

Aquatic Ecotoxicity of Cutback Bitumen

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Executive summary

Introduction

Most chipsealing in New Zealand is carried out using bitumen cutback (i.e. diluted) with kerosene. Under the new regulatory framework established by the Hazardous Substances and New Organisms (HSNO) Act (1996), bitumen with the addition of kerosene between 2.5–20% by weight has been classified as a 9.1C substance that is 'ecotoxic to the aquatic environment'. Other (non-ecotoxicity related) classifications also apply. Cutback bitumens with more than 20% kerosene are not classified.

The 9.1C ecotoxicity classification is derived from a calculation based on the aquatic toxicity of kerosene. Implicit in this classification is the assumption that the kerosene in cutback bitumen has the same bioavailability as pure kerosene. The object of this research was to establish whether this assumption is valid and whether the 9.1C classification for cutback bitumens is warranted. The research focused solely on aquatic ecotoxicity; other possible environmental affects of cutbacks in the atmosphere or terrestrial environment caused by toxicity or mechanical fouling were outside its scope.

As a review of the literature failed to find any experimental data on the aquatic ecotoxicity of cutbacks, an experimental programme was undertaken.

Experimental method

Bitumen and kerosene are multi-component substances that have very low solubilities in water. Testing the aquatic toxicity of such materials is difficult. The procedure generally used for preparing media for testing of aquatic toxicity of sparingly soluble materials is the water accommodated fraction (WAF) method. In this approach, the test material is brought in contact with water until those components that are soluble in water have reached an equilibrium concentration in the water phase. The water is separated from the insoluble material and test organisms are introduced. The concentration of the test substance is expressed as the bulk 'loading rate' (mg of substance per litre of water) rather than in terms of the aqueous concentration of the individual soluble components (which in most cases are unknown and impractical to measure).

In terms of modelling likely 'real-world' scenarios by which cutback may contaminate aquatic ecosystems, the WAF approach represents a worst-case scenario. These scenarios in which an equilibrium concentration could be reached are not completely unrealistic (for example, a tanker of kerosene-modified bitumen emulsion spilling into a small pond or lake) and cannot be discounted. In other scenarios, such as leaching of a cutback chipseal surface by rainwater, concentrations will probably be very much lower.

A cutback with a kerosene concentration of 9.8 % (13.6 pph) was used to prepare the WAF for aquatic ecotoxicity testing. This concentration is well above the levels typically in use on roads and represents the upper concentration of kerosene used. To determine the time needed for water-soluble kerosene components to reach equilibrium in the water phase, a spectrophotometric method was developed in which water samples were extracted with pentane and the absorbance at 215 nm measured.

Toxicity test results

Two 9.8% kerosene cutback loadings were tested with *Daphnia magna* (a minute crustacean): 10 mg/L and 100 mg/L. Two additional loadings of 1 mg/L and 100 mg/L were tested with algae. In each case, the WAF was a clear liquid with a kerosene odour. For all tests a blank WAF was also prepared following the standard procedure, but without cutback. Results of the *Daphnia* acute tests are given in Tables 1 and 2.

Table 1 *Daphnia* acute 48 hr toxicity test results: 100 mg/L loading.

Test Material	Survival (%)	Significant difference (p<0.05) to control	Significant difference (p<0.05) to blank WAF
Control	90.0	-	-
Blank WAF	90.0	No	-
Cutback WAF	86.0	No	No

Table 2 *Daphnia* acute 48 hr toxicity test results: 10 mg/L loading.

Test Material	Survival (%)	Significant difference (p<0.05) to control	Significant difference (p<0.05) to blank WAF
Control	98.0	-	-
Blank WAF	94.0	No	-
Cutback WAF	94.0	No	No

The *Daphnia* results indicate that acute toxicity will only occur at loadings of over 100 mg/L for the 9.8% cutback.

Algal growth tests are considered chronic tests because the effects are assessed over several generations during the usual 3–4 day exposure period. Significant toxicity to algae occurred at 100 mg/L (where growth was 81% of that in the control). No significant toxicity was observed at a loading of 1 mg/L. These results indicate that chronic toxicity occurs at a loading of 9.8% cutback between 1 and 100 mg/L.

Conclusion

ERMA provides four grades of aquatic toxicity. The object of this work was to determine whether the 9.1C classification for cutback bitumen was warranted. The *Daphnia* test results show that acute toxicity of 9.8% cutback bitumen occurs at loading levels above 100 mg/L, indicating that the 9.1C classification is too stringent. The algal test results show that chronic toxicity occurs at a loading of 9.8% cutback of 100 mg/L. Only two concentrations were tested. If more concentrations between 1 and 100 mg/L were tested, it is highly likely that the no-observed effect concentration (NOEC) would have been >1 mg/L especially given the relatively small effect on growth observed at the highest concentration of 100 mg/L. As such, the 9.1D classification may also not be warranted.

Furthermore, although it has been demonstrated that some kerosene components can migrate from the cutback into the water column (and kerosene has been shown previously to be not readily biodegradable and is bioaccumulative), the toxicological evidence presented here indicates that cutback bitumen may in fact meet the 'not classified' criteria. Once again it should also be noted that these tests were conducted with 9.8% cutback, adopting a 'worst-case' scenario. In practice, the level of kerosene present in cutbacks would usually be almost half of that used for the tests and therefore the current classification is certainly too stringent.

Abstract

Under the New Zealand regulations established by the Hazardous Substances and New Organisms (HSNO) Act (1996), bitumen to which between 2.5 and 20 % by weight kerosene is added is classified as a 9.1C substance that is 'ecotoxic to the aquatic environment'. This research aimed to establish whether this classification is warranted for cutback bitumens.

A cutback with 9.8% kerosene (13.6 pph) was used to prepare water accommodated fraction (WAF) samples for aquatic ecotoxicity testing. This concentration of kerosene is the highest actually used on roads. The concentration of kerosene components in the water phase was measured spectrophotometrically at 215 nm after extraction with pentane. Equilibration was achieved after 24 hours at 20°C.

The ecotoxicities of two cutback loadings in water were tested with *Daphnia magna* and freshwater algae. *Daphnia* 48 hr acute tests indicate that toxicity occurs at levels >100 mg/L. The 72 hour algal tests showed the average growth rate in the 100mg/L WAF to be 81% of the blank. The 1 mg/L loading showed no significant effect on growth rate. The algal results indicate that chronic toxicity occurs at a level >1 but <100 mg/L.

The results show that the current classification for cutback bitumens is too stringent and indicate that cutback bitumen may meet the 'not classified' criteria.

1. Introduction

Most chipsealing in New Zealand is carried out using bitumen cutback (i.e. diluted) with kerosene. Under the new regulatory framework established by the Hazardous Substances and New Organisms (HSNO) Act (1996), bitumen is not considered hazardous to the environment. However, bitumen to which between 2.5 and 20% by weight kerosene is added has been classified (NZ Gazette 2004) as a 9.1C substance that is 'ecotoxic to the aquatic environment' (see Table 1.1).

Other classifications which also apply to cutbacks are (Leary & Eng 2003):

- Cutback bitumen containing >10% kerosene: 3.1D Flammable, 6.3B Toxic
- Cutback bitumen containing >7% but <10 % kerosene: 3.1D Flammable
- Cutback bitumens with greater than 20% kerosene are not classified

The 9.1C ecotoxicity classification was derived from a calculation based on the aquatic toxicity of kerosene. Implicit in this classification is the assumption that the kerosene in cutback bitumen has the same bioavailability as pure kerosene. The object of this research was to establish whether this assumption is valid and whether the 9.1C classification for cutback bitumens is warranted. The research focused solely on aquatic ecotoxicity; other possible environmental effects of cutbacks in the atmosphere or terrestrial environment caused by toxicity or mechanical fouling were outside the scope of the current project.

Table 1.1 Environmental Risk Management Authority (ERMA) Aquatic ecotoxicity classifications (ERMA 2001b). Definitions of terms are given in Appendix 1.

Category	Aquatic Ecotoxicity
9.1A (very ecotoxic in the aquatic environment)	Acute ecotoxicity L(E)C ₅₀ ≤ 1.0 mg/L regardless of any persistence or bioaccumulation or chronic ecotoxicity information
9.1B (ecotoxic in the aquatic environment)	(Note: If there is chronic aquatic ecotoxicity data available that shows that the NOEC is greater than 1 mg/l, then this category does not apply) Acute ecotoxicity L(E)C ₅₀ between 1 and 10 mg/l AND persistent (lack of rapid degradability) OR Acute ecotoxicity L(E)C ₅₀ between 1 and 10 mg/l AND bioaccumulative OR Acute ecotoxicity L(E)C ₅₀ between 1 and 10 mg/l AND Persistent (lack of rapid degradability) AND bioaccumulative.
9.1C (harmful in the aquatic environment)	(Note: If there is chronic aquatic ecotoxicity data available that shows that the NOEC is greater than 1 mg/l, then this category does not apply) Acute ecotoxicity L(E)C ₅₀ between 10 and 100 mg/l AND persistent (lack of rapid degradability) OR Acute ecotoxicity L(E)C ₅₀ between 10 and 100 mg/l AND bioaccumulative OR Acute ecotoxicity L(E)C ₅₀ between 10 and 100 mg/l AND persistent (lack of rapid degradability) AND bioaccumulative.
9.1D (slightly harmful to the aquatic environment or otherwise designed for biocidal action)	Acute ecotoxicity L(E)C ₅₀ between 1 and 100 mg/l AND Not Persistent AND/OR Not Bioaccumulative OR Acute ecotoxicity L(E)C ₅₀ between 1 and 100 mg/l AND Persistent AND/OR bioaccumulative AND chronic ecotoxicity (NOEC) is greater than 1 mg/l OR Chronic aquatic ecotoxicity (NOEC*) less than or equal to 1 mg/l AND not persistent AND/OR not bioaccumulative (note: Acute ecotoxicity is > 1 mg/L) OR Persistent AND bioaccumulative AND no information that the chronic ecotoxicity (NOEC) is greater than 1 mg/l water OR Substance designed for biocidal action, other than biocidal action against a virus, protozoan, bacterium, or an internal organism in humans or in other vertebrates, but does not meet the criteria for any hazard classification in Class 9 other than 9.1D.
Not classified	Chronic ecotoxicity (NOEC) is greater than 1 mg/L AND Acute ecotoxicity is greater than 100 mg/L (regardless of whether it is persistent or Bioaccumulative).

*NOEC: No observed effect concentration

2. Background

2.1 The use of kerosene in cutback bitumen

Cutback bitumen is composed of a mixture of bitumen and kerosene. The purpose of the kerosene is to temporarily soften the binder so that surfacing chip can be manipulated by traffic to form a strong aggregate mosaic. The convention in the New Zealand road contracting industry is to express the concentration (C) of kerosene (and other additives) in a cutback in terms of parts of kerosene per hundred parts of bitumen (pph) on a by-volume (V) basis. The concentration in parts per hundred is calculated using the formula:

$$C_{pph} = (V_{\text{kerosene}} / V_{\text{bitumen}}) \times 100 \quad (\text{Equation 2.1})$$

The concentration in percent by volume ($C_{v\%}$) is calculated using C_{pph} :

$$C_{v\%} = 100 \times (C_{pph} / (100 + C_{pph})) \quad (\text{Equation 2.2})$$

Assuming bitumen and kerosene densities of 1.0 and 0.8 gcm⁻³ respectively, then the concentration in percent by weight ($C_{w\%}$) is:

$$C_{w\%} = 100 \times ((C_{pph} \times 0.8) / (100 + (C_{pph} \times 0.8))) \quad (\text{Equation 2.3})$$

A concentration of 10 pph for example is equal to 9.1 v% or 7.4 w%.

To convert from C_{pph} to $C_{w\%}$:

$$C_{pph} = (C_{w\%} \times 100) / (80 - (0.8 \times C_{w\%})) \quad (\text{Equation 2.4})$$

Unless otherwise stated, percent concentrations refer to $C_{w\%}$.

Transit New Zealand (TNZ) sealing specifications TNZ P/03 (TNZ 1995a) and TNZ P/04 (TNZ 1995b) allow up to 16 pph (11.3%) kerosene for use in cold weather. In practice, concentrations used are usually no greater than 7 to 8 pph (5.3 to 6.0%). An informal Roothing New Zealand survey of cutback sealing work completed by a representative range of contractors for the 2003–2004 season found the range of kerosene contents used as given in Table 2.1.

Table 2.1 Kerosene content of cutbacks used for sealing work in 2003–2004.

Kerosene content pph (%)	Volume of bitumen used (%)
0	40
0-5 (0–3.8%)	39
5-12 (3.8–8.8%)	21

Note

(a) Information from Alan Stevens of Roothing NZ (pers. comm. 2005)

In theory, new road surfaces can be primed with cutbacks containing around 50% kerosene, but use of this material for priming is very rare, if not extinct. Bitumen emulsions (used in approximately 10% of total seals) also often incorporate small amounts of kerosene, typically 2% or less of the bitumen content.

The success of a cutback seal depends on rapid evaporation of the kerosene. Field trials to monitor kerosene loss were conducted in Lower Hutt using 5 and 10 pph (3.8% and 7.7 %) cutback grade 3 chipseals (Ball 1992, Herrington & Ball 1994). The trials revealed that three minutes after spraying onto the road, 15% of the initial kerosene content at both sites had been lost. After five years about 80% of the added kerosene had evaporated (Figure 2.1).

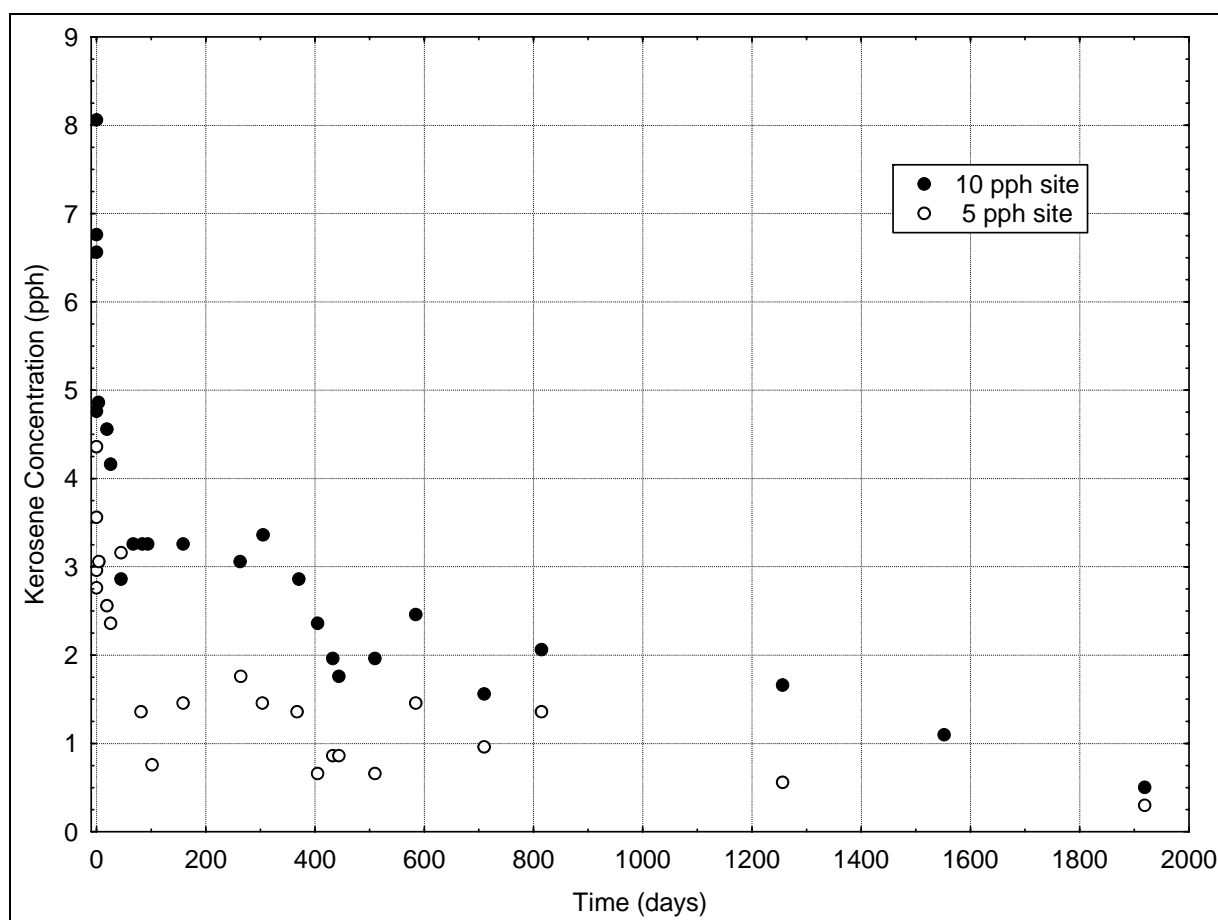


Figure 2.1 Kerosene loss from field trials in Lower Hutt.

Note:

(a) Data from an adjacent control site were used to correct for background losses caused by water etc.

Cutback bitumens are prepared by in-line blending and are transported in bitumen sprayers or tankers (of up to about 10 000 L capacity). Cutbacks are sprayed at around 160°C. At high kerosene concentrations, cutbacks have a consistency at room temperature similar to molasses; typical viscosities for sealing grade bitumen cut back with kerosene are given in

Table 2.2. Cutbacks are less dense than water and will float and spread slowly to form a thin layer over the surface of a body of water.

Table 2.2 Viscosities of common bitumen grades cutback at different concentrations.

Kerosene content (w%)	Viscosity at 60°C (Pa-s)	
	180/200 Grade bitumen	80/100 Grade bitumen
1	37.7	128.1
2	27.0	87.1
3	19.6	60.1
4	14.4	42.1
5	10.7	29.9
6	8.1	21.5
7	6.1	15.6
8	4.7	11.5
9	3.6	8.6
10	2.8	6.5

Accidental contamination of waterways from cutback bitumen can occur in a number of ways. Theoretically, accidental cutback spillage can occur from faulty pipelines on tankers or sprayers, but this would be rare as sprayers have to be inspected and relicensed annually. In an extreme case, a sprayer may overturn, either on or off the road. The insulation and outer sheaths on sprayers commonly act as buffers to reduce the loss of material in this situation. However, a number of instances of tankers rolling and discharging significant quantities of material into waterways have been reported in the last ten years (see Appendix B). Cutback bitumen could also enter the aquatic environment as run-off into gutters and storm-water drains from badly managed sealing or caused by a sudden heavy rainstorm during sealing. The possibility of significant levels of kerosene leaching into rain water on the surface of a finished seal is unlikely. The experimental approach taken to model cutback contamination of waterways is discussed in Chapter 3.

2.2 Constituents of cutback bitumen

2.2.1 Bitumen

2.2.1.1 Composition

Bitumens are the residues from the distillation of crude oil. The softest sealing grade used in New Zealand (180/200 grade) is produced by straight-run vacuum distillation (370°C, 60–70 mbar). Harder grades (130/150 and 80/100) are manufactured by air blowing and blending back into the 180/200 grade.

Bitumens consist mainly of a complex mixture of hydrocarbons of carbon number C_{25} and above. Average bitumen molecular structures (from molecular weight, elemental analysis and

Nuclear Magnetic Resonance (NMR) data) consist of one or two, 3 or 4-ring condensed aromatic systems with several aliphatic side chains and alicyclic systems attached. Bitumen comprises about 25–35% aromatic, 15–30% alicyclic and 35–60% aliphatic carbon (Branthaver et al. 1993, Herrington et al. 1994, Petersen 2000). Low levels of sulphur-containing compounds, mainly thiophenes and sulphides, are present as are pyridinic and pyrrolic nitrogen heterocycles. Metals, principally nickel and vanadium, are present largely as porphyrin-type complexes. Oxygen is present mainly as sulphoxide and ketone functionalities. Although there are differences in bitumen composition caused by the crude oil source, the types of species and functional groups present in bitumens are generally similar.

Measurement of bitumen molecular weight is difficult as inter-molecular association can lead to erroneously high results. Average values are typically 600–700 with the upper range probably in the region of 2000–3000 amu. (Moschopedis et al. 1990, Domin et al. 1999).

The most widely used bitumens in New Zealand are manufactured from Middle East crude oil. A typical analysis (using Safaniya bitumen) and average structural parameters are given in Table 2.3. Most 2–4 aromatic ring systems present are incorporated into larger molecules; hence concentrations of carcinogenic polyaromatic hydrocarbons (PAH) are low (Hangebrauck et al. 1967, Wallcave et al. 1971, Brandt et al. 1985). A PAH analysis for New Zealand Safaniya bitumen is given in Table 2.4.

Table 2.3 Safaniya bitumen composition (Herrington 2004).

Element or compound	Unit
Carbon	83.7 wt%
Hydrogen	10.8 wt%
Nitrogen	0.5 wt%
Sulphur	5.5 wt%
Nickel	18 ppm*
Vanadium	65 ppm
Asphaltene Content (n-heptane)	13.0 %

*parts per million

Note: The average molecular weight of Safaniya bitumen is 630 amu

Table 2.4 Safaniya bitumen analysis of selected PAH by gas chromatography mass spectrometry (GCMS) (Herrington et al. 1993).

Compound	Concentration (mg/kg)
Fluoranthene	Detected
Pyrene	Detected
Benzo[<i>a</i>]anthracene	Detected
Chrysene	Not detected
Benzo[<i>b</i>]fluoranthene	12.1
Benzo[<i>k</i>]fluoranthene	0.1
Benzo[<i>a</i>]pyrene	0.15
Dibenzo[<i>a,h</i>]anthracene	Not detected
Benzo[<i>a</i>]chrysene	5.0
Benzo[<i>g,h,i</i>]perylene	1.7

Note to Table 2.4: The detection limit was 0.002 mg/kg).

2.2.1.2 Fate of bitumen in the environment

No specific data are available relating to transport and distribution of bitumen among environmental media, environmental transformation and degradation, interaction with physical, chemical or biological factors, or bioconcentration (WHO 2004, Barksdale et al. 1993). Bitumen is thought to be highly stable in the environment. In water, bitumen is insoluble and is expected to show little migration (CONCAWE 1992). In soil, bitumen is likely to be both immobile and inert.

Although the constituents of bitumen have high log K_{ow} (the steady state ratio of the solubility of a substance in n-octanol to the solubility of that substance in water), which suggests they are potentially bioaccumulative, they have an extremely limited bioavailability (CONCAWE 1992). Their low water solubility and high molecular weights indicate that the bioaccumulation of bitumen is highly unlikely (King et al. 2001).

Some studies exist in which the leaching characteristics of bitumen or bitumen waste were studied (Townsend & Brantley 1998, Bowen, de Groot & Brandt 2000). Townsend & Brantley (1998) found no volatile organic compounds, PAHs or heavy metals in the leachate after performing a standard leachate test on asphalt road waste. Bowen et al. (2000) conducted static leaching tests and characterised the leaching behaviour of PAHs from nine different bitumens. They found that PAH concentration in leachate reached a steady state between days 4 and 9 and were predominantly naphthalene (n.d.: 371 ng/L) and phenanthrene (3–182 ng/L). These levels are below European limits for surface water and were not considered to pose a hazard to aquatic environments.

Kriech (2000) used the Environmental Protection Agency (EPA) SW846-1311 and SW846-351 Toxic Characteristic Leachability Procedure (TCLP) to study water leaching of hot mix asphalt (bitumen mixed with mineral aggregate). Naphthalene (250 ng/l) was detected but other PAHs and a range of semi-volatile organics were not present above detection limits (the detection limit was not given).

2.2.1.3 Ecotoxicity of bitumen

The predicted water solubility of bitumen is so low that no effects would be expected on aquatic organisms (King et al. 2001). The only ecotoxicity data for bitumen is a 56-day laboratory plant study where bitumen was shown to have no effect on growth of either beans (*Phaseolus vulgaris*) or corn (*Zea mays*) (Miller et al. 1980).

Trials beginning in the 1960s were conducted on the use of bitumen emulsion as an agricultural mulch. Thin films of bitumen were sprayed over the soil surface to increase crop yields without any apparent damaging effects on soil fauna (Morgan & Mulder 1995).

Aquatic toxicity data are available for 'Orimulsion', a stable emulsion of a natural Venezuelan (Orinoco) bitumen (70%) and water (30%) used as a fuel (Marcano et al. 1991, Svecevicus et al. 2003). Laboratory tests were conducted on rainbow trout exposed to the dispersed- and water-soluble fraction of Orimulsion added to water. The reported toxicity values are given in Table 2.5. The observed toxicity was thought to be partly caused by the soluble components (such as emulsifiers) of 'Orimulsion' and in part caused by small particles of dispersed bitumen blocking fish gills.

Table 2.5 Acute aquatic toxicity test data (96-h LC₅₀) for 'Orimulsion' in three stages of the rainbow trout life cycle (from Svecevicus et al. 2003).

Life stage	Value (mg/L)
Adults	2220
Larvae	60
Embryos	100

2.2.1.4 HSNO classification of bitumen ecotoxicity

Bitumen was originally classified as class 9.1D (slightly harmful to the aquatic environment) in the initial draft of the Transfer Regulations (see also Table 1.1):

A [9.1D substance is a] substance for which data indicate that:

(a) (i) the acute aquatic ecotoxicity value is greater than 1 milligram per litre of water but less than or equal to 100 milligrams of the substance per litre of water, but which does not meet the criteria for hazard classification 9.1B or 9.1C; or

(ii) the chronic aquatic ecotoxicity value is less than or equal to 1 milligram of the substance per litre of water, but which does not meet the criteria for hazard classification 9.1A, 9.1B, or 9.1C; or

(b) A substance that is designed for biocidal action, other than a substance that is designed for biocidal action against a virus, protozoan, bacterium, or an internal organism in humans or in other vertebrates, but does not meet the criteria for any hazard classification in Class 9 other than 9.1D; or

(c) A substance that is not rapidly degradable and that is bioaccumulative, unless the chronic aquatic ecotoxicity value is greater than 1 milligram of the substance per litre of water, but that does not meet the criteria for hazard classification 9.1A, 9.1B, or 9.1C. (ERMA 2001)

If the NOEC is greater than 1 mg/L the substance is excluded from this classification step.

However, subsequently this classification has been removed and bitumen is not classified as ecotoxic to the environment and will not be a substance controlled by HSNO (Annex 2 of Leary & Eng 2003).

2.2.2 Kerosene

2.2.2.1 Composition

Kerosene is obtained by atmospheric distillation of crude oil and consists mainly of normal and branched chain alkanes, cycloalkanes, alkyl benzenes and alkyl naphthalenes (Ellison et al. 1999). Aliphatic hydrocarbons are the primary components (80%) ranging from C₉ to C₁₆ with log K_{ow} values of about 5–8. Aromatic hydrocarbons make up about 20% of the components and consist mainly of single-ring compounds such as alkylbenzene. There are also some two-ringed compounds, mainly naphthalene and methylnaphthalene, with log K_{ow} values between 3.3 and 6. The boiling range is normally from 145°C to 300°C. Various grades of kerosene are manufactured by further processing of straight-run kerosene which alters the composition slightly. Chemical analyses of three European grades are given in Table 2.6.

In New Zealand, two grades of kerosene are routinely manufactured at the New Zealand Refining Company (NZRC) Marsden Point refinery: premium and Jet-A1 grades. The Jet-A1 grade is used principally for aircraft fuel. The premium grade is sold (under various trade names) for heating and industrial applications, and is the 'lighting' grade kerosene specified in the TNZ M/1 roading bitumen specification (TNZ 1995) for use as a bitumen diluent. This product, as supplied in New Zealand, is approximately equivalent to the hydrocracked product in Table 2.6. Typical properties of Premium grade kerosene are given in Table 2.7 (a detailed chemical analysis is not available).

Table 2.6 Hydrocarbon distributions for three different grades of kerosene (Peterson et al. 1996).

Analysis	Unit	Sweetened kerosene CAS* No. 91770-15-9	Hydro-desulphurised kerosene CAS No. 64742-81-0	Hydrocracked kerosene CAS No. 101316-80-7
Boiling range:	°C	151	156	187
Initial		257	255	288
Final				
Density at 16°C	kg/m ³	800	803	808
Sulphur	mg/kg	281	<20	<20
Nitrogen	mg/kg	1	1	1
Chloride	mg/kg	<5	<5	<5
Oxygen	mg/kg	290	290	290
Branched alkanes	%(m/m)	20.0	16.5	36.6
n-Alkanes	%(m/m)	22.2	19.4	5.8
n-Alkane range(<0.1%)	%(m/m)	C ₇ -C ₁₇	C ₈ -C ₁₅	C ₈ -C ₁₈
Cycloalkanes	%(m/m)	33.5	35.9	30.9
Alkylbenzenes	%(m/m)	15.4	20.4	14.3
Indanes and tetralins	%(m/m)	3.1	3.8	8.2
Indenes	%(m/m)	0.1	nd	0.2
2-ring aromatics	%(m/m)	5.5	3.8	3.5
3-ring aromatics	%(m/m)	0.2	0.2	0.3

*CAS = Chemical Abstracts Service

2.2.2.2 Fate of kerosene in the environment

As discussed in Chapter 2.1, when kerosene is released into the environment as a component of cutback bitumen in a chipseal, it is expected that at least 80% of the constituent hydrocarbons (of kerosene) will evaporate over a 5-year period. The less volatile components of kerosene will persist in the seal for longer periods.

Table 2.7 Properties of New Zealand kerosene used in cutbacks*.

Method	Analysis	Unit	Value
ASTM** D86	Boiling range: Initial Final	°C	171.7 231.1
ASTM D86	Density	kg/L	0.8003
ASTM D5453	Total sulphur	mg/kg	<10
IP†170	Flash point (Abel)	°C	52.5
ASTM D1322	Smoke point	mm	28.0
IP10	CHAR value	mg/kg	4.00

*D. Jacobsen, pers. comm.

**American Society for Testing and Materials

† Institute of Petroleum

In water, kerosene hydrocarbons have low solubility, with the aromatic hydrocarbons being more soluble than the aliphatic constituents (Ellison et al. 1999). Water solubility data for a number of representative kerosene components are given in Table 2.8.

Table 2.8 Water solubility at 25°C of some representative kerosene hydrocarbons (Mackay & Shiu 1981).

Compound	Solubility* (mg/L)
1,2,3-Trimethylbenzene	75.2
Napthalene	30.8
t-Butylbenzene	31.8
1-Methylnapthalene	28.6
Acenapthalene	3.8
1,2,4,5-Tetramethylbenzene	3.5
n-Decane	0.038
Tetradecane	0.00458

*Average of data from several sources.

Because of its low density relative to water (0.8 kg/L), kerosene entering waterways through accidental spills or similar will float and form a thin layer on the surface. Kerosene components will be rapidly lost from this layer by volatilisation, particularly the lighter components (CITGO 1999). This will be the predominant loss process because the low solubility of kerosene in water will ensure the liquid-air interface is maximised. Some of the aromatic hydrocarbons with a higher molecular weight may move into the water phase, and some of these may be adsorbed to sediments. In stagnant and slow-flowing waterways, the hydrocarbon layer can cover a significant surface area and can limit oxygen transfer, which results in an anaerobic environment and causes fish mortality (CITGO 1999). This hydrocarbon layer can also be physically harmful or fatal as it can coat plankton, algae, aquatic life, and water birds.

In soils, most components of kerosene are primarily volatilised over the first few hours (i.e. 99% of aromatics were desorbed from soil and volatilised in less than 2 h (Archer et al. 1989). The heavier weight aliphatics are slower to volatilise and are more likely to remain adsorbed on the soil. The mobility of the unvolatilised components of kerosene in a soil layer depends on the proportion of liquid phase remaining, as well as the moisture content of the soil, with greater rate and depth of movement experienced at higher moisture levels (Archer et al. 1989). However, in sandy soils and/or soils with a low organic content, there will be less binding and an increased likelihood of movement resulting in groundwater and surface water contamination.

Although the hydrocarbon components of kerosene are inherently biodegradable (i.e. degradable by microbes), adsorption onto sediment and soil can slow this degradation. Kerosene is also regarded as being not readily biodegradable in standard tests (Ellison et al. 1999), but this is caused by the poor solubility in water. Furthermore, because kerosene contains components that have log K_{ow} values greater than three, they have the potential to partition into organic material and subsequently bioaccumulate. Measured bioconcentration factors (BCF) for kerosene constituents were 61–159 (Klein & Jenkins 1983). Metabolic processes are thought to 'preclude the realisation of significant bioconcentration of kerosene components' (Ellison et al. 1999). However, CITGO (1999) reported that naphtha and kerosene mixtures can bioaccumulate in concentrations of up to 1–10 ppm in fish tissues (CITGO 1999).

2.2.2.3 Aquatic ecotoxicity of kerosene

It is expected that the water solubility of kerosene alkanes with chain lengths of greater than 11 carbons will be too low to give rise to acute aquatic toxicity (Peterson et al. 1996). The water solubility of the alkylbenzenes and two-ringed aromatics is expected to be high enough to contribute to aquatic toxicity. As mentioned above, spillages of kerosene into water can kill fish directly through toxicity, or indirectly via anaerobic conditions or through fouling the water. There are some reports of impacts on aquatic biota following such spillages with quite long recovery times (CONCAWE 1995).

Conducting aquatic toxicity tests on sparingly soluble and/or volatile compounds such as kerosene is problematic. Results can vary depending on the methodology used and, for complex mixtures like kerosene, difficulties also arise in suitably expressing the findings of the experiment so that they can be compared against classification criteria such as those described in the HSNO regulations. When low density hydrocarbons such as kerosene are mixed with water, some will dissolve but the bulk will remain as an insoluble film on the water surface. The approach recommended by CONCAWE in such cases is the WAF (water accommodated fraction) method, whereby the insoluble fraction is removed and the toxicity test is conducted using the remaining fraction. The methodology for conducting ecotoxicological testing of petroleum products is further discussed in Chapter 3.2.

The CONCAWE document that outlines the rationale for the environmental classification of petroleum substances (King et al. 2001) reports on acute ecotoxicity studies that have been conducted according to the recommended methodology outlined above. Although each study is referenced in the CONCAWE document, all of the data originate in other reports, some with limited distribution, or without direct reference to kerosene (e.g. Hedtkke & Puglisi 1982) making verification of the information difficult. King and colleagues also report on one chronic study conducted by Klein & Jenkins in 1983. An older document (a CONCAWE product dossier on kerosenes and jet fuels) contains a much broader list of toxicity data for fish, invertebrates and other species (CONCAWE 1995). However, the interpretation of this earlier data is much more complicated caused by the variety of testing methodologies involved. Some additional data have been obtained from material safety data sheets that did not reference their source and are therefore difficult to critique (presumably data are sourced from company tests, but even that is not clear).

Table 2.9 reproduces some of the ecotoxicity data for kerosene. In the case of the chronic study conducted by Klein & Jenkins (1983), King et al. (2001) reported that the no-observed effect concentration (NOEC) for the growth rate of American flagfish (*Jordanella floridae*) was 1.0 mg/L. On closer inspection of the original report by Klein & Jenkins, the NOEC for growth in juvenile flagfish is reported as 1.5 mg/L. Furthermore, in the same article, a chronic lowest observed effect concentration (LOEC) value for rainbow trout (*Oncorhynchus mykiss*) growth of 1.4 mg/L is reported (Klein & Jenkins 1983). This 1.4 mg/L was the lowest concentration in the trout study, which implies that the NOEC for rainbow trout growth is an undefined concentration less than 1.4 mg/L.

Table 2.9 Toxicity test data for kerosene using a selection of test organisms.

Animal type	Species	Parameters	mg/L	Reference
Fish	<i>Oncorhynchus mykiss</i>	96 hour LL ₅₀ 96 hour NOEC	18-25 1.4-6.8	Peterson et al. 1996
	<i>Oncorhynchus mykiss</i>	112 day study on larvae growth	1.4 LOEC	Klein & Jenkins 1983
	<i>Brachydanio rerio</i>	96 hour LL ₅₀	7.3	King et al. 2001
	<i>Lepomis macrochirus</i> , <i>Carassius auratus</i> , <i>Lebistes reticulatus</i>	24-96 hour LL ₅₀	10-200	CITGO 1999
	<i>Jordanella floridae</i>	128 day study on egg hatching and larvae growth	1.7, 3.1 (NOEC, LOEC time to hatch) 1.5, 3.0 (NOEC, LOEC growth)	Klein & Jenkins 1983
	<i>Pimephales promelas</i>	96 hour LC ₅₀	6.1	Fisher et al. 1985
	<i>Notemigonus chytsoleucas</i>	96 hour LC ₅₀	7.5	Klein & Jenkins 1983
Invertebrates	<i>Daphnia magna</i>	48 hour EL ₅₀	1.4-21	Peterson et al. 1996
	<i>Chaetogammarus marinus</i>	96 hour LL ₅₀	1.4	CONCAWE 1995
Algae	<i>Raphidocelis subcapitata</i>	72 hour IrL ₅₀	3.7-8.3	Peterson et al. 1996
	<i>Pseudokirchneriella subcapitata</i>	48 hour IrL ₅₀	2.0	Mayer et al. 2000
Mixed	<i>Oncorhynchus mykiss</i> , <i>Cancer magister</i> (crab) and <i>Squalius cephalus</i>	96 hour LL ₅₀ in seawater	5-20	CITGO 1999

Note to Table 2.9

- Unless specified, all tests were conducted using a WAF approach where the non-soluble fraction is removed after initial mixing (see text above for explanation of this methodology).
- IrL₅₀ is the loading rate of a substance that inhibits growth or growth rate of the test population of organisms by 50%.
- LL₅₀ is the lethal loading rate of a substance that causes mortality of 50% of the test population of organisms within the specified exposure period.
- LC₅₀ is the dissolved concentration of a substance that causes mortality of 50% of the test population of organisms within the specified exposure period. See the Glossary (Appendix A) for more detail.

2.2.2.4 Soil ecotoxicity of kerosene

If kerosene were to be spilt onto the soil, most would volatilise. However, the remaining constituents would move through the soil (under moist conditions) and/or bind to soil particles, so the potential does exist for soil ecotoxicity. Large spills have been reported to adversely affect the environment for prolonged periods (Das et al. 1985; Ellison et al. 1999).

2.2.3 HSNO classification of kerosene ecotoxicity

Kerosene is classified by ERMA as a 9.1B substance, which is one that is ecotoxic in the aquatic environment (Leary & Eng 2003). It appears that this classification has been made based on the acute toxicity data as well as a NOEC value of 1 mg/L. The full description of a 9.1B substance as given in schedule 6 of the Hazardous Substances (Classification) Regulations 2001 is as follows (see also Table 1.1):

Unless the chronic aquatic ecotoxicity value is greater than 1 milligram of the substance per litre of water, a [9.1B substance is a] substance:

(a) for which data indicate an acute aquatic ecotoxicity value greater than 1 milligram, but less than or equal to 10 milligrams, of the substance per litre of water; and

(b) that is not readily degradable or is bioaccumulative, or is not readily degradable and is bioaccumulative. (ERMA 2001)

If the NOEC is greater than 1 mg/L the substance is excluded from this classification step.

The acute aquatic toxicity values given in Table 2.9 range between 1 and 200 mg/L, with the majority being between 1 and 10 mg/L. With its potential for bioaccumulation and poor degradation according to the standard protocols, kerosene fits the criteria for a 9.1B substance.

Kerosene could also fit the criteria for a 9.1D substance, given that the data generated by Klein & Jenkins (1983) for flagfish growth indicate an NOEC of 1.5 mg/L. However, this needs to be considered in light of their rainbow trout growth data that give an LOEC of 1.4 mg/L. Since this was the lowest concentration tested, an NOEC was not reported for this test. The implication is that the NOEC for trout growth is likely to be <1.4 mg/L (and possibly less than the threshold of 1 mg/L). Furthermore, difficulties with unexplained mortalities were experienced in both the flagfish and the trout studies of Klein & Jenkins (1983), which cast doubt on the reliability of their results. Extrapolation of LOEC values to NOEC values usually involves the application of a 'conversion factor' between 2 and 10. Application of the least conservative conversion factor of 2 would result in a NOEC of <1mg/L. Therefore, the classification of kerosene as 9.1B appears reasonable, and it is very possible that the ERMA classification is based on more appropriate and/or more data than that presented in Table 2.9.

The European (including UK) classification for kerosene is 'N – *Dangerous to the environment*' with a risk phrase of R51/53 (i.e. toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment) (King et al. 2001; CPL Petroleum Limited 2003).

In Australia, as of 6 August 2004, kerosene did not appear to have been assessed or classified by the National Industrial Chemicals Notification and Assessment Scheme

(NICNAS). Material safety data sheets for kerosene products in use in Australia (e.g. Easygleam 2003) do not indicate the environmental and/or aquatic hazard identified in the European data sheets.

In the United States, kerosene does not contain chemicals identified as toxic by the Environmental Protection Agency (EPA) under its Code of Federal Regulations (CFR) part 372 (T. W. Brown Oil 1999).

2.3 Cutback bitumens

2.3.1 Components of cutback bitumen

Cutback bitumen is a mixture of bitumen (Chapter 2.2.1) and kerosene (Chapter 2.2.2). Other additives are routinely added to cutback bitumen, including adhesion agents, diesel oil and sometimes polymers of various types. The ERMA classification of cutbacks is based solely on the presence of kerosene, and the possible effect of components other than kerosene and bitumen was not considered in this study.

2.3.2 Fate of cutback bitumen

No original information was available on the fate of cutback bitumen in the environment, but based on the characteristics of kerosene and bitumen, it is highly unlikely that the bitumen will move through the environment. However, kerosene will be released into the environment as a component of cutback bitumen. As discussed in Chapter 2.1, it is expected that, in a chipseal, 80% of the constituent kerosene hydrocarbons will evaporate within five years after application in a chipseal (Ball 1992, Herrington & Ball 1994). Cutback bitumen is not considered to be readily biodegradable, nor is it soluble in water, and in soils it is expected that it will adsorb to soil particles and be immobilised (TOSAS 2000).

2.3.3 Ecotoxicity of cutback bitumen

Leary & Eng (2003) state that there appear to be no ecotoxicity data on cutback bitumen. However, the TOSAS material safety data sheet states that cutback bitumen is practically non-toxic to aquatic organisms with L(E)C₅₀ ratings between 50 and 100 mg/L, but it is not clear where these toxicity data for cutback bitumen originate from or whether they are estimates.

2.3.4 HSNO classification of cutback bitumen ecotoxicity

Although bitumen is not considered to be ecotoxic to the aquatic environment, cutback bitumen has been given a classification of 9.1C (harmful in the aquatic environment) on account of its kerosene content (Leary & Eng 2003).

Most likely, ERMA has applied a 'mixture' rule (ERMA 2001) to determine the ecotoxicity of cutback bitumen, as a mixture containing a certain percentage of this hazardous substance.

If a substance has not been tested, a number of approaches are available for classifying mixtures. Kerosene has been identified as the ecotoxic substance in cutback bitumen while bitumen itself has not been classified as ecotoxic to the aquatic environment (Leary & Eng 2003). In this kind of situation, where kerosene is expected to dominate the ecotoxicity of cutback bitumen and the bitumen component is expected to have no ecotoxic consequences, an additivity formula is applied (for this formula, 'ker' indicates kerosene):

$$L(E)C50(\text{mixture}) = \frac{100 \times L(E)C50(\text{ker})}{\text{concentration}(\text{ker})\% \text{ weight}} \quad (\text{Equation 2.5})$$

Therefore, if we take the lowest acute toxicity value for kerosene (an EC₅₀ of 1 mg/kg), the ecotoxicity of cutback bitumen can be calculated based on the percentage of kerosene that it contains, as shown in Table 2.10.

Table 2.10 EC₅₀ values for bitumen cut back with different concentrations of kerosene.

Kerosene concentration of cutback bitumen (%)	EC ₅₀ (in mg/L)
1	100
2.5	40
5	20
10	10

ERMA has recommended a classification for cutback bitumen of 9.1C (harmful in the aquatic environment). The full description of a 9.1C substance given in schedule 6 of the Hazardous Substances (Classification) Regulations 2001 is as follows:

Unless the chronic aquatic ecotoxicity value is greater than 1 milligram of the substance per litre of water, a [9.1C substance is a] substance:

(a) for which data indicate an acute aquatic ecotoxicity value greater than 10 milligrams, but less than or equal to 100 milligrams, of the substance per litre of water; and

(b) that is not readily degradable or is bioaccumulative, or is not readily degradable and is bioaccumulative. (ERMA 2001)

If the NOEC is greater than 1 mg/L the substance is excluded from this classification step.

Cutback bitumen with a kerosene content of less than 2.5% does not have a 9.1 classification (Leary & Eng 2003), although it is not entirely clear why not.

This classification of the hazard of cutback bitumen assumes that all ecotoxic components will enter the aquatic environment and cause ecotoxicity and does not account for the likely fate and behaviour of kerosene if cutback bitumen is released into the environment.

One could argue that, as some components of kerosene are rapidly lost to the atmosphere when cutback bitumen is initially released into the environment, then the hazard to the aquatic environment could be assessed based on the reduced proportions. Although a significant amount (15%) is lost during the actual spraying operation, the rate of loss after cooling is slow; about one month is required to lose about 50% and 5 years to lose 80% (see Chapter 2.1). Assuming an immediate 15% loss on cutback entering the environment in an accident, the threshold for percentage kerosene would only be slightly modified as shown in Table 2.11, and cutback bitumen containing greater than 2.5% kerosene would still be classifiable as 9.1C.

Table 2.11 Toxicity values of cutback bitumen, allowing for losses.

Original concentration of kerosene (%)	Concentration of kerosene remaining after losses (%)	EC ₅₀ (mg/L)
1	0.85	118
2.5	2.13	47
5	4.25	24
10	8.5	12

In Australia, cutback bitumen does not appear to have been assessed or classified by the National Industrial Chemicals Notification and Assessment Scheme (NICNAS) (www.nicnas.gov.au 2004). However, there it is recognised that cutbacks may harm the aquatic environment. In Victoria, the EPA has published a set of guidelines which outline a variety of precautions to be taken, dependent on the weather (EPA, Victoria 2002).

Precautions include:

- delaying work,
- checking weather regularly,
- locating and blocking of stormwater entry points,
- carrying spill response equipment, and
- re-checking sealing sites if heavy rain occurs within 24 hours after spraying.

In the European Union since July 2004, the classification of a preparation (mixture) containing ecotoxic chemicals is based on a simple content rule (Health & Safety Executive, UK 2004).

The relevant Chemical Hazard Information and Packaging (CHIP) classifications used by the Health & Safety Executive in the UK are:

- R50/53 – very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.
- R51/53 – toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment. Kerosene is classified under this label.

2. *Background*

- R52/53 – harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment (Health & Safety Executive UK 2004, ERMA 2001).

Thus, taking the case of kerosene (classified as R51/53 when undiluted):

- A mixture containing 25% or more is classified as R51/53,
- A mixture containing 2.5% or more is classified as R52/53,
- Below 2.5%, no classification is required.

For New Zealand cutbacks commonly used (which have 5–6% kerosene added), the strongest classification would be R52/53. In Europe, this classification only requires a risk and safety label as follows: 'Harmful to aquatic organisms, may cause long-term adverse effects in the aquatic environment'.

3. Experimental methodology

3.1 Introduction

Given the lack of data on the aquatic ecotoxicity of cutbacks, a testing programme was undertaken. The primary object was to determine whether the L(E)C₅₀ for cutbacks was higher than 100 mg/L of water. In that case, the 9.1C ERMA classification would not be applicable.

In theory, a blend of 99% kerosene and 1% bitumen is still a cutback, but in practice, kerosene concentrations used are generally below 6% (8 pph). For the present study, a cutback with a kerosene concentration of 9.8% (13.6 pph) was used for aquatic ecotoxicity testing. This concentration is well above typical levels in use and represents the upper limit of kerosene concentration used in practice.

3.2 Experimental approach

Bitumen and kerosene are multi-component substances that have very low solubilities in water. Testing the aquatic toxicity of such materials is difficult. Adding cutback bitumen to water will result in a two-phase system, except at impractically low concentrations. Attempting to measure aquatic toxicity directly using a two-phase system runs the risk of the physical fouling of the test organisms. This is especially the case if the medium is stirred to keep the insoluble material dispersed. The procedure generally used for preparing media for testing aquatic toxicity of sparingly soluble materials is the 'water accommodated fraction (WAF) method'. This method has been recommended by the OECD (Organisation for Economic Cooperation), the Group of Experts on the Scientific Aspects of Marine Environmental Protection (GESAMP), the United Kingdom Department of Conservation (UK DoE), Conseil Européen de l'Industrie Chimique (European Chemical Industry Council) (CEFIC) and CONCAWE (CONservation of Clean Air and Water in Europe) (King et al. 2001). In this approach the test material is brought into contact with water until those components that are soluble in water have reached an equilibrium concentration in the water phase. The water is separated from the insoluble material and test organisms are introduced. The concentration of the test substance is expressed as the bulk 'loading rate' (milligram of substance per litre of water) rather than in terms of the aqueous concentration of the individual soluble components (which are unknown and impracticable to measure in most cases). In the case of volatile compounds (in this instance kerosene) minimising volatilisation is also necessary to maintain constant aqueous concentrations and thus measure the inherent toxicity of the test substance.

To prepare test media with a range of test substance concentrations, a fresh WAF needs to be prepared for each separate loading rate to be tested. Although diluting a high loading rate WAF will produce test media with the same relative component concentrations as lower rates,

saturation concentrations of poorly soluble components may actually be reached at low loading rates and so relative component concentrations will vary with loading rate (Benkinney et al. 1993).

The WAF approach and experimental methods for producing WAFs are discussed in detail elsewhere (Girling 1989, OECD 2000, Benkinney et al. 1993, Peterson et al. 1996, King et al. 2001).

For modelling realistic scenarios by which cutback may contaminate aquatic ecosystems, the WAF approach represents a worst-case scenario. These scenarios in which an equilibrium concentration could be reached are not completely unrealistic (e.g. a tanker of kerosene modified bitumen emulsion spilling into a small pond or lake) and cannot be discounted. Of course, concentrations will probably be very much lower in other scenarios, such as leaching of a cutback chipseal surface by rainwater. In the latter case, the presence of aggregate will also both reduce the surface area of binder exposed to rainwater and may physically absorb kerosene from the binder.

3.3 Loading rate

The purpose of this work was to establish whether the 9.1C classification for cutback bitumens was justified. For this reason, the experimental programme was designed to establish the effect of loadings (mg cutback/L water) relevant to the ERMA classifications rather than determine definitive values for the chronic and acute toxicities.

3.4 Materials

Kerosene was obtained from a local roading contractor and blended with Safaniya 180/200 penetration grade bitumen manufactured by the NZRC at the Marsden Point refinery and meeting the TNZ M/1 1995 specification. The blend was mixed by hand at 120°C. To allow for evaporative losses during mixing, the precise kerosene concentration was determined by weighing the blend after cooling. The sample (500 g) was stored in an airtight tin at 4°C in a refrigerator.

Water used for the aquatic toxicity tests was supplied by NIWA (National Institute of Water and Atmospheric Research) and contained low concentrations of salts to sustain the test organisms. Water used for the equilibration measurements met the requirements of ASTM Type I water (ASTM D1193-99e 1999). Pentane (95% HPLC (High Pressure Liquid Chromatography) grade), naphthalene and t-butylbenzene were all >99% purity and used as received.

3.5 Test temperature

Potentially, the temperature used for preparing WAFs of petroleum products could have a significant affect on solubility but surprisingly, this is usually not specified in the literature. A

temperature of 20°C, close to that at which the toxicity tests are carried out, was adopted for the preparation of the WAF.

3.6 Equilibration measurements

The appropriate weight of cutback bitumen was coated onto a 6 mm diameter glass rod and placed upright into a 2 L glass bottle with an airtight polypropylene screw cap. The bottle was filled with water so that when a 50 mm x 8 mm Teflon-coated stir bar and the glass rod with cutback were added, the water reached the lip of the bottle (about 2.280–2.290 L). The bottle was placed in the dark in a temperature-controlled cabinet at $20.9 \pm 0.6^\circ\text{C}$ and the contents were stirred at 500 rpm. Some experiments were also conducted with an 80 ml headspace above the water surface. The rod was of a length that allowed it to be completely submerged as it leaned against the side of the bottle. A section of the rod which was not in contact with the sides of the bottle was coated with cutback bitumen at an average thickness of 1 mm. The bottle was fitted with a Teflon tap about 10 mm from the bottom for sampling.

After the chosen interval, the bottle was removed from the cabinet and allowed to stand for 15 to 20 minutes. A sample of water (50 ml or 250 ml) was taken from the bottle into a narrow-necked volumetric flask. Pentane (4 ml) was added and the flask shaken vigorously for two minutes then left to stand for a further eight minutes. The upper pentane phase was drawn off and the absorption at 215 nm was measured in a 1.0 cm quartz cuvette in an HP8453 UV-visible spectrophotometer.

3.7 Extraction efficiency

The efficiency of the extraction procedure was investigated using representative kerosene aromatics as standards. Standard solutions were prepared in water and 50 ml extracted with 4 ml of pentane. The pentane extract was diluted by a factor of 10 before measurement by UV-visible spectrophotometry at a wavelength near an absorbance maximum. Concentrations were calculated using calibration curves based on standards prepared in pentane. The results (Table 3.1) indicate an average extraction efficiency of about 86%.

Table 3.1 Extraction procedure efficiency test results.

Compound	Concentration (mg/L)	Extraction efficiency
Napthalene	21.0	90
t-Butylbenzene	17.24	82

3.8 Aquatic toxicity testing

3.8.1 *Daphnia* acute studies

Aquatic toxicity testing was carried out by the NIWA laboratory at Hamilton, using the crustacean *Daphnia magna*. *Daphnia* culture water was prepared according to Martin (2004) and used to prepare 24 hour cutback bitumen WAFs as outlined above. The toxicity tests were carried out according to a standard protocol (OECD 1981). Test conditions are outlined in Table 3.2.

Table 3.2 *Daphnia* acute toxicity test conditions.

Test parameter	Condition
test organisms	<i>Daphnia magna</i> (juveniles <24 h old)
source	laboratory culture
organisms / container	10
replicates	5
reference toxicant	zinc sulphate
test duration	48 hours
test chambers	250 ml glass bottles, glass stoppers, no headspace
lighting	16:8 h light:dark
temperature	20±1°C
aeration	no aeration
effect measured	immobility
test acceptability	mean control immobility no greater than 10%

Table 3.3 Algal growth rate test conditions.

Test parameter	Condition
test organisms	<i>Pseudokirchneriella subcapitata</i>
source	laboratory culture
test type	static
organisms / container	10,000 cells/ml at time zero
replicates	5
reference toxicant	zinc sulphate
test duration	72 hours
sample pre-treatment	nil
dilution water	NIWA algal growth medium
test chambers	100 ml stoppered glass flasks, no headspace
lighting	continuous
temperature	24°C
aeration	no aeration, but incubated on a shaker table
effect measured	growth (cells/ml)
test acceptability	cell concentration in control treatments should increase by at least 16x within 3 days; controls coeff. var. % <20%.

The mobility of *Daphnia* exposed to either a 10 mg/L loading of 9.8% cutback or (on another occasion) 100 mg/L of 9.8% cutback was compared to responses in unexposed *Daphnia* using a

one-tailed t-test at a significance level of 5%. The tests also checked immobility in control 'blanks' that had been subjected to the same WAF procedure but without cutback bitumen. In this test, immobility of *Daphnia* is considered the same as mortality.

3.8.2 Algal growth inhibition

The algal growth test was undertaken in accordance with OECD 201 (OECD 1984), but adapted as in Peterson et al. (1996). Test conditions are outlined in Table 3.3.

Algae were exposed to either a 1 mg/L loading of 9.8% cutback or (on another occasion) 100 mg/L of 9.8% cutback, and growth after 72 h was compared to growth in control 'blanks' that had been subjected to the same WAF procedure but without cutback bitumen. Algal growth in each of the cutback WAF samples were compared to growth in their appropriate blank using a one-tailed t-test at a significance level of 5%.

4. Results and discussion

4.1 Equilibration

The WAF procedure requires that an equilibrium concentration of soluble cutback bitumen components is reached in the water phase. A calibration curve of kerosene in pentane was constructed and used to estimate the kerosene concentration in the water phase. This is adequate for comparative measurements but, as the solubilities of the aromatic constituents of the kerosene vary, the overall average absorption coefficient at the measurement wavelength will differ slightly from that of the pure kerosene used to construct the calibration curve and thus introduce an error. Therefore, the calculated values are referred to as 'equivalent kerosene concentrations'. Aliphatic components are not detected by the spectrophotometric method used. This is also the case for the kerosene solutions used to prepare the calibration curve so the non-detection of aliphatics will have no net effect. In any case, the solubilities of kerosene aliphatics in water are very low compared to the aromatics present.

In preliminary studies a loading of 100 mg/L was used with an 80 ml headspace left above the water phase to enable better mixing, as in the kerosene aquatic toxicity studies of Peterson et al. (1996). Although the cutback bitumen remained on the glass rod, the film was disturbed and began to 'bead' noticeably after about 48 hours. After prolonged exposure (>100 hours), small particles were found to have broken off from the bulk material and were visibly suspended in the water. As a precaution, the water samples taken for UV-visible analysis were passed through a 0.25 μ nylon syringe filter using large capacity syringes to remove any particles of cutback dislodged by stirring. Comparative experiments made using 24 hour exposure samples (free from particulates) showed that the filtering step did not result in any measurable loss of dissolved kerosene components.

Equivalent kerosene concentrations rose initially but declined at longer intervals, presumably caused by volatilisation, as shown in Figure 4.1. Control experiments using 100 mg/L bitumen (without kerosene) found extractables equivalent to about 0.1 mg/L kerosene irrespective of exposure time. Data presented in Figures 4.1 to 4.3 have been corrected for this background absorption. Control experiments with water alone gave the same result, indicating that bitumen leaching was negligible under the conditions used.

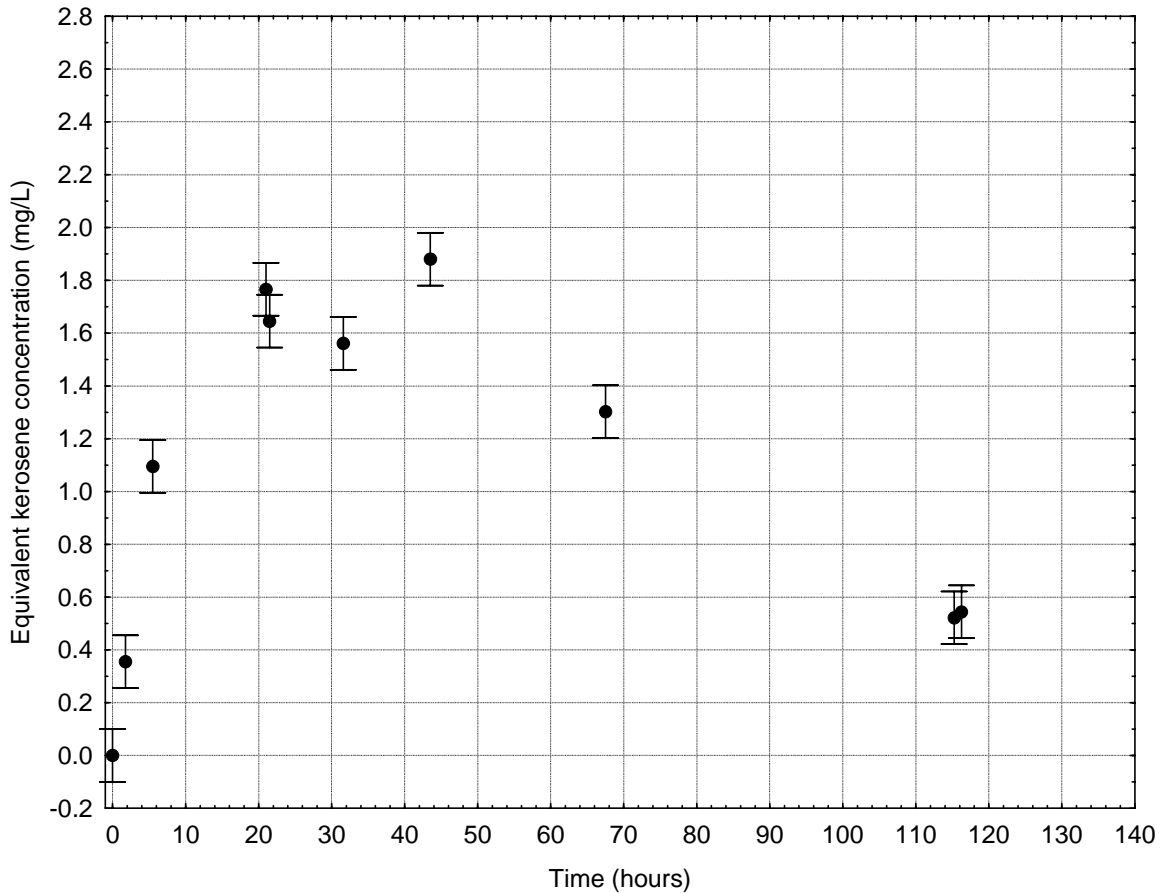


Figure 4.1 Equilibration of cutback bitumen (20°C, 100 mg/L loading with headspace).

Subsequent experiments were carried out with minimal headspace (about 1 ml), although adequate mixing still appeared to take place. By coating the cutback onto a glass rod, the specimen is kept submerged beneath the water surface so that mixing efficiency is less important than in the case of pure kerosene or other low density materials that tend to float on the surface. With minimal headspace, the equivalent kerosene concentration essentially reached equilibrium after about 24 hours. This period was used to prepare media for the aquatic toxicity tests. Similar behaviour was observed for a 10 mg/L loading (see Figure 4.2). The precision of the method was estimated as ± 0.2 mg/L, being the 95% confidence interval of four replicate 100 mg/L loadings with 52–53 hour exposure time measurements.

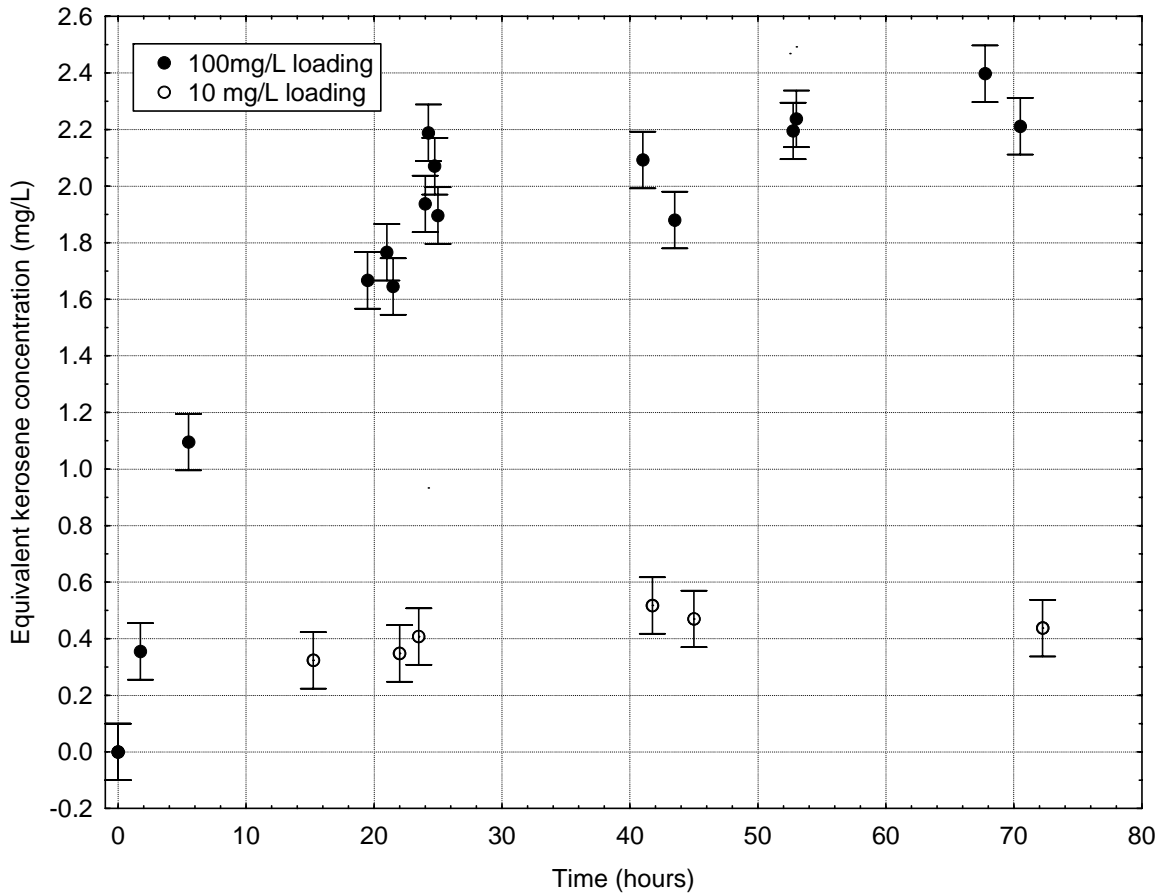


Figure 4.2 Equilibration of cutback bitumen (20°C, no headspace) with 10 mg/L and 100 mg/L cutback loadings.

Equivalent kerosene concentrations reached at equilibrium were about 2.1 mg/L and 0.4 mg/L for the 100 mg/L and 10 mg/L cutback loadings respectively. These concentrations represent solubilisation of about 20% and 40% of the available kerosene from the 100 mg/L and 10 mg/L loadings respectively. For comparison, Figure 4.3 shows the kerosene concentration in water from various loadings of pure kerosene after 24 hours mixing under the same conditions (although in this case the test bottles were allowed to stand undisturbed for an hour before sampling). With pure kerosene, equilibration was reached after only a few hours. At loadings of 100 mg/L and 10 mg/L, kerosene concentrations of about 25 and 6.5 mg/L respectively (25% and 65% of available kerosene) were measured in the water phase.

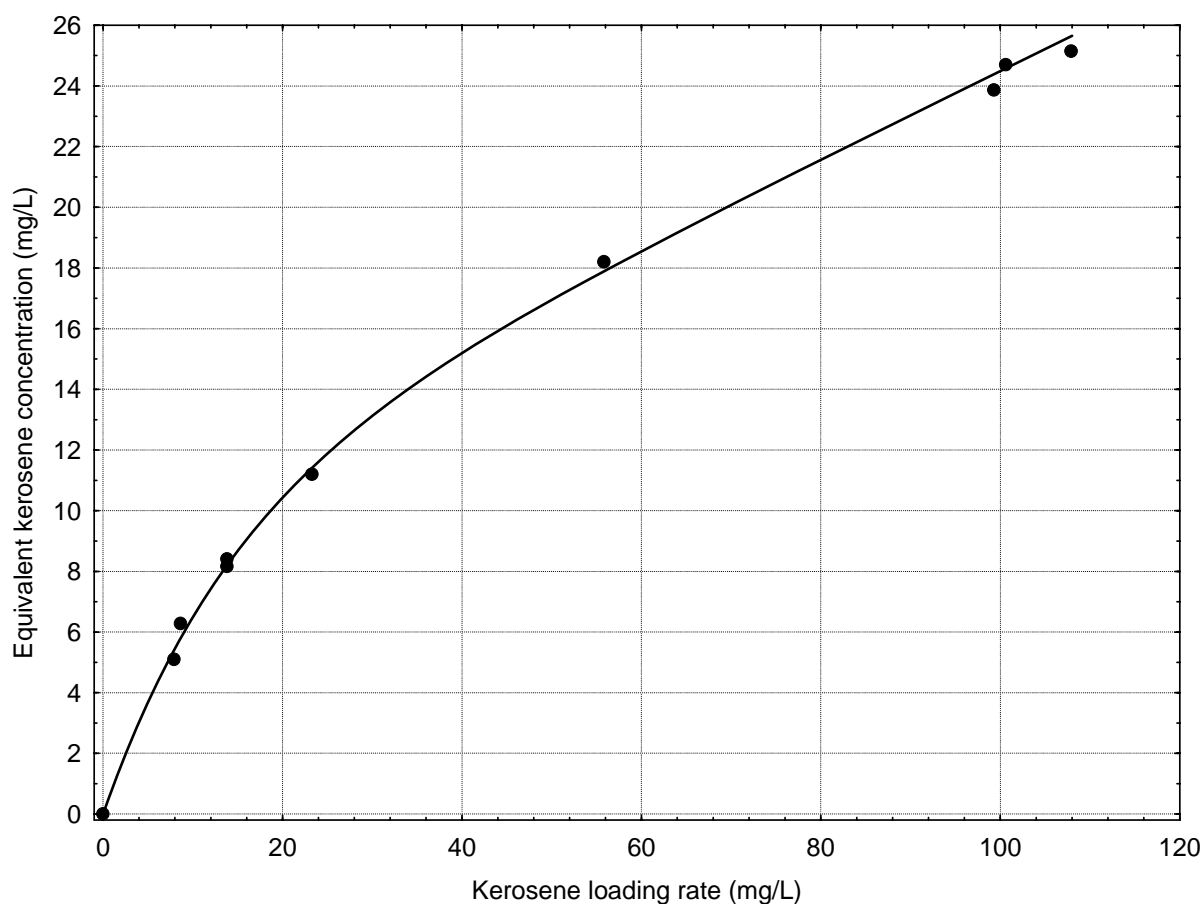


Figure 4.3 Kerosene concentration in water from various loadings ranging from 8 mg/L to 108 mg/L (20°C, 24 hours).

4.2 *Daphnia* acute studies

Two cutback loadings were tested: 10 mg/L 9.8% cutback and 100 mg/L 9.8% cutback. In each case, the WAF was a clear liquid with a kerosene odour. Blank WAFs were also prepared following the same procedure as for the cutback WAFs, but without bitumen. At the conclusion of the test, dissolved oxygen was above 2 mg/L and the pH was 7.28 and 7.27 for the 100 mg/L and 10 mg/L loading WAFs respectively. The conductivity of the 10 mg/L loading WAF was 175 $\mu\text{S}/\text{cm}$, which is within the acceptable range for *Daphnia* culture media. Results of the *Daphnia* acute tests are given in Tables 4.1 and 4.2.

Survival in the control tests was within the test acceptability criterion (<10% immobile after 48 h). There was no statistically significant ($p > 0.05$) reduction in mobility of the test organisms in the WAFs compared to the controls or compared to their respective blank WAFs. The results indicate that both the NOEC and the LL_{50} are greater than 100 mg/L for the 10% cutback.

Table 4.1 *Daphnia* acute 48 hr toxicity test results for 100 mg/L loading.

Test Material	Survival (%)	Significant difference (p<0.05) to control	Significant difference (p<0.05) to blank WAF
Control	90.0	-	-
Blank WAF	90.0	No	-
Cutback WAF	86.0	No	No

Table 4.2 *Daphnia* acute 48 hr toxicity test results for 10 mg/L loading.

Test Material	Survival (%)	Significant difference (p<0.05) to control	Significant difference (p<0.05) to blank WAF
Control	98.0	-	-
Blank WAF	94.0	No	-
Cutback WAF	94.0	No	No

4.3 Algal growth inhibition

Loadings of 1 mg/L and 100 mg/L 9.8% cutback were tested together with water blank WAFs as for the *Daphnia* studies. The results showed the average growth rate in the 100 mg/L WAF to be 81% that of the blank. The difference was significant at the 5% level (p<0.05). No significant difference in growth rate between the 1 mg/L loading and the blank was observed at the 5% level. The algal tests results show that that chronic toxicity occurs at a loading of 9.8% cutback of 100 mg/L. The NOEC is the concentration at which no effects are observed which, in this case, was 1 mg/L. In any ecotoxicology test, the reported NOEC is dependent upon the concentrations selected for the test (Chapman et al. 1996). In this research, only two concentrations were tested. If more concentrations between 1 and 100 mg/L had been tested, it is highly likely that the NOEC would be observed at concentrations >1 mg/L, especially given the relatively small effect on growth that was observed at 100 mg/L, which is the highest concentration in use.

5. Conclusion

ERMA provides four grades of aquatic toxicity as set out in Table 1.1. The object of this work was to determine whether the 9.1C classification for cutback bitumen was warranted. The *Daphnia* test results show that the acute toxicity for 9.8% cutback bitumen occurs at levels above 100 mg/L loading, indicating that the 9.1C classification is too stringent. The data from the algal test for chronic ecotoxicity also indicate that a 9.1D classification may not be warranted either.

It should also be noted that these tests were conducted with 9.8% cutback, representing a 'worst-case' scenario. In practice, the level of kerosene present in cutbacks would usually be almost half of that used in these tests. Furthermore, although it has been demonstrated that some kerosene components can migrate from the cutback into the water column (and kerosene has been shown previously to be not readily biodegradable and is bioaccumulative), the toxicological evidence presented here indicates that cutback bitumen may meet the 'not classified' criteria.

6. References

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Appendix A. Glossary and abbreviations

Acute ecotoxicity: toxicity observed in response to a short-term (48 or 96 h) exposure that generates LC_{50} (median lethal concentration) or EC_{50} (median effective concentration) ecotoxicity values. An example of an acute ecotoxicity test is the 96 h fish acute test where mortality is the measurement endpoint.

ASTM: American Society for Testing and Materials.

BCF (Bioconcentration factor): the steady state concentration of a substance in an aquatic organism divided by the concentration of the substance in the surrounding water.

Bioaccumulative: for the purposes of the **ERMA** classifications, any substance that has a **BCF** greater than or equal to 500 or, if **BCF** data is not available, a **log K_{ow}** greater than or equal to 4.

Biocidal action: in relation to a substance, means the substance causes mortality, inhibited growth, or inhibited reproduction in an organism.

BOD₅: the five-day Biochemical Oxygen Demand, being the mass of oxygen consumed by micro-organisms during oxidation of the substance in water over a period of five days (in mg oxygen consumed/mg of substance).

CAS: Chemical Abstracts Service.

CEFIC (Conseil Européen de l'Industrie Chimique): European Chemical Industry Council.

Chronic ecotoxicity: toxicity observed in a longer term exposure (compared to an acute exposure; see **acute ecotoxicity**) usually to a low concentration. Ecotoxicity values from chronic exposures include **NOEC**, **LOEC** and **EC(x)**. An example of a chronic ecotoxicity test is a 72 h algal growth inhibition test or a full life-cycle toxicity test on fish.

COD (chemical oxygen demand): the equivalent mass of oxygen from an oxidising agent (of a strength at least equal to the oxidising strength of potassium permanganate or potassium dichromate) that is consumed during oxidation of the substance in water (in mg oxygen consumed/mg of substance).

CONCAWE (CONservation of Clean Air and Water in Europe): an organisation set up in 1963 which includes most of the oil companies operating in Europe. CONCAWE's objectives are to acquire and communicate pertinent scientific, economic, technical and legal information on

environmental, safety and health issues relating to the refining of crude oil and the distribution and use of petroleum products.

Ecotoxicity test: the means by which the ecotoxicity of a substance is determined. An ecotoxicity test is used to measure the degree of response produced by exposure to a specific concentration or specific concentrations. Ecotoxicity values (**NOEC, LOEC, EC₅₀**, etc.) can be determined from ecotoxicity tests. Exposures may be acute (see **Acute ecotoxicity**) or chronic (see **Chronic ecotoxicity**).

EC₅₀: the dissolved concentration of a substance that causes an effect (e.g. reduction in growth rate) in 50% of the test population of organisms.

EC(X): the dissolved concentration of a substance that causes an effect (e.g. a reduction in growth rate) in x% of the test population of organisms.

EL₅₀: the effective loading rate of a substance that causes an adverse reaction (or a reduction in growth rate) in 50% of the test population of organisms.

ERMA: Environmental Risk Management Authority, New Zealand.

GCMS: Gas chromatography mass spectrometry.

GESAMP (The Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection): an organisation established in 1967 by a number of United Nations agencies. Its purpose is to provide advice to the agencies (and through them their member governments) on all scientific aspects of the prevention, reduction and control of the degradation of the marine environment's ability to sustain life support systems, resources and amenities.

IrL₅₀: the loading rate of a substance that inhibits growth or growth rate of the test population of organisms by 50%.

IP: Institute of Petroleum.

Log K_{ow}: the steady state ratio (k) of the solubility of a substance in n-octanol (o) to the solubility of that substance in water (w).

L(E)C₅₀: either LC₅₀ or EC₅₀ data.

L(E)L₅₀: either LL₅₀ or EL₅₀ data.

LL₅₀: the lethal loading rate of a substance that causes mortality of 50% of the test population of organisms within the specified period.

LC₅₀: the dissolved concentration of a substance that causes mortality of 50% of the test population of organisms within the specified exposure period. Also known as the median lethal concentration.

NIWA: National Institute of Water and Atmospheric Research, New Zealand.

NMR: Nuclear Magnetic Resonance.

NOEC (no-observed effect concentration): the highest concentration of a substance in an ecotoxicity test in which no statistically significant adverse effects on the exposed population of test organisms were observed compared with controls.

LOEC (lowest-observed effect concentration): the lowest concentration of a substance in an ecotoxicity test in which a statistically significant adverse effect on the exposed population of test organisms was observed compared with controls.

OECD: Organisation for Economic Co-operation and Development.

Rapidly degradable: for the purposes of the ERMA classifications, this means that:

- (a) 28 days after a solution containing the substance is inoculated with micro-organisms, there is at least:
 - (i) a 70% reduction in dissolved organic carbon in the solution; or
 - (ii) a 60% depletion of oxygen in the solution when compared with the maximum depletion of oxygen that would occur if the substance were completely degraded; or
 - (iii) a 60% generation of carbon dioxide in the solution when compared with the maximum generation of carbon dioxide that would occur if the substance were completely degraded.

or

- (b) if only COD and BOD₅ data are available, the ratio of BOD₅ to COD is greater than or equal to 0.5:1.

or

- (c) at least 70% of the substance can be degraded biotically or abiotically, in the aquatic environment within 28 days.

UK DoE: United Kingdom Department of the Environment.

Appendix B. Recently reported cases of tanker spillages in New Zealand

The Southland Times. 13/3/2001a, page 1. *Stricken tanker leaks tar.* A tanker jack-knifed and rolled, spilling 8000 litres into a ditch near the Titiroa Stream near State Highway 99.

The Southland Times. 25/10/2001b. *Slippery surface factor in fatal crash.* A tanker rolled on a corner and crushed a car on State Highway 99.

Waikato Times. 10/2/1998, page 2. *Fined for spillage.* A trailer overturned, spilling 900 litres into a Manakau Harbour tributary.

Aquatic Ecotoxicity of Cutback Bitumen

Land Transport New Zealand
Research Report 285