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Canadian Environmental Quality Guidelines for Sulfolane: Water and Soil

Scientific Supporting Document

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NOTE TO READERS

The Canadian Council of Ministers of the Environment (CCME) is the major intergovernmental forum in Canada for discussion and joint action on environmental issues of national, international and global concern. The 14 member governments work as partners in developing nationally consistent environmental standards, practices and legislation.

This document provides the scientific supporting information and rationale for the development of Canadian Water Quality Guidelines as well as Canadian Environmental and Human Health Soil Quality Guidelines for Sulfolane. For additional technical information regarding this document, please contact:

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Canadian Water Quality Guidelines are developed by the Water Quality Guidelines Task Group and Soil Quality Guidelines are developed by the Soil Quality Guidelines Task Group of CCME.

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ABSTRACT

This scientific supporting document provides the background information and rationale for the derivation of Canadian Soil Quality Guidelines and Canadian Water Quality Guidelines for sulfolane.

Sulfolane is a colourless, highly polar compound with good chemical and thermal stability. It has a low volatility and Henry's Law constant. Industrially, sulfolane is synthesized by hydrogenation of 3-sulfolene ($C_4H_6SO_2$), which is prepared through the reaction of butadiene (C_4H_6) and sulphur dioxide (SO_2). The total worldwide production of sulfolane was estimated between 18,000 and 36,000 tons per year (approximately 6.4×10^6 to 12.0×10^7 L).

Sulfolane has traditionally been used in the extraction of aromatics and in the removal of acid gases from a natural gas stream. Due to its combination of physical and chemical properties, sulfolane has also been used as an extraction distillation solvent, polymer solvent, polymer plasticizer, polymerization solvent, and in electronic/electrical applications.

Reports on the presence of anthropogenic sulfolane in the environment are limited to data collected from sour gas processing facilities in western Canada. At these facilities, a maximum soil sulfolane concentration of 701 $mg \cdot kg^{-1}$ was measured in clay-rich till. Maximum measured sulfolane concentrations in groundwater collected from contaminated aquifers beneath one of the gas processing facilities were 88 $mg \cdot L^{-1}$ in a bedrock aquifer and 800 $mg \cdot L^{-1}$ in a shallow till aquifer (Gieg *et al.* 1998). Maximum sulfolane concentrations reported in groundwater and creek water were 800 and 0.4 $mg \cdot L^{-1}$, respectively. The maximum measured sulfolane concentration in plants from a wetland was 256 $mg \cdot kg^{-1}$ while the highest measured sulfolane concentration in water within a wetland was 185 $mg \cdot L^{-1}$.

Sulfolane produced toxic signs indicative of central nervous system (CNS) stimulation or depression (dependent on dose) at acute concentrations in mammals. Acute toxicity testing of sulfolane on mammals yielded a range of LD50's from 632 and 2504 $mg \cdot kg^{-1}$ bw. Inhalation of atmospheres containing concentrations of 200 to 4,700 $mg \cdot m^{-3}$ of aerosolized sulfolane resulted in convulsions, vomiting, leukopenia and death in exposed guinea pigs, squirrel monkeys and dogs. None of these toxic effects were observed at exposures to concentrations of 20 $mg \cdot m^{-3}$ or lower. At dose concentrations from 2.5 and 250 $mg \cdot kg^{-1}$ bw it was found that shrinkage of white pulp in the spleen had occurred. Another study exposed rats to sulfolane in their drinking water for 13 weeks and found it to be well tolerated, with the only adverse effects being a nephropathy in male rats at the two highest doses, and reduced white blood cell (WBC) counts in females in the three highest dose groups. The stated NOAEL for male rats in this study, with nephropathy as the endpoint, was 8.8 $mg \cdot kg^{-1}$ day while NOAEL in female rats in the study was 2.9 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$. Based upon this study and the incorporation of a safety factor, a sulfolane TDI for humans was set at 0.0097 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$.

Acute toxicity tests on aquatic vertebrates reported LC_{50} values that ranged from 1,264 $mg \cdot L^{-1}$ (rainbow trout) to 4,800 $mg \cdot L^{-1}$ (goldfish). No adverse effect was observed on survival or growth of the fathead minnow at 1,000 $mg \cdot L^{-1}$. Acute toxicity tests on aquatic invertebrates reported an LC_{50} value from a test using *D. magna* that was 1,245 $mg \cdot L^{-1}$. LOEC toxicity results

for a reproduction endpoint for *Ceriodaphnia dubia*, ranged from 500 $mg \cdot L^{-1}$ to 1,000 $mg \cdot L^{-1}$. A chronic test using the aquatic duckweed (Lemna minor) plant resulted in an EC_{50} value for growth of >2,500 $mg \cdot L^{-1}$. EC_{50} values for a green alga (Selenastrum capricornutum) ranged from 723 $mg \cdot L^{-1}$ to > 1,000 $mg \cdot L^{-1}$.

An interim water quality guideline for sulfolane was calculated to be 50 $mg \cdot L^{-1}$ for the protection of freshwater aquatic life. The species maximum acceptable toxicant concentrations (SMATCs) for cereals, tame hays, and pasture crops are 46 $mg \cdot L^{-1}$ in loam and 15 $mg \cdot L^{-1}$ in poor soil. For other crops, SMATCs are 0.5 $mg \cdot L^{-1}$ in loam and in poor soil. Therefore, the interim irrigation water quality guideline protective of all crop species, regardless of soil type, is 0.5 $mg \cdot L^{-1}$. A source guidance value for groundwater was set at 0.09 $mg \cdot L^{-1}$.

Several soil studies provide evidence that sulfolane is readily biodegradable at concentrations up to 3,000 $mg \cdot L^{-1}$. Therefore, the assumption is made that sulfolane does not adversely affect microorganisms at these concentrations. Based upon these studies, the human health soil ingestion guideline for commercial land use is 2,400 $mg \cdot kg^{-1.}$ The agricultural and residential/parkland land use guidelines have been calculated to be 660 $mg \cdot kg^{-1}$. The industrial off-site migration check for human health endpoints for sulfolane is 9,000 $mg \cdot kg^{-1}$. The maximum sulfolane soil concentration that is protective of groundwater as a source of drinking water yields 0.8 $mg \cdot kg^{-1}$. The groundwater check is the limiting pathway for this media, therefore, the soil quality guideline for the protection of human health is 0.8 $mg \cdot kg^{-1}$.

The sulfolane environmental soil contact guideline for agricultural and residential/parkland land uses was calculated to be 210 $mg \cdot kg^{-1}$ while the soil contact guideline for commercial and industrial land was calculated 430 $mg \cdot kg^{-1}$. The value for the sulfolane off-site migration check for ecological endpoints is 3,000 $mg \cdot kg^{-1}$. The maximum sulfolane soil concentration that is protective of freshwater aquatic life was found to be 450 $mg \cdot kg^{-1}$. The soil contact guideline is the limiting pathway for this media, therefore, the soil quality guideline for the protection of environmental health is 210 $mg \cdot kg^{-1}$. The soil human health groundwater check is the limiting pathway for the overall recommended soil quality guideline for sulfolane, therefore, the overall value is set at 0.8 $mg \cdot kg^{-1}$.

RÉSUMÉ

Le présent document scientifique justificatif fournit l'information générale et l'explication pour l'élaboration des Recommandations canadiennes pour la qualité des sols et des Recommandations pour la qualité des eaux au Canada à l'égard du sulfolane.

Le sulfolane est un composé incolore et fortement polaire doté d'une excellente stabilité chimique et thermique. Sa volatilité et sa valeur de constante de la loi de Henry sont faibles. Dans l'industrie, le sulfolane est synthétisé par l'hydrogénation du 3-sulfolène ($C_4H_6SO_2$), lequel est issu de la réaction du butadiène (C_4H_6) et du dioxyde de soufre (SO_2). Selon les estimations, la production mondiale totale de sulfolane se situe entre 18 000 et 36 000 tonnes par an (entre 6,4 x 10^6 et 12,0 x 10^7 L environ).

Traditionnellement, le sulfolane a été utilisé pour extraire des aromatiques et pour enlever des gaz acides d'une source de gaz naturel. En raison de la combinaison de ses propriétés physiques et chimiques, le sulfolane a également été employé comme solvant d'extraction et de distillation, polymère solvant, polymère plastifiant et solvant de polymérisation, et utilisé dans des applications électroniques et électriques.

Les rapports concernant la présence de sulfolane anthropique dans l'environnement se limitent aux données recueillies dans les installations de transformation des gaz acides dans l'Ouest canadien. Dans ces installations, une concentration maximale de 701 $mg \cdot kg^{-1}$ de sulfolane dans le sol a été mesurée dans un till très argileux. Les concentrations maximales de sulfolane qui ont été mesurées dans les eaux souterraines recueillies dans des aquifères contaminés situés sous l'une des installations de transformation de gaz s'élevaient à 88 $mg \cdot L^{-1}$ dans un aquifère rocheux et à 800 $mg \cdot L^{-1}$ dans un aquifère de till superficiel (Gieg et coll., 1998). Les concentrations maximales de sulfolane rapportées dans les eaux souterraines et les eaux de ruisseau étaient de 800 et 0,4 $mg \cdot L^{-1}$, respectivement. La concentration maximale de sulfolane qui a été mesurée dans les plantes poussant dans une zone humide était de 256 $mg \cdot kg^{-1}$ tandis que celle mesurée dans l'eau d'une terre humide se chiffrait à 185 $mg \cdot L^{-1}$.

Le sulfolane produit des signes d'intoxication qui indiquent une stimulation ou une dépression (selon la dose) du système nerveux central (SNC) chez les mammifères lorsqu'ils sont exposés à des concentrations à effet aigu. Les essais de toxicité aiguë du sulfolane sur les mammifères ont donné des résultats de DL_{50} dont l'éventail se situe entre 632 et 2 504 $mg \cdot kg^{-1}$ de poids corporel. L'inhalation d'atmosphères contenant des concentrations de 200 à 4 700 $mg \cdot m^{-3}$ de sulfolane en aérosol provoque des convulsions, des vomissements, la leucopénie et même la mort chez les cochons d'Inde, les singes-écureuils et les chiens. Aucun de ces effets toxiques n'a été observé lors d'expositions à des concentrations de 20 $mg \cdot m^{-3}$ ou moins. Lorsque la concentration de la dose se situait entre 2,5 et 250 $mg \cdot kg^{-1}$ de poids corporel, il a été découvert que la pulpe blanche de la rate s'était rétrécie. Une autre étude ayant exposé des rats à du sulfolane dans leur eau potable pendant 13 semaines a conclu que les rats le toléraient bien, avec, comme seuls effets indésirables, une néphropathie chez les mâles exposés aux deux doses les plus élevées et une diminution du nombre de leucocytes (GB) chez les femelles exposées aux trois plus fortes doses. La DSENO établie pour les rats mâles de cette étude, dont la néphropathie constituait le critère d'évaluation, était de 8,8 $mg \cdot kg^{-1}$ par jour tandis que la DSENO pour les femelles de cette même

étude était de 2,9 $mg \cdot kg^{-1}$ de poids corporel par $jour^{-1}$. Selon cette recherche et l'introduction d'un coefficient de sécurité, la DJA de sulfolane pour les humains a été établie à 0,0097 $mg \cdot kg^{-1}$ de poids corporel par $jour^{-1}$.

Des essais de toxicité aiguë sur des vertébrés aquatiques ont rapporté des valeurs de CL_{50} se situant entre 1 264 $mg \cdot L^{-1}$ (truite arc-en-ciel) et 4 800 $mg \cdot L^{-1}$ (poisson rouge). Aucun effet indésirable n'a été observé à propos de la survie ou de la croissance de la tête-de-boule à 1 000 $mg \cdot L^{-1}$. Des essais de toxicité aiguë sur des invertébrés aquatiques ont rapporté une valeur de CL_{50} à partir d'un test utilisant *D. magna* qui étaie de 1 245 $mg \cdot L^{-1}$. Les résultats de toxicité d'une CMEO concernant les effets relatifs à la reproduction pour *Ceriodaphnia dubia* variaient de 500 $mg \cdot L^{-1}$ à 1 000 $mg \cdot L^{-1}$. Un essai de toxicité chronique dans lequel on a utilisé une lenticule mineure (*Lemna minor*) a permis d'obtenir une valeur de CE_{50} pour une croissance de >2,500 $mg \cdot L^{-1}$. Les valeurs CE_{50} pour une algue verte (*Selenastrum capricornutum*) se sont classées entre 723 $mg \cdot L^{-1}$ et > 1 000 $mg \cdot L^{-1}$.

Selon la recommandation provisoire pour la qualité des eaux, le taux de sulfolane devrait être de 50 $mg \cdot L^{-1}$ pour la protection de la vie aquatique en eau douce. Les concentrations maximales acceptables de toxiques pour une espèce (CMATE), soit pour les céréales, le foin cultivé et les pâturages, sont de 46 $mg \cdot L^{-1}$ dans les sols argileux-sableux et de 15 $mg \cdot L^{-1}$ dans les sols pauvres. Pour les autres cultures, les CMATE sont de 0,5 $mg \cdot L^{-1}$ dans les sols argileux-sableux et pauvres. Par conséquent, la recommandation provisoire pour la qualité de l'eau d'irrigation qui protège toutes les cultures, peu importe le type de sol, est de 0,5 $mg \cdot L^{-1}$. La valeur-guide pour les sources d'eau souterraine a été établie à 0,09 $mg \cdot L^{-1}$.

Plusieurs études de sols ont montré que le sulfolane est facilement biodégradable dans des concentrations qui s'élèvent à 3 000 $mg \cdot L^{-1}$. Par conséquent, on suppose que le sulfolane n'a pas d'effet indésirable sur les microorganismes à ces concentrations. Selon ces recherches, la recommandation relative à l'ingestion de sol pour la santé humaine en ce qui concerne l'utilisation commerciale des terres est de 2 400 $mg \cdot kg^{-1}$. Les recommandations en matière d'utilisation des terres agricoles et de celles à vocation résidentielle ou de parc ont été calculées à 660 $mg \cdot kg^{-1}$. La valeur de vérification de la migration industrielle hors site à l'égard des effets sur la santé humaine du sulfolane est de 9 000 $mg \cdot kg^{-1}$. La concentration maximale de sulfolane dans le sol qui protège les eaux souterraines comme source d'eau potable atteint 0,8 $mg \cdot kg^{-1}$. La vérification pour les eaux souterraines est la voie limite pour ce milieu, ainsi, la valeur recommandée pour la qualité du sol en vue de protéger la santé humaine est de 0,8 $mg \cdot kg^{-1}$.

La recommandation environnementale relative au sulfolane en contact avec le sol pour l'utilisation des terres agricoles ou à vocation résidentielle ou de parc a été calculée à 210 $mg \cdot kg^{-1}$ tandis que la recommandation concernant le contact avec le sol pour les terres commerciales et industrielles s'élève à 430 $mg \cdot kg^{-1}$. La valeur pour la vérification de la migration hors site du sulfolane en ce qui a trait aux effets sur l'écologie est de 3 000 $mg \cdot kg^{-1}$. La concentration maximale de sulfolane dans le sol qui protège la vie aquatique en eau douce est de 450 $mg \cdot kg^{-1}$. La recommandation relative au contact avec le sol est la voie limite pour ce milieu, ainsi, la valeur recommandée pour la qualité du sol en ce qui a trait à la protection de la santé de l'environnement est de 210 $mg \cdot kg^{-1}$. Le mécanisme de vérification aux fins de la santé humaine de l'exposition à des eaux souterraines en contact avec des sols contaminés constitue la voie

limite pour la recommandation générale de la qualité du sol à l'égard du sulfolane; par conséquent, la valeur globale est établie à 0,8 $mg \cdot kg^{-1}$.

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CHAPTER 1. INTRODUCTION

Canadian Soil Quality Guidelines are numerical concentrations or narrative statements that specify levels of toxic substances or other parameters in soil that are recommended to maintain, improve or protect environmental quality and human health. They are developed using formal protocols to ensure nationally consistent, scientifically defensible values. The guidelines are nationally endorsed through the Canadian Council of Ministers of the Environment (CCME).

This report reviews the sources and emissions of sulfolane, its distribution and behaviour in the environment, and its toxicological effects on soil micro-organisms, plants, animals, and humans.

Soil quality guidelines are derived according to "*A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines*" (CCME 1996), taking into consideration advances made during the development of the "*Canada-Wide Standard for Petroleum Hydrocarbons*" (CCME 2000) for various land uses: agricultural, residential/parkland, commercial and industrial (CCME 2003). In addition, various check mechanisms considering indirect pathways of exposure (*e.g.*, nutrient and energy cycling check and off-site migration of contaminants via wind and water erosion) are used to provide protection for resources and receptors not otherwise considered in the derivation of soil quality guidelines.

Water quality guidelines are derived according to "*A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life*" (CCME 1991), and "*Protocols for Deriving Water Quality Guidelines for the Protection of Agricultural Water Uses*" (CCME 1993).

The following derived values should be considered for general guidance purposes. However, in the application of these values, site-specific conditions should be considered. Because the guidelines may be applied differently in various jurisdictions, the reader should consult appropriate authorities for guidance in the application of these guidelines. The guidelines represent a limit below which no adverse impacts are expected, but site-specific information, should always be considered in the application of these guidelines.

CHAPTER 2. BACKGROUND INFORMATION

Synonyms

Sulfolane [126-33-0], $C_4H_8SO_2$, is known under a variety of synonyms including 2,3,4,5-tetrahydrothiophene-1,1-dioxide and tetramethylene sulfone. A full list of synonyms and trade names can be found in (CAPP 2001).

Physical and Chemical Properties

Published physical and chemical properties are summarized in Table 1. Sulfolane is a colourless, highly polar compound with good chemical and thermal stability. It has a low volatility and Henry's Law constant, a low octanol-water partition coefficient (Kow) and a low soil water partition coefficient (Kd). Sulfolane is highly water soluble and considered miscible at 25°C (Table 1). Its pKa value of 12.9 (Table 1) indicates that sulfolane does not dissociate significantly at typical environmental pH values (i.e., between 6 and 9).

Analytical Methods

There are currently no recommended methods for sulfolane analysis published by CCME or the United States Environmental Protection Agency (US EPA). Generally, sulfolane analysis is conducted by direct injection or solvent extraction, gas chromatographic (GC) separation, and detection by flame ionization (FID), mass-selective detection (MS), or electrolytic conductivity.

Analytical methods for sulfolane were described in the scientific literature for aqueous supernatants from biodegradation studies. Chou and Swatloski (1983) analyzed sulfolane by GC, but did not further specify analytical procedures. McLeod et al. (1992) extracted sulfolane from acidified water samples with dichloromethane and analyzed the extract by GC with a flame ionization detector (FID). CAPP (1997), Greene et al. (1998), Luther et al. (1998), and Greene et al. (1999) analyzed aqueous supernatants from laboratory cultures of biodegradation microcosm studies. Described methods involve direct injection and the use of a GC equipped with an FID. Reported detection limits varied between 0.5 and 5 mg·L-1, depending on the GC used.

Headley et al. (1999a,b) described a gas chromatography-mass spectrometry (GC-MS) method for analysis of sulfolane in vegetation samples from a sulfolane-contaminated wetland. Sample preparation included grinding and homogenizing frozen vegetation samples under liquid nitrogen. Ground samples were transferred into centrifuge tubes and allowed to warm to room temperature. Following addition of deionized water and equilibration for 45 minutes, samples were centrifuged for 45 minutes at 2,500 rpm. The supernatants were then filtered and transferred into a centrifuge tube. Supernatants were back-extracted serially with water-saturated toluene and analyzed by GC-MS.

TABLE 1. Physical and chemical properties of sulfolane.

Property	Units	Value	Reference
CAS registry number		126-33-0	
Molecular formula		$C_4H_8SO_2$	Kirk-Othmer (1999)
Molecular weight	$g \cdot mol^{-1}$	120.17	Lide (1996)
Melting point	ºC	28.5	Kirk-Othmer (1999)
Boiling point	ºC	287.3	Kirk-Othmer (1999)
Specific gravity			
30º C (sulfolane) /30º C (water)	-	1.266	Kirk-Othmer (1999)
100º C (sulfolane) /4º C (water)	-	1.201	Kirk-Othmer (1999)
Flashpoint	ºC	165-178	Kirk-Othmer (1999)
Density at 15º C	$g \cdot cm^{-3}$	1.276	Kirk-Othmer (1999)
Vapour density (air=1)	$g \cdot L^{-1}$	4.2	Shell Chemical Company (1976)
Vapour pressure			
20º C	mm Hg	0.01	Shell Chemicals Europe Limited (1994)
118º C	mm Hg	5	Verschueren (1996)
150º C	mm Hg	14.53	Mellan (1977)
160º C	mm Hg	21.55	Mellan (1977)
200º C	mm Hg	85.23	Mellan (1977)
210º C	mm Hg	115.1	Mellan (1977)
260º C	mm Hg	421.4	Mellan (1977)
n-Octanol-water partition coefficient (K_{ow})	log	-0.4	Travis and Arms (1988)
	log	-0.77	Shell Chemicals Europe Limited (1994)
Organic carbon partition coefficient (K_{oc})	log	0.07	Shell Chemicals Europe Limited (1994)
Henry's law constant	$atm \cdot m^{-3} \cdot mol^{-1}$	8.9×10^{-10}	Shell Chemicals Europe Limited (1994)
Solubility in water			
20º C	$g \cdot L^{-1}$	1,266	Shell Chemicals Europe Limited (1994)
25º C	$g \cdot L^{-1}$	379, miscible	Witzaney and Fedorak (1996)
30º C	$g \cdot L^{-1}$	miscible	Windholz (1983)
PKa	-log K	12.9	Coetzee (1977)
Soil water partition coefficient (Kd)			
montmorillonite	$L \cdot kg^{-1}$	0.94	Luther *et al.* (1998)
kaolinite	$L \cdot kg^{-1}$	0.18	Luther *et al.* (1998)
humus-rich soil	$L \cdot kg^{-1}$	0.099	Luther *et al.* (1998)
soils/aquifer materials (average of 4)	$L \cdot kg^{-1}$	0.08	Luther *et al.* (1998)
Dielectric constant	-	43.3	Kirk-Othmer (1999)
Dermal permeability coefficient (K_p)	$cm \cdot hour^{-1}$	0.0002	US EPA (1992)

Analytical methods used by two commercial laboratories that routinely conduct environmental sulfolane analysis of water and soil samples are summarized below:

One laboratory saturates water samples with NaCl and extracts sulfolane with ethyl ether/dichloromethane. Soil samples are subjected to Soxhlet extraction using dichloromethane. The extracts are analyzed by GC and sulfolane detection is achieved using a mass-selective detector in the selected ion monitoring mode. Detection limits are 0.001 $mg \cdot L^{-1}$ and 0.05 $mg \cdot kg^{-1}$ for water and soil, respectively.

The other commercial laboratory uses a direct injection, GC-FID technique for water samples with sulfolane concentrations exceeding 2 $mg \cdot L^{-1}$. Water samples containing sulfolane concentrations of less than 2 $mg \cdot L^{-1}$ are pre-concentrated using an extraction technique with a medium polarity solvent and extract concentration by evaporation. Soil samples are extracted with deionized water and are pretreated with a non-polar solvent if the soil sample contains significant concentrations of petroleum hydrocarbons. Samples or extracts are analyzed by GC using a polar column and an electrolytic conductivity detector operating in the sulphur-specific mode. Detection limits are 0.001 $mg \cdot L^{-1}$ and 0.01 to 1 $mg \cdot kg^{-1}$ for water and soil, respectively.

The accuracy, precision, and Type I and Type II errors associated with sulfolane water analyses conducted by the second commercial laboratory were investigated by Komex International Ltd. (Komex) in 1995 and 1998 (Komex 1999). The accuracy at sulfolane spike concentrations of 5, 10, and 50 µg L^{-1} ranged between 10 and 21%. Mean measured concentrations showed a positive bias (*i.e.*, measured value was higher than spike concentration) for nine out of twelve results. Sulfolane accuracy was not adversely affected by a matrix of local river water relative to a matrix of deionized water. Precision ranged from 0 to 66%, with an average precision of 22%. Blanks and matrix blanks yielded results below the detection limit (<0.001 $mg \cdot L^{-1}$), indicating no false positives (Type I errors) were obtained. All spikes and matrix spikes returned measurable concentrations indicating no false negatives (Type II errors) were obtained.

Production and Uses

This section on the production and uses of sulfolane was summarized from information in Kirk-Othmer (1999), except where otherwise indicated.

Production

Industrially, sulfolane is synthesized by hydrogenation of 3-sulfolene ($C_4H_6SO_2$), which is prepared through the reaction of butadiene (C_4H_6) and sulphur dioxide (SO_2). The reaction path is shown below:

$$C_4H_6 + SO_2 \rightarrow C_4H_6SO_2 \qquad \text{and} \qquad C_4H_6SO_2 + H_2 \rightarrow C_4H_8SO_2$$

Sulfolane manufacturing using butadiene and sulphur dioxide was patented by Shell in 1944. In 1951, sulfolane preparation by catalytic hydrogenation of sulfolene oxides was patented by Phillip Petroleum.

In North America, sulfolane is produced by Phillips Chemical Company (Borger, Texas, USA). Inspec Fine Chemicals Limited (United Kingdom) indicates they are the world's largest and the only European sulfolane manufacturer. According to Phillips Chemical Company, smaller producers of sulfolane in China and India have begun production within the last few years. The total worldwide production of sulfolane was estimated between 18,000 and 36,000 tons per year (approximately 6.4×10^6 to 12.0×10^7 L). Commercially, sulfolane is available as anhydrous sulfolane and as sulfolane containing 3% (wt.) deionized water.

Uses

Sulfolane has traditionally been used in the extraction of aromatics and in sour gas sweetening, (*i.e.*, removal of acid gases from a natural gas stream). Due to its combination of physical and chemical properties, sulfolane has also been used in a variety of new applications including as an extraction distillation solvent, polymer solvent, polymer plasticizer, polymerization solvent, and in electronic/electrical applications.

Gas Treating

Sulfolane is used as solvent in the Sulfinol process to remove acid gases from natural gas. The Sulfinol process was introduced by Shell in 1963 and consists of passing the sour natural gas stream through a mixture of sulfolane, diisopropanolamine (DIPA), or methyldiethanolamine, and water. Acid gases including hydrogen sulphide (H_2S), carbon dioxide (CO_2), carbonyl sulphide (COS), carbon disulphide (CS_2), and mercaptans (thiols) are physically absorbed by sulfolane and chemically absorbed by DIPA thereby "sweetening" the gas stream.

Sulfolane is used for other gas treatment processes including:

- hydrogen selenide removal from the gasification of coal, shale, or tarsands;
- olefin removal from alkanes;
- nitrogen, helium, and argon removal from natural gas;
- atmospheric CO_2 removal in nuclear submarines;
- ammonia and H_2S removal from waste streams;
- H_2S, HCl, N_2O, and CO_2 removal from various streams; and,
- H_2S and SO_2 removal from gas mixtures which differs from the Sulfinol process in that H_2S and SO_2 are converted directly to elemental sulphur.

Extraction Solvent

Sulfolane is used as an extraction solvent, predominantly to remove benzene, toluene, and xylene from aliphatic hydrocarbon mixtures (Kirk-Othmer 1999). This process is referred to as BTX processing (Broughton and Asselin 1968) and was introduced in 1959 by the Shell Development Company. The BTX process is licensed by Universal Oil Products. BTX processing involves sulfolane extraction of aromatic and some light non-aromatic hydrocarbons from the hydrocarbon feed. The non-aromatic fraction is subsequently stripped in an extractive stripper. The aromatic fraction is removed from the sulfolane solvent using a recovery column. In 1994, worldwide consumption was estimated at 6,974 tons per year of sulfolane for 137 extraction units (Kirk-Othmer 1999).

In addition, sulfolane is used as an extraction solvent for normal and branched aliphatic hydrocarbons, fatty acids, and fatty acid esters. In the latter process, sulfolane is used to enrich the unsaturation level of animal and vegetable fatty oil for use in paints, synthetic resins, food products, plastics, and soaps. Sulfolane is further used in a wood delignification process in which sulfolane extracts the lignin from wood chips thereby freeing the cellulose fibers.
Further extraction solvent applications include removing mercaptans and sulfides from sour petroleum, removing t-butylstyrene from t-butylethylbenzene, separating mixtures of close-boiling chlorosilanes and removing aromatics from kerosene, naphtha, and aviation fuel.

Extractive Distillation Solvent

Sulfolane is used for separating components in narrow boiling range mixtures such as alcohols, chlorosilanes, mono- and diolefins such as isoprene and butadiene, electrochemical fluorination products, water from organic acids, ethers, ketones, esters, cycloalkanes from alkanes, and aromatic hydrocarbons.

Polymer Solvent

Sulfolane is used as a solvent in the production of a variety of polymers including polyacrylonitrile (PAN), poly(vinylide cyanide), poly(vinyl chloride) (PVC), poly(vinyl fluoride), and polysulfones.

Polymer Plasticizer

Sulfolane is used to plasticize nylon, cellulose, and cellulose esters to improve flexibility and increase elongation of the polymer. Sulfolane is further utilized for the synthesis of cellulose hollow fibers as permeability membranes in reverse osmosis cells.

Polymerization Solvent

Sulfolane has been used alone or in combination with a co-solvent as a polymerization solvent for polyureas, polysulfones, polysiloxanes, polyether polyols, polybenzimidazoles, polyphenylene ethers, poly(1,4-benzamide), poly(imino-1,4-phenylenecarbonyl), silylated poly(amides), poly(arylene ether ketones), polythioamides, and poly(vinylnaphthalene/fumaronitrile) (Kirk-Othmer 1999). Sulfolane is used to increase polymerization rate, to facilitate polymer purification, better solubilizing characteristics, and improved thermal stability.

Electronic and Electrical Applications

Sulfolane has been tested as the solvent in lithium batteries due to its high dielectric constant, low volatility, solubilizing characteristics, and aprotic nature. Sulfolane has also been patented for use as a coil-insulating component, solvent in electronic display devices, as capacitor impregnant, and as a solvent in electroplating baths.

Miscellaneous Uses

Miscellaneous uses of sulfolane include the textile industry for preparation of dyes, fabric treating prior to dyeing, and fiber treating; curing of polysulphide-based sealants and

fluoropolymer rubbers; use as catalyst; detoxification of pesticides and chemical warfare agents; and co-surfactant in systems for enhanced petroleum recovery.

Existing Guidelines and Criteria in Various Media

No existing soil and water quality guidelines were found for sulfolane in any jurisdiction.

CHAPTER 3. LEVELS IN THE CANADIAN ENVIRONMENT

The occurrence of sulfolane in the environment has been reported in groundwater, surface water, soil, and plants in the vicinity of facilities where it has been used. It is anticipated, however, that in environments located away from such facilities (*i.e.,* most of Canada) sulfolane will not be present at measurable concentrations.

Reports on the presence of anthropogenic sulfolane in the environment are limited to data collected at three sour gas processing facilities in Alberta and British Columbia (CAPP 1997; Wrubleski and Drury 1997). At these facilities, a maximum soil sulfolane concentration of 701 $mg \cdot kg^{-1}$ was measured in clay-rich till. Maximum measured sulfolane concentrations in groundwater collected from contaminated aquifers beneath one of the gas processing facilities were 88 $mg \cdot L^{-1}$ in a bedrock aquifer and 800 $mg \cdot L^{-1}$ in a shallow till aquifer (Gieg *et al.* 1998). At one of the facilities, sulfolane-impacted groundwater discharged via a wetland into a creek. Levels within the wetland and the creek were significantly reduced compared to the discharging groundwater. Maximum sulfolane concentrations reported in groundwater and creek water were 800 and 0.4 $mg \cdot L^{-1}$, respectively.

Sulfolane uptake by wetland vegetation was studied as part of a CAPP research program to evaluate natural attenuation processes in contaminated wetlands (CAPP 1998; 1999; 2000). Roots, stems, leaves, flower heads, seed heads, and berries of cattail, dogwood, sedge, marsh reed grass, cow parsnip, and smooth brome growing in a sulfolane-impacted wetland were included in the study (CAPP 1999 and 2000; Headley *et al.* 1999b). Analytical results indicated highly variable sulfolane concentrations for different parts of the same species (*e.g.,* roots versus leaves), between different plant species (*e.g.,* cattail leaves versus sedge leaves), and even between different samples of the same part of the same species. The maximum measured sulfolane concentration in plants from the wetland was 256 $mg \cdot kg^{-1}$. The maximum measured sulfolane concentration in water within the wetland was 185 $mg \cdot L^{-1}$.

The only report of sulfolane occurring naturally in the environment was published by Barrow and Capon (1992). The authors identified sulfolane in a composite sample of a sponge (*Batzella*) and tunicate (*Lissoclinum*). The specimens contained approximately 50 $mg \cdot kg^{-1}$ dry weight of sulfolane.

CHAPTER 4. ENVIRONMENTAL FATE AND BEHAVIOUR

The fate and behaviour of a compound released to the subsurface environment is determined by the physical and chemical properties of the compound and the attenuation processes (including biodegradation) to which it is subjected. The relationship between compound properties and fate and behaviour can be used to predict the potential for the persistence and transport of sulfolane in the environment. Physical and chemical properties of sulfolane (Table 1) in combination with recently published sorption studies are discussed in the sections below to evaluate the environmental fate and behaviour of sulfolane.

Adsorption and Mobility

Sulfolane sorption parameters were investigated in batch equilibration studies by Luther *et al.* (1998) (Table 1). Sorbent materials included aquifer sediments from three sulfolane-contaminated sour gas treatment facilities, humus-rich soil, and reference montmorillonite and kaolinite clays. Sulfolane sorption isotherms were found to be linear in the range investigated. Sorption by soils and aquifer materials was reported to be very low with an average aqueous phase sediment partitioning coefficient (K_d) for the four soils/aquifer materials of 0.08 $L \cdot kg^{-1}$. The sulfolane K_d for clay minerals (0.18 to 0.94 $L \cdot kg^{-1}$) was higher than for humus-rich soil (0.099 $L \cdot kg^{-1}$). Cation exchange capacity (CEC) was found to be a reasonable predictor of sulfolane sorption by soils and aquifer materials with low organic carbon content (*i.e.*, <1%).

Sulfolane retardation coefficients calculated by Luther *et al.* (1998) for aquifer sediments were reported for weathered sandstone (1.0), weathered shale/sandstone (1.3), and clay-rich till (1.5). These values indicate sulfolane will migrate at a velocity close to that of the groundwater flow.

The organic carbon-water partition coefficient (K_{oc}) and the n-octanol-water partition coefficient (K_{ow}) represent the equilibrium ratio of sulfolane sorbed by organic carbon or octanol to its concentration in water, respectively, and are reported in Table 1. The low K_{oc}, K_{ow}, and pKa (negative logarithm of the acid dissociation constant) values, and the high water solubility of sulfolane are consistent with the findings of the sulfolane sorption study summarized above: there is a low potential for sulfolane to sorb to sediments or soils. Thus, sulfolane is predicted to be highly mobile in the subsurface.

Leaching and Lateral Movement

The leaching and lateral movement potential of sulfolane is determined by its low affinity for sorption, low retardation coefficients in sulfolane-contaminated aquifer sediments, and high solubility. CAPP (1997) used the classification system of McCall *et al.* (1980) to classify sulfolane mobility as very high. Thus, sulfolane is predicted to partition into water migrating downward through the vadose (*i.e.*, unsaturated) zone. Once in the saturated zone, the migration rate of sulfolane is likely a function of the hydraulic conductivity of the aquifer material, the hydraulic gradient, and the susceptibility of sulfolane to biological attenuation processes (*i.e.*, biodegradation).

Biodegradation

The biodegradation of sulfolane has been investigated in an activated sludge system, in wastewater treatment, in laboratory microcosm studies using contaminated aquifer sediments, and as part of a natural attenuation study in natural wetlands. Most studies have demonstrated that sulfolane is readily biodegradable in nutrient-enriched aerobic microcosms from a variety of sulfolane-contaminated environmental samples.

The ability of microorganisms to degrade sulfolane in refinery wastewater and groundwater using activated sludge or biologically activated carbon has been investigated by Bridié *et al.* (1979b), Chou and Swatloski (1983), Bagnall *et al.* (1984), Juhl and Clark (1990), McLeod *et al.* (1992), and Tian (1992). The findings of these studies were summarized by Witzaney and Fedorak (1996). The aerobic degradation of sulfolane by an activated sludge system was associated with a significant drop in pH that terminated microbial activity (Chou and Swatloski 1983). In an unbuffered system, a pH decrease from 7 to 4.5 and 5 occurred after degradation of approximately 10% of the sulfolane present. The stoichiometry of the complete oxidation of sulfolane was given by Greene *et al.* (1999) as:

$$C_4H_8O_2S + 6.5O_2 \rightarrow 4CO_2 + 3H_2O + 2H^+ + SO4^{2-}$$

Thus, the release of H_2SO_4, a strong acid, caused the observed drop in pH that resulted in termination of the microbial activity in the Chou and Swatloski (1983) study.

Salanitro and Langston (1988) conducted biodegradation studies on soil microcosms in response to a Sulfinol spill. Their findings are summarized in Appendix A-1.

A number of recent studies have investigated sulfolane biodegradation using nutrient-amended and unamended microcosms, under aerobic and anaerobic conditions, and at temperatures ranging from 8 to 28°C. Microcosm studies were conducted using water with sediments and soils from sulfolane contaminated aquifers. Sulfolane concentrations reported in these microcosm studies reflect chemical analysis of the supernatant liquid in $mg \cdot L^{-1}$. Sediments/aquifer materials ranged from sandstone, to till and sand, to wetland sediments. Materials, conditions, lag times, and biodegradation rates reported in microcosm studies are summarized in Appendix A-1.

Greene *et al.* (1998) conducted aerobic and anaerobic microcosm studies at 8° and 28°C using a variety of sediments from contaminated aquifers. This study documented aerobic sulfolane degradation at 8°C and 28°C following addition of the appropriate nutrients such as nitrogen and phosphate. Under aerobic conditions, nearly complete sulfolane removal occurred within 2 to 4 days at 28°C and within 8 to 12 days at 8°C. Results confirmed that previous exposure of aquifer materials to sulfolane and supplementing microcosms with nitrogen and phosphate (Fedorak and Coy 1996) enriches a microbial community, resulting in more rapid sulfolane degradation. Kinetic analyses indicated that sulfolane degradation is more accurately described by zero-order than first-order kinetics. Under anaerobic conditions, no evidence of sulfolane biodegradation was observed at 28°C or under Fe^{3+}, $SO4^{2-}$, and CO_2 reducing conditions at 8°C. In a limited number of microcosms, evidence for biodegradation was observed under Mn^{4+} and NO_3^-

reducing conditions. Thus, Greene *et al.* (1998) concluded that sulfolane biodegradation would not be significant in anaerobic aquifers.

Aerobic microcosm studies conducted at 8°C using sediments and groundwater from sulfolane-contaminated aquifer materials and background locations confirmed the presence of sulfolane degrading bacteria in all contaminated samples (Greene *et al.* 1999). Previously uncontaminated samples did not show evidence of sulfolane degradation even after nutrient (*i.e.*, nitrogen and phosphate) addition. This suggests that soil bacteria exposed to sulfolane adapt over time to be able to degrade sulfolane. Sulfolane biodegradation in previously contaminated aquifer materials was greatly enhanced by the addition of phosphate, whereas the addition of nitrogen provided little stimulation. Once started, sulfolane degradation continued to levels below the detection limit (<1 $mg \cdot L^{-1}$).

Kinetics

The majority of the studies discussed above find that sulfolane degradation is initially slow (presumably while microbial cultures build up, and then, once sulfolane degradation starts, the rate is relatively constant or increases. For this reason, most of the studies approximate the kinetics of the degradation process in terms of a lag time and a rate constant for the subsequent zero order decay (*e.g.*, Greene *et al.*, 1998,1999). However, the criterion for assessing persistence in surface water is based on half-life; a chemical is considered non- persistent if its half-life is less than 8 weeks (CCME 1999). Accordingly, a "pseudo-half life" was generated, where possible, for each result reported in Appendix A-1. A pseudo half-life is defined here as the half-life that correctly predicts the time taken for sulfolane to reach the analytical detection limit. The pseudo half life was generated by i) calculating the number of half lives required under first order kinetics for the initial concentration in each experiment to be reduced to the detection
limit (1 mg/L, referenced in the papers); ii) calculating the time required (including lag time) for sulfolane to be degraded from the initial concentration to the detection limit, and; iii) dividing the results from ii) by the results from i).

Appendix A-1 groups the microcosm experiments into 5 groups. The most relevant data to determining the environmental persistence of sulfolane in surface water are the "surface water studies", where wetland sediment together with corresponding surface water samples were spiked with sulfolane and incubated. These microcosms yielded pseudo half lives in the range of 5 to 11 days (Appendix A-1), and included microcosms with no nitrogen or phosphate supplementation. These pseudo half lives are significantly less than the criterion of 8 weeks noted above, and accordingly, sulfolane is considered a non-persistent variable in surface water.

The remainder of the microcosms in Appendix A-1 are relevant to groundwater rather than surface water, and are discussed in Section 3. Briefly, these data indicate that microcosms consisting of aquifer material and groundwater with the addition of phosphate can degrade sulfolane rapidly (pseudo half lives on the order of a few days) while similar microcosms without supplementary phosphate may not degrade at all.

The findings noted above are in accordance with field observations (Komex International Ltd., unpublished data) over a number of years which indicate that sulfolane can be persistent in

groundwater, however it degrades rapidly once the ground water discharges to a surface water body.

Metabolites

The only metabolite reported to be detected in microbial cultures was sulphate (Chou and Swatloski 1983). They further hypothesized that sulfolane degradation may produce butyrate, a fatty acid. Other metabolites of sulfolane have not been identified to date (Headley and Peru 2002). Bressler *et al.* (1999) reviewed the biodegradation of sulphur-heterocycles and suggested the cleavage of the sulfolane ring is most likely to occur by breaking a C-S bond. The metabolite produced would probably be a four-carbon sulfinic acid (CAPP 1997). Based on evidence from the microcosm studies referenced above, during biodegradation of sulfolane nearly stoichiometric amounts of sulphur are released. Hence, the C-S bond in the hypothesized sulfinic acid metabolite must be cleaved. If no C-C bonds are broken before the second C-S cleavage, an oxidized metabolite containing four C atoms would be formed. If one or more C-C bonds are broken before the second cleavage of a C-S bond, oxidized metabolites containing less than four C atoms would be formed. CAPP (1997) suggested that these hypothesized metabolites would be susceptible to further degradation and predicted sulfolane biodegradation should not generate an accumulation of organic carbon in the medium, except for biomass.

Volatilization

Volatilization potential is commonly expressed using the vapour pressure and the Henry's law constant of a compound. The Henry's law constant is the equilibrium ratio of the concentration in the gas phase to the concentration in the aqueous phase. This value is closely related to the vapour pressure of a compound, but is also dependent on its aqueous solubility and molecular weight and can be used to make a more accurate prediction of the volatility of a compound from an aqueous solution than a prediction based on solely on vapour pressure.

Lyman *et al.* (1982) used Henry's law constants to classify volatilization potential as follows:

- values less than 10^{-7} atm·m^3·mol^{-1} indicate the substance is less volatile than water and can be considered essentially non-volatile;
- values between 10^{-7} and 10^{-5} atm·m^3·mol^{-1} indicate the substance may volatilize slowly but the compound will still tend to partition into the aqueous phase;
- values between 10^{-5} and 10^{-3} atm·m^3·mol^{-1} indicate volatilization is significant; and,
- values greater than 10^{-3} atm·m^3·mol^{-1} indicate the majority of the mass of the compound will tend to partition into the gas phase.

The vapour pressure of a compound is the pressure that the vapour phase of a compound exerts at equilibrium with its liquid phase. Vapour pressures are reported for a given temperature and increase with increasing temperature. Compounds with high vapour pressures are more likely to volatilize than those with lower vapour pressures. Thus, the potential of vapour-phase transport of a compound increases with increasing vapour pressures.

The very low Henry's law constant of sulfolane (8.9 x 10^{-10} atm·m^3·mol^{-1}; Table 1), combined with a low vapour pressure (0.01 mg Hg @ 20°C; Table 1), suggest sulfolane can be considered essentially non-volatile in the environment. Thus, vapour-phase transport in the vadose zone is not expected to be significant.

Photolysis

No information on the susceptibility of sulfolane to phototransformation reactions was available at the time this report was prepared.

CHAPTER 5. BEHAVIOUR AND EFFECTS IN TERRESTRIAL BIOTA

Soil Microbial Processes

Specific studies designed to address the effects of sulfolane on nitrogen fixation, nitrification, carbon cycling, or nitrogen mineralization have not been conducted. However, a number of biological fate studies have been conducted to determine the biodegradation rate of sulfolane by indigenous soil bacteria.

Studies by Fedorak and Coy (1996) and Greene *et al.* (1998; 1999) were conducted with soil microcosms containing sulfolane and DIPA. These and other studies are summarized in Appendix A-1 and are discussed here because they provide concentrations at which soil dwelling bacteria were viable and capable of degrading sulfolane.

Several studies (Appendix A-1) provide evidence that sulfolane is readily biodegradable at concentrations up to 3,000 $mg \cdot L^{-1}$, and therefore the assumption is made that sulfolane does not adversely affect microorganisms at these concentrations. Greene *et al.* (1999) showed that mixed populations of indigenous bacteria were active in subsurface environments contaminated with up to 680 $mg \cdot L^{-1}$ sulfolane. Greene and Fedorak (1998) enumerated bacteria from the Greene *et al.* (1999) soil microcosms and identified a mixture of heterotrophs and sulfolane-degrading bacteria at concentrations of 104 to 106 BFU g^{-1}.

Terrestrial Plants

The toxicity of sulfolane to terrestrial plants is summarized in Appendix A-2. Two toxicity studies have been completed. Data for both studies are provided in CAPP (2001).

The first study (Komex 1999) conducted on lettuce (*Lactuca sativa*), consisted of a five day seed emergence test. Komex (1999) reported a LOEC for seed emergence of 160 $mg \cdot kg^{-1}$ for lettuce grown in artificial soil (Appendix A-2).

The terrestrial plant toxicity testing completed for CAPP (2001) (Appendix A-2) was conducted by Scientific Information Services (SIS) using an Environment Canada (1998a) draft protocol, four plant species (lettuce (*Lactuca sativa*), carrot (*Daucus carota*), alfalfa (Medicago sativa), and timothy (*Phleum pratense*)), and four soils (artificial soil, loam, sand and till) with differing texture, organic carbon content, and cation exchange capacity. The endpoints measured were emergence, biomass, root length, and shoot length after seven days of exposure (Appendix A-2). The majority of species/endpoint combinations were most sensitive to sulfolane in sand or till, and least sensitive in loam.

Terrestrial Invertebrates

The toxicity of sulfolane to terrestrial invertebrates is summarized in Appendix A-3. Two acute toxicity studies using an Environment Canada (1998b) draft protocol and measuring 7 and 14 day mortality endpoints have been conducted using earthworms (Eisenia fetida). Data for both studies are provided in CAPP (2001). Acute toxicity testing of earthworms is a widely used and

accepted method of assessing toxicity to terrestrial invertebrates (*e.g.*, OECD 1984; Greene *et al.* 1989).

Komex (1999) reported an LC_{25} value of 3,800 $mg \cdot kg^{-1}$ (Appendix A-3). The earthworm toxicity testing completed for CAPP (2001) (Appendix A-3), was conducted by SIS on four soils (artificial soil, loam, sand and till) with differing texture, organic carbon content, and cation exchange capacity, also using the Environment Canada (1998b) protocol. pH values for the tests ranged from 6.8 to 8.1. LC_{25} values were lowest for till (2,250 $mg \cdot kg^{-1}$) and highest for loam (15,210 $mg \cdot kg^{-1}$ Appendix A-3).

CHAPTER 6. BEHAVIOUR AND EFFECTS IN FRESHWATER AQUATIC BIOTA

Available data on the toxicity of sulfolane to freshwater and marine aquatic species are summarized in Appendix A-4. Toxicological studies on rainbow trout (*Oncorhynchus mykiss*) and the sideswimmer (*Hyalella azteca*) were commissioned by CAPP (2001). A full report on this work is included in CAPP (2001). Note that ERAC (1998) included a review of previous published and unpublished freshwater aquatic toxicological data, and a report on freshwater toxicological studies, which were commissioned for the ERAC (1998) report. References to ERAC (1998) in the following sections refer only to the new data commissioned for that report. Original references are used for other studies referenced in the ERAC (1998) report.

Aquatic Vertebrates

Data were available for five species of aquatic vertebrates (Appendix A-4). An acute lethality study on rainbow trout (*Oncorhynchus mykiss*) was completed for CAPP (2001). ERAC (1998) completed a 7-day survival and growth test on fathead minnows (*Pimephales promelas*). The results of acute lethality studies on goldfish (*Carassius auratus*), mosquito fish (*Gambusia* sp.), and stickleback (species not specified) were also available. Reported LC_{50} values for the acute tests ranged from 1,264 $mg \cdot L^{-1}$ (rainbow trout) to 4,800 $mg \cdot L^{-1}$ (goldfish). No adverse effect was observed on survival or growth of the fathead minnow at 1,000 $mg \cdot L^{-1}$ (the highest concentration used in the test).

Aquatic Invertebrates

Studies were available that considered the toxicity of sulfolane to three species of aquatic invertebrates (Appendix A-4). An acute lethality study on a sideswimmer (*Hyalella azteca*) was completed for CAPP (2001). Reported 48 hour LC_{50} values for *Daphnia magna* ranged widely from 40 $mg \cdot L^{-1}$ (Girling, 1987) to 3,274 $mg \cdot L^{-1}$ (ERAC, 1998). Studies from Shell 1984a,b were rejected because none reported controls and most did not report water chemistry data. Details of the test protocols for the three pre-existing *D. magna* studies were reviewed, but provided no insight into why the reported LC_{50} values vary by almost two orders of magnitude. One possible reason for the variability could be differing sensitivity of the *D. magna* cultures used in the testing. None of the pre-existing *D. magna* tests reported a reference toxicant test to confirm the sensitivity of the culture. An additional 48 hour LC_{50} *D. magna* toxicity test, including a reference toxicant test with NaCl and chemical analysis for sulfolane at the beginning and end of the test, was commissioned to help resolve this issue (Environment Canada 2003). The LC_{50} value from this test was 1,245 $mg \cdot L^{-1}$, based on mean measured sulfolane concentrations at the beginning and end of the test. This value was taken to be definitive due to: 1) the results of the reference toxicant test that were within quality control limits; 2) the chemical analysis for sulfolane and the beginning and end of the test; and, 3) the carefully controlled and reported conditions in this study. The LOECs for the non-lethal (reproduction) endpoint for *Ceriodaphnia dubia*, ranged from 500 $mg \cdot L^{-1}$ to 1,000 $mg \cdot L^{-1}$.

Aquatic Plants

Only one study for an aquatic vascular plant was available. SRC (1994) reported the 50th percentile effect concentration (EC_{50}) for duckweed (*Lemna minor*) growth to be >2,500 mg·L^{-1}. Three studies on the green alga *Selenastrum capricornutum* were available for various non-lethal endpoints. The lowest EC_{50} value was 723 mg·L^{-1} from the ERAC 1998 growth endpoint study. Other studies and other endpoints all gave EC_{50} values greater than 1,000 mg·L^{-1}.

Other Aquatic Biota

Other aquatic biota include all aquatic organisms not included in the animal or plant kingdoms. This covers organisms from the kingdoms Monera, Protista, and Fungi. A study by SRC (1994) measured ^{14}C uptake and nitrogen fixation by the cyanobacteria Aphanizomenon flos-aquae and ^{14}C uptake by the diatom *Cyclotella meneghiana*. The EC_{50} values reported were all greater than or equal to 500 mg·L^{-1}.

CHAPTER 7. BEHAVIOUR AND EFFECTS IN MARINE AQUATIC BIOTA

Marine Vertebrates

Literature data were not available for marine vertebrates.

Marine Invertebrates

Three studies considered the toxicity of sulfolane to marine invertebrates. Acute studies using the copepod Acartia tonsa (Girling 1987) and the oyster Crassostrea gigas (Fairhurst et al. 1992) yielded LC50 values ranging from 52 $mg \cdot L^{-1}$ (48 hour duration) to 460 $mg \cdot L^{-1}$ (24 hour duration). A NOEC of 150 $mg \cdot L^{-1}$ was obtained for the non-lethal (growth) endpoint of the mysid shrimp Mysidopsis bahia during a 7 day, chronic study (Wong et al. 1993).

Marine Plants

Literature data were not available for marine plants.

Other Marine Biota

Other marine biota include all marine organisms not included in the animal or plant kingdoms. This covers organisms from the kingdoms Monera, Protista, and Fungi. Two studies examined the effect of sulfolane on the luminescence of the marine bacterium Vibrio fischerii (SRC 1994; ERAC 1998). Reported EC50 values ranged from 30 to 59 $mg \cdot L^{-1}$.

CHAPTER 8. BEHAVIOUR AND EFFECTS IN HUMANS AND MAMMALIAN SPECIES

Adsorption, Biotransformation and Excretion

Research has indicated that sulfolane is rapidly and readily absorbed via the oral and inhalation routes, but poorly absorbed via the dermal route of administration (Andersen *et al.* 1976; Ursin *et al.* 1995). Andersen *et al.* (1976) conducted a number of absorption and metabolism studies in various species (*i.e.,* rats, guinea pigs, rabbits, and mice). Following an intraperitoneal administration of 100 mg of ^{35}S-sulfolane kg^{-1}, 85% of the radioactivity excreted in the urine during the first 24 hours was associated not with sulfolane itself, but with a metabolite, identified as 3-hydroxysulfolane (Andersen *et al.* 1976). Further excretion studies indicated that at low doses much of the sulfolane was excreted in its metabolized form in the urine and, with increasing dose, a larger proportion of the dose was excreted as unmetabolized sulfolane. These data indicate the presence of a saturable metabolic system.

Based upon blood-sulfolane decay curves obtained following intravenous injections of sulfolane, Andersen *et al.* (1976) estimated sulfolane was rapidly distributed throughout the body and then slowly removed from plasma with a half-life of 3.5 to 5 hours.

While route-specific bioavailability estimates cannot be predicted based upon an intraperitoneal administration, given that 85% of the sulfolane was excreted in a metabolized form, one would expect an internalized dose to be highly bioavailable.

Acute Toxicity Studies

There was minimal evidence of acute toxicity from sulfolane administered by various routes in rats, mice, guinea pigs, and rabbits. The toxicity of sulfolane to the four species was similar (Appendix A-5). Studies by Andersen *et al.* (1976) indicated little variation between the LD_{50} of oral, parenteral, and subcutaneous administered doses, while the intravenous LD_{50} was approximately half that seen with exposures via the other routes of exposure. Regardless of the route of administration or species, sulfolane produced toxic signs indicative of central nervous system (CNS) stimulation or depression (dependent on dose).

Inhalation Studies

Sulfolane has a low vapour pressure (Table 1), therefore, exposure via inhalation is unlikely at normal temperatures. Saturated vapours or mist suspensions can produce headache, nausea, vomiting, and decrease white blood cells (leukopenia). Neurological evidence of a response to inhaled sulfolane mists includes tremors and seizures. The effects observed in these exposures are reviewed in detail below in the section “Subchronic and Chronic Toxicity Studies”.

Oral Studies

In acute toxicity studies by Andersen *et al.* (1976), oral LD_{50} estimates for guinea pigs and rats were determined as 1,815 and 1,846 mg sulfolane kg^{-1} body weight (bw), respectively (Appendix A-5). Administration of sulfolane produced hyperactivity, followed by clonic-toxic convulsions.

Brown *et al.* (1966) reported a single dose, acute, oral LD_{50} of 2,100 $mg \cdot kg^{-1}$ bw in exposed guinea pigs (Appendix A-5). All animals that died, did so within 24 hours and typically in less than 3 hours. In each case, death was preceded by convulsions and gasping for breath.

Zhu *et al.* (1988) reported on the toxicokinetics of orally administered ^{3}H-sulfolane to the rat in a study that investigated the maximum allowable concentration of sulfolane in surface water. Acute oral LD_{50} values in white rats, mice and guinea pigs were determined as 2,504, 2,343, and 1,445 $mg \cdot kg^{-1}$ bw, respectively (Zhu *et al.* 1987; Appendix A-5). The authors indicate similar symptoms were immediately evident in each of the three test animals. The test subjects became more active, short of breath, and demonstrated rigid tails, twitching, rear leg shaking, and stiffening a few minutes following administration.

Percutaneous and Intravenous Administration

Andersen *et al.* (1976) reported parenteral LD_{50} values ranging from 1,270 to 1,598 $mg \cdot kg^{-1}$ bw in rats, mice, and guinea pigs, and intravenous LD_{50} values ranging from 632 to 1,094 $mg \cdot kg^{-1}$ bw for rats, mice, and rabbits exposed to sulfolane. Oral, parenteral, and intravenous exposures approaching, or in excess of the LD_{50}, resulted in toxic signs indicative of CNS stimulation.

Gordon *et al.* (1984) noted that a parenteral injection of approximately half the LD_{50} (799 $mg \cdot kg^{-1}$ bw) resulted in a depressed metabolic rate and hypothermia in rats, which lasted at least 2.5 hours. The authors speculated sulfolane toxicity may be partially due to its effects on body temperature (*i.e.*, depression of thermoregulation). Similar results were observed in studies by Ruppert and Dyer (1985).

Subcutaneous injections of 9, 100, 200, 400, 600, and 750 mg of sulfolane kg^{-1} bw at an ambient temperature of 10°C caused a dose-dependent decrease in the colonic temperature of rabbits (Mohler and Gordon 1988). The observed thermoregulatory response to sulfolane appeared to be a function of the ambient temperature.

Dermal and Ocular Studies

Dermal application of sulfolane resulted in no apparent skin irritation or damage in test rabbits (Brown *et al.* 1966). Furthermore, sulfolane did not produce signs of sensitization in either topical or intradermal tests. Undiluted sulfolane (0.2 ml) instilled into the right eyes of rabbits produced only a mild conjunctivitis, which cleared within a few hours.

Subchronic and Chronic Toxicity Studies

Three studies were available in this category (Appendix A-5). These studies are reviewed below.

Andersen et al. (1977)

Andersen *et al.* (1977) conducted subchronic (90 day) inhalation toxicity studies with rats, guinea pigs, beagle dogs, and squirrel monkeys. Animals were routinely evaluated for signs of potential toxic effects, such as alterations in physical appearance, locomotor activity, breathing patterns, appetite, or behaviour. Animals were also weighed and bled for hematological testing

after 30 and 60 exposure-days, and at the end of the study. Blood, major organs and tissues were also collected from each animal at the end of the study. Urinalysis examined pH, protein, sugar, ketone bodies, and occult blood at 24-hour intervals collected from the rats and guinea pigs. Six subchronic exposure studies were conducted: one study involved repeated exposure to 495 $mg \cdot m^{-3}$ for 8 hour day^{-1}, 5 days/week for 27 exposure days, and five studies looked at 23 hr day^{-1}, continuous exposures of approximately 90 day duration to 200, 159, 20, 4.0, and 2.8 $mg \cdot m^{-3}$.

Inhalation of atmospheres containing high concentrations (3,600 and 4,700 $mg \cdot m^{-3}$) of aerosolized sulfolane resulted in leukopenia and convulsions within 24 hours. Concentrations of 200 and 495 mg sulfolane$\cdot m^{-3}$ resulted in convulsions, vomiting, and death in exposed squirrel monkeys, while dogs convulsed, vomited, and were unusually aggressive during continuous exposure to 200 $mg \cdot m^{-3}$, but not during repeated exposures to 495 $mg \cdot m^{-3}$. While deaths of two squirrel monkeys were seen at the 200 $mg \cdot m^{-3}$ exposure level (on days 3 and 4), both monkeys were heavily infested with parasites, potentially playing a role in their susceptibility to sulfolane toxicity. While none of the rodents convulsed at any of the subchronic exposures, histological investigations indicated leukopenia and increased plasma transaminase activity in guinea pigs exposed to 200 $mg \cdot m^{-3}$, but not those exposed to 159 $mg \cdot m^{-3}$.

None of the toxic effects observed at 200 $mg \cdot m^{-3}$ in any of the test species were found on exposure to concentrations of 20 $mg \cdot m^{-3}$ or lower. As such, the exposure concentration of 20 $mg \cdot m^{-3}$ could be considered the no-observable-adverse-effect-level (NOAEL).

A study of the chronic toxicity of sulfolane administered orally to guinea pigs (which had just stopped breast-feeding) at dose levels of 0.25, 2.5, 25, and 250 $mg \cdot kg^{-1}$ bw was reported by Zhu *et al.* (1987). Forty guinea pigs, with equal numbers of males and females, were exposed to sulfolane for six months in each of the dose groups, and one control group. Biochemical and pathological evaluations were conducted on a subset of each dose group following three months of exposure, with minor effects observed in the 2.5, 25, and 250 $mg \cdot kg^{-1}$ bw dose groups. Pathological tissue inspection indicated the main pathological change involved shrinkage of white pulp in the spleen.

After six months of exposure, significant changes were observed in a number of liver biochemical indices for the 250 $mg \cdot kg^{-1}$ bw male guinea pig group, with some changes noted in the 25 $mg \cdot kg^{-1}$ bw group. Pathological examinations indicated a significant increase in fatty deposits in the liver tissue for the 2.5, 25, and 250 $mg \cdot kg^{-1}$ bw exposure groups. Shrinkage of spleen white pulp and decreasing cell counts in spinal marrow was also noted in these three dose groups. No biochemical or pathological changes were found in the 0.25 $mg \cdot kg^{-1}$ bw dosage group.

Based on these study results, the authors reported a chronic threshold and no-effect doses for sulfolane of 2.5 and 0.25 $mg \cdot kg^{-1}$ bw bodyweight, respectively, and a maximum allowable concentration (MAC) of 5 $mg \cdot L^{-1}$ in drinking water for humans (Zhu *et al.* 1987).

Huntingdon Life Sciences (HLS, 2001)

The Huntingdon Life Sciences (HLS 2001) study involved exposure of rats to sulfolane in their drinking water for 13 weeks at concentrations of 0, 25, 100, 400, and 1,600 $mg \cdot L^{-1}$, which was calculated by HLS to be equivalent to the following levels:

Males: 2.1, 8.8, 35, and 131.7 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$
Females: 2.9, 10.6, 42, and 191.1 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$

The sulfolane exposure was reported to be well tolerated, with the only adverse effects being a nephropathy in male rats at the two highest doses, and reduced white blood cell (WBC) counts in females in the three highest dose groups.

The nephropathy is typical of the well-known phenomenon specific to male rats that occurs following prolonged exposure to many hydrocarbons and derivatives, and is not considered to be of toxicological relevance to humans. The stated NOAEL for male rats in this study, with nephropathy as the endpoint, was 8.8 $mg \cdot kg^{-1}$ day (100 mg sulfolane L^{-1} drinking water).

The WBC reductions are consistent with observations from the Andersen *et al.* (1977) inhalation study. In the latter investigation they occurred after a single, high, 17.5 hour exposure, as well as after longer term exposures at the higher test concentrations in both sexes of rat (no data is given for female rats in the Andersen *et al.* (1977) paper, but male rats were definitely susceptible, whereas they were unaffected in the HLS (2001) study). WBC reductions were also observed in squirrel monkeys and guinea pigs exposed to high doses, but not in any of the four tested species after prolonged inhalation of 20 $mg \cdot m^{-3}$. A WBC reduction after a single exposure, as occurred in the Andersen *et al.* (1977) study, indicates a direct toxic effect on the WBCs. No pathological lesions were found in the females. The NOAEL in female rats in the HLS (2001) study was 2.9 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$ (25 $mg \cdot L^{-1}$ sulfolane L^{-1} drinking water).

Genotoxicity Studies

When evaluating data for genotoxicity, primary goals are to determine (1) the likelihood of occurrence of a key event and (2) whether that event might lead to heritable changes associated with any adverse effect *in vivo*, including cancer. The basis upon which a weight-of-evidence evaluation can be constructed includes the following:

- any statistically significant observations should be reproducible and biologically significant;
- a dose-response relationship should exist for effects;
- the effects should be permanent and progressive, as opposed to reversing upon cessation of chemical dosing;
- the nature of DNA effects should be characterized;
- the database should be consistent or inconsistencies adequately explained; and,
- the effects produced in the assay should be relevant to humans.

A central objective of the weight-of-evidence approach is to balance experimental test data with experience, and not to accord greater weight to any single result. For purposes of human hazard assessment, greater confidence is placed in those test systems that examine possible genetic effects from chemical exposure of animals, rather than in tests that rely on selected homogeneous cell populations raised and tested *in vitro*. Chemical exposures of biological systems carried out *in vitro* are much less realistic, and results of such tests can be determined by the effects of toxicity. Such toxicity can occur at unusually high exposure concentrations and/or be dependent on metabolic and detoxification capabilities. Finally, a weight-of-evidence evaluation seeks to establish a dose-response relationship. Greater attention should be given wherever there is a clear association between increased exposure and a genetic effect.

Sulfolane has never been assessed by mammalian cancer bioassays. The structurally related compound, 3-sulfolene was assessed by the National Cancer Institute and was found to be negative in a gavage carcinogenicity study in Osborne-Mendel rats and B6C3F1 mice (NCI 1978). Compared to sulfolane, 3-sulfolene has a higher degree of unsaturation, and may therefore differ in chemistry and toxicity.

The bacterial mutagenic activity of sulfolane was investigated in *Salmonella typhimurium* (strains TA1525, TA1537, TA1538, TA98, and TA100) and *Escherichia coli* (WP_2 and WP_2-*uvr A*) tester strains. Eucaryotic mutagenic activity was also examined in the yeast *Saccharomyces cerevisiae* (JD 1). These assays were conducted either in the presence or absence of an S9 microsomal fraction obtained from a liver homogenate from rats pretreated with Aroclor. At concentrations up to 4,000 µg per plate, sulfolane was not mutagenic to *E. coli* or *Salmonella* either in the presence or absence of a rat liver S9. Results in the *Saccharomyces* mitotic gene conversion assay with or without S9 also indicated sulfolane was non-mutagenic/genotoxic at concentrations up to 5 $mg \cdot ml^{-1}$ (Shell 1982). Similar assays on five *Salmonella typhimurium* strains (TA1535, TA1537, TA1538, TA98, and TA100) were also tested by Phillips (1984). Exposure to five graded doses of sulfolane in the presence of and in the absence of metabolic activation did not increase reversion rates of histidine prototrophy.

Phillips (1984) conducted an *in vitro* sister chromatid exchange (SCE) assay using Chinese hamster ovary cells and a minimum of five doses of sulfolane, with and without metabolic activation by an Aroclor-induced rat liver microsomal fraction. A statistically significant increase in the number of SCE per chromosome was observed only at the highest dose ($6.4\ mg \cdot ml^{-1}$) in the absence of metabolic activation. There were no significant increases observed at the remaining doses, so there was no evidence of a dose-response. Since only one dose of sulfolane exhibited a statistically significant increase in SCEs, but no dose produced an overall two-fold increase in SCE's, it was concluded the criteria for a positive test were not met. Therefore sulfolane was considered negative for the production of SCE in vitro (Phillips 1984).

In primary cell cultures of rat liver RL-4 cells, sulfolane at doses of 0.1, 0.25, and $1.0\ mg \cdot ml^{-1}$ in vitro was negative in a chromosomal aberration test (Shell 1982).

In the mouse lymphoma forward mutation assay performed in the L5178Y TK+/- a minimum of eight doses of sulfolane were tested with and without metabolic activation by an Aroclor-induced rat liver microsomal fraction. Sulfolane treatment resulted in an increased induction of forward

mutations at the TK locus for some doses, but failed to exhibit a dose-response relationship. Under the accepted criteria for the test, it was concluded that sulfolane was mutagenic in this assay (Phillips 1984).

Zhu *et al.* (1987) investigated the mutagenicity of sulfolane in three tests. In the Ames test, sulfolane was negative at all doses (0, 2, 20, 200, and 2,000 µg/container). In the mice spinal marrow micronucleus test sulfolane was administered orally to mice at doses of 62.5, 125, 250, 500, and 1,000 $mg \cdot kg^{-1}$. There was no statistically significant difference between the various dosage groups and the negative control; there was a difference between the various dosage groups and the positive control. Accordingly, it was concluded that sulfolane did not change the rate of micronucleus formation under the tested condition and the test was negative. Sulfolane was also tested at concentrations of 0.01, 0.1, 1, and 10 $mg \cdot ml^{-1}$ in an SCE test. Cell growth was inhibited in the 10 $mg \cdot ml^{-1}$ group. It was concluded that there was no statistical difference ($p>0.05$) between the test groups and the negative control group, and that sulfolane did not obviously affect SCE frequency of lymphocytes in human peripheral blood under the test conditions.

In the various mutagenicity and genotoxicity assays, sulfolane was not mutagenic in bacteria or yeast, and showed no evidence of being capable of producing structural alterations in vitro such as chromosomal aberrations in primary rat liver cultures, or SCE in either Chinese hamster ovary cells or lymphocytes in human peripheral blood. On the other hand, there is one report of a positive response at the highest dose in the mouse lymphoma assay, but no clear dose-response. Based on the criteria described, there is insufficient evidence to conclude that sulfolane is genotoxic, and the single mouse lymphoma assay response may suggest cytotoxicity at extremely high doses.

Reproductive and Developmental Toxicology Studies

Zhu *et al.* (1987) investigated possible teratogenetic effects of sulfolane on mice. Sulfolane was administered orally, once a day, at doses of 840, 280 and 93 $mg \cdot kg^{-1}$ (equivalent to 1/3, 1/9 and 1/27 of the LD_{50}) to mice on the 6th to 15th days of pregnancy. A sulfur-containing pesticide was used as positive control and distilled water as negative control. On the 18th day of pregnancy, the fetuses were taken out, the organs were examined and any skeletal changes noted.

No abnormality of body appearance and internal organs was observed for any of the test groups or the negative control group. For the 840 $mg \cdot kg^{-1}$ groups, the percentage of fetus absorption (30.16%) was significantly higher than that of the negative control (10.53%). Skeletal changes were found in 840 $mg \cdot kg^{-1}$ group ($P<0.01$), but no such changes were observed in the 280 $mg \cdot kg^{-1}$ group.

Tolerable Daily Intake (TDI)

The *Protocol for Developing Environmental and Human Health Soil Quality Guidelines* (CCME 2003) defines the Tolerable Daily Intake (TDI) as the intake to which it is believed a receptor can be exposed over a lifetime without deleterious effects. The TDI represents the combination of: (1) real values for toxicological endpoints at which no evidence of adverse effects can be

detected in experimental animals or humans; and, (2) uncertainty factors that account for possible differences between responses in the species tested and humans, sensitivity of human populations, and other factors that contribute to uncertainty. The introduction of uncertainty factors is a concept that has had wide acceptance in scientific and regulatory communities around the world.

The TDI is defined in Health Canada (1994) as:

$$TDI = \left(\frac{NOAEL\ or\ LOAEL}{Uncertainty\ Factor} \right)$$

The selection of the most appropriate study, selection of uncertainty factors and the calculation of the TDI is discussed in the three following sections.

Selection of Study

The three following chronic or subchronic studies for sulfolane were reviewed in the "Subchronic and Chronic Toxicity Studies" Section:

- Andersen *et al.* (1977);
- Zhu *et al.* (1987); and,
- Huntingdon Life Sciences (HLS 2001).

The human TDI was based on the HLS (2001) study. This study was preferred over the Andersen *et al.* (1977) study due to a more applicable route of administration (oral versus inhalation). Zhu *et al.* (1987) was not used to develop a human TDI due to uncertainties in the interpretation of some of the toxicological endpoints and the lack of data available to confirm that "good laboratory practice" GLP had been followed in this study.

The NOAEL in female rats in the HLS (2001) study was 2.9 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$ (25 $mg \cdot L^{-1}$ $sulfolane \cdot L^{-1}$ drinking water).

Selection of Uncertainty Factors

Guidance on developing uncertainty factors has been offered by a number of agencies. Health Canada (1994) propose:

1. A factor of 1 to 10 to account for interspecies variation;
2. A factor of 1 to 10 to account for intraspecies variation;
3. A factor of 1 to 100 to account for inadequacies in the database, which include, but are not limited to, lack of adequate data on developmental, chronic, or reproductive toxicity, use of a LO(A)EL versus a NO(A)EL, and inadequacies of the critical study; and,
4. A factor of 1 to 5 if there is information indicating the potential for interaction with other substances in the environment; and,
5. Exceptionally, an additional factor of 1 to 10 may be incorporated when deriving a TDI for severe effects.

The Joint European Committee on Food Additives (JECFA) proposed principles for determining a margin of safety, and has developed a methodology to establish an acceptable value for a factor that would directly link animal toxicological data to human health and safety (FAO/WHO 1958). The margin of safety allows for any species differences in susceptibility, the numerical differences between the test animals and the exposed human population, the greater variety of complicating disease processes in the human population, the difficulty of estimating the human intake, and the possibility of synergistic action. JECFA stated that the 100-fold margin of safety applied to the maximum ineffective dosage (expressed in $mg \cdot kg^{-1}$ body weight day^{-1}) was believed to be an adequate factor (FAO/WHO 1958). The value of 100 has been regarded as comprising two factors of ten to allow for interspecies and intraspecies variation (WHO 1994).

The validity and size of safety/uncertainty factors, and their application across many substances including pesticides has undergone periodic re-evaluation (Renwick and Lazarus 1998). By and large, the allocation of appropriate uncertainty factors is considered on a case-by-case basis, relying on analysis of the total weight of evidence including a consideration of data gaps (WHO 1990). WHO Scientific Groups have confirmed a 100-fold uncertainty factor as an adequate and useful guide, particularly when there are few toxicological data gaps (WHO 1967; 1994).

The National Research Council report on Pesticides in the Diets of Infants and Children (NRC 1993) indicated the current 10-fold intraspecies factor adequately protects for socioeconomic, nutritional, and health status factors that influence the vulnerability of children to environmental toxicants.

The uncertainty factor for sulfolane, using the HLS (2001) study, is based on the Health Canada (1994) uncertainty factors, and is broken down as follows:

Factor 1 - interspecies variation. An uncertainty factor of 10 is applied for interspecies variation.

Factor 2 - intraspecies variation. An uncertainty factor of 10 is applied for intraspecies variation (*i.e.,* sensitive individuals).

Factor 3 - database inadequacies, which include, but are not limited to, lack of adequate data on developmental, chronic, or reproductive toxicity, use of a LO(A)EL versus a NO(A)EL, and inadequacies of the critical study:

- Reproductive and developmental toxicity: there is one study (Zhu *et al.* 1987; reviewed under "Reproduction and Developmental Studies") which considers these endpoints. Skeletal abnormalities and fetus absorption were noted in the highest dose group, but as this dose was 1/3 of the LD_{50}, it is unclear whether this represents a true teratogenic response, or merely the effect of subjecting the parent to a close-to-lethal dose.
- Chronic toxicity: the 6 month Zhu *et al.,* (1987) study would be considered chronic; while the 3 month HLS (2001) study, which is the basis for the human TDI, would be considered sub-chronic. Accordingly some uncertainty factor is required to extrapolate from sub-chronic to chronic exposure. However, the fact that sulfolane is rapidly absorbed, metabolized and excreted in mammals (see the Section on "Absorption, Biotransformation,

and Excretion"), suggests that a smaller factor may be appropriate to make this extrapolation for sulfolane.

- Use of a LO(A)EL versus a NO(A)EL: a NOAEL is used, no uncertainty factor is required.
- Inadequacies of the critical study: HLS (2001) conforms in all respects to GLP. The sub-chronic duration of the critical study is addressed above.
- Carcinogenicity data: no mammalian cancer bioassays have been completed for sulfolane. However, the related compound 3-sulfolene was negative in a mammalian cancer bioassay, and the weight of evidence from various mutagenicity and genotoxicity assays was negative. On the whole, the evidence does not suggest that sulfolane is likely to be a mammalian carcinogen.
- Overall the dataset could be described as adequate, but not extensive.

The points raised in this section justify the application of an uncertainty factor. An uncertainty factor of 3 (approximate geometric mean of 1 and 10) was applied to account for 1) possible teratogenic response at very high doses; 2) subchronic to chronic extrapolation; and, 3) adequate, but not extensive dataset.

Factor 4 - interaction with other chemicals. There is no evidence to indicate that this is a concern, and accordingly no uncertainty factor is required.

Factor 5 - severe effects. The possible teratogenic response at very high doses was addressed in Factor 3 above. It should be noted that the NOAEL in the critical study (2.9 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$) is 2.5 orders of magnitude lower than the dose at which the possible teratogenic effects were seen. No uncertainty factor is applied for Factor 5.

In summary, a 300-fold uncertainty factor is proposed, consisting of the following:

Interspecies differences:	10-fold
Variability in human sensitivities (intraspecies variation):	10-fold
Adequate, but not extensive dataset; subchronic-chronic extrapolation; serious effects concerns:	3-fold

Calculation of Tolerable Daily Intake (TDI)

The TDI is calculated using the following formula:

$$TDI = \left(\frac{NOAEL \; or \; LOAEL}{Uncertainty \; Factor} \right)$$

Where:

TDI	=	tolerable daily intake;
NOAEL	=	no-observed-adverse-effect-level (2.9 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; see "Selection of Study" above); and,
Uncertainty Factor	=	300 (see "Selection of Uncertainty Factors" above).

Substituting these values in the above equation yields 0.0097 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$, which is the human TDI for sulfolane (Table 2).

TABLE 2. Tolerable daily intake of sulfolane for humans.

NOAEL ($mg\text{-}kg^{-1}$ $bw\text{-}day^{-1}$)	Uncertainty Factor	TDI ($mg\text{-}kg^{-1}$ $bw\text{-}day^{-1}$)	Relative Absorption Factors		
			Oral	Dermal	Inhalation
2.9	300	0.0097	1.0*	1.0*	1.0*

Notes:

* Assumed due to lack of data required to estimate differences in sulfolane absorbed from drinking water relative to sulfolane absorbed from soil ingestion, dermal soil contact, or soil inhalation (Zhu et al., 1987)

CHAPTER 9. DEVELOPMENT OF CANADIAN SOIL QUALITY GUIDELINES

Environmental Soil Quality Guidelines (SQG_E)

Canadian soil quality guidelines are designed to protect four different land uses: agricultural, residential/parkland, commercial, and industrial. Derivations of the environmental soil quality guidelines (SQG_E) for sensitive land uses (agricultural and residential/parkland) and less-sensitive land uses (commercial and industrial) are presented below. All data used in the following derivations were screened for ecological relevance and are presented in Tables 3, 4, and 5.

Agricultural and Residential/Parkland Land Uses

The derivation of the SQG_E for agricultural land use is equal to the lowest value obtained of two procedures; soil contact guideline and soil and food ingestion guideline with the SQG_E for residential/parkland use is based only on the soil contact guideline. The derivation procedure for SQG_E for these two land uses is the same when the soil and food ingestion guideline is not calculated for agricultural land use (see discussion below). Thus, these two land uses are discussed together.

Soil Contact Guideline

The derivation of the soil quality guideline for soil contact is based on the CAPP (2001) toxicological data for plants and soil invertebrates. The data reported in CAPP (2001) were expressed in terms of nominal concentrations. Appendix I explains how these data were adjusted to reflect analytical, rather than nominal concentrations. A methodology was provided in CCME (1996) for deriving Canadian soil quality guidelines for this pathway. Significant revisions in this methodology were published in CCME (2000, 2003). The methodology used in this document is based on the procedure in CCME (2000), but standardizes the effect at the 25th percentile level rather than the 50th percentile (as described in CCME 2003). The procedure used was as follows:

- Plant and terrestrial invertebrate toxicological data were screened for ecological relevance (*i.e.*, endpoints such as growth, reproduction, and mortality were selected).
- Data were standardized at a 25th percentile effect level (*i.e.*, EC_{25}/LC_{25}).
- Data based on nominal concentrations were corrected to reflect analytical measurements (Appendix I).
- If multiple data existed for the same species/endpoint/soil combination, only the data from the longest duration test were used; if multiple data points existed for the same test duration, they were combined and replaced by their geometric mean.
- The resulting data points (*i.e.*, one data point for each species/endpoint/soil combination) for plants and terrestrial invertebrates together were combined in a "species sensitivity distribution" in which the percentile was plotted against the EC_{25} values on a log scale (Figure 1).

- The 25th percentile of the species sensitivity distribution is the "no potential effects range" (NPER) for agricultural and residential/parkland land uses. The value of 420 $mg \cdot kg^{-1}$ is read directly from the species sensitivity distribution plot (Figure 1).

The soil quality guideline for soil contact (SQG_{SC}) is equal to the NPER divided by an optional safety factor (CCME 2003). In this case a safety factor is justified for the following reasons: 1) the protocol requires at least two invertebrate species; however, only earthworm data were available, and 2) while the available data exceed the minimum requirement of 10 discrete data points, the majority of it came from a single source. As such a safety factor of 2 was chosen. Therefore, the soil contact guideline for agricultural and residential/parkland land uses calculated for sulfolane based on the above procedure is 210 $mg \cdot kg^{-1}$ (Table 3).

Soil and Food Ingestion Guideline

The soil and food ingestion guideline (SQG_I) applies only to agricultural land use, and was not derived for sulfolane. The protocol for this guideline requires a minimum of three oral toxicological studies, of which at least two must be oral mammalian studies and one must be an oral avian study, and that a grazing herbivore with a high ingestion rate to body weight ratio should be considered in the minimum data set. The minimum data requirements for this guideline were not met, and the guideline was therefore not calculated. In addition, soil-to-plant bioconcentration factors would be required to calculate this guideline, and available plant concentration data were not suitable for calculating a bioconcentration factor.

Nutrient and Energy Cycling Check

The nutrient and energy cycling check was not calculated for residential/agricultural land use because sufficient data on the effect of sulfolane on microbial processes were not available. Sulfolane biodegradation was observed in soil microcosms at concentrations equal to or greater than 680 $mg \cdot L^{-1}$ (Appendix A-1 and references therein). Bagnall *et al.* (1984) reported sulfolane biodegradation at a concentration of 3,000 $mg \cdot L^{-1}$ but details of the microcosm material were not specified. While these data do not satisfy the requirements for the nutrient and energy cycling check, they do support the interpretation that at concentrations equal to or greater than 680 $mg \cdot L^{-1}$ and, perhaps, in excess of 3,000 $mg \cdot L^{-1}$, indigenous soil dwelling bacteria are active and capable of degrading sulfolane.

Commercial and Industrial Land Uses

Soil Contact Guideline

The derivation of the soil quality guideline for soil contact is based on the CAPP (2001) toxicological data for plants and soil invertebrates. The data reported in CAPP (2001) were expressed in terms of nominal concentrations. Appendix I explains how these data were adjusted and expressed in terms of analytical concentrations. A methodology was provided in CCME (1996) for deriving Canadian soil quality guidelines for this pathway. Significant revisions in this methodology were published in CCME (2000, 2003). The methodology used in this document is based on the procedure in CCME (2000), but standardizes the effect at the 25th percentile level rather than the 50th percentile (as described in CCME 2003). Moreover, both plant and invertebrate data were included for this land use. The procedure used was as follows:

- Plant and terrestrial invertebrate toxicological data were screened for ecological relevance (*i.e.*, endpoints such as growth, reproduction, and mortality were selected).
- Data were standardized at a 25th percentile effect level (*i.e.*, EC_{25}/LC_{25}).
- Data based on nominal concentrations were corrected to reflect analytical measurements (Appendix I).
- If multiple data existed for the same species/endpoint/soil combination, only the data from the longest duration test were used; if multiple data points exist for the same test duration, they were combined and replaced by their geometric mean.
- The resulting data points (*i.e.*, one data point for each species/endpoint/soil combination) for plants and terrestrial invertebrates together were combined in a "species sensitivity distribution" in which the percentile was plotted against the EC_{25} values on a log scale (Figure 1).
- The 50th percentile of the species sensitivity distribution is the "no potential effects range" (NPER) for commercial and industrial land uses. The value of 850 $mg \cdot kg^{-1}$ is read directly from the species sensitivity distribution plot (Figure 1).

The soil quality guideline (SQG_{SC}) is equal to the NPER divided by an optional safety factor (CCME 2003). In this case a safety factor is justified for the following reasons: 1) the protocol requires at least two invertebrate species; however, only earthworm data were available, and 2) while the available data exceed the minimum requirement of 10 discrete data points, the majority of it came from a single source. As such a safety factor of 2 was chosen. Therefore, the soil contact guideline for soil contact for commercial and industrial land uses calculated for sulfolane based on the above procedure is 430 $mg \cdot kg^{-1}$ (Figure 1; Table 3).

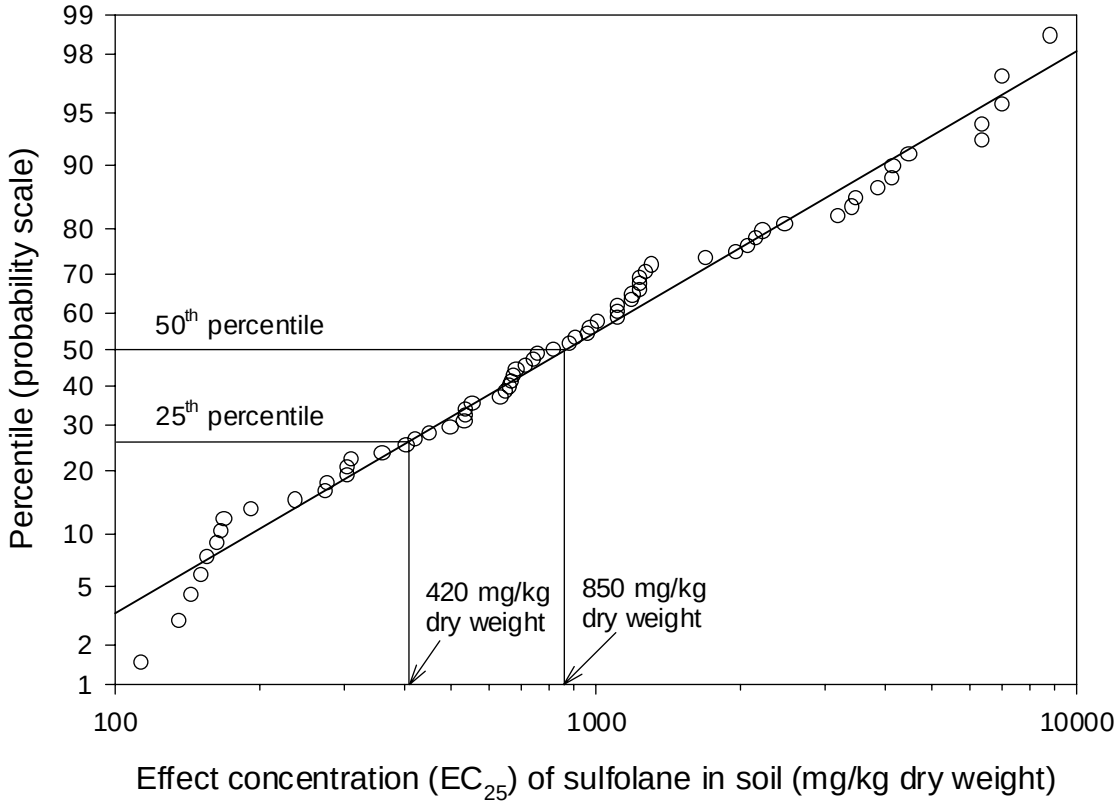

FIGURE 1. Canadian Environmental Soil Quality Guidelines For Sulfolane.

Note: Data was calculated using the distribution of effect concentrations (EC25) of plant and invertebrate species. The SQG_E (210 $mg \cdot kg^{-1}$ dry weight) for agricultural land use and for residential/parkland use are equal to the 25th percentile divided by a safety factor of 2 while the SQG_E (430 $mg \cdot kg^{-1}$ dry weight) for commercial and for industrial land uses are equal to the 50th percentile divided by a safety factor of 2.

Nutrient and Energy Cycling Check

The nutrient and energy cycling check was not calculated for commercial/industrial land uses because sufficient data on the effect of sulfolane on microbial processes was not available. See discussion above for Agricultural and Residential/Parkland Uses.

Off-Site Migration Check

The off-site migration check for ecological endpoints is calculated to ensure that wind and water erosion of contaminated material from an industrial site could not cause unacceptable contaminant concentrations on an adjacent residential property (CCME, 2003).

$$C_i = \frac{\{[D_m \cdot C_m] - [(D_m - D_d) \cdot BSC]\}}{D_d}$$

Where:

C_i	=	off-site migration check ($mg \cdot kg^{-1}$);
D_m	=	mixing depth (2 cm, CCME, 2003);
C_m	=	SQG_E for residential/parkland use (210 $mg \cdot kg^{-1}$, see Table 3);
D_d	=	depth of deposited material before mixing (0.14 cm; CCME, 2003); and,
BSC	=	background concentration of the contaminant in the receiving soil (0 $mg \cdot kg^{-1}$, assumed).

Substituting these values in the above equation gives 3,000 $mg \cdot kg^{-1}$. This value is the off-site migration check for ecological endpoints for sulfolane (Table 3).

Groundwater Check (Aquatic Life)

The groundwater check applies equally to all land uses and was performed using Appendix D of the CCME (1996) protocol. The formula used for the groundwater check was:

$$Groundwater\ Check\left(mg\ kg^{-1}\ soil\right) = DF \times C_{wa}\left(K_d + \theta_m\right)$$

Where:

DF	=	dilution factor (50; CCME 1996);
C_{wa}	=	concentration in the aquifer, which was set equal to the sulfolane freshwater aquatic life guideline (50 $mg \cdot L^{-1}$; see "Water Quality Guidelines - Freshwater Aquatic Life" below and Table 4);
K_d	=	sulfolane soil to water partition coefficient (0.08 ± 0.06 L kg^{-1} (Table 1) based on the average of four measurements fit to linear isotherms (Luther *et al.* 1998) from humus-rich soil, sand, till, and a fine-grained sandstone); and,
θ_m	=	field capacity moisture content (0.1 g g^{-1}; CCME 1996).

Substituting values from above, and rounding to two significant figures, yields 450 $mg \cdot kg^{-1}$, which represents the maximum sulfolane soil concentration that is protective of freshwater aquatic life (Table 4).

Data Gaps

With regards to the soil contact guideline, data on an invertebrate species other than earthworms are needed. Sufficient data were available to calculate the groundwater check for aquatic life. Additional information would be required to calculate the nutrient and energy cycling check. Specifically, a minimum of three studies would be required, addressing (preferably) nitrogen fixation and nitrification, or (less desirably) carbon cycling and nitrogen mineralization. In order to meet the minimum data requirements for the soil and food ingestion guideline, one oral study on an ungulate and one oral study on an avian species would be required.

Human Health Soil Quality Guidelines (SQG_{HH})

The human health guidelines for the four CCME land uses are discussed in the following sections. One parameter that warrants further discussion is the soil allocation factor (SF). The CCME (1996) protocol recommends using an SF of 0.2 to allow for the fact that, in theory, human exposure to contaminants can occur via five media: water, soil, air, food, and consumer products. However, more recent guidance (CCME 2000; CCME 2003) allows a consideration of which of these five media are realistic exposure pathways for the contaminant under investigation.

Based on physical and chemical properties, exposure to sulfolane at typical contaminated sites is likely to occur through soil, drinking water and food. Although there are no studies on detection of sulfolane in food, it has been shown to bioconcentrate and translocate significantly in wetland plants, with particularly high concentrations detected in leaf tips (Doucette et al., 2004; Leo et al., 2004), suggesting the potential for uptake in plants consumed by humans. Exposure to sulfolane through inhalation or consumer products is unlikely. Accordingly a soil allocation factor (SF) of 0.33 was used for sulfolane.

The protocol (CCME, 2003) assumes that absorption efficiency in an environmental exposure is equal to that of the experimental exposure unless other evidence exists. In cases where the experimental exposure occurs through a medium (e.g., drinking water) other than through soil, soil ingestion, dermal contact, and inhalation rates can be multiplied by a corresponding relative absorption factors (AF) to account for differences between absorption from drinking water and these soil-based routes of exposure. For sulfolane, the experimental exposure on which the TDI is based is through drinking water (HLS, 2001). No data exist, however, on the absorption of sulfolane from ingested water relative to ingested soil or to dermal contact or to inhalation. As a result, a relative absorption factor of one has been assumed for oral, dermal, and inhalation exposure routes (Table 2).

Agricultural and Residential/Parkland Uses

Soil Ingestion Guideline

For a threshold chemical such as sulfolane, the CCME (2003) protocol uses a fully exposed child aged 0.5 to 5 years to develop soil quality guidelines for agricultural and residential/parkland land use settings. This receptor is the most sensitive because it has the greatest exposure per unit bodyweight. The direct soil exposure pathways include ingestion, dermal contact, and particulate inhalation. However, based on professional risk assessment experience of the CCME Soil Quality Guidelines Task Group, the dermal and particulate inhalation pathways are not expected to be significant, and consequently, contact rates for these pathways were set to zero. The human health soil guideline was calculated using:

$$SQG_{HH} = \frac{(TDI - EDI) \times SF \times BW}{[(AF_1 \times IR) + (AF_D \times DR) + (AF_S \times SR)] \times ET} + [BSC]$$

Where:

SQG_{HH} = agricultural and residential/parkland human health soil quality guideline ($mg \cdot kg^{-1}$);
TDI = tolerable daily intake (0.0097 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; Table 2);
EDI = estimated daily intake (0 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; assumed);
SF = soil allocation factor (0.33; based on the assumption that sulfolane could be in soil, drinking water, or food, but is unlikely to be in air or consumer products);
BW = toddler body weight (16.5 kg; CCME 2000);
AF_I = relative absorption factor for gut (assumed 1; Table 2);
AF_D = relative absorption factor for lung (assumed 1; Table 2);
AF_S = relative absorption factor for skin (assumed 1; Table 2);
IR = soil ingestion rate for toddler (0.00008 kg d^{-1}; CCME 2003);
DR = soil inhalation rate (0; see above);
SR = soil dermal contact rate (0; see above);
ET = exposure term (1; defined for agricultural and residential/parkland uses; CCME 2003); and,
BSC = background soil concentration (0 $mg \cdot kg^{-1}$; assumed).

Substituting these values in the above equation yields 660 $mg \cdot kg^{-1}$, which is the agricultural and residential/parkland human health soil ingestion guideline (Table 3).

Produce, Meat and Milk Check

This check was developed to ensure soil quality guidelines do not result in an unacceptable contribution to the total daily intake of contaminants via home grown produce, meat, and milk. The check is applicable in agricultural and residential land use settings. The procedure outlined in the CCME (2003) protocol applies only to non-polar organic compounds, because polar compounds are not expected to bioconcentrate into food. The procedure is therefore not applicable to sulfolane, which is a highly polar compound (Table 1). Accordingly, this check was not calculated.

Inhalation of Indoor Air Check

The very low vapour pressure and Henry's law constant (0.01 mm Hg at 20°C and 8.9 x 10^{-10} $atm \cdot m^3 \cdot mol^{-1}$, respectively; Table 1), indicate that sulfolane is virtually non-volatile. Thus, vapour-phase transport of sulfolane in the subsurface will not be significant and, for this reason, the inhalation of indoor air check was not evaluated.

Commercial Land Use

Commercial sites are defined in the CCME (2003) protocol as sites at which commercial activities predominate. No manufacturing activities or residential occupancy are expected to occur. A commercial site is fully accessible to all age classes, but is used with less intensity, duration, and frequency than a residential site. An example of a commercial site would be an urban shopping mall or a daycare.

Soil Ingestion Guideline

For threshold contaminants, such as sulfolane, the CCME (2003) protocol assumes that a toddler is the most sensitive receptor (based on the greatest exposure per unit bodyweight) but that access is restricted to 10 hours per day, 5 days per week, and 48 weeks per year. The direct soil exposure pathways include ingestion, dermal contact, and particulate inhalation. However, based on professional risk assessment experience of the CCME Soil Quality Guidelines Task Group, the dermal and particulate inhalation pathways are not expected to be significant, and consequently contact rates for these pathways were set to zero. The human health soil guideline was calculated using:

$$SQG_{HH} = \frac{(TDI - EDI) \times SF \times BW}{[(AF_1 \times IR) + (AF_D \times DR) + (AF_S \times SR)] \times ET} + [BSC]$$

Where:

SQG_{HH} = commercial human health soil quality guideline ($mg \cdot kg^{-1}$);
TDI = tolerable daily intake (0.0097 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; Table 2);
EDI = estimated daily intake (0 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; assumed);
SF = soil allocation factor (0.33; based on the assumption that sulfolane could be in soil, water or food, but is unlikely to be in air or consumer products);
BW = toddler body weight (16.5 kg; CCME 2000);
AF_I = relative absorption factor for gut (assumed 1; Table 2);
AF_D = relative absorption factor for lung (assumed 1; Table 2);
AF_S = relative absorption factor for skin (assumed 1; Table 2);
IR = soil ingestion rate for toddler (0.00008 kg d^{-1}; CCME 2003);
DR = soil inhalation rate (0; see above);
SR = soil dermal contact rate (0; see above);
ET = exposure term (0.275; defined for commercial land use; CCME 2003); and,
BSC = background soil concentration (0 $mg \cdot kg^{-1}$; assumed).

Substituting these values in the above equation yields 2,400 $mg \cdot kg^{-1}$, which is the commercial human health soil ingestion guideline (Table 3).

Inhalation of Indoor Air Check

The very low vapour pressure and Henry's law constant (0.01 mm Hg at 20°C and 8.9 x 10^{-10} $atm \cdot m^3 \cdot mol^{-1}$, respectively; Table 1), indicate that sulfolane is virtually non-volatile. Thus, vapour-phase transport of sulfolane in the subsurface will not be significant and, for this reason, the inhalation or indoor air check was not evaluated.

Industrial Land Use

Soil Ingestion Guideline

Industrial lands typically have limited or restricted access to the public so that adult, occupational exposures predominate. The CCME (2003) protocol assumes that an adult at an industrial site is exposed to soil contact for 10 hours per day, 5 days per week, and 48 weeks per

year. Possible industrial land uses range from outdoor heavy earth-moving to high technology, ultra-clean environments.

Potential direct soil exposure pathways in industrial lands include ingestion, dermal contact, and particulate inhalation. However, based on professional risk assessment experience of the CCME Soil Quality Guidelines Task Group, the dermal and particulate inhalation pathways are not expected to be significant, and consequently contact rates for these pathways were set to zero. The human health soil guideline was calculated using:

$$SQG_{HH} = \frac{(TDI - EDI) \times SF \times BW}{[(AF_1 \times IR) + (AF_D \times DR) + (AF_S \times SR)] \times ET} + [BSC]$$

Where:

SQG_{HH} = industrial human health soil quality guideline ($mg \cdot kg^{-1}$);
TDI = tolerable daily intake (0.0097 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; Table 2);
EDI = estimated daily intake (0 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; assumed);
SF = soil allocation factor (0.33; based on the assumption that sulfolane could be in soil water or food, but is unlikely to be in air or consumer products);
BW = body weight (70.7 kg; CCME 2000);
AF_I = relative absorption factor for gut (assumed 1; Table 2);
AF_D = relative absorption factor for lung (assumed 1; Table 2);
AF_S = relative absorption factor for skin (assumed 1; Table 2);
IR = soil ingestion rate for adult (0.00002 kg d^{-1}; CCME 2003);
DR = soil inhalation rate (0; see above);
SR = soil dermal contact rate (0; see above);
ET = exposure term (0.275; defined for industrial land use; CCME 2003); and,
BSC = background soil concentration (0 $mg \cdot kg^{-1}$; assumed).

Substituting these values in the above equation yields 41,000 $mg \cdot kg^{-1}$, which is the industrial human health soil ingestion guideline (Table 3).

Inhalation of Indoor Air Check

The very low vapour pressure and Henry's law constant of sulfolane (0.01 mm Hg at 20(C and 8.9 x 10^{-10} $atm \cdot m^3 \cdot mol^{-1}$, respectively; Table 1), indicate that sulfolane is virtually non-volatile. Thus, vapour-phase transport of sulfolane in the subsurface will not be significant and, for this reason, the inhalation or indoor air check was not evaluated.

Off-Site Migration Check

The off-site migration check for human health endpoints is calculated to ensure that wind and water erosion of contaminated material from an industrial site could not cause unacceptable contaminant concentrations on an adjacent residential property (CCME, 2003).

$$C_i = \frac{\{[D_m \cdot C_m] - [(D_m - D_d) \cdot BSC]\}}{D_d}$$

Where:

C_i	=	off-site migration check ($mg \cdot kg^{-1}$);
D_m	=	mixing depth (2 cm, CCME, 2003);
C_m	=	soil ingestion guideline for residential/parkland use (660 $mg \cdot kg^{-1}$, see Table 3);
D_d	=	depth of deposited material before mixing (0.14 cm; CCME, 2003); and,
BSC	=	background concentration of the contaminant in the receiving soil (0 $mg \cdot kg^{-1}$, assumed).

Substituting these values in the above equation gives 9,000 $mg \cdot kg^{-1}$. This is the off-site migration check for human health endpoints for sulfolane (Table 3).

Groundwater Check (Drinking Water)

The groundwater check applies equally to all land uses and was performed using Appendices C and D of the CCME (1996) protocol. The formula used for the groundwater check was:

$$Groundwater\ Check\left(mg\ kg^{-1}\ soil\right) = DF \times C_{wa}\left(K_d + \theta_m\right)$$

Where:

DF	=	dilution factor (50; CCME 1996);
C_{wa}	=	concentration in the aquifer, which was set equal to the source guidance value for sulfolane in groundwater (0.09 $mg \cdot L^{-1}$; see "Water Quality Guidelines - Human Drinking Water" and Table 4);
K_d	=	sulfolane soil to water partition coefficient (0.08 ± 0.06 L kg^{-1} based on the average of four measurements fit to linear isotherms (Luther *et al.* 1998) from humus-rich soil, sand, till, and a fine-grained sandstone); and,
θ_m	=	field capacity moisture content (0.1 g g^{-1}; CCME 1996).

Substituting these values in the above equation yields 0.8 $mg \cdot kg^{-1}$, which represents the sulfolane soil concentration that is consistent with the source guideline value for groundwater calculated herein (Tables 3 and 4).

Data Gaps

Further data on bioconcentration of sulfolane into plants, and toxicity of sulfolane to livestock species would be required to calculate the soil and food ingestion guideline. Data on the toxicity of sulfolane to microbial processes would be required to calculate the nutrient and energy cycling check. Data on the bioconcentration of sulfolane into produce, milk, and meat would be required to calculate the produce, milk, and meat check.

TABLE 3. Soil quality guidelines and check values for sulfolane

	Land Use			
	Agricultural	Residential/ Parkland	Commercial	Industrial
	(mg·kg^{-1} dry weight)	(mg·kg^{-1} dry weight)	(mg·kg^{-1} dry weight)	(mg·kg^{-1} dry weight)
Recommended Guideline	0.8	0.8	0.8	0.8
Human health guidelines/check values				
SQG_{HH}				
Soil ingestion guidelines	660	660	2,400	41,000
Inhalation of indoor air check	NC	NC	NC	NC
Off-site migration check	—	—	—	9,000
Groundwater check (drinking water)	0.8	0.8	0.8	0.8
Produce, meat, and milk check	NC	NC	—	—
SQG_{HH}	0.8	0.8	0.8	0.8
Limiting pathway for SQG_{HH}	groundwater check	groundwater check	groundwater check	groundwater check
Environmental health guidelines/check values				
SQG_E				
Soil contact guidelines	210	210	430	430
Soil and food ingestion guideline	NC	—	—	—
Nutrient and energy cycling check	NC	NC	NC	NC
Off-site migration check	—	—	—	3,000
Groundwater check (aquatic life)	450	450	450	450
SQG_E	210	210	430	430
Limiting pathway for SQG_E	soil contact			

Notes:

SQG_{HH} = soil quality guideline for human health; SQG_E = soil quality guideline for environmental health; NC = not calculated; — = guideline/check value are not a part of the exposure scenario for that land use, or the pathway is not applicable, and therefore is not calculated.

CHAPTER 10. DEVELOPMENT OF CANADIAN WATER QUALITY GUIDELINES

Freshwater Aquatic Life

Freshwater aquatic life guidelines for sulfolane were developed using "*A Protocol for the Derivation of Water Quality Guidelines for the Protection of Aquatic Life*" (CCME 1991). The following sections summarize the requirements of the CCME protocol and discuss the available dataset in terms of these requirements. The toxicological dataset was summarized in Appendix A-4, and discussed in Chapter 5.

The CCME protocol defines (1) the requirements for a toxicological study to be acceptable for guideline derivation (data quality requirement), (2) the minimum required dataset for Full and Interim guideline development (data quantity requirement), and (3) the process for deriving guidelines. The following paragraphs provide a summary of the requirements of the CCME protocol, and assess the toxicological dataset.

Data Quality

The data quality requirement in the CCME protocol may be summarized as follows. For a toxicological study to be considered "secondary data," all relevant environmental variables (*e.g.*, temperature, pH, hardness, dissolved oxygen, *etc.*) should be measured and reported, and the survival of controls must be reported. For data to be considered "primary data", tests must employ currently acceptable practices, concentrations must be measured at the beginning and end of a test, and, in general, dynamic (*i.e.*, flow-through) tests are required. However, it should be noted that flow-through test set-ups are typically used only for fish, rather than invertebrates or algae. Data that do not conform to the requirements for primary or secondary data are classified as "unacceptable data."

The toxicological dataset is summarized in Appendix A-4 and data are classified as primary, secondary, or unacceptable. Only the work completed for CAPP (2001) or Environment Canada (2003) conformed to all the requirements for primary data. Studies by ERAC (1998) and Girling (1987) were classified as secondary data. All other studies were classified as unacceptable data. It should be noted that studies classified as "unacceptable Data" may, in fact, represent acceptable (*i.e.*, primary or secondary) data, but insufficient information was available to confirm this. According to the CCME protocol only primary or secondary data can be used in the guideline derivation process.

Data Quantity

The CCME protocol requirement for the quantity of primary and/or secondary data for Interim freshwater aquatic life guidelines may be summarized as follows. At least two studies on freshwater fish species and at least two studies on freshwater invertebrate species are required. The tests may be acute or chronic. One of the fish must be a cold water species, and two different classes of invertebrates must be represented, one of which includes a planktonic species resident in North America (*e.g.*, daphnid).

The CCME protocol requirements for an Interim guideline were met by the Primary and Secondary Data in Appendix A-4. The acute tests on rainbow trout and fathead minnow fulfill the requirement for tests of two freshwater fish species, with the rainbow trout fulfilling the requirement for a cold water species. Acceptable (*i.e.*, Primary or Secondary) test results are available for three species of invertebrate: *Daphnia magna* and *Ceriodaphnia dubia*, representing the Class Branchiopoda and *Hyalella azteca*, representing the Class Malacostraca.

Thus all the CCME protocol requirements for data quantity are met.

Guideline Derivation

"Guidelines are preferably derived from the lowest-observable-effect-level (LOEL) from a chronic study using a non-lethal endpoint for the most sensitive life stage of the most sensitive aquatic species investigated. The most sensitive LOEL is multiplied by an uncertainty factor of 0.1 to arrive at the guideline value" (CCME 1999). The lowest chronic LOEC for primary or secondary Data in this dataset is 500 $mg \cdot L^{-1}$ for the 7 day reproduction endpoint for *Ceriodaphnia dubia*. This yields a guideline value of 50 $mg \cdot L^{-1}$.

It should be noted that there is also a procedure in CCME for developing a freshwater aquatic life water quality guideline from acute data. This procedure can be used in the absence of sufficient chronic data or when a guideline based on the lowest chronic LOEC would not be protective of acute effects (*e.g.*, WQG for bromoxynil [CCME 1999]). In this procedure, the lowest LC_{50} result is multiplied by an application factor of 0.05 (for non-persistent variables) or 0.01 (for persistent variables) to give the guideline value. For sulfolane, the lowest LC_{50} result in Appendix A-4 is 40 $mg \cdot L^{-1}$ for *D. magna*. However, as discussed in Chapter 5, the range of *D. magna* results spanned almost two orders of magnitude, and the study commissioned to resolve this uncertainty (Environment Canada 2003) yielded a *D. magna* LC_{50} result of 1,245 $mg \cdot L^{-1}$. The LC_{50} value from this test was 1,245 $mg \cdot L^{-1}$, based on mean measured sulfolane concentrations at the beginning and end of the test. This value was taken to be definitive due to: 1) the results of the reference toxicant test that were within quality control limits; 2) the chemical analysis for sulfolane and the beginning and end of the test; and, 3) the carefully controlled and reported conditions in this study. Two statistical tests for outliers (Dixon Outlier Test and Box Plot) found the LC_{50} value of 40 $mg \cdot L^{-1}$ to be a significant outlier (alpha<0.01; Rohlf and Sokal 1995; Mendenhall and Beaver 1991). The LC_{50} value of 1,245 $mg \cdot L^{-1}$ multiplied by the application factor for non-persistent variables (*i.e.*, 0.05) yields a value of 62 $mg \cdot L^{-1}$. This value is greater than, but consistent with, the chronic guideline of 50 $mg \cdot L^{-1}$ derived above, and accordingly the freshwater aquatic life water quality guideline for sulfolane is 50 $mg \cdot L^{-1}$ (Table 4).

Irrigation

Irrigation water quality guidelines for sulfolane were developed using "Protocols for Deriving Water Quality Guidelines for the Protection of Agricultural Water Uses" (CCME 1993). The toxicological data set was sufficient to derive interim guidelines (Appendix A-2). Data in Appendix A-2 are classified as primary toxicological data by the CCME protocol. As laid out in the CCME protocol, species maximum acceptable toxicant concentrations (SMATC) were

calculated for (1) cereals, tame hays, and pasture crops (*e.g.*, alfalfa and timothy) and (2) other crops (*e.g.*, lettuce and carrot). The lowest SMATC is the interim irrigation guideline.

As can be seen in Appendix A-2, the sensitivity of plants to sulfolane varies strongly depending on soil type. For most plant species and endpoints, plants are most sensitive to sulfolane in sand or till and least sensitive in loam; the sensitivity of plants grown in artificial soil is usually in between these other two groups. The lowest LOEC, however, is for lettuce grown in artificial soil. In this study, no other soil types were tested (Komex 1999). Accordingly, species maximum acceptable toxicant concentration (SMATC) for "poor soil" (*i.e.*, sand or till) and loam were calculated separately, while for other crops, only one guideline based on the LOEC for lettuce in artificial soil was calculated (Table 4). The reason for this approach was to provide both an overall irrigation guideline, which was protective of crop growth on any soil type, and guidance on tolerable levels of sulfolane when cereals, tame hays, and pasture crops are being grown on typical, improved, agricultural soils. The overall irrigation guideline is the lowest of these three SMATCs. The detailed guideline derivation process is described below.

Prior to deriving the guideline value, data based on nominal concentrations were corrected for analytical recovery (see Appendix I). The next step was the calculation of the acceptable soil concentration (ASC), which is an estimate of the soil concentration that would not result in adverse effects on crops over the course of one growing season:

$$ASC\left(mg\,kg^{-1}\right)=\left(\frac{\sqrt{LOEC\times NOEC}}{UF}\right)$$

Where:

LOEC = lowest-observed-effect-concentration ($mg\cdot kg^{-1}$ soil; dry weight basis);
NOEC = no-observed-effect-concentration ($mg\cdot kg^{-1}$ soil; dry weight basis); and,
UF = uncertainty factor of 10 (CCME 1993).

The lowest calculated ASCs for each crop group and soil type were as follows:

- 28 $mg\cdot kg^{-1}$ - cereals, tame hays, and pasture crops, based on reduced biomass for timothy grown in loam;
- 10 $mg\cdot kg^{-1}$ - cereals, tame hays, and pasture crops grown in poor soil, based on reduced root length for alfalfa in till and on reduced biomass for timothy in sand;
- 3 $mg\cdot kg^{-1}$ - other crops, based on reduced seed emergence for lettuce grown in artificial soil

The final step in the guideline derivation process was to calculate species maximum acceptable toxicant concentration (SMATC), which is the maximum amount of contaminant allowed in a 1 ha (100 m x 100 m) plot. The SMATC was calculated as:

$$SMATC\left(mg\,L^{-1}\right)=\left(\frac{ASC\times\rho\times L\times W\times D}{IR}\right)$$

Where:

ASC	=	acceptable soil concentration ($mg \cdot kg^{-1}$);
ρ	=	soil bulk density (1,300 $kg \cdot m^{-3}$; dry weight basis);
L	=	length (100 m);
W	=	width (100 m);
D	=	leaching depth (1.5 m (cereals, tame hays, and pasture crops) or 0.15 m (other crops, see note below); and,
IR	=	irrigation rate per year (1.2×10^7 L ha^{-1}).

Note that the CCME protocol recommends a leaching depth of 0.15 m for other crops, and allows a leaching depth of up to 1.5 m for cereals, tame hays, and pasture crops. Lab studies (e.g., Luther et al., 1998) have shown that sulfolane interacts minimally with soil, and field studies (e.g., Komex, 1999) have confirmed that it can move through a significant thickness of soil to reach the water table. Accordingly the full 1.5 m was used as the leaching depth for cerals, tame hays, and pasture crops.

The SMATCs for cereals, tame hays, and pasture crops are 46 $mg \cdot L^{-1}$ in loam and 15 $mg \cdot L^{-1}$ in poor soil. For other crops, the SMATC is 0.5 $mg \cdot L^{-1}$ (artificial soil). Therefore, the recommended interim irrigation water quality guideline protective of all crop species, regardless of soil type, is 0.5 $mg \cdot L^{-1}$ (Table 4).

Livestock Watering

Insufficient data were available to meet the requirements of the CCME protocol for developing livestock watering guidelines ("Protocols for Deriving Water Quality Guidelines for the Protection of Agricultural Water Uses," CCME 1993). However, effective management of existing sites with sulfolane contamination requires a livestock watering guideline. Accordingly, preliminary livestock watering guidance values were developed for sulfolane following the CCME protocol as closely as possible; however these values are not guidelines. The minimum toxicological dataset required by the CCME protocol for derivation of Interim guidelines is two acute or chronic studies on two or more mammalian species raised in Canada including at least one livestock species, and at least one acute or chronic study on one or more avian livestock species. The minimum dataset requirements were not therefore met, but in spite of this, it was felt that it would be useful to calculate a preliminary livestock watering guidance value based on the available data.

Procedures exist in the CCME protocol for calculating a livestock watering guideline from either acute or chronic toxicological data. Available acute and chronic mammalian toxicological data for sulfolane were reviewed and discussed in Chapter 7. The acute studies by Zhu *et al.* (1987), Andersen *et al.* (1976), Alexander *et al.* (1959) and Brown *et al.* (1966) were considered for derivation of a preliminary guideline for livestock watering for the following reasons:

- the data set (Appendix A-5) includes 16 data points from four studies, using four species (rat, mouse, guinea pig, and rabbit) and four routes of administration (oral, intraperitoneal, intravenous, and subcutaneous);

- good agreement is seen between data for four different species from two mammalian orders (rodents and lagomorphs), providing some confidence in making an extrapolation to livestock species;
- good agreement is seen between data for four routes of administration;
- good agreement is seen between data from three different studies; and,
- overall, the data are very consistent.

The first step in the guideline derivation process laid down in the CCME protocol for acute data was the calculation of the TDI, which was based on an extrapolation of acute to chronic data (CCME 1993):

$$TDI\left(mg\,kg^{-1}\,bw\,day^{-1}\right)=\left(\frac{LD_{50}}{70\times UF}\right)$$

Where:

LD_{50} = lowest lethal dose to 50% of the population (632 mg·kg^{-1} bw·day^{-1}; Appendix A-5);
70 = extrapolation factor from acute to chronic data (CCME 1993); and,
UF = uncertainty factor (10; CCME 1993).

Based on the acute to chronic extrapolation, the TDI for sulfolane applicable to livestock is 0.9 mg·kg^{-1} bw·day^{-1}.

The next step in the guideline derivation process was to calculate reference concentrations (RCs) for various livestock species. A reference concentration is calculated using the body weight and water ingestion rate of particular species. Dairy cattle and beef cattle were selected to represent livestock; white leghorn chickens and deer were also considered to help assess possible risks to other species. RC for other species of interest may be calculated when the body weights and water intakes are known (CCME 1993). The equation used was:

$$RC\cdot\left(mg\,L^{-1}\right)=\left(\frac{TDI\times BW}{WIR}\right)$$

Where:

TDI = tolerable daily intake (0.9 mg·kg^{-1} bw·day^{-1}; calculated above);
BW = body weight (2.3 kg for white leghorn chickens; 862 kg for dairy cattle (CCME 1993), 730 kg for beef cattle (CCME 1993), and 68 kg for deer (Smith 1993); and,
WIR = daily water intake rate (0.61 L for white leghorn chickens; 137 L·day^{-1} for dairy cattle, CCME (1993), data for lactating cows at 21°C), 80 L day^{-1} for beef cattle (CCME 1993), and 4.4 L·day^{-1} for deer (Smith 1993).

The RCs for white leghorn chickens dairy cattle, beef cattle, and deer are 3, 6, 8, and 14 mg·L^{-1}, respectively. Livestock may be exposed to contaminants from sources other than polluted drinking water. As such, the RCs are multiplied by the percentage that drinking water

contributes to the TDI. In the absence of more specific data, the protocol recommends that a default value of 20% be used (CCME 1993).

Therefore, the preliminary livestock watering guidance values for white leghorn chickens dairy cattle, beef cattle, and deer are 0.6, 1, 2, and 3 $mg \cdot L^{-1}$, respectively. These values are not endorsed by the CCME (Table 4).

Human Drinking Water

Setting Canadian drinking water guidelines is undertaken by Health Canada, and is outside the jurisdiction of the CCME. However, no Canadian Guideline for Drinking Water Quality currently exists for sulfolane, yet a guideline value is required to calculate the groundwater check (drinking water) that makes up part of the soil quality guideline protocol (CCME 1996). Accordingly, the methods used by Health Canada to develop drinking water guidelines were used to develop a source guidance value for groundwater (SGVG) for sulfolane in this document. This value is not a Canadian Guideline for Drinking Water Quality. The process is discussed below.

The generic scenario assumed to develop a potable water protection value (referred to in this document as a source guidance value for groundwater) was the "Agricultural Land Use" scenario defined by the CCME (1996) protocol. Guidelines were calculated based on protection of an adult, following Health Canada (1994 and 2005) standard procedures.

Humans could be exposed to sulfolane in groundwater by (1) ingestion of drinking water and water used to cook and (2) dermal contact during bathing and washing. While individuals could be exposed to sulfolane in surface water via swimming and/or fishing, this exposure pathway will be minimal relative to those noted above. A dermal contact check is provided to evaluate the relative importance of this exposure pathway.

Ingestion of Drinking Water

The absorbed dose from ingestion of sulfolane in drinking water was calculated for humans using (US EPA 1989; CCME 1996):

$$Dose\left(mg\ kg\ bw^{-1}\ day^{-1}\right) = \left(\frac{C_W \cdot IR_W \cdot BIO_O \cdot EF}{BW \cdot AT}\right)$$

Where:

C_W = concentration of sulfolane in water ($mg \cdot L^{-1}$);
IR_W = drinking water ingestion rate (1.5 $L \cdot day^{-1}$ (adult); CCME 2000);
BIO_O = oral bioavailability (1; Table 2);
EF = exposure frequency (365 days; assumed);
BW = receptor body weight (70.7 kg (adult); CCME 2000); and,
AT = averaging time (365 days; assumed).

Absorbed dose calculations for drinking water and dermal contact are used to evaluate the relative importance of sulfolane exposure via oral and dermal routes (see dermal contact check below).

The above formula was re-arranged to yield a source guidance value for groundwater:

$$\textit{Source Guidance Value for Groundwater } \left(mg\,L^{-1}\right) = \left(\frac{BW \cdot TDI}{IR_W \cdot BIO_O}\right) \text{*DAF}$$

Where:
BW = receptor body weight (70.7 kg (adult); CCME 2000);
TDI = tolerable daily intake (0.0097 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$; Table 2);
IR_W = drinking water ingestion rate (1.5 L day^{-1} (adult); CCME 2000); and,
BIO_O = oral bioavailability (1; Table 2).
DAF= default allocation factor (0.2; Health Canada 2005)

The source guidance value for groundwater was calculated in this document is 0.09 $mg \cdot L^{-1}$ (Table 4).

Dermal Contact Check

To determine whether dermal contact was a significant exposure route relative to oral ingestion, dermal exposure modelling was conducted following US EPA (1992; 1997) protocols. Dermal exposure modelling is concerned with absorption and transport of chemicals through the outer skin layer (stratum corneum) and into the viable epidermis. The stratum corneum is the primary barrier to dermal absorption. This layer consists of a protein (keratin) and lipid matrix that channels chemicals through transcellular (aqueous) and intercellular (lipid) pathways.

The absorbed dose from dermal contact with sulfolane for an adult during bathing was calculated using (US EPA 1992):

$$Dose\left(mg\,kg^{-1}\,bw\,day^{-1}\right) = \frac{C_W \cdot SA \cdot ET \cdot PC \cdot EF}{BW \cdot AT \cdot 1000}$$

Where:

C_W	=	concentration of sulfolane in water ($mg \cdot L^{-1}$);
SA	=	skin surface area exposed during bathing (18,150 cm^2 mean of data for adult males and females; US EPA 1992);
ET	=	length of time the skin is in contact with water (0.5 $hours \cdot day^{-1}$; assumed);
PC	=	chemical specific dermal permeability constant (0.0002 $cm \cdot hour^{-1}$; calculated below);
EF	=	exposure frequency (365 days; assumed);
BW	=	receptor body weight (70.7 kg; CCME 2000); and,
AT	=	averaging time (365 days; assumed).

The value of 1000 was used to convert from cm^3 to L.

The chemical-specific dermal permeability constant (PC) for sulfolane was estimated using (US EPA 1992):

$$Log\ PC\left(cm\,hour^{-1}\right) = -2.72 + 0.71 \cdot \log K_{OW} - 0.0061 \cdot MW$$

Where:

$\log K_{ow}$ = logarithm (base 10) of the n-octanol-water partition coefficient (-0.4, unitless); and,

MW = molecular weight (120.17 $g \cdot mol^{-1}$).

Using the chemical/physical properties noted above (see also Table 1), the estimated dermal permeability constant for sulfolane was 0.0002 cm $hour^{-1}$.

Assuming a sulfolane concentration in water of 1 $mg \cdot L^{-1}$, and assuming a 0.5 hour bath each day, the calculated absorbed dermal dose for an adult was 3 x 10^{-5} $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$. The calculated absorbed dose for an adult drinking water was 0.021 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$, assuming 1 $mg \cdot L^{-1}$ sulfolane concentration in the drinking water supply. Based on these assumptions, therefore, dermal contact provides approximately 0.1% of the oral dose and can be safely disregarded.

Data Gaps

Freshwater Aquatic Life

The dataset for freshwater aquatic life was sufficient to derive interim guidelines. For a full freshwater aquatic life guideline to be developed, the following additional studies would be required:

- two chronic studies on freshwater fish species resident in North America;
- two chronic studies on two invertebrate species from different classes, one of which was a planktonic species resident in North America (*e.g.*, a daphnid); and,
- one study on a freshwater vascular plant or algal species resident in North America.

All the additional studies for a full guideline must be of primary data quality.

Marine Aquatic Life

The dataset for marine aquatic life guideline was not sufficient to derive interim guidelines. The following additional toxicity tests would be required in order to derive an interim marine water quality guideline:

- two acute or chronic studies on different marine fish species, including one temperate species; and,
- one acute or chronic study on a temperate marine invertebrate species from a different class to *Acartia tonsa*.

For a full marine guideline to be developed, the following additional studies would be required:

- three studies on three species of temperate marine fish of which at least two are chronic;
- two chronic studies on two temperate marine invertebrate species from different classes; and,
- one study on a temperate marine vascular plant or algal species.

All the studies for a full guideline must be of primary data quality.

Irrigation

Sufficient data were available to meet the requirements for an interim irrigation guideline. For a full irrigation guideline to be developed, the following additional studies would be required:

- two chronic (*i.e.*, full growing season) studies on cereal, tame hay, or pasture crops grown in Canada; and,
- two chronic (*i.e.*, full growing season) studies on three or more other crop species grown in Canada.

In addition, a third study on other crops (lettuce) should be conducted in all soil types to confirm the LOEC because the current to LOEC estimates for lettuce grown in artificial soil are separated by an order of magnitude (Appendix A-2; Komex 1999; CAPP 2001). All the additional studies for a full guideline must be of primary data quality.

Livestock Watering

To comply with the requirements of the CCME (1993) protocol for an Interim livestock watering guideline, the following additional studies would be required:

- two acute or chronic studies on mammalian species raised in Canada, of which one is a livestock species; and,
- one acute or chronic study on an avian livestock species.

In spite of this deficiency, preliminary livestock watering guidance values were derived, based on laboratory animal studies. These values are not endorsed by the CCME.

Drinking Water

Currently, no Canadian Guideline for Drinking Water Quality exists for sulfolane. The available mammalian toxicological data were considered acceptable to calculate a source guidance value for groundwater for sulfolane for the purposes of conducting a groundwater check in the derivation of the soil quality guidelines. The source guidance value for groundwater is not a Canadian Guideline for Drinking Water Quality. It was calculated for use in the derivation of Canadian Soil Quality Guidelines.

TABLE 4. Water Quality Guidelines for Sulfolane

	Water Use			
	Freshwater Aquatic Life	**Irrigation**	**Livestock Watering**	**Source Guidance Value for Groundwater**
	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)
Guideline	50	0.5	0.6	0.09
Guideline and other guidance values	50	Cereals, tame hays, and pasture crops 46 (loam) 15 (poor soil) Other Crops 0.5 (all soil types)	0.6 (leghorn chicken) 1 (dairy cow) 2 (beef cattle) 3 (deer)	0.09
Guideline Status	Interim	Interim	Preliminary †	Not a guideline*

Notes:

† Insufficient data are available to satisfy protocol requirements for an Interim guideline. These "preliminary" guidance values are not endorsed by the CCME.

* Calculation of a Canadian Guideline for Drinking Water Quality is outside the jurisdiction of the CCME. The source guidance value for groundwater presented here is calculated using the same principles and procedures as used by Health Canada (1994 and 2005) to allow the calculation of the soil quality guideline drinking water check (Table 3). This value is not a Canadian Guideline for Drinking Water Quality.

CHAPTER 11. DISCUSSION OF SOIL AND WATER QUALITY GUIDELINES

Soil Quality Guidelines

Soil quality guidelines were derived for the protection of human and environmental health. The results are summarized in Table 3.

Environmental Health

The soil contact guidelines and the groundwater check (aquatic life) were calculated. For agricultural and residential/parkland land uses, the limiting pathway for the environmental soil quality guideline was soil contact. For commercial and industrial land uses, the limiting pathway for the environmental soil quality guideline was the groundwater check (aquatic life). Insufficient data were available to calculate the soil and food ingestion guideline or the nutrient and energy cycling check. Data gaps were discussed in the preceding sections. However, information was presented which showed that some soil microbial processes occur at high sulfolane concentrations.

Human Health

The soil ingestion guideline, off-site migration check, and groundwater check were calculated. For each of the four land uses, the limiting pathway for the human health soil quality guideline was the drinking water check. Insufficient data were available to calculate the produce, meat, and milk check. Data gaps were discussed in the preceding sections. The inhalation of indoor air check was not calculated due to the low vapour pressure and Henry's law coefficient of sulfolane.

Overall, the recommended soil quality guideline for sulfolane in soil is 0.8 $mg \cdot kg^{-1}$, based on the groundwater check for drinking water. Note that this guideline is not based on a Canadian Guideline for Drinking Water Quality; rather it is based on a source guidance value for groundwater calculated herein specifically for the purposes of conducting the groundwater check. In certain circumstances this pathway may not be applicable, for instance where either the quantity, or the natural quality of the groundwater are unsuitable for use as drinking water. In this case, the next most sensitive applicable pathway would be used as the guideline.

Water Quality Guidelines

Water quality guidelines were calculated for four water uses: freshwater aquatic life, irrigation, livestock watering, and human drinking water. The recommended guidelines are summarized in Table 4.

Freshwater Aquatic Life

The Interim guideline for freshwater aquatic life was calculated to be 50 $mg \cdot L^{-1}$.

Irrigation

Three "species maximum acceptable toxicant concentrations" (SMATC) were calculated for irrigation. Based on the protocol (CCME 1993), guidelines are calculated for 1) cereals, tame hays, and pasture crops and 2) other crops. For the first group of plants, SMATCs were calculated for two soil types: loam and poor soil while for the second, the SMATC was based artificial soil because only this soil type was tested in the critical study. The SMATCs for cereals, tame hays, and pasture crops are 46 $mg \cdot L^{-1}$ in loam and 15 $mg \cdot L^{-1}$ in poor soil. For other crops, the SMATC is 0.5 $mg \cdot L^{-1}$ (artificial soil). Therefore, the recommended interim irrigation water quality guideline protective of all crop species, regardless of soil type, is 0.5 $mg \cdot L^{-1}$ (Table 4).

Livestock Watering

Insufficient data were available to meet the requirements of the CCME (1993) protocol for developing livestock watering guidelines. However, effective management of existing sites with sulfolane contamination requires a livestock watering guideline. Accordingly, preliminary guidance values for this water use were calculated for dairy cattle and beef cattle, to represent likely agricultural animals. In addition, guidance values were calculated for white leghorn chickens and deer, to assist in evaluating possible risks to other species. The most sensitive species was the white leghorn chicken, for which a guidance value of 0.6 $mg \cdot L^{-1}$ was calculated. The reason for the difference in sensitivity between life stages or species is related to how water consumption relates to body weight. In a situation where water was being used for the consumption of a single livestock species other than cattle, typical water ingestion rates and body weight could be used to calculate a species-specific guideline. It should be noted that these preliminary guidance values were based on studies on laboratory animals using appropriate uncertainty factors; no toxicological information was available for livestock species (either mammalian or avian). Should such data become available in the future, an interim guideline could be derived. At this time, the preliminary guidance values are not endorsed by the CCME.

Drinking Water

Setting Canadian Guidelines for Drinking Water Quality is undertaken by Health Canada, and is outside the jurisdiction of the CCME. However, no Canadian Guideline for Drinking Water Quality currently exists for sulfolane, and a guideline value is required to calculate the groundwater check (drinking water) that makes up part of the soil quality guideline protocol (CCME 1996). Accordingly, the methods used by Health Canada (1994 and 2005) to develop drinking water guidelines were used to develop a source guidance value for groundwater for sulfolane of 0.09 $mg \cdot L^{-1}$ in this document. This value is not a Canadian Guideline for Drinking Water Quality.

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APPENDIX A-1. Biodegradation studies for sulfolane.

Study	Initial Concentration ($mg \cdot L^{-1}$)	Microcosm Material	Conditions	Nutrients	Temperature (C)	Lag Time (days)	Biodegradation Rate ($mg \cdot L^{-1} \cdot day^{-1}$)	Pseudo Half-Life (days)
Surface Water Studies								
Greene et al. (1999)	120	Wetland sediment	aerobic	none	8	9	4.8	5
Greene et al. (1999)	120	Wetland sediment	aerobic	N, P	8	28	7.2	6
Greene et al. (1999)	120	Wetland sediment	aerobic	none	8	39	7.2	8
Greene et al. (1999)	120	Wetland sediment	aerobic	none	8	53	4.8	11
Greene *et al.* (1999)	120	Wetland sediment	aerobic	N, P	8	24	7.2	6
Greene *et al.* (1999)	120	Wetland sediment	aerobic	none	8	25	9.6	5
Groundwater Studies, Mineral Supplemented								
Bagnall *et al.* (1984)	3,000	na	aerobic	P	17-25	6	330	1
Fedorak and Coy (1996)	13	Sandstone	aerobic	N, P	8	3 to 7	4	3
Fedorak and Coy (1996)	20	Sandstone	aerobic	N, P	26	<3	7.5	<1
Fedorak and Coy (1996)	20	Till	aerobic	N, P	8	15	0.7	10

APPENDIX A-1. Biodegradation studies for sulfolane.

Study	Initial Concentration ($mg \cdot L^{-1}$)	Microcosm Material	Conditions	Nutrients	Temperature (C)	Lag Time (days)	Biodegradation Rate ($mg \cdot L^{-1} \cdot day^{-1}$)	Pseudo Half-Life (days)
Greene *et al.* (1998)	200	Sandstone	aerobic	N, P	8	1.3	31	1
Greene *et al.* (1998)	200	Sandstone	aerobic	N, P	28	0.7	154	0.3
Greene *et al.* (1998)	200	Till	aerobic	N, P	8	7.5	58	1
Greene *et al.* (1998)	200	Till	aerobic	N, P	28	1.0	110	0.4
Greene *et al.* (1998)	200	Sand	aerobic	N, P	8	2.1	46	0.8
Greene *et al.* (1998)	200	Sand	aerobic	N, P	28	1.2	118	0.4
Greene *et al.* (1999)	490	Till	aerobic	P	8	5	12	5
Greene *et al.* (1999)	680	Till	aerobic	P	8	29	7	13
Salanitro and Langston (1988)	100	Sandy loam	aerobic	N, P	10	14 to 28	35 to 42	<5
Groundwater Studies, Unsupplemented								
Fedorak and Coy (1996)	20	Sandstone	aerobic	none	26	<3	3.8	<2
Fedorak and Coy (1996)	20	Till	aerobic	none	8	22	0.6	13

APPENDIX A-1. Biodegradation studies for sulfolane.

Study	Initial Concentration ($mg \cdot L^{-1}$)	Microcosm Material	Conditions	Nutrients	Temperature (C)	Lag Time (days)	Biodegradation Rate ($mg \cdot L^{-1} \cdot day^{-1}$)	Pseudo Half-Life (days)
Greene *et al.* (1999)	490	Till	aerobic	none	8	220	0	nd
Greene *et al.* (1999)	680	Till	aerobic	none	8	220	0	nd
Groundwater Studies, Anaerobic								
Greene *et al.* (1998)	200	Sandstone	anaerobic	N, P	8	35	5	10
Greene *et al.* (1998)	200	Sandstone	anaerobic	N, P	8	34	5	10
Greene *et al.* (1998)	200	Sand	anaerobic	N, P	8	168	1	48

APPENDIX A-1. Biodegradation studies for sulfolane.

Study	Initial Concentration ($mg \cdot L^{-1}$)	Microcosm Material	Conditions	Nutrients	Temperature (C)	Lag Time (days)	Biodegradation Rate ($mg \cdot L^{-1} \cdot day^{-1}$)	Pseudo Half-Life (days)
Other Studies								
McLeod *et al.* (1992)	0.6	Acclimated sludge	aerobic	na	na	<1	>1.5	nc
McLeod *et al.* (1992)	1.4	Unacclimated sludge	aerobic	na	na	14	>1.1	nc

see text for definition of pseudo half life (Chapter 3)

na not available.

APPENDIX A-2. Toxicity of sulfolane to terrestrial plants.

Species	Scientific Name	Endpoint	Soil Type	NOEC ($mg \cdot kg^{-1}$)	LOEC ($mg \cdot kg^{-1}$)	EC_{25} ($mg \cdot kg^{-1}$)	EC_{50} ($mg \cdot kg^{-1}$)	Reference
Lettuce	*Lactuca sativa*	5-d emergence	Artificial	78	160	200	490	Komex (1999)
		7-d emergence	Artificial	944	1,890	1,530	2,690	CAPP (2001)
		7-d emergence	Loam	5,400	10,800	6,650	9,830	CAPP (2001)
		7-d emergence	Sand	911	1,820	1,030	1,430	CAPP (2001)
		7-d emergence	Till	440	940	940	1,410	CAPP (2001)
		7-d biomass	Artificial	944	1,890	462	1,780	CAPP (2001)
		7-d biomass	Loam	10,800	>10,800	>10,800	>10,800	CAPP (2001)
		7-d biomass	Sand	1,820	>1,820	>1,820	>1,820	CAPP (2001)
		7-d biomass	Till	1,880	>1,880	>1,880	>1,880	CAPP (2001)
		7-d root length	Artificial	944	1,890	1,370	2,470	CAPP (2001)
		7-d root length	Loam	2,700	5,400	7,000	9,840	CAPP (2001)
		7-d root length	Sand	455	911	526	1,070	CAPP (2001)
		7-d root length	Till	440	940	572	1,260	CAPP (2001)
		7-d shoot length	Artificial	1,890	3,780	2,520	>3,780	CAPP (2001)
		7-d shoot length	Loam	21,600	>21,600	>21,600	>21,600	CAPP (2001)
		7-d shoot length	Sand	455	911	650	>1,820	CAPP (2001)
		7-d shoot length	Till	940	1,880	1,690	>1,880	CAPP (2001)

APPENDIX A-2. Toxicity of sulfolane to terrestrial plants.

Species	Scientific Name	Endpoint	Soil Type	NOEC ($mg \cdot kg^{-1}$)	LOEC ($mg \cdot kg^{-1}$)	EC_{25} ($mg \cdot kg^{-1}$)	EC_{50} ($mg \cdot kg^{-1}$)	Reference
Carrot	*Daucus carota*	7-d emergence	Artificial	3,780	7,550	4,430	6,340	CAPP (2001)
		7-d emergence	Loam	10,800	21,600	11,600	19,400	CAPP (2001)
		7-d emergence	Sand	1,820	3,640	2,280	3,430	CAPP (2001)
		7-d emergence	Till	1,880	3,760	3,410	4,830	CAPP (2001)
		7-d biomass	Artificial	1,890	3,780	2,560	>7,550	CAPP (2001)
		7-d biomass	Loam	21,600	>21,600	>21,600	>21,600	CAPP (2001)
		7-d biomass	Sand	3,640	>3,640	2,770	>3,640	CAPP (2001)
		7-d biomass	Till	3,760	>3,760	>3,760	>3,760	CAPP (2001)
		7-d root length	Artificial	944	1,890	1,220	2,390	CAPP (2001)
		7-d root length	Loam	2,700	5,400	14,100	17,300	CAPP (2001)
		7-d root length	Sand	455	911	512	1,800	CAPP (2001)
		7-d root length	Till	440	940	807	2,390	CAPP (2001)
		7-d shoot length	Artificial	1,890	3,780	4,040	6,780	CAPP (2001)
		7-d shoot length	Loam	10,800	21,600	11,800	>21,600	CAPP (2001)
		7-d shoot length	Sand	1,820	3,640	2,420	>3,640	CAPP (2001)
		7-d shoot length	Till	1,880	3,760	3,070	>3,760	CAPP (2001)

APPENDIX A-2. Toxicity of sulfolane to terrestrial plants.

Species	Scientific Name	Endpoint	Soil Type	NOEC ($mg \cdot kg^{-1}$)	LOEC ($mg \cdot kg^{-1}$)	EC_{25} ($mg \cdot kg^{-1}$)	EC_{50} ($mg \cdot kg^{-1}$)	Reference
Alfalfa	*Medicago sativa*	7-d emergence	Artificial	3,780	7,550	5,760	8,180	CAPP (2001)
		7-d emergence	Loam	23,700	47,300	29,800	35,900	CAPP (2001)
		7-d emergence	Sand	3,640	7,290	4,320	5,740	CAPP (2001)
		7-d emergence	Till	3,760	7,510	4,180	5,340	CAPP (2001)
		7-d biomass	Artificial	944	1,890	2,210	>7,550	CAPP (2001)
		7-d biomass	Loam	23,700	>23,700	>23,700	>23,700	CAPP (2001)
		7-d biomass	Sand	7,290	>7,290	>7,290	>7,290	CAPP (2001)
		7-d biomass	Till	3,760	>3,760	>3,760	>3,760	CAPP (2001)
		7-d root length	Artificial	944	1,890	1,810	3,120	CAPP (2001)
		7-d root length	Loam	5,920	11,800	8,390	11,100	CAPP (2001)
		7-d root length	Sand	911	1,820	931	1,490	CAPP (2001)
		7-d root length	Till	235	440	490	1,530	CAPP (2001)
		7-d shoot length	Artificial	7,550	>7,550	>7,550	>7,550	CAPP (2001)
		7-d shoot length	Loam	23,700	>23,700	>23,700	>23,700	CAPP (2001)
		7-d shoot length	Sand	1,820	3,640	4,200	6,070	CAPP (2001)
		7-d shoot length	Till	3,760	>3,760	>3,760	>3,760	CAPP (2001)

APPENDIX A-2. Toxicity of sulfolane to terrestrial plants.

Species	Scientific Name	Endpoint	Soil Type	NOEC ($mg \cdot kg^{-1}$)	LOEC ($mg \cdot kg^{-1}$)	EC_{25} ($mg \cdot kg^{-1}$)	EC_{50} ($mg \cdot kg^{-1}$)	Reference
Timothy	*Phleum pratense*	7-d emergence	Artificial	1,890	3,780	2,990	4,630	CAPP (2001)
		7-d emergence	Loam	10,800	21,600	14,000	20,000	CAPP (2001)
		7-d emergence	Sand	455	911	2,320	3,160	CAPP (2001)
		7-d emergence	Till	1,880	3,760	2,150	3,070	CAPP (2001)
		7-d biomass	Artificial	7,550	>7,550	3,260	6,730	CAPP (2001)
		7-d biomass	Loam	675	1,350	1,050	2,960	CAPP (2001)
		7-d biomass	Sand	228	455	384	>3,640	CAPP (2001)
		7-d biomass	Till	3,760	>3,760	1,430	2,930	CAPP (2001)
		7-d root length	Artificial	472	944	1,030	1,990	CAPP (2001)
		7-d root length	Loam	1,350	2,700	4,050	9,350	CAPP (2001)
		7-d root length	Sand	455	911	562	911	CAPP (2001)
		7-d root length	Till	na	na	na	na	CAPP (2001)
		7-d shoot length	Artificial	1,890	3,780	3,310	5,300	CAPP (2001)
		7-d shoot length	Loam	5,400	10,800	13,100	18,400	CAPP (2001)
		7-d shoot length	Sand	911	1,820	1,530	2,560	CAPP (2001)
		7-d shoot length	Till	940	1,880	1,820	3,110	CAPP (2001)

Notes:

1. na = not available due to the impracticality of separating fine timothy roots from till soil
2. all data reported on a dry weight basis
3. all data reported as nominal concentrations

APPENDIX A-3. Toxicity of sulfolane to terrestrial invertebrates.

Species	Scientific Name	Endpoint	Soil Type	NOEC ($mg \cdot kg^{-1}$)	LOEC ($mg \cdot kg^{-1}$)	LC_{25} ($mg \cdot kg^{-1}$)	LC_{50} ($mg \cdot kg^{-1}$)	Reference
Earthworm	*Eisenia fetida*	14d survival	artificial	2,500	5,000	3,800	5,300	Komex (1999)
		14d survival	artificial	3,710	7,430	4,610	5,550	CAPP (2001)
		14d survival	loam	10,830	21,660	15,210	19,820	CAPP (2001)
		14d survival	sand	1,840	3,690	2,270	2,740	CAPP (2001)
		14d survival	till	1,800	3,600	2,250	2,700	CAPP (2001)
	Minimum Toxicity Values			1,800	3,600	2,250	2,700	

Notes:

all data reported on a dry weight basis

all data reported as nominal concentrations

APPENDIX A-4. Toxicity of sulfolane to aquatic species.

Type of Study	Type of Biota	Common Name	Species	Duration	Endpoint	NOEC	LOEC	LC_{50}/EC_{50}	Temperature	pH	DO	Hardness	Type of Control	Chemical Analysis?	Experimental Design	Protocol	Reference
						($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	(°C)		($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)					
Primary Freshwater Data																	
acute	vertebrate	Rainbow trout	*Oncorhynchus mykiss*	96 hours	survival	-	-	1,264	15.1	8.3	na	255	S	Y	S	ECP	CAPP (2001)
acute	invertebrate	sideswimmer	*Hyalella azteca*	96 hours	survival	-	-	1,516	23.1	8.3	na	255	S	Y	S	(ECP)	CAPP (2001)
acute	invertebrate	daphnid	*Daphnia magna*	48 hours	survival	-	-	1,245	23.1	8.2	8.5-8.7	255	S	Y	S	ECP	Environment Canada (2003)
Secondary Freshwater Data																	
acute	vertebrate	fathead minnow	*Pimephales promelas*	7 days	survival	1,000	>1,000	>1,000	25	6.8-8.4	5.3-8.8	na	S	N	S	ECP	ERAC 1998
acute	vertebrate	fathead minnow	*Pimephales promelas*	7 days	growth	1,000	>1,000	>1,000	25	6.8-8.4	5.3-8.8	na	S	N	S	ECP	ERAC 1998
acute	invertebrate	daphnid	*Daphnia magna*	48 hours	survival	-	-	3,274	na	na	na	na	S	N	S	ECP	ERAC 1998
acute	invertebrate	daphnid	*Daphnia magna*	48 hours	survival	-	-	40	18-22	7.8-8.2	8.6-9.4	168-178	S	N	S	S	Girling 1987
chronic	invertebrate	daphnid	*Ceriodaphnia dubia*	7 days	survival	500	1,000	>1,000	25	8.0-8.8	6.8-8.0	na	S	N	S	ECP	ERAC 1998
chronic	invertebrate	daphnid	*Ceriodaphnia dubia*	7 days	reproduction	250	500	635	25	8.0-8.8	6.8-8.0	na	S	N	S	ECP	ERAC 1998
chronic	plant/alga	green alga	*Selenastrum capricornutum*	72 hours	growth	500	1,000	723	na	na	na	na	S	N	S	ECP	ERAC 1998
Unacceptable Freshwater Data																	
acute	vertebrate	goldfish	*Carassius auratus*	24 hours	survival	-	-	4,800	na	na	na	na	na	na	na	na	Bridie *et al.* 1979a
acute	vertebrate	mosquito fish	*Gambusia sp.*	96 hours	survival	-	-	1,930	na	na	na	na	na	na	na	na	Shell 1984a
acute	vertebrate	mosquito fish	*Gambusia sp.*	48 hours	survival	-	-	4,600	na	na	na	na	na	na	na	na	Shell 1984a
acute	vertebrate	stickleback	*na*	96 hours	survival	-	-	1,760	na	na	na	na	na	na	na	na	Shell 1984a
acute	vertebrate	stickleback	*na*	48 hours	survival	-	-	1,820	na	na	na	na	na	na	na	na	Shell 1984a
acute	invertebrate	daphnid	*Daphnia magna*	24 hours	survival	-	-	270	20±2	7.9-8.4	9.0-9.4	180±10	na	N	S	S	Shell 1984b
acute	invertebrate	daphnid	*Daphnia magna*	24 hours	survival	-	-	160	na	na	na	na	na	na	na	S	Shell 1984b
acute	invertebrate	daphnid	*Daphnia magna*	48 hours	survival	-	-	94	20±2	7.9-8.4	9.0-9.4	180±10	na	N	S	S	Shell 1984b
acute	invertebrate	daphnid	*Daphnia magna*	48 hours	survival	-	-	95	na	na	na	na	na	na	na	S	Shell 1984b

APPENDIX A-4. Toxicity of sulfolane to aquatic species.

Type of Study	Type of Biota	Common Name	Species	Duration	Endpoint	NOEC	LOEC	LC_{50}/EC_{50}	Temperature	pH	DO	Hardness	Type of Control	Chemical Analysis?	Experimental Design	Protocol	Reference
						($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	(°C)		($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)					
chronic	invertebrate	daphnid	*Ceriodaphnia dubia*	7 days	reproduction	<375	375	-	na	na	na	na	na	na	na	na	Wong *et al.* 1993
chronic	invertebrate	daphnid	*Ceriodaphnia dubia*	7 days	survival	1,500	3,000	2,575	na	na	na	na	na	na	na	na	Wong *et al.* 1993
chronic	plant/alga	duckweed	*Lemna minor*	4-7 days	growth	-	-	>2,500	na	na	na	na	na	na	na	na	SRC 1994
chronic	plant/alga	green alga	*Selenastrum capricornutum*	24 hours	^{14}C uptake	-	-	10,000 - 50,000	na	na	na	na	na	na	na	na	SRC 1994
chronic	plant/alga	green alga	*Selenastrum capricornutum*	72-96 hours	biomass	-	-	>1,000	na	na	na	na	na	na	na	na	SRC 1994
chronic	plant/alga	green alga	*Selenastrum capricornutum*	96 hours	growth rate	-	-	>1,000	na	na	na	na	na	na	na	na	PSE Dossier 1993

APPENDIX A-4. Toxicity of sulfolane to aquatic species.

Type of Study	Type of Biota	Common Name	Species	Duration	Endpoint	NOEC	LOEC	LC_{50}/EC_{50}	Temperature	pH	DO	Hardness	Type of Control	Chemical Analysis?	Experimental Design	Protocol	Reference
						($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)	(°C)		($mg \cdot L^{-1}$)	($mg \cdot L^{-1}$)					
chronic	other	cyanobacteria	*Aphanizomenon flos-aquae*	24 hours	^{14}C uptake	-	-	500 - 1,000	na	na	na	na	na	na	na	na	SRC 1994
chronic	other	cyanobacteria	*Aphanizomenon flos-aquae*	24 hours	nitrogen fixation	-	-	5,000 - 10,000	na	na	na	na	na	na	na	na	SRC 1994
chronic	other	diatom	*Cyclotella meneghiana*	24 hours	^{14}C uptake	-	-	10,000 - 50,000	na	na	na	na	na	na	na	na	SRC 1994
	Secondary Marine Data																
acute	invertebrate	copepod	*Acartia tonsa*	24 hours	immobilization	-	-	350	18-22	7.8-8.2	6.8-7.8	na	Y	N	F	S	Girling 1987
acute	invertebrate	copepod	*Acartia tonsa*	48 hours	immobilization	-	-	52	18-22	7.8-8.2	6.8-7.8	na	Y	N	F	S	Girling 1987
	Unacceptable Marine Data																
acute	invertebrate	oyster	*Crassostrea gigas*	24 hours	na	-	-	460	na	na	na	na	na	na	na	na	Fairhurst *et al.* 1992
acute	other	bacterium (microtox)	*Vibrio fischerii*	na	luminescence	-	-	30	na	na	na	na	na	na	na	na	SRC 1994
acute	other	bacterium (microtox)	*Vibrio fischerii*	na	luminescence	-	-	59	na	na	na	na	na	na	na	na	ERAC 1998
chronic	invertebrate	mysid shrimp	*Mysidopsis bahia*	7 days	growth	150	-	-	na	na	na	na	na	na	na	na	Wong *et al.* 1993

Notes:
General: - = no data or not applicable; na = not available.

Controls Acceptable?: S = satisfactory; U = unsatisfactory.

Chemical Analysis?: N = no; Y = yes

Experimental Design: F = flow through; R = renewal; S = static.

Protocol: ECP = Environment Canada Protocol; (ECP) = Modified Environment Canada Protocol; S = Shell Internal Protocol.

APPENDIX A-5. Acute toxicity of sulfolane to mammalian species.

Species	Route of Administration	Exposure	LD_{50} (mg kg^{-1} bw)	Reference
Rat	intravenous	Single dose; death within 7 days	1,094	Andersen *et al.* 1976
	oral	single dose; death within 7 days Single	1,846	Andersen *et al.* 1976
	parenteral	single dose; death within 7 days Single	1,598	Andersen *et al.* 1976
	subcutaneous	single dose; death within 7 days Single	1,606	Andersen *et al.* 1976
	oral	N/A	2,504	Zhu *et al.* 1987
Mouse	intravenous	single dose; death within 7 days	632	Andersen *et al.* 1976
	intravenous	single dose; death within 7 days	1,080	Alexander *et al.* 1959
	parenteral	single dose; death within 7 days	1,270	Andersen *et al.* 1976
	subcutaneous	single dose; death within 7 days	1,360	Andersen *et al.* 1976
	oral	N/A	2,343	Zhu *et al.* 1987
Guinea pig	oral	single dose; death within 7 days	1,815	Andersen *et al.* 1976
	oral	single dose; death within 24 hours	2,100	Brown *et al.* 1966
	parenteral	single dose; death within 7 days	1,331	Andersen *et al.* 1976
	oral	N/A	1,445	Zhu *et al.* 1987
Rabbit	intravenous	single dose; death within 7 days	(640-850) *	Andersen *et al.* 1976
	subcutaneous	single dose; death within 7 days	(1,990-3,500) *	Andersen *et al.* 1976

Notes:

* not enough animals were used to calculate the LD_{50}, so only a range is given. Animals dosed with less than the lower dose indicated survived; those with more than the upper dose died; and,

† the low end of the range presented in the rabbit studies was used to calculate these values.

N/A information not available

APPENDIX A-6. Chronic toxicity of sulfolane to mammalian species.

Study	Duration	Species	NOAEL/NOAEC	Comment
		ORAL STUDIES		
HLS (2001)	13 week	Rat	2.9 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$	definitive sub-chronic study commissioned for guideline derivation
Zhu *et al.* (1987)	6 month	guinea pig	0.25 $mg \cdot kg^{-1}$ $bw \cdot day^{-1}$	concerns with study quality ; unable to confirm whether good laboratory practice had been followed
		INHALATION STUDIES		
Anderson *et al.* (1991)	90 day	rat guinea pig beagle dog squirrel monkey	20 $mg \cdot m^{-3}$	inappropriate exposure route

APPENDIX B-1. Correction of toxicity data to reflect analytically measured concentrations

Introduction

Plant and soil invertebrate toxicity tests for sulfolane were reported in CAPP (2001). No chemical analyses were performed in those tests, and test results were presented in terms of nominal concentrations expressed on a dry weight basis. Concerns were raised that nominal concentrations of sulfolane in soil might not be representative of the concentrations that would have been measured analytically at the start of the test. Possible reasons for this difference would include any biodegradation that might have occurred between the time that the sulfolane was introduced to the soil and the time the organisms were introduced, and also the possibility that the analytical extraction methodology did not recover 100% of the sulfolane from the soil. Accordingly an experimental program was initiated to spike soils with sulfolane and to submit the soils for analysis 24 hours later, to allow a correction of the toxicity data, and hence the resulting guideline values, for any losses of sulfolane.

Definition of Nominal and Analytical Concentrations

Throughout this Appendix, the concentration of a solution or a soil that is calculated from measured volumes and/or masses of sulfolane, water and/or soil is referred to as the "Nominal Concentration". The concentration of a solution or a soil that is determined by chemical analysis is referred to as the "Analytical Concentration". This Appendix describes the methodology used to determine the Analytical Concentrations, and the methodology used to correct the toxicity data to reflect analytically measured concentrations.

Soil Type

The scope of the Analytical Measurement project was limited to one soil type. A till soil similar to the one used in the toxicity tests reported in CAPP (2001) was selected as a surrogate for all soils. Biodegradation was expected to be similar for all four soil types used in the CAPP (2001) work, since none of them would have microbes that were already acclimated to sulfolane.

Preparation of Spiked Soils

Spiked soils were prepared according to the following steps which mimic the procedure used to prepare the soils in the CAPP (2001) toxicity tests:

- 1.5 kg of soil was prepared by drying overnight at 30°C, and sieving to 5 mm.
- 8 test units were prepared by measuring ~60 g dry weight of soil into 100 mm x 15 mm Petri dishes. The exact mass of soil added to each unit was recorded.
- 100 ml of ~90,000 $mg \cdot L^{-1}$ stock sulfolane solution was prepared by weighing ~9.0 g of sulfolane into a beaker, transferring to a volumetric flask, sequentially rinsing the beaker into the volumetric flask and diluting to the mark with deionized water. The exact mass of sulfolane added was recorded, and the Nominal Concentration calculated.
- 40 ml of the stock solution was placed in a second volumetric flask, and diluted to 100 ml by adding deionized water. Two further sequential dilutions were carried out to create a dilution series of 100%, 40%, 16%, and 6.4% of the stock solution.
- For each solution, 15 ml was added to each of two duplicate test units (randomly selected from the 8 prepared previously) and mixed by hand until uniform colour and moisture were

achieved (approximately 3 minutes). Test units were covered and allowed to equilibrate at room temperature for 24 hours.

- At the end of the 24 hour period, each pair of duplicate test units was composited by mixing by hand, and submitted to Maxxam Analytics Inc. in Calgary for sulfolane analysis.

Analytical Results

Analytical results for the stock solution and the spiked soils are summarized in Tables I-1 and I-2, respectively, and compared with the Nominal Concentrations calculated for each sample.

Dry Weight vs. Wet Weight Basis

Chemical concentrations in soil can be expressed on the basis of dry weight (*i.e.*, mg chemical per kg dry weight of soil) or wet weight (*i.e.*, mg chemical per kg wet weight of soil). The chemical analyses conducted for this work were presented by the laboratory on a wet weight basis. The CCME protocols (CCME 1993, 2003) require that that all soil toxicity data be presented on a dry weight basis. Accordingly the wet weight basis results in Table I-2 were converted to dry weight basis using the formula:

$$C_{dry} = C_{wet} \cdot \frac{M_{wet}}{M_{dry}}$$

Where:

C_{dry}	=	dry weight basis concentration (mg sulfolane / kg dry weight soil);
C_{wet}	=	wet weight basis concentration (mg sulfolane / kg wet weight soil);
M_{wet}	=	wet mass of soil (kg); and,
M_{dry}	=	dry mass of soil (kg).

Raw Toxicological Data

The available raw (*i.e.*, before the correction for analytical measurement) data for the toxicity of sulfolane to plants and terrestrial invertebrates were presented in CAPP (2001) and are summarized in Table I-3. Data were available for four plant species (lettuce (*Lactuca sativa*), carrot (*Daucus carota*), alfalfa (*Medicago sativa*), and timothy (*Phleum pratense*)), and one invertebrate species (earthworm, (*Eisenia andrei*)). The toxicity data were collected from four distinct soil types (artificial soil, loam, sand and till) with differing texture, organic carbon content, and cation exchange capacity. The endpoints measured were emergence, biomass, root length, and shoot length. The raw toxicological data are expressed on a dry weight basis.

Correction of Toxicological Data to Reflect Analytically Measured Concentrations

Figure I-1 shows a regression of Analytical vs. Nominal Concentrations for sulfolane in the spiked soil samples, expressed on a dry weight basis. An optimal fit to the data was achieved using the following regression, in which the intercept was fit through zero:

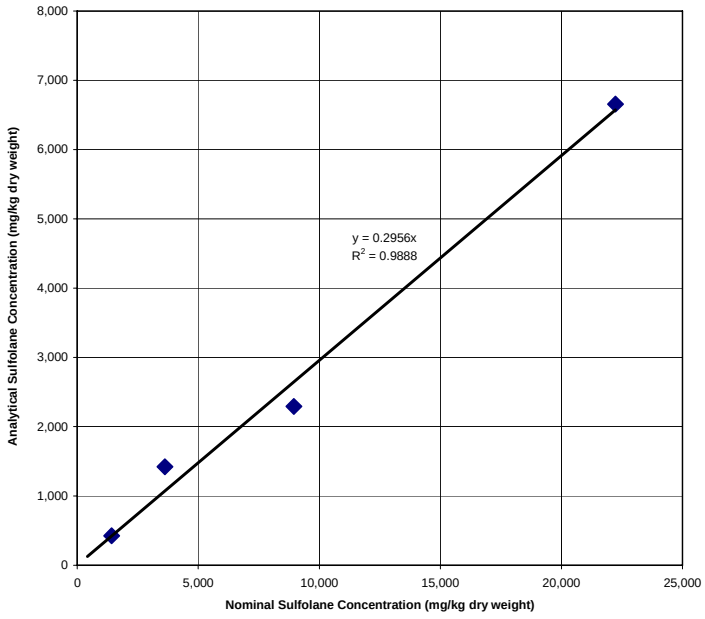
$$y = 0.2956x$$

Where x is the Nominal Concentration and y is the Analytical Concentration. This regression was used in Table I-4 to correct the raw (Table I-3) toxicity data to reflect analytically measured concentrations.

References

CAPP (Canadian Association of Petroleum Producers), 2001. Soil and water quality guidelines for sulfolane and diisopropanolamine (DIPA): environmental and human health. Unpublished report prepared by Komex International Ltd. File No. C50560000.

APPENDIX B-2 Analytical vs. Nominal Sulfolane in Soil (based on dry weights from Table I-2)



APPENDIX B-3. Nominal and Analytical Concentrations in Solutions

Solution	ID	Nominal Values Based on Volumetric Calculations			Analytical Concentration
		Mass of Sulfolane in 100 ml	Mass of Sulfolane in 15 ml	Nominal Concentration	
		(mg)	(mg)	(mg/L)	(mg/L)
Sulfolane Stock	S1	9,045.1	1,356.77	90,451	68,800
Sulfolane 1st Dilution - 40% of S1	S2	3,618.0	542.71	36,180	
Sulfolane 2nd Dilution - 40% of S2	S3	1,447.2	217.08	14,472	
Sulfolane 3rd Dilution - 40% of S3	S4	578.9	86.83	5,789	

APPENDIX B-4. Nominal and Analytical Concentrations in Soil

Individual Test Units			*Composited Test Units*				
Treatment	*Mass of Dry Soil (g)*	*Moisture %*	*Nominal Concentration (mg/kg ww)*	*Nominal Concentration (mg/kg dw)*	*Analytical Concentration* (mg/kg ww)*	*Analytical Concentration (mg/kg dw)*	*Analytical Recovery (%; dw)*
S1-A	61.687	24.4%	17,833	22,233	5,340	6,657	30%
S1-B	60.362	24.9%					
S2-A	60.628	24.5%	7,186	8,947	1,840	2,291	26%
S2-B	60.693	24.4%					
S3-A	60.457	24.4%	2,908	3,622	1,140	1,420	39%
S3-B	59.411	24.7%					
S4-A	62.488	23.6%	1,147	1,424	343	426	30%
S4-B	59.511	24.7%					

* Analytical concentrations were reported on a wet weight basis; therefore, they were converted to a dry weight basis before ploting on Figure I-1

APPENDIX B-5. Raw Plant and Invertebrate Toxicity Data

	PLANT DATA					
Species	**Soil**	**Effect Level**	**Emergence** (mg/kg dw)	**Biomass** (mg/kg dw)	**Root Length** (mg/kg dw)	**Shoot Length** (mg/kg dw)
Lettuce	Artificial Soil	EC25	200	nm	nm	nm
Lettuce	Artificial Soil	EC25	1,530	462	1,370	2,520
Alfalfa	Artificial Soil	EC25	5,760	2,210	1,810	7,550
Carrot	Artificial Soil	EC25	4,430	2,560	1,220	4,040
Timothy	Artificial Soil	EC25	2,990	3,260	1,030	3,310
Alfalfa	Loam	EC25	29,800	23,700	8,390	23,700
Carrot	Loam	EC25	11,600	21,600	14,100	11,800
Lettuce	Loam	EC25	6,650	10,800	7,000	21,600
Timothy	Loam	EC25	14,000	1,050	4,050	13,100
Alfalfa	Sand	EC25	4,320	7,290	931	4,200
Carrot	Sand	EC25	2,280	2,770	512	2,420
Lettuce	Sand	EC25	1,030	1,820	526	650
Timothy	Sand	EC25	2,320	384	562	1,530
Alfalfa	Till	EC25	4,180	3,760	490	3,760
Carrot	Till	EC25	3,410	3,760	807	3,070
Lettuce	Till	EC25	940	1,880	572	1,690
Timothy	Till	EC25	2,150	1,430	n/a	1,820

	INVERTEBRATE DATA		
Species	**Soil**	**Effect Level**	**Mortality** (mg/kg dw)
Earthworm	Artificial Soil	LC25	3,800
Earthworm	Artificial Soil	LC25	4,610
Earthworm	Loam	LC25	15,210
Earthworm	Sand	LC25	2,270
Earthworm	Till	LC25	2,250

Notes: na = not applicable
nm = not measured
1. Endpoints that were reported as greater than a certain value are consertatively presented here as that value (i.e., >1,700 presented as 1,700)
2. All data from CAPP (2001) and Komex (1999)

APPENDIX B-6. Toxicity Data Corrected to Reflect Analytically Measured Concentrations

	Moisture Content	
Artificial Soil	**35%**	**1.00**
Loam	**65%**	**1.00**
Sand	**25%**	**1.00**
Till	**25%**	**1.00**

Revised Regression Used to Correct for Analytical Measurements:
y = 0.2956x; r^2 = 0.9888

Species	Soil	Effect Level	PLANT DATA Emergence (mg/kg dw)	Biomass (mg/kg dw)	Root Length (mg/kg dw)	Shoot Length (mg/kg dw)
Lettuce	Artificial Soil	EC25	n/a	nm	nm	nm
Lettuce	Artificial Soil	EC25	n/a	137	405	745
Lettuce	Geometric Mean of Artificial Soil Data:		164	na	na	na
Alfalfa	Artificial Soil	EC25	1,703	653	535	2,232
Carrot	Artificial Soil	EC25	1,310	757	361	1,194
Timothy	Artificial Soil	EC25	884	964	304	978
Alfalfa	Loam	EC25	8,809	7,006	2,480	7,006
Carrot	Loam	EC25	3,429	6,385	4,168	3,488
Lettuce	Loam	EC25	1,966	3,192	2,069	6,385
Timothy	Loam	EC25	4,138	310	1,197	3,872
Alfalfa	Sand	EC25	1,277	2,155	275	1,242
Carrot	Sand	EC25	674	819	151	715
Lettuce	Sand	EC25	304	538	155	192
Timothy	Sand	EC25	686	114	166	452
Alfalfa	Till	EC25	1,236	1,111	145	1,111
Carrot	Till	EC25	1,008	1,111	239	907
Lettuce	Till	EC25	278	556	169	500
Timothy	Till	EC25	636	423	n/a	538

Species	Soil	Effect Level	INVERTEBRATE DATA Mortality (mg/kg dw)
Earthworm	Artificial Soil	LC25	n/a
Earthworm	Artificial Soil	LC25	n/a
Earthworm	Geometric Mean of Artificial Soil Data:		1,237
Earthworm	Loam	LC25	4,496
Earthworm	Sand	LC25	671
Earthworm	Till	LC25	665

Notes: n/a = not applicable
nm = not measured
1. Endpoints that were reported as greater than a certain value are consertatively presented here as that value (i.e., >1,700 presented as 1,700)
2. All data from CAPP (2001) and Komex (1999)

APPENDIX B-7. Toxicity Data Corrected to Reflect Analytically Measured Concentrations (Regression Used to Correct for Analytical Measurements: y = 0.2956x; r^2 = 0.9888)

Species	Scientific Name	Endpoint	Soil Type	NOEC ($mg \cdot kg^{-1}$ dry weight)	LOEC ($mg \cdot kg^{-1}$ dry weight)	Corrected NOEC ($mg \cdot kg^{-1}$ dry weight)	Corrected LOEC ($mg \cdot kg^{-1}$ dry weight)	ASC ($mg \cdot kg^{-1}$ dry weight)	SMATC ($mg \cdot L^{-1}$)	Reference
Alfalfa	*Medicago sativa*	biomass	Artificial	944	1,890	279	559	39	64	CAPP (2001)
Alfalfa	*Medicago sativa*	emergence	Artificial	3,780	7,550	1,117	2,232	158	257	CAPP (2001)
Alfalfa	*Medicago sativa*	root length	Artificial	944	1,890	279	559	39	64	CAPP (2001)
Alfalfa	*Medicago sativa*	shoot length	Artificial	7,550	>7,550	2,232	2,232	223	363	CAPP (2001)
Alfalfa	*Medicago sativa*	biomass	Loam	23,700	>23,700	7,006	7,006	701	1,138	CAPP (2001)
Alfalfa	*Medicago sativa*	emergence	Loam	23,700	47,300	7,006	13,982	990	1,608	CAPP (2001)
Alfalfa	*Medicago sativa*	root length	Loam	5,920	11,800	1,750	3,488	247	401	CAPP (2001)
Alfalfa	*Medicago sativa*	shoot length	Loam	23,700	>23,700	7,006	7,006	701	1,138	CAPP (2001)
Alfalfa	*Medicago sativa*	biomass	Sand	7,290	>7,290	2,155	2,155	215	350	CAPP (2001)
Alfalfa	*Medicago sativa*	emergence	Sand	3,640	7,290	1,076	2,155	152	247	CAPP (2001)
Alfalfa	*Medicago sativa*	root length	Sand	911	1,820	269	538	38	62	CAPP (2001)
Alfalfa	*Medicago sativa*	shoot length	Sand	1,820	3,640	538	1,076	76	124	CAPP (2001)
Alfalfa	*Medicago sativa*	biomass	Till	3,760	>3,760	1,111	1,111	111	181	CAPP (2001)
Alfalfa	*Medicago sativa*	emergence	Till	3,760	7,510	1,111	2,220	157	255	CAPP (2001)
Alfalfa	*Medicago sativa*	root length	Till	235	440	69	130	10	15	CAPP (2001)
Alfalfa	*Medicago sativa*	shoot length	Till	3,760	>3,760	1,111	1,111	111	181	CAPP (2001)
Carrot	*Daucus carota*	biomass	Artificial	1,890	3,780	559	1,117	79	13	CAPP (2001)
Carrot	*Daucus carota*	emergence	Artificial	3,780	7,550	1,117	2,232	158	26	CAPP (2001)
Carrot	*Daucus carota*	root length	Artificial	944	1,890	279	559	39	6	CAPP (2001)
Carrot	*Daucus carota*	shoot length	Artificial	1,890	3,780	559	1,117	79	13	CAPP (2001)
Carrot	*Daucus carota*	biomass	Loam	21,600	>21,600	6,385	6,385	638	104	CAPP (2001)
Carrot	*Daucus carota*	emergence	Loam	10,800	21,600	3,192	6,385	451	73	CAPP (2001)
Carrot	*Daucus carota*	root length	Loam	2,700	5,400	798	1,596	113	18	CAPP (2001)
Carrot	*Daucus carota*	shoot length	Loam	10,800	21,600	3,192	6,385	451	73	CAPP (2001)
Carrot	*Daucus carota*	biomass	Sand	3,640	>3,640	1,076	1,076	108	17	CAPP (2001)
Carrot	*Daucus carota*	emergence	Sand	1,820	3,640	538	1,076	76	12	CAPP (2001)
Carrot	*Daucus carota*	root length	Sand	455	911	134	269	19	3	CAPP (2001)
Carrot	*Daucus carota*	shoot length	Sand	1,820	3,640	538	1,076	76	12	CAPP (2001)
Carrot	*Daucus carota*	biomass	Till	3,760	>3,760	1,111	1,111	111	18	CAPP (2001)
Carrot	*Daucus carota*	emergence	Till	1,880	3,760	556	1,111	79	13	CAPP (2001)
Carrot	*Daucus carota*	root length	Till	440	940	130	278	19	3	CAPP (2001)
Carrot	*Daucus carota*	shoot length	Till	1,880	3,760	556	1,111	79	13	CAPP (2001)

continued

Species	Scientific Name	Endpoint	Soil Type	NOEC (mg·kg^{-1} dry weight)	LOEC (mg·kg^{-1} dry weight)	Corrected NOEC (mg·kg^{-1} dry weight)	Corrected LOEC (mg·kg^{-1} dry weight)	ASC (mg·kg^{-1} dry weight)	SMATC (mg·L^{-1})	Reference
Lettuce	*Lactuca sativa*	biomass	Artificial	944	1,890	279	559	39	6	CAPP (2001)
Lettuce	*Lactuca sativa*	emergence	Artificial	78	160	23	47	3	0.5	Komex (1999)
Lettuce	*Lactuca sativa*	emergence	Artificial	944	1,890	279	559	39	6	CAPP (2001)
Lettuce	*Lactuca sativa*	root length	Artificial	944	1,890	279	559	39	6	CAPP (2001)
Lettuce	*Lactuca sativa*	shoot length	Artificial	1,890	3,780	559	1,117	79	13	CAPP (2001)
Lettuce	*Lactuca sativa*	biomass	Loam	10,800	>10,800	3,192	3,192	319	52	CAPP (2001)
Lettuce	*Lactuca sativa*	emergence	Loam	5,400	10,800	1,596	3,192	226	37	CAPP (2001)
Lettuce	*Lactuca sativa*	root length	Loam	2,700	5,400	798	1,596	113	18	CAPP (2001)
Lettuce	*Lactuca sativa*	shoot length	Loam	21,600	>21,600	6,385	6,385	638	104	CAPP (2001)
Lettuce	*Lactuca sativa*	biomass	Sand	1,820	>1,820	538	538	54	9	CAPP (2001)
Lettuce	*Lactuca sativa*	emergence	Sand	911	1,820	269	538	38	6	CAPP (2001)
Lettuce	*Lactuca sativa*	root length	Sand	455	911	134	269	19	3	CAPP (2001)
Lettuce	*Lactuca sativa*	shoot length	Sand	455	911	134	269	19	3	CAPP (2001)
Lettuce	*Lactuca sativa*	biomass	Till	1,880	>1,880	556	556	56	9	CAPP (2001)
Lettuce	*Lactuca sativa*	emergence	Till	440	940	130	278	19	3	CAPP (2001)
Lettuce	*Lactuca sativa*	root length	Till	440	940	130	278	19	3	CAPP (2001)
Lettuce	*Lactuca sativa*	shoot length	Till	940	1,880	278	556	39	6	CAPP (2001)
Timothy	*Phleum pratense*	biomass	Artificial	7,550	>7,550	2,232	2,232	223	363	CAPP (2001)
Timothy	*Phleum pratense*	emergence	Artificial	1,890	3,780	559	1,117	79	128	CAPP (2001)
Timothy	*Phleum pratense*	root length	Artificial	472	944	140	279	20	32	CAPP (2001)
Timothy	*Phleum pratense*	shoot length	Artificial	1,890	3,780	559	1,117	79	128	CAPP (2001)
Timothy	*Phleum pratense*	biomass	Loam	675	1,350	200	399	28	46	CAPP (2001)
Timothy	*Phleum pratense*	emergence	Loam	10,800	21,600	3,192	6,385	451	734	CAPP (2001)
Timothy	*Phleum pratense*	root length	Loam	1,350	2,700	399	798	56	92	CAPP (2001)
Timothy	*Phleum pratense*	shoot length	Loam	5,400	10,800	1,596	3,192	226	367	CAPP (2001)
Timothy	*Phleum pratense*	biomass	Sand	228	455	67	134	10	15	CAPP (2001)
Timothy	*Phleum pratense*	emergence	Sand	455	911	134	269	19	31	CAPP (2001)
Timothy	*Phleum pratense*	root length	Sand	455	911	134	269	19	31	CAPP (2001)
Timothy	*Phleum pratense*	shoot length	Sand	911	1,820	269	538	38	62	CAPP (2001)
Timothy	*Phleum pratense*	biomass	Till	3,760	>3,760	1,111	1,111	111	181	CAPP (2001)
Timothy	*Phleum pratense*	emergence	Till	1,880	3,760	556	1,111	79	128	CAPP (2001)
Timothy	*Phleum pratense*	root length	Till	na	na	na	na	na	na	CAPP (2001)
Timothy	*Phleum pratense*	shoot length	Till	940	1,880	278	556	39	64	CAPP (2001)