Water, Air and Climate Change Branch

Ministry of Water, Land and Air Protection

Ambient Interim Water Quality Guidelines for Phenols

Prepared pursuant to Section 2(e) of the Environment Management Act, 1981

Summary Report

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TABLE OF CONTENTS

SUMMARY

This document is one in a series that establishes ambient water quality guidelines for British Columbia. The Canadian Council of Ministers of the Environment (CCME) has recently developed new guidelines of 4 micrograms/L for mono and dihydric phenols to protect freshwater aquatic life. The Ministry has published guidelines for chlorophenols, but needed to evaluate the CCME guidelines to decide which phenols were to be included as total phenols. Another factor that raised the priority of this review was that the Ministry is undertaking a Stage 2 Contaminated Sites Regulation amendment.

Suitable data documenting the effects of phenols for most water uses is lacking, therefore, we have only derived guidelines to protect aquatic life. Due to time and data constraints, and since the Ministry has guidelines for chlorinated phenols, this document only recommends interim water quality guidelines for non-halogenated phenols to protect freshwater aquatic life. These interim guidelines will need to be converted to more scientifically defensible guidelines when time and data permit.

At extremely low phenol values, there are two effects apparent in phenol-contaminated waters: 1.) toxicity to aquatic life, and 2.) the generation of an unpleasant taste in fish and shellfish. The data on which these interim guidelines for phenols are based are summarized in tables in the appendices to this report.

The interim water quality guidelines are summarized in the following table.

Table 1. Phenol Guidelines

Non-halogenated phenol species	**Guideline micrograms/L**
4-hydroxyphenol (hydroqinone, quinol)	4.5
3-hydroxyphenol (resorcinol)	12.5
Total of all other phenols*	50.0

*Total of all other Phenols = Total phenols minus (all chlorinated phenols plus hydroqinone plus resorcinol)

PREFACE

Establishing the Guidelines

THE MINISTRY OF WATER, LAND AND AIR PROTECTION is developing ambient water quality guidelines for British Columbia. This work has two goals:

- to provide guidelines for the evaluation of data documenting the effects on water, sediment and biota, and
- to provide guidelines for site-specific ambient water quality objectives

The guidelines represent safe conditions or safe levels of a substance, and are set to protect various water uses. A guideline is defined as "a maximum and/or a minimum value for a physical, chemical or biological characteristic of water, sediment or biota, which should not be exceeded to prevent specified detrimental effects from occurring to a water use, including aquatic life, under specified environmental conditions."

The guidelines are applied province-wide, but they are use-specific, and are being developed for the following:

- raw drinking water, public water supply and food processing*
- recreation and aesthetics*
- aquatic life and wildlife, and
- agriculture (livestock watering and irrigation).

The guidelines are established after considering the scientific literature, guidelines and criteria from other jurisdictions and environmental conditions in British Columbia. The scientific literature provides information about the effects of toxicants on various life forms. This information may not be conclusive since it is usually based on laboratory work that only approximates field conditions. To compensate for this uncertainty, the guidelines have built-in safety factors that are conservative, but reflect natural background conditions in the province.

The guidelines are subject to review and revision, as new information becomes available or as other circumstances dictate. The interim guidelines in this document are established using the best readily available published data.

* The guidelines apply to an ambient raw water source before it is diverted or treated for domestic use. The Ministry of Health regulates the quality of water for domestic use after it is treated and delivered by a water purveyor. Guidelines relating to public health at bathing beaches will be the same as those developed by the Ministry of Health, which regulates the recreation and aesthetic water use.

Using the Guidelines to Set Objectives

Water quality guidelines are used to set ambient water quality objectives for specific waterbodies. The objectives are based on present and future uses, waste discharges, hydrology, limnology, oceanography, and existing background water quality.

In most cases, the objectives will be the same as the guidelines. However, when natural background levels exceed the guidelines, the objectives could be less stringent than the guidelines. In rare instances, for example, if the resource is unusually valuable or of special provincial significance, using objectives that are more stringent than the guidelines could increase the safety factor. Another approach in special cases would be to develop site-specific guidelines by conducting toxicity experiments in the field. This approach is costly and time consuming, and is seldom used.

Neither the guidelines nor the objectives derived from them have any legal standing. Objectives may be used to calculate waste discharge limits. These limits are outlined in waste management permits that do have legal standing. Objectives are not usually incorporated as conditions of a permit. Objectives may also be used in the preparation of waste management orders and approvals. These documents also have legal standing.

Since there is an endless number of substituted phenols possible, all with somewhat different toxicity thresholds to individual species, and it is not practical to determine guidelines for each phenol, we recommend a site effluent-andspecies-specific determination for any given situation. This means that one should determine what species are present in the receiving water, choose several that are most likely to be very sensitive (amphibian tadpoles and salmonid fry are normally the species of choice) and carry out bioassays using a typical effluent mixture of phenols. The water quality objective developed for the local situation should be 0.05 of the LC_{50} determined by the assay in order to account for any more sensitive species and for atypical, more toxic, effluent mixtures.

INTRODUCTION

PHENOLS

In chemical terminology, a phenol is a single aromatic ring organic compound with an –OH group. An alkyl, straight chain or ring, organic compound with an –OH group is an alcohol. A double aromatic ring organic compound with an –OH group is a naphthol.

Phenol, formerly called carbolic acid, is an aromatic organic compound, C_6H_5OH. It is weakly acidic and resembles an alcohol in structure. The colourless, needlelike crystals of purified phenol melt at 43° C (109° F) and boil at 182° C (360° F). Phenol is soluble in organic solvents and slightly soluble in water at room temperature, and completely soluble above 66° C (150.8° F). It is a constituent of coal tar.

Phenol was first used as a disinfectant in 1867 by the British surgeon Joseph Lister for sterilizing wounds, surgical dressings, and instruments. Dilute solutions are useful antiseptics, but strong solutions are corrosive and scarring to tissue. Less irritating and more efficient germicides have replaced phenol, but it is widely used in the manufacture of resins, plastics, insecticides, explosives, dyes, and detergents. It is also used as a raw material for the production of medicinal drugs such as aspirin.

The term phenol is also used for any of a group of related acidic compounds that are hydroxyl derivatives of aromatic hydrocarbons. These include such substances as cresol, catechol, quinol, xylenol, guaiacol and resorcinol. For consistency and clarity these are all named as substituted phenols in this document. See Appendix 1 for a partial list of some phenol compounds.

The latest CCME document combines all of the 1- and 2-hydric phenols together into one group for setting guidelines based on toxicity. We have followed the same procedure for establishing these interim guidelines with the exception of setting separate guidelines for 4-hydroxyphenol (hydroquinone) and 3hydroxyphenol (resorcinol). There are several reasons for this.

There can be large differences in the toxicity of the various distinct phenol compounds, particularly when the substituents are strong electron donors or sinks. This can lead to overprotection for some of these compounds because the guideline is established to accommodate the most toxic phenol.

There is a paucity of existing reliable data that can be used to set guidelines for individual compounds. The guidelines are set to account for the most toxic phenols. If circumstances warrant, it is recommended that dischargers carry out Water Effect Ratio trials with their specific effluent and their ambient water to determine an acceptable site-specific phenol concentration.

Toluene and the xylenes are **not** phenols in their un-substituted form. Toluene is 1-methyl benzene and the xylenes are: 1, 2dimethyl benzene, 1, 3-dimethyl benzene or 1, 4-dimethyl benzene. However, if one of the other substitutions on the benzene ring is a hydroxy group, then they become a phenol, cresol or xylenol. Therefore, for example: 4-hydroxy toluene, 4methyl phenol, 1-methyl-4-hydroxy benzene, and 1-hydroxy-4methyl benzene are all the same compound, as are 3, 4-dimethyl phenol, 3, 4-dimethyl xylenol, 1-hydroxy-3, 4-dimethyl benzene and 2-methyl-4-hydroxy toluene.

One must be aware of all these alternate names when looking up data on phenol compounds. It is best to try to find one name in the Chemical Abstracts Service (CAS) registry that has a bewildering variety of alternate names listed. Using the substituted benzene or phenol nomenclature can reduce the ambiguity and confusion. In this document, we try to use only a few alternate names.

There are, in theory, an infinite number of phenols since up to 5 'R' groups (long-chain aliphatics) can be substituted and each of these can be very complex and substituted itself. In practice, there are far too many phenols to deal with individually but the toxic properties of many long-chain aliphatic substituted compounds will be quite similar. It is the toxicity of the phenols with simple substituents like methyl (-CH_3), hydroxyl (-OH), amino (-NH_2), nitro (-NO_2), methoxy (-CH_3O) and the halogens (-Cl, -Br, -I, -F) that are of most toxicological concern. Most phenols are used as bactericides, fungicides and herbicides;

particularly the halogenated phenols, and especially the chlorinated halophenols.

The environmental half–lives of most phenols are short, rarely as long as a month. Some are photo-degraded, especially in air. The microbial half-life is short, typically measured in days under aerobic conditions. Once a discharge ceases, environmental levels will drop rapidly due to bacterial breakdown. The half-life of phenols in fish is less than one day and phenols do not accumulate. Hence the existence of high levels in fish tissues indicates chronic or current exposure.

Microorganisms will alter their metabolic processes to utilize phenols. If they have not previously been exposed there will be an initial adaptation period until a large microbial population has been established. Any subsequent additions of phenols will be quickly degraded.

RECOMMENDED GUIDELINES

The following guidelines are based on readily available existing information that is summarized in Table 2. The Canadian Council of Ministers of the Environment (CCME) has set guidelines for all mono- and di-hydric phenols.

FRESHWATER AQUATIC LIFE

Aquatic Life is the only water use for which guidelines are being set in this document. They are interim guidelines subject to revision when more complete data become available. The maximum concentration of 4-hydroxyphenol (quinol, hydroquinone, 1,4-benzenediol) should not exceed 4.5 μg/L. The maximum concentration of 3-hydroxyphenol (resorcinol, 1,3-benzenediol) should not exceed 12.5 μg/L, and the maximum concentration of the total of all other non-halogenated phenols should not exceed 50 μg/L.

RATIONALE

The lowest LC_{50} data found for many phenols is presented in Table 2. The lowest effect for 4-hydroxyphenol (hydroquinone) was for *Daphnia magna*, at 0.09 mg/L. For 3-hydroxyphenol (resorcinol), the lowest effect level measured was at 0.25 mg/L, also for *Daphnia magna.* These were divided by a safety factor of 20:1 in order to estimate a safe minimal, or no effect, level for other freshwater species.

The next most toxic form of phenol was reported for fathead minnows using 4-phenylazophenol at 1.17 mg/L. We have assumed that the sum of all other phenols present (nonchlorinated) should not exceed this level since there are many phenol compounds with similar toxicity (see Table 2).Therefore, for all other phenols, we divided this level by a factor of 20 to estimate the safe level.

APPLICATION OF GUIDELINES

Chlorophenols, hydroquinone and resorcinol should be measured separately and compared to their respective proposed guideline values. A measurement of total phenols **minus** the sum of total chlorophenols, hydroquinone, and resorcinol allows one to determine if the guideline for total phenols is met.

TABLE 2 THE LOWEST RELIABLE FRESHWATER TOXICITY DATA, IN MG/L, FOR VARIOUS PHENOLS

TABLE 2.1 (sorted by the LC 50 value)

Phenol	**Species**	**Reference**	**LC_{50}**
4-hydroxyphenol (hydroquinone)	Daphnia	Bringmann *et al*, 1977	0.09
3-hydroxyphenol (resorcinol)	Daphnia	Ewell *et al*, 1986	0.25
4-phenylazophenol	Fathead	Geiger *et al*, 1984-1988	1.17
4-methylphenol (4-cresol)	Daphnia	Parkhurst *et al*, 1979	1.4
2,4-dinitro-6-methylphenol	Fathead	Geiger *et al*, 1984-1988	1.54
3-methylphenol (3-cresol)	Daphnia	Bringmann *et al*, 1977	1.6
4-tert-pentylphenol	Fathead	Geiger *et al*, 1984-1988	2.59
2,5-dinitrophenol	Fathead	Geiger *et al*, 1984-1988	3.36
2-hydroxyphenol (catechol)	Fathead	DeGraeve *et al*, 1980	3.5
phenol	Daphnia	Bringmann *et al*, 1977	3.9
2,4-dinitrophenol	Daphnia	LeBlanc, 1980	4.1
4-phenoxyphenol	Fathead	Geiger *et al*, 1984-1988	4.95
2-methylphenol (2-cresol)	Daphnia	Parkhurst *et al*, 1979	5.0
4-tert-butylphenol	Fathead	Geiger *et al*, 1984-1988	5.15
2-phenylphenol	Fathead	Geiger *et al*, 1984-1988	6.15
2,5-dimethylphenol	Daphnia	Devilliers *et al*, 1985	3.5-10
4-ethylphenol	Fathead	Geiger *et al*, 1984-1988	10.4
4-propylphenol	Fathead	Geiger *et al*, 1984-1988	11.0
2-allylphenol	Fathead	Geiger *et al*, 1984-1988	15.0
2,4-dimethylphenol	Fathead	Geiger *et al*, 1984-1988	16.6
4-nitrophenol	Daphnia	Bringmann *et al*, 1977	18
3-methyl-4-nitrophenol	Daphnia	Bringmann *et al*, 1977	18
3-nitrophenol	Daphnia	Bringmann *et al*, 1977	27
2-nitro-5-methylphenol	Daphnia	Bringmann *et al*, 1977	31
2,3-dimethylphenol	Daphnia	Devilliers *et al*, 1985	10-35
3,5-dimethylphenol	Daphnia	Devilliers *et al*, 1985	10-35
2-nitro-4-aminophenol	Fathead	Geiger *et al*, 1984-1988	36.2
2-nitrophenol	Daphnia	Bringmann *et al*, 1977	63
2-nitro-4-methylphenol	Daphnia	Bringmann *et al*, 1977	63
3-methoxyphenol	Fathead	Geiger *et al*, 1984-1988	74
2,4,6-trinitrophenol	Daphnia	LeBlanc, 1980	85
4-methoxyphenol	Fathead	Geiger *et al*, 1984-1988	110

TABLE 2.1

Phenol	**Species**	**Reference**	**LC_{50}**
2,4,6-trinitrophenol	Daphnia	LeBlanc, 1980	85 (n,48)
2,3-dimethylphenol	Daphnia	Devilliers *et al*, 1985	10-35
2,4-dimethylphenol	Fathead	Geiger *et al*, 1984-1988	16.6 (n,96)

TABLE 2.2 (sorted by the phenol compound)

Phenol	**Species**	**Reference**	**LC_{50}**
4-hydroxyphenol (hydroquinone)	Daphnia	Bringmann *et al*, 1977	0.09
3-hydroxyphenol (resorcinol)	Daphnia	Ewell *et al*, 1986	0.25
4-phenylazophenol	Fathead	Geiger *et al*, 1984-1988	1.17
4-methylphenol (4-cresol)	Daphnia	Parkhurst *et al*, 1979	1.4
2,4-dinitro-6-methylphenol	Fathead	Geiger *et al*, 1984-1988	1.54
3-methylphenol (3-cresol)	Daphnia	Bringmann *et al*, 1977	1.6
4-tert-pentylphenol	Fathead	Geiger *et al*, 1984-1988	2.59
2,5-dinitrophenol	Fathead	Geiger *et al*, 1984-1988	3.36
2-hydroxyphenol (catechol)	Fathead	DeGraeve *et al*, 1980	3.5
phenol	Daphnia	Bringmann *et al*, 1977	3.9
2,4-dinitrophenol	Daphnia	LeBlanc, 1980	4.1
4-phenoxyphenol	Fathead	Geiger *et al*, 1984-1988	4.95
2-methylphenol (2-cresol)	Daphnia	Parkhurst *et al*, 1979	5.0
4-tert-butylphenol	Fathead	Geiger *et al*, 1984-1988	5.15
2-phenylphenol	Fathead	Geiger *et al*, 1984-1988	6.15
2,5-dimethylphenol	Daphnia	Devilliers *et al*, 1985	3.5-10
4-ethylphenol	Fathead	Geiger *et al*, 1984-1988	10.4
4-propylphenol	Fathead	Geiger *et al*, 1984-1988	11.0
2-allylphenol	Fathead	Geiger *et al*, 1984-1988	15.0
2,4-dimethylphenol	Fathead	Geiger *et al*, 1984-1988	16.6
4-nitrophenol	Daphnia	Bringmann *et al*, 1977	18
3-methyl-4-nitrophenol	Daphnia	Bringmann *et al*, 1977	18
3-nitrophenol	Daphnia	Bringmann *et al*, 1977	27
2-nitro-5-methylphenol	Daphnia	Bringmann *et al*, 1977	31
2,3-dimethylphenol	Daphnia	Devilliers *et al*, 1985	10-35
3,5-dimethylphenol	Daphnia	Devilliers *et al*, 1985	10-35
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2-nitrophenol	Daphnia	Bringmann *et al*, 1977	63
2-nitro-4-methylphenol	Daphnia	Bringmann *et al*, 1977	63
3-methoxyphenol	Fathead	Geiger *et al*, 1984-1988	74
2,4,6-trinitrophenol	Daphnia	LeBlanc, 1980	85
4-methoxyphenol	Fathead	Geiger *et al*, 1984-1988	110

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2,4,6-trinitrophenol	Daphnia	LeBlanc, 1980	85 (n,48)
2,3-dimethylphenol	Daphnia	Devilliers *et al*, 1985	10-35
2,4-dimethylphenol	Fathead	Geiger *et al*, 1984-1988	16.6 (n,96)

Catechols, resorcinols, quinols, guaiacols, cresols and xylenols have been named as substituted phenols and 2,3,4 are used instead of o,m,p. Daphnia is *Daphnia magna* and

fathead is *Pimephales promelas.* n-nominal, m-measured, 24, 48, 96-duration of assay in hours.

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