

CHAPTER 6

SURFACE WATER AND GROUNDWATER ACCEPTANCE CRITERIA

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6.1 SURFACE WATER AND GROUNDWATER ACCEPTANCE CRITERIA

6.1 INTRODUCTION

6.1.1 Background

This chapter describes the development of acceptance criteria for potentially contaminated surface water and groundwater. The acceptable levels of contaminants in groundwater or surface water depend on a range of site-specific factors, including current and potential future uses.

When assessing contamination of groundwater or surface water associated with a particular timber treatment facility or contaminated site, it is necessary to critically review the potential uses of any groundwater or surface water, and to select acceptance criteria on the basis of these uses. Consideration may also be given to the designation of attenuation or mixing zones within which contaminant concentrations may exceed the nominated criteria, provided use is restricted.

As part of the development of acceptance criteria, the following potential uses of groundwater and surface water have been considered:

- potable water (human drinking);
- stock watering;
- irrigation
- primary contact recreation (bathing); and
- protection of aquatic ecosystems.

The guidelines have been developed following a review of published information from CCME, ANZECC, USEPA, WHO and other similar organisations. Where appropriate, health risk assessment procedures have been used in the development of acceptance criteria. The 'Australian Water Quality Guidelines for Fresh and Marine Waters' (ANZECC, 1992) are Australian guidelines and have no official status in New Zealand. (This is in contrast to the 'Australian and New Zealand Guidelines for the Assessment and Management of Contaminated Sites' (ANZECC, 1992), which have the status of government policy in New Zealand.)

The Ministry for the Environment is working towards the development of a framework for the protection of aquatic ecosystems. This will lead, in due course, to the adoption of the ANZECC Water Quality Guidelines, which are currently under review.

If site discharge limits are based on the criteria in this document, the criteria selected should be based on the use of the appropriate section of the receiving water, and then corrected to account for dilution, etc. It is more appropriate to apply the criteria directly to the appropriate receiving water as this recognises changes in the prevailing conditions and other external influences. However, this approach is frequently not possible and it is more practical to apply the criteria to the discharge, after allowing for typical dilution.

Guideline values for dioxins and furans (expressed as a 2, 3, 7, 8-TCDD toxic equivalent concentration) are included in Section 6.7 as interim values only; these values are those adopted for the 'Pentachlorophenol Risk Assessment Pilot Study' (NTG, 1992). Final acceptance criteria for dioxin and furan concentrations in groundwater and surface water will be determined as part of the Organochlorines Programme of the Ministry for the Environment.

6.1.2 Chapter Summary

This chapter presents acceptance criteria for the levels of timber treatment chemicals in water used for a range of purposes. The potential uses considered include: potable water, stock watering, irrigation and primary contact recreation (i.e. bathing). The protection of freshwater aquatic ecosystems is also discussed, but it is noted that further work on this topic is in process, and general guidelines are not proposed although some advice is offered.

For each of these potential uses, the guidelines propose maximum allowable levels of each of the contaminants of interest (i.e. arsenic, boron, chromium, copper and pentachlorophenol) and set out the reasons for adopting these levels, usually by reference to published criteria.

Table 6.3 presents the recommended water quality guidelines in summary form, allowing easy identification in terms of the water use or contaminant of interest to readers.

6.2 POTABLE USE

6.2.1 Introduction

This section presents guidelines for the concentration of contaminants in water intended for potable use (human drinking). These guidelines have been drawn from the 'Drinking Water Standards for New Zealand' (DWSNZ; MOH, 1995). The DWSNZ give consideration to:

- human health;
- aesthetic concerns; and
- protection of assets.

The DWSNZ are generally consistent with the WHO 'Guidelines for Drinking Water Quality' (WHO, 1993). The DWSNZ for the major contaminants of interest in timber treatment sites are summarised in Table 6.1.

6.2.2 Arsenic

Arsenic has been associated with a range of adverse, chronic, non-carcinogenic health effects, particularly associated with the central nervous system. Arsenic contamination of water supplies has also been linked to an increased incidence of skin cancer and arsenic is classified as a confirmed human carcinogen (Group A) by the USEPA (1992b). Both common forms of arsenic are readily bioavailable and toxic to humans. Based on an incremental lifetime risk of cancer of 10^{-5} and the USEPA IRIS database slope factors, the acceptable concentration of arsenic in drinking water can be estimated to be 2.4×10^{-4} mg/L. There is a higher degree of uncertainty associated with the USEPA carcinogenicity assessment for arsenic than with those for other carcinogens (USEPA, 1992), and this estimate may be overly conservative by at least one order of magnitude. More detailed consideration of the toxicology of arsenic is presented in Chapter 5.

Table 6.1
Summary of Drinking Water Standards for New Zealand (MOH, 1995)

Contaminant	Health Based MAV ⁽¹⁾ (mg/L)	Aesthetic Guideline Values (mg/L)
Arsenic	0.01	
Boron	0.3	
Chromium	0.03	
Copper	2	1
Pentachlorophenol	0.01	

Note: (1) MAV denotes maximum acceptable value.

The DWSNZ and the WHO guidelines nominate a limit of 10 µg/L for arsenic, which corresponds to an estimated incremental lifetime risk of skin cancer of 6×10^{-4} . However, only 1-14% of the arsenic related skin cancers are fatal, and therefore the estimated risk of fatal cancer spans the nominal threshold risk of 1×10^{-5} .

6.2.3 Boron

Boron is rapidly absorbed by humans, both orally and dermally, but is also readily excreted. Boron exposure may result in a range of non-carcinogenic health effects. Based on health risk assessment procedures, an acceptable concentration of boron in drinking water is estimated to be in the range 0.3 to 3 mg/L, corresponding to 10% to

100% of the acceptable daily intake (ADI). The DWSNZ and the WHO 'Guidelines for Drinking Water Quality' nominate a guideline value of 0.3 mg/L, corresponding to an allocation of 10% of the total exposure to drinking water.¹

6.2.4 Chromium

The environmental properties of Cr(VI) and Cr(III) differ markedly. Further, the human health effects associated with exposure to each form differ. Cr(VI) has been classified as a confirmed human carcinogen (Group A) by the USEPA via the inhalation route but is not classified as a carcinogen by the oral route. However, exposure to Cr(VI) via inhalation is of lesser relevance in the case of potable water supplies. Both Cr(III) and Cr(VI) cause irritation of the skin and mucous membranes and Cr(VI) has also been associated with sensitisation and ulceration of the skin and mucous membranes. Cr(VI) tends to be the dominant species in aerated or chlorinated water supplies (WHO, 1984), but is readily reduced to Cr(III) in the aquatic environment.

Most published guidelines for drinking water quality nominate limits for total chromium in the range 0.05 to 0.1 mg/L on the assumption that all chromium is present as Cr(VI). The DWSNZ and the WHO guidelines nominate a value of 0.05 mg/L for total chromium on the basis that all chromium is present as Cr(VI). Given the very low solubility of Cr(III) in most groundwaters and surface waters, there is some justification for this assumption.

Cr(III) and Cr(VI) can now be readily differentiated analytically and it is considered appropriate to set separate guidelines for the two species. Using health risk assessment procedures, the acceptable concentrations of chromium in water can be estimated to be 0.02 mg/L and 4 mg/L for Cr(VI) and Cr(III) respectively, based on allowing drinking water to contribute up to 10% of the acceptable intake.

6.2.5 Copper

Copper has been associated with a wide range of chronic and acute adverse health effects in humans, although these are generally only observed at relatively high doses. Quantitative dose-response information is limited for copper. Copper is not classified as a human carcinogen by the USEPA. Based on the available information, health risk assessment suggests that an acceptable concentration of copper in drinking water may be in the order of 0.2 mg/L. Tainting has been reported at copper concentrations in excess of 2.6 mg/L and staining of laundry has been reported at copper concentrations in excess of 1.0 mg/L for copper.

The DWSNZ and the WHO guidelines nominate a health-based MAV of 2.0 mg/L and an aesthetic guideline value of 1.0 mg/L for copper.

¹ MoH is reviewing the current MAV for boron.

6.2.6 Pentachlorophenol

Chronic exposure to pentachlorophenol (PCP) may result in a range of adverse health effects in humans, including irritation of the skin and mucous membranes, chloracne, neuroaesthesia, depression, headaches and changes in kidney and liver function. In addition, PCP has been classified as a probable human carcinogen (Group B2) by the USEPA, for exposure via the oral route. Prior to the recent reclassification of PCP as a carcinogen, drinking water quality criteria up to 60 mg/L were established for PCP on the basis of taste and odour considerations. The USEPA has indicated PCP concentrations in drinking water in the range 0.3 to 3 mg/L may be associated with an incremental lifetime risk of cancer in the range of 10^{-6} to 10^{-5} .

The DWSNZ nominate a provisional MAV of 10 µg/L for PCP based on an ADI of 3 µg/kg/d and allocation of 10% of the ADI to drinking water exposure.

6.3 STOCK WATERING

6.3.1 Introduction

This section sets out water quality guidelines for stock watering. The guidelines have been based principally on the Canadian Water Quality Guidelines (CCREM, 1991) and the Australian Water Quality Guidelines (ANZECC, 1992), which are based on published studies completed in the USA, Canada and Australia.

6.3.2 Arsenic

Arsenic is an essential element for livestock at low levels; however, at higher concentrations it is toxic. The toxicity of arsenic depends greatly on the chemical form in which it appears. Organic arsenic is sometimes used as a feed additive for pigs and poultry. Generally, published stock water quality guidelines for arsenic are in the range 0.2 to 0.5 mg/L, with concentrations up to 5 mg/L tolerated if arsenic intake from other sources, including feed, is low.

As arsenic associated with timber treatment is likely to be in inorganic form, a stock water quality guideline for arsenic of 0.5 mg/L has been nominated, which is consistent with the ANZECC (1992) water quality guidelines.

6.3.3 Boron

There is little information about the toxicity of boron, even at relatively high concentrations. For cattle, the consumption of water contaminated at 150 mg/L was associated with decreased hay consumption and weight loss, and the tolerance concentration for boron was estimated to be between 40 and 150 mg/L for cattle (Green, 1977). Previously published guidelines indicate that a boron concentration of

5 mg/L is acceptable, and on this basis a guideline value of 5 mg/L has been nominated, which is consistent with the ANZECC (1992) guidelines.

There is no evidence that boron concentrations at several times the guideline value would be associated with adverse effects (CCREM, 1991), and it is possible that further information about health effects at higher levels of exposure may indicate that higher values would be acceptable.

6.3.4 Chromium

For humans, Cr(VI) is of most concern, and, assuming domestic animals respond similarly, greatest concern should be focused on Cr(VI). Cr(III) has a very low solubility and is poorly absorbed by the gastrointestinal tract. By contrast, Cr(VI) is relatively soluble in water and is readily absorbed (Owen, 1990). Studies involving domestic animals indicated that a concentration of 5 to 6 mg/L of Cr(VI) did not cause tissue damage whereas a concentration of 10 mg/L resulted in chromium accumulation in the muscle.

Published guidelines for Australia, Canada and the USA each nominate an acceptable concentration of total chromium of 1.0 mg/L based on the effects of Cr(VI). A guideline value of 1.0 mg/L is nominated for Cr(VI). This guideline may also be used as the default for the assessment of total chromium concentrations: i.e. if the chromium is soluble it is likely to be Cr(VI). Given the lower toxicity of Cr(III), it is likely that higher concentrations of Cr(III) would be acceptable.

6.3.5 Copper

Copper is an essential trace element for animal growth. However, excess copper intake can lead to copper toxicosis. Excess copper intake by livestock is normally feed-related, but, because of the use of copper-based chemicals in agriculture, there is a need to set limits for stock water. Livestock species differ in their tolerance to copper, and the following limits have been adopted by the Canadian authorities, and are also proposed by ANZECC:

- Sheep – 0.5 mg/L
- Pigs and poultry – 1.0 mg/L
- Cattle – 5 mg/L

The above species-specific values have been adopted for the purposes of these guidelines.

6.3.6 Pentachlorophenol

None of the available published guideline for stock watering include reference to pentachlorophenol. Both the Canadian and ANZECC guidelines refer to drinking water guidelines for toxic organics, i.e. 10 µg/L for PCP. Higher values may be acceptable depending on the livestock use, the levels of risk that may be acceptable for livestock health, and the potential accumulation of PCP in livestock tissue and milk.

Appendix B presents the derivation of a preliminary guidelines value for stock watering based on consideration of both:

- protection of the health of consumers of livestock products; and
- protection of livestock health.

A preliminary stock watering guideline value for PCP of 0.15 mg/L is nominated, based on the protection of stock health (refer Appendix B). Where appropriate, the preliminary stock watering guideline for PCP may be modified to reflect site-specific information or additional information about the effects of PCP on livestock as it becomes available.

6.4 IRRIGATION

6.4.1 Introduction

This section sets out water quality guidelines for irrigation. They are based principally on the Canadian Water Quality Guidelines (CCREM, 1991) and the Australian Water Quality Guidelines (ANZECC, 1992), which are based on studies completed in the USA, Canada and Australia.

Note that the guidelines have generally been set to protect the most sensitive crop. Higher contaminant concentrations may be acceptable in irrigation water depending on site-specific considerations, such as the crop being grown, the irrigation regime and the capacity of the local soils to assimilate contaminants.

6.4.2 Arsenic

Generally, yield reduction and crop failure are the primary concerns associated with elevated arsenic concentrations in irrigation water and, consequently, soils. Arsenic does not generally accumulate in edible plant portions at levels potentially dangerous to consumers (ANZECC, 1992). Under some circumstances, arsenic uptake from contaminated soils may result in unacceptable contaminant concentrations in the root portions. Nutrient solutions containing 0.5 to 10 mg/L arsenic have been associated with toxic effects on crops. ANZECC and other authorities have adopted an irrigation water guideline concentration of 0.1 mg/L; however, arsenic concentrations up to 2.0 mg/L may be acceptable in neutral to alkaline soils, particularly clays, where

arsenic is adsorbed strongly on the soil particles. On this basis arsenic should not exceed a concentration of 0.1 mg/L in water applied to sandy and acidic soils, with concentrations up to 2 mg/L being acceptable in some circumstances.

6.4.3 Boron

The tolerance of various plant species to boron in the soil water varies considerably, from less than 0.5 mg/L for blackberries to 15 mg/L for asparagus. Boron in small quantities is necessary for the normal growth of plants but at higher concentrations is toxic. The allowable concentration of boron in irrigation water depends on the sorption capacity of the soil and, consequently, higher concentrations of boron in the irrigation water may be allowed where soils are alkaline. While a guideline suitable for all soils cannot be set, boron should not exceed a concentration of 0.5 mg/L for sensitive species, although concentrations up to 6 mg/L may be acceptable in some circumstances, as noted in the ANZECC guidelines.

6.4.4 Chromium

There is no evidence that chromium is essential to plant life. Yield reduction has been associated with chromium concentrations in the range 1 to 10 mg/L, for some plant species. Cr(III) and Cr(VI) are similarly bioavailable in nutrient solutions but in the soil environment, Cr(III) is readily adsorbed on soil particles and is generally less bioavailable.

The CCREM (1991) and ANZECC (1992) guidelines nominate an acceptable concentration of chromium in irrigation water of 0.1 mg/L. The US authorities (CCREM, 1991) indicate that chromium concentrations up to 0.1 mg/L are acceptable for continuous irrigation of acid, sandy soils but that concentrations up to 1.0 mg/L may be acceptable for up to 20 years on neutral to alkaline fine-textured soils. On this basis, an irrigation guideline value of 0.1 mg/L has been nominated for chromium (total).

6.4.5 Copper

Copper is necessary in soils at concentrations greater than 6 mg/kg in order to ensure healthy plant growth; however, at concentrations between 150 and 400 mg/kg copper is toxic to some plants. The toxicity of copper to plant life is pH-dependent, with higher concentrations being tolerated in fine-textured alkaline soils. The Canadian guideline values for copper in irrigation waters (CCREM, 1991) are as follows:

- continuous irrigation of all plant species on all soils – 0.2 mg/L
- low-sensitivity crops (e.g. cereals) – 1.0 mg/L
- neutral to alkaline soils for up to 20 years – 5.0 mg/L

The ANZECC (1992) guidelines nominate a value of 0.2 mg/L for all conditions; however, the Canadian guidelines are considered to represent a more flexible, site-specific approach. In the first instance a guideline value for copper of 0.2 mg/L may be used for assessment of irrigation water quality.

6.4.6 Pentachlorophenol

Published guidelines for pentachlorophenol in irrigation water were not identified. PCP is an effective biocide, with algae being sensitive at concentrations of 0.5 mg/L, and it is possible that some plant species will be sensitive at low concentrations. Sorption of PCP on soil particles may reduce the effective concentration to which plants are exposed. In dilute solution, PCP can be expected to degrade in the soil environment, and is unlikely to accumulate if irrigated at low concentration. In the absence of other information the potable use guideline of 10 µg/L may be used.

6.5 PRIMARY CONTACT RECREATION

Limited published information is available on acceptable concentrations of contaminants in water to be used for primary contact recreation, such as swimming. The ANZECC (1992) guidelines indicate that water containing chemicals which are either toxic or irritating to the skin or mucous membranes is unsuitable for primary contact recreation, and that the concentration of toxic substances should not exceed levels given for untreated drinking water.

Health risk assessment has been used to better quantify the potential adverse effects of bodily immersion in water containing contaminants, and the resulting health-risk-based acceptance criteria for recreational water are presented in Table 6.2. For details of the health risk assessment procedures, refer to Appendix A.

The guideline values presented in Table 6.2 have been developed on the context of regular swimming activities (1 hr/day, 150 day/year). Guideline values more typical of occasional recreational bathing are presented in Appendix A.

Table 6.2
Preliminary Health Risk Based Acceptance Criteria (refer Appendix A for details)
Primary Recreational Use of Surface Water

Receptor:	Children and adults resident onsite for up to 30 yrs.	Target Risk:	1E-05
		Target HI:	1
Exposure Frequency:	150 d/yr	Body Weight (4-10 yr):	30 kg
Averaging Time (carc.):	70 yrs	Body Weight (adult):	70 kg
(non-carc.)	6 yrs	Exposure Dur. (4-10 yr):	6 yrs
	24 yrs adult	Exposure Dur. (adult):	24 yrs
Ingestion Rate:	100 mL/event	Surface Area (4-10 yr):	8290 sq. cm (50th percentile)
Event Duration (t):	1 hr/d (av.)	Surface Area (adult):	18000 sq. cm (50th percentile)

Contaminant	SF (1/(mg/kg/d))		RfD (mg/kg/d)		Absorption in GI tract (%) ⁽²⁾	Acceptable CDI (mg/kg/d)				Permeability Constant (cm/h) ⁽⁴⁾	Preliminary Health-based Soil Acceptance Criteria (mg/kg)					
	Oral	Dermal ⁽³⁾	Oral	Dermal ⁽³⁾		Carcinogenic		Non-carcinogenic			Carcinogenic			Non-carcinogenic		
						Oral	Dermal	Oral	Dermal		Oral	Dermal	Combined	Oral	Dermal	Combined
<i>Metals:</i>																
Arsenic	0.15	0.21			70	6.75E-05	4.7E-05			8.0E-04	2.1E-01	1.3E+00	1.8E-01			
Boron			4.5E-02	4.5E-03	10			4.5E-02	4.5E-03	8.0E-04				3.3E+01	5.0E+01	2.0E+01
Chromium (III)			1.0E+00	4.0E-03	0.4			1.0E+00	4.0E-03	8.0E-04				7.3E+02	4.4E+01	4.2E+01
Chromium (VI)			5.0E-03	5.0E-04	10			5.0E-03	5.0E-04	8.0E-04				3.7E+00	5.5E+00	2.2E+00
Copper			5.0E-02	5.0E-03	10			5.0E-02	5.0E-03	8.0E-04				3.7E+01	5.5E+01	2.2E+01
<i>Organics:</i>																
PCP	0.12	0.15			80	8.3E-05	6.7E-05			6.5E-01	2.6E-01	2.2E-03	2.2E-03			

Note: (1) Preliminary water quality criteria for carcinogens based on average exposure over 30 years and for non-carcinogens on the six years of child exposure.
 (2) Owen (1990)
 (3) Dermal SF and RfD based on absorbed dose rather than administered dose.
 (4) USEPA (1992a)

6.6 PROTECTION OF AQUATIC ECOSYSTEMS

6.6.1 Introduction

The development of general guidelines for the protection of aquatic ecosystems is a difficult and uncertain practice. The acceptable level of a given contaminant in the aquatic environment can depend on a wide range of factors, including:

- the form of the contaminant discharged to the aquatic ecosystem;
- the water chemistry (e.g. pH, hardness, dissolved oxygen content, presence of complexing agents and/or organic matter, temperature);
- the frequency and intensity of discharges (e.g. shock loads vs continuous loads);
- the aquatic species present in that section of the aquatic environment;
- synergistic and antagonistic effects of other contaminants;
- the current state of the aquatic ecosystem and the level of protection to be afforded (i.e. other factors may lead to the degradation of the aquatic ecosystem, and applying guidelines set on the basis of protection of sensitive species in a pristine environment may be unwarranted); and
- the definition of mixing zones associated with discharges consented under the provisions of the RM Act and the requirements for protection of the ecosystem within the mixing zone¹.

Because of these factors, there is a need to assess the requirements for protection of aquatic ecosystems on a site-specific basis. This approach is consistent with the RM Act, which indicates that, where an aquatic ecosystem is to be protected, there should be an assessment of the sensitivity of the local ecosystem, an indication as to whether an adverse effect has occurred and a clear demonstration of where in the downstream water path the ecosystem has been examined.

Less stringent requirements for water quality may apply within the mixing zone: e.g. a requirement for no acute toxicity and a requirement that contaminant levels should not act as a barrier to the migration of aquatic life. Note that these guidelines relate to concentrations in the receiving water where the effect is likely to occur, external to a mixing zone where localised higher concentrations may be tolerated.

¹ Depending on conditions associated with the granting of a consent for a discharge to the environment less stringent requirements for the protection of aquatic ecosystems may apply within the mixing zone (e.g. a requirement that fish can pass through the mixing zone without adverse effect).

The Ministry for the Environment has embarked on a process of developing guidelines for the protection of aquatic ecosystems. The framework document 'A Process for the Development of Guidelines for the Protection of Aquatic Life in New Zealand' (MfE, 1995) has been the first stage. This will be followed in due course by the adoption of the ANZECC Water Quality Guidelines when the current revision is completed.

In this study the consideration of aquatic ecosystems has been restricted to freshwater receiving waters, as such systems are likely to be of primary concern given the location of most processing facilities. For information on potential ecosystem impacts in marine environments refer to the Canadian and ANZECC water quality guidelines.

Notwithstanding the desirability of undertaking a site-specific evaluation of the impacts on aquatic ecosystems, a number of published guidelines are available and are useful as part of an initial review.

6.6.2 Arsenic

The toxicity of arsenic depends on its form in the aquatic environment, although As(III) and As(V) exhibit similar bioavailability and toxicity to aquatic organisms (ANZECC, 1992). Because of its chemical similarity to phosphate, arsenate is readily absorbed by phytoplankton and thus enters the food chain (Sanders, 1980). Studies indicate the following toxicological information regarding arsenic in the aquatic environment (CCREM, 1991):

- Invertebrates exhibited signs of acute toxicity associated with As(III) at 812 µg/L.
- Adult fish exhibited signs of acute toxicity associated with As(III) at 13,300 µg/L upward.
- The alga *Scenedesmus obliquus* exhibited signs of toxicity at 48 µg/L.

A guideline concentration of 50 µg/L for total As has been recommended by CCREM (1991), Hart (1982) and ANZECC (1992). The USEPA recommends a concentration of 190 µg/L (4-day average) for As(III), not be exceeded more than once every three years.

6.6.3 Boron

There are no readily available published guidelines for boron for the protection of aquatic ecosystems. It may be argued that given impacts on plant life are some of the most sensitive effects associated with boron that guideline values nominated for irrigation may be used as a first indication of the likelihood of adverse impact on aquatic species, particularly plants. The USEPA refers to the irrigation guideline of 750 µg/L for sensitive crops. The ANZECC (1992) guidelines nominate a limit of 500 µg/L for sensitive crops.

Hickey (1989) conducted aquatic toxicity testing for a range of cladocerans, including some New Zealand species. Reported EC₅₀ values for boron ranged from 101 to 319 mg/L, while EC₁₀ values ranged from 38 to 250 mg/L. The lowest NOAEL reported for boron was 10 mg/L. It is understood unpublished information indicates some other species, particularly aquatic plants, are more sensitive to boron by a factor in the order of 3.

Based on the information outlined above, a preliminary aquatic ecosystem protection criterion for boron in the order of 0.75 mg/L is expected to be protective of the aquatic environment.

6.6.4 Chromium

The form of chromium, i.e. Cr(VI) or Cr(III), affects both its fate and toxicity in the aquatic environment. Cr(III) is much less soluble than Cr(VI) but may be present in the aquatic environment in suspension, or in solution complexed with organic anions. The ratio of Cr(III)/Cr(VI) is dependent on the organic matter present and the concentration of dissolved oxygen. Chromate, because of its chemical similarity to sulphate, is taken up by phytoplankton and can bioaccumulate in higher aquatic organisms. Studies indicate Cr(VI) is much more toxic to aquatic organisms than is Cr(III). The CCREM (1991) sets a guideline of 20 µg/L (total) for the protection of fish, and 2 µg/L (total) for protection of all aquatic life.

The Canadian water quality guidelines assume, for simplicity, that all chromium is present as Cr(VI), and set a value of 2 µg/L for total chromium for the protection of aquatic ecosystems (at a hardness of 50 mg/L). The ANZECC (1992) guidelines nominate a value of 10 µg/L (total). The USEPA provides separate guidelines for Cr(III) and Cr(VI) of 120 µg/L and 11 µg/L respectively. Given the differences in toxicity between Cr(VI) and Cr(III), it is considered appropriate that separate guidelines be set for each form. Where chromium concentrations are expected to be low, it may be appropriate to analyse for total chromium; however, where the concentration of total chromium exceeds the guidelines based on Cr(VI), analysis for each form becomes important.

The toxicity of Cr(III) to freshwater aquatic life is hardness-dependent; the USEPA guideline value for Cr(III) may be determined using the following relation:

$$\text{Acceptable chromium concentration (mg/L)} = e^{[0.819 \ln(\text{hardness (mg/L)}) + 1.561]}$$

6.6.5 Copper

The toxicity of copper to freshwater aquatic life is also dependent on the water hardness: toxicity increases with decreasing hardness. High concentrations of chelating agents and suspended solids lead to the formation of complexes that are less bioavailable, thus reducing the toxicity of copper. In the aquatic environment more than 98% of copper tends to be bound to organic material. The tolerances of fish,

invertebrates and freshwater plants to copper appear to be similar CCREM (1991). In assessing the impact of copper on aquatic ecosystems, the following should be considered:

- At a hardness of 50 µg/L, acute toxicity data for freshwater species ranged from 17 mg/L for *Ptychocheilus* to 10,000 mg/L for *Acroneuria* (USEPA in ANZECC, 1992).
- At a hardness of 50 µg/L, chronic toxicity values for 15 freshwater species ranged upward from 4 mg/L (USEPA in ANZECC, 1992).
- Changes in fish behaviour have been demonstrated at values as low as 4 µg/L (CCREM, 1991).
- CCREM (1991) developed a guideline of 2 to 6 µg/L depending on hardness.
- Hart (1982) established a criterion of 5 µg/L for filterable copper in soft waters.
- ANZECC (1992) established a guideline of 2 to 5 µg/L for copper in fresh waters, depending on water hardness.
- The USEPA has developed ambient water quality criteria for the protection of freshwater aquatic ecosystems such that the acceptable concentration of copper for chronic exposure is given by:

$$\text{Acceptable copper concentration (mg/L)} = e^{(0.8545 \ln [\text{hardness (mg/L)}] - 1.465)}$$

At a hardness of 50 mg/L, this expression results in an acceptable copper concentration for chronic exposure of 6.5 µg/L.

6.6.6 Pentachlorophenol

Studies involving PCP-contaminated freshwater lakes and ponds have shown that, although photolysis can result in rapid degradation of PCP, the chemical can persist for several months in water and fish, and for years to decades in sediments (Rao, 1978; Minister of Supply and Services, Canada, 1989). Fish were found to accumulate PCP and PCP degradation products rapidly from water, with fish liver and gill tissue exhibiting the highest concentrations of PCP. In addition, the persistence of PCP and its degradation products in sediments was found to provide a source of ongoing contamination of the aquatic environment (Rao, 1978; Minister of Supply and Services, Canada, 1989).

PCP, like many other chlorinated organic compounds, is soluble in fatty substances (ANZECC, 1991) and tends, therefore, to accumulate in the fatty tissues of living organisms. This process is known as bioaccumulation and it can occur by two pathways: bioconcentration, in which minute quantities of a chemical can be taken up and progressively concentrated in the fatty tissues; and biomagnification, in which the concentration of a chemical can be magnified several-fold by the consumption of organisms already contaminated with the chemical. Rainbow trout, which feed by predation, have been found to bioaccumulate PCP at up to 600 times the levels found

in the surrounding water by feeding on organisms which are already contaminated (ANZECC, 1991).

Several factors affect the toxicity of PCP in freshwater (ANZECC, 1990). PCP is more toxic to aquatic organisms at low pH, where concentrations of dissolved oxygen are low, or at elevated temperatures. These effects can either be species or life-stage specific.

The toxic effects of PCP have been studied in a range of organisms. Sensitivity can vary greatly between species. The 96 hour LC₅₀ values for fish, for example, can vary from 0.03 to 3 mg/L (ANZECC, 1990). The WHO monograph on PCP (WHO, 1987) provides additional toxicological information.

Canadian environmental authorities have developed various PCP limits for protection of receiving waters (Environment Canada, 1988). Generally these limits apply to the water column of receiving waters, and have the objective of protecting the most sensitive biological species within the relevant ecosystems. These limits have been formulated with respect to Canadian ecosystems, and there may be some differences in the sensitivity of New Zealand ecosystems.

The acceptable concentration of PCP in aquatic biota and the concentration at which chronic sublethal effects will be observed are not well-defined. The British Columbia Ministry of the Environment (Environment Canada, 1988) has proposed a maximum PCP concentration in fish muscle of 100 mg/kg (wet weight). However, this figure appears to be based on considerations of background concentrations and suitability for human consumption, and since there is uncertainty as to its relevance as an indicator of impact on aquatic ecosystems it is considered inappropriate for use as a criterion until its basis has been clarified.

Studies have shown that PCP at 0.03 mg/L in the water column causes tainting of the flesh of fish and other aquatic organisms; however, toxicity to aquatic species is found to be the limiting consideration compared to tainting of fish flesh.

Acceptable concentrations of PCP in sediments are not usually specified; however, the BC Ministry of the Environment has proposed a maximum PCP concentration in bottom surface sediments of 10 mg/kg based on background concentration considerations (Environment Canada, 1988).

Given the pH dependence of PCP toxicity, the USEPA (1986) has developed ambient water quality criteria for the protection of freshwater aquatic ecosystems based on the following relationships:

Acceptable PCP concentration – Acute ($\mu\text{g/L}$): $e^{(1.005(\text{pH}) - 4.830)}$ (1 hr average)

Acceptable PCP concentration – Chronic ($\mu\text{g/L}$): $e^{(1.005(\text{pH}) - 5.290)}$ (4 d average)

At pH 7, the above expression results in a chronic (4 d average) value of 5.7 $\mu\text{g/L}$.

While the ANZECC (1992) and CCREM (1991) guidelines adopt a similar approach for the development of guideline values protective of aquatic ecosystems, different values are nominated, reflecting differences in the toxicity data on which the guideline is based. The ANZECC (1992) guidelines have adopted the objective of 0.05 mg/L, based on an acute toxicity value of 4.4 µg/L for larval carp and an application factor of 0.01 (default value for a chemical which is persistent or which requires additional caution because of a limited data set). The CCREM (1991) guidelines nominate a value of 0.5 µg/L based on the lowest **mean** toxicity concentration of 55 µg/L for coho salmon, and an application factor of 0.01.

For the purposes of Chapter 7 it is necessary to nominate a PCP aquatic ecosystem protection guideline value for interim use. The recommended guideline values for the protection of aquatic ecosystems are:

- Modified ecosystems: 0.5 µg/L
- Pristine ecosystems: 0.05 µg/L

The interim recommendations will be reviewed as part of the Organochlorines Programme.

6.7 SUMMARY OF PROPOSED CRITERIA

The guidelines proposed for each contaminant and each potential use of groundwater or surface water are summarised in Table 6.3. Detailed consideration of the basis of the proposed values is presented in Sections 6.2 – 6.6.

The proposed guidelines have been based on total contaminant concentrations in groundwater and surface water, with the exception of chromium, for which separate values have been proposed for Cr(III) and Cr(VI). Where contaminant concentrations are low, as a first check, it may be appropriate to compare the results of total chromium analyses with the guideline value for Cr(VI).

In some cases the guidelines consist of a range rather than a single value, indicating that the application of the guidelines is particularly dependent on site-specific considerations.

As discussed in Section 6.6, contaminant concentrations associated with an adverse impact on aquatic ecosystems can vary significantly depending on the water chemistry, and the nature of the contaminant and aquatic flora and fauna. On this basis, no specific guideline values have been proposed for ecosystem protection (other than the interim values for PCP for use in Chapter 7), and it is recommended that the potential impact of contamination on aquatic ecosystems be reviewed on a site-specific basis, with reference to published guidelines as may be appropriate. Such an approach is considered to be consistent with the provisions of the RM Act, which may be interpreted as requiring consideration of the sensitivity of the local ecosystem and of whether an adverse effect has occurred. Published criteria may be used as a screening

tool, and site-specific evaluation should follow where appropriate (Hannah and McFarlane, 1992).

The guidelines in this document have been framed in terms of protecting different uses of surface waters and groundwaters, rather than being based on various classes or types of water body.

In applying the water quality guidelines it is important that a critical review be undertaken of the possible beneficial uses of a given groundwater or surface water body, and consideration be given to site-specific factors in any assessment of surface water or groundwater contamination. For example, natural water quality (e.g. salinity) and availability may restrict the potential beneficial uses of a groundwater or surface water body, and consequently it may not be appropriate to protect such water bodies for all beneficial uses. Further, the extent of a mixing zone, in which localised higher concentrations may be accepted, should be considered.

For these reasons the proposed guidelines should be viewed as being flexible and indicative only, with some variation being expected on a site-specific basis.

Water quality guidelines for dioxins and furans have not been specifically developed as part of these guidelines. A review of published water quality guidelines was undertaken as part of the 'Pentachlorophenol Risk Assessment Pilot Study' (NTG, 1992). The criteria adopted for dioxins and furans for the purposes of the NTG study are as follows:

- Potable use: 0.015 ng/L (TE)
- Aquatic ecosystem protection: 0.01 ng/L (TE)

These values may be used as interim criteria, which provide a preliminary indication of maximum acceptable dioxin and furan concentrations in surface water and groundwater.

Table 6.3
Summary of Water Quality Guidelines
(all values expressed in mg/L unless otherwise specified)

USE	Contaminant						
	Arsenic	Boron	Chromium			Copper	PCP
			(III)	(VI)	Total		
Potable	0.01	0.3			0.05	1	0.01
Stock watering	0.5	5		1	1	0.5 ⁽¹⁾	0.15
Irrigation	0.1 ⁽²⁾	0.5 ⁽³⁾			0.1	0.2 ⁽³⁾	0.01
Primary contact recreation	0.21	20	41.5	2.19		21.9	0.002
Aquatic ecosystem protection							
• CCREM (1991)	0.05	–		0.002	0.002	0.002-0.004	0.0005
• ANZECC (1992)	0.05	–		0.01	0.01	0.002-0.005	0.00005
• USEPA	0.19	–	0.12 ⁽⁴⁾	0.011		0.0065 ⁽⁴⁾	⁽⁴⁾
• Other		0.75					

Note: (1) Based on sheep – higher values may be tolerable for other livestock.
(2) Based on acid, sandy soils – higher values may be tolerable under other conditions.
(3) Based on sensitive crops – higher values may be acceptable depending on the crop.
(4) Refer expression relating guideline value to pH or hardness.

6.8 REFERENCES

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APPENDIX A

HEALTH RISK-BASED ACCEPTANCE CRITERIA FOR DRINKING WATER AND PRIMARY CONTACT RECREATION

A1. EXPOSURE ROUTES AND RECEPTOR GROUPS

A1.1 Drinking Water

For the purposes of this assessment the Maximum Acceptable Values (MAVs) nominated in the DWSNZ have been adopted as acceptance criteria for potable use of water. Therefore risk-based criteria for potable use have not been independently derived for any of the contaminants of concern; however, an approach similar to that presented in the following sections may be used if necessary.

In the case of drinking water exposure, the lifetime ingestion of water by adults is usually used as the basis for the derivation of criteria. While a child may be exposed to a weight-standardised rate approximately twice that of an adult, the duration of exposure for adults may be up to 10 times that for children. For some volatile contaminants, such as benzene, human exposure during showering and similar activities can be a significant exposure route. However, given the contaminants of concern in this assessment exhibit low volatility the primary exposure route for potable water supplies is considered to be ingestion of drinking water. The derivation of the DWSNZ reflects consideration of the ingestion of water only.

A1.2 Primary Contact Recreation

Primary contact recreational activities such as bathing necessarily involve intimate contact between those involved and the potentially contaminated water. Both children and adults are considered in this assessment. The intention is to quantify risks associated with regular swimming in surface water bodies. However, the criteria derived may also be applied to the assessment of groundwater used to fill swimming pools, except in the case where such pools are used for very regular training activities (>150 events/year, e.g. commercial swimming pools). The assessment therefore focuses on recreational bathing rather than regular training activities. Both incidental ingestion of water during bathing and dermal absorption have been considered in this assessment.

A2. RISK ASSESSMENT AND THE DEVELOPMENT OF RISK-BASED ACCEPTANCE CRITERIA

A2.1 General

A discussion of risk assessment principles and the process for the development of risk-based acceptance criteria is presented in Section 5.4. Such a process can be applied to the derivation of criteria for both soil and water.

The risk assessment process may be summarised in four steps as follows:

- Hazard Identification;
- Exposure Assessment;
- Toxicity Assessment; and
- Risk Characterisation.

In derivation of acceptance criteria, the above process is run in reverse, starting with definition of an acceptable level of risk.

A2.2 Toxicity Assessment

In order to relate estimates of exposure to the risk of adverse health effects in humans a range of dose response factors have been developed by various health and environmental agencies, based on a review of published toxicological and epidemiological information. The health effects associated with exposure to copper, chromium, arsenic, boron and pentachlorophenol, and the dose response factors nominated for each of these chemicals are discussed in Section 5.5. Also refer to Section 5.10.5 for details of the corrections to the adopted dose-response factors necessary to account for background exposure.

A2.3 Exposure Assessment

A2.3.1 Ingestion of Contaminated Water

The Chronic Daily Intake (CDI) may be determined by the following expression.

$$CDI = \frac{C \times IR_{adj} \times EF \times MF}{AT} \quad (A1)$$

where: C = concentration of contaminant in the water (mg/L)

IR_{Adj} = age adjusted ingestion rate (L/d)

$$= \frac{\sum ED_i \times IR_i}{B_{wi}} \quad (A2)$$

where: ED = exposure duration for age group 'i' (yr)

IR = ingestion rate for age group 'i' (mg/d)

BW = body weight for age group 'i' (kg)

EF = exposure frequency

AT = averaging time

= (ED x 365) days for non-carcinogens by convention or (70 years x 365) days for carcinogens, a lifetime, by convention

MF = matrix factor, accounts for reduced bioavailability of contaminant due to binding to the soil matrix. In the absence of necessary information, MF usually taken as 1.0.

A2.3.2 Dermal Absorption from Contaminated Water

The Chronic Daily Intake (CDI) for dermal absorption from contaminated soil may be determined from the following expression (based on USEPA, 1988):

$$CDI = \frac{t \times AV_{adj} \times C \times PC \times EF \times CF}{AT} \quad (A3)$$

where: t = duration of exposure (hours/event)

$$AV_{adj} = \text{age-adjusted skin surface area} \\ = \frac{\sum AV_i \times ED_i}{BW_i}$$

Where: AV_i = skin surface area for age group 'i' (cm²)

ED = exposure duration for age group 'i' (yr)

BW = body weight for age group 'i' (kg)

C = contaminant concentration in water (mg/L)

PC = dermal permeability constant (cm/hr)

EF = exposure frequency (event/yr)

AT = averaging time (days)

CF = conversion factor
= 10^{-3} L/cm³

Note, the USEPA (1992) has recently released further guidance regarding the estimation of dermal exposure. The above procedure is retained for the assessment of exposure to inorganics whereas some revision of the procedure has been adopted for organic contaminants. The revised approach may be described as follows:

$$CDI = \frac{DA_{event} \times ED \times EF \times AV}{BW \times AT} \quad (A4)$$

where: DA_{event} = Absorbed dose per event (mg/cm event)

DA_{event} is a function of the duration of each exposure event, the concentration of the contaminant in water and a number of contaminant specific parameters. Refer to USEPA (1992) for details.

Note, for the purposes of developing human health-based preliminary remediation goals for non-carcinogenic health effects, the most sensitive receptor, i.e. children, only is considered in the assessment of primary contact recreational exposure.

A3. DEVELOPMENT OF ACCEPTANCE CRITERIA FOR PRIMARY CONTACT RECREATIONAL USE

Health-based preliminary acceptance criteria for primary contact recreational use of water have been developed giving consideration to both the ingestion and dermal absorption exposure routes. The major exposure assumptions are summarised as follows:

- exposure duration = Child (4-10 yrs): 6 yrs
Adult (10-30 yrs): 20 yrs
- water ingestion rate = 130 mL/event (ANZECC, 1992)
- skin surface area = Child (4-10 yrs): 8290 cm² (USEPA, 1989a)
Adult (10-30 yrs): 18000 cm²
- body weight = Child (4-10 yrs): 30 kg (USEPA, 1989b)
Adult (10-30 yrs): 70 kg
- exposure frequency = 150 event/yr (USEPA, 1992)
- event duration = 1 hr/event (USEPA, 1992)

A4. REFERENCES

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APPENDIX B

DERIVATION OF STOCKWATERING GUIDELINE FOR PCP

B1. GENERAL

Two issues to be considered in deriving stockwater acceptance criteria are as follows:

- Protection of animal health
- Protection of human health (considering consumption of livestock products).

Information regarding the possible adverse health effects of PCP on livestock health is not readily available. Historically, in the absence of other information, the potable water quality guideline for PCP, which is protective of human health, has been used. In practice, a lower level of concern is attached to the protection of animal health, compared to the protection of human health. On this basis, while a potable guideline for PCP of 10 µg/L may be appropriate for the protection of human health, a higher value may be appropriate as a stockwater guideline.

B2. PROTECTION OF HUMAN HEALTH

Preliminary acceptance criteria for PCP for the protection of human health where water is used for stockwatering purposes have been derived based on:

- An incremental lifetime risk of cancer of 1 in 100,000;
- Typical livestock product consumption rates (Langley, 1996);
- Published correlations between intake of contaminants and concentrations in livestock products (ECETOC, 1990).

For the purposes of criteria derivation, cattle have been used as a representative species.

A correlation between the concentration of PCP in stockwater and the concentration of PCP in various cattle tissues/products based on published relationships (ECETOC, 1990).

$$I = C \times Q \quad (B1)$$

where I = PCP intake (mg/d)

C = Concentration of PCP in stockwater (mg/L)

Q = Consumption of water by cattle
= 55 L/day

$$C_p = I \times K_p \quad (B2)$$

where C_p = Concentration of PCP in the product (mg/kg)

I = Intake (mg/d)

K_p = Contaminant partition co-efficient for product 'p'

For organics

$$\log K_{\text{meat}} = -6.88 + 0.832 \log K_{\text{ow}} \quad (\text{B3})$$

$$\log K_{\text{milk}} = -6.786 + 0.731 \log K_{\text{ow}} \quad (\text{B4})$$

$$\log K_{\text{fat}} = -3.457 + 0.500 \log K_{\text{ow}} \quad (\text{B5})$$

Note: $\log K_{\text{ow}} (\text{PCP}) = 5.05$ (AERIS, 1991)

Average livestock product consumption rates (average of mean value for males and females) are summarised as follows (Langley, 1996):

- Meat: Male: 308 g/d
Female: 183 g/d
Average: 246 g/d
- Milk: Male: 356 g/d
Female: 247 g/d
Average: 302 g/d

Table B1 presents estimates of the intake of PCP by consumers of livestock products associated with exposure to 1 mg/L of PCP in stockwater. The acceptable concentration of PCP in stockwater can then be determined by ratio as required. On this basis a preliminary acceptance criterion for PCP in stockwater of 0.14 mg/L is nominated. The nominated criterion should be regarded as preliminary reflecting the uncertainty associated with modelling the uptake and accumulation of PCP in livestock.

B3. PROTECTION OF STOCK HEALTH

The derivation of water quality criteria protective of stock health presented below draws on that outlined in Appendix XV of the Canadian Water Quality Guidelines (CCME, 1993).

For the purpose of deriving acceptance criteria, cattle have been selected as a representative of livestock as it has been reported that the range of water consumption per unit body weight ratio is similar in both the larger (i.e. cattle) and the smaller animal (i.e. goat) (CCME, 1993).

The acceptance criteria may be derived as follows:

$$\text{Acceptance Criterion} = \frac{\text{Acceptable Daily Intake (ADI) x Body Weight}}{\text{Water Ingestion Rate}} \times \text{Proportion Assigned to Drinking Water} \quad (\text{B6})$$

where:

Body Weight	= 500 kg	(Shell, 1994)
Water ingestion rate	= 55 L/day	(Shell, 1994)
Proportion assigned to drinking water	= 0.5	

Table B1
Preliminary PCP Groundwater Acceptance Criteria Based on Protection of Human Health:
Exposure Via Consumption of Livestock

Oral slope	0.12 mg/kd/d ¹	Base water conc:	1 mg/L
Target risk	1.0E-05	Cattle ingestion rate:	55 kg/d
		Human body weight:	70 kg

Product Consumption (g/d)			
Product	Male	Female	Average
Meat	308	183	246
Milk	356	247	302

Cattle product	Partition coefficient	Total intake for cattle (mg/d)	Concentration (mg/kg, fresh weight)	Average consumption rate (g/d)	Estimated human intake (mg/d)	Body weight (kg)	CDI (mg/kg/d)	Dose response factors (mg/kg/d) ¹	Estimated cancer risk for 1 mg/kg PCP in soil
Meat	2.10E-03	5.50E+01	1.16E-01	246	2.8E-02	70	4.1E-04	0.12	4.86E-05
Milk	8.10E-04	5.50E+01	4.46E-02	302	1.3E-02	70	1.9E-04	0.12	2.30E-05
Combined					4.18E-02	70	6.0E-04	0.12	7.16E-05

Notes: (1) Equates to target risk

Acceptable groundwater concentration! 0.14 mg/L

In selecting the dose response factors (e.g. ADI) for use in establishing the stockwater acceptance criteria, it has been assumed that:

- Cancer is not a relevant endpoint for the establishment of stockwater criteria protective of cattle. The basis for this assumption relates to:
 - the lower level of protection that may be assigned to livestock compared to humans;
 - the relatively low risk of cancer expected at exposure levels consistent with protection against other adverse health effects; and
 - at least in the case of beef cattle, the relatively short duration of exposure compared to the natural life span of cattle; and
- Full protection of all sensitive sub-populations is not required.

On this basis, the ADI for the contaminants of concern has been determined from experimental data for a non-carcinogenic endpoint, assuming a threshold dose response relationship. The preliminary acceptance criteria for PCP based on the protection of livestock health, and the basis for the derivation, are summarised in Table B1.

Toxicological information for PCP is summarised in Section 5.5. Reference Doses/Acceptable Daily Intakes for PCP nominated by various agencies range from 0.03 mg/kg/day to 0.003 mg/kg/day. The DWSNZ nominate a NOAEL for PCP of 3 mg/kg/day and apply an Uncertainty Factor of 1000. On this basis an acceptable daily intake for the protection of stock health of 0.03 mg/kg/day has been used as the basis for the derivation of the stockwater acceptance criteria (i.e. Uncertainty Factor of 100 rather than 1000 reflecting the lower level of protection assigned to stock compared to humans). It may be argued that an acceptable intake of 0.3 mg/kg/day could be used for derivation of stock water criteria, given the Uncertainty Factor nominated in the DWSNZ includes some consideration of the potential carcinogenicity of technical grade PCP. However, in this case a conservative approach has been adopted for the derivation of preliminary criteria.

Based on the assumptions outlined above, a preliminary stockwater acceptance criterion for PCP, that is protective of stock health, of 0.015 mg/L has been nominated.

Considering both the protection of stock health and human health a preliminary acceptance criterion for PCP in stockwater of 0.15 mg/L is nominated.

B4. REFERENCES

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