

Environmental Effects of Emulsions

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Contents

Executive summary	7
Abstract	10
1. Introduction	11
2. Background	13
2.1 Constituents of sealing emulsions.....	13
2.2 The emulsion breaking and curing processes.....	13
2.3 Possible causes of unintended entry of emulsion components into the environment... 14	
2.3.1 Rainfall after sealing	14
2.3.2 Accidental spillage.....	14
3. Ecotoxicity data on sealing emulsion components	16
3.1 Bitumen.....	16
3.2 Natural rubber latex and SBS rubber	16
3.3 Kerosene	16
3.4 Acid.....	17
3.5 Calcium chloride	17
3.6 Cationic emulsifying agents	19
3.7 Application of ecotoxicity data to determine emulsion classification	21
3.8 The European Union method of mixtures for assessing ecotoxicity.....	22
4. Overseas research on bituminous emulsion toxicity	23
4.1 Introduction	23
4.2 Slurry seal runoff	23
4.3 Emulsifier elimination by micro-organisms	24
4.4 Current French research on cold mixes	24
4.5 Research on Orimulsion®	25
5. New Zealand research reported to date	26
6. Experimental methodology	27
6.1 Introduction	27
6.2 General experimental approach	28
6.3 <i>Daphnia magna</i> acute studies	29
6.4 Algal growth inhibition	30
7. Results and discussion	31
7.1 Introduction	31
7.2 Test emulsions.....	31
7.3 Crustacea.....	31
7.3.1 Results	31
7.3.2 Discussion	32
7.4 Algae.....	33
7.4.1 Results	33
7.4.2 Discussion	33
7.5 Potential ERMA classification.....	34
7.6 General application of results to emulsions.....	35
8. Summary and conclusions	36
9. Recommendations	38
10. References	39
Appendix	43

Executive summary

The great majority of bitumen emulsions used for chipsealing in New Zealand are cationic, i.e. the emulsifier provides the bitumen particles in the emulsion with a positive electrical charge. Continually increasing the use of these emulsions for chipsealing raises the question of the ecological risks and benefits of using these materials, as against the still more common method of using hot cutbacks, which are now classified by Environmental Risk Management Authority (ERMA) New Zealand as not ecotoxic (i.e. not toxic to the receiving environment).

The major potential environmental dangers of emulsion sealing in New Zealand are perceived to be:

- spillage and/or runoff into waterways from tanker accidents or mishaps during spraying, and
- rain washing emulsion off the road before it has set.

The emulsifying agent is the only component of the emulsion that will contribute significantly to ecotoxicity.

Cationic emulsifying agents used for road work are highly toxic (typically $LC_{50} < 1$ mg/L), while biodegradability varies widely from emulsifier to emulsifier (LC_{50} is the dissolved concentration of a substance that kills 50% of the test population of organisms within the specified exposure period). However, the emulsifier content of a typical emulsion is of the order of only 0.2%, of which a significant portion is bound in the bitumen particles. A calculation based on the published ecotoxicity data of an emulsifier, using an ERMA formula for mixtures, suggested that emulsifier aqueous phases would fall into ERMA ecotoxicology Class 9.1C (ecotoxic in the aquatic environment), if it is assumed that the No Observed Effect Concentration (NOEC) is less than 1 mg/L, or into Class 9.1D (slightly harmful to the aquatic environment or otherwise designed for biocidal action).

Overseas work with slurry seal runoff found that emulsifiers were strongly and irreversibly absorbed into soils. Accordingly, emulsion runoff may be a greater problem in urban (rather than rural) environments, where it may flow directly into stormwater drains rather than passing over grassed areas. On the other hand, steps to contain spillage may be more straightforward in urban areas.

French research on the ecotoxicity of runoff water from cold mixes confirmed the wide variability of results from emulsifier to emulsifier. Mixes produced with a tallow polyamine emulsifier produced a runoff approximately ten times more toxic than mixes with two other emulsifiers (tallow polyamine plus a mixture of imidazoline and amidoamine fat derivatives, and tallow polyamine plus tallow diamine).

Published research on the non-ionic bitumen emulsion Orimulsion™ (which is used as a power station fuel) reports toxicity to fish to be caused partially by the soluble components (principally the emulsifier) and partially by small particles of dispersed

bitumen blocking fishes' gills. Thus two components contribute to ecotoxicity: physical limitation of feeding and respiration by small particles, and chemical poisoning.

However, unlike non-ionic bitumen emulsions, cationic emulsions are unstable when diluted and, with rapid precipitation, the contribution of small particles to ecotoxicity should not be great.

The principal physical danger of emulsions is smothering by broken bulk bitumen. A toxic danger arises from compounds in the emulsion's water phase. The current work concentrated on investigating the effect of the emulsifier in determining ecotoxicity of this phase. Four emulsions containing four different types of emulsifier were selected for testing.

The aqueous phases of the emulsions were separated by centrifugation followed by filtering, and diluted to a target level of 1000 mg/L, using *Daphnia magna* culture water supplied by the National Institute of Water and Atmospheric Research (NIWA), Hamilton. NIWA tested these solutions for acute (short term) and chronic ecotoxicity to *D. magna* (a small crustacean) and algae.

The test results for algae gave no indication of ecotoxicity. However, the results for *D. magna* indicated that three of the four emulsion leachates qualified for the ERMA classification 9.1D, 'Slightly harmful to the aquatic environment.' Under standard ERMA procedures, a minimum set of three test species is needed to provide a classification, although this is not an invariable requirement.

If the results are modified to be expressed in terms of ecotoxicity of the full emulsion rather than its aqueous phase, all four emulsions would become 'not classified.' Classification according to the ecotoxicity of the aqueous phase only is the conservative option, which would possibly be preferred by regulatory bodies.

The measured aqueous phase LC₅₀ values for *D. magna* range from 67 to 331 mg/L, as opposed to the more ecotoxic 15 to 30 mg/L predicted for an emulsion with an N-tallow-1,3-diaminopropane emulsifier using ERMA mixing rules. This order of magnitude agreement indicates that pure emulsifier ecotoxicity data can give at least a conservative indication of the emulsion ecotoxicity.

The current indications are that chipsealing emulsions typically would be classified as safe or slightly harmful to the aquatic environment.

For the convenience of the chipsealing industry and clients concerned with the effect of chipseal emulsions on the environment, it would be helpful if all sealing emulsions could be classified as a group. This would require a number of matters to be addressed:

- The sealing industry as a whole would need to review the types of emulsifier and dosages being used to ascertain whether a representative set of emulsions has

been tested. If necessary, testing may be indicated for other types after the first two items listed below have been actioned.

- Discussions would need to be held with ERMA to:
 - explore the possibility of obtaining a group classification applicable to all cationic sealing emulsions,
 - to decide whether emulsion should be classified on the basis of the ecotoxicity of the aqueous phase only or on the inferred ecotoxicity of the emulsion as a whole (which may give a more ecologically favourable evaluation), and
 - to ascertain whether an ecotoxicity classification based on the known ecotoxicity of the emulsifier and calculated by ERMA's method of mixtures would be acceptable for an initial evaluation of any new type of emulsion.

Consideration should be given to specifying that all sealing emulsions meet ERMA's 'not classified' or 9.1D ecotoxicity level requirements.

A watching brief should be kept for innovations in continuing French research on emulsion ecotoxicity.

Abstract

This report describes a study, carried out in 2006–7, of the potential toxicity to the environment (ecotoxicity) of cationic bitumen emulsions used for chipsealing (surface dressing) in New Zealand. The ecotoxicities of the separate components of bitumen emulsions are reviewed to assess their contribution to emulsion ecotoxicity. Overseas reports on the environmental dangers of a non-ionic bitumen emulsion (a power station fuel) and runoff from cold mix asphalt are examined for relevant applications to sealing emulsions. Ecotoxicities are measured for four representative New Zealand emulsions. The implications of the findings for possible environmental classification of emulsions by environmental authorities are discussed.

1. Introduction

The purpose of the research reported here has been to evaluate the effect of chipsealing emulsions on aquatic flora and fauna by carrying out an ecotoxicological study of a selection of sealing emulsions supplied by contractors, using a modification of the methodology developed recently for a Land Transport New Zealand study on the ecotoxicity of cutbacks (Herrington et al. 2006).

Chipseals are by far the dominant surfacing for New Zealand roads. Traditionally, chipsealing has been carried out with hot bitumen binders cut back with kerosene, but increasingly, sealing has been carried out with bitumen based emulsions instead. Around 10% of state highway sealing is currently carried out with emulsions. For some local authority areas, emulsion is now the dominant sealing binder. Although they are typically 12% more expensive than cutbacks at present, emulsions are promoted on environmental grounds; in New Zealand, they have the potential of reducing greenhouse gas emissions from sealing work significantly (AUSTROADS 2002, Slaughter 2004). Many of the larger contractors who manufacture their own emulsions support the increased use of emulsions because they are considerably safer for sealing workers than cutbacks, which are commonly transported and sprayed above their flash points. The fact that smaller contractors cannot invest in emulsion manufacturing plant and must purchase emulsions from the larger contractors is a disincentive for them to use emulsions.

A Transit New Zealand study on the pros and cons of using emulsions for chipsealing rather than cutbacks (Ball 2005) found that the major environmental danger of emulsions was perceived to be spillage or runoff into waterways either through accidents with tankers and spraying procedures, or by rain before bitumen from the emulsion had had time to bond adequately to the sealing chip. However, no quantitative studies have been carried out on the actual significance of this perceived risk.

The New Zealand Environmental Risk Management Authority (ERMA) classified chipsealing cutbacks containing 2.5 to 10% kerosene as 'harmful in the aquatic environment', using standard methods for classifying mixtures of materials when no experimental data is available. Herrington et al.'s (2006) work demonstrated that the classification was not justified; as a result, the classification was removed. In view of the increased use of emulsions, it is to be expected that ERMA will eventually produce an emulsion ecotoxicity classification. Possibly, without experimental data, this classification could also be unnecessarily stringent compared to one based on laboratory testing as proposed in this research, and consequently inhibit the wider use of emulsions.

ERMA has four categories for aquatic ecotoxicity. These are listed in Table 1.1. The ecotoxicity of emulsion components will be discussed in this report in terms of these classification categories.

Table 1.1 ERMA aquatic ecotoxicity classifications (ERMA 2001).

Category	Aquatic ecotoxicity
9.1A (very ecotoxic in the aquatic environment)	Acute ecotoxicity $L(E)C_{50}^{ab} \leq 1.0$ mg/L Regardless of any persistence or bioaccumulation or chronic ecotoxicity information
9.1B (ecotoxic in the aquatic environment)	$1.0 < \text{Acute ecotoxicity } L(E)C_{50} \leq 10$ mg/L AND Lack of rapid degradability and/or bioaccumulative (UNLESS: Chronic ecotoxicity $NOEC^c > 1.0$ mg/L, in which case the substance is excluded from this classification step)
9.1C (harmful in the aquatic environment)	$10.0 < \text{Acute ecotoxicity} \leq 100$ mg/L AND Lack of rapid degradability and/or bioaccumulative (UNLESS: Chronic ecotoxicity $NOEC > 1.0$ mg/L, in which case the substance is excluded from this classification step)
9.1D (slightly harmful to the aquatic environment or otherwise designed for biocidal action)	$1.0 < \text{Acute ecotoxicity} \leq 100$ mg/L AND not persistent AND/OR not bioaccumulative OR $1.0 < \text{Acute ecotoxicity} \leq 100$ mg/L AND persistent AND/OR bioaccumulative AND chronic ecotoxicity ($NOEC$) > 1 mg/L OR Chronic aquatic ecotoxicity ($NOEC$) ≤ 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 ($NOEC$) > 1 mg/L water OR A 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 ($NOEC$) > 1 mg/L AND acute ecotoxicity > 100 mg/L (regardless of whether it is persistent or bioaccumulative)

Notes to Table 1.1:

- LC_{50} = the dissolved concentration of a substance that kills 50% of the test population of organisms within the specified exposure period. Also known as the median lethal concentration.
- EC_{50} = the median effective concentration, i.e. the concentration of a material in the water that is estimated to produce a specifically quantified effect on 50% of the test organisms. See glossary for more details.
- $NOEC$ = No observed effect concentration.

2. Background

2.1 Constituents of sealing emulsions

Emulsions used on New Zealand roads are mostly (if not completely) stabilised with cationic, organically-based emulsifiers activated with an acid (usually hydrochloric acid, though phosphoric acid may be used in the manufacture of some asphalt-emulsion products), and containing various additives (principally calcium chloride to counter the water-absorbing effect of salt in the bitumen and reduce settling, and various elastomers to modify the bitumen properties). A typical recipe would be roughly:

- ~0.2% emulsifier,
- ~0.1% concentrated hydrochloric acid (HCl),
- ~0.1 % calcium chloride (CaCl₂),
- 0–6% elastomer (latex or styrene-butadiene-styrene block copolymer (SBS)),
- ~1% kerosene (this aids emulsification, but a recent trend in New Zealand is to produce emulsion designs without kerosene),
- 70% binder (bitumen + any latex or SBS),
- water to 100%.

2.2 The emulsion breaking and curing processes

A cationic emulsion of the type used for sealing work consists of small, positively charged bitumen particles (diameter typically ranging over 0.1 to 10 microns) suspended in the aqueous phase.

The emulsifier molecules typically consist of an organic chain of carbon and hydrogen atoms with a number of amine (-NH-, -NH₂) and amide (O=CNR₁R₂ where R₁ and R₂ are alkyl groups or hydrogen) units at or near one end of the chain. In the acidic environment, the emulsifier molecules are positively ionised at the end of the molecule containing amine-amide; the other end of the emulsifier molecule is hydrophobic and is dissolved in the bitumen particles. Thus the charged ends point outwards from the bitumen particles' surfaces, giving the surfaces their positive charge. A significant proportion of emulsifier ions normally remains in solution.

Being positively charged, the bitumen particles repel each other, making the emulsion stable by negating any tendency for them to stick together. The stability of the emulsion against coagulation of the bitumen ('breaking') is controlled by the amount and type of emulsifier material, and by the pH level, which is set by the amount of acid.

Several processes occur when a bitumen emulsion comes in contact with sealing chip, and the balance of them will depend on emulsion formulation, aggregate chemistry and environmental conditions (Deneuvillers 2004, Holleran & Motina 2006). When the emulsion is sprayed on the road surface, some of the water and acid evaporates. With the

resulting change in pH level, the emulsifier starts to become deionised and bitumen particles begin to bond to each other. For the majority of chip types used in New Zealand (e.g. basalt and greywacke), wetting will result in negatively charged surfaces which will attract those bitumen particles that are still charged.

At this point, the emulsion has broken but the bitumen will not gain full strength, resulting in a stable chipseal, until it has fully cured by evaporation of the remaining water. The loss of water will have been accelerated for high bitumen content emulsions, which are sprayed at up to 90°C, but may not be effectively complete for several hours, depending upon ambient temperature and humidity, and the amount of traffic (imparting extra energy). In addition, water loss may be delayed by 'skinning', in which a bituminous layer forms across the surface of partially broken emulsions; controlled trafficking is needed to break the skin surface.

2.3 Possible causes of unintended entry of emulsion components into the environment

2.3.1 Rainfall after sealing

Until the emulsion has fully cured, residual water from the emulsion will be present, containing both bitumen particles and emulsifier. During this period, rain may wash the residual water off the road surface into the surrounding soil or (in urban areas) into the stormwater system. Although Fulton Hogan Limited, one of the larger New Zealand road maintenance and construction firms, takes precautions not to seal if the 24-hour weather forecast predicts rain, their environmental incident reports indicate that, combining both state highways and local authority roads, an average of two runoff events occur annually (Slaughter 2004). At present, around 10% of state highways are sealed with emulsion, of which Fulton Hogan seal around half. If this is typical of local authority roads as well, and given the possible scenario of eventually half the sealing being carried out with emulsions, it would not be unreasonable to expect around 40 or more runoff incidents a year.

Precautions such as blocking access to waterways and drains before sealing can limit the dangers of such runoffs, although it would be necessary to maintain these precautions for several hours after sealing to ensure no detrimental runoff occurs. The economic costs of doing this while sealing sprayers have moved on to further work sites could count against use of emulsions rather than hot cutbacks for sealing in rain-prone areas.

2.3.2 Accidental spillage

Situations in which accidental spillage is likely to occur are:

- **Accidental spills during transfer or sealing.** Precautions can be taken to reduce the danger, e.g. blocking access to drains and waterways before sealing, and carrying equipment to isolate and clean up spillages.
- **Tanker rollover** – a rare but occasional event. A probability for this type of event of approximately 0.3% per year from front line spray units has been estimated (Vercoe et al. 2006).

Emulsions can retain their colour even when highly diluted after spilling. Figure 2.1 shows various dilutions of the same 70% bitumen emulsion photographed together shortly after preparation. Even at 10000:1, dilution the solution is clearly coloured.

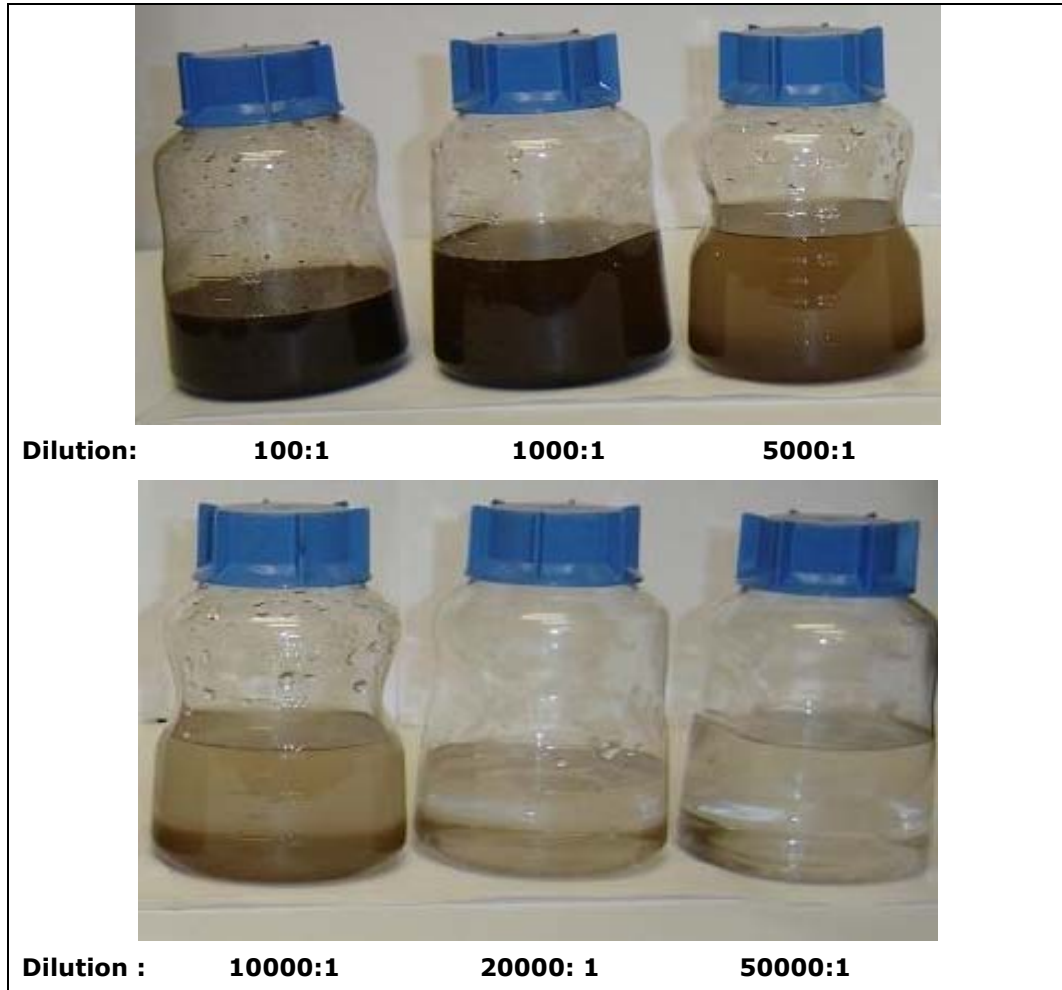


Figure 2.1 Cationic CRS-2 70% bitumen emulsion diluted at different levels with tap water.

3. Ecotoxicity data on sealing emulsion components

3.1 Bitumen

For a detailed discussion of the effect of bitumen on the environment, see Herrington et al. (2006), Chapter 2.2.1. This discussion concludes that the constituents of bitumen have extremely limited bioavailability, and their low water solubility and high molecular weights make bioaccumulation of bitumen highly unlikely. Bitumen is not classified by ERMA as toxic to the environment (Annex 2 of Leary & Eng 2003).

3.2 Natural rubber latex and SBS rubber

Natural rubber latex (Chemical Abstracts Service (CAS) Reference 9006-04-6) is widely used and although frequent allergic reactions to its products are recorded, a library search revealed no evidence that it is seen as being ecologically dangerous (PAN Pesticides Database 2008). No ecotoxicity information for SBS rubber (CAS Reference 9003-55-8) has been developed, but on the basis of the ecotoxicology of similar products, it is expected to be practically non-toxic (see, for example, Kraton Polymers SBS D Series Products Material Safety Data Sheet 2007).

3.3 Kerosene

Kerosene is classified by ERMA as a 9.1B substance, which is one that is ecotoxic in the aquatic environment (see Table 1.1). In the case of emulsions, the kerosene is added to adjust bitumen viscosity primarily to achieve an improved binder particle size distribution. The kerosene is therefore incorporated into the bitumen and will not be easily available to an aqueous environment. The availability from a bitumen cut back with kerosene has been studied by Herrington et al. (2006). It was found that with 9.8% kerosene in the binder, acute toxicity (EC_{50}) for the test organism, *Daphnia magna*, was greater than 100 mg/L. This has resulted in cutbacks with 10% kerosene or less becoming unclassified, as defined in Table 1.1. The measurements were carried out on the water accommodated fraction (WAF)¹, produced by keeping water in contact with the binder until an equilibrium was reached. For emulsions with kerosene, the kerosene content in the binder is around 1%, well below the 9.8% dosage assessed for cutbacks, and no environmental problems from kerosene are therefore expected. In any case, the trend is for producers to make emulsions without kerosene as their design processes become more sophisticated.

¹For a fuller discussion of the water accommodated fraction, see Appendix A.

3.4 Acid

Concentrated hydrochloric acid is toxic to aquatic organisms. However, in cationic bituminous emulsions, it typically constitutes around only 0.2% of the aqueous carrier and is therefore strongly diluted.

ERMA provides the classifications shown in Table 3.1 for various concentrations of hydrochloric acid. For the meaning of the ecotoxicological classifications 9.1A to 9.1D, see Table 1.1. The term 'not classified,' which will be used throughout this work, means that ERMA would assess the material as having no measurable ecotoxicity.

Table 3.1 ERMA classifications for hydrochloric acid (HCl).

Substance description	CAS#	Ecotoxicity classification
Hydrochloric acid, >25% aqueous solution	7647-01-0	9.1D
Hydrochloric acid, >10–25% aqueous solution	7647-01-0	'not classified'
Hydrochloric acid, >2–10% aqueous solution	7647-01-0	'not classified'
Hydrochloric acid, 0.5–2% aqueous solution	7647-01-0	'not classified'

ERMA ecotoxicity classifications indicate that below 25% concentration, hydrochloric acid is not regarded as significantly ecotoxic. Industrial strength acid used for emulsion manufacture contains roughly 33% hydrogen chloride. For a typical high temperature emulsion with 30% water, use of 0.1% acid results in an aqueous solution of hydrochloric acid of $(0.1/30) \times 100\% = 0.33\%$. This concentration is not classified by ERMA.

3.5 Calcium chloride

Solid calcium chloride occurs in two forms, anhydrous calcium (CaCl_2) and hydrated calcium ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). Table 3.2, taken from an Organisation for Economic Co-operation and Development (OECD) assessment report (2002), summarises many studies carried out on the ecotoxicological properties of this material. This table tells us several things as follows:

- Calcium chloride's vapour pressure is negligible and its water solubility is 745 g/L at 20°C. Calcium chloride is readily dissociated into calcium and chloride ions in water. These physico-chemical properties indicate that calcium chloride released into the environment is distributed into local water in the form of calcium and chloride ions.
- Acute toxicity studies (lowest effect values) reveal a 72-hour EC_{50} of 2900 mg/L for algae (*Pseudokirshneriella subcapitata*), a 48-hour EC_{50} of 1062 mg/L for daphnids (*D. magna*) and a 96-hour LC_{50} of 4630 mg/L for fish (*Pimephales promelas*).
- The chronic toxicity study with *D. magna* shows that a 16% impairment of reproduction (EC_{16}) is caused at the concentration of 320 mg/L. The 72-hour EC_{20} for *P. subcapitata* determined by the OECD TG 201 study is 1000 mg/L. All the data compiled on the acute and chronic toxicity are greater than 100 mg/L.

Table 3.2 Results of ecotoxicological studies on calcium chloride (CAS # 10043-52-4) from OECD 2002.

ECOTOXICOLOGY	PROTOCOL	SPECIES	RESULTS Concentrations are of anhydrous CaCl ₂
Acute/prolonged toxicity to fish	EPA/600/4-90/027, EPA/600/6-91/003	<i>Pimephales promelas</i>	LC ₅₀ (96 hr) = 4630 mg/L
	NA*	<i>Lepomis macrochirus</i>	LC ₅₀ (96 hr) = 9500-11 300 mg/L LC ₅₀ (96 hr) = 10 650 mg/L
	NA	<i>Gambusia affinis</i>	LC ₅₀ (96 hr) = 13 400 mg/L
Acute toxicity to aquatic invertebrates e.g. <i>Daphnia magna</i>	OECD TG 202	<i>D. magna</i>	EC ₅₀ (48 hr) = 2400 mg/L (immobilisation)
	EPA/600/4-90/027, EPA/600/6-91/003	<i>D. magna</i>	LC ₅₀ (48 hr) = 2770 mg/L
	NA	<i>D. magna</i>	EC ₅₀ (48 hr) = 1062 mg/L (immobilisation) LC ₅₀ (48 hr) = 1285 mg/L
	NA	<i>D. hyaline</i>	LC ₅₀ (48 hr) = 8300 mg/L
	EPA/600/4-90/027, EPA/600/6-91/003	<i>Ceriodaphnia sp.</i>	LC ₅₀ (48 hr) = 1830 mg/L
	NA	<i>Cyclops abyssorum prealiinus</i>	LC ₅₀ (48 hr) = 19 400 mg/L
	NA	<i>Eudiaptomus padanus padanus</i>	LC ₅₀ (48 hr) = 11 100 mg/L
	NA	<i>Nitocra spinipes</i>	LC ₅₀ (96 hr) = 1600 mg/L
	NA	<i>Tubifex tubifex</i>	EC ₅₀ (96 hr) = 780 mg/L (immobilisation)
	NA	<i>Caenorhabditis elegans</i>	LC ₅₀ (24 hr) = 44 400 mg/L
Toxicity to aquatic plants e.g. algae	OECD TG 201	<i>Selenastrum capricornutum</i>	EC ₅₀ (72 hr) = 2900 mg/L (biomass) EC ₂₀ (72 hr) = 1000 mg/L (biomass) EC ₅₀ (72 hr) = >4000 mg/L (growth rate) EC ₂₀ (72 hr) = 2700 mg/L (growth rate)
Chronic toxicity to aquatic invertebrates	NA	<i>D. magna</i>	EC ₁₆ (21 d) = 320 mg/L (reproduction) EC ₅₀ (21 d) = 610 mg/L (reproduction) LC ₅₀ (21 d) = 920 mg/L

* Protocols for these tests were not given in the source.

3.6 Cationic emulsifying agents

Not every manufacturer publishes details of their emulsifiers or quantitative information on the ecotoxicities. However, AKZO provide a full set of safety data sheets on their website, and these can be used to gain an indication of the range of ecotoxicities to be expected.

Table 3.3 lists ecotoxicological data obtained from the AKZO Nobel website (AKZO 2008).

These different agents may be blended according to the emulsion properties sought. It is apparent from the Table 3.3 that:

- although a range of compounds is used for emulsifying agents, all the industrial products are highly ecotoxic, with 50% mortality figures quoted at less than 1.0 mg/L;
- however, the quoted figures are almost always estimates, based on the behaviour of similar compounds; and
- biodegradability varies from emulsifier to emulsifier, and could be a consideration in choosing which emulsifiers to use.

The European Commission European Chemicals Bureau (2000) has produced an IUCLID dataset for N-tallow-1,3-diaminopropane (marketed as Redicote™ E9, Duomeen™ T paste ROADCHEM 406HA, and probably under several other trademarks) which gives more definite ecotoxicological data for this compound than the AKZO Nobel safety data sheet. The data are reproduced in Table 3.4.

A minimum LC₅₀ for this material is 0.1 mg/L (Table 3.4, Fish *Brachydanio rerio*). This figure will be used to estimate the ecotoxicity that would be assigned by ERMA to an emulsion.

Table 3.3 Published ecotoxicological data for AKZO Nobel emulsifiers (AKZO 2008).

Agent/materials	Ecotoxicological information
REDICOTE™ N39L Brown liquid Reaction product with tall oil fatty acid and aminoethylpiperazine: 40–60% N-oleyl-1,3-diaminopropane: 30–60% 2-Ethylhexanoic acid: 5% 2-Piperazine-1-ylethylamine: 1–3%	Reaction product with tall oil fatty acid and aminoethylpiperazine: <ul style="list-style-type: none"> • LC₅₀ 96 hours <i>Brachydanio rerio</i> (fish) <1 mg/L • EC₅₀ 48 hours <i>Daphnia</i>^a <1 mg/L • Very toxic to aquatic organisms. • Not readily biodegradable. <60% BOD^b, 28 days N-Oleyl-1,3-diaminopropane: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish[†] < 1 mg/L^c • EC₅₀ 48 hours <i>Daphnia</i>[†] <1 mg/L • IC₅₀^d 72 hours algae^a <1 mg/L^c • Very toxic to aquatic organisms. • Readily biodegradable. >60% BOD, 28 days 2-Ethylhexanoic acid: <ul style="list-style-type: none"> • LC₅₀ 96 hours <i>Leucisus idus</i> (fish) >250 mg/L • EC₅₀ 48 hours <i>Daphnia magna</i> 85.4 mg/L • EC₅₀ 72 hours <i>Scenedesmus subspicatus</i> (algae) 61 mg/L • Harmful to aquatic organisms. • Readily biodegradable. BOD₅ >70%.
REDICOTE™ RM007 Yellow liquid Alkylamine ethoxylate: 35–45% Alkyldiamine ethoxylate: 55–65%	Contains substance(s) classified very toxic to aquatic organisms. Alkylamine ethoxylate: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a <1 mg/L^c • EC₅₀ 48 hours <i>Daphnia</i>^a <1 mg/L^c • Readily biodegradable. >60% BOD, 28 days Alkyldiamine ethoxylate: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a <1 mg/L^c • Very toxic to aquatic organisms. • Not readily biodegradable^c
REDICOTE™ EM24 Yellow liquid Tallow amine propoxylate: 30–60% N-oleyl-1,3-diaminopropane: 30–60%	Contains substance(s) classified very toxic to aquatic organisms. Not readily biodegradable Tallow amine propoxylate: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a <1 mg/L^c • EC₅₀ 48 hours <i>Daphnia</i>^a <1 mg/L^c • Very toxic to aquatic organisms. Not readily biodegradable N-oleyl-1,3-diaminopropane: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a <1 mg/L^c • EC₅₀ 48 hours <i>Daphnia</i>^a <1 mg/L • IC₅₀ 72 hours algae^a <1 mg/L^c • Very toxic to aquatic organisms. Readily biodegradable. >60% BOD, 28 days
REDICOTE™ EM22 Brown liquid N-oleyl-1,3-diaminopropane: 45% Tall oil fatty acids polyamine condensates: 25–35% Diethylene glycol: 20–25%	Very toxic to aquatic organisms. Not readily biodegradable N-oleyl-1,3-diaminopropane: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a <1 mg/L^c • EC₅₀ 48 hours <i>Daphnia</i>^a <1 mg/L • IC₅₀ 72 hours algae^a <1 mg/L^c • Very toxic to aquatic organisms. Readily biodegradable. >60% BOD, 28 days Diethylene glycol: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a >1000 mg/L • EC₅₀ 48 hours <i>Daphnia</i>^a >100 mg/L • ICLo 7 days algae^a >1000 mg/L Degradation >70% DOC ^e , 28 days. Readily biodegradable. No bioaccumulation is expected.
REDICOTE™ E-9 Off white paste N-tallow-1,3-diaminopropane: >92%	<ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a < 1 mg/L • EC₅₀ 48 hours <i>Daphnia</i>^a < 1 mg/L^c • IC₅₀ 72 hours algae^a < 1 mg/L^c Very toxic to aquatic organisms. Readily biodegradable. >60% BOD, 28 days
REDICOTE™ 103 Light yellow paste N-tallow-1,3-diaminopropane: 40–60% (Hydrogenated tallow) amine: 40–60%	Contains substance(s) classified very toxic to aquatic organisms. The product is classified as readily biodegradable and contains only readily biodegradable substances. N-tallow-1,3-diaminopropane: <ul style="list-style-type: none"> • LC₅₀ 96 hours fish^a <1 mg/L • EC₅₀ 48 hours <i>Daphnia</i>^a <1 mg/L^c • IC₅₀ 72 hours algae^a <1 mg/L^c Very toxic to aquatic organisms. Readily biodegradable. >60% BOD, 28 days

Notes to Table 3.3:

a Species not identified in published data sheet

b BOD: Biochemical oxygen demand

c These data were estimated from tests on similar products.

d IC₅₀: Mean inhibition concentration, i.e. the concentration estimated to cause a 50% reduction in growth compared to a control.

e DOC: Dissolved organic carbon die-away test (OECD 1992)

Table 3.4 Results of ecotoxicology studies with N-tallow-1,3-diaminopropane (CAS # 61791-55-7), taken from European Chemicals Bureau, 2000.

ECOTOXICOLOGY	PROTOCOL	SPECIES	RESULTS
Acute/prolonged toxicity to fish	OECD Guideline 203	<i>Brachydanio rerio</i>	LC ₅₀ (96 hr) = 0.1 mg/L LC ₁₀₀ (96 hr) = 0.15 mg/L NOEC = LC ₀ (96 hr) = 0.069 mg/L
Acute toxicity to aquatic invertebrates e.g. <i>Daphnia magna</i>	ISO 6341 15	<i>D. magna</i>	LC ₅₀ (24 hr) = 0.27 mg/L LC ₁₀₀ (24 hr) = 0.75 mg/L NOEC = LC ₀ (24 hr) <0.1 mg/L
	ISO 6341 15	<i>D. magna</i>	LC ₅₀ (48 hr) = 0.13 mg/L LC ₁₀₀ (48 hr) = 0.60 mg/L NOEC = LC ₀ (48 hr) <0.1 mg/L

3.7 Application of ecotoxicity data to determine emulsion classification

The ERMA *User Guide to the HSNO Thresholds and Classifications, Part VII Substances with Ecotoxic Properties* (ERMA 2001) provides an additive formula for determining the ecotoxicity level of mixtures:

$$\frac{100}{L(E)C_{50mix}} = \sum_{i=1}^{\eta} \frac{C_i}{L(E)C_{50i}} \quad \text{[Equation 1]}$$

where:

- C_i = concentration of ecotoxic component (weight percentage)
- $L(E)C_{50i}$ = LC₅₀ or EC₅₀ for component i (mg/L)
- η = number of ecotoxic components

We take the emulsifier content at 0.2% by weight with LC₅₀ = 0.1 mg/L, and CaCl₂ (0.1% by weight) with LC₅₀ = 100 mg/L. With a high temperature bitumen emulsion, we have approximately 30% water, and, assuming that the emulsifier and CaCl₂ are completely present in the aqueous phase, concentrations as percents of the aqueous phase become 0.67% and 0.33% respectively. Therefore, we have;

$$\frac{100}{LC_{50mix}} = \frac{0.67}{0.1} + \frac{0.33}{100} \quad \text{[Equation 2]}$$

and, solving this for LC_{50mix} , we obtain

$$LC_{50mix} = 14.9 \text{ mg/L.} \quad \text{[Equation 3]}$$

The contribution of calcium chloride to this figure is negligible and is only apparent at the fifth significant figure.

If we assume that only half of the emulsifier is available in the aqueous phase, we obtain:

$$LC_{50mix} = 30.3 \text{ mg/L.} \quad \text{[Equation 4]}$$

In either case, the acute ecotoxicity LC_{50} lies between 10 and 100 mg/L.

Based on Table 1.1, this places the material in Class 9.1C (harmful in the aquatic environment) if it is not readily biodegradable or Class 9.1D if it is. Redicote™ E-9 is readily biodegradable. Considering Table 3.3, we find that in the event of their acute ecotoxicity meeting the requirements of Equation 5 (which, it must be emphasised, has only been calculated for Redicote™ E-9 or other products with CAS # 61791-55-7 at present), emulsions based on the emulsifiers listed in Table 3.3 would meet the requirements of Class 9.1C or 9.1D. The classification of 9.1C would only apply if the NOEC is less than 1 mg/L.

Redicote™ N39L, Redicote™ RM007, Redicote™ EM24 and Redicote™ EM22 contain components which are not readily biodegradable. Emulsions based on these would meet the Class 9.1C requirement unless the emulsifiers possess relatively high NOEC values (undetermined), in which case they would meet the Class 9.1D requirement of '1.0 < Acute ecotoxicity \leq 100 mg/L AND persistent AND/OR bioaccumulative AND chronic ecotoxicity (NOEC) > 1 mg/L.'

Redicote™ E-9 and Redicote™ 103 would meet the Class 9.1D requirement '1.0 < Acute ecotoxicity \leq 100 mg/L AND not persistent AND/OR not bioaccumulative'.

3.8 The European Union method of mixtures for assessing ecotoxicity

The method of mixtures is used in the European Union to assign ecotoxicity in the absence of testing a mixture. Thus, if an R50 compound (very toxic to aquatic organisms) is present to $\geq 25\%$ of the mixture, the classification remains as R50. If not, for $\geq 2.5\%$, we have an R51 classification (toxic to aquatic organisms); for $\geq 0.25\%$, an R52 classification (harmful to aquatic organisms). Typical emulsifiers are classified as R50. Hydrochloric acid is classified as R50/53 (very toxic to aquatic organisms; may cause long-term adverse effects in the aquatic environment). With the emulsifier and acid combining to make up approximately 0.3% of a typical emulsion, emulsions would be classified as R52/53 (harmful to aquatic organisms; may cause long-term adverse effects in the aquatic environment) – the R53 label is maintained under dilution.

4. Overseas research on bituminous emulsion toxicity

4.1 Introduction

Overseas work has concentrated mainly on emulsion mixes (slurries and cold mixes), with the principal ecological danger being seen as emulsifier in water produced in the breaking process after placement. The emulsifier dosages in these products tend to be higher than for chipsealing, at least partly because more stable emulsions are required for mix work.

4.2 Slurry seal runoff

A set of studies was reported from AKZO Nobel on runoff from a slurry seal (James 1998, Campbell et al. 2000, James & Thorstensson 2002). Findings in these papers that are relevant to the present study include:

- Runoff from a dense graded slurry containing 13.4% emulsion (1.2% Redicote™ EM 26, 65% bitumen) contained less than 0.5mg/l of emulsifier (approximately 0.5 ppm).
- The aquatic toxicity (LC₅₀ and EC₅₀) of emulsifiers is of the order of 0.1 to 10 mg/l (James & Thorstensson 2002).
- Emulsifier was strongly and irreversibly absorbed in soils. Tests with three soil types obtained 99.99% absorption (emulsifier in soils may be eliminated by biological action – see 6.3). (As a general rule, cationic surfactants adsorb strongly to natural sediments, soil and clay (Boethling 1994)). Small amounts of humic acid added to a solution of cationic surfactant in water resulted in much reduced morbidity for fish, daphnia and algae.

It follows from this that runoff may be a greater problem in urban (as opposed to rural) environments where it may flow directly into stormwater drains rather than travelling over grassed berms.

The only result reported for a chipsealing emulsifier was that no detectable emulsifier was found in air samples taken around and in a sprayer sealing with CRS-2 emulsion containing approximately 0.2% tallow diamine emulsifier (this would be a hot emulsion). Minute quantities of ammonia in the parts per billion range were observed.

4.3 Emulsifier elimination by micro-organisms

AKZO Nobel and other manufacturers reported results of a laboratory study at 28°C of the elimination of a commercial tallow alkyl amine by soil micro-organisms (European Commission European Chemicals Bureau 2000). Seventy-five percent of the material had been eliminated at seven days, and 84% at 28 days. The IUCLID dataset notes that 'a high geoaccumulation potential is not expected, due to high biodegradation.' The AKZO Nobel data on emulsifiers in Table 3.3, however, indicate that not all emulsifier products are biodegradable.

4.4 Current French research on cold mixes

SFERB (2004) (Section des Fabricants d'Émulsions Routières de Bitume – French Road Emulsion Manufacturers' Association) granted Institut National de l'Environnement Industriel et des Risques (INERIS) a research budget to develop a standardised method to conduct impact studies and risk assessments related to the road use of asphalt cationic emulsions.

INERIS is a public independent laboratory under the supervision of the French Secretary of the Environment. The purpose of the development work is to assess the impact of the runoff water resulting from the emulsion's breaking process as well as of the wash-off waters resulting from early rainfalls following application to the road.

To date, the research has focused on cold mix material (Gay et al. 2006). By the nature of its manufacture, the cold mix will produce runoff as it is compacted, whereas entry of water into the surrounding land and water environment from chipsealing is an unintended phenomenon. Cold mixes generally have higher emulsifier concentration in the emulsion than do chipseals; 0.4 to 1.5% surfactant content is typical. The emulsion is designed to break fully under the mechanical stresses induced by laying or rolling the mix, rather than rapidly upon contact with the aggregate, as is the aim for chipsealing.

Gay et al. (2006) have developed a standardised laboratory protocol for predicting the environmental impact of asphalt emulsions in cold mixes. The test emulsion is mixed with a standard graded aggregate. The mixture is then centrifuged to separate the aggregate and its adhering bitumen from the aqueous phase of the broken emulsion. Three sets of standard ecotoxicological tests are carried out on the aqueous phase:

1. The effect of the aqueous phase (corresponding to water as it emerges from cold mix) on *Daphnia* mobility and algal growth is examined.
2. Standard test soils are impregnated with the aqueous phase, and the effect on earthworm mortality, and plant leaf and root growth is studied. This is meant to reproduce the effect of runoff water on the immediate road environment.
3. The impregnated soil is leached, and the effect of the leachate on *Daphnia* and algae is measured. This is meant to assess the effect of rain leaching material from soil into waterways.

Results for three emulsions were reported. It is noteworthy that one of the emulsions (with a tallow polyamine emulsifier) is approximately ten times more toxic, as measured by the above approach, than the two that were produced with different emulsifier combinations (tallow polyamine + mixture of imidazoline and amidoamine fat derivatives, tallow polyamine + tallow diamine).

In New Zealand, the present concern is with emulsions used for chipsealing rather than for cold mix or slurry manufacture, because this is by far the principal use, and because the possibility of accidental spillage into the environment during or after sealing is viewed as a much more likely occurrence than significant water loss to the environment from cold mixes. Nevertheless, the variation of ecotoxicity resulting from the different emulsifiers serves as a warning that the ecotoxicity of a fully representative range of chipseal emulsions needs to be assessed.

4.5 Research on Orimulsion®

A considerable number of investigations have been carried out to assess the ecotoxicity of the bitumen emulsion product Orimulsion® and its current version Orimulsion-400® (e.g., Environmental Protection Agency 2001, National Academy of Science 2002, Svecevičius et al. 2003, Williams et al. 2003). These products are designed as a fuel and consist of Venezuelan bitumen and water in an approximately 70:30 mix, with a small amount of non-ionic emulsifier (0.135% alcohol ethoxylate) and stabiliser (0.11% monoethanolamine). Concerns have been raised about the effect of accidental spillage into freshwater and saltwater environments.

In Svecevičius et al's 2003 work, laboratory tests were conducted on rainbow trout (*Oncorhynchus mykiss*) exposed to Orimulsion® diluted with artesian water. The reported toxicity values are given in Table 4.1. The observed toxicity was thought to be caused partially by the soluble components (principally the emulsifier) of Orimulsion® and partially by small particles of dispersed bitumen blocking fish gills.

Table 4.1 Acute aquatic toxicity test data (96hr LC₅₀) for 'Orimulsion-400®' for rainbow trout life stages (from Svecevičius et al. 2003).

Life stage	LC ₅₀ (mg/L)
Adult	2220
Larvae	60
Embryos	100

Orimulsion-400® is stable when diluted by fresh or salt water, although in fresh still water, the bitumen particles tend to sink as the bitumen is slightly denser than the water (Williams et al. 2003). A cationic chipsealing emulsion will be unstable in fresh water and only the smallest particles would be expected to remain in solution for long, so that the mechanical effect of small particles may be much less than any chemical effect.

5. New Zealand research reported to date

Fulton Hogan (2003) reported test results for runoff from artificial cutback and emulsion seals constructed in the laboratory and sprayed with water at various times after construction. The total petroleum hydrocarbons (TPH) were measured in each instance, and converted to runoff per square metre and runoff per lane-kilometre values. Indicated TPH values for emulsions on spraying half an hour after preparation were above the 15 mg/l limit proposed in the Ministry for the Environment (1998) Environmental Guidelines.

Report recommendations include:

- Further research should be carried out to determine what the concentrations of TPH in waterways are, and also the effect that pavement temperature will have on the curing time.
- Any road sealing operations that require the use of emulsion should not proceed without a positive weather forecast for at least the following day.

6. Experimental methodology

6.1 Introduction

In the absence of any reported testing, the review of research work in Chapters 4 and 5 indicates the need to measure sealing emulsion ecotoxicity. The laboratory approach must be appropriate to the actual risks encountered by the environment.

- Danger to the environment will be a combination of physical effects and chemical poisoning.
- The physical effects would consist of smothering by broken bulk bitumen in the immediate vicinity of a spill or of a large spillage arising from a tanker accident (ecotoxicity is irrelevant in this case), and the action of small suspended bitumen particles hindering breathing and feeding of small organisms. Published research on Orimulsion® indicates the LC₅₀ levels caused only by small particle size should be greater than 60mg/L (Table 4.1). The Orimulsion® results are for a material for which breaking does not occur easily (the emulsifiers are neutral rather than cationic or anionic) and the bitumen particles remain suspended in solution. Cationic emulsions will break on dilution in streams or ponds, and the concentration of bitumen particles should be much reduced compared to that of Orimulsion®. The rate of precipitation of particles from the water will depend on many local environmental factors, such as stream speed, irregularity of flow, and stream bed profile and composition. It is not practical to devise a laboratory test for the effect of small particles that would be applicable to all situations. Generally, it is accepted that undiluted emulsion will kill small aquatic or terrestrial organisms through a physical effect, but that this risk will diminish with dilution.
- In view of the discussion in Chapter 3, the likely cause of any chemical poisoning would be emulsifier diluted in any water environment. Any kerosene present may also theoretically contribute to ecotoxicity levels but (as noted in Chapter 3.3) this effect should not be important.

We wish to evaluate the ecotoxicity of the aqueous phases of the emulsions. In general, runoff resulting from rain after chipsealing will be from partially broken material. While this could be environmentally problematic, the more extreme case is spillage of completely unbroken emulsion. It was therefore proposed, in the first instance, to test the ecotoxicity of the aqueous phase of the original emulsions.

6.2 General experimental approach

The testing procedure used aimed to separate the aqueous phase from the bitumen and test it for ecotoxicity at various concentrations. Plastic vessels were used throughout the work. Cationic bitumen emulsions are designed to break on contact with siliceous aggregate surfaces, and the same thing would be expected to happen with chemically similar glass vessels. In addition, a significant portion of the emulsifier in an aqueous solution may be absorbed on to glass surfaces.

The emulsions were received from the manufacturers in capped plastic containers. Each emulsion was stored at approximately 50°C for at least 24 hours and then inverted several times to ensure a representative sample. A small sample was weighed into a polypropylene vessel and diluted with approximately a litre of *Daphnia* culture water (Martin 2004) (the culture water is designed to replicate typical stream water and provide nourishment for the test organisms). The diluted material was centrifuged for two hours in 250 mL polypropylene centrifuge cups at approximately 3400 gs (4000 rpm, maximum centrifuge speed). The centrifuged liquid was then filtered under suction through a 0.22 µm polyethersulfone filter (Millipore Stericup-GP 500 mL filter unit). After weighing to determine the proportion of the liquid recovered after filtering, the filtrate was diluted with more *Daphnia* culture water, aiming to bring the concentration of the emulsion's aqueous phase to 1000 mg of aqueous phase per litre, i.e. 1 gm of aqueous phase diluted to a litre. This material was bottled in high density polyethylene flagons and despatched to the NIWA Ecotoxicity Laboratory in Hamilton for testing at a range of dilutions. A blank sample of *Daphnia* culture water was prepared for comparison by the same process (centrifuging and filtering).

The NIWA laboratory carried out acute (48 hour *D. magna* survival) and chronic (72 hour algal growth rate) toxicity tests on the received solutions.

6.3 *Daphnia magna* acute studies

Test conditions for this work are outlined in Table 6.1. The tests were carried out according to a NIWA protocol based on an OECD method (OECD 1984).

Table 6.1 *Daphnia* acute toxicity test conditions in the study on emulsions.

Test parameter	Condition
test protocol	NIWA SOP 10.1 (NIWA 1995)
test organisms	<i>Daphnia magna</i> (juveniles <24 h old)
source	laboratory culture
organisms/container	10
test concentrations	Control, 0.1, 1.0, 5.0, 10.0, 25.0%
replicates	5 for controls, 3 for treatments
reference toxicant	zinc sulphate
test duration	48 hours
dilution water	NIWA <i>D. magna</i> culture water
test chambers	55 ml polystyrene beakers
lighting	16:8 h light: dark
temperature	20 ± 1°C
aeration	nil
effect measured	mortality
test acceptability	mean control mortality no greater than 10%
test compliance	achieved

The mortality of *D. magna* exposed to a series of concentrations of the aquatic phase of the emulsions was compared to responses in unexposed *D. magna*. The tests also checked survival in control 'blanks' that had been subjected to the same solution preparation procedures (centrifuging and filtering) apart from inclusion of emulsion.

The 48 hour tests were followed immediately by one hour's exposure to ultraviolet (UV) radiation and reassessment of mortality. The UV irradiation procedure has been developed as a result of the studies of Ahrens et al. (1992), Ankley et al. (1994) and Monson et al. (1995), who found increased mortality which was attributed to photo-activation of polyaromatic hydrocarbons (PAHs) absorbed by the test organisms. Results before UV exposure would apply to emulsions spilling into sheltered environments; in open water expanses, the results after UV exposure are applicable, especially for New Zealand, where relatively high UV exposure in aqueous environments is to be expected. Test samples were considered toxic when a statistically significant ($\alpha=0.05$) dose-dependent effect on survival occurred.

6.4 Algal growth inhibition

The algal growth test followed the protocol established by Golding (1994) from a method developed by Environment Canada (1992). Test conditions are outlined in Table 6.2.

Table 6.2 Algal growth rate test conditions in the study on emulsions.

Test parameter	Condition
test organisms	<i>Pseudokirchneriella subcapitata</i> *
source	University of Texas, USA
test protocol	NIWA SOP 15.2 (Golding 2004)
test type	Static, serial dilution
organisms/container	10 000 cells/mL at time zero
test concentrations	Control, 0.2, 0.4, 0.8, 1.56, 3.13, 6.25, 12.5, 25, 50, 100%
replicates	10 for controls, 4 for dilutions
reference toxicant	zinc sulphate
test duration	72 hours
sample pre-treatment	0.45 µm filtration
dilution water	0.2 µm filtered UV deionised water
test chambers	96 well polystyrene microplates
lighting	Continuous overhead lighting
temperature	24 ± 1°C
aeration	nil
effect measured	growth inhibition relative to controls (cells/mL)
test acceptability	Cell concentration in control treatments could increase by at least 16× within 3 days; control coeff. var. < 20%
test compliance	achieved

* Formerly *Selenastrum capricornutum*

Algae growing exponentially were exposed to a series of concentrations of the aquatic phase of the emulsions and growth after 72 hours was compared to growth in control 'blanks' that had been subjected to the same solution preparation procedure (centrifuging and filtering) but without emulsion. Algal growth in each emulsion aqueous phase sample was compared to growth in the appropriate blank. Test samples were considered toxic when a statistically significant ($\alpha=0.05$), dose-dependent inhibition of algal growth occurred.

7. Results and discussion

7.1 Introduction

Complete details of the testing methodology and results are given in the NIWA report by Bremner & Martin (2007). A summary of the toxicity testing results is presented below.

7.2 Test emulsions

Table 7.1 lists basic properties of the emulsions tested. The emulsions were chosen to give a variety of cationic emulsifier types.

Table 7.1 Characteristics of emulsions evaluated in the toxicity testing.

Sample reference	Emulsion type	Percent binder ^a	Emulsifier description
6/07/67	CRS-2	70	fatty diamine
6/07/86	CRS-2	70	tallow and fatty diamines + tallow amine propoxylates
6/07/89	Cat 60	60	fatty piperazines + fatty diamines
6/07/91	PME ^b	75	tallow propylene diamine.

Notes to Table 7.1:

a Percentage binder quantities supplied by manufacturer

b Polymer modified cationic emulsion

7.3 Crustacea

7.3.1 Results

Table 7.2 lists toxicity results reported by NIWA for the aqueous phases of the emulsions and the supplied blank (Sample Reference 6/07/115 – see Chapter 6.2 for details of preparation).

Table 7.2 Summary of the *Daphnia magna* test results (48 hour survival).

Sample	Emulsion aqueous phase concentration (mg/L)					
	LC ₅₀ ^a	NOEC ^b	LOEC ^c	TEC ^d	LC ₅₀ ^a after 1hr UV exposure	Evidence of photo-activation
6/07/67	331	100	250	158	231	Yes
6/07/86	71	50	100	71	63	Yes
6/07/89	45	10	50	22	45	No
6/07/91	67	50	100	71	67	No
6/07/115	>1000	>1000	>1000	>1000	-	-

Notes to Table 7.2:

a. The lower the LC₅₀, the greater the toxicity, which indicates that a higher dilution was required to cause a 50% effect on the test organisms.

b. NOEC = No observed effect concentration

c. LOEC = Lowest observed effect concentration

d. TEC = Threshold effect concentration = $\sqrt{\text{NOEC} \times \text{LOEC}}$

7.3.2 Discussion

All four emulsion extracts significantly affected the *Daphnia* survival, but a seven-fold difference in survival was noted between leachates (least toxic: 6/07/67, LC₅₀ = 331 mg L⁻¹; most toxic: 6/07/89, LC₅₀ = 45 mg L⁻¹).

UV exposure for one hour increased mortality significantly for sample 6/07/67 (331 to 221 mg/L), although even after this, the toxicity was less than in all the other samples. Sample 6/07/86 had a slight reduction of 8 mg/L in the LC₅₀ value, while the other two samples were unaffected. Increased toxicity of the type observed has been attributed to the photoactivation of specific PAHs absorbed into the organism tissues (Ahrens et al. 1992, Ankley et al. 1994, Monson et al. 1995). The increased mortality following UV exposure found for samples 6/06/67 and 6/07/86 indicates that photoactive PAHs (or possibly other unidentified photoactive compounds) were present, and in greater concentrations in 6/07/67 than in 6/07/86.

The pH and dissolved oxygen of each of the test dilutions at the end of the tests were all within normal physiological range and therefore did not account for any of the toxicity observed.

The results of Table 7.2, as noted above, are for the aqueous phase of the emulsions. To express them in terms of the total emulsion, they must be multiplied by a factor of $\frac{100}{100 - \text{Binder percentage}}$. Carrying out this conversion gives the results shown in Table 7.3.

Table 7.3 Summary of *Daphnia magna* test results predicted for full emulsion.

Sample	Bitumen emulsion concentration (mg/L)				
	LC ₅₀	NOEC	LOEC	TEC	LC ₅₀ 1hr UV
6/07/67	1103	333	833	526	770
6/07/86	237	167	333	237	210
6/07/89	113	25	125	55	113
6/07/91	268	200	400	284	268

These figures do not account for any additional toxicity caused by the binder but, as discussed previously, the binder's contribution to toxicity is expected to be negligible.

7.4 Algae

7.4.1 Results

Table 7.4 lists toxicity results reported by NIWA for the aqueous phases of the emulsions and the supplied blank (Sample 6/07/115).

Table 7.4 Summary of algae (*Pseudokirchneriella subcapitata*) test results (72 hour cell growth inhibition).

Emulsion aqueous phase concentration (mg/L)				
Sample	EC ₅₀	NOEC	LOEC	TEC
6/07/67	>1000	1000	>1000	-
6/07/86	399	100	500	224
6/07/89	301	100	499	223
6/07/91	284	100	500	224
6/07/115	>1000	>1000	>1000	>1000

Note: The lower the EC₅₀, the greater the toxicity, which indicates that a higher dilution was required to cause a 50% effect on the test organisms. NOEC, LOEC and TEC are defined as for Table 7.2.

7.4.2 Discussion

Sample 6/07/67 showed no toxic effect on the algae at the highest test concentration (NOEC = 1000 mg L⁻¹). For the other three samples, the NOEC is 100 mg/L. Toxicity is, by definition, deemed to occur at the TEC value, i.e. 224, 223 and 224 mg/L for samples 6/07/86, 89 and 91, respectively.

Converting these toxicities so as to express quantities in terms of the full emulsions gives the results shown in Table 7.5.

Table 7.5 Summary of algae (*Pseudokirchneriella subcapitata*) test results predicted for full emulsion.

Bitumen emulsion concentration (mg/L)				
Sample	EC ₅₀	NOEC	LOEC	TEC
6/07/67	>3333	3333	>3333	-
6/07/86	1330	333	1667	745
6/07/89	753	250	1248	559
6/07/91	1136	400	2000	894

7.5 Potential ERMA classification

Bremner & Martin (2007) used the toxicity test results for algae and *D. magna* to classify bitumen emulsion leachates provisionally according to the ERMA (2001) ecotoxicity classification scheme (Table 7.6).

Although none of the samples had a 72 hour algal growth EC_{50} of 100 mg/L or less, three of the leachates (6/7/86, 98 and 91) would require ERMA classification, as they had a *D. magna* 48 hour LC_{50} of 100 mg/L or less. The chronic *D. magna* NOEC of each of the leachates was estimated to be greater than 1 mg/L. Under the classification scheme, the emulsions may be classified as: 9.1 D or 'slightly harmful to the aquatic environment'.

The increase in toxicity through ultraviolet photo-activation does not change the classification.

Table 7.6 ERMA (2001) classification of bitumen emulsion leachates.

Sample	Emulsion concentrations (mg/L)				ERMA classification
	Acute EC_{50} or LC_{50}		Chronic NOEC		
	Algae	<i>Daphnia</i>	Algae	<i>Daphnia</i> *	
6/07/67	>1000	331	>1000	33.1	'not classified'
6/07/86	399	71	100	7.1	9.1D
6/07/89	301	45	100	4.5	9.1D
6/07/91	284	67	100	6.7	9.1D

*Estimated by acute $LC_{50}/10$ to allow for chronic affects (ANZECC 2000).

The *D. magna* and algae results provide an indication of the likely classification. ERMA requires a minimum set of three test species to provide an accurate classification. Therefore a definitive classification cannot be made at this time, unless ERMA allows a dispensation to use only two species (see Chapter 9 for a fuller discussion on establishing classification).

7.6 General application of results to emulsions

The emulsifier is the major contributor to the ecotoxicity of emulsions. An approximately seven-fold variation in ecotoxicity (for *D. magna*) has been observed in the four emulsions tested. A wide range of emulsifier types is available. This could potentially lead to a wide range of potential ecotoxicities. In addition to the emulsifier type, ecotoxicity will be effected by:

- emulsifier concentration – this may be varied by the manufacturer to control emulsion viscosity, storage stability, setting rate and binder adhesiveness; and
- the concentration of the emulsifier in the aqueous phase of the emulsion.

The emulsion aqueous phases tested fall comfortably into ERMA's 'not classified' category or Class 9.1 D ('slightly harmful to the aquatic environment'). If the results are modified to be expressed in terms of ecotoxicity of the full emulsion (Tables 7.3 and 7.5), all four emulsions become 'not classified.'

The range of emulsifier types tested is believed to be representative of the industry, although only a survey of all New Zealand bitumen emulsion manufacturers could confirm this. Manufacturers of emulsions know details of the chemical nature of the products they use in their emulsion recipes, but will not make these generally available for commercial reasons.

For the convenience of the chipsealing industry, it would be helpful if all sealing emulsions could be classified as a group. Testing individual emulsions would cost several thousand dollars per emulsion. A number of matters would need to be resolved.

Firstly, ERMA would need to accept the results as a valid indication of ecotoxicity for emulsions as a group; they fall into Class 9.1D 'slightly harmful to the aquatic environment'. This would (at least) require manufacturers to indicate that the emulsifiers they were using fell into the range of types tested. In the instance that a manufacturer was using a different type of emulsion, independent testing would be needed.

Secondly, the question of whether an emulsion should be classified on the basis of the ecotoxicity of the aqueous phase only or on the inferred ecotoxicity of the emulsion as a whole (which may give a more ecologically favourable evaluation) needs to be addressed.

The measured *D. magna* LC₅₀ values for the aqueous phase extract ranged from 67 to 331 mg/L, as opposed to the 15 to 30 mg/L values calculated using ERMA mixture rules for an emulsion with an N-tallow-1,3-diaminopropane emulsifier (Chapter 3.7). This is only an order of magnitude agreement, but it indicates that calculations based on emulsifier ecotoxicity data may provide a conservative indication of the emulsion ecotoxicity. The measured results are more ecologically protective than the calculated one.

8. Summary and conclusions

Continually increasing use of cationic bitumen emulsions for chipsealing in New Zealand raises the question of the ecological risks and benefits of using this material, as against the still more common method of using hot cutbacks, which are now classified by ERMA New Zealand as not ecotoxic.

The major potential environmental dangers of emulsion sealing in New Zealand have been perceived to be:

- spillage and/or runoff into waterways from tanker accidents or mishaps during spraying, and
- rain washing emulsion off the road before it has had time to set.

With the principal physical danger of emulsions being established as smothering by broken bulk bitumen, the decision was made to concentrate on investigating the effect of the emulsifier in determining ecotoxicity. Four emulsions containing four different types of emulsifier were selected for testing.

The emulsifying agent is the only component of the emulsion that will contribute significantly to ecotoxicity (toxicity in receiving environments).

Cationic emulsifying agents used for road work are highly toxic (typically $LC_{50} < 1$ mg/L), while biodegradability varies widely from emulsifier to emulsifier. However, the emulsifier content of a typical emulsion is of the order of only 0.2%, of which a significant portion is bound in the bitumen particles which will precipitate out on use or accidental spillage.

The aqueous phases of the emulsions were separated by centrifugation followed by filtering, and diluted to a target level of 1000 mg/L, using *D. magna* culture water supplied by NIWA, Hamilton. NIWA tested these solutions for acute and chronic ecotoxicity to *D. magna* (crustacean) and algae.

The test results for algae gave no indication of ecotoxicity. However, the results for *D. magna* indicated that three of the four emulsion leachates qualified for the ERMA classification 9.1D, 'slightly harmful to the aquatic environment'. Under standard ERMA procedures, a minimum set of three test species is needed to provide a classification, although this is not an invariable requirement.

If the results were modified to be expressed in terms of ecotoxicity of the full emulsion (Tables 7.3 and 7.5), all four emulsions would become 'unclassified.' Classification according to the ecotoxicity of the aqueous phase only would be the conservative option, possibly preferred by regulatory bodies.

The measured aqueous phase 48 hour LC_{50} values for *D. magna* ranged from 67 to 331 mg/L, as opposed to the 15 to 30 mg/L values predicted using an ERMA mixture rule for

an emulsion with an N-tallow-1,3-diaminopropane emulsifier. This order of magnitude agreement indicates that emulsifier ecotoxicity data may provide a conservative estimate of the emulsion ecotoxicity.

Current indications are that chipsealing emulsions typically would be classified as safe or 'slightly harmful to the aquatic environment' (ERMA Class 9.1D).

9. Recommendations

For the convenience of the chipsealing industry and clients concerned with the effect of chipseal emulsions on the environment, it would be helpful if all sealing emulsions could be classified as a group. This would require a number of matters to be addressed:

- The sealing industry as a whole would need to review the types of emulsifier and dosages being used to ascertain whether a representative set of emulsions has been tested. If necessary, testing may be indicated for other types after the items below have been actioned.
- Discussions would need to be held with ERMA to:
 - explore the possibility of obtaining a group classification applicable to all cationic sealing emulsions,
 - to decide whether to classify ecotoxicity by complete emulsion or aqueous phase (the former results in a slightly less ecotoxic evaluation), and
 - to ascertain whether an ecotoxicity classification based on known ecotoxicity of the emulsifier and calculated by ERMA's method of mixtures would be acceptable for an initial evaluation of any new type of emulsion.

New emulsifiers and new emulsion recipes are expected to be produced over time to give greater efficiencies and economies of emulsion production. Some new emulsion products may turn out to have greater ecotoxicity than current materials. The state highway and local authorities could guard against this by specifying that all sealing emulsions meet ERMA's 'not classified' or 9.1D ecotoxicity level requirements. Consideration should be given to doing this.

A watching brief should be kept for innovations in continuing French research on emulsion ecotoxicity (see Chapter 4.4).

10. References

Ahrens, M.J., Nieuwenhuis, R., Hickey, C.W. 2002. Sensitivity of juvenile *Macomona liliiana* (Bivalvia) to UV-photoactivated fluoranthene toxicity. *Environmental Toxicology* 17(6):567–577.

Ankley, G.T., Collyard, S.A., Kosian, P.A., Monson, P.D. 1994. Influence of ultraviolet light on the toxicity of sediments contaminated with polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry* 13(11):1791–1796.

ANZECC. 2000. *Australian and New Zealand Guidelines for Fresh and Marine Water Quality*. Canberra: Australian and New Zealand Environment and Conservation Council & Agriculture and Resource Management Council of Australia and New Zealand.

AUSTROADS. 2002. Environmental assessment of emulsions. *Report Number AP-R153*.

AZKO. 2008. Safety data sheets.

http://www.surface.akzonobel.com/prodsearch_app.cfm?App=63&AppArea=15.

Ball, G.F.A. 2005. Implications of increased emulsion sealing on state highways. *Central Laboratories Report 05-521095.00*. Wellington: Opus International Consultants.

Boethling, R.S. 1994. Environmental aspects of cationic surfactants. Pp 95–135 in *Cationic Surfactants: Analytical and Biological Evaluation* (eds Cross, J., Singer, E.J.). New York: Marcel Dekker, Inc.

Bremner, D., Martin, M. 2007. Toxicity of bitumen emulsion leachates: May 2007. *NIWA Client report: HAM2007-113, July 2007; NIWA Project: OIC07205*. Hamilton: National Institute of Water and Atmospheric Research. 23 pp.

Campbell D., James A., Redelius, P., Thorstenson B.-A. 2000. *Chemical Emissions from Asphalt Emulsion Applications*. Paper presented at Inroads 2000 American Emulsion Manufacturers' Association 27th Annual Conference, Florida, USA.

Deneuvillers C. 2004. *Interactions between Surfactants, Aggregates and Bitumen – Understanding the Breaking Mechanism of Bitumen Emulsions*. Paper presented at the Fourth International Symposium on Asphalt Emulsion Technology, Washington DC, USA, October 2004.

Environment Canada. 1992. Biological test method: growth inhibition using the freshwater algae *Selenastrum capricornutum*. *Environmental Protection Series Report EPS1/RM/25*. Ontario, Canada: Environment Canada.

Environmental Protection Agency. 2001. Environmental Impacts of the Use of Orimulsion® EPA-600/R-01-056a. <http://www.epa.gov/appcdwww/aptb/OrimulsionV1.pdf>.

ERMA. 2001. User guide to the HSNO thresholds and classification. Part VII: substances with ecotoxic properties. Environmental Risk Management Authority ER-UG-03-1 08/01. <http://www.ermanz.govt.nz/resources/publications/pdfs/ER-UG-03-1.pdf>.

European Commission European Chemicals Bureau. 2000. *IUCLID dataset: Substance 61790-33-8, Tallow Alkyl Amines*.

Fulton Hogan Ltd. 2003. *Emulsified and Cutback Bitumen Runoff Experiment, February 2003*. Internal study. Christchurch: Fulton Hogan Ltd.

Gay, G., Schnuriger, B., Pandard, P., Ismert, M. 2003. *Élaboration d'une Méthodologie de Qualification Environnementale des Eaux de Rupture des Émulsions de Bitume dans leurs Applications Routières [Development of a Methodology to Assess the Environmental Impact of Water Resulting from Breaking of Bitumen Emulsions Used in Roading Applications]*. Paper presented at the 4th World Congress on Emulsions, 3–6 October 2006, Lyon, France.

Golding, L. 2004. Freshwater algae *Selenastrum capricornutum* chronic toxicity test protocol. *Standard Operating Procedure 15.2*. Hamilton, New Zealand: National Institute of Water and Atmospheric Research Ltd. 43 p.

Herrington, P., Ball, G., O'Halloran, K., Tremblay, L. 2006. Aquatic ecotoxicity of cutback bitumen. *Land Transport New Zealand Research Report 285*. Wellington: Land Transport New Zealand. 52pp.

Holleran, G., Motina, I. 2006. *Coalescence and Curing and their Measurement in Chipsealing Emulsions*. Paper presented at the Transit New Zealand and New Zealand Institute of Highway Technology 8th Annual Conference, Auckland, New Zealand, 15–17 October 2006.

James, A. 1998. *Chemical Emissions from Slurry Surfacing*. Paper presented at the 36th Annual conference of the International Slurry Surfacing Association, San Diego, California USA.

James, A., Thorstensson, B-A. 2002. *Environmental and Safety Aspects of Cationic Bitumen*. Paper presented at the Third World Congress on Emulsion, Lyon.

Kraton Polymers SBS D Series Products Material Safety Data Sheet. 2007. [http://docs.kraton.com/tl_warehouse/technical_literature/docs/Rev.%2025%20-%20SBS-D%20Series%20\(01-26-07\).pdf](http://docs.kraton.com/tl_warehouse/technical_literature/docs/Rev.%2025%20-%20SBS-D%20Series%20(01-26-07).pdf).

Leary, G., Eng, A. 2003. Substances to be transferred to the HSNO Act under section 160(1)9a: Petrol and petroleum products. *ERMA New Zealand Transfer Report*. 123p.

Martin, M. 2004. *Daphnia magna* culture procedure. *Standard Operating Procedure Number 11.2*. Hamilton, New Zealand: National Institute of Water and Atmospheric Research. 11 pp.

Ministry for the Environment. 1998. *Environmental Guidelines for Water Discharges from Petroleum Industry Sites in New Zealand*. Wellington: Ministry for the Environment.

Monson, P.D., Ankley, G.T., Kosian, P.A. 1995. Phototoxic response of *Lumbriculus variegatus* to sediments contaminated by polycyclic aromatic hydrocarbons. *Environmental Toxicology and Chemistry* 14(5): 891–894.

National Academy of Science. 2002. Spills of emulsified fuels: risks and response. <http://www.nap.edu/openbook/030908301X/html/>.

NIWA. 1995. Daphnid acute toxicity test procedure. *Standard Operating Procedure Number 10*. Hamilton, New Zealand: National Institute of Water and Atmospheric Research. 11pp.

OECD. 1984. *Daphnia* sp., acute immobilisation test and reproduction test. Part 1 – 24 h EC₅₀ acute immobilisation test. *OECD Guidelines for Testing of Chemicals No. 202*. Paris: Organisation for Economic Co-operation and Development. 15pp.

OECD. 1994. Guidelines for the testing of chemicals: test No. 301: ready biodegradability. <http://caliban.sourceoecd.org/vl=4360477/cl=13/nw=1/rpsv/ij/oecdjournals/1607310x/v1n3/s2/p1>.

OECD. 2002. *SIDS Initial Assessment Report for SIAM 15 (Calcium Chloride, CAS# 10043-52-4)*. Paris: Organisation for Economic Co-operation and Development.

PAN Pesticides Database – Chemicals. 2008. http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34307.

SFERB. 2004. Environmental impact and risk assessment for cationic asphalt emulsion based road applications. http://www.ibef.net/_doc/Environmental_impact_and_risk.pdf.

Svecevičius G., Kazlauskienė, N., Vosylienė, M.Z. 2003. Toxic effects of Orimulsion™ on rainbow trout *Oncorhynchus mykiss*. *Environmental Science and Pollution Research*, Vol 10(5): 281–283.

Slaughter, G. 2004. *Environmental Comparison of Cutback Bitumen and Bitumen Emulsions for Sealing Roads*. Paper presented at the Towards Sustainable Land Transport conference 21–24 November 2004, Wellington, New Zealand.

- Vercoe, J., Perriam, B., Starr, J., Hutchison, D. 2006. *Chipseals and Emulsions versus Cutbacks*. Paper presented at 'Transport and the Pursuit of Excellence', the New Zealand Institute of Highway Technology and Transit New Zealand 8th Annual Conference, 2006.
- Williams J., Roderick, C., Alexander, R. 2003. Sublethal effects of Orimulsion-400[®] on eggs and larvae of Atlantic herring (*Clupea Harengus L.*). *Environmental Toxicology and Chemistry*, Vol 22(12): 3044–3048.

Appendix A Glossary and abbreviations

Acute ecotoxicity: Toxicity observed in response to a short-term (48 or 96 h) exposure relative to the life stage of the test organism that generates **LC₅₀** or **EC₅₀** ecotoxicity values. An example of an acute ecotoxicity test is the 96 h fish acute test where death is the measurement endpoint.

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 are not available, a **log K_{ow}** greater than or equal to 4.

Biocidal action: This means that a substance kills, inhibits growth or inhibits 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.

Chronic ecotoxicity: Toxicity observed in a longer term exposure (compared to **acute ecotoxicity**) relative to the life stage of the organism, 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 fish full life cycle toxicity test or a 72 hour algal growth inhibition test.

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).

DOC: Dissolved organic carbon die-away test.

Ecotoxicity test: The means by which the ecotoxicity of a substance is determined on a group of selected organisms under defined conditions. An ecotoxicity test is used to measure the degree of response produced by exposure to a specific concentration/ or specific concentrations of the test material. Ecotoxicity values (**NOEC**, **LOEC**, **EC₅₀** etc.) can be determined from ecotoxicity tests. Exposures may be acute (see **acute ecotoxicity**) or chronic (see **chronic ecotoxicity**). A toxicity test usually measures either (a) the proportions of organisms affected (quantal) as measured by **EC₅₀**, or (b)

the degree of effect shown (graded or quantitative) after exposure to specific concentrations of whole effluents or receiving water as measured by an **IC₅₀**.

EC₅₀: The median effective concentration (i.e. the concentration of a material in water that is estimated to produce a specifically quantified effect on 50% of the test organisms). The EC₅₀ and its 95% confidence limits are usually derived by statistical analysis of a quantal 'all or nothing' response (such as death, fertilisation, germination or development) in several test concentrations after a fixed period of exposure. The duration of exposure must be specified (e.g., 72 h EC₅₀).

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

ERMA: Environmental Risk Management Authority.

IC₅₀: The median inhibition concentration, i.e. the concentration estimated to cause a 50% reduction in growth compared to a control. The exposure time must be specified, e.g. IC₅₀ (72 h)', for a growth rate derived IC₅₀ and a test duration of 72 h.

INERIS: Institut National de l'Environnement Industriel et des Risques (National Institute for Environmental Technology and Hazards).

Log K_{ow}: The steady state ratio of the solubility of a substance in n-octanol to the solubility of that substance in water.

L(E)C₅₀: Either **LC₅₀** or **EC₅₀** data.

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.

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 compared with controls was observed.

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

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 to the controls.

OECD: Organisation for Economic Co-operation and Development.

PAH: Polyaromatic Hydrocarbons.

PME: Polymer modified cationic emulsion.

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

- 28 days after a solution containing the substance is inoculated with micro-organisms, at least the following should be observed:
 - a 70% reduction in dissolved organic carbon in the solution,
 - 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
 - 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:

- if only **COD** and **BOD₅** data are available, the ratio of BOD₅ to COD is greater than or equal to 0.5:1;

or:

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

SFERB: La Section des Fabricants d'Emulsions Routières de Bitume (French Road Emulsion Manufacturers' Association).

TEC: Threshold Effect Concentration = $\sqrt{\text{NOEC} \times \text{LOEC}}$.

TPH: Total Petroleum Hydrocarbons.

UV: Ultraviolet.

WAF: Water Accommodated Fraction. The WAF method is generally used for preparing sparingly soluble materials (such as bitumen containing kerosene) for testing of aquatic toxicity. 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 containing the WAF is then separated from the insoluble material and test organisms are introduced. In terms of modelling likely 'real-world' scenarios by which a kerosene based cutback may contaminate aquatic ecosystems, the WAF approach represents a worst-case scenario. Such 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.

Environmental Effects of Emulsions

Land Transport New Zealand
Research Report 343