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Canadian Soil Quality Guidelines for

Phenol: Environmental

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NOTICE

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

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

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

Ce document technique de soutien n'est disponible qu'en anglais avec un résumé en français présenté à la page vii.

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ABSTRACT

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

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

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

The following soil quality guidelines are recommended by the CCME based on the available scientific data. For phenol, the environmental soil quality guideline (SQG_E) relative to agricultural and residential/parkland land uses is $20 \text{ mg}\cdot\text{kg}^{-1}$ soil and it is $170 \text{ mg}\cdot\text{kg}^{-1}$ soil for commercial and industrial land uses. These environmental soil quality guidelines are optimized for soils within the pH range of 4 to 9 as the toxicological studies on which they are based were conducted within this pH range.

RÉSUMÉ

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

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

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

Les recommandation pour la qualité des sols suivantes, proposées par le CCME, sont fondées sur les données scientifiques disponibles. Pour le phénol, la recommandation pour la qualité des sols en vue de la protection de l'environnement (RQS_E) relative aux terrains à vocation agricole et résidentielle/parc est de $20 \text{ mg}\cdot\text{kg}^{-1}$ de sol et elle est de $170 \text{ mg}\cdot\text{kg}^{-1}$ de sol pour les terrains à vocation commerciale et industrielle. Ces recommandations pour la qualité des sols en vue de la protection de l'environnement sont à leur optimum dans des sols avec pH entre 4 et 9 puisque les études toxicologiques utilisées pour leur élaboration ont été effectuées dans ces mêmes conditions de pH.

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1. INTRODUCTION

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

This report reviews the sources and emissions of phenol, its distribution and behaviour in the environment and its toxicological effects on terrestrial mammals, plants and soil organisms. This information is used to derive guidelines for phenol to protect environmental receptors according to the processes outlined in *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME 1996) for agricultural, residential/parkland, commercial and industrial land uses.

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

2. BACKGROUND INFORMATION

2.1 Physical and chemical properties

Phenol is an aromatic hydroxy compound and belongs to the non-chlorinated monohydric phenol group. The major physical and chemical properties of phenol are presented in Table 1. Phenol is a colourless white to light pink solid crystal with a melting point of 43°C and a boiling point of 182°C. It has a characteristic acrid smell and a sharp burning taste. Despite its moderate vapour pressure (2.7×10^{-2} kPa at 20°C), phenol has a low Henry's law constant (3.97×10^7 atm·m³·mol⁻¹). It is moderately volatile at room temperature (Howard 1989). It is very soluble in water and in most organic solvents. Phenol reacts as a weak acid. Phenol is oxidized to various products such as dihydroxy- and trihydroxybenzenes and quinones depending on the oxidizing agent and the reaction conditions. It can also undergo many electrophilic substitution reactions, such as halogenation and sulfonation. Phenol reacts rapidly with chlorine to form chlorophenols (ENVIRO TIPS 1985). Phenol reacts with carbonyl compounds in both acidic and alkaline media. The octanol/water partition coefficient of phenol is low relative to other compounds that share a benzene sub-structure (i.e., 1.46 (WHO 1994)). Thus bioaccumulation is expected to be nonsignificant (Verschuere 1983; Windholtz et al. 1983; Howard 1989; Shiu et al. 1994).

2.2 Analytical methods

The analytical techniques used for the detection of phenol are: gas chromatography in combination with flame ionization detection (GC/FID); high-performance liquid chromatography (HPLC) in combination with ultraviolet detection; and gas chromatography in combination with mass spectrometry (GC/MS). The GC/MS method is more sensitive than FID (WHO 1994).

CCME (1993) recommended the Capillary Column Technique (U.S. EPA method 8270B, Rev 2) with Gas Chromatography/Mass Spectrometry for the determination of phenol in soils. Soil samples are extracted ultrasonically for three minutes with a mixture of methylene chloride and acetone (1:1), dried in a column with anhydrous sodium sulphate and concentrated to 1 mL. The extracts are spiked with 10 μ L of internal standard solution and analyzed with GC/MS. The detection limit of this method is 0.66 mg phenol \cdot kg⁻¹ of wet soil.

2.3 Production and uses in Canada

The available information on phenol production, importation and total consumption in Canada is presented in Table 2. Phenol was produced in Canada until 1992. In 1992, 71 kt of phenol was consumed in Canada, of which 10 kt was produced locally and the rest was imported (SRI 1993). The demand for phenol is expected to grow by 2.5% per annum from 1992 to 1997 (SRI 1993). The most commonly used method of production of phenol in Canada is from cumene *i.e.* isopropylbenzene (ENVIRO TIPS 1985; SRI 1993). It is also produced from chlorobenzene and toluene (WHO 1994).

Phenol is a major by-product of the coal-tar, coking and petroleum industries. Terrestrial vegetation contains many phenolic compounds that are solubilized during degradation of plant materials and are released to the soil environment (Dobbins et al. 1987).

Phenol is used as a disinfectant, antiseptic, bactericide, and antimicrobial agent (CCREM 1987). It is widely used in the manufacture of resins, dyes, drugs, explosives, fertilizers, rubber, paint, coke, textiles, plastics, perfumes, and pharmaceutical preparations. The major use of phenol in Canada is in the production of phenolic resins which consumes approximately 93% of production (SRI 1993). Phenol is also used as a disinfectant in the petroleum, leather, paper, soap, toy, dye and agricultural industries.

The most important source of phenol emissions results from phenolic resins (WHO 1994), which are used as a binding material in insulation materials, chipboard, paints, and casting sand foundries. These materials contain phenol from 2% to > 50% and the emissions are approximately proportional to the concentration of free phenol which is present as a monomer in these materials (Bollig and Decker 1980). Phenol is also released to the environment through industrial activities such as production of phenol and its derivatives, resins, and insulation materials, distillation of coal and wood, oil refining, pulp and paper mills (CCREM 1987). Phenol is also released through exhaust gases of

automobiles (Verschuere 1983), cigarette smoke (Groenen 1978; Health Canada 1994), gases from incinerators and wood-burning in homes (Den Boeft et al. 1984).

2.4 Levels in Canadian environment

Phenol may occur naturally in soils as the decomposition product of plants, decaying vegetation, animal and human wastes. Liquid manure contains about $30 \text{ mg}\cdot\text{kg}^{-1}$ of phenol (RIVM 1986). They may also be formed during degradation of pesticides in soil (McNeely et al. 1979). Industrial effluents and domestic sewage may also contribute significant quantities of phenol to aquatic and terrestrial environments. A summary of concentrations of phenol in the Canadian environment is presented in Table 3. Information concerning phenol levels in Canadian ambient air was not found

Very little information is available regarding phenol concentrations in the Canadian terrestrial environment. In Ontario, soil samples collected throughout the province from undisturbed old urban and rural parklands not impacted by local point source of pollution were analyzed for a variety of chemicals to determine average background concentrations known as "Ontario typical range" (OTR_{98}) (OMEE 1993). These OTR_{98} values correspond to the 98th percentile of the sample population analyzed. For phenol, the OTR_{98} value for old urban parkland was established at $27 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ soil while a provisional value of $14 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ was obtained for rural parkland (OMEE 1993). Phenol has been detected at contaminated sites, with levels ranging from background to $26,900 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ being reported (Pakdel et al. 1992; Marchand 1992). Marchand (1992) reported concentrations of non-chlorinated phenols ranging from 400 to $26,900 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ at a contaminated site near a petroleum refinery in Montreal.

Total phenolic concentrations in surface water across Canada are reported to be generally below $2 \text{ }\mu\text{g}\cdot\text{L}^{-1}$, whereas groundwater concentrations range from 0.5 (detection limit) to $10000 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ (CCREM 1987). Concentrations below $100 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ were reported in groundwater and piezometer well samples in Prince Edward Island (NAQUADAT 1985). Sithole and Williams (1986) detected phenol in three of 120 raw water samples with concentrations ranging from 0.12 to $0.357 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ in a Canadian national survey of drinking water samples.

Concentrations in the order of $1000 \text{ }\mu\text{g}\cdot\text{L}^{-1}$ of phenol have been reported downstream from pulp and paper and chemical industries in northern Ontario (CCREM 1987; Health and Welfare Canada 1980). Munro et al. (1985) reported concentrations of phenol ranging from 0.001 to $10 \text{ mg}\cdot\text{L}^{-1}$ in the waters of the St. Clair river.

Phenol levels ranging from <0.1 (detection limit) to $33.3 \text{ }\mu\text{g}\cdot\text{kg}^{-1}$ in sediment samples from various rivers in Quebec have been reported by Laliberté (1990). Phenol has also been detected in the sediments of the Ottawa river basin with values up to $0.2 \text{ mg}\cdot\text{kg}^{-1}$ (Paul and Laliberté 1987).

2.5 Existing criteria and guidelines

Existing criteria and guidelines for phenol in soils are presented in Table 4. The CCME (1991) interim remediation criteria for phenol are 0.1, 1.0 and 10.0 mg·kg⁻¹ for agricultural, residential/parkland and commercial/ industrial land uses, respectively. In Ontario, proposed soil remediation guidelines are based upon an assessment of the potential for a contaminant to leach from soil and contaminate groundwater (OMEE 1994). For surface soils with potable and non-potable groundwater, the cleanup criteria are 40 mg·kg⁻¹ for all land uses, whereas for subsurface soils with potable and non-potable groundwater, the corresponding criteria are 64 and 390 mg·kg⁻¹.

3. ENVIRONMENTAL FATE AND BEHAVIOUR IN SOILS

The soil factors that determine the fate and behaviour of phenol in the terrestrial environment are pH, organic matter, clay content, and texture. The major physical processes that determine the mobility and distribution of phenol in the terrestrial environment are volatilization, adsorption and desorption, chemical reactions, leaching, photolysis and biodegradation. The environmental fate and behaviour of phenol are summarized below:

Volatilization

Phenol has a moderate vapour pressure of 0.524 mm Hg at 25°C or 2.7×10^{-2} kPa at 20°C and a Henry's law constant of 3.97×10^{-7} atm·m³·mole⁻¹. Therefore, volatilization is expected to be rapid from surface soils (WHO 1994). In the atmosphere, phenol exists predominantly within the vapour phase (Eisenreich et al. 1981). The estimated half-life in air generally varies between four and five hours (WHO 1994), but values ranging from 2.28 h to 22.8 h have been reported in the literature (Howard et al. 1991)

Adsorption/Desorption

In soil, phenol is readily adsorbed by clays such as montmorillonite, kaolinite and illite, with the rate of adsorption being influenced by sorptive concentration (Hamphill and Swanson 1963; Zhang and Sparks 1993). Adsorption reduces the rate of phenol biodegradation in soils, although sorption to clay surfaces is reversible (Knezovich et al. 1988; Saltzman and Yariv 1975). Vapour phase adsorption of phenol to Na-montmorillonite and Na-kaolinite has also been reported (Luh and Baker 1970). Relative to other mono-substituted benzene derivatives, phenol has a low K_{OC} and K_{OW} and hence, sorption to organic matter is expected to be low. In acidic soil, low adsorption and high mobility has been reported for phenol (Howard 1989; Scott et al. 1982)

Ionization

In solution, phenol reacts as a weak acid. Based on its high pKa (9.99), phenol is not expected to dissociate in the environment at pH < 9. Howard (1989) suggests that phenol may exist in a partially dissociated state in water and in moist soils.

Hydrolysis

Phenol has no hydrolysable functional groups and is therefore not expected to hydrolyse under normal conditions (Howard et al. 1991)

Mobility

Since phenol is soluble in water and moderately volatile, it is very mobile in soils (Howard 1989). Therefore, phenol can readily leach through soils and contaminate groundwater

Photolysis and Oxidation

Phenol absorbs light in the range of 290 to 330 nm and therefore may be subject to photo-degradation (WHO 1994). Exposing phenol to radiation of 290 nm wavelength has been reported to result in a 32.5% reduction in the concentration of the parent compound (Freitag et al. 1985). An atmospheric photolysis half-life ranging from 46 h to 173 h has been reported in the literature (Howard et al. 1991). Phenol is sensitive to oxidizing agents (including metal ions such as manganese and iron) and may autooxidize to form coloured complexes such as quinones (WHO 1994; Rineheart 1973). Products of the atmospheric photochemical transformation of phenol include dihydroxybenzenes, nitrophenols, and numerous ring cleavage products (WHO 1994).

Biodegradation

Phenol is an abundant and naturally occurring chemical, and thus tends to biodegrade rapidly in the environment (i.e. within 2 to 5 days) (Baker and Mayfield 1980; Howard 1989). Both aerobic and anaerobic soil microorganisms are capable of utilizing phenol as a growth substrate, although decomposition under aerobic conditions is more rapid than under anaerobic conditions (Howard 1989; Scott et al. 1982). The complete mineralization of phenol to form carbon dioxide (under aerobic conditions) or carbon dioxide plus methane (anaerobic conditions) will occur under appropriate environmental conditions (Aquino et al. 1988; Dobbins et al. 1987; Fedorak and Hrudey 1986; Tschuch and Fuchs 1987; WHO 1994). Intermediate products of the biotransformation process include benzoate, catechol, *cis-cis*-muconate, β -ketoadipate, succinate and acetate (Krug et al. 1985; Knoll and Winter 1987; Paris et al. 1982). Bacteria of the genera *Pseudomonas* (e.g. *Pseudomonas putida*) are believed to play a major role in the degradation of phenol in soils and sediments (Bayly and Wigmore 1973; Haider et al. 1974; Knezovich et al. 1988). Other genera, such as *Achromobacter*, *Azotobacter*, *Arthobacter*, *Bacillus*, *Brevibacterium*, *Clostridium*, *Flavobacterium*, *Micrococcus* and *Sarcina* have also been shown to actively degrade phenol (Visser et al. 1977; Haider et al. 1974).

Factors such as soil horizon, soil physico-chemical composition, phenol concentration, bacterial abundance, temperature, and the presence of other nutrients and pollutants are important determinants of phenol biodegradation and the potential for groundwater contamination (Dobbins et al. 1987; WHO 1994). The estimated half-life of phenol in aerobic soil studies varies between 1 and

10 days (Howard et al. 1991). Biodegradation of up to 41% of applied amount in activated sludge has been reported in the literature (Freitag et al. 1985).

Bioaccumulation

Relative to other substituted benzene derivatives, phenol has low octanol water partition coefficient ($\log K_{ow}=1.46$) (WHO 1994). Therefore, phenol is not expected to bioaccumulate significantly (Howard 1989; Verschueren 1983; Windholtz et al. 1983; WHO 1994). Based upon $\log K_{ow}$ data for phenol, a bioconcentration factor (BCF) of 7.6 has been calculated (Lyman et al. 1982). In the literature, K_{oc} values for phenol ranging from 1.21 to 1.96 have been reported (Branson 1978; USEPA 1989; Verschueren 1983; Windholtz et al. 1983; WHO 1994). The K_{ow} of phenol is pH dependent and the reported range of K_{oc} values probably reflects experimental variation in pH (WHO 1994)

4. BEHAVIOUR AND EFFECTS IN BIOTA

4.1 Soil Microbial Processes

Consulted information concerning the toxicity of phenol to terrestrial microorganisms and microbial processes is presented in Table 5. Very few studies concerning the effects of phenol on terrestrial microorganisms and microbial processes are available. Megharaj et al. (1991) reported that low levels of phenol (5 to 20 $\text{mg}\cdot\text{L}^{-1}$) were found to significantly increase the production of chlorophyll-a, proteins and carbohydrates. Phenol was likewise observed to stimulate CO_2 -fixation, nitrate reductase and glutamine synthetase activities when an exogenous source of carbon was added to the culture medium.

Several studies have shown that phenol inhibits nitrification significantly, especially at concentrations higher than 500 $\text{mg}\cdot\text{kg}^{-1}$ (Beccari et al. 1980; Benmoussa et al. 1986; Neufeld et al. 1980; Stafford 1974; Tomlinson et al. 1966). Other studies have shown allelopathic effects resulting from phenolic acids, but no such studies are available for phenol itself (Gallet 1994; Inderjit and Dakshini 1994; Pellissier 1993; Pellissier and Trosset 1989).

4.2 Terrestrial Plants

Plant toxicity studies selected for use in soil quality guidelines derivation, as well as additional plant studies that were consulted but not used in guidelines derivation, are presented in Table 6. Phenol may be taken up by plants via root absorption and stored in different parts of the plant. Shafer and Schonherr (1985) reported that phenol was absorbed and stored in cuticle membranes of tomato (*Lycopersicon*), green pepper (*Capsicum*) fruits and in rubber plant leaves. Absorption of C^{14} labeled phenol by roots in soybeans (*Glycine max.* L.) was reported by McFarlane et al. (1987). The absorbed phenol was stored in roots and not translocated to shoots, an observation that the authors attributed to *in vivo* metabolism of phenol to less mobile compounds.

Phenols occur naturally in plants and soils. Since phenol and phenolics are relatively water soluble, they are present in the soil solution and are easily taken up by plants (Kuiters and Denneman 1987). They also occur naturally in most plant species and play an important role in resistance to insect damage (Leszczynski et al. 1985). Harborne (1985), Haslam (1988), and Rhodes (1985) reported that plant phenols act as defence agents against herbivores. In allelopathic studies, significant promotion in root growth of mustard (*Brassica juncea*) has been reported by Inderjit and Dakshini (1994). However, many investigations have also revealed that phenolics can seriously interfere with metabolic processes during germination, seedling and later growth stages (Kuiters 1989; Williams and Hoagland 1982).

4.3 Terrestrial Invertebrates

Invertebrate toxicity studies selected for use in soil quality guidelines derivation are presented in Table 7.

The relationship between phenol concentration and earthworm (*Eisenia fetida*) mortality was studied by Neuhauser et al. 1985. These authors, using an artificial soil medium, reported an LC_{50} of $401 \text{ mg}\cdot\text{kg}^{-1}$. Environment Canada 1995, also studying *Eisenia fetida*, reported a NOEC of $160 \text{ mg}\cdot\text{kg}^{-1}$ and a LC_{50} of $270 \text{ mg}\cdot\text{kg}^{-1}$.

Callahan et al. 1994 used a Weibull function to summarize the shape of the concentration-response curves of four species of earthworms. Sensitivity to phenol, in soil tests, is as follows: *Eisenia fetida* < *Perionyx excavatus* < *Allolobophora tuberculata*. No data was available for *Eudrilus eugenia*. Only the relative LC_{50} 's, generated to rank the species among them, are reported (Callahan, personal communication). These LC_{50} 's have no meaning out of their context and are thus not reported here.

4.4 Mammals and Birds

Consulted information concerning the toxicity of phenol to mammalian and avian species is presented in Table 8. Phenol poisoning in animals is usually associated with respiratory failure causing death (Deichmann and Keplinger 1981). It may also cause damage to lungs, liver, kidneys, heart and genitourinary tract (Deichmann and Keplinger 1981).

Phenol is readily absorbed (both orally and dermally) by animals (Clarke and Clarke 1975). The extent of dermal absorption depends primarily on the area of the skin exposed. Liao and Oehme (1980) reported that phenol absorption was influenced to a greater extent by the surface area of skin exposed than by the concentration of the applied solution. Phenol vapours are also absorbed into the pulmonary circulation (Deichmann and Keplinger 1981). After absorption, most of the phenol is oxidized and conjugated with sulfuric, glucuronic and other acids.

Studies on the metabolism of phenol in experimental animals showed that phenol is excreted mainly as conjugates of glucuronic acid and sulphate, and that urinary elimination is the major route for the

excretion of phenol metabolites. Traces of free phenol are eliminated with the feces and expired air (Deichmann and Keplinger 1981). Kao and Bridges (1979) reported that, following oral administration of phenol ($25 \text{ mg}\cdot\text{kg}^{-1} \text{ bw}$) in sheep and pigs, a high proportion of the dose is rapidly excreted through urine (in 3h, 85% in sheep and 84% in pigs was recovered). Less than 0.5% was excreted in feces, suggesting that a considerable amount of phenol was absorbed. Phenyl phosphate was also reported as urinary metabolite of phenol in sheep.

Acute studies on oral administration of phenol to rats, mice and rabbits show that the LD_{50} values range from 300 to $600 \text{ mg}\cdot\text{kg}^{-1} \text{ bw}$, whereas for dermal exposure, the LD_{50} values ranged from 670 to $1400 \text{ mg}\cdot\text{kg}^{-1} \text{ bw}$. Phenol toxicity was reported in pigs when phenyle (2.9% phenol) was used to disinfect the pig pen (Reid et al. 1982). The observed toxicological effects included skin ulcerations and nervous symptoms.

5. DERIVATION OF ENVIRONMENTAL SOIL QUALITY GUIDELINES

5.1 Introduction

Canadian soil quality guidelines are designed to protect four different land uses: agricultural, residential/parkland, commercial, and industrial. The Canadian soil quality guidelines for naphthalene are based on the procedures described in CCME (1996).

All data selected for use in the following derivations have been screened for ecological relevance and are presented in Tables 6 and 7. Toxicological studies that have been consulted but not used in guideline derivation are presented in Tables 5 and 8. Studies were excluded from use because of one or more of the following reasons:

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

There were insufficient data available for the derivation of a soil quality guideline based on soil and food ingestion (SQG_i), or to perform the nutrient and energy cycling check, for each of the land use categories. However, sufficient data are available to derive a soil quality guideline for soil contact (SQG_{sc}), as well as guidelines for the protection of groundwater.

5.2 Soil quality guidelines for agricultural, and residential/parkland land uses

5.2.1 Soil quality guidelines for soil contact (SQG_{sc})

The derivation of the SQG_{sc} is based on toxicological data for vascular plants and soil invertebrates. After examination of the toxicological data for phenol, it was determined that the LOEC method was the most appropriate for guidelines derivation as insufficient data was available for the preferred weight of evidence method.

The threshold effects concentration (TEC) was calculated as follows:

$$\text{TEC} = \text{lowest LOEC} / \text{UF}$$

where;

$$\begin{aligned}\text{TEC} &= \text{threshold effects concentration (mg phenol}\cdot\text{kg}^{-1}\text{)} \\ \text{LOEC} &= \text{lowest observed effects concentration (mg phenol}\cdot\text{kg}^{-1}\text{)} \\ \text{UF} &= \text{uncertainty factor}\end{aligned}$$

The lowest selected endpoint was determined to be 79 mg phenol·kg⁻¹ from the Environment Canada (1995) test on lettuce seedling emergence resulting in a 23% reduction in germination success.

An uncertainty factor of four, out of a possible five, was applied because only the minimum number (3) of studies were selected and only three taxonomic groups with acute studies were tested. Additional uncertainty arises from the lack of data on the effects of phenol to soil microorganisms and processes. The negative effect of phenol on microbial populations and processes is documented (section 4.1 and table 5), and this is also incorporated into the uncertainty factor.

$$\text{LOEC} = 79 \text{ mg}\cdot\text{kg}^{-1} \text{ soil}$$

$$\begin{aligned}\text{TEC} &= 79/4 \\ &= 19.75 \text{ rounded to } 20 \text{ mg}\cdot\text{kg}^{-1}\end{aligned}$$

Nutrient and Energy Cycling Check

Nitrification and nitrogen fixation data are considered primary data, whereas nitrogen mineralization, denitrification and carbon cycling data are considered secondary data when performing the nutrient and energy cycling check. The nutrient and energy cycling check cannot be performed as minimum data requirements have not been met (CCME 1996). Therefore, the SQG_{sc} for agricultural and residential/parkland land uses is equivalent to the TEC of 20 mg phenol·kg⁻¹ soil.

5.2.2 Soil quality guidelines for soil and food ingestion (SQG_I)

The soil quality guideline for soil and food ingestion applies only to agricultural land use. The derivation of SQG_I is based on the toxicological data for mammalian and avian receptors. Minimum toxicological data requirements (three grazing herbivore oral toxicological studies) for the derivation of SQG_I for phenol have not been met.

5.3 Soil quality guidelines for commercial and industrial land use

5.3.1 Soil quality guidelines for soil contact (SQG_{sc})

The derivation of SQG_{sc} is based on toxicological data for vascular plants and soil invertebrates. However, for commercial and industrial land uses, only the effects data are used and uncertainty factors are not applied. The LOEC method was determined to be the most appropriate method for deriving the SQG_{sc} for commercial and industrial land use since minimum data requirements were met for this method. This method uses the geometric mean of acceptable LOEC data considered biologically significant. EC₂₅ data can be substituted for LOEC data if the EC₂₅ is lower than the LOEC in the same study.

The Effects Concentration Low (ECL) is calculated as:

$$\text{ECL} = \{(\text{LOEC or EC}_{25})^1 \times (\text{LOEC or EC}_{25})^2 \times (\text{LOEC or EC}_{25})^n\}^{1/n}$$

where;

ECL = effects concentration low (mg·kg⁻¹)

LOEC = lowest observed effects concentration (mg·kg⁻¹)

EC₂₅ = 25% effects concentration (mg·kg⁻¹)

n = number of available LOECs

$$\text{ECL} = (125 \times 79 \times 210 \times 401)^{1/4} = 169.81 = 170 \text{ mg} \cdot \text{kg}^{-1}$$

The ECL was calculated to be 170 mg phenol·kg⁻¹.

Nutrient and Energy Cycling Check

Nitrification and nitrogen fixation data are considered to be primary data, whereas nitrogen mineralization, denitrification and carbon cycling data are considered secondary data when performing the nutrient and energy cycling check. The nutrient and energy cycling check cannot be performed as minimum data requirements have not been met (CCME 1996). Therefore, the SQG_{sc} for commercial and industrial land uses is equivalent to ECL of 170 mg phenol·kg⁻¹.

5.4 Groundwater check

Soils are hydrologically linked to groundwater systems. A major concern with soil contamination is that it can and does lead to groundwater contamination. Thus, soil quality guidelines must be designed to prevent unacceptable transfers of contaminants to groundwater systems. Prudent assumptions are that an aquifer underlying a remediated site may be used by humans as a drinking water source, or may have the potential to enter surface water bodies. Therefore, the following check is used to calculate the concentration in soil which will not cause an exceedence of groundwater concentrations above existing water quality guidelines for the protection of raw water for drinking or for the protection of freshwater aquatic life. The groundwater check follows the rationale and calculation procedure recommended in the protocol (CCME 1996). It is based on equilibrium partitioning between solid and aqueous phases. For most non-ionic organics, including phenol at ambient pH, the following equation is used:

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

where,

Y	=	concentration of contaminants in soil (mg substance·kg ⁻¹ dry soil)
DF	=	dilution factor = 50 (default)
C _{wa}	=	water protection value
K _d	=	distribution coefficient
θ _m	=	soil moisture content = 0.1 (default)

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

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

A default value of 0.3% (or 0.003) is used for f_{oc} (CCME 1996) while, for consistency, the sorption partition coefficient should be evaluated using the octanol-water partition coefficient based on the following equation (Mackay et al. 1993):

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

For phenol, log K_{ow} has been evaluated at 1.46 (WHO 1994) and a value of 0.001 mg·L⁻¹ has been established for the protection of freshwater aquatic life.

Therefore;

$$\begin{aligned} K_{ow} &= 28.84 \\ K_{oc} &= 11.824 \\ K_d &= 0.035 \end{aligned}$$

For the protection of freshwater aquatic life:

$$\begin{aligned} Y &= 50 \times 0.001 (0.035 + 0.1) \\ &= 0.007 \text{ mg phenol} \cdot \text{kg}^{-1} \text{ dry soil.} \end{aligned}$$

The groundwater check indicates that for the protection of freshwater aquatic life, the level of phenol in soil should not exceed $0.007 \text{ mg phenol} \cdot \text{kg}^{-1}$.

5.5 Derivation of the Final Environmental Soil Quality Guidelines (SQG_E)

The following environmental soil quality guidelines (SQG_E) are optimized for soils within the pH range of 4 - 9. The toxicological studies upon which these guidelines are based were conducted within this pH range. At a pH greater than 9, phenol will likely dissociate and the groundwater protection model as utilized in this document will not be applicable (see CCME 1996). A summary of all the derived soil quality guidelines is presented in Table 9.

Agricultural land use:

The final SQG_E of $20 \text{ mg phenol} \cdot \text{kg}^{-1}$ is based upon the SQG_{SC} for agricultural land use.

Residential/Parkland land uses:

The final SQG_E of $20 \text{ mg phenol} \cdot \text{kg}^{-1}$ is based upon the SQG_{SC} for residential/parkland land uses.

Commercial and Industrial land uses:

The final SQG_E of $170 \text{ mg phenol} \cdot \text{kg}^{-1}$ is based upon the SQG_{SC} for commercial/industrial land uses.

Soil guidelines for phenol that will be protective of freshwater aquatic life was calculated to be $0.007 \text{ mg phenol} \cdot \text{kg}^{-1}$.

6. DATA GAPS

A review of literature showed that there is a lack of data on toxicity of phenol to mammals, birds and terrestrial microorganisms. It is recommended that research be conducted in these areas. Also, while the minimum data requirements for criteria derivation have been met with respect to phenol toxicity to terrestrial plants and invertebrates, additional greenhouse experiments on the toxic effects of soil-incorporated phenol to seedling emergence, root elongation and early stages of plant growth is recommended. Further research on the toxicity of phenol with well defined concentrations to earthworms in an artificial soil is desirable. Additional data on levels of phenol compounds in the vicinity of Canadian point sources are also needed.

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TABLES

Table 1: Physical and chemical properties of phenol

Property	Parameter
Empirical formula	C ₆ H ₆ O
Molecular weight	94.11
CAS registry number	108-95-2
Common synonyms	carbolic acid, hydroxy benzene, oxybenzene, phenic acid, phenylhydroxide, phenylic acid, phenyl hydrate
Physical state (25 °C)	colourless white to light pink crystalline solid
Melting point (°C)	43 (40.85 for ultrapure material)
Boiling point (°C)	182
Density (g·mL)	1.071
Vapour pressure (kPa at 20° C) (mm Hg at 25° C)	2.7x10 ⁻² 0.524
Henry's law constant (atm·m ³ ·mole ⁻¹)	3.97 x 10 ⁻⁷
Dissociation constant (pKa)	9.994 9.686
Log K _{oc}	1.21 (range 1.21 to 1.96)
Log K _{ow}	1.46
Solubility in water at 25 °C (mg·L ⁻¹)	87,000
Solubility in ethanol, acetone, and diethyl ether	very soluble

Sources: U.S.EPA 1991; Windholz et al. 1983; Howard 1991; Howard 1989; WHO 1994; Riddick et al. 1986

Table 2: Production, importation and consumption of phenol in Canada

Year	Production ktons	Importation ktons	Exportation ktons	Consumption ktons
1983	34	22.6	0	57
1984	25.5	34	0	59.5
1987	53	27	1	79
1992	10	61	0	71

Sources: CCREM 1987; SRI 1993

Table 3: Concentrations of phenol in the Canadian environment

Environment	Concentration	Remarks	Reference
Soil ($\mu\text{g}\cdot\text{kg}^{-1}$)	14 26	Background concentrations: rural parkland sites urban parkland sites	OMEE 1994
	1 to 10 (12350 at one site)	Contaminated site at Ville-Mercier, Quebec	Pakdel et al. 1992
	400 to 26,900	Contaminated site near refinery, Montreal (non-chlorinated phenols)	Marchand 1992
Water ($\mu\text{g}\cdot\text{L}^{-1}$)	0.001 to 10,000	St. Clair river near east Montreal (near petroleum refinery)	Munro et al. 1985
	10 to 150	St. Lawrence	Visser et al. 1977
	ND* to 83 ND* to 28	Pacific region sampled prior to 1980	NAQUADAT 1985 (CCREM 1987)
	2 [†] to 250 1 [‡] to 38	Western region: sampled prior to 1980 sampled in 1980 to 1985	
	ND* to 10000 ND* to 94	Central region: sampled prior to 1980 sampled in 1980 to 1985	
	5 [‡] to 70	Atlantic region: sampled in 1980 to 1985	
	120 to 357 $\text{ng}\cdot\text{L}^{-1}$	National survey of drinking water samples	Sithole and Williams 1986
	up to 1050	downstream near pulp and paper industry in northern Ontario	Health and Welfare Canada 1980
Sediments ($\mu\text{g}\cdot\text{kg}^{-1}$)	ND* to 200	Ottawa river basin	Paul and Laliberté 1987
	<0.1 to 33.3	Quebec	Laliberté 1990

*ND = not detected

[†] = detection limit is 0.5 $\mu\text{g}\cdot\text{L}^{-1}$

[‡] = detection limit is 1 $\mu\text{g}\cdot\text{L}^{-1}$

Table 4: Existing environmental quality guidelines and criteria for phenol

Jurisdiction	Category		Conc (mg·kg ⁻¹ soil)	Reference
Canada (Interim)	Assessment Criteria		0.1	CCME 1991
	Remediation Criteria: Agricultural land use Residential/parkland land use Commercial/industrial land use		0.1 1.0 10.0	
Alberta	Tier I: Assessment Criteria: Tier II: Site Specific		0.1 NA	Alberta Environment 1990
	Clean-up criteria: Level I(High Sensitive Site) Level II(Medium Sensitive Site) Level III(low Sensitive Site)		0.05 1.0 10.0	Alberta MUST 1991
British Columbia	Level A (Background Level) Level B (Remediation Criteria, Agricultural, Residential/parklands) Level C (Commercial/industrial Lands)		0.1 1.0 10.0	BCMOC 1989
Ontario (proposed clean-up guidelines)	Surface soil with potable groundwater situation (pH 5 to 9)	Agr R/P C/I Groundwater criteria for all uses	40 40 40 4.2 mg·L ⁻¹	OMEE 1994
	Surface soil with non-potable groundwater situation (pH 5 to 9)	R/P C/I Groundwater criteria for both uses	40 40 26 mg·L ⁻¹	
	Sub-surface soil with potable groundwater situation (pH 5 to 11)	R/P C/I	64 64	
	Sub-surface soil with non-potable groundwater situation (pH 5 to 11)	R/P C/I	390 390	
Quebec	Level A (Background level) Level B (Remediation criteria) Level C (Immediate clean-up)		0.1 1.0 10.0	MENVIQ 1988
Canada	CCME Drinking Water Quality Guidelines		0.002 mg·L ⁻¹	HWC 1980
The Netherlands	Target value Intervention value		0.05 40	MHSPE 1994
US	Preliminary remediation goals (health based): Residential soil Industrial soil		23000 100000	USEPA 1993
New Jersey	Soil clean up standards: Residential surface soils Residential subsurface soils Non-residential surface soils		10000 50 10000	New Jersey Register 1992
Australia	Background level		0.03 to 0.5	ANEC 1992

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

Table 5: Consulted microbial toxicological studies for phenol

Species	Effect ^(a) (% decrease)	Endpoint	Phenol concentration	pH	Test substrate	Reference
<i>Nostoc linckia</i> (cyanobacterium)	growth and metabolic activities {chlorophyll a, protein, carbohydrates, nitrogen fixation, CO ₂ uptake, nitrate reductase and glutamine synthetase activities}	NOEC	100 mg·L ⁻¹	NR	culture medium (Allen's medium)	Megharaj et al. 1991
Nitrifying bacteria	nitrification (75%)	EC	15900 mg·kg ⁻¹	7.5 to 8	activated sludge	Den Blanken 1993
Nitrifying bacteria	nitrification nitrification (75%) nitrification (100%)	NOEC EC EC	2.0 mg·L ⁻¹ 5.6 mg·L ⁻¹ 10 mg·L ⁻¹	7.6	activated sludge	Stafford 1974
<i>Nitrosomonas</i>	ammonia oxidation (50%)	EC	25 mg·L ⁻¹	NR	culture medium (nitrifying organisms)	Neufeld et al. 1980
Nitrifying bacteria	ammonia oxidation (75%)	EC	5.6 mg·L ⁻¹	NR	activated sludge	Downing et al. 1964
Nitrifying bacteria	ammonia oxidation (75%)	EC	5.6 mg·L ⁻¹	NR	activated sludge	Tomlinson et al. 1966
Microbial respiration	O ₂ consumption	IC ₅₀	799 mg·L ⁻¹	7.5	activated sludge	Klecka et al. 1985
Nitrifying bacteria	inhibition of nitrification	significant inhibition	> 500 mg·kg ⁻¹	NR	activated sludge	Beccari et al. 1980

a: The EC endpoints represent the effects concentration as calculated by the CCME from the data presented by the author(s)

NR: not reported

Table 6: Consulted and selected plant toxicological studies for phenol

Species	Exposure period	Effect ^(a)	Endpoint (% decrease)	Effect concentration	pH	Test Substrate	Reference
Consulted Toxicity Data							
<i>Raphanus sativa</i> (radish)	72 h	root elongation	NOEC EC (37%) EC ₂₅ EC ₅₀	51 mg·L ⁻¹ 86 mg·L ⁻¹ 64 mg·L ⁻¹ 138 mg·L ⁻¹	NR	nutrient solution	Environment Canada 1995
<i>Lactuca sativa</i> (lettuce)	120 h	root elongation	NOEC EC (63%) EC ₂₅ EC ₅₀	86 mg·L ⁻¹ 178 mg·L ⁻¹ 114 mg·L ⁻¹ 159 mg·L ⁻¹	NR	nutrient solution	Environment Canada 1995
<i>Panicum miliaceum</i> (millet)	96 h	root elongation	EC ₅₀	170 mg·L ⁻¹	6.7 - 7.1	filter paper test	Wang 1985a
<i>Panicum miliaceum</i> (millet) <i>Raphanus sativa</i> (radish) <i>Abutilon theophrasti</i> (velvetleaf)	96 h	seed biomass weight	EC ₅₀	259 mg·L ⁻¹ 230 mg·L ⁻¹ 324 mg·L ⁻¹	6.7 - 7.1	filter paper test	Wang 1985b
Selected Toxicity Data							
<i>Raphanus sativa</i> (radish)	72 h	seedling emergence	NOEC EC (41%) EC ₂₅ EC ₅₀	79 mg·kg ⁻¹ 158 mg·kg ⁻¹ 125 mg·kg ⁻¹ 170 mg·kg ⁻¹	4-4.2	Artificial soil: sand 72 to 75%; clay 16 to 19%; silt 8 to 9%; moisture 80% WHC; OM 4.7 to 6.3%	Environment Canada 1995
<i>Lactuca sativa</i> (lettuce)	120 h	seedling emergence	NOEC EC (23%) EC ₂₅ EC ₅₀	40 mg·kg ⁻¹ 79 mg·kg ⁻¹ 83 mg·kg ⁻¹ 131 mg·kg ⁻¹	4-4.3	Artificial soil: sand 67 to 75%; clay 16 to 21%; silt 8 to 12%; moisture 80% WHC; OM 4.7 to 7.1%	Environment Canada 1995

(a) The EC endpoints represent the effects concentration as calculated by the CCME from the data presented by the author(s)

NR: not reported

Table 7: Consulted and selected invertebrate toxicological data for phenol

Species	Exposure period	Effect ^(a)	Endpoint (% decrease)	Phenol concentration mg·kg ⁻¹	pH	Test substrate	Reference
<i>Selected Toxicological Data</i>							
<i>Eisenia fetida</i> (earthworm)	14 d	mortality	NOEC EC (74%) LC ₂₅ LC ₅₀	160 320 210 270	4-4.2	Artificial soil: sand 72 to 75%; clay 16 to 19%; silt 8 to 9%; moisture 80% WHC; org. matter 4.7 to 6.3%	Environment Canada 1995
<i>Eisenia fetida</i> (earthworm)	14 d	mortality	LC ₅₀	401	6 ±0.5	Artificial soil: sand 69%; clay 20%; peat 10%; CaCO ₃ 1%; moisture 35% WHC	Neuhauser et al. 1985

(a) The EC endpoints represent the effects concentration as calculated by the CCME from the data presented by the author(s)
NR: not reported

Table 8: Mammalian and avian oral toxicological studies for phenol

Species	Exposure period	Exposure concentration (mg·kg ⁻¹ bw)	Exposure route	Endpoint	Effect concentration (mg·kg ⁻¹ bw)	Reference
<i>Agelaius phoeniceus</i> (redwinged blackbird)	acute	18 h	oral	LD ₅₀	> 113	Schafer, Jr. et al. 1983
Rat	14 d	NA	oral	LD ₅₀ (estimated)	400	Schlicht et al. 1992
Mouse	acute	NA	oral	LD ₅₀	300	Von Oettingen and Sharples 1946
Mouse	acute	NA	oral	LD ₅₀	427	Kostovetskii and Zholdakova 1971
Rat	acute	NA	oral	LD ₅₀	340 to 530	Deichmann and Witherup 1944
rat	acute	NA	oral	LD ₅₀	512	Kostovetskii and Zholdakova 1971
Rat	acute	NA	dermal	LD ₅₀	670	Connig and Hayes 1970
Rabbit	acute	NA	dermal	LD ₅₀	850	Flickinger 1976
Rabbit	acute	NA	dermal	LD ₅₀	1400	Vernot et al. 1977
White rat	15 d (sublethal)	100 mg·m ³	inhalation	central nervous system	100 mg·m ³	Dalin and Kristoffersson 1974
Rat	12 m	0,800,1200,1600 and 2400 mg·L ⁻¹	oral	depressed weight	200 (> 2000 mg·L ⁻¹)	Deichmann and Oesper 1940
Rabbit	18 d (5 h/d, 5 d/week)	64 to 380	dermal	skin irritation systemic effects (tremors and death)	190 130	Deichmann et al. 1950
Rat	NA	NA	oral	LD ₅₀	445 to 550	Thompson and Gibson 1984
Guinea-pig	12 d (7 h/d, 5 d/week)	100 to 200 mg·m ³	inhalation	LD ₄₂	100 to 200 mg·m ³	Deichmann 1944
lamb (newborn)	used during lambing time	200 to 300 mL of terebene sheep balsam (3.7% phenol w/w)	dermal (due to use of phenol containing disinfectant)	poisoning: fever, convulsion, diarrhoea	82 mg·L ⁻¹ (plasma)	Eales et al. 1981

Species	Exposure period	Exposure concentration (mg·kg ⁻¹ bw)	Exposure route	Endpoint	Effect concentration (mg·kg ⁻¹ bw)	Reference
<i>Agelaius phoeniceus</i> (redwinged blackbird)	acute	18 h	oral	LD ₅₀	> 113	Schafer, Jr. et al. 1983
Pig	2 to 4 weeks prior to investigation (used as a disinfectant in the pig pen)	Phenyl (2.9% phenol)	inhalation and dermal	poisoning: ulcerations, nervous symptoms and convulsions	NA	Reid et al. 1982

NA= not available

Table 9. Summary of environmental soil quality guidelines for phenol

Guideline	Land use		
	Agricultural (mg·kg ⁻¹)	Residential/parkland (mg·kg ⁻¹)	Commercial/industrial (mg·kg ⁻¹)
TEC or ECL*	20	20	170
Nutrient and energy cycling check	Insufficient data	Insufficient data	Insufficient data
SQC _{sc}	20	20	170
SQC ₁	Insufficient data	NA	NA
SQC ₂	20	20	170
Groundwater check for the protection of aquatic life	0.007	0.007	0.007
CCME interim criteria§	0.1	1.0	10.0

*As per the CCME 1996 protocol, the TEC for agricultural and residential/parkland land uses corresponds to the 25th percentile of the distribution when using the weight of evidence method, while the ECL for commercial/industrial land use corresponds to the 25th percentile of the effects data distribution.

†NA = not applicable.

§CCME 1991.



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