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WATER STEWARDSHIP DIVISION
MINISTRY OF ENVIRONMENT

Ambient Water Quality Guideline for Naphthalene to Protect Freshwater life

Overview Report
First Update

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SUMMARY

This document is one in a series that establishes ambient water quality guidelines for British Columbia. It is an update to a previous report originally published in 1993. This update assesses the most recent information on the subject published in the literature and the information developed by B.C. Ministry of Environment under contract at the Simon Fraser University laboratory. The guidelines are safe conditions or levels that have province-wide application. This overview report is based on a technical document prepared by BWP Consulting under contract to B.C. Ministry of Environment; the most recent important information from the technical report is summarized in the appendix to make it stand alone.

A major use of the guidelines is to set ambient water quality objectives. The objectives are the guidelines modified or adopted to protect the most sensitive designated water use in a particular body of water. The objectives are used in the preparation of waste management plans, pollution prevention plans, waste management permits, orders or approvals. The latter three are the only documents that have legal status. The guidelines are also used as a basis for evaluating contaminated sites and determining remediation requirements.

The maximum concentration to protect freshwater aquatic life from adverse effects of naphthalene should not exceed one μg/L. The recommended guideline remains unchanged in the light of new information.

PREFACE

The B.C. Ministry of Environment develops province-wide ambient water quality guidelines for variables that are important in the surface waters of British Columbia. This work has the following goals:

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

The definition adopted for a guideline is as follows:

> 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 province-wide in application, are use-specific, and are developed for some or all of the following specific water uses:

- Source water for drinking, public water supply and food processing
- Aquatic life and wildlife
- Agriculture (livestock watering and irrigation)
- Recreation and aesthetics
- Industrial (water supplies)

The guidelines are set after considering the scientific literature, guidelines from other jurisdictions, and general conditions in British Columbia. The scientific literature gives information on the effects of toxicants on various life forms. This information is not always conclusive because it is usually based on laboratory work which, at best, only approximates actual field conditions. To compensate for this uncertainty, guidelines have built-in safety factors which are conservative but reflect natural background conditions in the province.

Ambient water quality objectives for specific waterbodies will be based on the guidelines and also consider present and future uses, waste discharges, hydrology/limnology/ oceanography, and existing background water quality. The process for establishing water quality objectives is more fully outlined in Principles for Preparing Water Quality Objectives in British Columbia, copies of which are available from Water Quality Section of the Water Management Branch.

Neither guidelines nor objectives which are derived from them, have any legal standing. The objectives, however, can be used to calculate allowable limits or levels for contaminants in waste discharges. These limits are set out in waste management permits and thus have legal standing. The objectives are not usually incorporated as conditions of the permit.

The site-specific water quality objectives are, in many cases, the same as guidelines. However, in some cases, such as when natural background levels exceed the guidelines, the objectives could be less stringent than the guidelines. In relatively rare instances, for example if the resource is unusually valuable or of special provincial significance, the safety factor could be increased by using objectives which are more stringent than the guidelines. Another approach in such special cases is to develop site-specific guidelines by carrying out toxicity experiments in the field. This approach is costly and time-consuming and therefore seldom used.

Guidelines are subject to review and revision as new information becomes available, or as other circumstances dictate.

Recommended Guidelines

The maximum concentration of naphthalene should not exceed 1μg/L, a level consistent with the CCME guideline and the recent information developed by the Ministry of Environment (Kennedy, 2006).

The freshwater aquatic life guideline is based on the 1993 document "Ambient Water Quality Guidelines for Polycyclic Aromatic Hydrocarbons (PAHs), as well as a review of more recent literature, and includes a discussion of a toxicity study conducted by Kennedy (2006) with the aid of a grant from the B.C. Ministry of Environment.

Rationale

The criterion recommended to protect freshwater aquatic life from long-term effects (1.0 μg/L) in 1993 was based on chronic toxicity of naphthalene to rainbow trout (*O. mykiss*) exposed to 11 μg/L of naphthalene for 27 days (geometric mean of the two LOELs; Black *et al*., 1983). The chronic value of 11 μg/L was the lowest concentration at which an effect of naphthalene was recorded in freshwater organisms. Based on the recommendations in the CCME and B.C. Environment protocols for the derivation of water quality guidelines, an application factor of 0.1 was applied to derive the recommended interim criterion. The proposed guideline is consistent with the interim freshwater guideline recommended by CCME, and was derived using the same methodology from the same data.

The recent study contracted out by the Ministry of Environment (Kennedy, 2006) corroborated the earlier results by Black *et al.* (1983). The 28-day flow-through tests with rainbow trout eggs found EC_{20} values (hatching success and survival of fry) of 10 μg/L, similar to that determined by Black *et al.* (1983) in their chronic study. For this reason, no change from the existing guideline was recommended.

APPLICATION OF THE GUIDELINES

Naphthalene is a very volatile substance. The water quality guideline recommended in this document is based primarily on controlled, laboratory bioassays that do not account for factors that may modify the toxicity of naphthalene in the field.

SETTING WATER QUALITY OBJECTIVES

Care must be exercised when the water quality guidelines are applied to assess environmental impacts of naphthalene, since there will be situations where naphthalene concentrations are continuously renewed, e.g., discharge from an industrial operation, or with the potential for only a minimal amount of volatilization e.g., under ice cover. In these types of situations, a site-specific study should be undertaken and appropriate site-specific water quality objectives developed based on species present and actual naphthalene persistence and concentrations.

In many cases, water quality objectives will be the same as the guidelines. In some cases, socioeconomic or other factors may justify objectives that are less stringent than the guidelines. Site-specific impact studies would be required in such cases.

Methods (*e.g.*, water effects ratio, resident species toxicity in the field, etc.) are available to adapt the recommended guidelines to a given site. Where necessary, these methods can be employed to set site-specific water quality objectives. Because these approaches are costly and time consuming, they are seldom used.

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Appendix

This information briefly discusses toxicity studies that have been conducted on various freshwater organisms, and forms the basis for the guideline proposed in Section 1.0.

Literature Data

Lethal and acute effects

The acute (96-h LC_{50}) and lethal effects of naphthalene in the freshwater environment are shown in Table 1.

In general, fish appear to be the most sensitive of the aquatic organisms to PAHs, and rainbow trout the most sensitive of the fish species tested. The toxic mode of action for naphthalene is termed nonpolar narcosis, in that it acts as an anesthetic (Broderius *et al.*, 1995; Lee *et al.*, 2002). The threshold for 50% mortality is relatively constant (2-8 mmol/kg wet weight for acute mortality), and is also chemical and species independent for narcotic compounds (Lee *et al.*, 2002). Gert-Jan de Maagd *et al.* (1997) found that the lethal body burden (LBB) for fathead minnow (*Pimephales promelas*) was 8 ± 3 mmol/kg wet weight.

Another factor affecting naphthalene toxicity is exposure to sunlight. This photoinduced toxicity is a result of two processes: photosensitization and photomodification. Many of the photoproducts of PAHs are more toxic than their parent (Huang *et al.*, 1993, 1995 and McConkey *et al.*, 1997 in El-Alawi *et al.*, 2002).

Sublethal and chronic effects

Sublethal and chronic effects of naphthalene on growth and physiological processes of aquatic algae and plants are shown in Table 2.

The data suffer from some major drawbacks: (a) short exposure periods, (b) exposure levels higher than naphthalene aqueous solubilities, and (c) lack of constancy in the naphthalene concentration during the experiments. Bastian and Toetz (1982) exposed *Anabaena flos-aquae* in open flasks to several PAHs for 14 days. Within 7 days, a number of the LPAHs including naphthalene completely disappeared from solution. In the study on nitrogen fixation by *Anabaena flos-aquae,* Bastian and Toetz (1985) used short-term exposure (2 h) to minimize losses of PAHs during the experiment. Naphthalene was observed to reduce the nitrogen fixation by the alga, but the long-term effects of naphthalene are difficult to predict from these short-term studies (Table 2).

The data on long-term or chronic effects of PAHs on freshwater animals are few and generally suffer from the same drawbacks as noted above for aquatic plants (Table 3).

Sarojini *et al.* (1995a) exposed female crayfish (*Procambarus clarkii*) to 10,000 µg/L of naphthalene and examined its effect on ovarian development. Ovaries were removed for examination after 1, 2, 4, 6, 8, 10, 12, and 15 days of exposure, and ovarian weight decreased gradually over this period until it was approximately 10% of the control by 15 days. Upon being returned to clean freshwater, the crayfish depurated a high proportion of the accumulated naphthalene within 7 days. They also measured naphthalene concentrations at various sites within the body and found that the main accumulation site in both males and females was the hepatopancreas, followed by the ovaries in females and muscle in the males (Sarojini *et al.*, 1995b). Damage caused to the hepatopancreas was reversible during the 7-day depuration period. Naphthalene exposure at this level (10,000 µg/L) resulted in a significant decrease in live cells in the hepatopancreata, but numbers began to increase when crayfish were returned to clean water (Sarojini *et al.* 1993).

Mutagenicity and carcinogenicity

Several PAHs, especially those containing 4 to 6 aromatic rings in their structure, have been shown to be mutagenic, carcinogenic, and inducers of tumors in mammals exposed to high doses of the contaminants in the laboratory. The US Environmental Protection Agency (EPS) reports that no carcinogenic effects were seen in rats exposed to naphthalene in their diet and by injection, but that mice exposed by inhalation showed increased alveolar/bronchiolar adenomas and carcinomas (USEPA, 2000). The USEPA has classified naphthalene as Group C, a possible human carcinogen (USEPA, 2000). Djomo *et al.* (1995) found that naphthalene was genotoxic to the newt *Pleurodeles waltl* at levels of 500 μg/L, but not at 125 μg/L. In their study, Gravato and Santos (2002) showed that exposure of sea bass (*D. labrax*) to naphthalene at a concentration of 346 μg/L for 8 hours resulted in a significant increase in erythrocytic micronuclei and erythrocytic nuclear abnormalities. Finally, Johnson and Long (1998) designated naphthalene as having a positive genotoxicity based on Mutatox® tests on Vibrio bacterium.

B.C. Ministry of Environment Toxicity Testing

A study was undertaken by Kennedy (2006) at Simon Fraser University in British Columbia under contract to the B.C. Ministry of Environment to address deficiencies in previous studies as mentioned above. Specifically, a special intermittent flow-through bioassay system was developed to ensure that naphthalene concentrations remained constant for the duration of the testing period.

Three trials were conducted on rainbow trout (*Oncorhynchus mykiss*) eggs which were fertilized not more than one hour prior to their exposure to the naphthalene solution. In each trial, 100 eggs were exposed to naphthalene at concentrations of 0, 5, 15, 50, 100, 150, 200 and 250 μg/L. Trout from the egg stage to button-up fry were examined a minimum of three times daily, and percent survival of eggs, hatching success and survival of fry at several stages were recorded. Finally, dead fish as well as those surviving to the end of the test were examined by light microscopy for deformities and teratogenic effects. The EC_{50} for naphthalene was found to be 50 µg/L with a 95% confidence interval of 30 to 60 µg/L, and the EC_{20} was 10 µg/L (Table 2). The EC_{20} is almost identical to the geometric mean of the 97% and 91% hatchability concentrations determined by Black *et al.* (1983) (11 µg/L; Table 3) for the same species. Most of the toxicity occurred following hatch. Teratogenic deformities were seen in <1% of all fry examined.

Table 1. Lethal and Acute Toxicity of PAHs to Freshwater Aquatic Life

Organism	**EC_{50}/LC_{50} (µg/L)**	**Duration (hours)**	**System***	**References**
Alga (*S. capricornutum*)	2,960	4	S,U	Millemann *et al*., 1984
Diatom (*N. palea*)	2,820	4	S,U	Millemann *et al*., 1984
Alga (*C. vulgaris*)	33,000	48	S,U	Kauss & Hutchinson, 1975
Cladoceran (*D. magna*)	8,570	48	S,U	USEPA, 1978
D. magna	17,000	24	S,U	LeBlanc, 1980
D. magna	8,600	48	S,U	LeBlanc, 1980
D. magna	6,600-13,200	24	S,U	Crider *et al*., 1982
D. magna	3,400-4,100	48	S,U	Crider *et al*., 1982
D. magna	2,128-2,497	24	S,U	Muńoz and Tarazona, 1993
D. magna	1,958-2,459	48	S,U	Muńoz and Tarazona, 1993
D. magna	2,160	48	S,M	Millemann *et al*., 1984
Cladoceran (*D. pulex*)	3,400	48	S,U	Geiger & Buikema Jr., 1981
D. pulex	2,920-3,890	48	S,U	Geiger & Buikema Jr., 1982
D. pulex	1,000	96	S,M	Trucco *et al* ., 1983
Amphipod (*G. minus*)	3,930	48	S,M	Millemann *et al*., 1984
Amphipod (*H. azteca*)	1,632	240	SR, M	Lee *et al*. 2002
Midge (*C. tentans*)	2,810	48	S,M	Millemann *et al*., 1984
Snail (*P. gyrina*)	5,020	48	S,M	Millemann *et al*., 1984
Dragonfly (*S. cingulata*)	1,000-2,500	96	S,U	Correa and Coler, 1983
Crimson-spotted Rainbowfish (*Melanotaenia fluviatilis*)	1,210	72	S,M	Pollino and Holdway, 2002
M. fluviatilis	510	96	S,M	Pollino and Holdway, 2002
Mosquitofish (*G. affinis*)	220,000	24	S,U	Wallen *et al*., 1957
G. affinis	165,000	48	S,U	Wallen *et al*., 1957
G. affinis	150,000	96	S,U	Wallen *et al*., 1957
Fathead minnow (*P. promelas*)	7,900	96	FT,M	DeGraeve *et al*., 1982
P. promelas	6,140	96	FT,M	Broderius *et al*. 1995
P. promelas	1,990	96	FT,M	Millemann *et al*., 1984
Largemouth Bass (*M. salmoides*)	680	168	FT,M	Millemann *et al*., 1984
Rainbow trout (*O. mykiss*)	1,600	96	FT,M	DeGraeve *et al*., 1982
O. mykiss	120	648	FT,M	Millemann *et al*., 1984
O. mykiss	110	648	FT,M	Black *et al* ., 1983
Coho salmon (*O. kisutch*)	5,600	<6		Holland *et al*., 1960
O. kisutch	2,100	96	FT,M	Moles *et al*., 1981
O. kisutch	3,200	96		Neff, 1985

- **S= static; SR= static with replacement; FT= flow through; M= measured; U= unmeasured**

Table 2. Sublethal and Chronic Toxicity of Naphthalene to Freshwater Algae, Plants and Protozoans

Organism	*Conc* (µg/L)	Effects	References
Blue-green alga (*A. flos-aquae*)	15,480	30-50% decrease in the N_2 fixation rate in 2 h	Bastian & Toetz, 1985
A. flos-aquae	2,080	16% decrease in the N_2 fixation rate in 2 h	Bastian & Toetz, 1985
A. flos-aquae	14,851	56% increase in biomass in 14 d	Bastian & Toetz, 1982
Chlamydomonas angulosa	8,960	EC_{50} for photosynthesis in 3 h exposure	Hutchinson *et al*., 1980
Alga (*C. vulgaris*)	330- 30,000	decrease in growth rate	Kauss & Hutchinson, 1975
Duckweed (*Lemna gibba*)	2,000	increase in toxicity when exposed to VU-B radiation	Ren *et al.*, 1994
Protozoan (*Spirostomum ambiguum*)	38	24h EC_{50} (cell deformation)	Nalecz-Jawecki and Sawicki, 1999)

Table 3. Sublethal and Chronic Toxicity of Naphthalene to Freshwater Animals.

Organism	*Conc.* (μg/L)	Effect	References
Cladoceran (*D. magna*)	>5,000	decreased motility, sluggish behavior; decreased haemoglobin concentration	Crider *et al*., 1982
Cladoceran (*D. magna*)	1,000	1.3-fold induction of monooxygenase activities	Sturm and Hansen, 1999
Cladoceran (*D. pulex*)	330- 680	longer lifespan; greater or equal number of live young than controls	Geiger and Buikema Jr., 1982
Prawn (*M. kistnensis*)	595.7	decreased protein levels, increased amino acid concentration, and amino acid enzyme activity	Sarojini *et al* ., 1987
Mussel (*Elliptio complanata*)	1.3	initial stimulation of heat rate, O_2 consumption, no irreversible damage to gill tissue	Cheney *et al*., 2001
Crayfish (*Procambarus clarkii*)	10,000	decreased ovarian index, degeneration of pre-vitellogenic and vitellogenic oocytes	Sarojini *et al.,* 1995
Newt (*Pleurodeles waltl*)	125	not genotoxic to larvae micronucleii	Djomo *et al.* 1995
Newt (*Pleurodeles waltl*)	500	genotoxic to larvae micronucleii	Djomo *et al.* 1995
Fathead minnow (*P. promelas*)	>850	reduced egg hatchability; reduced fry length & weight	DeGraeve *et al*., 1982
P. promelas	>4,380	100% mortality	DeGraeve *et al*., 1982
Bream (*Abramis brama*) and Mozambique tilapia (*Oreochromis mossambicus*)	1,500	no significant alteration to fish gut carbohydrase activity after 60 days	Golovanova *et al.,* 1994
Mozambique tilapia (*Oreochromis mossambicus*)	1,500	slight increase in proteolytic activity, increased thyme proteinase and intestineal proteolytic activity,	Kuz'mina *et al*., 1999
Coho salmon (*O. kisutch*)	400- 700	less aggressive feeding behavior; reduced growth rate	Moles *et al*., 1981
Rainbow trout (*O. mykiss*)	6,154	cytotoxic to gill cell line	Schirmer *et al*., 1998
O. mykiss	8	97% hatchability at embryo-larval stages	Black *et al*., 1983
O. mykiss	15	91% hatchability at embryo-larval stages	Black *et al*., 1983
O. mykiss	46	85% hatchability at embryo-larval stages	Black *et al*., 1983

Organism	***Conc.* (μg/L)**	**Effect**	**References**
O. mykiss	230	35% hatchability at embryo-larval stages; gross anomalies in 7% of exposed fish	Black *et al*., 1983
O. mykiss	10	80% hatchability at embryo-larval stage	Kennedy, 2006
Largemouth bass (*M. salmoides*)	239	gross anomalies in 6% of exposed fish vs 1% in fish exposed to 28 μg NA/L	Black *et al*., 1983