THE WALKERTON INQUIRY

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SOURCES, PATHWAYS, AND RELATIVE RISKS OF CONTAMINANTS IN WATER

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Abstract

Pathogenic contamination of drinking water, the cause of countless disease outbreaks and poisonings, is the most significant global health risk to humans. However, non-pathogenic, toxic contaminants, often present in drinking water, pose significant risks to both human and environmental health. This paper discusses 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 to human and environmental health.

Our discussion follows the classical risk assessment paradigm, with emphasis on risk characterization. We focus on toxic contaminants with a demonstrated or potential effect on human health via drinking water. To address (and reduce) uncertainty in estimating the likelihood of exposure, we must understand the sources and pathways for contaminants in the environment. This enables us to quantify effects through accurate measurement and testing and to predict their likelihood, based on empirical models. It also provides critical information for making decisions on regulatory initiatives, remediation, monitoring, and management.

Our discussion has two primary themes: first, the major sources of contaminants from anthropogenic activities to aquatic surface- and groundwater and the pathways along which they move; and, second, the health significance of the contaminants reported and the uncertainties associated with exposures and potential effects.

Loading of contaminants occurs via two primary routes: (1) point source pollution and (2) non-point source pollution. Point source pollution has discrete sources whose inputs into aquatic systems can often be defined explicitly, e.g., industrial effluents, municipal sewage treatment plants and combined sewage–storm water overflows, mining, and land disposal sites. Non-point source pollution, in contrast, has poorly defined, diffuse sources that typically occur over broad areas, e.g., agricultural runoff, stormwater and urban runoff, and atmospheric deposition. Within each source, we identify the most important contaminants that either have been demonstrated to pose significant risks to human health and/or aquatic ecosystem integrity or are suspected of posing such risks, e.g., nutrients, metals, pesticides, persistent organic pollutants (POPs), chlorination by-products, and pharmaceuticals. We confine our discussion to those chemicals which pose risks to human health via exposure through drinking water.

We use information on specific chemicals to determine their relative risk by the hazard quotient (HQ) approach, in which the exposure concentration of a stressor, either measured or estimated, is compared to an effect. A key goal is to develop a perspective on the relative risks of toxic contaminants in drinking water. For many common contaminants, there is insufficient environmental exposure (concentration) information in Ontario drinking water and groundwater. Hence, we limit our assessment to specific compounds within major contaminant classes including metals, disinfection by-products, pesticides, and nitrates. For each contaminant, the HQ is estimated by expressing the maximum concentration recorded in drinking water as a function of the water quality guideline for that compound.

Our goal is not to conduct a comprehensive, in-depth assessment of risk for each chemical but, rather, to provide the reader with an indication of the relative risk of major contaminant classes as a basis for understanding the risks posed by the myriad forms of toxic pollutants in aquatic systems and drinking water.

For most compounds, the estimated HQs are <1, indicating that there is little risk. There are some exceptions, yielding HQs of >1, e.g., nitrates in many rural areas and lead, total trihalomethanes, and trichloroacetic acid in some treated distribution waters (water distributed to households). The latter compounds are further assessed using a probabilistic approach. These assessments indicate that the maximum allowable concentrations (MAC) or Interim MACs for the respective compounds are exceeded less than 5% of the time, i.e., the probability of finding them in drinking water at levels posing a risk to humans is low.

Our review follows the conventional principles of risk assessment, which requires rigorous data on both exposure and toxicity to adequately characterize potential risks of contaminants to human health and ecological integrity. Weakness caused by poor data, or lack of data, in either the exposure or effects stage significantly reduces confidence in the overall risk assessment. Although our review suggests selected instances of potential risks to human health from exposure to contaminants in drinking water, we also note that information on exposure levels for many contaminants in this matrix is lacking, which significantly limits the ability to conduct sound risk assessments and introduces considerable uncertainty into the management of water quality. 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. A tiered risk approach could be used, beginning with a hazard quotient assessment, for example. Potentially problematic compounds would then be subjected to more comprehensive risk assessments using probabilistic methods, if sufficient data exist to do so. Generating this information is critical.

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1 Introduction

1.1 Background

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.[1] 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 a year.[2] 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 was recently emphasized in the publication of the agenda-setting book *The Freshwater Imperative*.[3]

> Changes in the distribution, abundance, and quality of water and freshwater 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.

Although this quote makes reference to the 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 to Canada and other countries. 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 that induced by petroleum products in the 20th century.

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[1] D.C. Gibbons, 1986, *The Economic Value of Water* (Washington, D.C.: Resources for the Future).

[2] Canada, Environment Canada, 1991, *The State of Canada's Environment* (Ottawa: Environment Canada), En21-54/1991E.

[3] R.J. Naiman et al., 1995, *The Freshwater Imperative: A Research Agenda* (Washington, D.C.: Island Press).

Most Canadians perceive Canada as a land with an abundant supply of freshwater, and this perception is reflected in our daily use patterns. In terms of total water use, the average Canadian drew approximately 4,500 L per person per day; in terms of personal use, we drew 340 L per person per day.[4] 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 one-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 centres 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 of those (5 million) living in rural areas.[5] In Ontario, close to 30% of residents rely on groundwater as a source of drinking water.[6] 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 to provide perspective on the relative risks that these compounds pose to human health and ecosystem integrity. This is a significant and daunting undertaking in light of the large number of toxic contaminants that are 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 throughout history countless poisonings and disease outbreaks have resulted from poorly treated or untreated water. Issues surrounding the history of disease outbreaks in Ontario are discussed in a separate Commissioned Paper by Krewski et al.[7] However, significant risks to human

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[4] Canada, Environment Canada, 1996, *The State of Canada's Environment* (Ottawa: Environment Canada), En21-54/1996E.

[5] Canada, Environment Canada, 2001, "Groundwater – Nature's hidden treasure," Freshwater Series A-5 [online], [cited October 23, 2001], <www.ec.gc.ca/water/en/info/pubs/FS/e_FSA5.htm>.

[6] M.J. Goss et al., 1998, "Contamination in Ontario farmstead domestic wells and its association with agriculture. 1. Results from drinking water wells," *Journal of Contaminant Hydrology,* vol. 32, pp. 267–93.

[7] D. Krewski et al., 2002. *Managing Health Risks from Drinking Water* (Toronto: Ontario Ministry of the Attorney General), Walkerton Inquiry Commissioned Paper 7, Walkerton Inquiry CD-ROM, <www.walkertoninquiry.com>.

health may also result from exposure to non-pathogenic, 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.[8] 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.[9] 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 will be 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 are shared with, those which 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,[10] even though the merits of doing so have been debated at length.[11] 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.

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[8] S.J. Larson et al., 1997, “Pesticides in surface waters: Distribution, trends, and governing factors*,”* *Pesticides in the Hydrologic System* (Chelsea, Mich.: Ann Arbor Press, Inc.), vol. 3.

[9] U.S. National Research Council, 1999, *Hormonally Active Agents in the Environment* (Washington, DC.: National Academy Press).

[10] D.J. Schaeffer et al., 1988, “Ecosystem health 1. Measuring ecosystem health,” *Environmental Management*, vol. 12, pp. 445–55.

[11] G.W. Suter, 1993a, “A critique of ecosystem health concepts and indices,” *Environmental Toxicology and Chemistry*, vol. 12, pp. 1533–39; J. Lancaster, 2000, “The ridiculous notion of assessing ecological health and identifying the useful concepts underneath,” *Human and Ecological Risk Assessment,* vol. 6, pp. 213–22.

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, 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 their way into drinking water. A list of the toxic chemicals identified in Canadian drinking water is presented in table A1 (Appendix A), 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.[12] 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 their environmental fate, distribution, and potential risks to humans and ecosystems begun to receive scientific scrutiny.[13] 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 the current paper. 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 will restrict our discussion primarily to toxic contaminants that have had a demonstrated or

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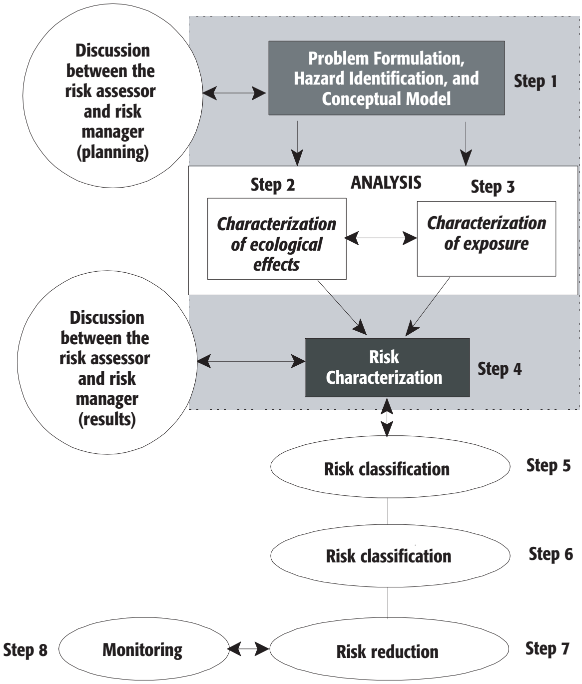
[12] T. Colborn et al., 1996, *Our Stolen Future* (New York: Dutton Press).

[13] C.G. Daughton and T.A. Ternes, 1999, “Pharmaceuticals and personal care products in the environment: Agents of subtle change?” *Environmental Health Perspectives,* vol. 107 (Suppl. 6), pp. 907–38.

potential effect on humans through drinking water. Some of these are listed in table A1. In doing so, we will only briefly consider sources, pathways, and relative risks of pathogens originating in water as these are addressed in greater detail in a separate paper submitted to the Commission.[14] In addition, apart from some examples for selected contaminant classes, we will not address issues of contaminant remediation and management.[15] 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 Commissioned Paper.

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

Figure 1-1 Risk Assessment Framework



Source: U.S., National Research Council, 1983, *Risk Assessment in the Federal Government* (Washington, D.C.: National Academy Press).

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[14] M.J. Goss et al., 2002, *The Management of Manure in Ontario with Respect to Water Quality* (Toronto: Ontario Ministry of the Attorney General), Walkerton Inquiry Commissioned Paper 6, Walkerton Inquiry CD-ROM, <www.walkertoninquiry.com>.

[15] Interested readers can obtain information on remediation and management technologies from U.S. Environmental Protection Agency, 2000b, *Site Remediation Technology InfoBase: A Guide to Federal Programs, Information, Resources, and Publications on Contaminated Site Cleanup Technologies* (Washington, D.C.: US EPA), EPA 542-B-00-005.

assessment framework outlined in figure 1-1. 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.[16] The key components of this risk assessment framework are hazard identification, dose-response (effects) evaluation, exposure (sources/pathways) evaluation, and risk characterization. The latter 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.

1.2 Objectives

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

1. To identify and describe key point and non-point 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.

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[16] U. S. National Research Council, 1983, *Risk Assessment in the Federal Government* (Washington, D.C.: National Academy Press).

2 Sources and Pathways of Contaminants in Aquatic Systems and Drinking Water

2.1 Sources of Water Contamination

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 2-1). Point source contributions of contaminants originate from discrete sources whose inputs into aquatic systems 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.[17] 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 through-put 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.

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[17] K.M. Kleinow and M.S. Goodrich, 1994, "Environmental aquatic toxicology," in L.G. Cockerham and B.S. Shane (eds.), *Basic Environmental Toxicology* (Boca Raton, Fla.: CRC Press), pp. 353–84.

Table 2-1 Major Point Source and Non-point Sources of Contaminants to Surface Waters, Groundwater, 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, anti-microbials, 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, polycylic 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
NON-POINT 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
Habitat Modification	Removal of riparian vegetation, streambank 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

Source: U.S., Environmental Protection Agency, Risk Assessment Forum, 1998, *Guidelines for Ecological Risk Assessment* (Washington, D.C.: US EPA).

In addition to the traditional point and non-point sources listed in table 2-1, 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 modification can result in significantly increased sediment loading in streams, with a corresponding loss of benthic productivity and fish habitat.[18] In fact, siltation was identified by the U.S. EPA as the most significant pollutant causing degradation of streams in the United States (table 2-2). Indirectly, however, changes in the physico-chemical 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.[19] 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.

Table 2-2 Five Leading Pollutants Causing Water Quality Impairment in Various Surface Waters of the U.S.

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.
Source: U.S., Environmental Protection Agency, 1998.

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[18] T.F. Waters, 1995, *Sediment in Streams: Sources, Biological Effects, and Control* (Bethesda, Md.: American Fisheries Society), Monograph 7.

[19] W.F. Ritter, 1998, "Reducing impacts of nonpaint source pollution from agriculture: A review," *Journal of Environmental Science and Health*, vol. A23.

Following release to the environment from any of the point and non-point sources identified in table 2-1, 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 non-toxic 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 the degree to which aquatic biota and humans may be exposed to it, depend largely on the physico-chemical 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 non-point sources of contamination, section 2.3). Polar compounds generally do not bioaccumulate (but see the atmospheric transport section, 2.3.2, 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, non-polar (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 water has long been used as a sink for many forms of anthropogenic waste; however, it also serves as the primary source of drinking water. Approximately three-quarters of water used for drinking purposes in Canada and Ontario, particularly in urban centres, 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 kilometres, and in depth from only a few metres to several hundred metres.[20]

In Canada, groundwater serves as the primary source of drinking water for approximately 7.9 million people or about 26% of the population.[21] 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.[22] 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 2-3). The spatial extent and intensity of groundwater contamination depend upon many factors that collectively distinguish detection, treatment, and management of this resource 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.[23] 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 the impact on aquatic ecosystems has 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

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[20] Canada, Environment Canada, 2001.

[21] Canada, Environment Canada, 1996.

[22] Canada, Health Canada, 1997, "Water," in *Health and Environment: Partners for Life* [online], Ottawa: Health Canada, [cited February 5, 2002], <www.hc-sc.gc.ca/ehp/ehd/catalogue/general/97ehd215.htm>.

[23] D.W. Miller, 1980, *Waste Disposal Effects on Groundwater: A Comprehensive Survey of the Occurrence and Control of Groundwater Contamination* (Berkeley, Calif.: Premier Press).

safe and proper construction of 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 in greater detail below in relation to the various point and and non-point sources of pollution.

Table 2-3 Sources of Groundwater Contaminants

Category 1: Sources designed to discharge substances

1 Sub-surface percolation from septic tanks/cesspools

2 Injection Wells

Hazardous waste

Non-hazardous waste (e.g., brine disposal)

Non-waste (e.g., solution mining)

3 Land Application

Wastewater (spray irrigation)

Wastewater by-products (biosolids)

Hazardous waste

Non-hazardous waste

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

1 Landfills

Industrial hazardous waste

Industrial non-hazardous waste

Municipal sanitary

2 Open dumps, including illegal dumping

3 Residential disposal

4 Surface impoundments

Hazardous waste

Non-hazardous waste

5 Materials stockpiles (non-waste)

6 Graveyards

7 Animal burial

8 Above-ground storage tanks

Hazardous waste

Non-hazardous waste

Non-waste

9 Underground storage tanks

Hazardous waste

Source: M. Barcelona et al., 1990, “Contamination of groundwater: Prevention, assessment, and restoration,” *Pollution Technology Review*, vol. 184.

Finally, it is important to note that historical approaches and philosophies regarding the governance and management of groundwater/surface water research have treated these two water systems as separate entities.[24] 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.

2.2 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 will identify the major contaminants that have had demonstrated or potential risks to human health via drinking water. In doing so, we will 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 will be 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.

2.2.1 Industrial and Resource Extraction

Industrial applications constitute a significant source of toxic contaminants to surface waters, sediments, and groundwater in Canada, and many have been detected in drinking water. In Canada, three primary industries 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

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[24] R.J. Naiman and H. Descamps, 1997, "The ecology of interfaces," *Annual Review of Ecology and Systematics*, vol. 28, pp. 621–58; P.B. Duncan, 1999, "Groundwater-surface water interactions: No longer ignoring the obvious at superfund sites," *SETAC News*, vol. 19, no. 5, pp. 20–21.

and directly employ over one million people.[25] 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 groundwater. In either case, industrial-borne contaminants have had broad impacts on aquatic ecosystems and many pose risks to human health.[26]

Keith reviewed the occurrence and frequency of detection of organic contaminants and metals in industrial wastewaters in a 1979 survey conducted by the USEPA.[27] 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.[28]

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 wastewater impoundments and hazardous waste wells into nearby groundwater aquifers. Industrial contaminants may also enter aquatic environments via the atmospheric transport of smokestack emissions that are either deposited 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 below under non-point source pollution (section 2.3). In each case, contamination of drinking water supplies

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[25] Canada, Environment Canada, 1991.

[26] Canada, Environment Canada, 1996.

[27] L. J. Keith, 1979, "Priority pollutants. I. A perspective view," *Environmental Science and Technology*, vol. 13.

[28] E.P. Jorgensen, 1989*, The Poisoned Well: New Strategies for Groundwater Protection,* Sierra Club Legal Defense Fund (Washington, D.C.: Island Press); D.I. Gustafson, 1993, *Pesticides in Drinking Water* (New York: Van Nostrand Reinhold).

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., the food processing industry), these are relatively minor compared to the above industries in terms of both their economic importance and their 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 space 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, 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 micro-nutrients and are essential at specific concentration ranges for the health of biological organisms. Owing to their natural and anthropogenic origins and their ubiquitous occurrence in surface and groundwater, we have purposefully departed from the general organizational structure of the document to consider both point and non-point sources of metals together.

2.2.1.1 *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 (bioavailable) 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 evaluating the human health and environmental risk and in determining the contaminant's behaviour. Indeed, the degree of trace metal toxicity depends largely on the form of the metal and on the 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 2-4.

Sources of Metals 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 evaluating trace metal contamination. In some cases, naturally occurring concentrations of trace metals in some regions exceed safe-limit criteria established in particular jurisdictions. Burning of fossil fuels, mining operations, and the industrial use of metals and mineral compounds are prime human-influenced sources of trace metals in the environment. Sources of trace metals in the environment can be described under 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.[29]

Table 2-4 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

Source: P. Brezonik, 1976, "Analysis and speciation of trace metals in water supplies," in Alan J. Rubin (ed.), *Aqueous-Environmental Chemistry of Metals* (Ann Arbor, Mich.: Ann Arbor Science Publishers, Inc.).

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[29] S.L. Williams et al., 1976, "Sources and distribution of trace metals in aquatic environments," in A.J. Rubin (ed.), *Aqueous Environmental Chemistry of Metals* (Ann Arbor, Mich.: Ann Arbor Science Publishers, Inc.), pp. 77–127.

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 the total value of the non-fuel mineral production in Canada for that year.[30] Of the four mining stages, only mining and milling and post-operational waste management contributed to the contamination of surface water and groundwater resources.[31] Another important source of elevated metal concentrations in receiving environments is domestic wastewater (table 2-5) since many household and personal products contain metals.[32] Corrosion of plumbing pipes and fixtures also contributes metals to wastewater.[33] 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.

Table 2-5 Concentrations of Trace Metals in Municipal Wastewater in ppb

Metal	St. Paul, Minn.	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

Sources: St. Paul data from Costner and Thornton, 1989; L.A. from Southern California Coastal Water Research Project, 1992; N.Y. from Baccay and Ahmed, 1996; Ont. from Atkins and Hawley, 1978.

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[30] B.J. Alloway , 1995, *Heavy Metals in Soils,* 2nd ed. (New York: Chapman & Hall).

[31] Ibid.

[32] E. Atkins and J. Hawley, 1978, *Sources of Metals and Metal Levels in Municipal Wastewaters*, Research Program for the Abatement of Municipal Pollution under Provisions of the Canada-Ontario Agreement on Great Lakes Water Quality (Ottawa and Toronto: Environment Canada and Ontario Ministry of the Environment), Research Report No. 80.

[33] L. Millette and D.S. Mavinic, 1988, "The effect of pH adjustment on the internal corrosion rate of cast-iron and copper water distribution pipes," *Canadian Journal of Civil Engineering*, vol. 15, pp. 79–90.

Non-point sources of trace metal contamination include the burning of fossil fuels, agricultural practices, and atmospheric deposition.[34] Deliberate application of trace metals in fertilizers, manure, sewage sludge, and pesticides makes agricultural runoff a key non-point 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 non-point source of pollution. Common sources of trace metals in urban runoff are automobile fuel exhaust and the wear and corrosion of automobile components such as tires, brake linings, and exhaust systems.[35] Corrosion from ship traffic on the Great Lakes is also important as a mobile non-point source of trace metal contaminants.

Contaminated sediments can also be sources of metal pollution.[36] 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. Marys Rivers, along with the Toronto and Hamilton harbours. 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.[37]

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.[38] Many of these phenomena depend on interactions between organic and inorganic species present in solution and physical effects at the solid–solution interface. The chemical and

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[34] Williams, 1976.

[35] R.T. Bannerman et al., 1993, "Sources of pollutants in Wisconsin stormwater," *Water Science and Technology,* vol. 28, pp. 241–59.

[36] J.D. Smith and T.E. Hamilton, 1992, "Trace metal fluxes to lake sediments in south-eastern Australia," *The Science of the Total Environment*, vol. 125, pp. 227–33.

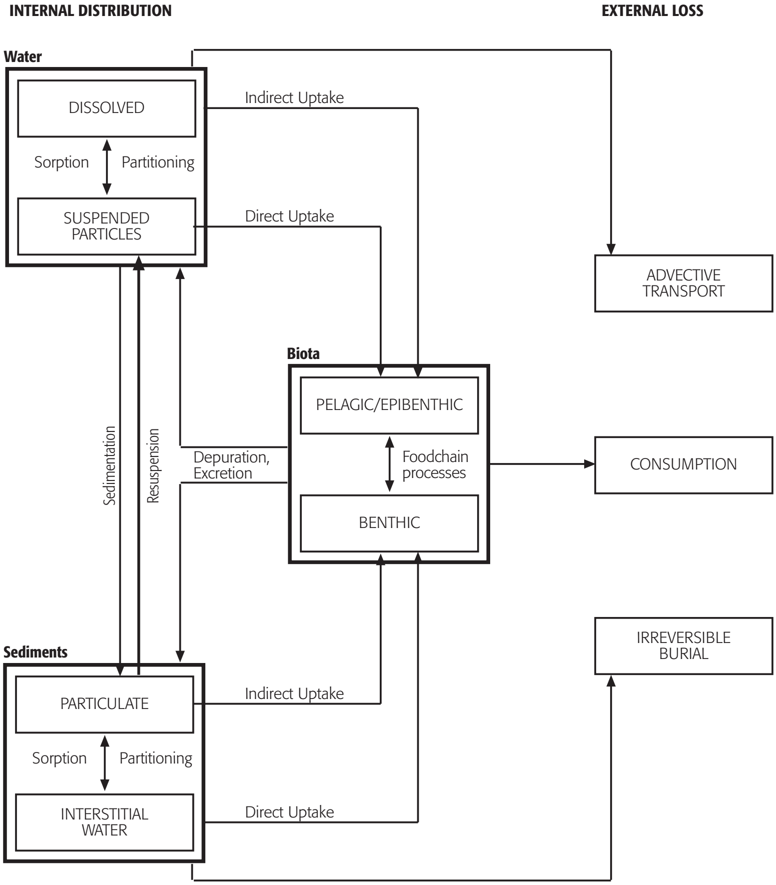
[37] S.C. Sheppard, 1998, "Geophagy: who eats soil and where do possible contaminants go?" *Environmental Geology,* vol. 33, pp. 109–114.

[38] J.O. Leckie and R.O. James, 1976, "Control mechanisms for trace metals in natural waters," in A.J. Rubin (ed.), *Aqueous-Environmental Chemistry of Metals* (Ann Arbor, Mich.: Ann Arbor Publishers, Inc.), vol. 1, p. 76; Parametrix, Inc., 1995, *Persistence, Bioaccumulation and Toxicity of*

physical properties of trace metals influence their availability for uptake by biological organisms and their potential to be toxic to organisms, as well as their transport mechanisms in natural waters. For example, fish take up dissolved metals relatively easily, so these metals are more bioavailable than those which are complexed to large organic molecules such as humic acids.

Once trace metals enter natural water systems, they are subject to very complex chemical and biochemical reactions that affect their chemical behaviour and partitioning between the different phases, as indicated in figure 2-1. Interactions of these trace metal ions involve many processes including: exchange reactions, adsorption/desorption processes, and oxidation-reduction reactions.[39]

Figure 2-1 Complex, Heterogeneous Environment of a Natural Water System



Metals and Metal Compounds, prepared for the International Council on Metals and the Environment (Ottawa: International Council on Metals and the Environment).

[39] Leckie and James, 1976; A. Demayo et al., 1978, *Forms of Metals in Water* (Ottawa: Environment Canada, Inland Water Directorate, Water Quality Branch), Scientific Series No. 87.

There are many pathways and transport mechanisms by which trace metals partition between the different components of the environment.[40] Many competing processes interact to determine the movement and fate of metals.[41]

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.[42] 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.[43] The critical role of pH on trace metal speciation has a direct influence on the bioavailability and potential for toxicity of metal contaminants.

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.[44]

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

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[40] R.M. Harrison, 1990, "Cycles, fluxes and speciation of trace metals in the environment," in J.W. Patterson and R. Passino (eds.), *Metal Speciation, Separation and Recovery,* vol. 2 (Boca Raton, Fla..: Lewis Publishers Inc.).

[41] B.D. Honeyman and P.H. Santaschi, 1988, "Metals in aquatic systems," *Environmental Science and Technology,* vol. 22, pp. 862–71; J.F. Elder, 1988, *Metal Biogeochemistry in Surface-Water Systems: A Review of Principles and Concepts* (Denver, Colo.: U.S. Geological Survey), U.S. Geological Survey Circular 1013.

[42] Elder, 1988.

[43] Leckie and James, 1976; T.A. Black et al., 1973, "The significance of physiochemical variables in aquatic bioassays of heavy metals," in G.E. Glass (ed.), *Bioassay Techniques and Environmental Chemistry* (Ann Arbor, Mich.: Ann Arbor Science Publishers, Inc.), pp. 259–75.

[44] J.F. Pankow, 1991a, "Solubility behaviors of simple mineral salts, and metal oxides, hydroxides and oxyhydroxides," *Aquatic Chemistry Concepts* (Chelsea, Mich.: Lewis Publishers Inc.), pp. 219–42.

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 behaviour.[45] 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 sulphate. 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.[46]

Hardness Water hardness is a measure of the amount of dissolved salts in water (especially calcium, magnesium and iron [II]). It has been shown that increasing hardness, usually expressed as equivalents of $CaCO_3$, decreases the 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 of 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. Figure 2-2 shows the effect of alkalinity and hardness on the toxicity of copper to rainbow trout.

Carbonates Dissolved carbon dioxide (CO_2) in water can equilibrate as three carbonate species (H_2CO_3, HCO_3^-, and CO_3^-) depending on the pH of the water. These carbonate species form the main buffering system in natural waters.

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[45] P.C. Singer, 1974, *Trace Metals and Metal-Organic Interactions in Natural Waters* (Ann Arbor, Mich.: Ann Arbor Science Publishers, Inc.).

[46] B. Allard et al., 1987, "The importance of sorption phenomena in relation to trace metal speciation and mobility," in L. Lander (ed.), *Speciation of Metals in Water, Sediment and Soil Systems* (New York: Springer-Verlag); L.I. Bendell-Young and H.H. Harvey, 1992b, "Geochemistry on Mn and Fe in lake sediments in relation to lake acidity," *Limnology and Oceanography*, vol. 37, pp. 603–13.

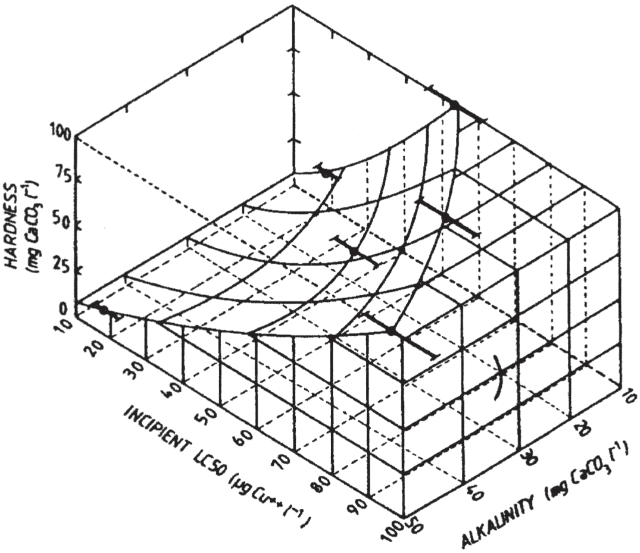
Metals can bond or become coordinated with species in solution such as carbonates.[47]

Since trace metal toxicity depends on its form or speciation, equilibrium concentrations of the carbonate anions influence solution pH and the pH, in turn, has a direct influence on the speciation of the metal. Thus, carbonates help determine the behaviour 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 behaviour 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

Figure 2-2 Effects of Hardness, Alkalinity, and pH on the Toxicity of Copper to Rainbow Trout (*Oncorhynchus mykiss*)



Source: T.G. Miller and W.C. Mackay, 1980, "The effects of hardness, alkalinity, and pH of test water on the toxicity of copper to rainbow trout (*Salmo gairdneri*)," *Water Research*, vol. 14.

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[47] J.F. Pankow, 1991b, "Solubility behavior of metal carbonates in closed systems," in his *Aquatic Chemistry Concepts* (Chelsea, Mich.: Lewis Publishers Inc.).

influence 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.[48] 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.[49]

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 behaviour 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 which 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 that significantly change their toxicity.[50] One such reaction is the methylation of Hg to methylmercury (CH_3Hg) or dimethyl mercury $(CH_3)_2Hg$.[51] 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.

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[48] V.L. Snoeyink and D. Jenkins, 1980, "Oxidation-reduction reactions," *Water Chemistry* (Toronto: J. Wiley & Sons), pp. 316–430.

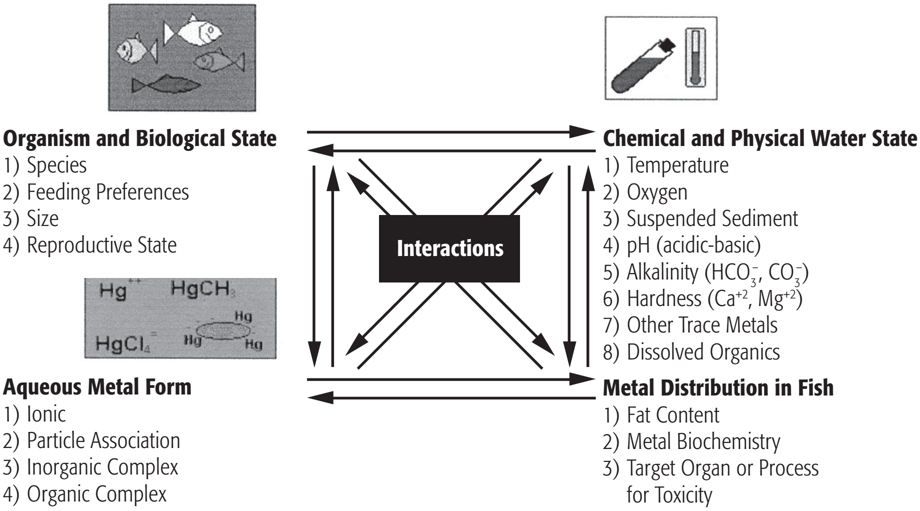
[49] P.G.C. Campbell et al., 1988, *Biologically Available Metals in Sediments*, Associate Committee on Scientific Criteria for Environmental Quality (Ottawa: National Research Council) NRCC no. 27694.

[50] J.E. Fergusson, 1990, "Methyl compounds of the heavy elements," *The Heavy Elements: Chemistry, Environmental Impact and Health Effects* (Toronto: Pergamon Press), pp. 429–57.

[51] A. Jernelöv, 1974, "Factors in the transformation of mercury to methylmercury," in R. Harting and B.D. Dinman, *Environmental Mercury Contamination* (Ann Arbor, Mich.: Ann Arbor Science Publishers, Inc.), pp.167–172.

Summary Trace metal compounds can undergo transformation processes, and this is key to their distribution, environmental fate, and effects within a natural water system. The transport and pathways of trace metal contaminants in watersheds are strongly influenced by the form of the metal in solution. Many trace metal complexes can exist in the environment for very long periods of time in non-bioavailable forms, and thus competing fate processes in receiving environments control the form and species of bioavailable contaminants. Other fate processes that may determine concentrations of bioavailable fractions of trace metal contaminants include: sorption processes, burial, volatility, and physical advection. 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 2-3.

Figure 2-3 Distribution of Trace Metals in the Different Phases of Aquatic Ecosystems



2.2.1.2 *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 influence 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.[52]

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, stormwater 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.[53]

Storage of some waste material or tailings from mine operations in regions where high concentrations of sulphide 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 sulphuric acid that can solubilize metals and potentially compromise the quality of drinking water drawn from surface water or groundwater.[54]

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

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[52] P.E. Rasmussen, 1998, "Long-range atmospheric transport of trace metals: The need for geoscience perspectives," *Environmental Geology,* vol. 33, pp. 96–108.

[53] J. Marsalek and H. Schroeter, 1988, "Annual loadings of toxic contaminants in urban runoff from the Canadian Great Lakes basin," *Water Pollution Research Journal of Canada*, vol. 23, pp. 360–78.

[54] N.F. Gray, 1998, "Acid mine drainage composition and the implications for its impact on lotic systems," *Water Resources,* vol. 32, pp. 2122–34.

anthropogenic complexing agents such as NTA, which can "protect" the metal from some precipitation and adsorption reactions.[55]

The 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.[56] 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.[57] Some of the binding sites hold the contaminants very strongly, while others only hold the contaminants weakly. This illustrates the

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[55] Grout et al., 1999, "Analysis of colloidal phases in urban stormwater runoff," *Environmental Science and Technology*, vol. 33, pp. 831–39; R. Gadh et al., 1991, "Determination of different soluble species in Yamuna River Waters," *Environmental Technology,* vol. 12, pp. 363–69.

[56] Smith and Hamilton, 1992; W.G. Wilber and J.V. Hunter, 1979, "The impact of urbanization on the distribution of heavy metals in bottom sediments of the Saddle River," *Water Resources Bulletin,* vol. 15, pp. 790–800.

[57] Bendell-Young and Harvey, 1992b.

concept of bioavailability. Those contaminants which are weakly held are easily available to organisms and the environment, while those which are strongly bound are not as bioavailable. Therefore, the total concentration of a contaminant in sediment is not indicative of its bioavailability and, consequently, 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.[58] 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, whereas the water would have to become very acidic in order for the trace metals sequestered in the residual phase to become available for uptake by organisms.

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 associated with sediment. Sediments can release some of their contaminant load when environmental conditions change.[59] 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 the occurrence of physical and chemical reactions 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.[60] Complex processes occur at the sediment–water interface that result in fluxes of contaminants between the sediment and the 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.

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[58] Bendell-Young and Harvey, 1992b; A. Tessier et al., 1979, "Sequential extraction procedure for the speciation of particulate trace metals," *Analytical Chemistry,* vol. 51, pp. 844–51.

[59] A. Tessier et al., 1994, "Processes occurring at the sediment-water interface: Emphasis on trace elements," in J. Buffle and R.R. Devitre (eds.), *Chemical and Biological Regulation of Aquatic Systems* (Boca Raton, Fla.: CRC Press), pp. 137–73.

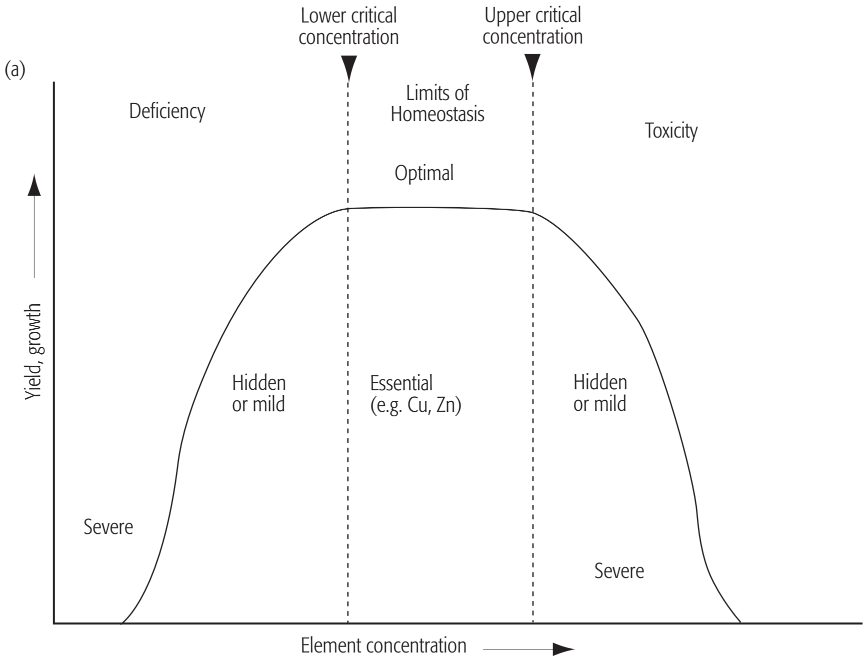
[60] R. Carigan et al., 1985, "Sediment porewater sampling for metal analysis: A comparison of techniques," *Geochemica et Cosmochimica Acta,* vol. 49, pp. 2493–97.

2.2.1.3 *Concentrations of Trace Metals and Effects in the Environment*

Several trace metals are essential to the overall health of organisms at low concentrations and yet have the potential to become toxic to the organism when tolerable concentrations are exceeded. Figure 2-4a illustrates this unique quality of some trace metals. In contrast, some trace metals are non-essential but do not demonstrate toxic effects below a critical threshold concentration (figure 2-4b). The tolerable concentration range between thresholds that satisfy fundamental nutritional requirements and levels above which the element becomes toxic to organisms varies between trace metals.

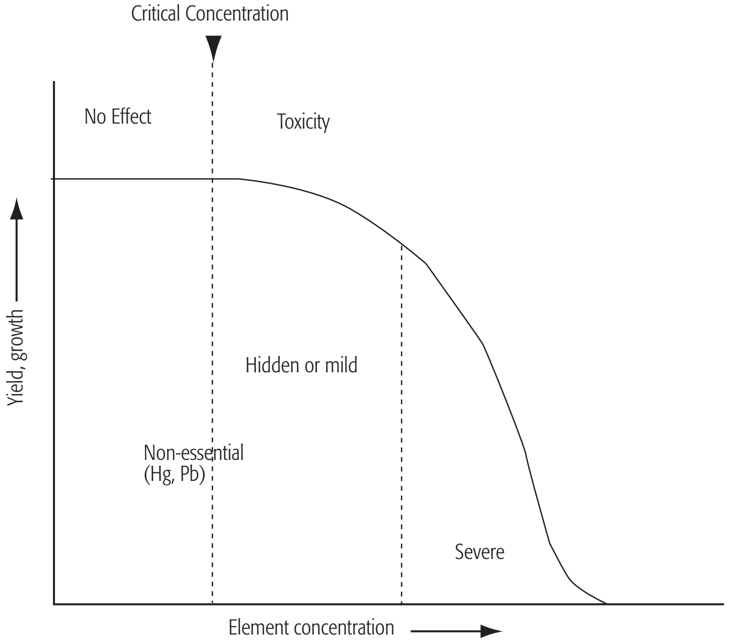
Essential elements such as copper, zinc, nickel, and selenium have played a critical role in the evolutionary development of life. Nature became conditioned to the natural levels of metals present in the environment, but this delicate balance can be disturbed by human input of metals. These essential elements can be toxic at concentrations that are too high, but 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

Figure 2-4a Typical Dose-Response Curve for Essential Metals



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. Non-essential 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. 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

Figure 2-4b Typical Dose-Response Curve for Non-essential Metals



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 2-6. Sediment quality guidelines have recently been developed by CCME and are shown in table 2-7, along with the probable effects level (PEL). The PEL is the concentration at which toxic effects can be expected to occur in aquatic organisms.

Table 2-6 Various Drinking Water Guidelines and Drinking Water Objectives for Trace Metals in μg/L

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

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
^ Interim maximum acceptable concentration (MAC)
a Aesthetic objective
b pH dependent
* Depends on hardness

Sources: Canada, Health Canada, 1996; Canadian Council of Ministers of the Environment, 1995; Ontario, Ministry of the Environment and Energy, 1994.

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 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 four samples out of approximately 1,000. A few water supplies had high copper and lead concentrations, 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 harbours, St. Marys River, Niagara River, and many others. A list is maintained by the EPA at <www.epa.gov/glnpo/sediment/gpra/index.html>.

The following information about the characteristics, sources, environmental concentrations, toxicology, routes of exposure, and effects of the individual

Table 2-7 CCME Sediment Quality Guidelines (mg/kg)

Metal	ISQG	PEL
As	5.9	17.0
Cd	0.6	3.5
Cr	37.3	90.0
Cu	35.7	197
Pb	35.0	91.3
Hg	0.170	0.486
Zn	12.3	315

ISQG Interim sediment quality guidelines
PEL Probable effects level
Sources: Canadian Council of the Ministers of the Environment, 1995.

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 <www.hc-sc.gc.ca/ehp/ehd/catalogue/bch_pubs/dwgsup_doc/dwgsup_doc.htm> along with other valuable water quality information. A good discussion of many of these individual metals can also be found in *Heavy Metals in Natural Waters* by Moore and Ramamoorthy.[61]

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 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 that 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 an average of 0.16 ppm. At these levels, individuals would have to consume over 100 litres 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 ALS, Parkinson's, and Alzheimer's. However, this has neither been proven nor disproven, 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). It can also be a contaminant of other minerals such as pyrite (FeS_2). Arsenic is the twentieth most common element in the earth and the twelfth most common element in the human body. Sources of As include natural weathering of geologic material, especially that found near gold and other metal-rich areas, pesticides, wood preservatives, and smelting. Arsenic is used in semiconductor manufacturing, in pigments, and in glass production, and has many other minor uses.[62]

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

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[61] J. Moore and S. Ramamoorthy, 1984, *Heavy Metals in Natural Waters* (New York: Springer-Verlag).

[62] J.O. Nriagu (ed.), 1994, *Arsenic in the Environment: Part 1: Cycling and Characterization* (Toronto: J. Wiley & Sons).

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.[63]

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 of arsenic. The USA Environmental Protection Agency (EPA) recently concluded an extensive study on As in water and recommended lowering their 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 as the cause of a very common type of skin cancer, along with cancers of 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 g/day 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. In 1972, 560 tons of Cd were emitted into the atmosphere. Much of this is eventually deposited back on the earth's surface while some may be washed into water bodies. 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, most of it being exported. It is used in metal plating, alloys, pigments, and 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.

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[63] W. Cullen and K. Reimer, 1989, "Environmental arsenic chemistry," *Chemical Reviews*, vol. 89.

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 of Cd. Levels found in Lake Erie and Lake Ontario were below 1 ppb in most cases,[64] with a few samples as high as 2 ppb. Cd has been found in Ontario sewage sludge at concentrations between 4 and 9 ppm.[65] 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 non-toxic 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 and 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 and 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. It has also been suggested that smoking makes significant contributions to Cr exposure in humans.[66]

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 were 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.

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[64] J.O. Nriagu et al., 1996, “Dissolved trace metals in lakes Superior, Erie, and Ontario,” *Environmental Science and Technology,* vol. 30, pp. 178–87.

[63] Canada, National Research Council, 1979, *Effects of Cadmium in the Canadian Environment* (Ottawa: National Research Council), NRCC no. 16743.

[64] Canada, National Research Council, 1976, *Effects of Chromium in the Canadian Environment* (Ottawa: National Research Council), NRCC no. 15017.

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 (1,000 g/L), which is set to prevent staining of plumbing fixtures. Much of the Cu found in tap water is due to leaching from copper pipes that are used to distribute water in homes. Studies of tap water 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 manganese 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 g/L for Fe and Mn, respectively) are set to prevent precipitates from forming in pipes and to prevent undesirable tastes and colour.

Lead The average lead (Pb) concentration in the earth's crust is 10 ppm. Lead has many commercial uses. Over 250,000 tonnes of Pb were 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 after 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 non-essential 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 minutes before drinking should significantly decrease the exposure to Pb. Soil, dust, and paint are the major sources of Pb exposure for children. Lead exposure is of particular concern for young children, as the body absorbs a high percentage of Pb, which is thought to impair mental function. Most Pb exposure to humans is through food.[67]

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[67] Canada, National Research Council, 1978, *Effects of Lead in the Canadian Environment* (Ottawa: National Research Council), NRCC no. 16736.

Mercury Mercury (Hg) is a natural and anthropogenic contaminant. It is released naturally from volcanoes and from the weathering of soils. In its elemental state it has a high vapour 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 sulphide 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. Chlor-alkali 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. Until 1960, a plant near Sarnia released up to 90 kg of Hg a day into the water. Creation of hydroelectric reservoirs also results in high Hg concentrations in the water and the fish in the reservoir. This is attributable to mercury release from the decomposing vegetation and soils in the flooded zone.[68] Sang and Lourie reported that 5,138 kg of Hg are released by humans into Ontario's environment each year.[69] 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 estimated that 39 tonnes of Hg were released into the Canadian environment in 1990, half of this from non-ferrous metal production.[70]

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 against the consumption of fish from the Great Lakes have been issued, due to high levels of Hg in the fish. It is a candidate to be banned in the Great Lakes.[71] Hg is not an essential element and causes neurological and renal problems in humans. The alkylated forms are teratogenic, meaning they cause harm to

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[68] G. Mierle and R. Ingram, 1991, "The role of humic substances in the mobilization of mercury from watersheds," *Water, Air, Soil Pollution,* vol. 56, pp. 349–58.

[69] S. Sang and R. Lourie, 1995, "Mercury in Ontario: An inventory of sources, use and releases," in Proceedings of the 1995 Canadian Mercury Network Workshop, workshop held September 29–30, 1995, York University, Toronto.

[70] J.O. Nriagu, 1997, *Origin, Long-range Transport, Atmospheric Deposition, and Associated Effects of Heavy Metals in the Canadian Environment*, prepared for the Atmospheric Environment Service (Downsview: Environment Canada).

[71] Sang and Lourie, 1995.

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 whether excessive amounts 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 as the result of 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, and has numerous other uses. Smelters release significant quantities of Zn into the air. Over 1,000,000 tonnes of Zn were 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 for adults. Unpolluted freshwater usually has less than 15 ppb of Zn. The concentrations of Zn in air are higher in southern Ontario, as compared with northern Ontario. Higher concentrations of Zn were found in precipitation near smelting operations, such as those 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 been discussed above. 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 of Ni is possible in regions such as Sudbury.[72] 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 tributyl tin (TBT) are used as anti-fouling 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.[73]

2.2.1.4 *Exposure to Metals from Sources Other Than Water*

The primary pathways of trace metals to humans are through consumption of food, occupational exposure, smoking, air, and drinking water. Trace metal concentration within food sources is important to humans as dominant members of the food chain. We must realize that we are linked with the environment. Therefore, these sources of exposure are intimately linked and must be considered in any assessment. All watersheds contain background levels of trace metals, and this must be considered in trace metal contaminant assessments. Some other sources of exposure to individual metals are covered in the section above. Many pharmaceutical and therapeutic products also contain metals and may be a significant route of exposure for some individuals.

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[72] J.O. Nriagu et al., 1998, "Saturation of ecosystems with toxic metals in Sudbury basin, Ontario," *The Science of the Total Environment,* vol. 223, pp. 99–118.

[73] L. Randall et al., 1986, "Determination of inorganic tin, methyltin and butyltin compounds in sediments," *Environmental Technology Letters,* vol. 7, pp. 571–76.

2.2.1.5 *Risk Assessment and Management of Metals*

The risk assessment of trace metals and metal compounds requires an understanding of the fundamental differences between inorganic metal compounds and organic compounds. Trace metals have unique attributes that must be considered in all steps of the risk assessment process. Since they are naturally occurring substances that persist over time in altered forms, the risk associated with the toxicity of each trace metal element must be carefully examined in the context of its species, form, and bioavailability. Many metals are essential for the health of organisms, and thus the contamination of waters with non-metallic contaminants that reduce essential trace metal bioavailability is as much of a concern as the excessive loading of trace metal contaminants.

Identification of trace metal exposure hazards relies on information about toxicity, persistence, and the potential to bioaccumulate in an ecosystem food chain. Although toxicity is the universal measure of hazard potential applied to all substances, not all substances demonstrate a toxic response. In the case of metals, this is important because some relatively non-toxic 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.

2.2.1.6 *Conclusions*

Metal contamination of treated drinking water does not appear to be a widespread problem in Ontario, and only lead is found in concentrations that may pose a risk to humans (see section 3 below). However, there are some localized and possible long-term problems in surface waters and sediments. For example, contaminated sediments in some Great Lakes areas continue to be a concern for aquatic ecosystem health. Aesthetic concerns such as high levels of Al, Fe, Mn, salts, and minerals may contribute to public perception of poor water quality.

While metals in water may not have immediate health effects on individuals, the cumulative effects of mixtures of metals and other contaminants, combined with chronic exposure, may lead to health effects in the future. The principal pathways of exposure of metals in Ontario seem to be food or workplace exposure.[74] Human exposure to metals via drinking water is a less significant pathway of exposure. Increasing urbanization and intensive agriculture may be possible sources of metals that should continue to be monitored in the future. Routine monitoring of municipal water supplies should detect elevated metal levels; however, individual well owners should be encouraged to test their wells periodically, especially in areas where high levels of metals may occur.

Possible avenues of further research with metals include investigating the effects of mixtures of metals and mixtures of different classes of contaminants that are routinely found in the environment. Research into metal speciation is increasing and may provide valuable information about routes of exposure and bioavailability.

2.2.1.7 *Petroleum*

There are currently seven petroleum refineries in Ontario. Wastewater discharged from these industries may contain a wide range of organic and metallic pollutants, including phenols, oil and grease, sulphides, ammonia nitrogen, and polycyclic aromatic hydrocarbons (PAHs).[75] Some of these are used or produced during the process of refining, but many are already contained in the crude oil itself.[76] 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.[77] From a human risk perspective, PAHs constitute a significant health concern because some, such as benzo[a]pyrene, have been shown to be carcinogenic. It is important to note that PAHs have been detected in groundwater as the result

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[74] Canada, Health Canada, 2001, *Guidelines for Canadian Drinking Water Quality – Supporting Documents* [online], [cited October 23, 2001], <www.hc-sc.gc.ca/ehp/ehd/catalogue/bch_pubs/dwgsup_doc/dwgsup_doc.htm>.

[75] Canada, Environment Canada, 1996.

[76] Ibid.

[77] R.J. Huggett et al., 1992, "The effects of contaminated sediments in the Elizabeth River," in G.A. Burton Jr., (ed.), *Sediment Toxicity Assessment* (Boca Raton, Fla.: Lewis Publishers), pp. 405–30.

of leaching of oils or creosote from spills, untreated discharges, or poor waste management practices.[78] For example, a common waste disposal method in the petrochemical industry is the use of deep wells (see below). 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. The Goss team found no evidence of petroleum derivatives in well water from wells that were located within at least 60 m of a fuel storage tank on 160 farms.[79] This suggests that there were few incidences of petroleum 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, with its associated PAHs, is the most common contaminant in refinery effluent, but much of this is typically treated and recovered for reuse in the refinery using separators before it enters into the final mill effluent. Sludge produced during this process is treated in the sludge disposal system to produce inert solids for land disposal.[80]

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. It should be noted that the dissolved organics occurring in some effluents are not amenable to biological degradation and require tertiary treatment using activated carbon adsorption or reverse osmosis for removal.[80] A final holding basin downstream of the treatment system allows for

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[78] J.G. Mueller et al., 1989, "Creosote-contaminated sites: Their potential for remediation," *Environmental Science and Technology*, vol. 23, pp. 1197–1201.

[79] Goss et al., 1998.

[80] S. Finelt and J.R. Crump, 1980, "Pick the right water reuse system," in James D. Wall (ed.), *Environmental Management Handbook for the Hydrocarbon Processing Industries* (Houston: Gulf Publishing Company).

[81] M.R. Beychok, 1980, "State-of-the-art wastewater treatment," in James D. Wall (ed.), *Environmental Management Handbook for the Hydrocarbon Processing Industries* (Houston: Gulf Publishing Company).

[82] Ibid.

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.[82]

While making a strong effort to meet regulations by reducing environmental impact, 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*.[83] These regulations limit the amount of oil and grease, phenols, sulphide, ammonia nitrogen, and total suspended matter that can be discharged by a refinery in a 24-hour or month-long period.[84] The 1996 *Compliance Inspection Summary Report* gave a 99% compliance rate for the 84 company reports received.[85] 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.[86] 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 persist over discharges of carcinogenic substances and other potentially toxic metal and organic contaminants to surface waters.[87] Moreover, localized areas of sediment contamination, particularly in some Great Lakes Areas of Concern (e.g., Hamilton Harbour in Ontario and the St. Louis River system in Duluth, Minnesota), continue to store and release hydrocarbon compounds, such as PAHs, contributed historically by the petroleum industry.[88]

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[83] Canada, Environment Canada, 1997, *Ontario Region Compliance Inspection Summary Report 1996/97*, August 14 [online], [cited October 23, 2001], <www.on.ec.gc.ca/glimr/data/summary-report/intro.html>.

[84] Canada, Fisheries and Oceans Canada, 2000b, *Petroleum Refinery Liquid Effluent Regulations* [online], April 30, [cited October 23, 2001], <canada.justice.gc.ca/en/laws/f-14/CRC-c828/index.html>.

[85] Canada, Environment Canada, 1997.

[86] Canada, Environment Canada, 1996.

[87] Ibid.

[88] P.K. Sibley et al., 1999, "An exposure apparatus for the *in situ* assessment of sediment toxicity and bioaccumulation," *Environmental Toxicology and Chemistry,* vol. 18, pp. 2325–36.

2.2.1.8 *Pulp and Paper*

The process of converting wood to fibre produces hundreds of individual compounds that are discharged to surface waters in pulping effluents.[89] 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.[90] 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.[91] However, a significant contaminant was discovered in effluents from plants that used chlorine to bleach pulp: 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.[92]

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.[93] Areas affected in this manner were typically characterized by complete loss of benthic habitat and associated benthic communities.[94] However, considerable research on fish

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[89] J.W. Owens, 1991, "The hazard assessment of pulp and paper effluents in the aquatic environment: A review," *Environmental Toxicology and Chemistry,* vol. 10, pp. 1511–40.

[90] L.R. Suntio et al., 1988, "A review of the nature and properties of chemicals present in pulp mill effluents," *Chemosphere,* vol. 17, pp. 1249–90.

[91] N. Bonsor et al., 1988, *Kraft Mill Effluents in Ontario,* report prepared for Ministry of the Environment [Toronto].

[92] U.S.Environmental Protection Agency, Office of Water, Regulations, and Standards, 1988, *U.S. EPA/Paper Industry Cooperative Dioxin Screening Study* (Washington, D.C.: US EPA), EPA-440/1-88-025; O. Svanberg and B.-E. Bengtsson, 1996, "Impact of bleached pulp mill effluents on the aquatic environment (The Swedish Environment/Cellulose Project) – a case study," *Resource Conservation and Recycling,* vol. 16, pp. 189–99; C.C. Travis and A.G. Nixon, 1996, "Human exposure to dioxin," in R.E. Hester and R.M. Harrison (eds.), *Chlorinated Organic Micropollutants*, the Royal Society of Chemistry, Issues in Environmental Science and Technology series, vol. 6, pp. 17–30.

[93] Owens, 1991.

[94] Canada, Environment Canada, 1987, *Aquatic Toxicity of Pulp and Paper Mill Effluent: A Review* (Ottawa: Environment Canada), report EPS 4.PF/1; G.J. Scrimgeour, 1989, "Effects of bleached kraft mill effluent on macroinvertebrate and fish populations in weedbeds in a New Zealand hydro-electric lake," *New Zealand Journal of Marine and Freshwater Research*, vol. 23, pp. 373–79; Owens, 1991; P.K. Sibley et al., 2000, "Impact of bleached kraft mill effluent on benthic community structure in relation to environmental factors," *Journal of Aquatic Ecosystem Stress and Recovery,* vol. 7, pp. 256–69.

populations in both Sweden and Canada also clearly demonstrated significant biochemical and physiological impacts.[95] 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.[96] 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.[98]

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 pollutant loadings to aquatic environments. At the mills themselves, internal changes (e.g., to in-mill processes such as substituting or eliminating the use of chlorine to bleach pulp) and external changes (e.g., installation of secondary treatment facilities) 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%.[98] At

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[95] M.E. McMaster et al., 1991, “Changes in hepatic mixed-function oxygenase (MFO) activity, plasma steroid levels and age at maturity of a white sucker (*Catostomus commersoni*) population exposed to a bleached kraft pulp mill effluent,” *Aquatic Toxicology,* vol. 21, pp. 199–218; S.M. Adams et al., 1992, “Responses of fish populations and communities to pulp mill effluents: A holistic assessment,” *Ecotoxicology and Environmental Safety*, vol. 24, pp. 347–60; K.R. Munkittrick et al., 1994, “Survey of receiving-water environmental impacts associated with discharges from pulp mills: 2. gonad size, liver size, hepatic EROD activity and plasma sex steroid levels in white sucker,” *Environmental Toxicology and Chemistry,* vol. 13, pp. 1089–1111; J.A. Tana et al., 1994, “Assessing impacts on Baltic coastal ecosystems with mesocosm and fish biomarker tests: A comparison of new and old wood pulp bleaching technologies,” *The Science of the Total Environment,* vol. 145, pp. 213–34; L. Forlin et al., 1995, “Biochemical and physiological effects in fish exposed to bleached kraft mill effluents,” *Ecotoxicology and Environmental Safety,* vol. 30, pp. 164–170; Svanberg, 1996.

[96] McMaster, 1991.

[97] M. Personen and T. Anderson 1992, “Toxic effects of bleached and unbleached paper mill effluents in primary cultures of rainbow trout hepatocytes,” *Ecotoxicology and Environmental Safety*, vol. 24, pp. 63–71; Munkittrick et al., 1994.

[98] Canada, Environment Canada, 1996.

present, as demonstrated by toxicity tests with fish and invertebrates, most pulp mill effluents in Canada are no longer toxic. 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*.

2.2.2 Sewage Treatment and Combined Stormwater 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 centres in Ontario showed that flow volume varied considerably among jurisdictions in relation to precipitation events.[99] For example, in dry weather conditions, flow volumes varied between 17 and 65% for storm water, 1 and 6% for combined sewer overflows, and 35 and 80% for WWTP effluents. However, in wet weather conditions, the flow volume proportions changed to approximately 80%, 7%, and 13% for each source, respectively.

Effluents from WWTPs are derived predominantly from household and industrial sources.[100] The effluent may contain solids, suspended and dissolved

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[99] H.O. Schroeter, 1997, "Toxic contaminant loadings from municipal sources in Ontario areas of concern," *Water Quality Research Journal of Canada*, vol. 32, pp. 7–22.

[100] P.A. Chambers et al., 1997, "Impacts of municipal wastewater effluents on Canadian waters: A review," *Water Quality Research Journal of Canada,* vol. 32, pp. 659–713.

substances that may incur a biological oxygen demand in receiving waters, nutrients, pathogens, organic chemicals, metals, and oil and grease.[101] 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.[102] There is also emerging evidence that WWTP effluents contain numerous pharmaceuticals, the environmental fate and effects of which are virtually unknown.[103] Below, 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 stormwater runoff are treated separately below under non-point source pollution (section 2.3).

2.2.2.1 *Pathogens*

The most significant form of pollution from sewage treatment and combined stormwater overflows is pathogenic. Sewage treatment plants contribute numerous species of potentially infectious agents, including *Salmonella,* coliforms, viruses, and protozoans to surface waters (table 2-8). These pathogens are commonly detected in treated wastewater treatment effluents, often long distances below the point of discharge.[104] Drinking-water intake pipes of

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[101] Ontario, Ministry of the Environment, Water Resources Branch, 1988, *Thirty-seven Municipal Water Pollution Control Plants: Pilot Monitoring Study,* vols. 1 and 2 [Toronto: Ministry of the Environment]; Chambers et al., 1997; J. Li and P. MacAteer, 2000, “Urban oil spills as a non-point pollution source in the Golden Horseshoe of Southern Ontario,” *Water Quality Research Journal of Canada,* vol. 35, pp. 331–40.

[102] D.T. Bennie, 1999, “Review of the environmental occurrence of alkylphenols and alkylphenol ethoxylates,” *Water Quality Research Journal of Canada*, vol. 34, pp. 79–122 ; M.R. Servos, 1999, “Review of the aquatic toxicity, estrogenic responses and bioaccumulation of alkylphenols and alkylphenol polyethoxylates,” *Water Quality Research Journal of Canada,* vol. 34, pp. 123–77.

[103] B. Halling-Sorensen et al., 1998, “Occurrence, fate, and effects of pharmaceutical substances in the environment – a review,” *Chemosphere,* vol. 36, pp. 357–93; B.G. Koenig et al., 2000, “Drugs in sewage treatment plant effluents in Canada,” abstract from the 21st annual meeting of the Society of Environmental Toxicology and Chemistry, Nashville, Tenn., abstract 342.

[104] E.E. Geldreich, 1996, *Microbial Quality of Water Supply in Distribution Systems* (Boca Raton, Fla.: CRC Press).

municipalities located downstream of such effluent discharge points may then draw large 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 USEPA found

Table 2-8 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 poliomyelitis	Human feces
Hepatitis A	Infectious hepatitis	Human feces
Norwalk virus	Gastroenteritis	Human feces
Reovirus	Mild upper respiratory irritation	Human/animal feces
Rotavirus	Gastroenteritis	Human feces
Coxsackie virus	Aseptic meningitis	Human feces
Protozoans		
Balantidium coli	Balantidiasis (dysentery)	Human feces
Cryptosporidium	Cryptosporidiosis	Human/animal feces
Entamoeba histolytica	Amoebic dysentery	Human feces
Giardia lamblia	Giardiasis (gastroenteritis)	Human feces

Sources: V.P. Olivieri, 1986, “Human pathogens, disinfection, and chlorine,” in R.L. Jolley et al. (eds.), *Water Chlorination: Chemistry, Environmental Impact, and Health Effects*, vol. 5 (Chelsea, Mich.: Lewis Publishers Inc.); E.E. Geldreich, 1990, “Microbiological quality of source waters for water supply,” in G.A. McFeters (ed.), *Drinking Water Microbiology* (New York: Springer-Verlag).

that approximately 32% of degraded river miles in U.S. rivers in a nation-wide survey could be attributed to pathogenic pollution.[105] This compares to 51% by siltation and 40% by nutrient enrichment (see table 2-2). 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.[106] 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 below; see also Walkerton Inquiry Commissioned Paper 6 by Goss et al.[107]).

2.2.2.2 ***Nutrients***

Household sewage represents the largest point source discharge of nitrogen and phosphorus to the Canadian environment (table 2-9).[108] However, relative to non-point 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, the Chambers team, in their 1997 article, 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.[109] Indeed, as discussed below, it is not uncommon to observe a relatively high proportion of exceedences of nitrate water quality criteria in rural well waters.[110] 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 below, section 2.3.5.4). They may also impart undesirable tastes and odours in

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[105] United States, Environmental Protection Agency, Office of Water, 1998a, *National Water Quality Inventory: 1998 Report to Congress,* [online], [cited October 23, 2001], <www.epa.gov/305b/98report/toc.html>.

[106] Ibid.

[107] Goss et al., 2002.

[108] P.A. Chambers et al., 2001, *Nutrients and Their Impact on the Canadian Environment*, Agriculture and Agri-Food Canada, Environment Canada, Fisheries and Oceans Canada, Health Canada, and Natural Resources Canada [online], [cited February 2, 2002], <www.durable.gc.ca/group/group7/report/index_e.phtml>.

[109] Chambers et al., 1997.

[110] D.R. Briggens and D. E. Moerman, 1995, "Pesticides and farm well water quality in Kings County, Nova Scotia," *Water Quality Research Journal of Canada*, vol. 30, 443–68; R. Frank et al., 1990, "Survey of farm wells for pesticides, Ontario, Canada, 1986 and 1987," *Bulletin of Environmental Contamination and Toxicology,* vol. 44, pp. 410–419.

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.

2.2.2.3 *Hormonally Active Agents*

In recent years, there has been increasing concern regarding the potentially adverse human and environmental health effects of various contaminants that act on the endocrine system.[111] 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 is provided by Keith;[112] some of these are listed in table 2-10. Toxicological concerns have arisen from evidence that these compounds may, under conditions of high exposure, mimic the action of the female sex hormone, causing

Table 2-9 Comparison of Nitrogen and Phosphorus Loading (103 Tonnes/Year) to Canadian Surface 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
Indusry[1]	11.8	2.0
Agriculture[2]	293	55
Aquaculture	2.3	0.5
Atmospheric deposition to water	182	N/A

[1] Industrial N loads are based on NO3+NH3 and are thus dissolved inorganic nitrogen and not total nitrogen.
[2] 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.

Source: Chambers et al., 2001.

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[111] T. Colborn et al., 1993, "Developmental effects of endocrine disrupting chemicals in wildlife and humans," *Environmental Health Perspectives,* vol. 101, pp. 378–84; Colborn et al., 1996; U.S. National Research Council, 1999.

[112] L.H. Keith, 1997, *Environmental Endocrine Disruptors: A Handbook of Property Data* (New York: Wiley Interscience).

developmental and reproductive effects in wildlife. Strong evidence for such action has been observed among bird populations that feed on contaminated fish.[113] More recently, several studies have demonstrated the potential for endocrine disruption in a wide variety of organisms, ranging from invertebrates to mammals.[114] It is important to note that some scientists have hypothesized that human exposure to hormonally active agents may produce similar effects on reproduction and development and may be involved in the increasing incidence of breast cancer in human populations.[115] Further, dietary exposure to PCBs has been correlated with intellectual deficits in children who have been breast-fed in some Great Lakes areas.[116]

Table 2-10 Estrogenic Potencies of Some Common Xenoestrogens, Relative to 17-β Estradiol (e2)

		Vitellogenin Induction	
Compound	**LOEC[1] μM**	**Maximum % of Max E2**	**Potency Relative to E2**
17-β estradiol	0.002	100	1
Diethylstilbestrone (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[2]	ND	ND
Toxaphene	ND	ND	ND
β Endosulphan	ND	ND	ND
Dieldrin	ND	ND	ND

1 Lowest Observed Effect Concentration – see glossary for definition.
2 Not Detected.
Source: Smeet et al., 1999.

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[113] G.A. Fox, 1992, "Epidemiological and pathobiological evidence of contaminant-induced alterations in sexual development in free-living wildlife," in T. Colborn and C. Clement (eds.), *Chemically-Induced Alterations in Sexual and Functional Development: The Wildlife-Human Connection* (Princeton, N.J.: Princeton Scientific Publishing), pp. 147–58; J.P. Giesy et al., 1994, "Deformities in birds of the Great Lakes region: Assigning causality," *Environmental Science and Technology*, vol. 28, pp. 128A–35A.

[114] U. S. National Research Council, 1999.

[115] D.L. Davis et al., 1993, "Medical hypothesis: Xenoestrogens as preventable causes of breast cancer," *Environmetal Health Perspectives*, vol. 101, pp. 372–77.

[116] 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.[117] However, concentrations of 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.[118] 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.

2.2.2.4 *Pharmaceuticals*

Despite widespread use in numerous sectors of society, until recently, pharmaceuticals (or medical substances) have received little attention as potential contaminants in drinking water. However, considerable evidence is emerging that pharmaceutical compounds are relatively widespread in the surface waters of many countries, especially in water bodies receiving effluent from sewage treatment facilities.[119] In most cases, the concentrations of pharmaceuticals in surface waters occur in the ng/L to g/L 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

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[117] M.O. James and K.M. Kleinow, 1994, "Trophic transfers of chemicals in the aquatic environment," in D.C. Mallins and G.K. Ostrander (eds.), *Aquatic Toxicology: Molecular, Biochemical, and Cellular Perspectives* (Boca Raton, Fla.: Lewis Publishers), pp. 1–35.

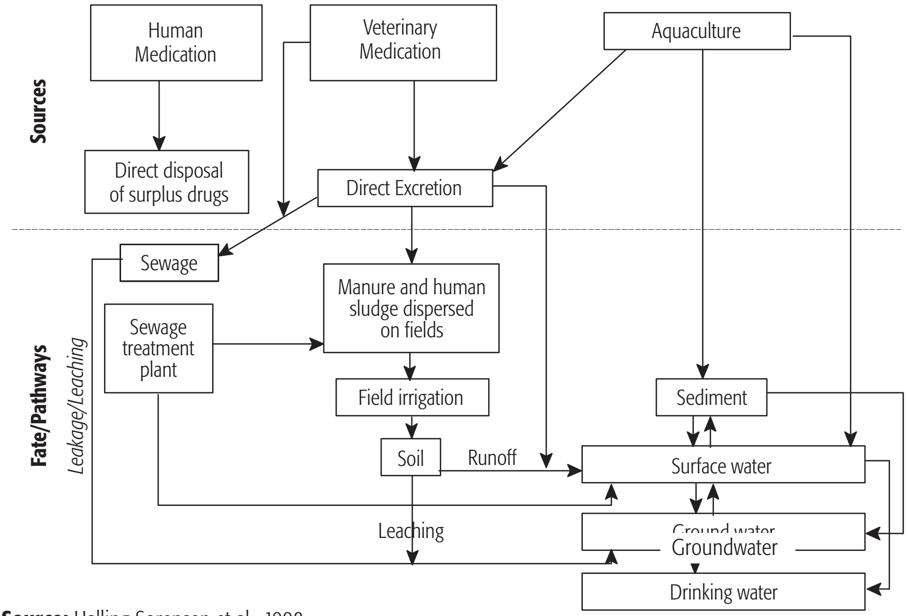
[118] R. Pearson et al., 1996, "PCBs in Lake Michigan water revisited," *Environmental Science and Technol*ogy, vol. 30, pp. 1429–36; D.T. Bennie et al., 1997, "Occurrence of alkylphenols and alkylkphenol mono- and diethoxylates in natural waters of the Laurentian Great Lakes basin and upper St. Lawrence River," *The Science of the Total Environment,* vol. 193.

[119] Halling-Sorensen, 1998; H.R. Buser et al., 1999, "Occurrence and environmental behavior of the chiral pharmaceutical drug Ibuprofen in surface waters and in waste water," *Environmental Science and Technology,* vol. 33, pp. 2529–35; Daughton, 1999.

are remote from points of sewage discharge,[120] 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 2-5. In Ontario, sewage treatment plants are probably the primary source of pharmaceuticals in surface waters, and many have been detected in sewage discharges.[121] However, it is likely that pharmaceuticals will also be detected in other aquatic matrices in Ontario, as they have been in other countries. For example, pharmaceuticals have been detected in groundwater via leachates from landfill sites[122] and in sediments in conjunction with aquacultural practices.[123] In the latter source, those antibiotics administered

Figure 2-5 Sources and Pathways of Pharmaceutical Compounds in Aquatic Environments



Source: Halling-Sorensen et al., 1998.

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[120] Daughton, 1999.

[121] Koenig et al., 2000.

[122] W.P. Eckel et al., 1993, "Pentobarbital found in ground water," *Ground Water,* vol. 31, pp. 801–04; J.V. Holm et al., 1995, "Occurrence and distribution of pharmaceutical organic compounds in the groundwater down-gradient of a landfill (Grinsted, Denmark)," *Environmental Science and Technology,* vol. 29, pp. 1415–20.

[123] P. Jacobsen and L. Berglind, 1988, "Persistence of oxytetracycline in sediments from fish farms," *Aquaculture*, vol. 70, pp. 365–70; J. Kerry et al., 1995, "Fish feed as a source of oxytetracycline-resistant bacteria in the sediment under fish farms," *Aquaculture,* vol. 131, pp. 101–13.

to fish which 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 the spreading of manure. The same situation may exist in relation to the 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.[124] Interestingly, the Hirsch team found little evidence of groundwater contamination by pharmaceuticals in areas influenced by agriculture or when sewage was applied to fields.[125]

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.[126] 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.[127] 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.

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[124] Halling-Sorensen et al., 1998.

[125] R. Hirsch et al., 1999, "Occurrence of antibiotics in the aquatic environment," *The Science of the Total Environment,* vol. 225, pp. 109–18.

[126] H.J. Stan et al., 1994, "Occurrence of clofibric acid in the aquatic system – Is the use in human medical care the source of the contamination of surface, ground, and drinking water?" *Vom Wasser,* vol. 83, pp. 57–68.

[127] J. Kerry et al., 1995; K. Kummerer, 2000, "Health risk potential from drinking water polluted with domestic sewage and excreta: Drugs, diagnostic agents, and disinfectants in waste water," *Schrift des Ver Wasser Boden und Lufthyg,* vol. 15, pp. 59–66.

2.2.3 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.[128] Water may be disinfected using a number of treatment methods:[129] (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 used only for short-term disinfection), (5) ozonation, in which water is injected with ozone to destroy organic compounds that impart taste or odour to drinking water, and (6) irradiation with ultraviolet 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. A common perception that the latter methods are too expensive to operate makes many municipalities reluctant to incorporate either of them as the sole method to control pathogens in their treatment systems. Although issues associated with the treatment and disinfection of water are considered extensively in separate Walkerton Inquiry Commissioned Papers by Doyle et al.,[130] 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.[131] 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

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[128] Naiman et al., 1995.

[129] World Health Organization, 1993, *Guidelines for Drinking-water Quality: Volume 1, Recommendations,* 2nd ed. (Geneva: WHO).

[130] E. Doyle et al., 2002a, *Production and Distribution of Drinking Water* (Toronto: Ontario Ministry of the Attorney General), Walkerton Inquiry Commissioned Paper 8, Walkerton Inquiry CD-ROM, <www.walkertoninquiry.com>; E. Doyle et al., 2002b, *Wastewater Collection and Treatment* (Toronto: Ontario Ministry of the Attorney General), Walkerton Inquiry Commissioned Paper 9, Walkerton Inquiry CD-ROM, <www.walkertoninquiry.com>.

[131] D.G. Crosby, 1998, *Environmental Toxicology and Chemistry* (New York: Oxford University Press).

residual organic matter generally occurs at higher concentrations in surface waters than in groundwater, the formation of DBPs 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 DBPs also depend upon the chlorine dose, pH, temperature, contact time, and bromide ion concentration.[132] A list of the DBPs identified from a national survey conducted in Canada in 1993 is provided in table 2-11.

There are three main classes of DBPs in drinking water that present potential risks to human health (table 2-5 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).[133] Of the several phenolic DBPs produced during chlorination, 2,4,6 trichlorophenol has been reported to induce lymphomas, leukemia, and hepatic tumours 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.[134] However, the evidence in support of the association between bladder cancer and DBPs is considered to be inadequate by the International Agency for Research on Cancer.[135] 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.

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[132] A.A. Stevens et al., 1989, "Formation and control of non-trihalomethane disinfection by-products," *Journal of the American Water Works Association,* vol. 81, pp. 54–60.

[133] World Health Organization, 1993.

[134] C.J. Mills et al., 1999, "Health risks of drinking water chlorination by-products: Report of an expert working group," *Chronic Diseases in Canada,* vol. 19, pp. 91–102.

[135] World Health Organization, 1993.

Table 2-11 Identity and Ranges of Concentrations for Disinfection By-products (DBPs) Analyzed in Treated Water (Immediately Prior to Distribution)

Disinfection By-product	**MAC[1] or IMAC (Canada)**	**WHO[2,3] Guideline (µg/L)**	**IARC Designation[4]**	**Concentration Range (µg/L)[5]**	
				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 DBPs					
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

[1] MAC = Maximum Allowable Concentration; IMAC = Interim MAC

[2,3] From WHO (1996). Level determined as the concentration of drinking water associated with a life-time cancer risk of 10^{-5}.

[4] 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.

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

Source: Canada, Health Canada, 1995.

Dichloroacetic acid has been used pharmaceutically and has been shown to induce hepatic tumours in mice; however, evidence in support of cancer in humans is considered to be insufficient.[136] Trichloracetic acid has been used as a herbicide and the acetate form has been found to induce hepatic tumours 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 g/L, respectively.

Debates on the merits and potential risks of chlorination versus other forms of disinfection have been prevalent for many years in scientific and trade journals and in public fora. The refusal by the people of Erickson, British Columbia, to chlorinate their water supply is testimony to the intensity and passion aroused by the subject. The issues surrounding DBPs illustrate the relative nature of risk: although both chlorination and non-chlorination pose inherent risks to human health, failing to treat water is generally deemed to hold greater risk than disinfecting water. Indeed, in most jurisdictions, the failure to treat water in some manner is recognized to have significant human health risks, most notably 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.[137] However, where local circumstances require that a choice be made between meeting either microbiological quality or guidelines for disinfectants or disinfectant by-products, microbiological quality must always take precedence.[138] In the absence of new, risk-free technologies for water disinfection, the challenge, therefore, is to manage water disinfection in a manner that maximizes the reduction of risk without compromising disinfection efficiency.[139]

Although not a disinfection by-product per se, fluoride is another commonly encountered halogen in drinking water. As with chlorine, the addition of fluorine to water has been a matter of public controversy. Fluoride, a widespread, naturally occurring element, accounts for approximately 0.3 g/kg of the earth's crust and occurs widely in surface waters.[140] Although fluoride can be obtained

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[136] World Health Organization, 1993.

[137] Ibid.

[138] Ibid.

[139] Canada, Health Canada, 1996, *A One-year Survey of Halogenated Disinfection By-products in the Distribution Systems of Treatment Plants Using Three Different Disinfection Processes* (Ottawa: Health Canada), Report 960-EHD-206.

[140] World Health Organization, 1993.

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.[141] 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.[142] 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.[143]

2.2.4 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.[144] Numerous historical examples have been documented of how, throughout North America, waste disposal practices have led to significant contamination of groundwater resources. The most significant environmental problem associated with waste disposal is leaching of contaminants into groundwater (figure 2-6). These leachates typically comprise 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.[145] In the 1980s, a Canadian study of groundwater contamination showed that 60% of contaminated sites resulted from landfills, industrial waste sites, septic systems, deep-well injection of wastes; over 20% resulted from underground leaking storage tanks, spills, aboveground material storage, and other industrial operations.[146] Cherry and Harmon examined 92 groundwater sites reputed to be contaminated by organic chemicals; this represented only a small fraction of the estimated number of existing sites.[147] Although more recent containment systems are generally constructed using elaborate leak prevention systems, there are still significant

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[141] Canada, Health Canada, 1996; World Health Organization, 1993.

[142] Crosby, 1998, *Environmental Toxicology and Chemistry* (New York: Oxford University Press).

[143] World Health Organization, 1984, *Fluorine and Fluorides* (Geneva: WHO), Environmental Health Criteria 36.

[144] Miller, 1980; Jorgensen, 1989.

[145] Canada, Environment Canada, 1996.

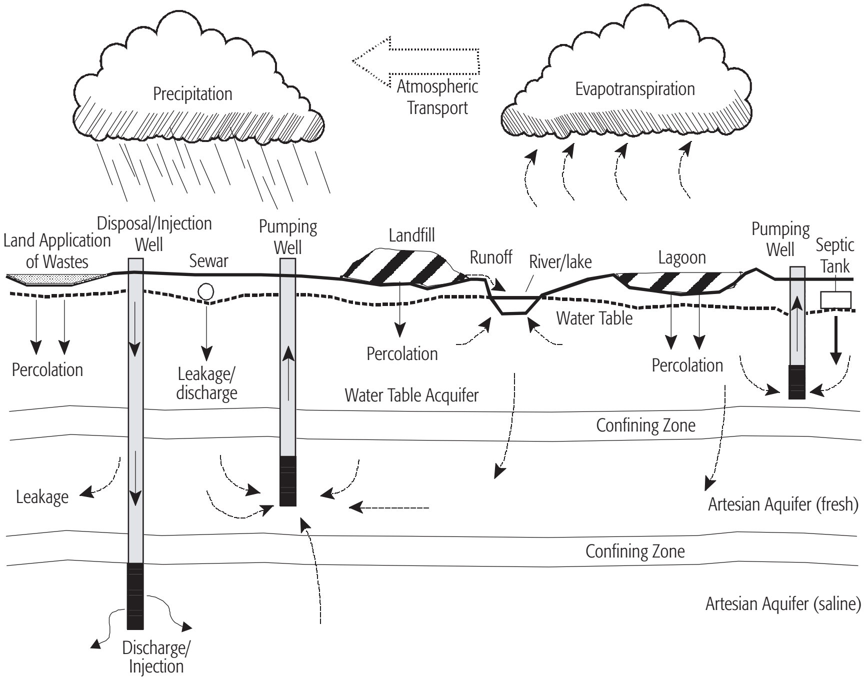
[146] Canada, Statistics Canada, 1994, *Human Activity and the Environment 1994* (Ottawa: Industry Canada).

[147] J.A. Cherry and J. Harmon, 1994, “Organic chemicals in Canadian groundwater,” *Hazardous Materials Management,* vol. 6, 47–49.

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.[148] 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.[149] Sources and pathways of contaminants from landfills, leachates, and containment systems are considered briefly below; other aspects are also discussed in detail elsewhere in this paper.

Figure 2-6 Sources of Contaminants to Groundwater and Surface Water via Landfills, Leachates, and Disposal Wells



Source: Miller, 1980.

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[148] Jorgensen, 1989.

[149] Miller, 1980; J.S. Devinny, 1990, "The composition of hazardous waste," in J.S. Devinny et al. (eds.), *Subsurface Migration of Hazardous Wastes* (New York: Van Nostrand Reinhold), pp. 15–39; S.R. Qasim and W. Chiang, 1994, *Sanitary Landfill Leachate: Generation, Control, and Treatment*, (Lancaster, Pa.: Technomic Publishing); K.L. Shah, 2000, *Basics of Solid and Hazardous Waste Management Technology* (Columbus, Ohio: Prentice Hall).

2.2.4.1 *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.[150] 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.[151]

Once treated, the liquid waste is primarily discharged to local surface waters; residual waste solids resulting from the waste treatment process are incinerated, or applied to land (this is common for solid waste material from municipal, agricultural, and some pulp and paper waste treatment), or sent to a landfill 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; some of these were discussed in greater detail above.

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.

2.2.4.2 *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.[152] When leaks (referred to as LUSTs) occur in these tanks due to age, neglect, or improper maintenance, there is significant potential for widespread groundwater contamination. For example, a single litre of

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[150] Miller, 1980.

[151] Jorgensen, 1989; Shah, 2000.

[152] J.S. Devinny and J.C.S. Lu, 1990, "Introduction," in J.S. Devinny et al. (eds.), *Subsurface Migration of Hazardous Wastes* (New York: Van Nostrand Reinhold), pp. 15–39; Swaigen, 1995.

gasoline leaked from a underground storage tank can contaminate up to one million litres of groundwater.[153] 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.[154] Based on the assumption that Ontario has approximately 17% of the gas stations in Canada,[155] there are potentially between 1,700 and 3,400 leaking tanks in the province of Ontario.

From both an environmental and a human health perspective, the primary toxicological concern with underground storage tanks 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.[156] The other three compounds are currently regulated on the basis of aesthetic objectives (taste and odour) and have no established maximum allowable concentrations in drinking water in Canada[157] or Ontario.[158]

2.2.4.3 *Landfills an d 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.[159] 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.[160]

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[153] Canada, Fisheries and Oceans Canada, 2000b, *Petroleum Refinery Liquid Effluent Regulations* [online], April 30, [cited October 23, 2001], <canada.justice.gc.ca/en/laws/f-14/CRC-c828/index.html>.

[154] Swaigen, 1995.

[155] Ibid.

[156] Canada, Health Canada, Federal-Provincial Subcommittee on Drinking Water, 1996, *Guidelines for Canadian Drinking Water Quality.* 6th ed. (Ottawa: Health Canada), Cat. # H48-10/1996E.

[157] Ibid.

[158] J.-D. Phyper and B. Ibbotson, 1994, *The Handbook of Environmental Compliance in Ontario,* 2nd ed. (Ontario: McGraw-Hill Ryerson), pp. 90–93 and 102–104.

[159] Miller, 1980.

[160] Ibid.

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.[161] 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 be of concern 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 detected in the water and biota throughout the Niagara River have been traced to leachates from hazardous waste dump sites located adjacent to the river in New York.[162] These compounds eventually find their way into Lake Ontario and undoubtedly into the influent water abstracted by water treatment facilities to supply municipalities with drinking water.

2.2.4.4 *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.[163] For this reason, potential risks to human health from this source are predominantly associated with the 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, there may also be significant local odour problems. Nitrates in groundwater may also constitute a significant problem (nutrients are discussed in greater detail below), although it is not known how much these originate in septic systems rather than other sources. Potential risks to human health are greatest in rural areas, where bacterial contamination of drinking water extracted from private wells may occur. For example, in 1995, Goss and Barry reported that approximately one-third of

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[161] Qasim and Chiang, 1994.

[162] Canada, Environment Canada, 1996.

[163] Miller, 1980.

the wells on 1,200 rural farms were contaminated with bacteria.[164] However, in rural areas, it is often difficult to tell whether contamination was due to runoff and leaching of animal manure or to faulty septic systems.[165] If septic systems are properly maintained, bacterial contamination of groundwater can be negligible.[166] Interestingly, in 1993, Rudolph and Goss found no significant correlation in the proximity of a well head to the septic tank or weeping bed at distances up to 300 feet in rural areas.[167]

2.2.4.5 *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 more common and can represent an environmentally responsible method of disposing of residual waste materials and recycling nutrients to the soil.

Municipal (sewage treatment) and industrial sludge is the residual material that remains after treatment of wastewater. In agriculture, farmers have applied residual waste materials from both municipal (human wastes) and farming (animal wastes) origins for many years. With the use of one of several best management practices, residual waste materials can be applied in a manner that minimizes losses via runoff and leaching, thereby ensuring the maintenance of environmental quality. 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 farm 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.

2.2.4.6 *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,

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[164] M.J. Goss and D.A.J. Barry, 1995, "Groundwater quality: Responsible agriculture and public perceptions," *Journal of Agricultural and Environmental Ethics*, vol. 8, pp. 52–64.

[165] M.J. Conboy and M.J. Goss, 1997, "Is *Escherichia coli* an effective predictor of health risks and source of water contamination for rural populations?" *Toxicology and Exotoxicology News*, vol. 4, pp. 156–157.

stormwater, and agricultural drainage.[168] The primary concern with disposal wells is the contamination of groundwater aquifers. Drainage wells are particularly common in agriculture, where they are used to remove surface and subsurface drainage and maintain favourable soil moisture levels.[169] However, they may also channel agricultural contaminants, such as pathogens and nutrients, directly into underground aquifers[170] that 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 litres) of industrial waste are disposed of annually in deep injection wells,[171] a practice that has resulted in the contamination of groundwater supplies in a number of jurisdictions.[172] Comparable statistics for Ontario and Canada could not be found, although this technology for waste disposal is used both nationally and provincially.

A common form of disposal well is the deep injection well, principally used by industry to dispose of hazardous wastes and popular because of its relatively low cost.[173] As the name implies, deep disposal wells are drilled deep into the ground, often between 1,000 and 6,000 feet, to the point at which an appropriate geological formation for holding the wastes can be located.[174] Such a formation usually consists of permeable, brackish sandstone or limestone/dolomite deposits confined by layers of relatively impermeable geological deposits.[175] The water associated with these deposits is characteristically saline and unpotable. In most situations, disposal of wastes using deep disposal wells can be practised safely. However, chemicals contained in the waste material

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[166] P. Seyfried and D. Joy, 1995, "Pathogenic viruses in septic systems and their removal," in *Alternative Systems: Nutrient Removal and Pathogenic Microbes*, conference proceedings, Septic System Conference (Waterloo, Ont.: Waterloo Centre for Groundwater Research, University of Waterloo), pp. 5–15.

[167] Goss, 1998.

[168] Miller, 1980.

[169] G.A. Tobin and R. Rajagopal, 1990, "Expert opinion and groundwater quality: The case of agricultural drainage wells," *Journal of Soil Water Conservation,* vol. 45, pp. 341–36.

[170] J.L. Baker et al., 1985, "Impact of agricultural drainage wells on groundwater quality," *Journal of Soil Water Conserv*ation, vol. 40, pp. 516–20; Tobin and Rajagopal, 1990.

[171] L.H. Wickstrom and M.T. Baranoski, 2000, "Industrial waste disposal wells in Ohio," Ohio Department of Natural Resources, Division of Geological Survey [online], [cited February 5, 2002], <www.dnr.state.oh.us/geosurvey/gen/environment/Class1a.htm>.

[172] Jorgensen, 1989.

[173] Ibid.

[174] Shah, 2000.

[175] Jorgensen, 1989.

may enter into useable groundwater supplies through small cracks and fissures in the well casings or the geological formation itself if the latter were 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.

2.2.4.7 *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.[176] In these areas, the principal problem has been contamination of surface waters via direct discharge of saline effluent waters or contamination of groundwater via leaching of the effluent from unlined pits. Occasionally, metals may also be present in the brine solutions and may 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.[177] However, in the United States, deep disposal wells (see above) 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.[178] 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. Further discussion of the petroleum industry, and its relationship to surface water and groundwater contamination, is provided above under industrial sources of contamination.

2.2.4.8 *Disposal of Animal Feedlot Wastes*

Issues related to the sources and pathways of contaminants associated with animal wastes are described in separate sections above and below. For additional information on this subject, the reader is referred to the Goss team's Walkerton Inquiry Commissioned Paper 6[179] and the book by Miner et al.[180] Given recent concerns over the construction of so-called factory farms and the disposal of

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[176] Miller, 1980.

[177] Ibid.

[178] Shah, 2000.

[179] Goss et al., 2002.

[180] J.R. Miner et al., 2000, *Managing Livestock Wastes to Preserve Environmental Quality* (Ames, Iowa: Iowa State University Press).

the large volumes of animal waste generated from such farms, it is likely that pathogenic and nutrient contamination related to the management of feedlot wastes will continue to be issues for some time.

2.2.4.9 *Abandoned/Poorly Constructed Wells*

An area of potentially significant, yet little understood, groundwater contamination is that originating from abandoned and poorly constructed wells. In Ontario, there may be as many as 100,000 abandoned wells. These, along with existing, older wells, which may be poorly constructed and do not meet current standards, represent a direct conduit for contaminants to groundwater.[181] Indeed, in a study of Nebraska wells, Exner and Spaulding in 1985 found a strong correlation between well construction quality and the likelihood of groundwater contamination.[182] In most cases, the greatest environmental and human health concerns involve 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, and thus cannot be plugged as stipulated in current regulations (regulation 903 pursuant to the *Ontario Water Resources Act*).[183] Moreover, the cost of plugging and/or repairing poorly constructed wells may be high (up to $10,000), so owners often lack the incentive to report existing wells that are no longer in service or to repair those requiring it.

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

- Optimal placement on the land surface. Avoid low spots and keep away from contaminant sources, such as pesticide storage areas or treated fields.

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[181] Gustafson, 1993.

[182] M.E. Exner and R.F. Spaulding, 1985, "Groundwater contamination and well construction in southeast Nebraska," *Ground Water,* vol. 23, pp. 26–34.

[183] See also Ontario, Ministry of the Environment, 1998, "Water wells and groundwater: Recommended methods for plugging abandoned water wells, *Green Tips*, [Toronto: Ministry of the Environment.] 1M-09-98; Ontario, Ministry of Agriculture, Food, and Rural Affairs, 1998, "Water wells," Infosheet #2 [online], [cited October 23, 2001], <www.gov.on.ca/OMAFRA/english/environment/EFP/efp2-water_wells.htm>.

- 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.

- 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.[184]

2.3 Non-point Sources of Contamination

2.3.1 Agriculture

Agriculture constitutes the most important non-point 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 (see table 2-2).[185] However, pesticides and nutrients can also have significant impacts on ecosystem structure and function in regions of intense agriculture, where they may either be toxic to water and sediment-dwelling organisms or promote eutrophication and habitat degradation.[186] 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 non-point agricultural impacts on aquatic ecological integrity at higher geographical scales, including

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[184] Gustafson, 1993.

[185] J.R. Karr et al., 1985, "Fish communities of mid-western rivers: A history of degradation," *BioScience,* vol. 35, pp. 90–95; C.F. Rabeni and M.A. Smale, 1995, "Effects of siltation on stream fishes and the potential mitigating role of the buffering riparian zone," *Hydrobiologia,* vol. 303, pp. 211–19; Waters, 1995.

[186] B.K. Ferguson, 1994, *Stormwater Infiltration* (Boca Raton, Fla.: CRC Press); M.E. Fenn et al., 1998, "Nitrogen excess in North American ecosystems: Predisposing factors, ecosystem responses, and management strategies," *Ecological Applications*, vol. 8, pp. 706–33; R. Schultz and M. Liess, 1999, "A field study of the effects of agriculturally-derived insecticide input on stream macroinvertebrate dynamics," *Aquatic Toxicology,* vol. 46, pp. 155–76.

catchment, watershed, and landscape perspectives.[187] Approaches that incorporate higher levels of scale may be particularly useful in assessing and managing risks to ecosystem integrity associated with non-point 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 is considered in greater detail below.

2.3.1.1 *Pathogens*

Because pathogens in animal wastes and in drinking water is well researched, we provide only a brief contextual description of pathogenic pollution in relation to agricultural activities and potential human health risks.[188]

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:O157 variant of *E. 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

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[187] C. Richards et al., 1993, "Identification of predominant environmental factors structuring stream macroinvertebrate communities within a large agricultural catchment," *Freshwater Biology,* vol. 29, pp. 285–94; J.D. Allan et al., 1997, "The influence of catchment land use on stream integrity across multiple scales," *Freshwater Biol*ogy, vol. 37, pp. 149–61; L.B. Johnson and S.H. Gage, 1997, "Landscape approaches to the analysis of aquatic ecosystems," *Freshwater Biology*, vol. 37, pp. 113–132; J.S. Harding et al., 1999, "Changes in agricultural intensity and river health along a river continuum," *Freshwater Biology,* vol. 42, pp. 345–57; M. Lammert and J.D. Allan, 1999, "Assessing biotic integrity of streams: Effects of scale in measuring the influence of land use/cover and habitat structure on fish and macroinvertebrates," *Environmental Management*, vol. 23, pp. 257–70; *see also* L.A. Kapustka, ed., 2000, "Ecosystem vulnerability," *Environmental Toxicology and Chemistry*, vol. 19, Special Issue, no. 4, part 2 (April).

[188] The origin, transport, and management of pathogens associated with animal wastes and agriculture are reviewed by Goss et al., 2002. Further information on pathogens in farm animal wastes may also be obtained from Miner et al., 2000. Information on pathogens in drinking water in Ontario may be obtained from Geldreich, 1996; Conboy and Goss, 1997, and Conboy and Goss, 1999, "Contamination of rural drinking water wells by fecal origin bacteria – survey findings," *Water Quality Research Journal of Canada*, vol. 34; Goss et al., 1998; and Rudolph et al., 1998, "Contamination in Ontario farmstead domestic wells and its association with agriculture. 2. Results from multilevel monitoring well installations," *Journal of Contaminant Hydrology*, vol. 32.

private wells via surface runoff or groundwater. Below-grade or poorly sealed wells are particularly susceptible to contamination via surface runoff; whereas old, deteriorated, or poorly constructed wells 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 revealed relatively high levels of bacterial contamination. For example, Conboy and Goss 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.[189] This study showed the association of bacterial contamination with an increase in the proportion of individuals experiencing diarrhea; no other illnesses were noted and the greater incidence of diarrhea did not increase the number of visits to the hospital. Interestingly, between the early 1950s and the mid-1990s there has been a significant rise in the number of wells with *E. coli* contamination.[190]

2.3.1.2 *Pesticides*

Pesticides have been used widely to control pests in agriculture since the 1950s. Many of the early pesticides were chlorinated organics (e.g., DDT, chlordane, dieldrin) that were subsequently discovered to have serious environmental effects, including significant risks to human health, due to their propensity to bioaccumulate. These problems were brought to the attention of the public by Rachel Carson in her book *Silent Spring*, and with it the environmental movement was born.[191] 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 section 2.3.2 on atmospheric transport below). Moreover, there has been renewed concern about the potential risks of these persistent pesticides 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.[192]

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[189] Conboy and Goss, 1999.

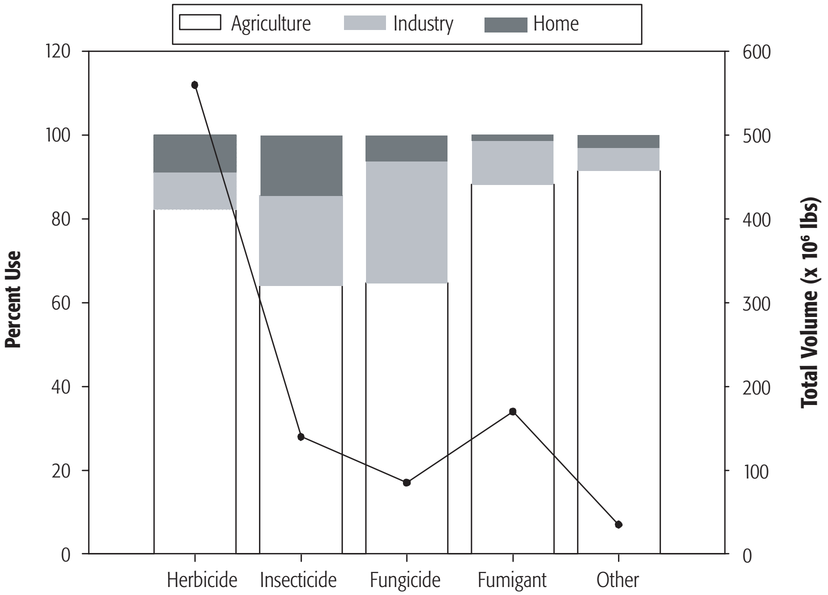
[190] Ibid.

[191] R. Carson, 1962, *Silent Spring* (New York: Houghton Mifflin).

[192] U.S. National Research Council, 1997, *Contaminated Sediments in Ports and Waterways: Cleanup Strategies and Technologies* (Washington, D.C.: National Academy Press).

Today, pesticides continue to be an integral component of crop protection and pest management. In both Canada and the United States, most pesticide use (about 80%) occurs in agriculture (figure 2-7). Other sources include forestry and household applications (these are discussed in greater detail below). From all sources, the quantity of pesticides applied annually in the United States is approximately 500,000 kg, a trend that has been relatively stable since 1978.[193] In Canada, 70% of pesticides applied in agriculture are herbicides; these were applied to approximately 8.7 million hectares in 1990.[194] In Ontario, Hunter and Magee found that pesticide use decreased from 7,200 t to 6,200 t of active ingredient between 1988 and 1993.[195] Among major pesticide classes, herbicide use has increased significantly since the 1960s in both Canada and the United States.[196] Over this same 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

Figure 2-7 Relative Proportion of Pesticides by Use in the United States



Line graph = total volume of pesticide used as shown on right axis.
Bar graph = % of pesticide class used in each category shown on left axis.
Source: Nowell et al., 1999.

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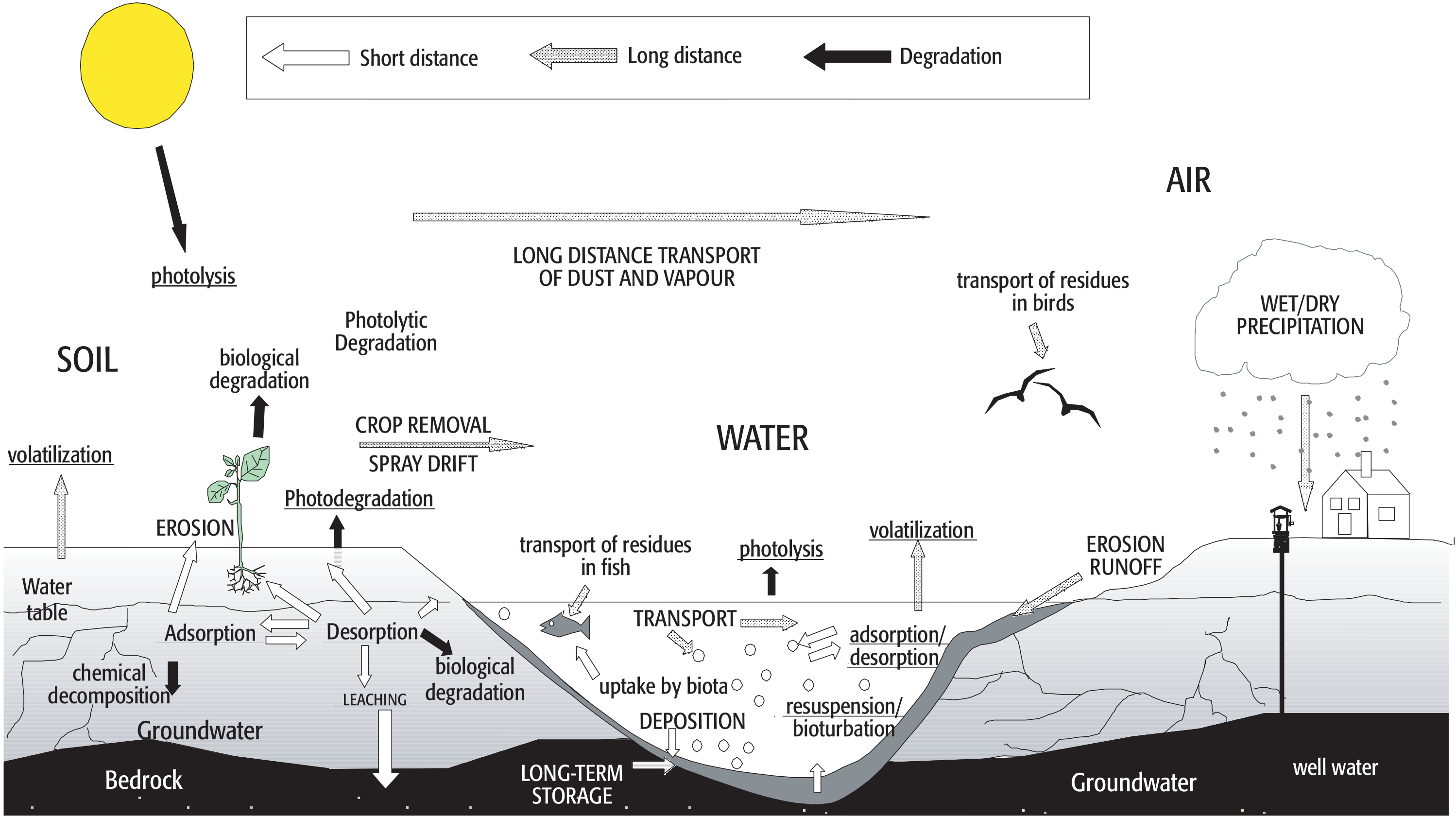
[193] L.H. Nowell et al., 1999, "Pesticides in stream sediment and aquatic biota: Distribution, trends, and governing factors," *Pesticides in the Hydrologic System*, vol. 4 (New York: Lewis Publishers).
[194] Canada, Environment Canada, 1996.
[195] C. Hunter and B. McGee, 1994, *Survey of Pesticide Use in Ontario, 1993* (Toronto: Ontario Ministry of Agriculture, Food and Rural Affairs), Economics Information Report no. 94–01.
[196] Canada, Environment Canada, 1996.

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.

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 overspraying. 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 which can significantly alter their mobility, environmental fate, and toxicity (figure 2-8). 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, endosulphan) 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, the 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, the risks to human health from ingestion of drinking water, especially when 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 currently used 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. reported in 1999 that more than 95% of samples collected from streams and 50% of

Figure 2-8 Sources, Sinks, Pathways, and Movement of Pesticides in Terrestrial and Aquatic Environments



samples collected from wells across the United States contained at least one pesticide.[197] 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.[198] A survey of mid-western streams in the United States detected atrazine in 98% (n = 149) of the streams sampled.[199] In southern Ontario, atrazine was detected in most surface waters flowing into the Great Lakes.[200] In a comprehensive probabilistic environmental risk assessment of atrazine in North American surface waters, Solomon et al., in 1996, concluded that this compound does not pose a significant risk to the aquatic environment.[201] 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.[202] 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.[203] 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.[204] Atrazine is commonly detected in drinking water supplies drawn

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[197] R.J. Gilliom et al., 1999, "Testing water quality for pesticide pollution," *Environmental Science and Technology,* vol. 33, pp. 164A–169A.

[198] G.R. Halberg, 1989, "Pesticide pollution of groundwater in the humid United States," *Agriculture, Ecosystems and Environment,* vol. 26, pp. 299–367; K.R. Solomon, 1996, "Overview of recent developments in ecotoxicological risk assessment," *Risk Analysis,* vol. 16, pp. 627–633.

[199] E.M. Thurman et al., 1991, "Herbicides in surface waters of the Midwestern United States: The effect of the spring flush," *Environmental Science and Technology,* vol. 25, pp. 1794–96.

[200] Frank, R. et al., 1982, "Triazine residues in suspended solids (1974–1976) and water (1977) from mouths of the Canadian streams flowing into the Great Lakes," *Journal of Great Lakes Research,* vol. 5, pp. 131–138.

[201] Solomon et al., 1996.

[202] Gustafson, 1993.

[203] J.E. Barbash et al., 1999, *Distribution of Major Herbicides in Groundwater of the United States* (Sacramento: U.S. Geological Survey), United States Geological Survey, Water Resources Investigation Report 98-4245.

[204] B. McCrae, 1991, *The Characterization and Identification of Potentially Leachable Pesticides and Area Vulnerable to Groundwater Contamination by Pesticides in Canada* (Ottawa: Agriculture Canada, Food Production and Inspection Branch), Backgrounder 91-01.

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 2-12). Goss et al. wrote in 1998 that they detected atrazine in 6.6 and 10.5% of approximately 1,300 domestic wells sampled in the winter and summer, respectively.[205] Briggins and Moerman found atrazine in 32% of wells (n = 102) in Nova Scotia, although none were above the Canadian water quality criterion of 5 μg/L.[206] Other pesticides detected in that study (<4% of wells) included simazine, metribuzin, alachlor, metolachlor, captan, chlorothalonil, dimethoate, and permethrin.[207]

Table 2-12 Pesticides Detected in Wells Drawn from Groundwater During a Monitoring Program Conducted by the Ontario Ministry of the Environment

Pesticide	1985 Survey		1986 Survey	
	# of Detections (%)	Maximum Concentration (µg/L)	# of Detections (%)	Maximum Concentration (µg/L)
Alachor	15	20	5	2.3
Atrazine	-----	-----	43	4.2
Atrazine & deethyl atrazine[1]	48	354	50	10.5
Deethyl atrazine	-----	-----	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 & deethyl atrazine	3	23	ND	
2,4-D/2,4-DB	1	5800	ND	
Total Detections	51		50	

1 Atrazine and deethyl atrazine combined in 1985 survey.

Source: Halberg, 1989.

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[205] Goss et al., 1998.

[206] Briggens and Moerman, 1995.

[207] Ibid.

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 far 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.[208] 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. found no evidence to support a shift in sex ratio in this species.[209]

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 drinking 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.[210] The first survey was directed at agricultural areas and, to a lesser extent, areas that were hydrogeologically susceptible to contamination.[211] In total, nine pesticides, all herbicides, were detected in the wells. At least one pesticide was detected in 51% of the wells sampled, while 21% contained residues of at least two pesticides (table 2-12). 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.[212] 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

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[208] S.I. Dobson et al., 1999, "Low exposure concentrations of atrazine increase male production in *Daphnia pulicaria*," *Environmental Toxicology and Chemistry*, vol. 15, pp. 1568–73.

[209] A. Hosmer et al., 2000, "Effects of atrazine on the sex ratio of *Daphnia pulicaria*," *Abstract* from the 21st Annual Meeting of the Society of Environmental Toxicology and Chemistry, Nashville, Tenn., abstract PTP139.

[210] Ontario, Ministry of the Environment, 1985, *Alachlor Monitoring of Ontario Drinking Water, May-November 1985,* Report of the Water Resources Branch (Toronto: Ministry of the Environment).

[211] Ontario, Ministry of the Environment, 1987a, *Pesticides in Ontario Drinking Water, 1985*, Report of the Water Resources Branch (Toronto: Ministry of the Environment).

[212] Ontario, Ministry of the Environment, 1987b, *Pesticides in Ontario Drinking Water, 1986*, Report of the Water Resources Branch (Toronto: Ministry of the Environment).

detections and maximum concentrations was generally lower. A key finding of these surveys was that contamination of the wells was due almost equally to surface water and groundwater contamination. In a series of studies on pesticide contamination of farm wells and groundwater in Ontario, Frank et al. 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.[213] In surveys conducted between 1979 and 1984 on a broader range of pesticides, 71% of wells (n = 359) contained pesticide residues.[214] In a survey of pesticide contamination of wells in different soil types carried out in 1981–1982 and 1984, Frank et al. 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).[215] Finally, in a series of surveys conducted in 1984, 1986, and 1987, another Frank team 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.[215] 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 from direct spills, three from runoff immediately following an application event, and four 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. 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.[217] In that study, 20% of wells (n = 126) contained pesticide residues; atrazine was found in 15% of wells, MCPA (monochloro phenoxyacetic 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 exist.

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[212] R. Frank et al., 1979, “Herbicide contamination and decontamination of well waters in Ontario, Canada, 1969–1978,” *Pesticide Monitoring Journal*, vol. 13, pp. 149–67.

[213] R. Frank et al., 1987a, “Investigations of pesticide contaminations in rural wells, 1979–1984, Ontario, Canada,” *Archives of Environmental Contamination and Toxicology*, vol. 16, pp. 9–22.

[214] R. Frank et al., 1987b, “Survey of farm wells for pesticide residues, Southern Ontario, Canada, 1981–1982, 1984,” *Archives of Environmental Contamination and Toxicology*, vol. 16, p. 108.

[215] Frank et al., 1990.

[216] B. Ripley et al., 1998, “The contribution of well water to overall farm family pesticide exposure,” *Toxicological Sciences,* vol. 42, p. 767.

In Ontario, monitoring programs for the detection of pesticide residues in treated drinking water are virtually non-existent. 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 is more likely to be contaminated by pesticides due to their proximity to various agricultural practices. Goss et al. then and Rudolph with Barry and Goss conducted a survey of contaminants (pathogens, nutrients, and pesticides) in approximately 1,300 domestic wells and multilevel monitoring well installations at 144 farms in Northern and Southern Ontario.[218] 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.

2.3.1.3 *Non-agricultural Sources of Pesticides*

Although agriculture accounts for 70–80% of pesticides found in surface water, groundwater, and drinking water in North America,[219] a number of other significant sources exist. Some of these may constitute 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.[220] Some applications include: (1) forestry, (2) transportation (to control weeds along roadsides, railways, and rights-of-way), (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 lumber yards), and (5) lakes and streams for control of aquatic weeds and nuisance organisms (e.g., pestifierous midges). The various sources of pesticides used in non-agricultural applications are provided in figure 2-9. Below, we briefly discuss these non-agricultural sources of pesticides with respect to their loading to, and movement in, aquatic environments.

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[218] Rudolph and Goss, 1998; Rudolph et al., 1998.

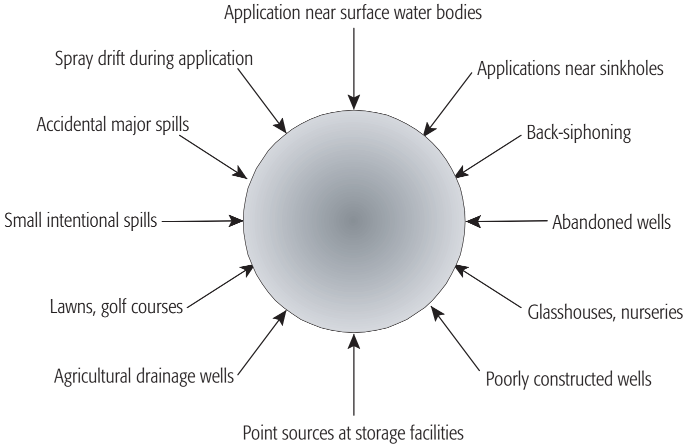
[219] A.L. Apselin, 1994, *Pesticide Industry Sales and Usage: 1992 and 1993 Market Estimates* (Washington, D.C.: United States Environmental Protection Agency, Office of Pesticide Programs, Biological and Economic Analysis Division, Economic Analysis Branch), Report 733K-92–001.

[220] Larson et al., 1997; Nowell et al., 1999.

Forestry The amount of pesticides applied in forestry, and the corresponding areal coverage, represents a small fraction of the amount used and the areal coverage in agriculture.[221] In Canada, the total area receiving herbicide treatments in 1993 was 235,000 ha, most of which was 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 but are more typically directed at controlling pest outbreaks (e.g., gypsy moth, spruce budworm) in localized areas. Here, 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 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.[222]

Figure 2-9 Potential Sources of Pesticides Other Than Crop Protection That Can Lead to Drinking Water Contamination



Source: Gustafson, 1993.

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[221] Canada, Environment Canada, 1996.
[222] Ibid.