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Canadian Soil Quality Guidelines for

Naphthalene: Environmental

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NOTICE

This final draft document provides the information supporting the derivation of environmental soil quality guidelines for naphthalene. Development of these soil quality guidelines was initiated through the National Contaminated Sites Remediation Program (NCSRP) which officially ended in March 1995. Given the need for national soil quality guidelines for contaminated sites management and many other applications, development was pursued under the direction of the CCME Soil Quality Guidelines Task Group after the end of the NCRSP.

This document is a working document that was released shortly after the publication of "A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines" (CCME 1996). The CCME recognizes that some refinements or changes to the Protocol may become necessary upon application and testing. If required, amendments to the Protocol will be made and the guidelines will be modified accordingly. For this reason guidelines are referred to in this document as CCME Recommended Guidelines. Readers who wish to comment or provide suggestions on the Protocol or on the guidelines presented in this document should send them to the following address:

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This document is a supporting technical document. It is available in English only. A French Abstract is given on page vii.

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ABSTRACT

Canadian environmental quality guidelines, developed under the auspices of the Canadian Council of Ministers of the Environment (CCME), are numerical concentrations or narrative statements recommended to support and maintain designated resource uses. CCME Canadian soil quality guidelines can be used as the basis for consistent assessment and remediation of contaminants at sites in Canada.

This report was prepared by the Guidelines Division of the Science Policy and Environmental Quality Branch (Environment Canada), which acts as Technical Secretariat for the CCME Soil Quality Guidelines Task Group. The Guidelines were derived according to the procedures described in *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996).

Following the introduction, chapter 2 presents chemical and physical properties of naphthalene and a review of the sources and emissions in Canada. Chapter 3 discusses naphthalene's distribution and behavior in the environment while chapter 4 reports the toxicological effects of naphthalene on microbial processes, plants, and animals. These informations are used in chapter 5 to derive soil quality guidelines for naphthalene to protect environmental receptors in four types of land uses: agricultural, residential/parkland, commercial, and industrial.

The following soil quality guidelines are recommended by the CCME based on the available scientific data. For naphthalene, the available data were insufficient/inadequate to derive soil quality guidelines according to the CCME 1996 Protocol. Therefore, the Provisional Method, described in CCME (1997) and hereafter was used to derive provisional environmental soil quality guidelines for naphthalene. The provisional environmental soil quality guideline (SQG_E—provisional) for agricultural and residential/parkland land uses is 0.6 $mg \cdot kg^{-1}$ soil whereas for commercial and industrial land uses it is 22 $mg \cdot kg^{-1}$ soil.

RÉSUMÉ

Les recommandations canadiennes pour la qualité de l'environnement, élaborées sous les auspices du Conseil Canadien des Ministres de l'Environnement (CCME), sont des concentrations ou des énoncés décrivant les limites recommandées dans le but d'assurer le maintien et le développement durable d'utilisations désignées des ressources. Les recommandations canadiennes pour la qualité des sols proposées par le CCME peuvent être utilisées comme base pour l'uniformisation des processus d'évaluation et d'assainissement des terrains contaminés au Canada.

Le présent document a été préparé par la Division des Recommandations de la Direction de la Qualité de l'Environnement et de la Politique Scientifique (Environnement Canada), qui agit comme secrétaire technique pour le Groupe de Travail du CCME sur les Recommandation pour la Qualité des Sols. Les Recommandations ont été élaborées selon les procédures décrites dans le *Protocole d'élaboration de recommandations pour la qualité des sols en fonction de l'environnement et de la santé humaine* (CCME 1996).

Faisant suite à une brève introduction, le chapitre 2 présente les propriétés physiques et chimiques du naphtalène de même qu'un survol des sources et des émissions au Canada. Le chapitre 3 discute du devenir et du comportement de cette substance dans l'environnement alors que le chapitre 4 rapporte ses effets toxicologique sur les processus microbiens, les plantes et les animaux. Ces informations sont utilisées au chapitre 5 afin d'élaborer des recommandations pour la qualité des sols relatives au naphtalène en vue de la protection de l'environnement dans le cadre de quatre types d'utilisations de terrains: agricole, résidentiel/parc, commercial et industriel.

Les recommandation pour la qualité des sols suivantes, proposées par le CCME, sont fondées sur les données scientifiques disponibles. Pour le naphtalène, les données disponibles sont insuffisantes/inadéquates pour permettre l'élaboration de recommandations selon les procédures décrites dans le Protocole du CCME (1996). Ainsi, la Méthode provisoire, décrite dans un document du CCME (1997) et ci-après, à été utilisée pour élaborer des recommandations provisoires pour la qualité des sols relatives au naphtalène en vue de la protection de l'environnement. La recommandation provisoire pour la qualité des sols en vue de la protection de l'environnement (RQS_E—provisoire) visant les terrains à vocation agricole et résidentielle/parc est de 0.6 $mg \cdot kg^{-1}$ de sol, alors que pour les terrains à vocation commerciale et industrielle, elle est de 22 $mg \cdot kg^{-1}$ de sol.

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1. INTRODUCTION

The Canadian Council of Ministers of the Environment's (CCME) Canadian Environmental Quality Guidelines are numerical limits for contaminants in soil and water intended to maintain, improve, or protect environmental quality and human health. CCME Canadian Soil Quality Guidelines can be used as the basis for consistent assessment and remediation of contaminants at sites in Canada along with CCME guidelines issued for the protection of water quality, sediment quality and tissue quality. In response to the urgent need to begin remediation of high priority "orphan" contaminated sites, an interim set of criteria was adopted from values currently in use in various jurisdictions across Canada (CCME 1991). Many of the CCME interim soil remediation criteria do not have a complete supporting scientific rationale and are being updated based on current scientific information.

This report reviews the sources and emissions of naphthalene, its distribution and behaviour in the environment and its toxicological effects on terrestrial plants, microbial processes and animals. This information is used to derive criteria for naphthalene to protect ecological receptors according to the processes outlined in CCME (1996) for agricultural, residential/parkland, commercial and industrial land uses.

The values derived herein are environmental soil quality guidelines and are intended as general guidance. Site-specific conditions should be considered in the application of these values. The values may be applied differently in various jurisdictions, therefore, the reader should consult the appropriate jurisdiction for application of the values.

2. BACKGROUND INFORMATION

2.1 Physical and Chemical Properties

Polyaromatic Hydrocarbons (PAHs) are a group of organic compounds consisting of two or more fused benzene rings. The physical and chemical characteristics of PAHs are dependant upon their molecular weight and structure (i.e. number of aromatic rings and stereochemistry) (see Table 1). For example, PAH resistance to oxidation, reduction and vaporization increases with increasing molecular weight, whereas aqueous solubility decreases (Nagpal, 1993). Thus the environmental mobility, behaviour, and fate of naphthalene differs from higher molecular weight PAH compounds such as benzo(a)pyrene, although many PAH compounds share similar modes of formation.

Naphthalene ($C_{10}H_8$) is the simplest structured PAH, having the lowest molecular weight (128.16 g), lowest density (1.162 $g \cdot ml^{-1}$) and highest water solubility (31.7 $mg \cdot L^{-1}$) of this family of chemicals. The physical and chemical properties of naphthalene are listed in Table 2. Purified naphthalene is a white, crystalline solid, with a characteristic moth ball type odour. Similar to many non-polar organic chemicals, naphthalene is only slightly soluble in water but very soluble in organic solvents such as benzene. The log-octanol water partition coefficient (log K_{OW}), a measure of a chemical's affinity to partition between aqueous phase and an organic solvent, is approximately 3.37 for naphthalene (Mackay et al. 1992). This indicates that naphthalene has the potential to accumulate within fatty

tissues of exposed organisms. However, the degree of bioconcentration is influenced by exposure conditions as well as the rate of biological depuration (metabolism plus excretion), and therefore cannot be predicted solely from log K_{OW} data.

Although naphthalene is more dense than water, volatilization from aquatic and terrestrial environments is considered to be an important transport and dispersal mechanism. Unlike higher molecular weight PAH compounds such as benzo(a)pyrene, naphthalene readily volatilizes at ambient environmental temperatures.

2.2 Analytical Methods

Two analytical methods are recommended by the CCME for determining the amount of naphthalene in soils: U.S. EPA method 8260A, Revision 1 and U.S. EPA Method 8270B, Revision 2. The detection limits for these methods are 0.04 µg·L, and 0.66 mg·kg wet soil, respectively. Both of these methods use capillary gas chromatography/mass spectrometry (GC/MS) and are also suitable for the analysis of naphthalene in groundwater. Three methods which may be used to detect naphthalene in surface and ground water are U.S. EPA Method 502.2 Revision 2, U.S. EPA Method 524.2 Revision 3 and Spectrometric Method 6410B. Details of these methods are found in CCME, 1993.

2.3 Production and Uses

Naphthalene is primarily used as a raw material for the production of phthalic anhydride, a chemical used to produce indigo, indanthrene and triphenylmethane dyes (United Technology Science Inc.1978; Merck 1989). This use alone accounts for a majority of all commercial grade naphthalene produced in the United States (U.S. EPA 1986b). Naphthalene is also used as a feedstock for manufacturing carbaryl insecticides, beta-naphthol, tanning agents, moth repellents, synthetic resins, smokeless powders and surfactants (Nagpal 1993 and Merck 1989). The use of naphthalene as an insecticide and moth repellent has declined in recent years due to increased use of chlorinated compounds such as *p*-dichlorobenzene (Merck 1989).

Naphthalene was first isolated from coal tar distillates in 1820 (United Technology Science Inc. 1978). Naphthalene is the most abundant compound present in coal tar creosote, accounting for approximately 11% of creosote dry weight (Merck 1989). The specific composition of creosote and the relative abundance of naphthalene will vary depending upon the stock: a sample of Canadian produced creosote contained approximately 17.5% naphthalene (EC&HW 1993). Coal tar creosote is used as a wood preservative, disinfectant and insecticide, although the use of creosote has declined substantially since the early part of the 20th Century. This has been partly attributable to the introduction of alternative wood preservatives such as pentachlorophenol and copper arsenates, and in part due to diminishing demand for new railway ties (EC&HW 1993).

Commercial naphthalene is derived from coke or petroleum sources and is sold in the form of white scales, powder, balls, or cakes (U.S. EPA 1986b; Merck 1989). Based upon voluntary reporting of

commercial activities for the Domestic Substances List, 1,000 tonnes of naphthalene were produced or manufactured in Canada in 1986, with 10 - 100 tonnes being imported.

2.4 Levels in the Canadian Environment

2.4.1 Inputs to the Canadian Environment

Naphthalene may be formed by the thermal decomposition of any organic material containing carbon and hydrogen. The two major mechanisms resulting in the formation of naphthalene are pyrolysis and the carbonization process (e.g. during the formation of mineral oil and coal), with biosynthetic formation representing an additional source (Bjørseth and Ramdahl 1985). Several natural processes contribute naphthalene to the environment; including volcanoes, forest fires and the biodegradation of vegetal and animal matter. Anthropogenic sources of naphthalene include emissions from aluminum smelters, steel mills, coal fired generating plants, petroleum refineries, creosote wood preserving facilities, municipal incinerators and leachate from municipal/industrial landfill sites (U.S. EPA 1986a; 1986b). Naphthalene is also released from a wide variety of indirect sources, including creosote treated telephone poles and railway ties, petroleum spills, waste crankcase oil, cigarette smoke, and vehicle exhaust (Nagpal 1993)

Naphthalene is a common constituent of wastewater from industries that produce or use creosote. Treated effluent (via activated charcoal filter) from a wood preserving plant in Quebec had a naphthalene concentration of 16 $\mu g \cdot L^{-1}$ (LGLA, 1993). In wastewater effluents from coal operations, naphthalene was detected at levels greater than 10 $\mu g \cdot L^{-1}$ (Nagpal, 1993). A water sample obtained from a ditch receiving drainage from creosote treated utility poles in Vancouver had a concentration of 488 $\mu g \cdot L^{-1}$ (Nagpal 1993).

Data pertaining to total naphthalene emissions to the Canadian environment are not available. Estimated total (atmospheric) PAH emissions from Canadian sources totalled 4 314 metric tonnes in 1990, with 47% (2 010 t) of this sum originating from forest fires, 21% (925 t) from aluminum plants, 11% (474 t) from wood stove exhaust, 8.3 % (358 t) from open air fires and agricultural burnings, 5.8% (249 t) from tepee burner exhaust (forestry industry), 4.6 % (200 t) from diesel and gasoline combustion, and 2.3% (98 t) from other sources (LGLA 1993). Significant sources of PAH emissions in Ontario include residential fuelwood combustion (140 tonnes per year), ferroalloy production (53.5 tonnes per year), metallurgical coke production (26.2 tonnes per year), emissions from gasoline and diesel fuel vehicles (24.5 tonnes per year), open fires and prescribed burning (17.4 tonnes per year), and electrical power generation (8.8 tonnes per year) (Ortech 1992).

Approximately 11 500 U.S. tonnes of naphthalene per year are discharged to the U.S. environment from select tallied sources; including coal tar production/distillation, combustion, commercial uses, contained petroleum sources, oil spills, tire wear, waste water treatment, and wood preserving applications (U.S. EPA 1982). Of this estimated total, 92 % (10 600 t) is discharged to the atmosphere, 3 % (314 t) is discharged to the terrestrial environment, and 5% (577 t) is discharged to the aquatic environment.

The utilization of fossil fuels and petroleum products contributes naphthalene to the Canadian environment. A sample of Kuwait crude oil was determined to contain approximately 400 $mg \cdot kg^{-1}$ naphthalene. However, since crude oil is composed of a complex mixture of hydrocarbons whose relative proportions depend upon the origin of the crude, naphthalene concentrations vary in different crude stocks (Neff 1979 as cited by Nagpal 1993).

Significant concentrations of naphthalene are present in refined oils and gasoline products. Samples of Bunker C residual oil and No. 2 fuel oil were found to contain naphthalene concentrations of 1000 $mg \cdot kg^{-1}$ and 4000 $mg \cdot kg^{-1}$, respectively (Neff 1979 as cited by Nagpal 1993). Canadian diesel fuels contain up to 17,000 $mg \cdot kg^{-1}$ total naphthalenes (including substituted naphthalene derivatives), whereas Canadian gasolines contain between 1,500 and 3,600 $mg \cdot kg^{-1}$ total (non-substituted) naphthalene (1993 test data) (CPPI 1994). Low octane gasolines contain higher concentrations of naphthalene than do high octane gasolines (see Table 3). A distinction is evident between winter and summer naphthalene concentrations in Canadian gasoline, with summer concentrations ranging substantially higher than winter concentrations (CPPI 1994). Although the nature of this discrepancy is not certain, a decrease in volatile components (e.g. benzene, toluene, ethyl benzene and xylene) during summer months may increase the relative proportions of naphthalene and other less volatile components.

Smoking contributes 11.2 mg of vapour-phase naphthalene to the atmosphere per cigarette consumed (Gundel et al. 1995). Operation of a four stroke outboard motor running on unleaded gasoline was found to contribute 1.3 mg naphthalene per minute to the water environment via exhaust emissions (Jütner 1994). Naphthalene emissions from the open combustion of scrap tires in a controlled experiment ranged from 486 - 815.9 mg naphthalene per kg tire (Lemieux and Ryan 1993). Effluents discharged from the Hamilton water pollution control plant in 1983 contained naphthalene levels between 0.0 - 0.68 $\mu g \cdot L^{-1}$ with an average concentration of 0.28 $\mu g \cdot L^{-1}$; resulting in an annual loading of 30.3 kg (Zukovs et al. 1984).

2.4.2 Distribution of Naphthalene in the Canadian Environment

The current literature data concerning PAH concentrations in the Canadian environment is dominated by studies of higher molecular weight compounds such as anthracene, chrysene and benzo(a)pyrene. Since the physico-chemical behaviour and environmental fate of naphthalene differs from that of other PAHs, data concerning higher molecular weight PAHs do not provide an accurate indication of naphthalene levels in the environment. However, based upon the literature data, it is apparent that naphthalene is widely distributed in the Canadian environment (see Table 4). Residues have been detected in all media including air, water, soil, groundwater and biota.

Soil

There is little information available concerning naphthalene levels in Canadian soils. In general, a majority of existing data relates to investigations at industrial sites where PAH contamination is known or expected. Soil in the vicinity of industrial operations which have historically involved the

use of creosote, coal or petroleum products typically contain significant quantities of naphthalene. Concentrations of naphthalene as high as 4400 $mg \cdot kg^{-1}$ were reported in soils obtained from a Quebec cokery prior to site remediation (Ringuette et al., 1993). Soil samples obtained from various creosote utilizing wood treatment facilities across Canada have been found to contain up to several thousand milligrams of naphthalene per kilogram of soil (EC&HW, 1993).

Soil samples collected throughout Ontario from undisturbed old urban and rural parklands not impacted by local point sources of pollution were analyzed for a variety of chemicals to determine average background concentrations known as "Ontario Typical Range" (OTR_{98}) (OMEE 1993). These OTR_{98} values correspond to the 98th percentile of the sample population analyzed. For naphthalene, the provisional OTR_{98} value for old urban parkland land use was established at 0.09 $mg \cdot kg^{-1}$ while a provisional concentration of 0.006 $mg \cdot kg^{-1}$ was obtained for rural parkland.

Water

There is little available information concerning naphthalene levels in Canadian surface or ground waters. At the head of the Niagara river, in Fort Erie, Ontario, water was determined to contain median and maximum naphthalene levels of 3.65 $ng \cdot L^{-1}$ and 10.76 $ng \cdot L^{-1}$, respectively (n=51), whereas at the mouth of the Niagara river (in Lake Ontario), a median naphthalene concentration of 4.98 $ng \cdot L^{-1}$ and a maximum naphthalene concentration of 11.86 $ng \cdot L^{-1}$ were reported (n=40) (Kuntz 1990 as cited in Ringuette et al. 1993). Samples of annual snow deposition obtained from the Agassiz Ice Cap on Ellesmere Island contained 0.035-0.66 $\mu g \cdot L^{-1}$ total PAH over the period 1963-1993, with naphthalene accounting for an overall mean of 88% of the total quantity (Peters et al. 1995). Railway ditch water flowing to salmon streams in lower mainland, B.C., was found to have a median naphthalene concentration of < 0.1 $\mu g \cdot L^{-1}$ and a maximum of 0.8 $\mu g \cdot L^{-1}$ (n=6) (Wan 1991).

Sediments

Sediments from Canadian harbours and lakes typically contain <1 mg naphthalene$\cdot kg^{-1}$, although sediments sampled in water bodies receiving industrial effluent often contain higher concentrations (see table 4). The median naphthalene concentration of 25 sediment samples obtained from Hamilton harbour between 1988 and 1989 was 19.8 $mg \cdot kg^{-1}$ (Murphy et al. 1993). A 1985-1986 survey of Vancouver harbour sediment detected a median and maximum naphthalene concentration of 0.1 $mg \cdot kg^{-1}$ and 1.17 $mg \cdot kg^{-1}$ (n=24), respectively. Follow up testing in 1987 found a median/maximum naphthalene concentration of 0.4 $mg \cdot kg^{-1}$ and 0.7 $mg \cdot kg^{-1}$, respectively (n=23) (Goyette 1989).

Surficial sediments obtained from twelve locations along the St. Marys River had a median naphthalene concentration of 0.69 $mg \cdot kg^{-1}$ and maximum of 29 $mg \cdot kg^{-1}$ (Kauss and Hamdy 1991). Railway ditch sediments collected from six locations in lower mainland, B.C., had a median naphthalene concentration of 0.46 $mg \cdot kg^{-1}$ and a maximum concentration of 1.09 $mg \cdot kg^{-1}$ (n=6) (Wan 1991).

Atmosphere

Most PAHs present in air are sorbed to aerosols, especially soot, and PAH deposition is usually associated with particulate deposition (Pierce and Katz 1975; Uthe 1991). However, atmospheric naphthalene primarily exists in the vapour phase and does not appreciably sorb to particulate matter (Biermann et al. 1985; U.S. EPA 1986a). Air samples obtained from the vicinity of the Niagara River had a mean gas-phase concentration of naphthalene of 2.4 $ng \cdot m^3$ ($\pm$1.6 $ng \cdot m^3$) during the month of September and 3.2 $ng \cdot m^3$ ($\pm$1.2 $ng \cdot m^3$) during January (Hoff and Chan 1987). In contrast, particulate-phase naphthalene in air sampled from the vicinity of the Niagara River had a mean concentration of 1.0 $ng \cdot m^3$ ($\pm$0.671 $ng \cdot m^3$) during the month of September and 0.16 $ng \cdot m^3$ ($\pm$0.17 $ng \cdot m^3$) during the month of January (Hoff and Chan 1987).

Environment Canada has measured ambient air PAH concentrations in British Columbia, Manitoba, the Northwest Territories, Ontario, Quebec and Nova Scotia since the 1970s. The highest PAH concentrations have been measured in industrial areas, particularly near aluminum smelting operations. Naphthalene has been surveyed in air samples obtained from Kitimat, B.C., and at numerous sites in Quebec (see Table 4). The highest naphthalene concentrations have been measured at Sept-Iles (396.88 $ng \cdot m^3$; wood heating), Jonquiere (126.67 $ng \cdot m^3$; aluminum smelting), and Shawinigan (77.79 $ng \cdot m^3$; aluminum smelting). The highest median naphthalene concentrations have been measured in urban settings (Cap-de-la-Madeleine, 18.08 $ng \cdot m^3$; station Duncan and Decarie, Montreal, 14.49 $ng \cdot m^3$), indicating that the urban environment has a higher ambient concentration of naphthalene than non-urban settings.

2.5 Existing Criteria, Guidelines and Standards

Existing guidelines, criteria, or standards for naphthalene in soil and groundwater from provincial, national, and international agencies are summarized in Table 5.

3. ENVIRONMENTAL FATE AND BEHAVIOUR

3.1 Soil

Volatilization and biodegradation are considered to be the two principal processes governing naphthalene persistence in soils (U.S. EPA 1986; Sims and Overcash 1984). The residence time of naphthalene in the soil profile increases with increasing depth, since volatilization and microbial transformation processes are less prominent below the zone of aeration. Due to its mobility and chemical stability, naphthalene can penetrate the soil profile and contaminate groundwater (Ehrlich 1983).

Abiotic Fate and Behaviour

The scientific literature reports varying sorptive behaviour for naphthalene in soil. Some studies

suggest that naphthalene is not strongly adsorbed to subsurface sediments (Ehrlich 1983; Goerlitz 1985), and limited sorption or rapid desorption of naphthalene from soils have been predicted (Ehrlich 1983; U.S. EPA 1986). On the other hand, Bedient et al. 1984 reported that naphthalene was still present in the soil of and abandoned creosote facility in Conroe, Texas, ten years after the facility was closed, and that up to 84% of the naphthalene measured was found in the top 5 feet of soil depth.

Naphthalene has a high vapour pressure relative to other PAH compounds (see table 1). Therefore, naphthalene can volatilize and dissipate from surface soils over the course of a few days (Moore and Ramamoorthy1984, as cited in Nagpal 1993). The volatilization half life ($T_{1/2}$) for naphthalene in a soil containing 1.25% organic carbon has been estimated at 1.1 days for a depth of 1 cm, and 14 days for a depth of 10 cm (Jury et al. 1984). The mean percent volatilization of naphthalene from a Kidman fine sandy loam and McLaurin sandy loam over a 48 hour study period were reported to be 32.3% and 29.2%, respectively (Park et al. 1990). Since soil adsorption effectively inhibits PAH volatilization, it is unlikely that volatilization alone can result in the complete removal of naphthalene from the soil profile .

Microbial Biotransformation

Biological transformation by bacteria and fungi is an important mechanism of naphthalene removal from terrestrial environments. Depending upon environmental conditions and biological factors, naphthalene may be completely mineralized to CO_2 or transformed to a wide variety of intermediate products (Jeffrey 1975, U.S. EPA 1986, Sims and Overcash 1983). Naphthalene provides a source of carbon and energy for microbial cell synthesis. However, at very high naphthalene levels, microbial growth can be inhibited in a manner directly proportional to the concentration (Calder and Lader 1976 as cited by Sims and Overcash 1983).

Due to resonance stabilization, the fused benzene rings of polyaromatic hydrocarbons are resistant to chemical and biological degradation (Sims and Overcash 1983). Electrons belonging to the carbon atoms forming the aromatic rings are shared across the entire structure, resulting in a delocalization of charge throughout the molecule. Nevertheless, under favourable conditions certain species of bacteria and fungi are capable of catalyzing the degradation of polyaromatic hydrocarbons through the use of molecular oxygen. The microbial incorporation of molecular oxygen into the chemical structure of naphthalene is an activation step rendering the molecule less stable as well as providing a substrate for enzyme catalyzed fission of the aromatic ring. These initial reactions eventually yield to central metabolism pathways such as the Krebs cycle (Sims and Overcash 1983).

Within a complex microbial population, two or more microbial species may work in conjunction to metabolize polyaromatic hydrocarbons. Such cometabolism occurs when one type of microorganism inadvertently initiates biotransformation of a compound while carrying out normal cellular functions. This initial metabolite then provides a suitable growth substrate for other microorganisms to continue the transformation process. The role of cometabolism in naphthalene degradation is not certain, although it has been cited as a key mechanism enabling the biotransformation of high molecular weight polyaromatic hydrocarbons (Sims and Overcash 1983).

Enzymes capable of catalyzing the oxidation of naphthalene are classified as oxygenases. Polyaromatic oxygenases require either NADH or NADPH as an electron donor in order to complete the reaction (Jeffrey et al. 1975). The specific enzymes involved in the reaction vary depending upon whether the cell is a eucaryote (e.g. fungi and multicellular organisms) or a prokaryote (i.e. bacteria) (see Table 6). The microbial oxidation of naphthalene is a dioxygenase-catalyzed reaction, while fungal biotransformation is typically accomplished through a monoxygenase-catalyzed reaction. The fungal route of biotransformation resembles mammalian metabolization due to the shared mechanism of cytochrome P-450 mixed function oxidase enzymes (MFOs) (Cerniglia et al. 1979; 1982). For example, the fungus *Cunningham elegans* degrades naphthalene via an arene oxide and *trans*-naphthalene dihydrodiol pathway (Table 6), which is also a characteristic process of mammalian metabolization systems.

Under acidic conditions, the soil microflora is dominated by fungi while at a neutral pH, bacteria tend to dominate (Bulman et al. 1985; Sims and Overcash 1983). Certain soil bacteria (e.g. *Pseudomonas putida, Flavobacterium* sp.) can use naphthalene as a source of carbon and energy to support cell growth (Jeffrey et al. 1975; Sims and Overcash 1983). A broad range of fungi are also capable of degrading naphthalene (Cerniglia et al.1979). Naphthalene was biotransformed by 55% of tested fungi in a survey of eighty-six species belonging to sixty-four genera from the major fungal taxa.(Cerniglia et al.1979). The intermediate products of naphthalene biodegradation by the fungi *Cunninghamella elegans* include trans-naphthalene diol, 4-hydroxy-1-tetralone, 1,2-naphthoquinone, 1,4-naphthoquinone, 1-naphthol and 2-naphthol (Cerniglia et al. 1979; 1982).

The rate of naphthalene biotransformation in soil is dependant upon environmental factors and the structure of the microbial community. Rate determining environmental factors include temperature, pH, oxygen concentration, soil moisture content, soil mineral composition, concentrations of other contaminants or cosolvents, and the relative abundance of limiting soil nutrients. These variables strongly influence diversity within the soil microbial community, as measured by total species counts and/or the proportion of bacterial to fungal populations. Another important factor influencing biodegradation rate is the exposure period of microbial colonies to the contaminated media (i.e. the acclimatization period). Over time, elevated levels of PAHs in soil leads to the growth of microbial populations capable of degrading them (Herbes 1981).

Estimates of naphthalene biodegredation kinetics are prone to error because abiotic loss (e.g. volatilization) may compromise the validity of experimental results (Bulman et al. 1985). Studies which fail to accurately measure abiotic loss rates and subtract these from total loss kinetics tend to overestimate the importance of biodegredation in removing naphthalene from the soil profile. Since naphthalene degradation is often studied in conjunction with higher molecular weight PAHs which do not significantly volatilize at ambient environmental temperatures, this aspect of total loss kinetics is frequently overlooked (e.g. Herbes and Schwall 1978).

A total residence time of 12 days (abiotic and biotic loss) was established for naphthalene in a Donnybrook sandy loam (2.3% organic matter, pH 7.0) following application of a mixture of 8 PAH congeners to the test soil (Bulman et al. 1985). The half life for microbial biodegredation of commercial grade naphthalene applied to a Kidman sandy loam (0.5% organic matter, pH 7.9) was

evaluated at 2.1 days, whereas a half-life of 2.2 days was established for a McLaurin sandy loam (1.1% organic matter, pH 4.8) (Park et al. 1990).

3.2 Water

The principal mechanisms controlling the fate of naphthalene in aquatic and marine ecosystems are evaporation, photochemical oxidation, sedimentation, and biological uptake (Eisler, 1987). Biodegredation is also considered to be a significant processes responsible for the loss of naphthalene from aquatic and marine environments (Lee et al. 1978). In experiments using controlled marine ecosystem enclosures, up to 5% of naphthalene per day was biotransformed (Lee et al. 1978).

Volatilization of naphthalene is considered to be an important removal process from aquatic and marine environments. Southworth (1979) estimated the volatilization half-life of naphthalene to be sixty hours for an aquatic system with a current velocity of 0.1 m/second and a wind velocity of 2 m/sec, decreasing to five hours in a situation with a current velocity of 1 m/second and a wind velocity of 3 m/second.

Photoinduced oxidation of naphthalene in aquatic and marine environments results from chemical reactions with singlet oxygen, ozone, hydroxide radicals and other oxidants (Nagpal, 1993). The half-life constants for naphthalene undergoing reactions with singlet oxygen or peroxy radicals are estimated to be quite long; thus these processes are not expected to significantly affect the fate of naphthalene in water (U.S. EPA, 1986). The half-life for photolysis of naphthalene in water is estimated to be approximately 140 hours (U.S. EPA, 1986).

Relative to higher molecular weight PAHs, naphthalene does not appreciably settle from the water column or accumulate in bottom sediments (Lee et al. 1978). It has been reported that approximately 15% of the total amount of naphthalene in a shallow, rapidly flowing stream becomes sorbed to sediments (U.S. EPA, 1986).

3.3 Atmosphere

In the atmosphere, naphthalene may be transformed by photooxidation and photolysis processes or undergo reactions with nitrous oxides, sulphur dioxide, hydroxide radicals or ozone (Germain et al., 1993). The estimated atmospheric half-lives for naphthalene due to reaction with hydroxide radicals, ozone, nitrogen pentoxide and nitrate are estimated to be 8 - 12 hours, >40 days, >7 days and 15 hours, respectively (U.S. EPA, 1986). At an assumed OH radical concentration of 1×10^6 cm^{-3}, the atmospheric lifetime for naphthalene is estimated to be approximately 12 hours (Biermann et al. 1985). Although the reaction of gas-phase naphthalene with OH radicals is expected to be the dominant daytime fate process, reaction with NO_3 may be a significant fate process at night . Naphthalene may also be removed from the atmosphere via wet and dry precipitation to the aquatic and terrestrial environments, although this is not believed to be a major fate process (Mackay et al. 1992, U.S.EPA 1986a).

The atmospheric photooxidation half-life for naphthalene has been estimated to range from 2.96 to 29.6 hours, while the photolysis half-life is estimated to range from 1,704 - 13,200 hours (Germain et al., 1993). The U.S. EPA (1986) estimates the photooxidation half-life of naphthalene to be three days. The rates of photooxidation and photolysis vary considerably, depending in part upon the composition of the particulate matter onto which naphthalene may be adsorbed.

3.4 Environmental Fate Modelling

The environmental behaviour and chemical fate of a contaminant can be simulated by constructing partitioning models that are based upon established physico-chemical test data. The fugacity Level III model incorporates expressions for twelve intermedia transport rates that encompass both diffusive and non-diffusive processes (Mackay, Shiu and Ma, 1991). For the purposes of the Level III model, four environmental "compartments" (air, water, soil and sediment) are considered in relation to contaminant transport, accumulation and degradation processes. Transport mechanisms that are evaluated within the scope of this model include deposition, precipitation, evaporation, diffusion and resuspension. Biota are not considered within the context of this model, neither as a transport mechanism nor as a compartment.

Level III fugacity modelling predicts that naphthalene will primarily remain in the environmental media where it was initially released (see Table 7). The model also predicts that the primary route of naphthalene loss from the soil environment is via reaction/ degradation pathways. Advection would appear to play a marginal role in governing the fate of naphthalene present in the soil environment. Aerial deposition of naphthalene also appears to be limited, with an estimated 4.45% of total air emissions of naphthalene partitioning to the soil compartment (see Table 7). This is probably a consequence of rapid chemical decomposition within the air compartment (estimated half-life of 17 hours).

4. BEHAVIOUR AND EFFECTS IN BIOTA

4.1 Metabolization and Biochemical Effects

The environmental toxicity of a chemical is a direct function of its biological activity. Elucidating the biochemical basis of an observed toxic response is desirable, since this information helps to explain differences in chemical sensitivity between species and/or between different tissues within a single species. Within biological systems, chemical contaminants are subject to numerous biochemical conversion processes resulting in various metabolites. These processes may result from biological defence mechanisms (such as enzyme mediated response) or proceed due to spontaneous chemical reactions; usually both processes work in tandem to yield a succession of metabolic conversion steps.

Polycyclic aromatic hydrocarbons are subject to common biochemical reactions (Guengerich and Liebler 1984; Sims and Overcash 1983). In mammals, naphthalene metabolization is precipitated by

the cytochrome P-450 mixed-function oxidase class of enzymes which are found in greatest abundance in the smooth endoplasmic reticulum of liver cells, and to a lesser degree in other tissues and organs (Nagpal 1993; Kaminsky and Fasco 1992; Pasanen and Pelkonen 1994). These enzymes catalyze the reaction of naphthalene with oxygen, resulting in the formation of the reactive epoxide metabolite 1,2-naphthalene oxide (Nagpal 1993; Sims and Overcash 1983; Iyer et al. 1991). This primary metabolite rapidly undergoes further transformation to a variety of secondary and tertiary metabolites (Jeffrey 1975, U.S. EPA 1986, Sims and Overcash 1983).

Once 1,2-naphthalene oxide forms during the biotransformation process, this metabolite can undergo several secondary reactions. The epoxide metabolite may react with glutathione to produce a glutathione conjugate, a process which effectively detoxifies the compound (Iyer et al., 1991). Alternatively, the epoxide may covalently bind to cellular macromolecules at nucleophilic sites (Jerina et al., 1990). This binding leads to oxidant stress and can initiate lipid peroxidation of exposed tissue (Wells, 1989).

The metabolite 1,2-naphthalene oxide may also be re-arranged in vivo to form 1-naphthol (Jerina et al., 1990). Cytochrome P-450 enzymes may further metabolize 1-naphthol to form 1,4-naphthoquinone, a known cytotoxicant used as a non-selective fungicide in the past (D'Arcy Doherty and Cohen, 1984). The toxicity of 1,4-naphthoquinone relates to its ability to covalently bind to macromolecules and generate reactive oxygen species via redox cycling of the quinone (Thornally et al, 1984). Finally, 1,2-naphthalene oxide may undergo epoxide hydrolysis to form naphthalene-1,2-dihydrodiol. This tertiary metabolite can undergo further reaction to 1,2-naphthoquinone which is believed to be responsible for the formation of cataracts in naphthalene exposed rabbits (Van Heyningen, 1979).

4.2 Plants

Uptake and Distribution

Low molecular weight PAHs such as naphthalene are absorbed and translocated within plants more readily than high molecular weight PAH compounds (Wild and Jones 1991). Terrestrial plants may take up naphthalene through the following mechanisms (Edwards 1983, as cited in Wild and Jones 1991):

- uptake through the root tissues
- adsorption to the root surfaces
- foliar uptake of compounds volatilized from the soil surface
- adsorption from the atmosphere to the leaf surface
- natural biosynthesis within the plant cells

PAHs are lipophilic substances and form strong associations with organic matter in the soil, resulting in limited plant uptake through the roots (Wild and Jones 1991). The authors examined commercially grown carrots in the U.K. for 15 different PAHs. The highest concentrations were found in the peel,

with low molecular weight PAHs such as naphthalene being the most abundant. The distribution of naphthalene throughout different carrot tissues ranged from 23.3 $\mu g \cdot kg^{-1}$ dry weight in the peel to 4.9 $\mu g \cdot kg^{-1}$ in the core (Wild and Jones 1991).

Toxicity

A summary of consulted plant toxicity data is presented in Table 8.

Environment Canada (1995a) studied the effects of naphthalene on lettuce (*Lactuca sativa*) seed germination in an artificial soil at a pH of 4.2-4.3. Based on nominal concentrations, the resulting NOEC, LOEC, EC_{25} and EC_{50} were evaluated at 350, 700, 470 and 630 mg naphthalene$\cdot kg^{-1}$ dry soil, respectively. The average LOEC value corresponded to a 62% decrease in seedling emergence (Environment Canada 1995a). In another study using *L. sativa*, lettuce seeds were exposed to naphthalene for 120 hours in a similar artificial soil matrix but under different experimental conditions (Environment Canada 1995b). This experiment resulted in a NOEC, LOEC, EC_{25} and EC_{50} of 8, 16, 10 and 144 mg naphthalene$\cdot kg^{-1}$, respectively. The LOEC in this second study corresponded to a 37% reduction in seedling emergence relative to controls (Environment Canada, 1995b).

The effect of naphthalene on the germination success of radish (*Raphanus sativa*) seeds grown in artificial soil was also reported by Environment Canada (1995b). The NOEC, LOEC, EC_{25} and EC_{50} values were reported as 63, 125, 66 and 90 mg naphthalene$\cdot kg^{-1}$ dry soil, respectively. The LOEC corresponded to an 85% decrease in seedling emergence (Environment Canada 1995b).

Root elongation was examined for lettuce (*L. sativa*) seedlings exposed to naphthalene in solution (Environment Canada 1995a). The resulting NOEC, LOEC, EC_{25} and EC_{50} were 2000, 4000, 2300 and 3100 mg naphthalene$\cdot L^{-1}$, respectively. The LOEC resulted in an 86% decrease in lettuce root growth (Environment Canada 1995a). In a second study on *L. sativa* using an experimental protocol designed to compensate for the volatility of naphthalene, the NOEC, LOEC, EC_{25} and EC_{50} values for root elongation in solution averaged 63, 125, 109 and 363 mg naphthalene$\cdot kg^{-1}$, respectively. The average LOEC corresponded to a 27% decrease in root length (Environment Canada 1995b).

Root elongation was also examined for radish (*R. sativa*) exposed to naphthalene in solution (Environment Canada 1995a). The resulting NOEC, LOEC, EC_{25} and EC_{50} were 4000, 8000, 4400 and 6000 mg naphthalene$\cdot L^{-1}$, respectively, with the LOEC corresponding to a 22% decrease in radish root length (Environment Canada 1995a). In another study on *R. sativa* using an experimental protocol designed to compensate for the volatility of naphthalene, the NOEC, LOEC, EC_{25} and EC_{50} values for root elongation in solution were reported as 16, 31, 41 and 167 mg naphthalene$\cdot kg^{-1}$, respectively. The LOEC resulted in a 19% decrease in root length (Environment Canada 1995b).

4.3 Terrestrial Invertebrates

Very little information is available concerning naphthalene uptake and distribution in terrestrial invertebrates. A summary of consulted invertebrate toxicity data is presented in Table 8.

The results of a study on earthworm *(Eisenia fetida)* mortality following 14 days of exposure to naphthalene in artificial soil was reported by Environment Canada (1995a). Based on measured values, the NOEC, LOEC, EC_{25} and EC_{50} were estimated at 204, 408, 287 and 362 $mg \cdot kg^{-1}$, respectively. The LOEC resulted in 56% earthworm mortality (Environment Canada, 1995a). In another study, *E. fetida* earthworms were exposed for 7 days to naphthalene in a similar artificial soil matrix but under different experimental conditions (Environment Canada 1995b). The NOEC, LOEC, EC_{25} and EC_{50} for this second study were estimated to be 63, 125, 97 and 137 $mg \cdot kg^{-1}$, respectively, with the LOEC resulting in 47% earthworm mortality (Environment Canada, 1995b).

Walton (1980) studied acute and chronic toxicity of naphthalene to crickets (*Acheta domesticus*) via oral and dermal routes of administration. The twenty-four hour LD_{50} when naphthalene was administered orally and topically to crickets was >15,000 and >580 $mg \cdot kg^{-1}$, respectively. In the chronic oral toxicity test, crickets were fed for 18 days on diets consisting of 0.1% naphthalene (100 $mg \cdot kg^{-1}$ wet weight of food). The time required for 50% mortality (LT_{50}) was 12.0±0.41 days. In the chronic topical experiments, naphthalene was applied at a dosage equalling 0.1% of the average weight of food consumed by the crickets over the course of the study. The cumulative topical dose for the 18 day period was 1.224 mg naphthalene per cricket, an application rate resulted in 25% mortality (other endpoints not specified by the author).

4.4 Mammals

Uptake and Distribution

Very little quantitative information is available concerning naphthalene absorption and distribution in mammals. Rats administered naphthalene via gavage at concentrations of 30, 75 and 200 $mg \cdot kg^{-1}$ exhibited an increase in urinary excretion of thioethers proportional to the dose. This result suggests that the absorption rate of naphthalene in rats remains fairly constant up to 200 $mg \cdot kg^{-1}$ (Summer et al. 1979, U.S. EPA 1986). In laying pullets fed ^{14}C-labelled naphthalene via oral intubation, the major site of deposition was the kidney, followed in decreasing order by fat, lung, and liver (Eisele 1985). Naphthalene and/or naphthalene metabolites were also detected in the light and dark meat (muscle tissue), heart and spleen of the pullets, and in the yolk and albumen of eggs (Eisele 1985).

In an acute study where ^{14}C-labelled naphthalene was provided via oral intubation, growing swine showed a rapid accumulation of radioactivity (i.e. naphthalene and/or naphthalene metabolites) in fat tissue, with the liver and kidneys accumulating less than one-tenth the amount contained in fat (Eisele 1985). Following a chronic exposure period of 31 days, little radioactivity was observed in the fat or major organs of swine, indicating that chronic exposure leads to increased elimination capability. In contrast to swine, dairy cows exposed to an acute dose of ^{14}C-labelled naphthalene via oral intubation showed little accumulation in fat (Eisele 1985). The difference may be attributable to the lower body fat content of lactating dairy cattle relative to swine. Following acute and chronic exposure, naphthalene and/or naphthalene metabolites were detected in the liver, loin, flank, heart,

spleen, kidneys, lungs and milk of the lactating cow (Eisele 1985).

Toxicity

Few studies are available concerning naphthalene toxicity to mammals. The available scientific literature is dominated by non-ingestion exposure studies of the effects of naphthalene on laboratory rodents.

Shopp *et al.* (1984) evaluated acute oral toxicity and sub-chronic toxicity of naphthalene administered in corn oil to CD-1 mice. The fourteen day oral LD_{50} of naphthalene was found to be 533 and 710 $mg \cdot kg^{-1}$ for male and female mice, respectively. During the 14 and 90 day sub-chronic effects study, mice were administered naphthalene via oral gavage on a daily basis. The doses administered for the 14 day study were 27, 53 and 267 $mg \cdot kg^{-1}$. For the female mice, a 5% mortality rate was observed only at the highest dosage group (267 $mg \cdot kg^{-1}$). This dose also resulted in a significant decrease in spleen weight and an increase in lung weight. Male mice exhibited 10% mortality at the highest treatment level, although this may have been attributable to aggressive behaviour amongst the male group (Shopp et al. 1994). In addition to the observed mortality, a 30% decrease in thymus weight was apparent in the 267 $mg \cdot kg^{-1}$ dosage group. The 90 day sub-chronic experiments used daily oral doses of 5.3, 53 and 133 $mg \cdot kg^{-1}$ and resulted in no mortalities at all treatment levels. However, female mice exhibited reduced spleen weight at the highest dose while organ weights were unaffected in the males (Shopp et al. 1994).

Naphthalene has been found to cause ocular cataracts in rabbits (Ghetti and Mariani, 1956 as cited in Wells et al. 1989) and mice (Wells et al. 1989). Cataracts were formed in a dose dependent manner in C57BL16 mice exposed to 500 - 2000 $mg \cdot kg^{-1}$ (body weight) via intraperitoneal administration. The incidence of cataractogenesis was enhanced by simultaneous treatment with the cytochrome P-450 inducer phenobarbital and the glutathione depletor diethyl maleate (Wells et al. 1989).

Plasterer et al. (1985) examined the developmental effects of prenatal exposure to naphthalene in female CD-1 mice. Naphthalene doses of 125, 250, 500, 1,200 and 2,000 $mg \cdot kg^{-1}$ were administered by oral gavage for eight consecutive days, resulting in an LD_{50} of 353.6 $mg \cdot kg^{-1}$. The reported maternal lethality (15%) was considered statistically significant for mice treated with naphthalene. Total numbers of live offspring were significantly reduced in the treated groups, with control mice averaging 1.5 more pups per litter than treated mice.

5. DERIVATION OF ENVIRONMENTAL SOIL QUALITY GUIDELINES

5.1 Introduction

Canadian soil quality guidelines are designed to protect four different land uses: agricultural, residential/parkland, commercial and industrial. The derivation procedures are described in *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996).

There were insufficient data available to meet the minimum data requirements described in the Protocol (CCME 1996), for the derivation of soil quality guidelines based on soil contact (SQG_{SC}), soil and food ingestion (SQG_I) or the nutrient and energy cycling check for any of the categories of land use. Studies were excluded from use because of one or more of the following reasons:

- soil pH was not recorded;
- soil pH was below 4 (as this is considered outside the normal pH range of most soils in Canada)
- no indication of soil texture was provided;
- inappropriate statistical analysis was used;
- test was not conducted using soil or artificial soil;
- test soil was amended with sewage sludge or a mixture of toxicants;
- test did not use controls.

Therefore, the Provisional Method, described in CCME (1997) and hereafter was used to derive Provisional Canadian Soil Quality Guidelines for naphthalene. Results are presented in Table 9.

5.2 Provisional Soil Quality Guidelines

Provisional Soil Quality Guidelines Derivation Method

Limitations in the availability of quality soil toxicity data hinder the derivation of soil quality guidelines since the methods described in the Protocol (CCME 1996) are all limited by minimum data requirements. However, litterature searches often yield data which do not meet the requirements of the 1996 Protocol, but still provide some toxicity information. Also, toxicity tests using standard methodologies may produce data that do not meet the regular quality standards defined by toxicologists, due to difficulties in handling and evaluating certain substances such as volatile organic chemicals in the context of a soil contact test for example.

While acknowledging the need for toxicity data of the highest quality, it is the opinion of the Subcommittee that guidelines based on limited toxicity information are still more practical and scientifically defensible than the absence of guidelines or than guidelines that are not risk based. Thus, a provisional method for deriving environmental soil quality guidelines was proposed (CCME 1997). The guidelines derived using this method are called "provisional" to clearly indicate that the underlying data do not meet the requirements of the Protocol (CCME 1996) and that there is an urgent need for additionnal research. Also, given the increased uncertainty surrounding the provisional soil quality guidelines, such provisional guidelines may not be used to raise an existing criteria or guideline, such as the 1991 interim criteria, but only to lower it if the provisional value indicates that the existing criteria or guideline is not adequately protective.

The guiding principles described in the Protocol (CCME 1996) are to be followed while applying relaxed data requirements in order to allow the derivation of provisional soil quality guidelines. When the data requirements of one of the derivation methods described in the Protocol (CCME 1996) are met, regular soil quality guidelines must be derived. However, when the available data do not meet

those requirements, professionnal jugement is used to evaluate the available information and to recommend a provisional soil quality guideline. The derivation of provisional soil quality guidelines is directed by the following landmarks:

- be precautionary: use higher safety factors where degree of uncertainty is high;
- use soil contact data for plants and invertebrates preferentially over mammalian data, equilibrium partitioning data or other data;
- rely on equilibrium partitioning data only to justify additional safety factors and to assist in professional judgement;
- use microbial data as a check mechanism, follow the method described in the protocol (use geometric mean of soil contact number and microbial value where microbial value is lower);
- keep in mind that provisional soil quality guidelines for agricultural and residential/parkland land uses are intended to approximate no appreciable effect levels where those for commercial/industrial land use allow for a low level of effects;
- be consistent with the spirit of the 1996 Protocol.

Derivation of Provisional Soil Quality Guidelines

Table 9 presents a summary of the results of the Provisional derivation procedures and a comparison with the CCME (1991) interim remediation criteria.

The available data was insufficient to meet the minimum data requirements for the derivation of a guideline based on soil contact. However, the available data based on direct soil contact was used in the following manner to derive a SQG_E—provisional. Only the reported EC_{25} endpoints based on direct soil contact experiments, and for these endpoints, only the recovered (measured) concentrations were considered.

For Agricultural and Residential/Parkland land uses, the lowest of the considered values was divided by an uncertainty factor of 5 and the result was taken as the SQG_E—provisional. Thus, from Table 8, the available EC_{25} endpoints based on direct soil contact experiments are: 61 $mg \cdot kg^{-1}$ for radish seedling emergence, 3 $mg \cdot kg^{-1}$ for lettuce seedling emergence, and 54 $mg \cdot kg^{-1}$ for earthworm survival. Hence, the SQG_E—provisional for Agricultural and Residential/Parkland land uses is:

$3 / 5 = 0.6\ mg \cdot kg^{-1}$

For Commercial and Industrial land uses, the SQG_E—provisional was taken as equal to the geometric mean of the available EC_{25} endpoint values listed above, which are based on direct soil contact experiments. Hence, the SQG_E—provisional for Commercial and Industrial land uses is:

$(61 \times 3 \times 54)^{1/3} = 21.5 = 22\ mg \cdot kg^{-1}$

5.3 Groundwater Check

Soils are hydrologically linked to groundwater systems. A major concern with soil contamination is that it can and does lead to groundwater contamination. This check is designed to prevent unacceptable transfers of contaminants to groundwater to protect aquatic life. Thus, the lowest value between the Provisional guideline and the values derived using this check should be used in areas with underlying groundwater systems.

Prudent assumptions are that an aquifer underlying a remediated site may have the potential to enter surface water bodies. Therefore, the following equations are used to calculate the concentration in soil which will not cause an exceedence of groundwater concentrations above existing water quality guidelines for the protection of freshwater aquatic life. The groundwater check follows the rationale and calculation procedure recommended in *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996). It is based on equilibrium partitioning between solid and aqueous phases. For most nonionic organics, including naphthalene, the following equation is used:

$$Y = DF \times C_{WA} (K_d + \theta_m)$$

where,
Y = concentration of contaminant in soil ($mg \cdot kg^{-1}$ dry soil)
DF = dilution factor (50 by default) (CCME 1996)
C_{WA} = water protection value ($mg \cdot L^{-1}$)
θ_m = soil moisture content (0.1 by default) (CCME 1996)

The distribution coefficient (K_d) is directly related to the organic matter content and can be derived using the sorption partition coefficient (K_{oc}) and the organic fraction of dry soil (f_{oc}) as described by the following equation:

$$K_d = K_{oc} \cdot f_{oc}$$

A default value of 0.3% (or 0.003) is used for f_{oc} (CCME 1996). For consistency, the sorption partition coefficient (K_d) is predicted from the octanol-water partition coefficient using the following equation (Mackay *et al.* 1993).

$$K_{oc} = 0.41 \cdot K_{ow}$$

For naphthalene, log K_{ow} has been evaluated at 3.37 (Mackay et al. 1992). Therefore;

K_{ow} = 2344.2
K_{oc} = 961.1
K_d = 2.88

Currently, there are no Canadian water quality guidelines for naphthalene (CCME 1991). The

groundwater check for the protection of aquatic life was therefore performed using a biologically relevant aquatic threshold value. A target maximum concentration of 0.015 mg naphthalene·L^{-1} was obtained, corresponding to the LOEC (9% reduction) on hatchability at embryo-larval stages in rainbow trout (Black et al. 1983).

For the protection of aquatic life;

$$Y = 50 \cdot 0.015\ (2.88+0.1)$$
$$Y = 2.2\ mg \cdot kg^{-1}$$

6. DATA GAPS

Very few studies that evaluate the ecological effects of naphthalene are currently available. The existing literature is predisposed towards aquatic toxicity and laboratory rodent testing, with terrestrial herbivores, invertebrates, microorganisms and avian organisms being poorly represented in the scientific literature. Due to the limitations of the available literature base, it is not currently possible to derive soil quality guidelines for naphthalene based on soil contact (SQG_{SC}), or soil and food ingestion(SQG_I).

As a soil contaminant, naphthalene is often found in close association with other PAHs. Consideration of the combined terrestrial toxicity of groups of PAHs and/or PAH metabolites is therefore necessary. Since soil fungi metabolize naphthalene and higher molecular weight PAH congeners via the monooxygenase pathway, toxic metabolites may persist within the terrestrial environment following the disappearance of the parent compound. Remediation guidelines established for single PAH constituents do not presently account for these toxicologically significant processes.

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TABLES

Table 1: Physical and Chemical Properties of Selected Polyaromatic Hydrocarbons

PAH Compound	Molecular Formula	Molecular Weight	No. of Aromatic Rings	Solubility @ 25°C (μg/L)	Log Kow	Vapour Pressure@ 25°C (mm Hg)
Naphthalene	$C_{10}H_8$	128.16	2	12, 500 - 34, 000	3.37 - 3.5	1.8×10^{-2}
Anthracene	$C_{14}H_{10}$	178.22	3	45 - 59	4.5	2.4×10^{-4}
Phenanthrene	$C_{14}H_{10}$	178.22	3	435	4.46 - 4.5	6.8×10^{-4}
Pyrene	$C_{16}H_{10}$	202.24	4	133 - 135	4.88	6.9×10^{-7}
Chrysene	$C_{18}H_{12}$	228.28	4	1.9	5.63	4.0×10^{-6}
Perylene	$C_{20}H_{12}$	252.30	5	2.4	6.21	7.0×10^{-7}
Benzo[a]pyrene	$C_{20}H_{12}$	252.30	5	3.8	6.06	5.5×10^{-9}
Dibenz[a,h]-anthracene	$C_{22}H_{14}$	278.33	5	0.4	6.86	1.3×10^{-9}
Benzo[g,h,i]-perylene	$C_{22}H_{12}$	276.4	6	0.3	6.78	1.0×10^{-10}
Coronene	$C_{24}H_{12}$	300.3	7	0.14	7.36	1.5×10^{-11}

Source: (Nagpal, 1993; Merck and Co., 1989; Germain et al., 1993; Mackay, Shiu and Ma, 1991)

Table 2: Physical and Chemical Properties of Naphthalene

Property	Value	Source
Common Name:	Naphthalene	
Synonyms:	naphthene, camphor tar, mothballs, albo carbon	Merck 1989
Chemical Name:	naphthalene	Merck 1989
Chemical Family:	polyaromatic hydrocarbon (PAH), polynuclear aromatic (PNA), aromatic hydrocarbon	Merck 1989
CAS Registry No.:	91-20-3	Merck 1989
Physical State at 25°C:	crystalline solid	Merck 1989
Colour:	white	Merck 1989
Odour:	mothball odour	Merck 1989
Molecular Formula:	$C_{10}H_8$	Merck 1989
Molecular Weight:	128.18	Merck 1989
Melting Point:	80.2°C	Merck 1989
Boiling Point:	217.9°C	Merck 1989
Water Solubility:	31.7 $mg \cdot L^{-1}$	Merck 1989
Density at 20°C:	1162 $mg \cdot L^{-1}$	Merck 1989
Henry's Law Constant:	48.6 $Pa \cdot m^3 \cdot mole^{-1}$	U.S. EPA 1982
Vapour Pressure:	11.99 Pa @ 25C	U.S. EPA 1982
Octanol/Water Partion Coefficient (log K_{ow}):	3.37	Mackay et al. 1992
Soil/Carbon Partition Coefficient (log K_{oc}):	3.11	Mackay et al. 1992

Table 3: Naphthalene Levels in Canadian Gasolines (1993)

	Premium Unleaded		Mid-Range Unleaded		Regular Unleaded	
	Summer ($mg \cdot kg^{-1}$)	Winter ($mg \cdot kg^{-1}$)	Summer ($mg \cdot kg^{-1}$)	Winter ($mg \cdot kg^{-1}$)	Summer ($mg \cdot kg^{-1}$)	Winter ($mg \cdot kg^{-1}$)
Minimum	600	400	1300	400	1500	200
Maximum	4900	5100	5100	5000	5600	5100
Average	2800	1500	3300	1800	3600	2200
Std. Dev.	1200	1000	1000	1100	1000	1400

* Based upon 21 samples (premium), 20 samples (mid-range) and 21 samples (regular) collected from across Canada for each of the winter and summer sampling periods. Data source (CPPI, 1994).

Table 4: Naphthalene Concentrations in the Canadian Environment

Compartment	No. of Samples	Naphthalene Concentration			Sampling Location	Reference
		Mean	Med.	Max.		
Soil ($mg \cdot kg^{-1}$)					*Background concentrations:*	OMEE 1994.
		—	0.05	—	Rural parkland sites	
		—	0.2	—	Urban parkland sites	
	5	1.64	—	8	Contaminated site at Pincher Creek, Alberta	ETL 1994.†
	15	450.6	0.7	4400	Site of the old Sorel cokery, Quebec (prior to site restoration)	Laboratoire Sondage Universel Inc.1989.†
Sediments ($mg \cdot kg^{-1}$)	8	0.27	0.24	0.36	Luxton and Mountain Lake, Kejimkujik National Park, P.E.I.	Keizer 1990.†
	38	0.93	0.05	7.80	Sydney harbour, Nova Scotia	Kieley et al. 1988.†
	12	—	0.69	29.0	St. Mary's River (surficial sediments)	Kauss and Hamdy 1991
	3	2.267	0.053	6.724	St. Mary's River	Nagy et al. 1989.†
	24	0.17	0.10	1.17	Vancouver harbour (1985-1986)	Goyette 1989.†
	23	0.43	0.40	0.70	Vancouver harbour (1987)	
	6	0.18	0.14	0.51	Kitimat, British Columbia	Goyette 1991.†
	11	<0.08	<0.08	<0.08	Fraser River Estuary, British Columbia	Harding et al. 1988.†
	42	0.5	0.2	6.3	Montreal harbour	Bélanger 1989.†
	35	0.014	<0.002	0.152	Quebec City harbour	Bélanger 1989.†
	11	<0.01	<0.01	<0.01	Trois-Rivières, Quebec	Bélanger 1989.†
	17	0.02	<0.01	0.08	Lake St. Louis, Quebec	Champoux and Sloterdijk 1988.†
	3	0.057	0.020	0.193	Hamilton Harbour (near Randal Reef)	Murphy et al. 1993.†
	2	1.414	1.414	2.827	Hamilton Harbour, Ontario	Nagy et al. 1989.†
	3	11.937	0.089	35.655	Lake Ontario	Nagy et al. 1989.†

Compartment	No. of Samples	Naphthalene Concentration			Sampling Location	Reference
		Mean	Med.	Max.		
Water ($ng \cdot L^{-1}$)	40	5.38	4.98	11.86	Niagara on the Lake, Ontario (at the mouth of the Niagara River)	Kuntz 1990.†
	51	3.57	3.65	10.76	Fort Erie, Ontario	Kuntz 1990.†
Air ($ng \cdot m^{-3}$).					Niagara River vicinity	Hoff and Chan (1987).
	19	3.2	—	—	January (vapour phase)	
	19	0.16	—	—	January (particulate phase)	
	5	2.4	—	—	September (vapour phase)	
	5	1.0	—	—	September (particulate)	
	24	3.10	2.00	13.00	Kitimat, British Columbia (aluminum smelting)	Johnson 1991.†
	16	18.08	10.39	55.01	Cap-de-la-Madeleine, Quebec (urban)	LEI 1992a, LEI 1992b.†
	17	26.00	3.26	126.67	Jonquiere, Quebec (aluminum smelting)	LEI 1992a, LEI 1992b.†
	20	0.41	0.12	1.84	Nouvelle, Quebec (wood heating)	LEI 1992a, LEI 1992b.†
	24	43.74	1.29	396.88	Sept-Iles, Quebec (wood heating)	LEI 1992a, LEI 1992b.†
	31	12.45	4.33	77.79	Shawinigan, Quebec (aluminum smelting)	LEI 1992a, LEI 1992b.†
	31	4.99	0.21	58.24	Station Riv. des Prairies, Montreal. (wood heating)	LEI 1992a, LEI 1992b.†
	10	14.84	14.49	31.69	Station Duncan and Decarie, Montreal. (urban transportation)	LEI 1992a, LEI 1992b.†

† As reported in Ringuette et al. 1993.

Table 5: Existing Soil and Groundwater Quality Guidelines and Criteria for Naphthalene

Jurisdiction	Category		Conc ($mg \cdot kg^{-1}$ soil)	Reference
Canada (Interim)	Assessment Criteria		0.1	CCME 1991
	Remediation Criteria: Agricultural land use Residential/Parkland land use Commercial/Industrial land use		0.1 5.0 50.0	
British Columbia	Level A (Background Level) Level B (Remediation Criteria, Agricultural, Residential/Parklands) Level C (Commercial/Industrial Lands)		0.1 5.0 50.0	BCMOE 1989
Ontario (proposed clean-up guidelines)	Surface soil with potable groundwater situation (pH 5 to 9)	Agr R/P C/I Groundwater criteria for all uses	4.6 4.6 4.6 21 $\mu g \cdot L^{-1}$	OMEE 1994
	Surface soil with non-potable groundwater situation (pH 5 to 9)	R/P C/I Groundwater criteria for both uses	40 40 5900 $\mu g \cdot L^{-1}$	
	Sub-surface soil with potable groundwater situation (pH 5 to 11)	R/P C/I	4.6 4.6	
	Sub-surface soil with non-potable groundwater situation (pH 5 to 11)	R/P C/I	1300 1300	
Quebec	Level A (Background level) Level B (Remediation criteria) Level C (Immediate clean-up)		0.1 5.0 50.0	MENVIQ 1988
The Netherlands	Target value Intervention value		0.015 NA	MHSPE 1994
New Jersey	Soil clean up standards: Residential surface soils Residential subsurface soils Non-residential surface soils		230 100 4200	New Jersey Register 1992

Agr=Agricultural lands; R/P=Residential/Parklands; C/I=Commercial/Industrial lands
NA=Not available

Table 6: Principal Metabolic Pathways of Naphthalene Biotransformation

Category of Biodegrading Organism	Example of Naphthalene Degrading Genera	Metabolizing Enzyme Systems	Chemical Substrate Specificity	Oxygen Incorporation	Initial Metabolic Products
Fungi	*Cunninghamella* sp. *Saccharomyces* sp. *Syncephalastrum* sp.	Cytochrome P-450 Mixed Function Oxidase (mono-oxygenases)	non-specific	singlet oxygen	Arene oxides, *trans*-1,2-dihydrodiols
Bacteria	*Pseudomonas* sp. *Flavobacterium* sp.	various dioxygenases	specific	molecular oxygen	Dioxetanes, *cis*-1,2-dihydrodiols

Source: Sims and Overcash 1983; Cerniglia et al. 1979; Jefferey et al. 1975.

Table 7: Fugacity Level III Modelling of Naphthalene Partitioning Behaviour

	Predicted Environmental Partitioning Behaviour			
Initial Point of Release	Air (% total)	Water (% total)	Soil (% total)	Sediment (% total)
Air	92.87	2.56	4.45	0.116
Water	2.88	92.78	0.14	4.2
Soil	0.154	0.166	99.67	0.0075
Air/Water/Soil (6:3:1)	5.1	17.3	76.8	0.78

Source: Mackay et. al. 1992.

Table 8. Consulted Invertebrate and Plant Toxicity Studies for Naphthalene

Organism	Effect Parameter (length of exposure)	Endpoint*	Concentration $mg \cdot kg^{-1}$ Nominal and (measured)	Soil pH	Test substrate	Extraction method	Reference
Earthworm *(Eisenia fetida)*	Mortality (14 days)	NOEC LOEC (56%) EC_{25} EC_{50}	204 408 287 362	4.2-4.3	Artificial Soil, OM 4.1 - 7.1%	Nominal	Environment Canada 1995 (a)
	Mortality (7 day)	NOEC LOEC (47%) EC_{25} EC_{50}	63 (33) 125 (70) 97 (54) 137 (77)	4.2	Artificial Soil, OM 6.1%	Nominal (EPA method 3550 / 8000)	Environment Canada 1995 (b)
Lettuce *(Lactuca sativa)*	Seed germination (120 hours)	NOEC LOEC (62%) EC_{25} EC_{50}	350 700 470 630	4.2-4.3	Artificial Soil, OM 4.1 - 7.1%	Nominal	Environment Canada 1995 (a)
		NOEC LOEC (37%) EC_{25} EC_{50}	8 (2) 16 (5) 10 (3) 144 (64)	4.2	Artificial Soil, OM 6.1%	Nominal (EPA method 3550 / 8000)	Environment Canada 1995 (b)
Radish *(Raphanus sativa)*	Seed germination (72 hours)	NOEC LOEC (85%) EC_{25} EC_{50}	63 (58) 125 (121) 66 (61) 90 (86)	4.2	Artificial Soil, OM 6.1%	Nominal (EPA method 3550 / 8000)	Environment Canada 1995 (b)

*The EC endpoints represent the percentage of adverse effect, compared to controls, as calculated by the CCME from the data presented by the author(s).

Table 9. Summary of Environmental Soil Quality Guidelines for Naphthalene

Guidelines	Land use		
	Agricultural ($mg \cdot kg^{-1}$)	**Residential/parkland** ($mg \cdot kg^{-1}$)	**Commercial/industrial** ($mg \cdot kg^{-1}$)
TEC or ECL[a]	Insufficient data	Insufficient data	Insufficient data
Nutrient and energy cycling check	Insufficient data	Insufficient data	Insufficient data
SQG_{SC}	Insufficient data	Insufficient data	Insufficient data
SQG_I	Insufficient data	NA	NA
Groundwater Check for the Protection of Aquatic life	2.2	2.2	2.2
Provisional SQG_E	0.6	0.6	22
CCME interim criteria§	0.1	5.0	50.0

(a) As per the CCME (1996) protocol, the TEC for Agricultural and Residential/Parkland land uses corresponds to the 25th percentile of the effects and no effects data distribution when using the Weight of Evidence method, while the ECL for Commercial/Industrial land use corresponds to the 25th percentile of the effects data distribution.

NA = not applicable.

§CCME 1991.

CANADIAN SOIL QUALITY GUIDELINES FOR NAPHTHALENE: ENVIRONMENTAL

CANADIAN SOIL QUALITY GUIDELINES FOR NAPHTHALENE: ENVIRONMENTAL