
solids from agricultural activities and forestry to aquatic systems (Peterjohn
& Correll, 1984; Gregory et al., 1991). Wetlands have been shown to
function similarly in this capacity (Richardson, 1999). Riparian zones and
wetlands may also serve to impede the movement of, or permanently re-
tain, water- and particle-borne toxic contaminants such as pesticides.
From a functional standpoint, regardless of the class of pollutant, the in-
creased contact time afforded by retention within the soil or sediment
matrix of the riparian zone or wetland provides significantly increased
opportunity for attenuation and degradation of the contaminants via chemi-
cal and microbial processes. Constructed wetlands have been shown to be
very effective as treatment systems for reducing contaminant and pathogen
concentrations and toxicity of point source effluents and non-point source
pollution (Richardson, 1999; Rodgers et al., 1999; Huddleston et al., 2000).
Increasing the proportion of riparian and wetland structures also signifi-

cantly improves habitat quality, thereby improving the overall health of the ecosystem (Naiman et al., 2000).

Recognition of the important role of riparian zones and wetlands in this regard has led to the initiation of a number of restoration initiatives throughout North America. For example, in 1997, the U.S. Department of Agriculture initiated the National Conservation Buffer Initiative program, in which financial assistance and technical guidance is provided to landowners to develop buffer strips in both rural and urban settings to reduce non-point-source pollutant loadings to aquatic environments (Federal Interagency Stream Restoration Working Group, 1998). The goal of this ambitious program is to have a total of 3.2 million km of buffer strips in place along the nations waterways by the year 2002. A similar program was launched in 1999 in Prince Edward Island, Canada, wherein the province has legislated the requirement of vegetative buffers for all watercourses. Similar "buffer strip" initiatives are being proposed in Ontario through various conservation authorities.

Cooling-Water Effluent   Effluent discharged as a result of cooling operations in industry represents a form of point source pollution to aquatic environments. This form of pollution does not contribute toxic chemicals to surface waters per se, so there is little risk to human health. However, cooling-water effluents can have a significant effect on receiving waters ecosystems. In streams, large fluctuations in temperature can significantly effect species richness due to the elimination of thermal cues needed to break egg diapuase, reduction in degree days needed to complete development, and loss of synchrony in life cycles (Allan, 1995). In both streams and lakes, a change in temperature profile can also alter the type of fish community present.

Radionuclides   Exposure to radionuclides may occur from both natural and artificial sources. The former accounts for approximately 82% and includes sources of cosmic, internal, and terrestrial origin as well as exposure to radon (NRC, 1990). Artificial sources account for 18% of exposure and include medical applications, occupational exposure, nuclear fuel cycle, and fallout. On average, Canadians are exposed to a 2.6 mS/yr, which is slightly higher than the average global exposure of 2.4 mS (Health Canada, 1996b).

Radionuclides are frequently detected in both surface and groundwater sources that supply drinking water; however, the contribution of drinking water to total exposure is very small and is primarily the result of the presence of naturally occurring radionuclides in the uranium and thorium decay series (Health Canada, 1996b). Sources of radionuclides to surface waters include atmospheric deposition to both surface waters and soil, loss from soils due to surface runoff and leaching to soil water, and direct addition from effluent radionuclides associated with industrial activities (Cockerham & Cockerham, 1994).

Radon is the major source of naturally occurring radiation exposure for humans (Health Canada, 1996b). Exposure occurs as the result of ingestion

of water in which radon is dissolved or via inhalation of atmospheric radon. Because radon is volatile, surface water concentrations tend to be low, typically in the order of 0.01 Bq/L. However, groundwater may contain higher levels, often in the range of 10–75 Bq/L (Health Canada, 1996b). In some jurisdictions in the United States, radon represents a significant contaminant of drinking water, particularly in locations in which radon occurs at high natural concentrations in groundwater, or when it is found at high indoor atmospheric concentrations (Nero, 1988; Health Canada, 1996b). However, in Canada, it has been concluded that radon poses little risk to humans via drinking water exposure (Health Canada, 1996b). For this reason, a MAC has not been established for this radionuclide; however, it is recommended that in situations in which indoor air concentrations of radon exceed the acceptable level of 800 Bq/m^3 (as an annual average concentration in a normal living space), groundwater supplies should be examined to determine levels in that matrix.

In Ontario, the radionuclide of primary concern in drinking water is tritium, and it is routinely monitored as part of the Ontario Drinking Water Surveillance Program (ODWSP, 2000). Average tritium concentrations have been shown to range from 5 to 10 Bq/L in surface waters across Canada, between 7 and 10 Bq/L in Great Lakes surfaces waters, and to average 6 Bq/L in Ontario surface waters based on samples taken from various locations (Health Canada, 1996b). These values are all well below the Canadian Drinking Water Quality Maximum Allowable Concentration (MAC) for tritium of 7000 Bq/L. Moreover, data from the ODWSP indicate that tritium has never been found above the Ontario Drinking Water Objective, although the provincial drinking water objective for tritium is currently under review (ODWSP, 2000).

The ODWSP also undertakes periodic measurements of gross beta and alpha particles, which are used as preliminary screens for all radionuclides in water other than tritium. As with tritium, the ODWSP data indicate that these too are rarely detected in Ontario's drinking water (Table 17).

Natural Toxins   There are numerous examples of naturally occurring toxins in aquatic environments. Of primary concern from a human health perspective in drinking water are toxins that originate from cyanobacteria. Cyanobacteria grow in surface waters of freshwater lakes and rivers throughout the year, but are typically most prevalent during the warm mid to late summer months, when they may bloom to high concentrations (Tang et al., 1997; Lee, 1999). These algae proliferate during this time of the year because they have superior light-capturing capacity relative to some other algae, have a high affinity for nitrogen and phosphorus when supplies are limited, can regulate their position in the water column via gas vacuoles to better exploit areas of higher nutrient enrichment, and have relatively high temperature optima for growth (Tang et al., 1997). Not surprisingly, it is during this time of the year that they pose the greatest threat to humans and wildlife due to poisoning following ingestion. These algae occur across Canada, but they are particularly prevalent

TABLE 17. Concentration Ranges for Radionuclides Measured in Various Stages of Water Treatment

Compound	Concentrations ranges		
	Influent (surface)	Treated	Distribution
Southern region			
Gross alpha radiation (Bq/L)	0.08–0.31 (24/4/2)[a]	10.05–0.72 (23/23/23)	0.05–0.84 (47/15/10)
Gross beta radiation (Bq/L)	0.04–0.19 (24/22/22)	0.04–0.32 (23/23/23)	0.04–0.34 (47/7/6)
Tritium	6.0–11.0 (24/6/5)	— (23/1/0)	6.0–8.0 (47/7/6)
Radium	— (24/6/0)	— (23/1/0)	— (47/8/0)
Northern region			
Gross alpha radiation (Bq/L)	— (9/1/0)	0.04–0.12 (6/3/3)	0.05–0.06 (15/4/2)
Gross beta radiation (Bq/L)	0.04–0.07 (9/7/7)	0.05–0.21 (6/6/6)	0.04–0.13 (15/12/12)
Tritium	— (9/2/0)	— (6/1/0)	— (15/3/0)
Radium	— (9/0/0)	— (6/0/0)	— (15/0/0)

Note. Data taken from the Ontario Drinking Water Surveillance Program (ODWSP, 2000).

[a]First number in parentheses represents number of municipal water treatment plants searched, second number represents number of municipal water treatment plants that tested for presence of compound, and third number represents the number of municipal water treatment plants that detected compound on at least one occasion.

in the prairies where cyanobacterial poisoning has resulted in a number of livestock deaths (Manitoba Environment, 1998). However, there has been an increase in the number of cyanbacterial blooms in the Great lakes, so there may be increased risks to humans in these (and other) areas that use this water for drinking purposes. Interestingly, it has been hypothesized that one of the reasons for the apparent increase in these blooms in the Great Lakes region is a corresponding general increase in lakewide measurements of nitrogen (Chambers et al., 1997). Although studies to investigate this apparent relationship are lacking, it clearly underscores the potential interactive nature of many contaminants in aquatic environments. More importantly, it has important implications for the management of environmental contaminants in aquatic environments insofar as regulation of single compounds may not be appropriate, nor sufficiently protective, for both humans and aquatic biota, if interactions with other

compounds or abiotic factors exert a strong influence on the behaviour and concentration of the contaminant to which the regulation(s) is/are directed.

Some cyanobacteria produce toxins (cyanotoxins) of which there are two basic types: neurotoxins and hepatotoxins (Bell & Cobb, 1994). Neurotoxins are alkaloids (low-molecular-weight nitrogen-containing compounds) that block the transmission of nerve impulses between neurons and between neurons and muscles. Hepatotoxins are inhibitors of protein phosphatases 1 and 2A (Arment & Carmichael, 1996) and cause bleeding of the liver. There are two types of hepatotoxins: microcystins (produced by several species) and nodularins (produced by a single species). The former is most commonly encountered in freshwater and poses the greatest risk to humans and wildlife that drink contaminated water. The occurrence of these toxins in drinking water is most likely to occur in areas that do not have water treatment. However, these toxins may also occur in treated water even when the water is chlorinated. Indeed, although suitable analytical methods are poorly developed, it appears that a reduction in toxicity due to these neurotoxins in treated water can only be achieved using activated carbon or ozonation treatment processes (WHO, 1996).

The proposed guideline for consumption of algal toxins from drinking water in Canada is 1.5 µg/L, which is slightly higher than the World Health Organization guideline of 1.0 µg/L. However, these guidelines do not address risks associated with the potential for cancer from these toxins, which have been shown to promote tumor development. Interestingly, in a recent survey of drinking water in the United States and Canada, algal toxins were found to exceed World Health Organization guidelines in a number of jurisdictions (e.g., Winnipeg, Regina, cental Alberta). In the lower Great Lakes, particularly Lake Erie, the frequency of recent blue-green-dominated algal blooms appears to be increasing. Possible causes for these increases are unknown, but they may reflect lakewide increases in nitrogen or possibly an indirect effect of the invasive zebra mussel, whose filtering activity may be removing species that would otherwise compete with these algae. Similar competitive interactions have been shown between zebra mussel and the deepwater amphipod, *Diporiea* spp. It has been hypothesized that population densities of the latter are declining in southern Lake Michigan due to removal of diatoms, its primary food base, via feeding (filtering) activity of the zebra mussels (Landrum et al., 2001).

Another natural toxic agent that has recently emerged as a significant threat to human and aquatic ecosystem health and that has been connected to intense agricultural practices is *Pfiesteria*. Outbreaks of *Pfiesteria piscicida*, a dinoflagellate marine algae, are uncommon in Canada, but it has been a significant problem in the U.S. estuaries, particularly in South Carolina, where it has been connected with large hog farming practices (U.S. EPA, 1998b). These outbreaks occur largely due to poor watershed management practices such as inadequate protection from agricultural runoff and provide a dramatic indication of the intimate relationship between humans

and ecosystems and the effect that each can have on the other (Silbergeld et al., 2000).

Pfiesteria poses risks to both humans and ecosystems, although our understanding of the latter is much better than the former (Silbergeld et al., 2000). In fish, *Pfiesteria* cause characteristic lesions, the origin of which is hypothesized to result from a toxin secreted by the alga that damages the mucus/skin of the fish, allowing penetration of harmful bacterial or fungal species present in the water (Noga et al., 1996). In humans, potential routes of exposure and mechanisms of toxicity are poorly understood. Glasgow et al. (1995) reported that individuals having contact with *Pfiesteria*–contaminated water exhibited symptoms of headaches, skin lesions, and skin burning. Unfortunately, there is currently little information on occurrence of *Pfiesteria* in drinking-water supplies in areas where this organism occurs, so potential exposure via this route is virtually unknown.

Summary of Sources and Pathways

Although necessarily brief in scope and conceptually general, we have attempted to identify the most significant point and nonpoint sources of contaminants, the transport pathways (e.g., erosion, leaching, deposition) through which the contaminants move, and some of the factors (e.g., hardness, pH) that affect their composition and toxicity in the environment as they become incorporated into the groundwater and surface-water resources that supply our drinking water. Although we have attempted to be as thorough as possible in our consideration of the various sources and pathways of water contamination, we realize that some important aspects (e.g., specific compounds) have not been addressed at a level of detail that might otherwise be warranted based on their perceived or actual importance. However, it must be realized that our goal was not to provide a comprehensive assessment in this regard, but rather to provide the reader with an introduction to, and appreciation of, the myriad sources, pathways, and types of contaminants that occur in surface waters, groundwater, and drinking water, to serve as a basis for assessing the relative risks posed by selected contaminants in drinking water to human health. We have provided the reader with numerous references that may be used as a starting point for additional investigation. With these thoughts in mind, we now turn our attention to issues of risk assessment, with the goal of describing risk assessment methodologies and the risks that selected compounds in drinking water pose to human health.

ASSESSING RELATIVE RISK AND RISK CHARACTERIZATION

Risk assessment has traditionally been done by comparison of the exposure concentration of the stressor(s) to the responses reported for that stressor(s) in laboratory tests. These comparisons usually make use of response data from surrogate species such as laboratory rats and mice for

assessing risks in humans and fish and other wildlife for assessing risks in the environment. Risk assessments for humans usually employ a number of conservative steps to ensure that the population is protected from almost all eventualities; however, for environmental risk assessment, some effects may be tolerated, especially if the activities that produce the risks also bring benefits, such as the use of pesticides in the production of food.

Deterministic Versus Stochastic Effects in Risk Assessment

Prior to a discussion on the process of risk assessment, it may be valuable to explain the difference between deterministic and stochastic effects in the context of risk assessment. Effects for which the severity of the damaged caused is proportional to the dose and for which a threshold dose exists below which they do not occur are called *deterministic effects* (Health Canada, 1996b). Effect endpoints that measure toxicity, such as mortality or growth inhibition, are examples of deterministic endpoints. On the other hand, effects for which the probability of occurrence, rather than severity, is proportional to the dose are referred to as *stochastic effects*. It is assumed that there is no threshold below which stochastic effects do not occur. Cancer is the primary example of a stochastic effect. Deterministic effects may be categorized as either somatic or developmental, whereas stochastic effects may be categorized as somatic, hereditary, or teratogenic.

A key difference between these two categories of health effect in terms of applying risk assessment methodologies is that approaches such as hazard quotient assessments (discussed later), which are referenced to deterministic endpoints (e.g., no observed effect concentrations), may not be appropriate for assessing risks associated with stochastic effects. In this sense, the approach to risk assessment and the ensuing development of regulatory criteria differ for each category of effect. Specifically, although deterministic approaches, such as the use of hazard quotients, may be suitable for endpoints for which thresholds can be defined, probabilistic approaches may be more appropriate for stochastic endpoints (see also later discussion). For example, stochastic effects are the most important consequence of exposure to environmental levels of radiation and hence form the basis of the current radiological guidelines (Health Canada, 1996b).

Tiers in Risk Assessment

For logistical reasons, it is frequently necessary to divide complex tasks into smaller components that can be more easily managed or divided among workers. Nowhere is this more true than in risk assessment, where relationships between exposure and responses can be very complex. The use of tiers or steps in the process of risk assessment is one method used to reduce complexity and narrow the focus of risk assessments to the key issues and has been recommended frequently for use in risk assessments (NRC, 1993; U.S. EPA, 1992, 1998c; ECOFRAM, 1999). The use of tiered

approaches in risk assessment has several advantages. The initial use of conservative criteria allows substances that truly do not present a risk to be eliminated from the risk assessment process, thus allowing the focus of expertise to be shifted to more problematic substances or situations. As one progresses through the tiers, the estimates of exposure and effects become more realistic as uncertainty is reduced through the acquisition of more or better quality data. Tiers are normally designed such that the lower tiers in the risk assessment are more conservative (less likely to pass a hazardous substance or activity) while the higher tiers are more realistic, with assumptions more closely approaching reality. Because lower tiers are designed to be protective, failing to meet the criteria for these tiers does not necessarily mean that a disaster is imminent; rather, it is an indication that an assessment based on more realistic data is needed before a regulatory decision can be reached.

The First Tier of Risk Assessment—Classification Systems Classification systems only make use of the physical or biological properties of the stressor and have been used over the years by a large number of organizations for the purposes of ranking and selecting substances for further regulatory action (International Joint Commission, 1993; Ontario Ministry of the Environment and Energy, 1990; Environment Canada, 1994).

The basic principle of a scoring system is to assign a rank or priority to a list of potential stressors. This is usually accomplished by assigning a score to several of the properties of the substances being assessed, manipulating these scores in some way or another, and then using the scores to rank (and select) some of these substances for further action. Some scoring systems use single criteria (above or below a threshold) for a property, while others may use multiple criteria which are assigned numerical scores. Very few scoring systems use decision criteria for multiple values, that is, where different authors report different values. Some systems use the smallest value, regardless of source or provenance (validity of the methods used to determine the value). Some scoring systems use mathematical formulas where scores are added, multiplied, or subtracted to give a combined score. The combined score is then ranked to identify compounds of higher or lower priority. Yet other scoring systems use the scores in a taxonomic key where, after the scores have been evaluated in a series of questions, the compound is classified into a particular category. This has the advantage that scores may be combined in specific ways for different combinations of properties and that the system may be integrated into a computerized expert system.

Correctly used, scoring systems have been used to rank substances in order of priority for further assessment. This is usually in the first tier of risk assessment. Further assessment is normally required because the scoring systems commonly make use of worst-case data and they do not handle missing values, weighting, or scaling in clear or appropriate ways. The rank numbers produced from combinations of scores have no meaning in the

real world; their only use is to allow prioritization of substances for more detailed assessment.

The Use of Quotients for Assessing Hazard

The most widely used method of assessing risk is the hazard quotient method (HQ), by which the exposure concentration of a stressor, either measured or estimated, is compared to an effect concentration such as an LC50 or no-observed-effect concentration (NOEC) (Urban & Cook, 1986; Calabrese & Baldwin, 1993). These are simple ratios of single exposure and effects values and may be used to express hazard or relative safety. For example:

$$\text{Hazard} = \frac{\text{exposure concentration}}{\text{effect concentration}} \quad \text{or} \quad \text{Margin of safety} = \frac{\text{effect concentration}}{\text{exposure concentration}}$$

The calculation of hazard quotients has normally been conducted by utilizing the effect concentration of the most sensitive organism or group of organisms and comparing this to the greatest exposure concentration measured or estimated in the environmental matrix. In this case, if the hazard ratio is greater than 1, a hazard exists. Many HQ assessments incorporate some form of uncertainty factor, either explicitly as part of the calculation itself or in the criteria for acceptance of the HQ (CWQG, 1999), as illustrated in Table 18.

Because they frequently make use of worst-case data, HQs are designed to be protective of almost all possible situations that may occur. However, reduction of the probability of a type II error (false negative) through the use of very conservative application factors and assumptions can lead to the implementation of expensive measures of risk mitigation for stressors that pose little or no threat to humans or the environment (Moore & Elliott, 1996; Lee & Jones-Lee, 1995). A common error in the interpretation of HQs is the assumption that the HQ itself is exactly proportional to the "risk." As the concept of risk should always incorporate an element of probability, the HQ is biased because it assumes that the conditions of the HQ exist on every

TABLE 18. Uncertainty Factors in Assessing Risks from Substances in Humans

From	To	Uncertainty factor
Average	Sensitive human	≥10
Animal	Human	≥10
LOAEL	NOAEL	≥10
Subchronic	Chronic	≥10
Database inadequacies		≥10
Modifying factors		0

occasion and in every location. In addition, the HQ is based on a point estimate of effect (EC50 or NOEC) and does not consider the relationship between the concentration and the effect (the dose-response). Although very great HQs are obviously more important than small HQs, small differences between these ratios should not be considered significant. At the other end of the scale, HQs that are less than 1, no matter how small, are all indicative of low risks, provided that appropriate uncertainty factors have been considered. Because of this, the HQ approach is only really useful for early tiers or preliminary risk assessments and for the elimination of substances from the need for further assessment.

The Probabilistic Approach

The probability of occurrence of a particular event is, and has been, widely used in the characterization of risk from many physical and medical events in humans (the insurance industry) and for protection against failure in mechanical and civil engineering projects (time between failures, one-in-one-hundred-year floods, etc.). Probabilistic risk assessment procedures make use of distributions of values for exposures and effects to estimate the likelihood that a particular combination of exposure and response will occur. Probabilistic approaches offer an additional refinement to HQ approaches.

Distributional approaches have been used in the regulation of food additives (Munro, 1990) for the protection of human health for several years. The idea of using these distributions for setting environmental quality guidelines originated from early work in the Netherlands (van Straalen, 1989, personal communication) (Kooijman, 1987) and the United States (Stephan et al., 1985). Other authors who have expanded upon the probabilistic risk estimation process include Van Straalen and Denneman (1989), Wagner and Løkke (1991), Aldenberg and Slob (1991, 1993), and Okkerman et al. (1991, 1993). Comparing distributions of species sensitivity directly to distributions of exposure concentrations (Cardwell et al., 1993) was recommended for pesticide risk assessment by the Aquatic Risk Assessment Dialogue Group (SETAC, 1994), demonstrated for metals and other substances (Parkhurst et al., 1996), and incorporated in a computer program (Cadmus Group, Inc., 1996).

Probabilistic risk assessment has been recommended for regulatory risk assessment of pesticides (ECOFRAM, 1999). The general concepts as they apply to ecological and human health risk assessment have been reviewed and extensively discussed (Suter et al., 1993; Forbes & Forbes, 1993, 1994; Balk et al., 1995; Solomon, 1996; Richardson, 1996; Anderson & Yuhas, 1996; Burmaster, 1996; Power & McCarty, 1996; Bier, 1999; Roberts, 1999; Postuma et al., 2001).

The major advantage of probabilistic risk assessment is that it uses all relevant data and allows quantitative estimation of risks. In addition, the data may be revisited, the decision criteria become more robust with addi-

tional data, and the method is transparent and consistent—producing the same results with similar data sets. The method does have some disadvantages. More data are usually needed. For new substances not yet used in the environment, models must be used to estimate exposures and have not been widely validated for these uses. Probabilistic approaches are also less easily applied where exposure is from multiple sources.

It is important to recognize that, as for risk assessment in general, all probabilistic risk assessment methods are essentially similar; however, they may be used for different purposes. As for risk assessments, some uses include the setting of environmental guidelines and criteria, while in others, probabilistic risk assessment is used to assess risks in situations where exposures are known and their significance is being assessed.

For the setting of criteria, an a priori decision must be made as to what level of protection is acceptable (Balk et al., 1995; Forbes & Forbes, 1993). For example, the U.S. EPA method of setting environmental water quality criteria (Stephan et al., 1985) uses a 95% protection level (with an extrapolation factor of 2) but applies this to acute, chronic, and tissue residues. Similar techniques have been recommended for water quality determination in the North American Great Lakes Initiative (U.S. EPA, 1995).

The other use of probabilistic risk assessment is in assessing risks from situations that already exist, such as where a substance has been released or is about to be released into the environment and a risk assessment is needed to apply to a risk-benefit regulatory decision. In this case, no predefined percentage of species to protect is needed as this will vary from one situation to another, depending on other lines of evidence, such as the types of organism most likely to be affected or the toxicological properties of the substance. Unlike the process of criteria setting, it may be very appropriate to exclude certain types of organisms from the assessment or, based on biological knowledge, to tolerate more frequent exceedences of species response values for some groups of organisms than others. Because the potential adverse effects of measured or estimated exposures are being assessed in this method, combination or segregation of exposure data sets adds significant utility to the risk assessment process. It allows more realistic toxicity and exposure information to be applied to ranking of exposure scenarios for the purposes of mitigation or regulatory decision making. Because risk assessment considers both likelihood of exposure concentrations and likelihood of effects, risk can be expressed as a joint probability, for example, that n% of organisms will be affected x% of the time or in y% of the locations, depending on the type of exposure data collected. These risks can be expressed as the probability of exceeding a fixed criterion of response (Solomon et al., 1996) or as an exceedence profile (EP, Figure 13), which is relatively simple and offers a useful tool for communication of risks (ECOFRAM, 1999).

Application of distributional analysis to concentrations of substances in the environment must be done with due consideration for the fact that
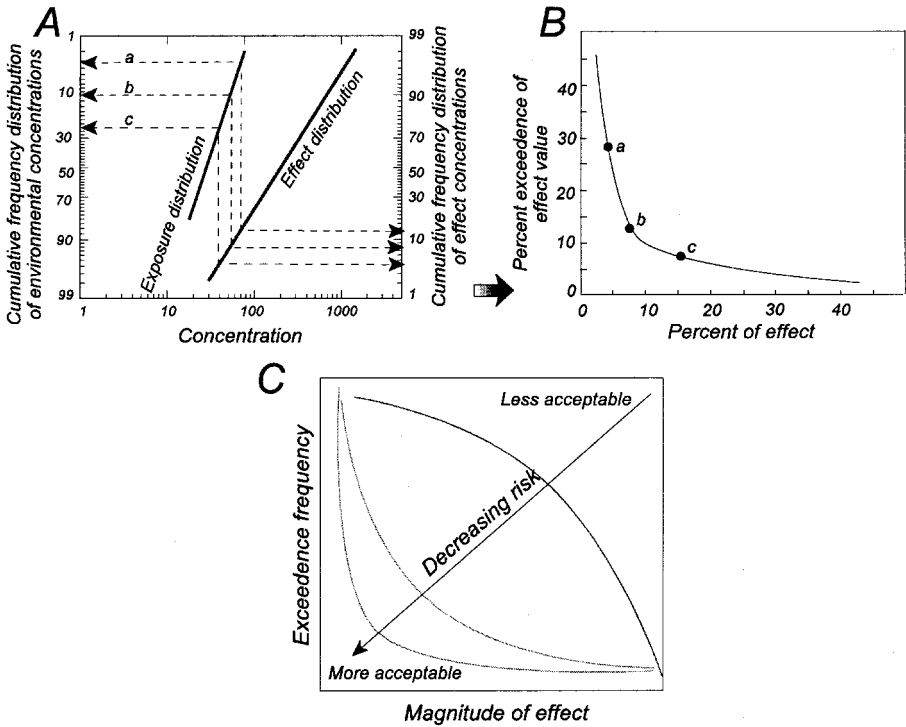
FIGURE 13. Presentation of exceedence probabilities (A) as a continuum of likelihoods in (B) an exceedence profile (EP) and (C) the use of these curves in decision making. Adapted from ECOFRAM (1999).

these data are usually censored by the limits of analytical detection (Figure 14). In practice, all exposure concentration data below the limit of detection (LOD) or limit of quantization (LOQ) are assigned a dummy value of zero. These data are used in the calculation of the total number of samples (*n*) but are not used to estimate centiles directly. The assumption used here is that the values below the LOD lie on the same distribution as the values above the LOD. With recent advances in analytical chemistry, values below the LOD are usually of little toxicological significance; however, the regression equation for the distribution may be used to estimate the concentration of data points below the LOD for the purposes of developing an exceedence profile. The substitution of a value of half the LOD for all the data points below the LOD—a practice used for estimating mean concentration of a data set—results in a biased data set that will be difficult to fit to any model.

Probabilistic risk assessment has been applied to a number of substances as part of higher tiered and more realistic assessment of their ecological risks. While probabilistic risk assessment provided tools to more thoroughly address these assessments and to handle large data sets, other

lines of evidence were also important in reaching the final conclusions. These risk assessments were intensive of a broad range of expertise and resources and were most easily carried out where good data sets for toxicity and exposure values were available. Probabilistic risk assessment is a significant improvement on the traditional HQ approach but it will likely continue to evolve as the entire science moves forward and as exceptions test the interpretation of the methods. As has been pointed out, one of the major hurdles that probabilistic risk assessment will face is its acceptance by the public and regulators (Solomon, 1999; Roberts, 1999). Risk managers will likely continue to demand, or at least interpret, probabilistic risk estimates as point estimates of high certainty (Moore & Elliott, 1996; Chapman, 1995; Richardson, 1996). Decision makers want to know whether it is safe or not and prefer being told what will happen, not what might happen (Morgan, 1998). Similarly, the public demands absolute safety but has less understanding of probability and also greatly misperceives risks to themselves, fellow humans, and the environment (Slovic, 1987).

Risk Perception

Once risk has been characterized, it will almost always be necessary to develop a risk communication strategy. Effective risk communication is not easy to achieve, especially if the result of the assessment is contrary to conventional wisdom or to the interests of certain stakeholder groups. Information about risks often involves using terms that are not part of the public
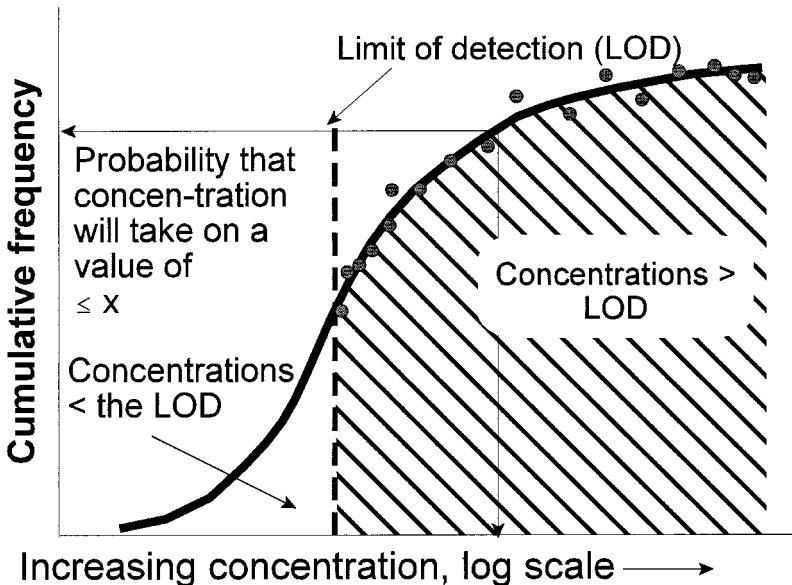

FIGURE 14. Illustration of censoring of a distribution of measured concentration data by the level of detection of the analytical method.

vocabulary and hence may be difficult for the public to understand (NOELs, MATCs, uncertainty, etc.). Understanding risk means dealing with a large amount of information. An audience can only assimilate a certain amount of the data given, and this is often greatly oversimplified in the process of assimilation.

Perceptions of human health risk are based on our social structures and morals, and it is necessary to take these into account when communicating risks to the public. A person's perception of risk will also be determined by that person's implicit "worldview" and knowledge or assumptions of who (or what) receives the benefits and who (or what) pays the costs for the risk management decisions (Lackey, 1995). While the scientific definition of risk is usually taken as the probability that a particular event will occur (i.e., an automobile accident), the public perception of risk is a summation of ob-servability (knowledge) and controllability (Morgan, 1993). Thus, the public will perceive a different risk for a voluntary versus a coerced activity or one controlled by the individual versus one controlled by society, government or another group. The perception of individual and societal risks also varies with expertise and knowledge (Slovic, 1980).

As an example of risk perception, there is a determinant philosophy among the public that cancer rates are rising and that these "increases" are directly linked to exposure to chemicals in drinking water or food. In some cases this perception is correct and statistics will bear this out. In many cases, however, medical statistics on cancer are incongruent with this per-ception of increasing cancer rates. For example, of the leading types of cancer in men and women in Canada, many have either declined or re-mained comparable relative to their rates of 20 years or so ago (Figure 15). In essence, the perception of the public represents uncertainty that can be ascribed to some of the reasons already discussed. Uncertainty is dis-cussed in the next section.

Uncertainty

One of the most elusive concepts in risk assessment to convey to the public is the relative nature of risk. Uncertainty analysis is an important step in the risk assessment process as it both identifies and, to the extent possible, quantifies the uncertainty in entire process of problem formula-tion, analysis, and risk characterization (Warren-Hicks & Moore, 1998). In addition, an assessment of uncertainty may allow identification of ways in which uncertainty can be reduced. Uncertainties in risk assessment have three sources: ignorance or imperfect knowledge, systematic errors, and nonsystematic errors.

The first is ignorance or imperfect knowledge of things that should be known—for example, not knowing that a pathogen or potentially toxic sub-stance is present in a water source. Uncertainty from lack of knowledge can never be addressed to the complete satisfaction of everyone; however, the more data that are available, the less likely it is that errors from lack of
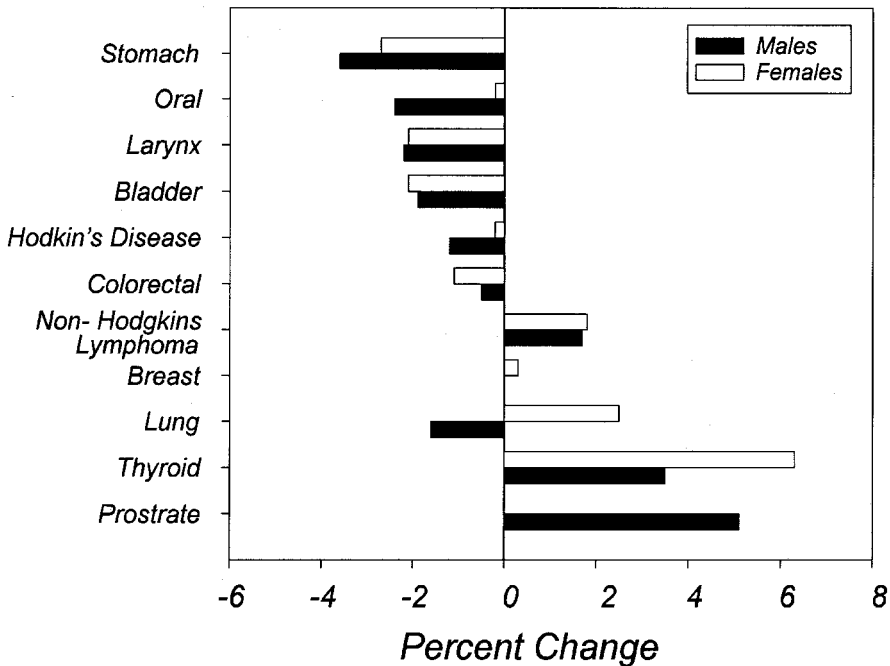
FIGURE 15. Annual percent change in age-standardized incidence rates for selected cancer sites (1988–1995). Adapted from Health Canada (2000).

knowledge will occur. Uncertainty resulting from co-occurring stressors and possible interactions in mixtures is an area of current concern. Uncertainty from insufficient data is considered in the probabilistic process as the estimated exceedences are responsive to the number of data points.

Systematic errors in the risk assessment process are those that may occur through computational mistakes (incorrect position of the decimal, data entry errors) or through incorrect instrumental calibration. Provided that these errors can be identified, they can be addressed through better quality control and quality assurance or through a correction factor. Systematic errors include errors in sampling where nonrepresentative samples are taken, errors in analysis such as a lack of correction for recovery of the analytical method, errors in analytical techniques where systematic but different errors occur at different concentrations, and incomplete data collections that do not fully represent the entire year and will result in samples biased toward seasonal drivers that are present during that particular time of the year.

Nonsystematic errors are random or stochastic errors that result from the random nature of the system being assessed and, unlike systematic errors, are just as likely to give a value that is too low as one that is too high. These types of errors can be described and quantified but cannot be avoided or corrected for. For example, in the analysis of small concentra-

tions of substances, recoveries are more variable and quantification techniques are subjected to relatively greater interference from matrix effects. Similarly, variability in the results of toxicity tests for a given species tested in different experiments or by different laboratories is a potential source of random (or systematic) errors. This type of error can be addressed by taking the smallest value in the set (worst-case, conservative approach) or by using the geometric mean of all the data points for the species.

Exposure Values and Water Quality Guidelines Used in HQ Assessment

To provide insight into the relative risks of toxic contaminants found in drinking water to human health, we conducted an assessment of selected compounds using the HQ approach. Criteria for the selection of compounds were (1) whether they pose a known or potential concern to human health (see Table A1), and/or (2) availability of measurements in drinking water. The compounds selected for the HQ assessment are identified in Table 19. The respective Ontario, Canadian, and World Health Organization Water Quality Guideline values for these and other compounds are listed in Table A2.

Assessments were conducted on both treated water and domestic wells. Hazard assessments on treated water were based on information derived from the Ontario Drinking Water Surveillance Program (DWSP). These are available online at http://www.ene.gov.on.ca/envision/dwsp9899/dwsp.htm. The DWSP was initiated in 1986 to provide reliable and current information about the quality of municipal drinking water. Participation by municipal water treatment plants (MWTPs) in this program is voluntary, although inclusion in the program is also based on the population served, geographic location, and risk of contamination. In theory, each MWTP monitors a wide range of water quality parameters and toxic compounds, although this is not consistent between plants. Metals, chloroaromatic compounds, chlorophenols, n-nitrosodimethylamine (NMDA), disinfection by-products, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, volatile organics, pesticides, radionuclides, and taste- and odor-impairing compounds are monitored with varying frequency. In practice, however, only metals, nitrates, disinfection by-products, atrazine, and a few individual organic compounds are routinely monitored; it is from these groups of substances that we selected individual contaminants for the current assessment (Table 19). Measurements at the MWTPs are typically made at three stages of water treatment prior to human consumption: (1) raw (influent) water, drawn from surface or groundwater sources, (2) treated laboratory water, and (3) distribution water, which is measured at various locations within the municipality.

For assessments on municipal water treatment, concentrations of the compounds listed in Table 19 were taken from 47 randomly selected MWTPs in 4 regions of Ontario, 12 from each of the 3 southernmost regions and 11 from the eastern region (Figure 16). Of the 47 plants, 24 (6 per region) were selected that extracted water from surface-water sources

TABLE 19. Concentration Ranges for Contaminants in Various Stages of Water Treatment

Class	Compound	Concentration ranges		
		Influent	Treated	Distribution
Pesticides (µg/L)	Atrazine (ATR)	0.05–0.95 (81/36/30)[a]	0.05–0.56 (119/58/54)	—[b]
	2,4-D	0.24 (81/2/1)	0.02–0.16 (119/3/2)	—
	Dicamba (DIC)	0.06-0.51 (81/3/2)	0.06–0.20 (119/4/3)	
	Dinoseb (DIN)	— (81/0/0)	0.023 (119/1/1)	—
	Diquat (DIQ)	— (81/0/0)	0.80 (119/1/1)	
	Paraquat (PAR)	0.20–0.80 (81/3/2)	0.20 (119/3/1)	—
	Prometryne (PRO)	0.08 (81/2/1)	0.05 (119/2/1)	—
	Simazine (SIM)	0.06–0.07 (81/3/2)	— (119/2/0)	—
Inorganic (µg/L)	Nitrates	0.01–9.4 (24/23/23)	0.006–5.7 (23/23/23)	0.01–5.7 (47/29/29)
Metals (µg/L)	Arsenic (AS)	0–2.37 (24/23/23)	0–7.78 (23/23/23)	0–7.2 (47/45/45)
	Cadmium (CD)	0–0.13 (24/23/23)	0–43 (23/23/23)	0–0.21 (47/45/45)
	Chromium (CR)	0–17.8 (24/23/23)	0–31.5 (23/23/23)	0–33.3 (47/45/45)
	Lead (PB)	0–5.99 (24/23/23)	0–8.45 (23/23/23)	0–22.3 (47/44/44)
DBPs (µg/L)	Trihalomethanes (TTHM)	0.5–50.5 (24/23/11)	1.0–52 (23/21/4)	0.5–238 (47/43/43)
	Dichloroacetic acid (DCA)	0.1–13.7 (24/23/14)	0.1–14.8 (23/23/11)	0.2–36.9 (47/45/45)
	Trichloroacetic acid (TCA)	0.5–9.3 (24/22/19)	0.05–36.7 (23/22/13)	0.1–138 (47/43/42)
	Bromodichloromethane (BDM)	0.1–12.6 (24/23/8)	0–6.2 (23/22/4)	0.4–24.4 (47/44/44)
	Bromoform (BRO)	0.5 (24/18/1)	0–7.0 (23/15/2)	0.2–8.5 (47/32/24)
	Chloroform (CHL)	0.1–38.6 (24/23/17)	0–44.6 (23/23/8)	0.2–122 (47/45/44)

TABLE 19. Concentration Ranges for Contaminants in Various Stages of Water Treatment (*Continued*)

Class	Compound	Concentration ranges		
		Influent	Treated	Distribution
Organics (µg/L)	Carbon tetrachloride (CT)	— (81/14/0)	—	0.2–1.6 (119/18/6)
	1,4-Dichlorobenzene (DCB)	0.02–0.15 (81/21/9)	—	0.05–0.5 (119/24/14)
	Nitrosodimethylamine (NMDA)	0.001–0.005 (81/53/34)	—	0.001–0.005 (119/4/4)
	Pentachlorphenol (PCP)	0.01–0.016 (81/2/2)	—	— (119/0/0)
	Tetrachlorethylene (TCE)	0.05–0.15 (81/16/7)	—	0.05–4.75 (119/23/9)

[a]In order of appearance, numbers in parentheses represent number of municipal water treatment plants searched, number of municipal water treatment plants that tested for presence of compound, and number of municipal water treatment plants that detected compound on at least one occasion.

[b]Not measured.

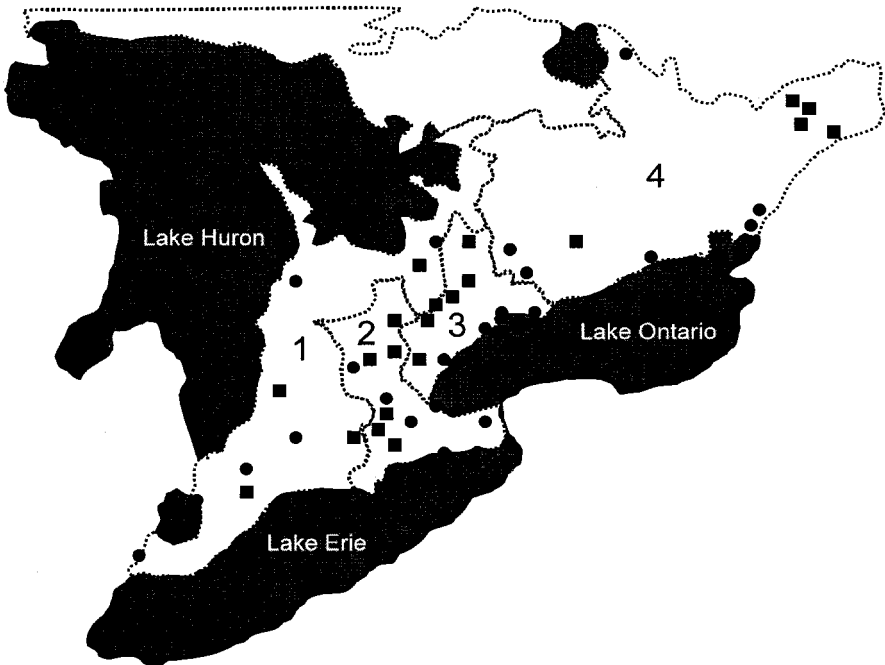**FIGURE 16.** Location of the 47 randomly selected municipal water treatment stations in 4 regions of Ontario used in the hazard quotient (HQ) assessment for metals, pesticides, disinfection by-products, and nitrates. Region 1, southwestern; Region 2, west central; Region 3, central; Region 4, eastern. Circles (●) indicate water drawn from surface water; square (■) indicates water drawn from groundwater.

(streams, lakes), and 23 from groundwater sources. At each plant, we re-
corded the minimum and maximum value measured for each compound in
the influent (surface or ground) and distribution stages of water treatment
from the 24 surface-water stations and the 23 groundwater stations. How-
ever, because few MWTPs regularly monitor levels of pesticides and conta-
minants, we searched all water treatment plants in southern Ontario (119
plants in total) for pesticide concentration data. Hazard quotients were
determined for each of the metals, disinfection by-products, nitrates, pesti-
cides, and organics selected from the drinking water database. In all cases
except pesticides, the HQ estimates were based on maximum concentra-
tions in the distribution water (48 stations), as we felt that these concentra-
tions would be most representative of those to which humans would be
exposed via ingestion of water. In the case of pesticides, which were not
routinely measured in distribution waters in the DWSP, we used values
from the treatment stage.

For untreated well water, we assessed only pesticides and nitrate con-
centrations. For these compounds, we used the information from Ontario
Ministry of the Environment (1987a), Frank et al. (1990), Rudolph and Goss
(1993), and Briggins and Moerman (1995). As with treated water assess-
ments, we used the maximum value in the HQ assessment; however, we
were careful to differentiate between normal contamination levels (e.g,,
those that might occur as a result of groundwater contamination or normal
runoff events) and those due to spills, back-siphoning, or other unusual
events that could bias the estimates. Thus, HQ values based on mean and
median exposures were also included where this information was provided.

For both treated and untreated water, the HQ assessment was deter-
mined as the ratio of the maximum measured concentration in either the
treated or well water and the Provincial Water Quality Criterion for that
compound (Canadian guidelines were used when provincial guidelines
were not available):

$$\text{Hazard} = \frac{\text{maximum exposure concentration}}{\text{water quality guideline concentration}}$$

This approach is highly conservative for two reasons. First, some water
quality criteria typically incorporate uncertainty factors to enhance protec-
tion. Second, by using the maximum concentration detected, we are essen-
tially evaluating a worst-case scenario. That is, the HQ that we calculate in
most cases is likely to much greater than would be predicted had we used
mean or median values for the data. Overall, this approach allows us to
better detect "meaningful violations" and hence to gain a better sense of
potential risk to human health.

Where we found HQ values >1 (an indication of potential risk), these
were further analyzed using a probabilistic risk assessment. For this
analysis, we constructed cumulative frequency distributions of data points
corresponding to all measured concentrations of each substance in distri-

bution water from the DWSP database for the 47 water treatment plants. The number of measurements, and hence data points, for each compound for each water treatment plant varied widely in this database, ranging from one to several; all available data points were used in the assessment. The data was plotted separately according to whether it originated from surface water (24 stations) or groundwater (23 stations).
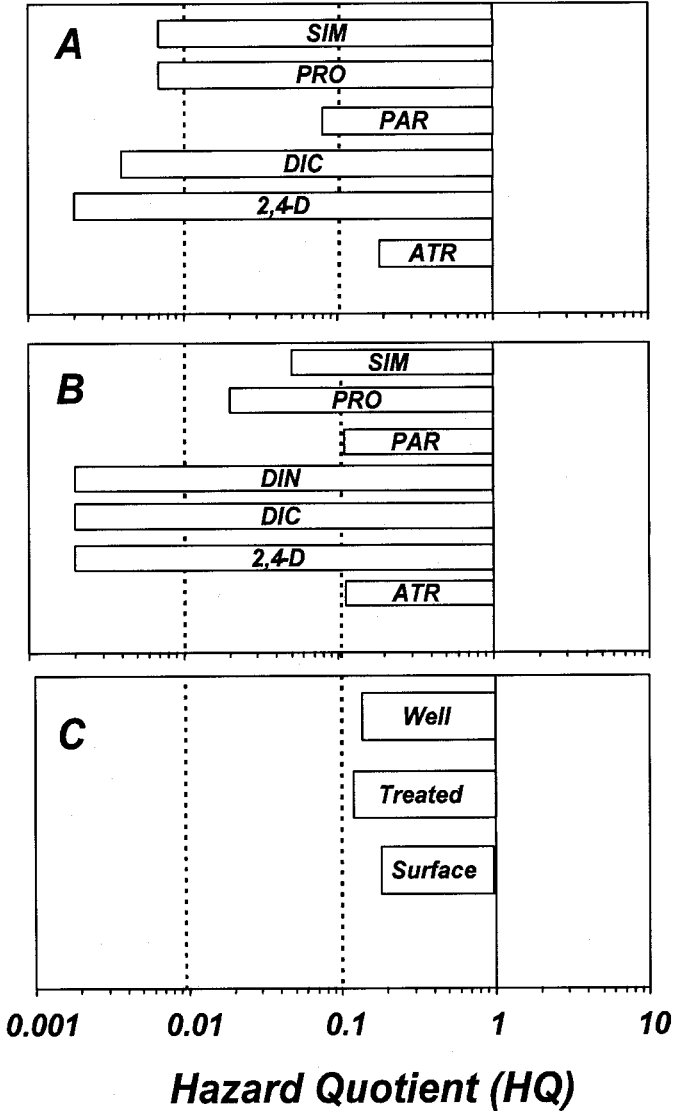

FIGURE 17. Hazard quotient values for selected pesticides in (A) influent and (B) treated water from the Ontario Drinking Water Surveillance Program, and (C) comparison of municipal water to well water for atrazine. See Table 19 for pesticide acronyms.
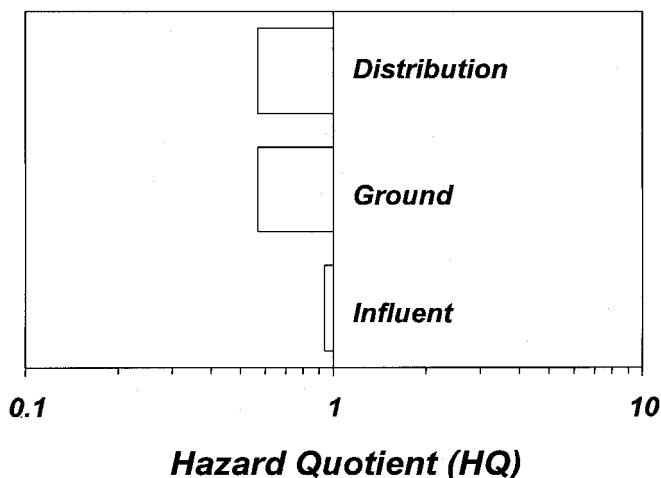
FIGURE 18. Hazard quotient values for nitrates in influent (surface and ground) and distribution water in municipal water treatment plants participating in the Ontario Drinking Water Surveillance Program.

Where possible, we have provided an indication of the frequency with which these compounds are detected in drinking water or in surface waters, if the former was not available. For some compounds, frequency-of-detection data have been presented in the preceding sections.

Results of HQ Assessment

The ranges of concentrations for each compound at each stage of the water treatment process from the DWSP are provided in Table 19. Our assessment of these data in drinking water showed that the HQ values for most contaminants were well below 1 (Figures 17–20). These data suggest that there is little risk to humans from exposure to these substances through ingestion of water. In fact, the HQs that we report here are based on highest exposure levels (maximum concentrations), so it likely that the HQs based on the average or median concentrations, and the implied level of risk, would be even lower as illustrated by the pesticide HQ esti-mates from well water (Table 20).

Pesticides

All of the pesticides evaluated from treated municipal water had HQ values <1 (Figure 17). HQ values ranged from 0.002–0.190 for surface water samples (Figure 17A) and 0.002–0.112 for groundwater samples (Figure 17B). For both sources, atrazine generally yielded the highest HQ values, with surface waters (0.190) being slightly higher than groundwater (0.112). It must be kept in mind that the data used to estimate the HQs for pesticides, other than atrazine, were based on very few data points because pesticides are not routinely measured as part of the DWSP. The
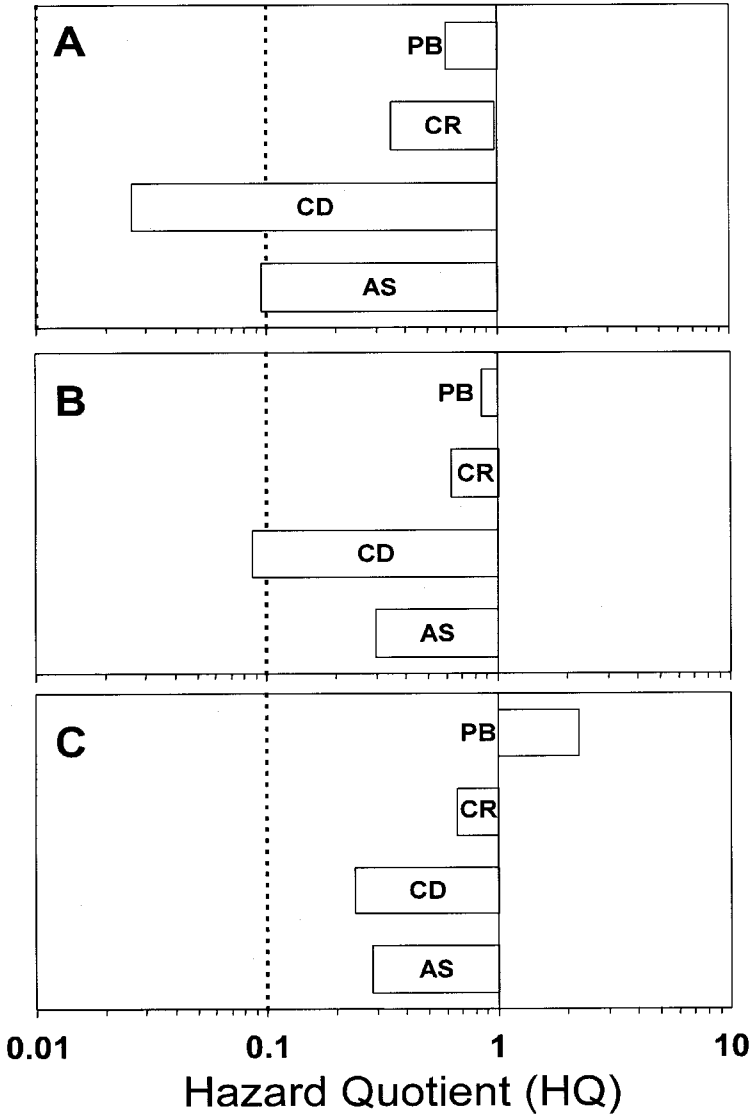
FIGURE 19. Hazard quotient values for selected metals in (A) influent, (B) treated, and (C) distribution water from the Ontario Drinking Water Surveillance Program.

HQ value for the mean concentration of atrazine measured in well water (from study of Rudolph & Goss, 1993) was 0.138 (Figure 17C). The HQ value for the maximum concentration recorded in that study (18 µg/L) was 3.6. A number of other pesticides detected in that survey had HQ values >1 (Table 20); however, these occurred very infrequently and, based on median values, the majority yielded HQ values well below 1. Only 6 out of the 1292 wells (0.46%) sampled in that survey contained pesticides above the provincial MAC (Goss et al., 1998).

Nitrates

HQ estimates for nitrates in water sampled from each stage of the treatment process in municipal water treatment plants were <1 (Figure 18); however, the HQ value for the highest concentration in surface water was just below 1 (0.94). In contrast, based on several studies, HQ values >1 were frequently determined for the highest nitrate concentrations in rural water wells (Table 21). This result is consistent with the relatively high number
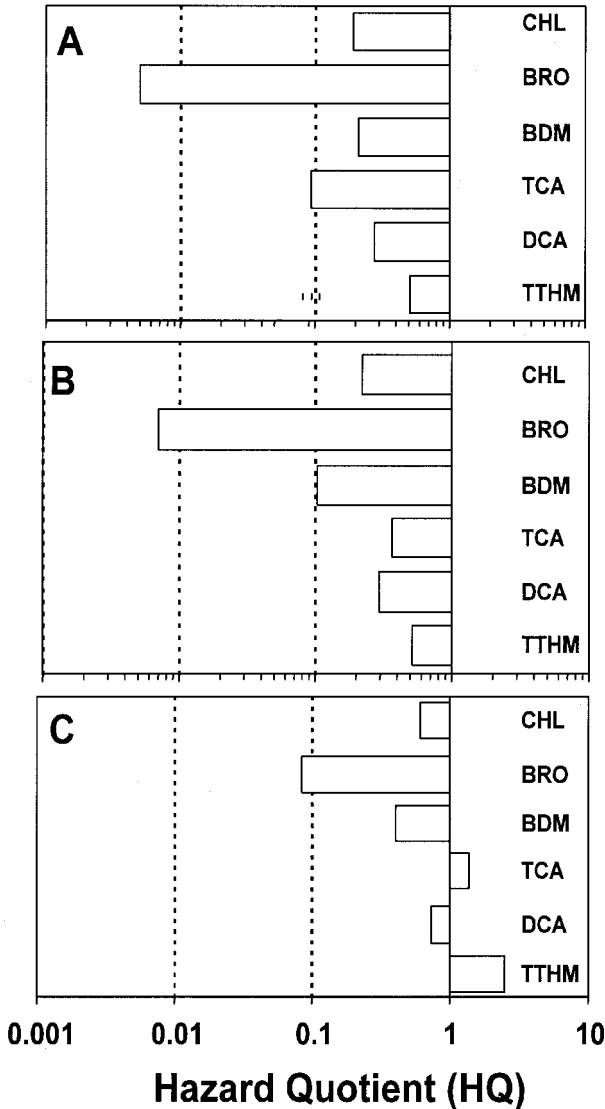

FIGURE 20. Hazard quotient values for selected disinfection by-products in (A) influent, (B) ground, and (C) distribution water from the Ontario Drinking Water Surveillance Program. See Table 19 for acronyms.

TABLE 20. Summary of Pesticide Findings from a 1991/1992 Survey of Ontario Rural Wells (Rudolph & Goss, 1993)

Pesticide	Frequency of detection (number of wells)	Frequency of detection (%)	Concentrations (µg/L)		
			Maximum	Mean	Median
Alachlor	1	0.1	15.0 (0.75)[a]	15.0 (0.75)	NA
Atrazine	126	10.5	18.9 (3.6)	0.69 (0.14)	0.30 (0.06)
Diethyl atrazine	76	6.3	8.2 (2.3)	0.98 (0.20)	0.72 (0.14)
Cyanazine	3	0.3	3.6 (0.36)	1.7 (0.17)	1.2 (0.12)
Metribuzin	9	0.3	0.69 (0.009)	0.61 (0.008)	0.63 (0.008)
Metolachlor	3	0.8	93 (1.9)	17.3 (0.35)	1.7 (0.60)

Note. Numbers in parentheses represent hazard quotient (HQ) estimates (derived from Canadian Water Quality Guidelines unless indicated otherwise).
[a]Based on WHO (1996) drinking water guideline.

of exceedences of the nitrate water quality guideline reported for well water in rural areas in Ontario and elsewhere in Canada (Frank et al., 1991; Briggins & Moerman, 1995; Goss et al., 1998).

Metals

Except for lead in distribution water, for which we estimated an HQ value of 2.23, the HQ values for chromium, cadmium, and arsenic were <1 (Figure 19) in all water treatment stages. Elevated lead levels in distribution water is not surprising due to the occurrence of lead piping in some older architecture. The lead data are analyzed in greater detail below using a probabilistic approach.

Organics

The HQ estimates for all of the organic compounds for which data were collected from the DWSP database were <1, ranging from 0.005–0.57 in influent (surface) water to 0.1–0.56 in distribution water (Table 22).

TABLE 21. Summary of Nitrate Concentrations in Well Water from Various Studies and Estimated Hazard Quotients (in Parentheses)

Study	Concentrations (µg/L)		
	Maximum	Mean	Median
Briggins and Moerman (1995)	46.1 (4.61)	4.61 (0.46)	2.68 (0.27)
Frank et al. (1990)–1986	55 (5.5)	NA	NA
Frank et al. (1990)–1987	43 (4.3)	NA	NA
Rudolph and Goss (1993)–summer	87 (8.7)	NA	NA
Rudolph and Goss (1993)–winter	77 (7.7)	NA	NA
Ontario Ministry of Environment (1985)	60 (6.0)	NA	NA

Note. Canadian Water Quality Guideline value for nitrate is 10 mg/L.

TABLE 22. Hazard Quotient Estimates for Selected Organic Substances in Drinking Water Derived from the Ontario Drinking Water Surveillance Program

Compound	Influent (surface) water	Distribution water
Benzene	0.4	0.17
Carbontetrachloride	—	0.32
1,4-Dichlorobenzene	0.11	0.1
Nitrosodimethylamine (NDMA)	0.57	0.56
Pentachlorophenol	0	—
Tetrachloroethylene	0.005	0.32

Disinfection By-Products

The HQ values for the maximum concentration of total trihalomethanes were 0.505, 0.520, and 2.38 for surface water, groundwater, and distribution water, respectively (Figure 20). Except for trichloracetic acid in distribution water (HQ = 1.38), the HQ estimates for each of the individual components of THMs (di- and trichloroacetic acid, bromodichloromethane, bromoform, and chloroform) did not exceed 1. The HQ values for these compounds were generally higher in distribution water; this is not surprising because DBPs are formed, in part, as a result of interactions with naturally occurring organic precursors in surface and groundwater during and after the treatment process.

Probabilistic Assessment

Those compounds for which the estimated HQ was >1 in the assessment of treated municipal water (trichloroacetic acid, total trihalomethanes, and lead) were subsequently analyzed using a probabilistic assessment based on cumulative frequency distributions to estimate the likelihood of the measured values exceeding the respective MACs. The regression coefficients for the cumulative frequency distributions (Table 23) were used to estimate the likelihood of the measured values exceeding the MAC (Table

TABLE 23. Regression Coefficients and Intercepts for Various Contaminants in Drinking Water

Data source	$y = ax + b$				Regression intercepts (µg/L) 90%	Probability of exceeding the MAC
	a	b	r^2	MAC		
TCA surface water	1.72	3.74	0.95	100	30	1.44
TCA groundwater	1.25	5.04	0.99	100	10	0.54
THM surface water	2.97	0.77	0.98	100	72	4.36
THM groundwater	1.77	3.77	0.99	100	26	1.05
Lead surface water	1.14	5.83	0.92	10	2	2.39
Lead groundwater	1.62	5.96	0.96	10	2	0.48

Note. Values for the regression are based on a linear regression analysis on the log- and probability-transformed values from the plotted data.

A2). For all three compounds, >95% of the measured values fell below the MAC in surface water, and 100% of values fell below the MAC in groundwater (Figures 21–23). While these exceedences are relatively low, they must be considered in the context of the sampling base from which they were drawn. Analyses for these substances are conducted relatively infrequently (every 3–6 mo in most locations), so these samples may not represent the entire period between samples. In the absence of analyses for the intermediate times, the distribution analyses suggest that exceedences could be of relatively long duration. As might be expected for TCA and total THMs, exceedences of the MAC in the distribution water drawn from surface water were greater than those from groundwater (no exceedences). Exceedences of the MAC for lead were also greater in surface water than in groundwater. While this may be the result of contamination from lead pipes, it is more likely from contaminants other sources such as in runoff from contaminated soil or from atmospheric deposition.

SUMMARY AND CONCLUSIONS

Addressing issues of drinking water quality and management requires a thorough understanding and evaluation of the types and environmental

FIGURE 21. Probability distributions for total trihalomethane (THMs) concentrations in surface water and groundwater. MAC, provincial maximum allowable concentration.
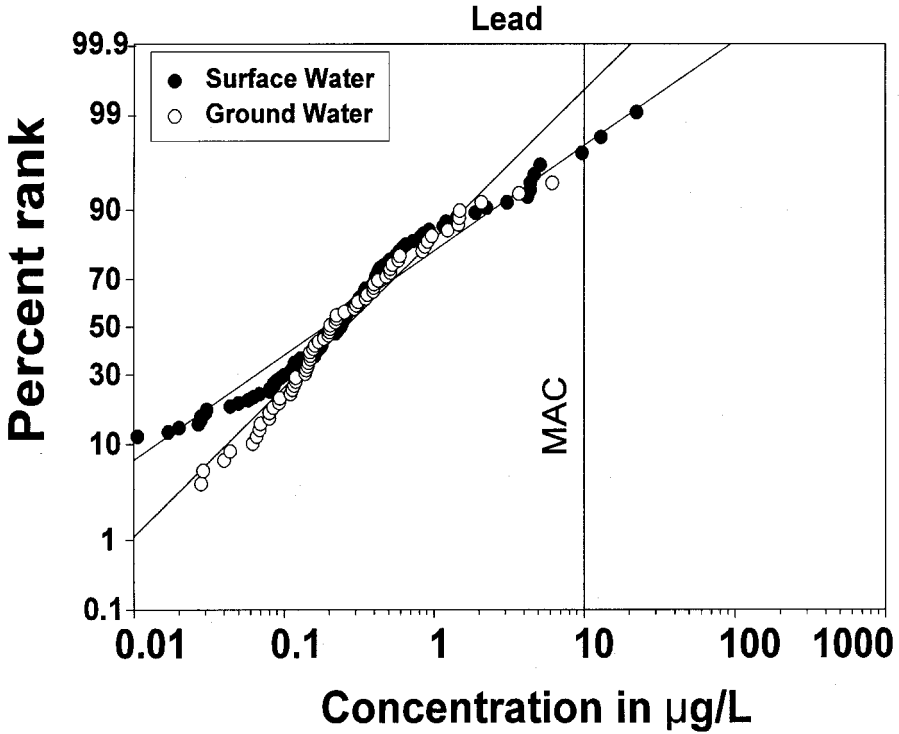
FIGURE 22. Probability distributions for lead (Pb) concentrations in surface water and groundwater. MAC, provincial maximum allowable concentration.

behaviour of contaminants that lead to impairment of this critical resource. A key aspect of this evaluation is the need for an enhanced understanding of the sources and nature of contaminant loadings to, and the transport pathways within, the primary water systems that serve as sources of drinking water for humans and a place of residence for aquatic organisms. While the tragic events at Walkerton were precipitated by pathogenic contamination of the drinking water supply, it is important to realize that water quality issues in Ontario and other jurisdictions extend well beyond issues of pathogenic contamination and its associated risks to human health. Indeed, significant risks to human health may result from exposure to nonpathogenic, toxic contaminants, many of which are globally ubiquitous in waters from which drinking water is derived. In this context, we undertook the current review to address two important objectives: (1) to identify the major sources of contaminants from anthropogenic activities to aquatic surface waters and groundwater and the pathways through which they move, and (2) to assess the health significance of selected contaminants in drinking water and identify some of the inherent uncertainties in terms of exposures and potential effects.

The loading of contaminants to surface waters, groundwater, sediments, and ultimately drinking water occurs as either point-source or non-point-
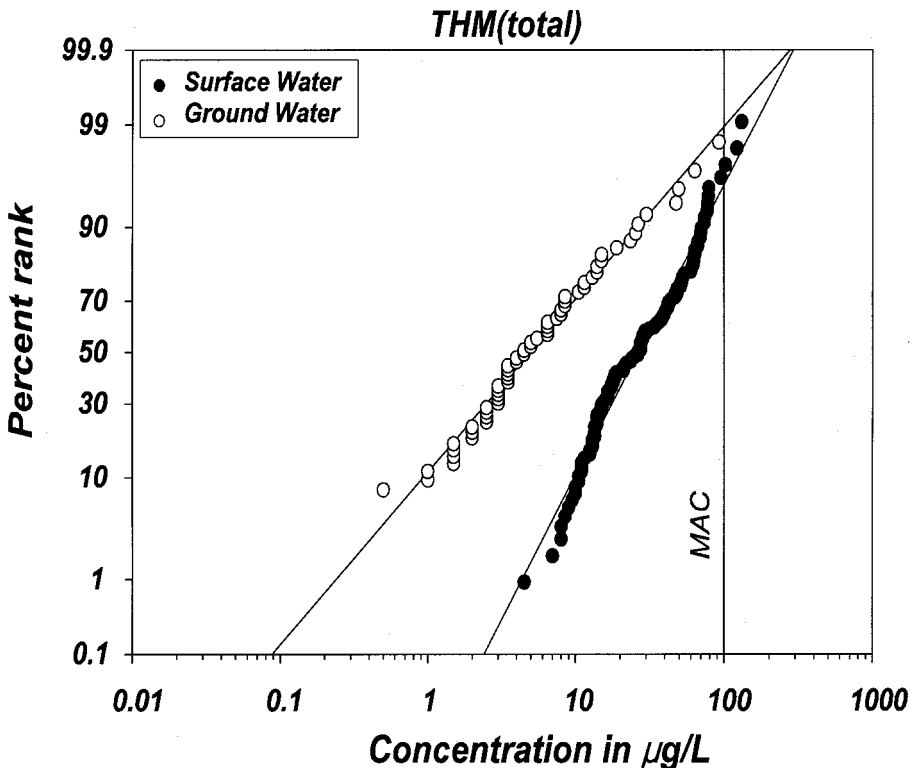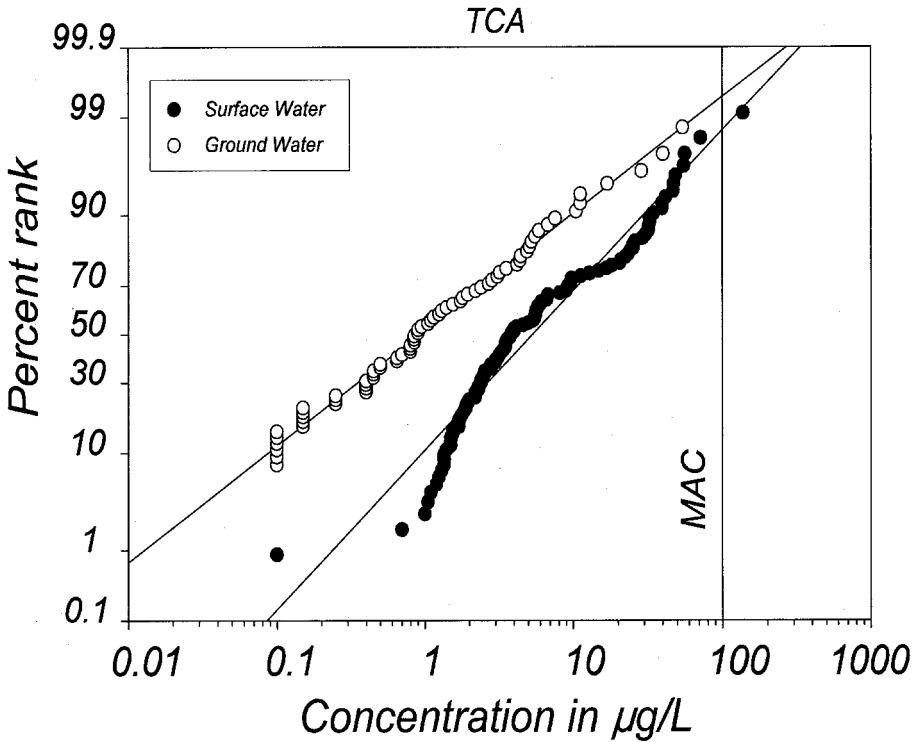
FIGURE 23. Probability distributions for trichloracetic acid (TCA) concentrations in surface water and groundwater. MAC, provincial maximum allowable concentration.

source pollution. Point-source pollution originates from discrete sources whose inputs into aquatic systems can often be defined in a spatially explicit manner. Examples of point-source pollution include industrial effluents from pulp and paper mills and steel refineries (hazardous waste materials), municipal sewage treatment plants and combined sewage–storm-water overflows (pathogens, nutrients, heavy metals), resource extraction (mining), and land disposal sites (landfill sites, industrial impoundments). Non-point-source pollution, in contrast, originates from poorly defined, diffuse sources that typically occur over broad geographical scales. Examples of non-point-source pollution include agricultural runoff (pesticides, pathogens, and fertilizers), storm-water and urban runoff, and atmospheric deposition (wet and dry throughput of persistent organic pollutants).

In most cases, pollutant loading to surface waters, either as direct deposition of effluents or via atmospheric deposition, represents the primary route for contaminants to become incorporated into drinking water. Since the drinking-water supply of most Canadians is derived from surface-water sources, this likely represents the most significant route for exposure to anthropogenic contaminants and the associated potential risks to human

health. Contamination of surface waters and associated sediments is certainly the most significant route by which aquatic communities are exposed to anthropogenic contaminants and associated risks that threaten the ecological integrity of aquatic systems. Despite this fact, apart from some focused regional studies (e.g., Struger et al., 2000), there has been surprisingly little effort to undertake comprehensive, national monitoring programs of contaminants in Canadian surface waters. Such programs can be very expensive to undertake; however, as demonstrated by recent national monitoring programs in the United States (e.g., by the U.S. Geological Survey and U.S. Environmental Protection Agency), they can also provide important spatial and temporal information about surface-water contamination that can feed into the risk assessment process, and can aid managers in regulatory initiatives on both a regional and national level.

Pollutant loading to groundwater occurs through direct exchange with contaminated surface water or leaching of contaminants through soil. Although fewer Canadians draw their drinking water from groundwater sources, this route is the most significant source for exposure of humans to contaminants in drinking water in rural communities. Risks to human health may be much higher in rural areas because drinking water, particularly that associated with privately owned wells, is often not treated. In this context, although several comprehensive studies have been conducted to evaluate levels and distributions of relevant contaminants in rural well water, no structured monitoring program exists.

Historical approaches regarding the governance and management of groundwater/surface-water research has been to treat surface water and groundwater as distinctly separate water systems (Naiman et al., 1995; Duncan, 1999). However, that the intimate chemical and biological connections between groundwater and surface waters form an integral component of the hydrological cycle has gained wide acceptance by scientists and greater appreciation by environmental managers. Understanding the nature of groundwater–surface-water relationships is a crucial step to understanding the pathways through which contaminants may be exchanged between these two systems and how this may affect exposure of humans and aquatic biota to contaminants. Thus, it is imperative that future assessment and management of water quality be conducted in a manner that recognizes the intimate connection between these two systems.

For selected compounds in both surface water and groundwater subjected to the hazard assessment, most of the estimated HQs were <1. This indicates that there is little risk associated with exposure from drinking water to the compounds tested. There were some exceptions. For example, nitrates were found to commonly yield HQs >1 in drinking water taken from many rural areas. Some pesticides from well water also yielded HQs >1. In treated distribution waters (water distributed to households), lead, total trihalomethanes, and trichloroacetic acid each yielded HQs >1. These latter compounds were further assessed using a probabilistic approach;

these assessments indicated that the maximum allowable concentrations (MACs) or interim MACs for the respective compounds were exceeded <5% of the time. In other words, the probability of finding these compounds in drinking water at levels that pose risks to humans through ingestion of drinking water is very low.

Our review was carried out in accordance with the conventional principles of risk assessment. Application of the risk assessment paradigm requires rigorous data on both exposure and toxicity in order to adequately characterize potential risks of contaminants to human health and ecological integrity. Uncertainty rendered by poor data, or lack of data, in either the exposure or effects stages of the risk assessment process significantly reduces the confidence that can be placed in the overall risk assessment.

Overall, while our review suggested selected instances of potential risks to human health from exposure to contaminants in drinking water, we also noted a distinct paucity of information on exposure levels for many contaminants in this matrix. We suggest that this represents a significant limitation to conducting sound risk assessments and introduces considerable uncertainty with respect to the management of water quality. In this context, future research must place greater emphasis on targeted monitoring and assessment of specific contaminants in drinking water for which there is currently little information. Such a undertaking need not be resource intensive nor cost prohibitive as long as research priorities are directed to problem compounds identified using the appropriate tools of sound risk assessment. This could be accomplished by using a tiered risk approach, beginning with, for example, assessments based on the use of hazard quotients. Ideally, these would not be used as a basis for rendering final management decisions, although this is often the practice. Potentially problematic compounds identified in these preliminary assessments would then be subjected to more comprehensive risk assessments using probabilistic methods, if sufficient data exist to do so. On this latter point, there is often a lack of adequate exposure and/or toxicity information for many compounds (e.g., pharmaceuticals) from which to construct distributions to estimate the probability of risk, thus providing little opportunity to undertake adequate ecological or human risk assessments. In such cases, basic research into exposure and toxicity must be conducted.

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TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Alachlor	Pesticide (OC)	Herbicide used mainly on corn and soybeans to control the growth of weeds.		Yes
Aldrin	Pesticide (OC)	A pesticide used to control soil insects.		Yes
Aluminum	Metal(I)	Found naturally in the form of very fine particles of aluminosilicate clay.	PSL 2	No
Arsenic	Metal(I)	Arsenic is sometimes found at higher levels in groundwater in hard rock areas in Ontario through the dissolution of arsenic containing minerals, in some mine drainage waters and in some mine waste leachates.		Yes
Atrazine	Pesticide	A triazine pesticide used mainly as a preemergent herbicide on corn for annual grass control.		Yes
Azinphos-methyl	Pesticide	A broad-spectrum insecticide used against foliage-feeding insects.		Yes
Barium	Metal(I)	Barium is a common constituent in sedimentary rocks such as limestone and dolomite.		Yes
Bendiocarb	Pesticide	Bendiocarb is a carbamate insecticide used to control specific insects in buildings and greenhouses.		Yes
Benzene	Organic	Benzene is present in small amounts in gasoline and other refined petroleum products. Benzene is reported to occur in vehicle emissions and cigarette smoke. Drinking water is not considered a significant source of benzene because of its objectionable taste and odor in water.	PSL 1	Yes
Benzo[a]pyrene	Organic	Formed during the incomplete burning of organic matter and is found in poorly adjusted diesel exhaust and in coal/coking tar.		Yes

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Boron (borate)	Inorganic	Acute boron poisonings have resulted from the use of borates as antiseptic agents and from accidental ingestion; however, the consumed amounts were much higher than would be encountered through drinking water.		Yes
Bromoxynil	Pesticide	Herbicide used in Ontario for the control of specific weed seedlings in grain crops.		Yes
Cadmium	Metal(I)	Cadmium is a relatively rare element that is extremely unlikely to be present as a significant natural contaminant in drinking water. Cadmium compounds used in electroplated materials and electroplating wastes may be a significant source of drinking-water contamination.	PSL1	Yes
Carbaryl	Pesticide	Carbaryl is a commonly used broad-spectrum carbamate insecticide used in agriculture and forestry for control of foliar pests and as a home and garden product for specific garden and lawn pests. It is also used for the control of parasites on livestock and pets.		Yes
Carbofuran	Pesticide	It is a broad-spectrum carbamate insecticide used in agriculture for control of foliar pests.		Yes
Carbon tetrachloride	Organic	Carbon tetrachloride is likely to be found only in ground water from old industrial sites where chlorinated solvents were made or used.		Yes

(*Table continues on next page*)

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Chloramines	Organic	Chloramines are produced when ammonia is added to chlorinated water during the disinfection process. Chloramine is a weak disinfectant that usually results in lower levels of trihalomethanes and other chlorination by-products in the drinking water.	PSL2	Yes
Chlordane	Pesticide (OC)	Chlordane is an organochlorine insecticide that was once used extensively in agriculture as a soil insecticide and for domestic control of cockroaches, ants, and termites. Chlordane is very persistent in soil. Chlordane was banned in Ontario in 1994.		Yes
Chloride	Inorganic	Chloride is a common non-toxic material present in small amounts in drinking water and produces a detectable salty taste. Chloride is widely distributed in nature, generally as the sodium (NaCl), potassium (KCl), and calcium (CaCl$_2$) salts.		No
Chloroform	Organic	A common by-product of water disinfection using chlorination.	PSL2	Yes
Chlorpyrifos	Pesticide	Common organophosphate insecticide used for the control of insects on agricultural crops, domestic use, and for flea and tick control.		Yes
Chromium	Metal(I)	Trivalent chromium, the most common and naturally occurring state of chromium, is not considered to be toxic. However, chromium present in untreated water may be oxidized to a harmful hexavalent form during chlorination. Chromium in the more highly oxidized form may be present in older yellow paints and in residues from plating operations and around old recirculating water-cooling systems.		Yes

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Copper	Metal(I)	Copper occurs naturally in the environment, but is rarely found in untreated water. Copper is used extensively in domestic plumbing, in tubing and fittings, and is an essential component of food. Drinking water has the potential to be corrosive and to cause copper to dissolve in water.		No
Cyanazine	Pesticide	A triazine herbicide registered for control of weeds in crop and noncrop areas.		Yes
Cyanide	Inorganic	Widely used in metals plating and refining industries, and industrial effluents are the major potential sources of cyanide contamination.		Yes
Diazinon	Pesticide	An organophosphate insecticide used to control foliar and soil pests. Also used to control flies in barns, ants, and cockroaches.		Yes
Dicamba	Pesticide	A benzoic acid herbicide that is used for control of broadleaf weeds in grains, corn, flax, sorghum, pastures, and weed control in lawns.		Yes
1,2-Dichlorobenzene	Organic	Used in a variety of specialty chemical blends (e.g., degreasing agents, imported dye carriers).	PSL1	Yes
1,4-Dichlorobenzene	Organic	A persistent synthetic material with a strong "medicinal" smell. It has been used widely in toilet pucks and mothballs.	PSL1	Yes
1,2-Dichloroethane	Organic	Used principally as a starting material for vinyl chloride production, as a solvent and a fumigant. It is released into the environment via atmospheric emissions and the discharge of industrial wastewaters.	PSL1	Yes

(*Table continues on next page*)

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
1,2-Dichloroethylene	Organic	This chemical is not produced in Canada; however, it is imported for use in the food industry and the textile industry for furniture and automotive upholstery, drapery fabric, and outdoor furniture.		Yes
Dichloromethane	Organic	Used extensively as an industrial solvent for paint stripping and as a degreasing agent.	PSL1	Yes
2,4-Dichlorophenol	Organic	Chlorophenols are highly odorous synthetic materials that are most often present in drinking water due to the action of chlorine on phenolic precursors. Lighter phenols are found in water only as a result of industrial contamination.		Yes
2,4-D (2,4-dichloro-phenoxy acetic acid)	Pesticide	Commonly used herbicide for control of broadleaf weeds in cereal crops and lawns.		Yes
Diclofop-methyl	Organic, pesticide	A chlorophenoxy derivative that is used for control of annual grasses in grain and vegetable crops.	Yes	
Dieldrin	Pesticide (OC)	A pesticide used to control soil insects.		Yes
Dimethoate	Pesticide	Organophosphate miticide and insecticide used on a wide range of plants for control of mites and both sucking and leaf-feeding insects. It is also used for fly control in livestock pens.		Yes

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Dioxins	Organic (OC)	Dioxins are formed in very small amounts in combustion processes, particularly combustion of chlorine containing materials such as scrap tires and, potentially, in some poorly controlled industrial processes such as bleached paper manufacturing.	PSL1	Yes
Diquat	Pesticide	Herbicide used primarily as a crop desiccant in seed crops and as an aquatic herbicide.		Yes
Diuron	Pesticide	A substituted urea-based herbicide used for the control of vegetation in crop and noncrop areas, including sites and rights-of-way.		Yes
Ethylbenzene	Organic	A component of gasoline additives used for octane rating boosting. It is also used in solvent-based paint formulations.		No
Fluoride	Inorganic	Where fluoride is added to drinking water, it is recommended that the concentration be adjusted to the optimum level for control of tooth decay to prevent excessive human exposure.	PSL2	Yes
Glyphosate	Pesticide	Broad-spectrum, nonselective herbicide used for weed control on rights-of-way, forestry plantations, and in-site preparations for planting of crops, as well as for domestic control of plants.		Yes

(*Table continues on next page*)

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Hardness (caused by dissolved calcium and magnesium)	Inorganic	Hardness is caused by dissolved calcium and magnesium, and is expressed as the equivalent quantity of calcium carbonate. On heating, hard water has a tendency to form scale deposits and can form excessive scum with regular soaps. However, certain detergents are largely unaffected by hardness.		No
Iron	Metal(I)	Iron may be present in ground-water as a result of mineral deposits and chemically reducing underground condi-tions. It may also be present in surface waters as a result of anaerobic decay in sediments and complex formation.		No
Lead	Metal(I)	Lead is only present in drinking water as a result of corrosion of lead solder, lead-containing brass fittings, or lead pipes, which are found close to or in domestic plumbing and the service connection to buildings.		Yes
Lindane	Pesticide (OC)	Organochlorine insecticide used in seed treatment; may also be used in pharmaceutical preparations of human lice and mite shampoos.		Yes
Malathion	Pesticide	Broad-spectrum organophosphate insecticide used on fruits and vegetables, as well as for mosquito, fly, and tick control.		Yes
Manganese	Metal(I)	Present in some groundwaters because of reducing conditions underground, coupled with the presence of manganese mineral deposits. Manganese also occasionally present, seasonally, in surface waters when anaerobic decay processes in sediments are occurring.		No

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Mercury	Metal(0)	Sources of mercury in drinking water include air pollution from coal combustion, waste incineration, and from metal refining operations and from natural mineral deposits in some hard rock areas. Food is the major source of human exposure to mercury, with freshwater fish being the most significant local source.		Yes
Methane	Organic	Occurs naturally in some groundwater and acts as a stimulant for microbiological fouling in the water distribution system. If methane is allowed to accumulate in confined areas, the potential for explosive combustion exists.		No
Methoxychlor	Pesticide (OC)	An organochlorine insecticide. It is nonaccumulative in biological tissues, making it an attractive insecticide for use on products nearing harvest, in dairy barns for housefly control, and as either a larvicide or adulticide against black flies and mosquitoes.		Yes
Metolachlor	Pesticide	A selective herbicide used for preemergence and preplant broadleaf weed control in corn, soybeans, peanuts, grain sorghum, pod crops, woody ornamentals, and sunflowers.		Yes
Metribuzin	Pesticide	Triazine herbicide used for the control of broadleaf weeds and grasses infesting agricultural crops. It is used selectively on soybeans and potatoes, all crops that are highly sensitive to most other triazine herbicides.		Yes

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Monochloro-benzene (chloro-benzene)	Organic	Used in the production of chloronitrobenzene and diphenyl ether, as a rubber intermediate, and as a solvent in adhesives, paints, waxes, polishes, and inert solvents. Also used in metal-cleaning operations and may be present in industrial discharges.	PSL1	Yes
Nitrate	Inorganic	Present in water (particularly groundwater) as a result of decay of plant or animal material, the use of agricultural fertilizers, domestic sewage or treated wastewater contamination, or geological formations containing soluble nitrogen compounds.		Yes
Nitrite	Inorganic	Rapidly oxidized to nitrate and is therefore seldom present in surface waters in significant concentrations. Nitrite may occur in groundwater sources; however, if chlorination is practiced the nitrite will usually be oxidized to nitrate.		Yes
NTA (nitrilotriacetic acid)	Organic	NTA is mainly used in laundry detergents, most of which is eventually disposed of in domestic wastewater.		Yes
NDMA (*N*-nitroso-dimethylamine)	Organic	NDMA is used industrially but has been used as an antioxidant, as an additive for lubricants, and as a softener of copolymers. It has been detected in some foods, particularly smoked foods, and very occasionally in treated river/lake water in heavily farmed locations.	PSL2	Yes

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Paraquat	Pesticide	Highly toxic herbicide used as a contact herbicide and for desiccation of seed crops. It is also used for noncrop and industrial weed control.		Yes
Parathion	Pesticide	Broad-spectrum, organophosphate insecticide used in agriculture against foliar pests and adult stage of root maggots.		Yes
Pentachlorophenol	Organic (OC)	Rarely found in commercial use today but was used extensively as a pesticide and wood preservative. It is the most environmentally persistent of the chlorophenols.		Yes
Phorate	Pesticide	An organophosphate insecticide used for control of sucking insects, larvae of the corn rootworm and leaf-eating beetles.		Yes
Picloram	Pesticide	A phenoxyalkanoic acid herbicide used for broadleaf weed and brush control on right-of-ways and roadsides.		Yes
Polychlorinated biphenyls (PCBs)	Organic (OC)	Among the most ubiquitous and persistent pollutants in the global ecosystem. In the past, PCBs have been marketed extensively for a wide variety of purposes but are no longer manufactured or used.	PSL1	Yes
Prometryne	Pesticide	Herbicide used to selectively control annual grasses and broadleaf weeds in crops and noncrops.		Yes

(*Table continues on next page*)

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Selenium	Metal(I)	Occurs naturally in waters at trace levels as a result of geochemical processes such as weathering of rocks. Food is the main source of selenium intake other than occupational exposure. Selenium is an essential trace element in the human diet.		Yes
Simazine	Pesticide	A triazine herbicide used for pre-emergence weed control in annual row crops. Simazine is least soluble of all triazines and is easily leached to groundwater, where it may persist for years.		Yes
Sodium	Inorganic	Sodium is not toxic. The average intake of sodium from water is only a small fraction of that consumed in a normal diet. Softening using a domestic water softener increases the sodium level in drinking water and may contribute a significant percentage to the daily sodium intake for a person on a sodium restricted diet.		No
Sulfate	Inorganic	High levels of sulfate may be associated with calcium, which is a major component of scale boilers and heat exchangers. In addition, sulfate can be converted into sulfide by some anaerobic bacteria, creating odor problems and potentially greatly accelerating corrosion.		No
Sulfide	Inorganic	Sulfide is undesirable in water supplies mainly because, in association with iron, it produces black stains on laundered items and black deposits on pipes and fixtures.		No
Temephos	Pesticide	Organophosphate insecticide used to control mosquito and black-fly larvae.		Yes
Terbufos	Pesticide	Terbufos is an organophosphate insecticide used for insect control in corn.		Yes

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Tetrachloro-ethylene (perchloro-ethylene)	Pesticide	No longer produced in Canada but continues to be imported primarily as a solvent for the dry cleaning and metal cleaning industries. It has been found in groundwater, primarily after improper disposal or dumping of cleaning solvents.	PSL1	Yes
2,3,4,6-Tetra-chlorophenol	Organic	2,3,4,6-Tetrachlorophenol was used extensively, along with pentachlorophenol, to preserve wood.		Yes
Toluene	Organic	Used in gasoline and other petroleum products and in the manufacture of benzene derived medicines, dyes, paints, coating gums, resins, and rubber. It may be found in industrial effluents.	PSL1	No
Triallate	Pesticide	A thiocarbamate herbicide used for control of wild oats in grain crops, mustard, and sugar beets.		Yes
Trichloroethylene	Organic	Mostly used in dry cleaning. Some is used in metal degreasing operations and in tetrachloroethylene production. Trichloroethylene may be introduced into surface water and groundwater through industrial spills and illegal disposal of effluents.	PSL1	Yes
2,4,6-Trichlorophenol	Organic	Used in the manufacture of pesticides.		Yes
2,4,5-T (2,4,5-Tri-chlorophenoxy-acetic acid)	Pesticide	A phenoxy alkanoic acid herbicide that was once an important stem/foliage treatment for deciduous brush control on roadsides and power lines. 2,4,5-T is no longer used in Ontario.		Yes
Trifluralin	Pesticide	A dinitroaniline herbicide used for weed control in summer fallow and annual grasses in wheat, barley, and canola.		Yes

(*Table continues on next page*)

TABLE A1. Chemicals That Have Been Detected in Drinking Water in Ontario, Their Priority Substance List (PSL) Designation, and Status Regarding Human Health Concerns (*Continued*)

Chemical	Class	Description of use/origin	CEPA priority pollutant? (PSL1/2)[a]	Human health concern? (yes/no)
Trihalomethanes (e.g., chloroform, bromodichloro-methane, chloro-dibromomethane, and bromoform)	Organic	Trihalomethanes are the most widely occurring synthetic organics found in chlorinated drinking water. The principal source of trihalomethanes in drinking water is the action of chlorine with naturally occurring organic (precursors) left in the water after filtration.	PSL1	Yes
Uranium	Metal(I)	Uranium is normally present in biological systems and aqueous media as the uranyl ion (UO_2^{2+}).		Yes
Vinyl chloride (chloroethene)	Organic	Vinyl chloride is a synthetic chemical with no known natural sources. It is used in making PVC (polyvinyl chloride) plastic items such as water-main pipe, siding, and many other common plastic items, all of which are now made in such a way that there is no trace of vinyl chloride present in them.		Yes
Xylenes	Organic	There are three isomers of dimethyl benzene, which are almost identical chemically and are collectively called xylenes. Xylenes are used as industrial solvents and as an intermediate for dyes and organic synthesis. They are a component of household paints and paint cleaners and gasoline and other petroleum products.	PSL1	No
Zinc	Metal(I)	The concentration of zinc may be considerably higher at the drinking water tap in standing water because of corrosion taking place in galvanized pipes.		No

Note. Adapted from Ontario Ministry of the Environment (2000). Abbreviations used in this table: OC, organochlorine; I, inorganic; O, organic.

[a]PSL, priority substance list 1 or 2. Contaminants on this list have been designated in CEPA (Canadian Environmental Protection Act) as this.

TABLE A2. Chemicals of Health Significance in Drinking Water and Associated Water Quality Guidelines/Criteria (mg/L)

	WHO drinking water quality value	Canadian drinking water quality guideline		Provincial water quality guideline/objective	Ontario drinking water quality guideline		Used in HQ assessment?
Inorganic constituents							
Antimony	0.005[a]			7000[c]			
Arsenic	0.01[a,b]	0.025	IMAC	100,000	1	MAC	Yes
Barium	0.7	1	MAC				
Beryllium	NAD			100,000[c]			
Boron	0.3	5	IMAC		5	IMAC	
Cadmium	0.003	0.005	MAC	200	0.05	MAC	Yes
Chromium	0.05[a]	0.05	MAC	100,000			Yes
Copper	2[a]	1.0	AO	5000			
Cyanide	0.07	0.2	MAC		0.2	MAC	
Fluoride	1.5	1.5	MAC		1.5[g]	MAC	
Lead	0.01	0.01	MAC	[d]	0.01	MAC	Yes
Manganese	0.5[a]	0.05	AO				
Mercury (total)	0.001	0.001	MAC	200	0.001	MAC	
Molybdenum	0.07			10,000[c]			
Nickel	0.02			25,000			
Nitrate (as NO_3^-)	50[e]	45			10	MAC	Yes
Nitrite (as NO_2^-)	3[a,e]	3.2[f]			1	MAC	
Selenium	0.01	0.01	MAC		0.01	MAC	
Uranium	NAD	0.1	MAC	100,000	0.1	MAC	
Organic constituents							
Chlorinated alkanes							
Carbon tetrachloride	2	0.005	MAC		0.005	MAC	Yes
Dichloromethane	20	0.05	MAC		0.05	MAC	
1,1-Dichloroethane	NAD			200,000			
1,2-Dichloroethane	30[b]	0.005	IMAC	100,000	0.005	IMAC	
1,1,1-Trichloroethane	2000[a]			800,000			
Chlorinated ethenes vinyl chloride	5[b]	0.002	MAC		0.002	MAC	
1,1-Dichloroethene	30						
1,2-Dichloroethene	50						
Trichloroethene	70[a]						Yes
Tetrachloroethene	40						

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TABLE A2. Chemicals of Health Significance in Drinking Water and Associated Water Quality Guidelines/Criteria (mg/L) *(Continued)*

	WHO drinking water quality value	Canadian drinking water quality guideline		Provincial water quality guideline/objective	Ontario drinking water quality guideline		Used in HQ assessment?
Aromatic hydrocarbons							
Benzene	10^b	0.005	MAC	$100,000^c$	0.005	MAC	Yes
Toluene	700	0.024	AO	800^c			
Xylenes	500	0.3	AO				
Ethylbenzene	300	0.0024	AO	8000^c			
Styrene	20			4000^c			
Benzo[a]pyrene	0.7^b	0.00001	MAC		0.00001	MAC	
Chlorinated benzenes							
Monochlorobenzene	300	0.08	MAC	15,000	0.008	MAC	
1,2-Dichlorobenzene	1000	0.2	MAC	2500			
1,3-Dichlorobenzene	NAD			2500			
1,4-Dichlorobenzene	300	0.005	MAC	4000			
Trichlorobenzenes (total)	20						Yes
Miscellaneous							
Di(2-ethylhexyl)adipate	80						
Di(2-ethylhexyl)pthalate	8						
Acrylamide	0.5^b			600			
Epichlorohydrin	0.4^a						
Hexachlorobutadiene	0.6			70^c			
Edetic acid (EDTA)	200^a						
Nitrilotriacetic acid	200	0.4	MAC		0.4	MAC	
Pesticides							
Dialkyltins	NAD						
Tributyltin oxide	2			0.04^c			
Alachlor	20^b				0.005	IMAC	
Aldicarb	10				0.009	MAC	
Aldrin/dieldrin	0.03	0.0007	MAC	1	0.0007	MAC	
Atrazine	2	0.005	IMAC		0.06	IMAC	Yes
Bentazone	30						
Carbofuran	5	0.09	MAC		0.09	MAC	
Chlordane	0.2			60	0.007	MAC	
Chlorotoluron	30						
DDT	2	NG		3	0.03	MAC	

1,2-Dibromo-3-chloropropane	1[b]						
2,4-D	30	0.1	IMAC		0.1	MAC	Yes
1,2-Dichloropropane	20[a]						
1,3-Dichlropropane	NAD						
1,3-Dichloropropene	20[b]						
Ethylene dibromide	NAD						
Heptachlor and heptachlor epoxide		0.03	NG		0.003	MAC	
Hexachlorobenzene	1[b]			1			Yes
Isoproturon	9			6.5			
Lindane	2			10	0.004	MAC	
MCPA	2						
Methoxychlor	20	0.9	MAC	40	0.9	MAC	
Metolachlor	10	0.05	IMAC		0.05	IMAC	
Molinate	6						
Pendimethalin	20			500			
Pentachlorophenol	9				0.06	MAC	Yes
Permethrin	20						
Propanil	20						
Pyridate	100						
Simazine	2	0.01	IMAC	10,000	0.01	IMAC	Yes
Trifluralin	20	0.045	IMAC		0.045	IMAC	
Other chlorophenoxy herbicides							
2,4-DB	90						
Dichlorprop	100						
Fenoprop	9						
MCPB	NAD						
Mecoprop	10						
2,4,5-T	9				0.2	MAC	
Disinfectants							
Monochloroamine	3				3	MAC	
Di- and trichloramine	NAD						
Chlorine	5			2000			
Chlorine dioxide	NAD						
Iodine	NAD						
Disinfectant by-products							
Bromate	25[a,b]						
Chlorate	NAD						
Chlorite	200[a]						

TABLE A2. Chemicals of Health Significance in Drinking Water and Associated Water Quality Guidelines/Criteria (mg/L) *(Continued)*

	WHO drinking water quality value	Canadian drinking water quality guideline		Provincial water quality guideline/objective	Ontario drinking water quality guideline		Used in HQ assessment?
Chlorophenols							
2-Chlorophenol	NAD	NAD			NAD		
2,4-Dichlorophenol	NAD	0.9	MAC		0.9	MAC	
2,4,6-Trichlorophenol	200[b]	0.005	MAC		0.005	MAC	
Formaldehyde	900						
MX	NAD						
Trihalomethanes							
Bromoform	100				0.1	MAC (total)	Yes
Dibromochloromethne	100				0.35	MAC	
Dibromodichloromethane	60[b]				0.35	MAC	
Chloroform	200[b]				0.35	MAC	
Chloroacetone	NAD				0.35	MAC	
Halogenated acetonitriles							
Dichloroacetonitrile	90[a]						
Dibromoacetonitrile	100[a]						
Bromochloroacetonitrile	NAD						
Trichloroacetonitrile	1[a]						
Cyanogen chloride (as CN)	70						
Chloropicrin	NAD						

Note. MAC, maximum acceptable concentration; IMAC, interim maximum acceptable concentration; AO, aesthetic objective; NG, no guideline available; NAD, no available data. Sources of information used to compile this table included: (1) Health Canada (1996b), pp. 19–77, (2) Phyper and Ibbotson (1994), pp. 90–93 & 102–104; (3) World Health Organization (1993), pp. 174–178.

[a] Provisional guideline value, used for constituents for which there is some evidence of a potential hazard but where the available information on health effects is limited; or where an uncertainty factor greater than 1000 has been used in the derivation of the tolerable daily intake (TDI).

[b] For substances that are considered to be carcinogenic, the guideline value is the concentration in drinking water associated with an excess lifetime cancer risk of 10⁻⁵ (1 additional cancer per 100,000 of the population ingesting drinking water containing the substance at the guideline value for 70 yr). Concentrations associated with estimated excess lifetime cancer risks of 10⁻⁴ and 10⁻⁶ can be calculated by multiplying and dividing, respectively, the guideline value by 10.

[c] These values represent propsed Provincial Water Quality Guidelines/Objectives.

[d] PWQO/G is either a narrative, or dependent on pH, alkalinity, or hardness.

[e] The sum of the ratio of the concentration of each to its respective guideline value should not exceed this.

[f] In cases where nitrate and nitrite are determined separately.

[g] The MAC for naturally occurring fluoride in drinking water is 2.4 mg/L. A MAC of 1.5 mg/L was established to ensure that when fluoride is added to drinking water the concentration (1.2 ± 0.2 mg/L) is maintained such that the population obtains optimal benefit.