

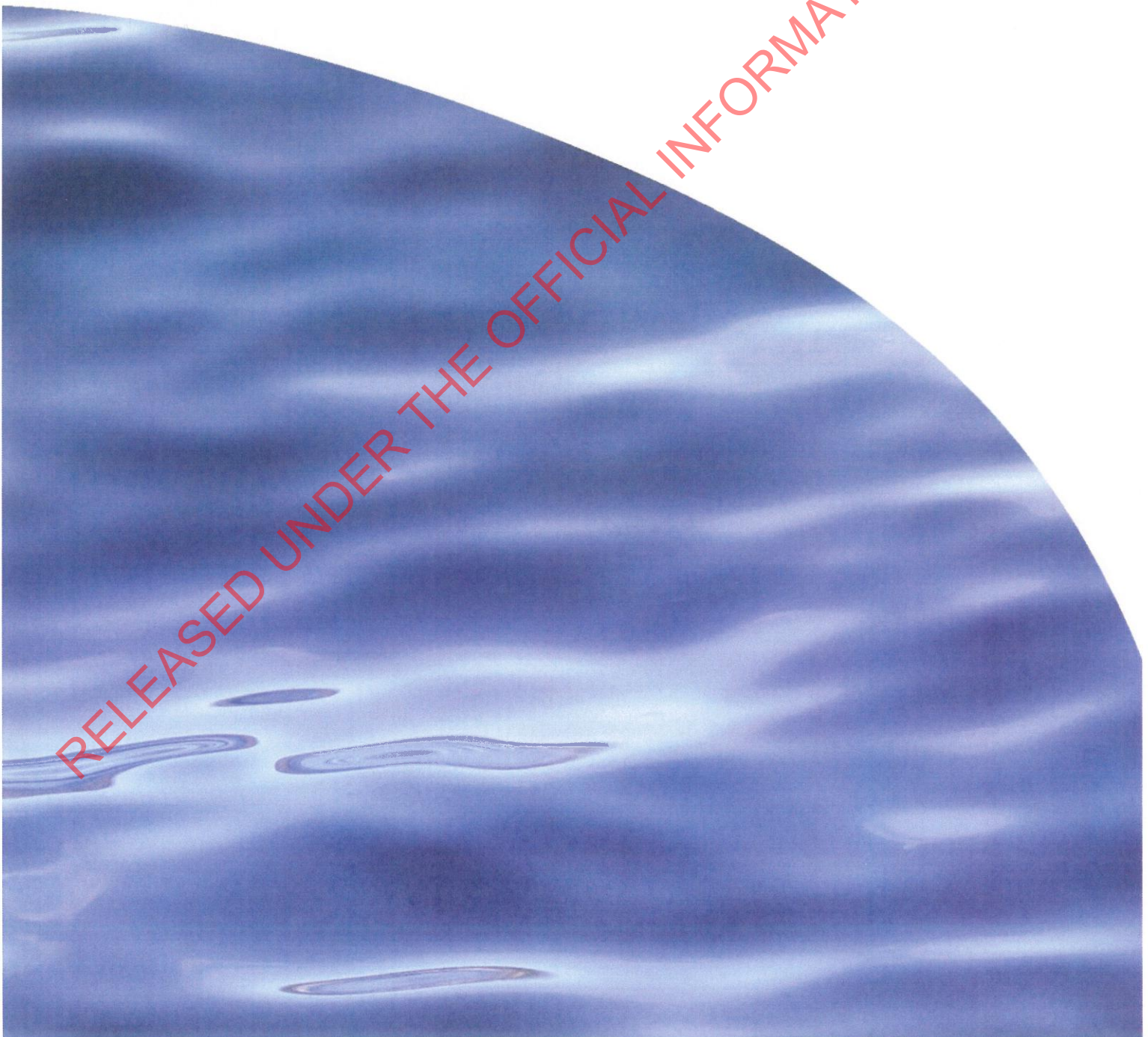


CAWTHRON
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REPORT NO. 3241

**POTENTIAL ECOLOGICAL EFFECTS OF
HERBICIDE USE ON STATE HIGHWAY 6, NELSON
DISTRICT**

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POTENTIAL ECOLOGICAL EFFECTS OF HERBICIDE USE ON STATE HIGHWAY 6, NELSON DISTRICT

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Prepared for Tasman Journeys

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EXECUTIVE SUMMARY

The New Zealand Transport Agency (NZTA) is applying to Nelson City Council (NCC) and Tasman District Council (TDC) for renewal of discharge consents for the use of herbicide active ingredients to control pest plants on NZTA-administered land within the Nelson and Tasman districts (adjacent to State Highway 6). The application proposes the use of the following herbicide active ingredients:

- Glyphosate, for use in all areas within legal road, including in or near waterways
- Metsulfuron, for use in all areas within legal road, including in or near waterways
- Terbutylazine, for use in all areas within legal road, except in or near waterways
- Triclopyr 600 g/L, for use in all areas within legal road, except in or near waterways.

In 1993, the Cawthron Institute produced an assessment of permit applications for herbicide spraying on roadsides and riverbeds for TDC, NCC and Transit New Zealand (now NZTA). The assessment included a review of the toxicity of the herbicides to non-target plants and animals. The present report provides an update to the information provided by Roberts (1993) to support the discharge consent renewal.

Toxicity to non-target organisms

Glyphosate exists primarily as either glyphosate technical acid or as various salts of glyphosate. The variety of forms of glyphosate complicates the application of toxicological data to assessments of the risk from the use of glyphosate-based herbicides. Glyphosate has low acute toxicity to mammals, birds and earthworms. Toxicity to fish is low-moderate and toxicity to aquatic invertebrates, aquatic plants and algae is low for the active ingredient but moderate for the glyphosate-trimesium formulation and for the first breakdown product. It is considered practically non-toxic to honeybees on an acute oral and acute contact basis. However, recent work has suggested that glyphosate may have long-term adverse effects on honeybees by perturbing their gut microbiota.

Metsulfuron has low acute toxicity to mammals, birds and earthworms. It is considered practically non-toxic to honeybees on an acute contact basis although some toxicity data suggest moderate toxicity. Toxicity to fish and aquatic invertebrates is low. Toxicity to algae is moderate but toxicity to aquatic plants is high.

Terbutylazine has moderate toxicity to mammals, birds and honeybees but low toxicity to earthworms. Toxicity to fish, aquatic invertebrates, aquatic plants and algae is moderate.

Triclopyr is applied in the form of an ester and is converted to the parent acid (triclopyr) several days after application. The toxicity of the ester is much higher than that of the parent compound and is considered more relevant for present purposes. Triclopyr has moderate toxicity to mammals, birds, honeybees and earthworms. Toxicity to fish is slight-moderate. Toxicity to aquatic invertebrates is widely variable and is high for at least one common New Zealand aquatic insect. Toxicity to aquatic plants (based on tests on duckweed) is moderate but toxicity to algae is low.

Of the four herbicides considered here, triclopyr is the compound with the highest toxicity to aquatic fauna. Applications are intended to be on land adjacent to State Highway 6, but caution is warranted to minimise potential risk from spraying into nearby streams or ditches.

Most herbicides are toxic to a range of plants, often including crop species. One of the major potential impacts of the proposed spraying is its effect on non-target plants, including pasture grass, horticultural crops, shelter belts and native vegetation. It is most likely that these effects will arise from the drift of spray through the air, but contamination of irrigation water may also be of concern in small water bodies or storage dams fed from roadside water tables. The concentrations of herbicides washed from sprayed channels by rainfall have been shown to cause damage to sensitive crops in some cases. The main cause for concern is when irrigation channels are sprayed directly. In the case of the present consent application, the areas sprayed will not carry irrigation water directly (but may drain into waterways from which irrigation water is taken). The extra dilution provided by runoff from the unsprayed parts of the catchment should reduce the herbicide concentrations to levels that are harmless to non-target plants on the land and in streams and rivers.

Exposure pathways

Non-target animals and plants could be exposed to active ingredients used to control noxious pest plants on NZTA-administered land along State Highway 6 via several pathways:

- Direct spraying – including onto non-target plant surfaces and into waterways
- Accidental spills – in terms of the concentration and volume of herbicide involved, this represents the highest environmental risk
- High rainfall events – rainfall will wash herbicides off target vegetation but will also increase dilution and dispersal
- Via groundwater from normal application – likely to represent a negligible source under normal conditions

The review suggests that there is a risk of adverse effects on aquatic organisms from some of the active ingredients, indicating that it is important that adequate precautions are taken to avoid contamination of waterbodies during spraying. There is also some risk to mammals, birds, honeybees and earthworms from some of the herbicides. Moreover, given the doubt that has been cast on the quality and applicability of toxicological data for herbicides, even those that are widely used, it is appropriate to take a precautionary approach to mitigation.

Mitigation methods

Suggested mitigation options include:

- Restrictions on spraying operations, such as timing in relation to forecast rain or when vegetation is wet, or in relation to water courses or water bodies
- Specification of maintenance of spraying equipment
- Keeping of spray diaries
- Reporting of incidents.

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GLOSSARY

Acronym	Definition
ai	Active ingredient
as	Active substance
ANZECC	Australian and New Zealand Environment Conservation Council
BCF	Bioconcentration factor
bw	Body weight
DPR	Department of Pesticide Regulation of California
DT ₅₀	Degradation Time of the substance to reach 50% of its the initial concentration ($\frac{1}{2}$ life)
d.	Day
d. wt.	Dry weight
EC ₅₀	Effective Concentration that leads to half-maximal response
ECHA	European Chemicals Agency
g	Gram
ha	Hectare
HC5	Hazardous concentration for 5% of the species
IC ₅₀	50% Inhibitory Concentration
kg	Kilogram
K _{oc}	Organic-carbon partition coefficient (adsorption coefficient in soil)
K _{ow}	Octanol-water partition coefficient
L	Litre
LC(D) ₅₀	50% Lethal Concentration (Dose)
LOEC	Lowest Observed Effect Concentration
LR ₅₀	Median Lethal Tissue Residue Values
MAC	Maximum Acceptable Concentration
MCL	Maximum Contaminant Level
mg	Milligram (10^{-3} gram)
µg	Microgram (10^{-6} gram)
ng	Nanogram (10^{-9} gram)
Pa	Pascal
NOEC	No Observed Effect Concentration
PNEC	Predictable No-Effect Concentration
Rfd	Reference dose
s	Second
US EPA	United States Environmental Protection Agency
wt	Weight
WHO	World Health Organisation

DEFINITIONS

Term	Definition
Acute toxicity	<p>This is the intrinsic property of a substance to be injurious to an organism in a short-term exposure to that substance. Lethality is the endpoint associated with acute toxicity in this document where the benchmarks of toxicity are LC₅₀s. It is usually determined in controlled laboratory animal exposure studies.</p> <ul style="list-style-type: none"> • Mammals, birds <ul style="list-style-type: none"> > 2000 mg/L = Low 100–2000 mg/L = Moderate < 100 mg/L = High • Honeybees, fish, aquatic invertebrates, sediment dwelling organisms <ul style="list-style-type: none"> > 100 mg/L = Low 0.1–100 mg/L = Moderate < 0.1 mg/L = High • Algae, aquatic plants <ul style="list-style-type: none"> > 10 mg/L = Low 0.01–10 mg/L = Moderate < 0.01 mg/L = High
BCF	<p>The concentration of the pesticide in tissue per concentration of chemical in the ambient environment. This describes the accumulation of pollutants through chemical partitioning from, for instance, the aqueous phase into an organic phase, such as the gill of a fish. The higher the value the higher is the potential for bioaccumulation.</p>
Chronic toxicity	<p>This state implies adverse effects during or after relatively long-term exposures to one or more contaminants. In this document it is associated with effects that are related to changes in reproduction, growth metabolism, mobility, or other sub-lethal biological variables (e.g. behaviour) being observed.</p>
EC_{x-t}	<p>Effective Concentration is the generic term for a concentration of substance or material that is estimated to cause some defined effect on a proportion (x%) of the test organisms after a defined period of exposure (t). This kind of endpoint allows the classification and the comparison of the toxic potency or intensity of different chemicals. More terms can be derived to describe specific effects (e.g. lethality, inhibition):</p> <ul style="list-style-type: none"> - LC_{x-t} (Lethal Concentration) is the concentration of substance or material that is estimated to be lethal to a proportion (x%) of the test organisms after a defined period of exposure (t). This is an acute toxicity indicator. - IC_{x-t} (Inhibitory Concentration) is the concentration of substance or material that is estimated to have an inhibitory effect (e.g. growth, mobility) on a proportion (x%) of the test organisms after a defined period of exposure (t). This is a chronic toxicity indicator.
Half-life (DT₅₀)	<p>Time required for the pesticide concentration under defined conditions to decline (break down into degradation products) to 50% of the original amount after an application. This time is often expressed as a range (for example, 1-3 days, etc.) because the rate of pesticide breakdown depends on a variety of factors including temperature, soil pH, soil microbe content and whether the pesticide is exposed to light, water and oxygen. It is worth noting that many of the breakdown products themselves are toxic and may have significant half-lives as well.</p>

Term	Definition
Half-life (DT₅₀), continued	<p>Soil degradation (days)</p> <p>< 30 = Non-persistent 30–100 = Moderately persistent 100–365 = Persistent > 365 = Very persistent</p> <p>Aqueous photolysis (DT₅₀ in days at 20°C, pH 7)</p> <p>< 1 = Fast 1–14 = Moderately fast 14–30 = Slow > 30 = Stable</p> <p>Aqueous hydrolysis (DT₅₀ in days at 20°C, pH 7)</p> <p>< 30 = Non-persistent 30–100 = Moderately persistent 100–365 = Persistent > 365 = Very persistent</p>
HC5	Hazardous concentration for 5% of the species; this concentration derived from literature data is expected to protect 95% of species.
Henry's Law Constant	<p>Amount of gas absorbed by a given volume of liquid at a given temperature. This amount is directly proportional to the partial pressure of that gas in equilibrium with that liquid. As such it provides an indication of the preference of a chemical for air relative to water i.e. its volatility. Henry's Law Constant is usually quoted either in Pa.m³/mole or in mm Hg.m³/mole (or in a dimensionless form) at a given temperature (20 °C).</p> <p>Henry's Law constant (Pa.m³/mole):</p> <p>> 100 = Volatile 0.1–100 = Moderately volatile < 0.1 = Non-volatile</p> <p>(Unit conversion: 1 atm = 760 mm Hg = 101.325 kPa)</p>
K_{oc}/K_{foc} (mL/g) (adsorption coefficient)	<p>The adsorption coefficient, K_{oc}, is a measure of how strongly a chemical adheres to soil in preference to remaining dissolved in water. K_{oc} is formally defined as the ratio of the mass of pesticide adsorbed per unit mass of soil to the mass of the pesticide remaining in solution at equilibrium. Pesticides with high K_{oc} values (> 1000) are typically not very water soluble and will preferentially adhere to soils rather than be dissolved in water. This means that pesticides in this class are unlikely to be carried off-site in runoff as dissolved substances; instead, they are transported on sediment particles.</p> <p>Chemicals with lower values (< 500) tend to move more with water than be adsorbed to sediment. Some pesticides are strongly bound to other soil components such as clay surfaces. For some pesticides K_{oc} will be very pH sensitive.</p> <p>< 15 = Very mobile 15–75 = Mobile 75–500 = Moderately mobile 500–4000 = Slightly mobile > 4000 = Non-mobile</p>

Term	Definition
K_{ow} (partition coefficient)¹	<p>The octanol-water partition coefficient (K_{ow}) is a measure of how a chemical will distribute between two immiscible solvents: water (a polar solvent) and octanol (a relatively non-polar solvent). Pesticides with a long half-life and high K_{ow} have been shown to bioaccumulate in the food chain. It is expressed as a logarithm (base 10). The lower values correspond to higher water solubility. Compounds with larger log are more likely to bioaccumulate in tissue:</p> <p style="text-align: center;"> < 2.7 = Low bioaccumulation $2.7-3$ = Moderate > 3.0 = High </p> <p> Log K_{ow} = 1 means 10:1 Organic: Aqueous Log K_{ow} = 0 means 1:1 Organic: Aqueous Log K_{ow} = -1 means 1:10 Organic: Aqueous </p>
LOEC	Lowest Observed Effect Concentration is the lowest concentration of a test substance or material which is observed to have a statistically significant adverse effect on the test organisms for a defined time of exposure and under the test conditions, relative to the control.
Mobility	Ability of a substance to be transported through the environment.
MCL	Maximum Contaminant Level. The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the MCLG (maximum contamination level goal) as feasible using the best available analytical and treatment technologies and taking cost into consideration. MCLs are enforceable standards.
NOEC	No Observed Effect Concentration is the highest concentration of a test substance or material which is observed not to have a statistically significant adverse effect on the test organisms for a defined time of exposure and under the test conditions, relative to the control.
pKa (dissociation constant)	<p>Strengths of acids and bases can be indicated on a common scale at 25 °C. Defined as the negative logarithm of the acidity constant Ka. The lower the pKa the stronger the acid. For example, acetic acid has a pKa of 4.75 whilst sulphuric acid has a pKa of -3.0. pKa is used here as an indicator of the potential of a compound to form ions in water.</p> <p>Many pesticide active substances are either permanently ionic or will change ionic state somewhere in the range of the pH of environmental soils and water. Knowing the ionic state of a pesticide provides important information on its potential mobility and persistence in the environment.</p>
RfD	Reference Dose. An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.
Ten-day Health Advisory (HA)	The concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for up to ten days of exposure. The Ten-day HA is also intended to protect a 10-kg child consuming 1 L of water per day.

¹ EU database: http://sitem.herts.ac.uk/aeru/ppdb/en/docs/Background_and_Support.pdf

Term	Definition
Vapour pressure	<p>The pressure at which a liquid is in equilibrium with its vapour at 25 °C. It is a measure of the tendency of a material to vapourise. The higher the vapour pressure the greater the potential.</p> <p>$< 1 \times 10^{-6}$ = Non-volatile 1×10^{-4} to 1×10^{-6} = Intermediate state $> 1 \times 10^{-4}$ = Volatile</p>

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1. INTRODUCTION

The New Zealand Transport Agency (NZTA) is applying to Nelson City Council (NCC) and Tasman District Council (TDC) for discharge consents for the use of herbicide active ingredients to control pest plants on NZTA-administered land within the Nelson and Tasman districts (adjacent to State Highway 6). This is a renewal of NCC Discharge Consent RM095012, which expires on 27 May 2019 and TDC Discharge Consent RM090020, which expires on 04 March 2019. The present applications seek to enable the continued legal use of herbicides for the control of unwanted plants.

Consistent with the present consent, the application proposes the use of the following herbicide active ingredients:

- Glyphosate, for use in all areas within legal road, including in or near waterways
- Metsulfuron, for use in all areas within legal road, including in or near waterways
- Terbutylazine, for use in all areas within legal road, except in or near waterways
- Triclopyr 600 g/L, for use in all areas within legal road, except in or near waterways.

In 1993, the Cawthron Institute produced an assessment of permit applications for herbicide spraying on roadsides and riverbeds for TDC, NCC and Transit New Zealand (now NZTA) (Roberts 1993). The assessment included a review of the toxicity of the herbicides² to non-target plants and animals and included, as appendices, data on the herbicides' toxicity to freshwater aquatic life, mobility, persistence and other properties.

The present report provides an update to the information provided by Roberts (1993) to support the discharge consent renewal.

² The original assessment referred to herbicides by their proprietary names: Roundup® (active ingredient glyphosate), Gardoprim® (active ingredient terbutylazine), Escort® (active ingredient metsulfuron), Velpar® (active ingredient hexazinone), atrazine and Gallant® (active ingredient haloxyfop). A variation to a subsequent discharge consent replaced proprietary names with the four active ingredients considered in the present report.

2. METHODS

The information presented in the present report is derived from the wider review by Champeau and Tremblay (2013) of 26 agri-chemicals (herbicides, fungicides and insecticides) for the control of vegetation and pests in parks and reserves administered by Nelson City Council, with subsequent updates. Data in those reviews were mainly obtained from the World Health Organisation (WHO), United States Environmental Protection Agency (ToxNet and PAN), European Chemicals Agency (ECHA), Canada (Health Canada), France (AGRITOX database on plant protection substances), Australian and New Zealand Environment and Conservation Council (ANZECC) and Rotterdam Convention database of chemicals. There are some inconsistencies in the use of units and missing information for some chemicals, e.g. missing values, no studies, no regulatory information available. This reflects the variety of sources used for Champeau and Tremblay's review or is an information gap in the database consulted.

Champeau and Tremblay (2013) provided the following information for each agri-chemical:

- chemical structure and other forms
- physico-chemical properties
- toxicology and ecotoxicology information
- environmental fate information
- environmental standards or regulations
- important user information.

3. ASSESSMENT OF POTENTIAL ENVIRONMENTAL EFFECTS

The assessments below are based on the information on the proposed herbicides from Champeau and Tremblay 2013 (summarised in Table 1 and presented in more detail in Appendix 1), with additional sources of information noted where applicable.

3.1. Toxicity to non-target organisms

3.1.1. Glyphosate

Glyphosate is not one single clearly defined compound, but a family of chemicals that can be produced via different chemical processes that, in turn, create various qualitative differences e.g., impurities and by-products. (Cuhra et al. 2016). Glyphosate exists primarily as either glyphosate technical acid or as various salts of glyphosate. Glyphosate-based herbicides are normally formulated as a salt, such as the potassium or isopropylamine salts, to enhance absorption into plants. The salts used are selected to ensure the formulated product handles well, is compatible with other products that might be included in the spray formulation and will not cause adverse responses in crops. When it reaches the leaf surface, glyphosate is often not associated with the salt that it is formulated with.

Cuhra et al. (2016) illustrated how the variety of forms of glyphosate has created confusion over the applicability of toxicological data to assessments of the risk from the use of glyphosate-based herbicides. They suggest that this is a possible explanation for the wide range (spanning orders of magnitude) of published EC₅₀ values for glyphosate.

Glyphosate has low acute toxicity to mammals, birds and earthworms. It is considered practically non-toxic to honeybees on an acute oral and acute contact basis (US EPA 1993), although the parent compound (acid) has an acute oral LD₅₀ of 100 µg/bee (the lower limit of Champeau and Tremblay's [2013] 'moderate' toxicity category: Appendix 1). Recent work has, however, suggested that glyphosate may have long-term adverse effects on honeybees by perturbing their gut microbiota, affecting the bees' resistance to pathogens (Motta et al. 2018) and larval survival and growth rates (Dai et al. 2018).

Toxicity to fish is low-moderate (acute 96-h LC₅₀ > 93 mg/L for the propylamine salt and 38 mg/L for the parent acid). Toxicity to aquatic invertebrates, aquatic plants and algae is low for the active ingredient (the isopropylamine salt of glyphosate) but moderate for the glyphosate-trimesium formulation of the product and for the first breakdown product (glyphosate acid). Bioconcentration in aquatic organisms is likely to be low (based on bioconcentration factors for fish).

3.1.2. Metsulfuron

Metsulfuron has low acute toxicity to mammals, birds and earthworms. It is considered practically non-toxic to honeybees on an acute contact basis (48-h LD₅₀ > 100 µg/bee: US EPA 2008). However, Champeau and Tremblay (2013) cite an LD₅₀ value of > 25 µg/bee for contact toxicity and > 44.3 µg/bee for oral toxicity (both moderately toxic in their classification: see Appendix 1).

Toxicity to fish and aquatic invertebrates is low. Toxicity to algae is moderate but toxicity to aquatic plants is high (based on an acute EC₅₀ to duckweed, *Lemna gibba*, of 0.00036 mg/L). Bioconcentration in aquatic organisms is likely to be low.

3.1.3. Terbutylazine

Terbutylazine has moderate toxicity to mammals, birds and honeybees, but low toxicity to earthworms (14-d LC₅₀ > 141.7 mg/kg).

Toxicity to fish, aquatic invertebrates, aquatic plants and algae is moderate. Bioconcentration in aquatic organisms is likely to be low.

3.1.4. Triclopyr

Triclopyr is applied in the form of an ester and is converted to the parent acid (triclopyr) over a period of several days after application. The toxicity of the ester is much higher than that of the parent compound and is considered more relevant for present purposes. The ester represents the worst-case compound and the one that would dominate in any contamination soon after application. The confusion over toxicity data for different forms of the active ingredients of glyphosate-based herbicides that was described by Cuhra et al. (2016) may also apply to data for triclopyr.

Triclopyr has moderate toxicity to mammals, birds, honeybees and earthworms. Toxicity to fish is described as slight to moderate by Champeau and Tremblay (2013), although the acute 96-h LC₅₀ for rainbow trout is 117 mg/L (> 100 mg/L is classed as 'low' toxicity: Champeau & Tremblay 2013). Toxicity to aquatic invertebrates is widely variable and is high for at least one common New Zealand aquatic insect (acute 96-h LC₅₀ for *Deleatidium* spp. 0.01 mg/L). Toxicity to aquatic plants (based on tests on duckweed) is moderate but toxicity to algae is low. Bioconcentration in aquatic organisms is likely to be low.

Of the four herbicides considered here, triclopyr is the compound with the highest toxicity to aquatic fauna. Applications are intended to be on land adjacent to State Highway 6, but caution is warranted to minimise potential risk from spraying into nearby streams or ditches.

Table 1. Summary of information on the toxicity and factors affecting mobility in soil of the four herbicides, derived from Roberts (1993) and a more recent review (Champeau & Tremblay 2013). See Appendix 1 for more detail.

Compound/ Reference	Toxicity										K _{oc}
	Mammals	Birds	Bees	Earthworms	Fish	Aquatic inverts	Aquatic plants	Algae	Bioaccumulation/BCF	Solubility in water	
Glyphosate											
Roberts	Low (p43)				Low-moderate (rainbow trout 96h LC ₅₀ 1.3mg/L) (Attachment 3)	Low-moderate (p39). Effects unlikely (p40)	'Do not appear to be dramatically affected by aerial spraying and...unlikely to be affected by proposed ground based spraying'		Taken up but not strongly accumulated and readily excreted (p39)	Very soluble (900,000mg/L). Binds strongly to SS	Low mobility, binds strongly to SS and soils (K _{oc} 24,000)
Champeau & Tremblay	Low (>2,000mg/kg bw)	Low (>2,000mg/kg bw)	Low-moderate (>=100ug as/bee)	Low (>480mg as/kg)	Low (>1000mg/L, 38mg/L for 1st metabolite, glyphosate acid)	Low (930mg/L). Moderate for G-trimesium (12mg/L)	Low (long-term EC ₅₀ 53.6mg/L but moderate for glyphosate trimesium: 1mg/L)	Low chronic (EC ₅₀ 72.9mg/L)	'bioconcentration in aquatic organisms is low' (p62)	Very (10,500mg/L)	Not or only slightly mobile (K _{oc} 2,600-4,900)
Champeau & Tremblay	Low (>2,000mg/kg bw)	Low (>2,000mg/kg bw)	Low-moderate (>=100ug as/bee)	Low (>5000mg as/kg)	Low-moderate (48-h EC ₅₀ 93mg/L for isopropylamine, >1227mg/L for potassium salt, 38mg/L for glyphosate acid)	Low-moderate (48-h EC ₅₀ 93mg/L for isopropylamine, >1227mg/L for potassium salt, 40mg/L for glyphosate acid)	Low (acute 7-d EC ₅₀ 88.4mg/L)	Low-moderate (72-h EC ₅₀ >72.9mg/L for isopropylamine, >86mg/L for potassium salt, 4.4mg/L for glyphosate acid)	'bioconcentration in aquatic organisms is low' (p23)	Very (11,600mg/L)	Variable with soil type (K _{oc} 0.9-51.6L/g)
Metsulfuron											
Roberts	Low (p43)				Low (rainbow trout 96h LC ₅₀ >150mg/L) (Attachment 3)	Low (p38)	No data (p38)		ND ('readily metabolised and eliminated' according to manufacturer)	Very soluble (9,500mg/L), readily washed off sprayed surfaces	Low soil adsorption (K _{oc} 35) so high mobility
Champeau & Tremblay	Low (>5,000mg/kg bw)	Low (>2,510mg/kg bw)	Moderate (>44.3ug /bee)	Low (>1000mg as/kg)	Low (96h LC ₅₀ >150mg/L)	Low (<i>Daphnia</i> 48h EC ₅₀ >150mg/L)	High (EC ₅₀ <i>Lemna</i> 0.00036mg/L)	Moderate (72h EC ₅₀ 0.045mg/L)	'bioconcentration in aquatic organisms is low' (p103)	Moderately-very (pH dependent: ph 7 2,790mg/L)	Low soil adsorption (K _{oc} 57) so mobile
Champeau & Tremblay	Low (>5,000mg/kg bw)	Low (>2,510mg/kg bw)	Moderate (>44.3ug/bee)	Low (>1000mg as/kg)	Low (96h LC ₅₀ >150mg/L)	Low (<i>Daphnia</i> 48h EC ₅₀ >150mg/L)	High (EC ₅₀ <i>Lemna</i> 0.00036mg/L)	Moderate (72h EC ₅₀ 0.045mg/L)	'bioconcentration in aquatic organisms is low' (p28)	Moderately-very (pH dependent: ph 7 2,790mg/L)	Low soil adsorption (K _{oc} 57) so mobile
Terbuthylazine											
Roberts	Low (p43)				Low-moderate (rainbow trout 96h LC ₅₀ 3.8mg/L) (Attachment 3)			High (based on single sp)	No data	Low solubility (8.5mg/L)	Low mobility in soils (depends on soil type)
Champeau & Tremblay	Moderate (>100mg/L)	Moderate (>100mg/L)	Moderate (>22.6mg/L)	Low (>141.7mg/kg)	Moderate (2.2mg/L)	Moderate (<i>Daphnia</i> 48h EC ₅₀ 21.2mg/L, <i>Americamysis</i> 96h EC ₅₀ 0.167mg/L)	Moderate (<i>Lemna</i> 7d EC ₅₀ 0.0128mg/L)	Moderate (algal 72h EC ₅₀ 0.012mg/L)	'potential for bioconcentrations is low' (p126)	Low solubility (6.6mg/L)	Slight - despite indication of moderately mobile (K _{oc} 231) forms strongly bound residues
Triclopyr											
Roberts	Low (p43)				Moderate at time of application as ester of triclopyr (96h LC ₅₀ for rainbow trout 0.7mg/L; Attachment 3), low toxicity once converted to parent acid over several days	Ester: moderate to high	No data (p40)		No data (but product pamphlet states that it 'does not accumulate in aquatic or terrestrial food chains' - no supporting data presented)	Low solubility (23mg/L)	Doesn't bind strongly to soils (K _{oc} 780) 'high mobility in soils'
Champeau & Tremblay	Moderate (630mg/kg)	Moderate (1698mg/L)	Moderate (>100ug as/bee)	Moderate (>521mg/kg)	'Slight to moderate' (p131: 96h LC ₅₀ 117mg/L)	Low (<i>Daphnia</i> 48h EC ₅₀ 131mg/L)	Moderate (<i>Lemna</i> 7d EC ₅₀ 0.8mg/L)	Low (algal 72h EC ₅₀ 75.8mg/L)	'potential for bioconcentrations is low' (p130)	Sparingly (440mg/L)	'Not expected to bind strongly to suspended solids', moderate-very mobile (K _{oc} 1.5-134)
Champeau & Tremblay	Moderate (577mg/kg)	Moderate (1698mg/L)	Moderate (>100ug as/bee)	Moderate (>521mg/kg)	'moderate to high' (p42: 96h LC ₅₀ 117mg/L)	Low (<i>Daphnia</i> 48h EC ₅₀ 131mg/L) to high (<i>Deleatidium</i> 96-h EC ₅₀ 0.01mg/L)	Moderate (<i>Lemna</i> 7d EC ₅₀ 0.8mg/L)	Low (algal 72h EC ₅₀ 75.8mg/L)		Ester: low (7mg/L) acid: sparingly (440mg/L)	Ester: Slightly mobile (K _{oc} 780). Acid: Not expected to bind strongly to suspended solids, moderate-very mobile (K _{oc} 1.5-134)

3.2. Effects on non-target plants

Most herbicides are toxic to a range of plants, often including crop species. One of the major potential impacts of the proposed spraying is its effect on non-target plants, including pasture grass, horticultural crops, shelter belts and native vegetation. It is most likely that these effects will arise from the drift of spray through the air, but contamination of irrigation water may also be of concern in small water bodies or storage dams fed from roadside water tables.

The physical properties of a herbicide partly determine the potential for it to affect non-target plants. Herbicides that do not bind strongly to soils that are highly water-soluble are more likely to move from the plants and soil with runoff (see Section 3.3).

The concentrations of herbicides washed from sprayed channels by rainfall have been shown to cause damage to sensitive crops in some cases. The main cause for concern is when irrigation channels are sprayed directly. In the case of the present consent application, the areas sprayed will not carry irrigation water directly (but may drain into waterways from which irrigation water is taken). The extra dilution provided by runoff from the unsprayed parts of the catchment should reduce the herbicide concentrations to levels that are harmless to non-target plants on the land and in streams and rivers. It is also unlikely that irrigation will be occurring at times when rainfall might carry herbicides from roadsides into streams, and any herbicide that does reach plants may be washed off by rain before it has any harmful effect. The situation in which impacts on non-target plants via irrigation are most likely to occur is when water-storage dams are filled with water draining from sprayed water tables or very small creeks.

Roberts (1993) suggested that limited monitoring of the concentrations of selected herbicides in roadside runoff be undertaken to provide a preliminary assessment of potential effect on non-target plants. This monitoring was to include metsulfuron, which is highly mobile, and terbutylazine, which is toxic to algae. However, monitoring was not included in the consent conditions and, as far as we are aware, no monitoring has been done to date.

Spray drift through the air is more likely to affect non-target plants than runoff from sprayed areas. It is very important that spray drift is adequately controlled. Various conditions have been included in previous consents to achieve this, and they are recommended below (Section 4).

3.3. Environmental fate

3.3.1. Glyphosate

Glyphosate binds strongly to soils (as indicated by its high K_{oc} value) and is therefore likely to have low mobility. It is moderately persistent in soils. Volatilisation from moist soil surfaces is not expected to be an important fate process because glyphosate exists as a zwitterion at environmental pH (5-9) and ionic species do not volatilise. The relatively low vapour pressure of glyphosate suggests that volatilisation from dry soil surfaces is not an important process. The biodegradation (breakdown by microbes in the soil) half-lives of glyphosate in a sandy loam and silt loam soil were 1.85 and 2.06 days, respectively under laboratory-controlled (25 °C) aerobic conditions. In eight field studies, in which glyphosate was applied at maximum usage rates to bare ground plots, the median dissipation half-time was 13.9 days.

Glyphosate is expected to adsorb to suspended solids and sediment in the water column (as indicated by its high K_{oc} value). Volatilisation from water surfaces is not expected to be an important fate process because ionic compounds do not volatilise. The aerobic and anaerobic biodegradation half-lives of glyphosate in a flooded silty clay loam sediment was 7 and 8.1 days, respectively. Glyphosate was stable to hydrolysis at pH 5, 7, and 9 at 5–35 °C.

3.3.2. Metsulfuron

Metsulfuron-methyl (the active ingredient in proprietary forms such as Escort®) does not bind strongly to soils (as indicated by its low K_{oc} value) and is therefore likely to have relatively high mobility, particularly in alkaline soils. Volatilisation from moist soil surfaces is not expected to be an important fate process based on the compound's estimated Henry's Law constant. The relatively low vapour pressure of metsulfuron-methyl suggests that volatilisation from dry soil surfaces is not an important process. Metsulfuron-methyl is expected to biodegrade in soil based on half-lives of 17-69 days for this substance in non-sterile soil compared with half-lives of 54-139 days in sterile soil. Reported half-life values for soil include: clay—178 days; sandy loam—102 days; clay loam—14–105 days; silty loam—120–180 days. Breakdown in soil is dependent on temperature, moisture content and pH.

Metsulfuron-methyl is expected to have little to no adsorption to suspended solids and sediment in water (as indicated by its low K_{oc} value). It is expected to biodegrade in water based on its behavior in soil. Volatilisation from water surfaces is not likely to be an important fate process based upon this compound's estimated Henry's Law constant. Metsulfuron-methyl is stable to hydrolysis at neutral and alkaline pH but may undergo direct photolysis by UV irradiation.

3.3.3. Terbutylazine

If released to soil, terbutylazine is expected to have only slight mobility based upon field observations. Although K_{oc} values of 151-514 suggest moderate mobility, terbutylazine interacts in soil to form strongly bound residues. Volatilisation from moist soil surfaces is not likely to be an important fate process. Some sensitised photodegradation may occur on soil surfaces exposed to sunlight. Terbutylazine has been shown to degrade more rapidly in natural soil than in sterilised soil. Field studies in biologically active soil have reported terbutylazine dissipation half-lives ranging from 6.5-149 days.

If released into water, terbutylazine is expected to adsorb to suspended solids and sediment based upon the K_{oc} . Volatilisation from water surfaces is not expected to be an important fate process based upon this compound's Henry's Law constant. Hydrolysis is not expected to be an important environmental fate process given half-lives of 73, 205 and 194 days at pH 5, 7 and 9, respectively. Sensitised photodegradation may have some importance in natural waters exposed to sunlight. In river, seawater and groundwater die-away tests, terbutylazine had half-lives ranging from 44 to 196 days.

3.3.4. Triclopyr

The more toxic ester form of triclopyr degrades rapidly in soils to form the parent acid, with a half-life of approximately 13 d under aerobic conditions and 27 d under anaerobic conditions. Under aerobic conditions, triclopyr biodegrades with half-lives of 8 and 18 d in silty clay loam and silty loam soils, respectively. Triclopyr acid's relatively low K_{oc} (1.5 to 134) suggest that it is mobile in soils. Volatilisation from moist soil surfaces is not likely to be an important fate process.

Triclopyr acid is non-persistent in surface water. It has limited mobility and low to medium persistence in soil. Considering its adsorptive characteristics and that it dissipates via multiple pathways such as photolysis, plant metabolism, and microbial degradation, its potential to leach to depth in soil and to contaminate groundwater is low.

3.4. Relative risk rankings of the proposed herbicides

To facilitate the interpretation of information relevant to the potential environmental effects of each of the 26 agri-chemicals (herbicides, fungicides and insecticides) in their review, Champeau and Tremblay (2013) developed a ranking system based on a system described by McBrien (1987). The scored parameters were weighted to reflect their relevance and importance to the risk characterisation (e.g. $K_{ow} \times 1$, $K_{oc} \times 1$, $BCF \times 2$, half-life $\times 2$, $HC5 \times 4$; see Table 2—only the 14 herbicides are shown). Each chemical was assigned to one of three categories, with each category defined as

being a third of the range covered by the scores of the 26 chemicals; the lowest scores in green, medium in yellow and highest in red.

The colour ranking is an approach to best estimate the potential environmental risk of the pesticides. For instance, a green-coded pesticide will potentially have a lesser impact than a yellow or red, but Champeau and Tremblay (2013) stress that this should not be interpreted as an endorsement for its unrestricted use. This approach reinforces and confirms the overall assessment that was derived from the available information in the databases.

In the case of the four herbicides proposed for use by NZTA, triclopyr had a relatively low rank compared to the other chemicals reviewed by Champeau and Tremblay (2013: Table 2). Metsulfuron and terbutylazine had intermediate scores. Triclopyr's low rank was largely due to its relatively short half-life in water and intermediate hazardous concentration for aquatic animals (HC5). Metsulfuron had a similar overall rank to triclopyr but was placed in the intermediate (yellow) category because its relatively low HC5 rank was based on very limited data. Glyphosate had a similar ranking to terbutylazine but was precautionarily placed in the highest category of scores (red) because of concerns about carcinogenicity (Champeau & Tremblay 2013, their Appendix 2).

Table 2. Weighted scores of the parameters used to derive the colour ranking for the 14 herbicides assessed by Champeau and Tremblay (2013). Herbicides reviewed in the present report are in bold text.

Agri-chemical	Category ranking							Environmental ranking
	log K_{ow}	K_{oc}	GUS \pm	BCF	Half-life water hydrolysis	Half-life in soil	HC5	
Picloram	1	1	6.03	6	20	8	12	48
Triclopyr	1	3	3.69	6	2	6	20	38
Mecoprop	1	2	2.29	4	20	2	36	65
Dicamba	1	2	1.75	6	6	4	20	39 R
Dichlorprop	4	3	2.39	4	20	5	36	72
2,4-D	1	3	1.62	4	20	6	12	46 R
Ethofumesate	3	3	3.19	6	20	10	20	62
Glyphosate	3	5	-0.49	2	20	10	20	60*
Metsulfuron	1	2	n/r	6	20	6	4	39 P
Terbutylazine	4	3	3.07	6	20	10	20	63
Haloxypop	3	3	2.03	6	20	6	44	82
MCPA	1	2	2.94	4	20	4	36	67
MCPB	2	3	1.66	4	20	2	4	35 R
Paclobutrazole	4	3	3.44	6	20	10	36	79

Note: Category descriptions

- K_{ow} : Partition coefficient, is a measure of how a chemical will distribute between two immiscible solvents: water (a polar solvent) and octanol (a relatively non-polar solvent).
- K_{oc} : Adsorption coefficient is a measure of how strongly a chemical adheres to soil in preference to remaining dissolved in water.
- BCF: bioconcentration factor, describes the accumulation of toxicants (i.e. from the water to the organism), for aquatic animals.
- GUS: Groundwater Ubiquity Score, an indicator of a chemical potential for leaching into groundwater (\pm not taken into account for the ranking hence use of grey font). Refer to Definitions table for the leaching likelihood).
- HC5: A hazardous substance for 5% of the species population (95% protection level). Derived from aquatic animals' data.
- P: Precautionary ranking (lack of data)
- R: Regulatory ranking (banned or pending approval)
- Grey cells indicate non-reported values replaced by intermediate score
- * Precautionary from vertebrate studies (non- reported in the table)

3.5. Exposure pathways

Non-target animals and plants could be exposed to herbicide active ingredients used to control noxious pest plants on NZTA-administered land along State Highway 6 via several pathways:

- direct spraying—including onto non-target plant surfaces and into waterways
- accidental spills—in terms of the concentration and volume of herbicide involved, this represents the highest environmental risk
- high rainfall events—rainfall will wash herbicides off target vegetation but will also increase dilution and dispersal
- via groundwater from normal application—likely to represent a negligible source under normal conditions.

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4. MITIGATION OF RISKS

The review presented here suggests that there is a risk of adverse effects on aquatic organisms from some of the herbicides, indicating that it is important that adequate precautions are taken to avoid contamination of waterbodies during spraying. There is also some risk to mammals, birds, honeybees and earthworms from some of the herbicides. Moreover, given the doubt that has been cast on the quality and applicability of toxicological data for herbicides, even those that are widely used, it is appropriate to take a precautionary approach to mitigation.

These risks can be mitigated by precautions prescribed in consent conditions. The present consents (RM095012, granted by NCC in 2009 and RM090020, granted by TDC in 2009) include conditions proposed by Roberts (1993) to mitigate environmental risk. These are listed below (numbered as in the consent: this is not an exhaustive list of the conditions) and we suggest that these be carried over into the new consent, if granted:

4.1. Restrictions on spraying operations

2. The spraying authorised by this permit applies only to the use of the herbicide active ingredients listed below. Those marked with an asterisk are not to be used on the slopes or bed of water tables or other drainage channels.

Active ingredient	Area for use
Glyphosate	All areas within legal road, including in or near waterways
Metsulfuron	All areas within legal road, including in or near waterways
Terbuthylazine*	All areas within legal road, except in or near waterways
Triclopyr 600 g/L*	All areas within legal road, except in or near waterways

Herbicides may be supplemented with Boost™ penetrant, Pulse® penetrant, Multi-film Extra® surfactant, Teepo™ or similar products where necessary to increase the efficacy of the herbicide product and/or to avoid or reduce adverse effects of spray drift. No product shall be discharged at a concentration higher than that specified on the product label instructions.

3. Herbicides shall only be discharged to vegetation rooted in road reserve.
4. Herbicides shall be discharged from land-based herbicide applicators only.
5. Herbicides shall not be sprayed directly over, onto or into water and the spray plume shall be directed away from water as far as is practicable. Spraying is authorised into dry waterways.
6. No spraying shall be carried out when vegetation is wet.
7. Spraying of glyphosate shall not occur when rain is forecast to fall within 6 hours in the area being sprayed.

8. Spraying of other authorised chemicals shall not occur when rain is forecast to fall within 12 hours in the area being sprayed.
9. There shall be no spray drift beyond the boundary of the road reserve.
Advice note: Spraying should not be carried out when wind speed exceeds 15 kilometres per hour. Drift control measures are required at lower wind speeds.
10. There shall be no discharge of herbicide onto flood protection plantings or other vegetation planted for aesthetic or economic purposes.
11. All reasonable precautions shall be taken to avoid disturbing nesting birds and other wildlife.
12. There shall be no spraying on the frontage of those properties registered as 'no spray' areas for the Chemical Control of Vegetation on State Highways, as described in Condition 31.

4.2. Herbicide transport, preparation and discharge

13. Notwithstanding the conditions of this discharge permit, the Consent Holder shall ensure that the discharge does not contravene any requirements specified on the product label instructions.
14. Notwithstanding the conditions of this discharge permit, the Consent Holder shall ensure the management, transport, storage, use and application of herbicide, the disposal of containers and emergency preparedness of the spraying contractor are carried out in accordance with the 'New Zealand Standard: Management of Agrichemicals, NZS 8409:2004' or subsequent version of that document.
15. Containers holding undiluted herbicide shall be kept closed at all times, except during the preparation of the spray mix, to prevent accidental spillage.
16. All preparation of the spray mix and cleaning of equipment shall be undertaken at locations where spillage will not result in any of the spray mix or undiluted herbicide being able to enter surface water or any stormwater drain.
17. If any watercourse, surface water body or stormwater drain is used as a source of water for spray mix, the Consent Holder shall ensure that backflow of water from the spray equipment to that watercourse, water body or stormwater drain does not occur. If water is pumped or siphoned to the spray equipment, or otherwise transferred directly between the water source and the equipment, the pump, siphon or spraying equipment shall be fitted with a device that prevents backflow.
18. All the spray equipment shall be fitted with valves that, when closed, prevent the spray mix from leaving the holding tanks.

4.3. Maintenance of spraying equipment

21. Spraying equipment that is susceptible to rupturing or leakage (e.g. hoses, joins, compressors) shall be inspected prior to use during the spray programme.
Equipment shall be maintained as necessary to minimise the risk of accidental

chemical spillage. Maintenance checks shall be recorded in the spray diary required to be kept by Condition 22.

4.4. Spray diary to be kept

22. The Consent Holder shall ensure that a written spray diary is kept as a record of all herbicide use associated with this resource consent. The spray diary shall be written each day that spraying is undertaken, and submitted on request to Council's Monitoring Officer. The diary shall record:
- a. Date of spraying
 - b. Spraying times
 - c. Spraying location (including New Zealand Map Grid co-ordinates)
 - d. Chemicals used and their application rates (both volume and concentration)
 - e. Weather conditions during spray operations
 - f. Method of discharge
 - g. Any conflicts that arose during the spraying, such as conflicts between the spray mix and the target plant
 - h. Any adverse effects on the environment resulting from spraying (including any chemical spills)
 - i. The dates of equipment maintenance and checks.

4.5. Incidents

23. The Consent Holder shall ensure that an adequate spill kit is available on site and at a distance of no more than 200 metres at all times during the spraying.
24. In the event of an accidental spill of herbicide at any of the application sites, the Consent Holder shall:
- a. Take immediate action to remedy and contain the spill and minimise any potential for the herbicide to reach any stormwater drains or unpaved areas
 - b. Advise Council's Monitoring Officer of the spill and the action being taken to remedy the problem as soon as practicable
 - c. Complete the Incident and Complaints Log in accordance with Condition 25
 - d. Forward a copy of the Incident and Complaints Log to the Council's Monitoring Officer within one week of the incident.

Ceasing of spraying operations

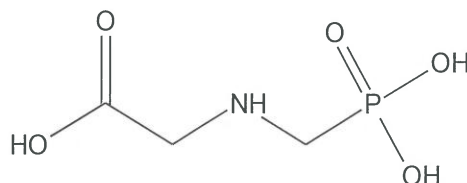
30. The Council's Monitoring Officer or his delegate may order that spraying cease immediately if, in their opinion, spraying is causing unacceptable environmental damage and/or the discharge is resulting in a noxious or dangerous level of herbicide beyond the property boundary.

5. REFERENCES

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6. APPENDIX 1 PROPERTIES OF HERBICIDES IN THE CONSENT APPLICATION

6.1. Glyphosate



Glyphosate is a weak acid herbicide. The parent acid of glyphosate (CAS 1071-83-6) is effective as a herbicide, but doesn't make a stable formulation or mix well with other products and can be associated with salts like the isopropylamine salt (CAS 38641-94-0) or the potassium salt (CAS 70901-12-1). Since the glyphosate that reaches the leaf surface often is not associated with the salt that it is formulated with, properties, fate and regulations are indicated for the parent compound (acid), and toxicities for parent and related compounds (potassium and isopropylamine salts).

6.1.1. Physico-chemical properties

Cas number	1071-83-6
Name (IUPAC)	N-(phosphonomethyl)-glycin
Use class	herbicide
Chemical class	Phosphonoglycine
Mode of action	Systemic; Inhibition of the EPSP synthase
Appearance	Colourless crystals
Vapour pressure	EU: $1.31 \cdot 10^{-5}$ Pa (25 °C, acid) ToxNet: $9.8 \cdot 10^{-8}$ mm Hg at 25°C
Henry's law constant (at 25 °C)	EU: $2.1 \cdot 10^{-7}$ Pa · m ³ /mol
Solubility in water	EU: pH 2: 10.5 ± 0.2 g/L (20 °C, 995 g/kg) PAN: 11.6 g/L
Dissociation constants (pKa)	EU: 2.34 (25 °C) ToxNet: 2, 2.6, 5.6, 10.6
Partition coefficient (log K_{ow})	EU: -3.2 (pH 5–9) at 25 °C
Adsorption coefficient (K_{oc})	EFSA (2015): 0.9–20.1 L/g PAN: 6920 ToxNet: 2600–4900
Hydrolysis half-life	EU: pH 5, 7 and 9: stable at 25 °C ToxNet: pH 5, 7 and 9: stable from 5 to 35 °C PAN: 35 d
Photostability in water (DT₅₀)	33 d (pH 5), 69 d (pH 7), 77 d (pH 9) (Xenon lamp)
Aerobic soil half-life	ToxNet: 1.85–7 d (up to 140.6 d in colder temperate climate) PAN: 96 d EU: Lab studies DT ₅₀ range 1.0-67.7 days, DT ₉₀ range 9.3-1661 days; field studies DT ₅₀ range 5.7-40.9 days, DT ₉₀ range 66.9-386.6 days,
Anaerobic soil half-life	PAN: 22 d

6.1.2. Environmental fate

The production of glyphosate may result in its release to the environment through various waste streams. Its use as a broad spectrum non-selective, post-emergent herbicide will result in its direct release to the environment.

If glyphosate is released to air, a vapour pressure of 1.31×10^{-5} Pa (25 °C) indicates that glyphosate will exist solely in the particulate-phase in the ambient atmosphere. Particulate-phase glyphosate will be removed from the atmosphere by wet and dry deposition.

If released to soil, glyphosate mobility is variable, based on K_{oc} values in the range of 0.6 to 5.10^5 . Volatilisation from moist soil surfaces is not expected to be an important fate process because glyphosate exists as a zwitterion at environmental pH (501509) and ionic species do not volatilise. Volatilisation from dry soil surfaces is not expected to be an important environmental fate process based on the vapour pressure. Glyphosate is moderately persistent in soil, with an estimated average half-life of 47 days. The biodegradation half-lives of glyphosate in a sandy loam and silt loam soil were 1.85 and 2.06 days respectively, under laboratory-controlled (25 °C) aerobic conditions. In eight field studies, in which glyphosate was applied at maximum usage rates to bare ground plots, the median dissipation half-time (DT_{50}) was 13.9 days. Reported field half-life estimates range from 1 to 174 days.

If released to water, glyphosate is expected to adsorb to suspended solids and sediment in the water column based upon the K_{oc} values. Volatilisation from water surfaces is not expected to be an important fate process because ionic compounds do not volatilise. The aerobic and anaerobic biodegradation half-lives of glyphosate in a flooded silty clay loam sediment were 7 and 8.1 days, respectively. Glyphosate was stable to hydrolysis at pH 5, 7, and 9 at 5 to 35 °C. According to a classification scheme, bioconcentration factor (BCF) values of 0.2 to 0.63 measured in fish suggest bioconcentration in aquatic organisms is low.

Transport of glyphosate may be caused by an interaction of high rainfall events shortly after application on wet soils, showing the presence of preferential flow paths. Glyphosate-based pesticides (including the degradation product AMPA (Figure A1.1) have been found to contaminate drinking water via rainwater, surface runoff and leaching in ground water with AMPA being more mobile in soil than glyphosate (Duke & Powles 2008).

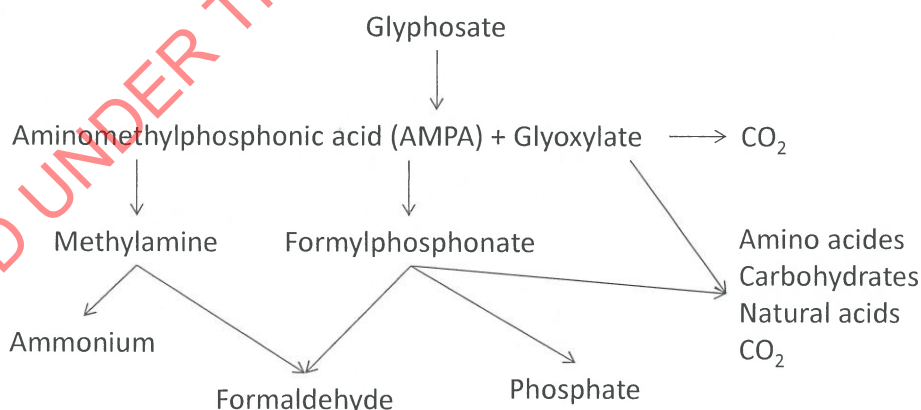


Figure A1.1 Glyphosate degradation pathway³.

³ cdpr.ca.gov/docs/emon/pubs/fatememo/glyphos.pdf

6.1.3. Toxicology and ecotoxicology

Glyphosate is not classified as a human carcinogen by the European Chemical Agency⁴ (although it maintains its classification as a substance causing serious eye damage and being toxic to aquatic life with long-lasting effects) nor the US EPA⁵. In December 2017, the European Union renewed the approval of glyphosate for five years (until 2022)⁶. At the time of writing (September 2018), glyphosate is undergoing registration review with the US Environmental Protection Agency⁷.

Toxicity information toward humans (US EPA)

- acute toxicity: slight
- carcinogenicity: not likely (but see above)
- endocrine disruption: not listed
- reproductive and developmental toxicity: not listed
- ground water contaminant: potential.

⁴ <https://echa.europa.eu/-/glyphosate-not-classified-as-a-carcinogen-by-echa>, accessed 27 September 2018.

⁵ https://cfpub.epa.gov/ncea/iris/iris_documents/documents/subst/0057_summary.pdf, accessed 27 September 2018.

⁶ <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A32017R2324>, accessed 27 September 2018.

⁷ <https://www.regulations.gov/docket?D=EPA-HQ-OPP-2009-0361>, accessed 27 September 2018.

Toxicity information toward other organisms

Organisms - Endpoint	Isopropyl-amine	Potassium salt	Acid	Species	Toxicity level
Terrestrial organisms					
Mammals					
Acute oral LD ₅₀ (mg/kg)	> 2000	> 2000	> 2000	Rat	Low
Short term dietary (mg/kg)			150	Rat	Moderate
Birds					
Acute LD ₅₀ (mg/kg)		> 2241	> 2250	<i>Colinus virginianus</i>	Low
			> 4640 mg/kg/feed	unknown species	
Honey bees					
Acute oral LD ₅₀ (µg/bee)			100		Moderate
Acute contact LD ₅₀ (µg/bee)		> 100	> 100		Low
Earthworms					
Acute 14-d LC ₅₀ (mg/kg)	> 5000		> 5600	<i>Eisenia foetida</i>	Low
Chronic 14-d NOEC, reproduction (mg/kg)	28.8		> 28.8		Moderate
Aquatic organisms					
Fish					
Acute 96-h LC ₅₀ (mg/L)	> 93	> 1227	38	<i>Oncorhynchus mykiss</i>	Low to moderate
Chronic 21-d NOEC (mg/L)			25	<i>Oncorhynchus mykiss</i>	Low
Aquatic invertebrates					
Acute 48-h EC ₅₀ (mg/L)	> 93	> 1227	40	<i>Daphnia magna</i>	Low to moderate
Chronic 21-d NOEC (mg/L)			30	<i>Daphnia magna</i>	Low
Acute 96-h LC ₅₀ (mg/L)			40	<i>Americamysis bahia</i>	Moderate
Aquatic plants					
Acute 7-d EC ₅₀ , biomass (mg/L)	88.4			<i>Lemna paucicostata</i>	Low
Acute 7-d EC ₅₀ , biomass (mg/L)			12	<i>Lemna gibba</i>	Low
Acute 72-h EC ₅₀ , growth (mg/L)	> 72.9			<i>Scenedesmus subspicatus</i>	Low
Acute 72-h EC ₅₀ , growth (mg/L)		35		<i>Selenastrum capricornutum</i>	Low
Acute 72-h EC ₅₀ , growth (mg/L)			4.4	<i>Scenedesmus quadricauda</i>	Moderate
Chronic 96-h NOEC, growth (mg/L)			2	Unknown species	Low

HC5 = 4436 (2616–7520) µg/L derived from LC₅₀ of aquatic animals exposed up to 4 days.

6.1.4. Environmental standards/regulations

Water standards and criteria

ANZECC - Freshwater		Concentrations µg/L - unless noted 370 (99% protection), 1200 (95% protection)
Canadian Water Quality Guidelines for the Protection of Aquatic Life (freshwater)		65
US National Drinking Water Standards and Health Criteria		
	Maximum contaminant level (MCL)	700
	Maximum contaminant level goal (MCLG)	700
	One day exposure health advisory level	20000
	Ten days exposure health advisory level	20000
	Reference dose	2000 (µg/kg/day)
	U.S. Drinking Water Equivalent Level	70000
WHO Water Quality Criteria		30
Canada - Standards and Criteria		
Drinking water	Maximum acceptable concentration (MAC)	280
Canada - Water Quality Guidelines for the Protection of Aquatic Life	Freshwater	800
Canada - Water Quality Guidelines for the Protection of Agricultural Water uses	Livestock	280
Australian Drinking Water Guideline		100
	ANZECC trigger value (99% protection level)	370
French Water Quality Guideline		
	France – Threshold value freshwater PNEC	28
	France – Maximum acceptable concentration	64
	France – Environmental quality guideline	0.1

Regulations

Registered for use in: 28 countries (including Australia, Canada, European Union, India, New Zealand, United States).

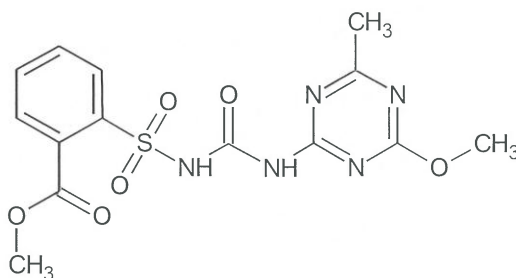
6.1.5. Important user information

Based on the proposed and supported uses, the following issues have been identified as requiring particular and short-term attention from users, as appropriate:

- Groundwater: users must pay particular attention to the protection of the groundwater in vulnerable areas, in particular with respect to non-crop uses.

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6.2. Metsulfuron-methyl



6.2.1. Physico-chemical properties

Cas number	74223-64-6
Name (IUPAC)	Methyl 2-(4-methoxy-6-methyl-1,3,5-triazin-2-methylcarbamoylsulfamoyl)benzoate
Use class	Herbicides
Chemical class	Sulfonylurea
Mode of action	Selective, systemic with contact and residual action. Inhibits plant amino acid synthesis—acetohydroxyacid synthase AHAS
Appearance	White to pale yellow solid with characteristic odour (ester-like)
Relative density (g/mL)	1.45
Vapour pressure	ToxNet: 2.5×10^{-12} mm Hg at 25 °C EU: 1.4×10^{-8} mPa at 25 °C 3.2×10^{-9} – 1×10^{-8} Pa at 25 °C
Henry's law constant	1.32×10^{-16} atm.m ³ /mole at 25 °C (est.) 1.6×10^{-9} Pa.m ³ /mol at 25 °C EU: 2.87×10^{-6} Pa.m ³ /mol at 25 °C
Solubility in water (g/L)	0.548 (pH 5), EU: 2.79 (pH 7), 213 (pH 9) (25 °C)
Dissociation constant (pKa)	3.8–4.8 (20°C)
Partition coefficient (log K _{ow})	1 (pH 4), EU: -1.87 (pH 7)
Adsorption coefficient (K _{oc})	ToxNet: 4–345 EU K _{foc} : 12 PAN: 57
Photostability in water (DT ₅₀)	EU pH7: stable
Hydrolysis half-life	EU: pH 5: 22 d at 25 °C, stable at pH 7 and 9 PAN: 30
Aerobic soil half-life	ToxNet: 10 to 71 d PAN: 24 d EU: lab studies DT ₅₀ range 6.4–48.8 days, DT ₉₀ range 48–175 days; field studies DT ₅₀ range 7.3–37.1 days, DT ₉₀ range 24.3–123 days
Anaerobic soil half-life	PAN: 65 d

6.2.2. Environmental fate

If metsulfuron-methyl is released to air, a vapour pressure of 2.50×10^{-12} mmHg at 25 °C indicates it will exist solely in the particulate phase in the atmosphere. Particulate-phase metsulfuron-methyl will be removed from the atmosphere by wet or dry deposition. Metsulfuron-methyl may undergo direct photolysis based on 50% and 76% degradation of this substance in an aqueous solution after 15 and 36 hours exposure to UV irradiation (greater than or equal to 290 nm), respectively. If released to soil, metsulfuron-methyl is expected to have moderate to very high mobility based upon K_{oc} values ranging from 4–345. Volatilisation from moist soil surfaces is not expected to be an important fate process based upon an estimated Henry's Law constant of 1.32×10^{-16} atm.m³/mole. The pKa of metsulfuron-methyl is 3.8, indicating that urea nitrogen in this compound will exist primarily in anion form in the environment and anions generally do not adsorb more strongly to organic carbon and clay than their neutral counterparts. Metsulfuron-methyl is not expected to volatilise from dry soil surfaces based upon its vapour pressure. Metsulfuron-methyl is expected to biodegrade in soil based on half-lives of 27, 60, and 17–69 days for this substance in non-sterile soil compared with half-lives of 54, 108, and 99–139 days in sterile soil. Reported half-life values for soil include: clay—178 days; sandy loam—102 days; clay loam 14 to 105 days; silty loam—120 to 180 days.

The half-life of metsulfuron-methyl (200 g/kg in an herbicide formulation) applied to a field was 33 days at an application rate of 20.0 g/ha and 23 days at an application rate of 10.0 g/ha.

Half-lives measured for 4.3 µg metsulfuron-methyl in different flasks containing 50 g of Horitiu sandy loam were 36 days at 10°C; 22, 23, and 29 days at 22°C; and 8 days at 30°C. Half-lives of 10 and 11 days were measured for metsulfuron-methyl applied to fields of Horitiu sandy loam at application rates of 30 and 60 g/ha, respectively. Metsulfuron-methyl was dissipated by 50% after 16 days and by 90% after 54 days in a soil flow-through test system at both initial concentrations of 0.1 and 1.0 ppm. Half-lives corresponding to the degradation of 10 µg metsulfuron-methyl applied to different samples containing 50 g of silt loam (pH 8, 22 g/kg organic carbon) that had been previously stored for 0, 3, and 6 months at 4°C were 45, 60, and 62 days, respectively. The half-lives measured in soil stored for 0, 3, and 6 months at 20°C were 45, 71, and 58 days, respectively.

If released into water, metsulfuron-methyl is expected to have little to no adsorption to suspended solids and sediment based upon the range of K_{oc} values. Metsulfuron-methyl is expected to biodegrade in water based on its behaviour in soil. Volatilisation from water surfaces is not expected to be an important fate process based upon this compound's estimated Henry's Law constant. BCF values ranging from 1–17 suggest bioconcentration in aquatic organisms is low. Metsulfuron-methyl is expected to undergo hydrolysis in the environment based on measured half-lives of 4–9.6, 116,

99–139, and 87 days at pH 5.2, 7.1, 8.2, and 10.2, respectively and temperatures of 25–28°C.

Metsulfuron-methyl is not expected to bioaccumulate. Metsulfuron-methyl is stable in water at pH 7 and 9 but hydrolysed at pH 5. In water the substance is transformed into sulphonamide (IN-D5803), saccharin (IN-00581), and triazine amine (IN-A4098). The primary degradation occurs with DT₅₀ 81–148 days. Metsulfuron-methyl is slowly degraded in water/sediment systems, with DT₅₀ 15–25 weeks for the entire systems. The major metabolite in water-sediment systems is bis-O-demethyl metsulfuron-methyl (IN-JX909). The metabolite occurs in both water and sediment. Toxicity tests have been performed of metabolite (IN-JX909) showing low toxicity towards aquatic organisms.

Degradation of metsulfuron-methyl was observed in an *in situ* enclosure deployed in a mixed-wood/boreal forest lake. Half-lives were less than 84 days and approximately 30 days at initial concentrations of 1000 and 10,000 ug/L, respectively.

6.2.3. Toxicology and ecotoxicology

Toxicity information toward humans (U.S EPA)

- acute toxicity: slight
- carcinogenicity: not likely
- endocrine disruption: not listed
- reproductive and developmental toxicity: not listed
- ground water contaminant: potential.

Toxicity information toward other organisms

Terrestrial organisms

Acute toxicity to mammals

LD50 (rats) > 5 000 mg/kg

Long term oral toxicity to mammals:

NOAEL (90 d, rats) = 100 ppm

Acute toxicity to birds:

NOAEL (90 d, rat) = 100 ppm

Dietary toxicity to birds:

LD50 (mallard duck) > 2 510 mg/kg

Reproductive toxicity to birds:

LC50 (bobwhite quail) > 5 620 ppm

LC50 (mallard duck) > 5 620 ppm

NOEC = 1 000 ppm

Honeybees

Acute oral toxicity:

LD50 > 44.3 microg a.s./bee

Acute contact toxicity:

LD50 > 25 microg a.s./bee

Other arthropod species*Chrysoperla carnea*

E (beneficial effect) = - 3.5 % (WG 20%)

Typhlodromus pyri

E (beneficial effect) = - 1.2 % (WG 20%)

Poecilus cupreus

E (mortality) = 3.5 % (WG 20%)

E (prey consumption) = 3%

Aleochara bilineata

E (beneficial effect) < 30 % (WG 20%)

Aphidius rhopalosiphii

E (beneficial effect) = 19.3 % (WG 20%)

Earthworms

Acute toxicity:

LC50 > 1 000 mg a.s./kg dry soil

Metabolites

LC50 > 1 000 mg IN-A4098/kg dry soil

LC50 > 1 mg IN-00581/kg dry soil

LC50 > 1 mg IN-B5067/kg dry soil

LC50 > 1 mg IN-NC148/kg dry soil

Reproductive toxicity:

No data submitted

Soil micro-organisms

Nitrogen mineralization:

0.2 mg a.s./kg: No effect

Carbon mineralization:

0.2 mg a.s./kg: No effect

Aquatic organisms

Active substance:

Acute toxicity fish:

Chronic toxicity fish:

Bioaccumulation fish:

Acute toxicity invertebrate:

Chronic toxicity invertebrate:

Acute toxicity algae:

Acute toxicity (aquatic plants):

Chronic toxicity sediment dwelling organism:

LC50 (96 h) > 150 mg/l

NOEC (21 d) = 68 mg/l

log P_{ow} = - 1,7 (pH 7.0)
whole fish: < 1

EC50 (48 h, *D. magna*) > 150 mg/l

NOEC (21 d, daphnids) = 150 mg/l

EC₅₀ (72 h, *S. capricornutum*) = 0.045 mg/l

EC50 (*L. gibba*) = 0.00036 mg/l

not required

Preparation (WG 20%):

Acute toxicity fish:

Acute toxicity invertebrate:

LC50 (trout, 96 h) > 1 000 mg/l

EC50 (daphnids) > 1 000 mg/l

Metabolites:

Acute toxicity fish:

Acute toxicity invertebrate:

Acute toxicity algae:

Acute toxicity (aquatic plants)

LC50 (trout) = 981 mg IN-JX909/l

EC50 (daphnids) = 971 mg IN-JX909/l

EC50 (*S. capricornutum*) = 64 mg IN-JX909/l

EC50 (*L. gibba*) = 30 mg IN-JX909/l

EC50 (*L. gibba*) > 10 mg IN-A4098/l

Indicative HC5 calculated at 75.3 mg/L (no 95% CI) derived from LC₅₀ of fish exposed four days. The reliability of this value is very low due to the low number of studies.

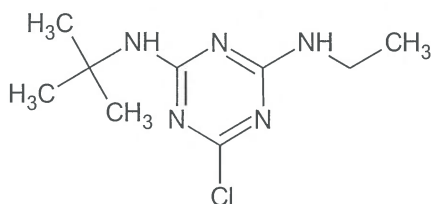
Environmental standards/regulation

ANZECC trigger value for freshwater (moderate reliability): 3.4 µg/L.

The European water quality standard applied from the derived PNEC is 0.003 µg/L.

Australian Drinking Water Guideline: 40 µg/L.

6.3. Terbutylazine



6.3.1. Physico-chemical properties

Cas number	5915-41-3
Name (IUPAC)	N2-tert-butyl-6-chloro-N4-ethyl-1,3,5-triazine-2,4-diamine
Use class	Algaecide, herbicide, microbiocide
Chemical class	Triazine
Melting point	176 °C
Vapour pressure	1.2×10^{-4} Pa at 25 °C
Henry's law constant	1.64×10^{-6} Pa.m ³ /mole at 25 °C
Solubility in water	6.6 mg/L
Solubility (g/L) in organic solvents (at 20°C)	acetone: 41 toluene: 9.8 n-hexane: 0.41
Partition coefficient (log K _{ow})	3.4
Adsorption coefficient (K _{oc})	231
Dissociation constants (pK _a)	1.9
Hydrolytic stability (DT ₅₀)	stable
Photostability in water (DT ₅₀)	stable
Aerobic soil half-life	75.1

6.3.2. Environmental fate

The production of terbutylazine and use as a laboratory analytical standard may result in its release to the environment through various waste streams and its use as a herbicide will result in its direct release to the environment.

If released to air, a vapour pressure of 1.2×10^{-4} Pa at 25 °C indicates terbutylazine will exist in both the vapour and particulate phases in the ambient atmosphere. Vapour-phase terbutylazine will be degraded in the atmosphere by reaction with photochemically-produced hydroxyl radicals; the half-life for this reaction in air is estimated to be 35 hrs. Particulate-phase terbutylazine will be removed from the atmosphere by wet and dry deposition. Terbutylazine has been detected in ambient

rain and snow samples. Direct photolysis is not an important fate due to weak absorption at wavelengths > 290 nm.

If released to soil, terbuthylazine is expected to have only slight mobility based upon field observations. Although K_{oc} values of 151-514 suggest moderate to low mobility, terbuthylazine interacts in soil to form strongly bound residues. Volatilisation from moist soil surfaces is not expected to be an important fate process based upon an estimated Henry's Law constant of 1.64×10^{-6} Pa.m³/mole at 25 °C and results of soil volatilisation tests. Some sensitised photodegradation may occur on soil surfaces exposed to sunlight. Terbuthylazine has been shown to degrade more rapidly in natural soil than in sterilised soil (22-27 vs 82 d half-lives). Field studies in biologically activate soil have reported terbuthylazine dissipation half-lives ranging from 6.5 to 149 days.

If released into water, terbuthylazine is expected to adsorb to suspended solids and sediment based upon the K_{oc} . Volatilisation from water surfaces is not expected to be an important fate process based upon this compound's Henry's Law constant. An estimated BCF of 25 suggests the potential for bioconcentration in aquatic organisms is low. Hydrolysis is not expected to be an important environmental fate process given half-lives of 73, 205 and 194 days at pH 5, 7 and 9, respectively. Sensitised photodegradation may have some importance in natural waters exposed to sunlight. In river, seawater and groundwater die-away tests, terbuthylazine had half-lives ranging from 44 to 196 days.

Occupational exposure to terbuthylazine may occur through inhalation and dermal contact with this compound at workplaces where terbuthylazine is produced or used. Workers may be exposed to terbuthylazine during applications in commercial/industrial settings. Monitoring data indicate that the general population may be exposed to terbuthylazine *via* ingestion of contaminated drinking water and dermal contact with this compound. People (including children) may be exposed while wading or swimming in treated ornamental ponds or fountains.

6.3.3. Toxicology and ecotoxicology

Terrestrial organisms

Mammals - Acute oral LD ₅₀ (mg/kg)	> 1000	Rat	Moderate
Mammals - Short term dietary NOEL (mg/kg)	> 0.22	Rat, 2 year	High -
Birds - Acute LD ₅₀ (mg/kg)	> 1236	<i>Colinus virginianus</i>	Moderate
Birds - Short term dietary LC ₅₀ /LD ₅₀ (mg/kg bw day)	> 395	<i>Anas platyrhynchos</i>	
Honeybees - Acute 48-hour LD ₅₀ (µg/bee)	> 22.6	Oral	Moderate
Earthworms - Acute 14-day LC ₅₀ (mg/kg)	> 141.7	<i>Eisenia fetida</i> , corr.	Moderate
Other arthropods LR ₅₀ (g/ha)	0.75	Mortality <i>Typhlodromus pyri</i>	Harmful at 1 kg/ha
Other arthropods LR ₅₀ (g/ha)	0.75	Mortality <i>Aphidius rhopalosiphii</i>	Harmful at 1 kg/ha
Soil micro-organisms	Nitrogen mineralisation: No significant effect Carbon mineralisation: No significant effect	Dose: 10.9 mg/kg soil	-

Aquatic organisms

Fish - Acute 96-hour LC ₅₀ (mg/L)	2.2	<i>Oncorhynchus mykiss</i>	Moderate
Fish - Chronic 21-day NOEC (mg/L)	0.09	<i>Oncorhynchus mykiss</i>	-
Aquatic invertebrates - Acute 48-hour EC ₅₀ (mg/L)	21.2	<i>Daphnia magna</i>	Moderate
Aquatic invertebrates - Chronic 21-day NOEC (mg/L)	0.019	<i>Daphnia magna</i>	-
Aquatic crustaceans - Acute 96-hour LC ₅₀ (mg/L)	0.167	<i>Americamysis bahia</i>	Moderate
Sediment dwelling organisms - Chronic 28-day NOEC, static, water (mg/L)	0.5	<i>Chironomus riparius</i>	Moderate
Aquatic plants - Acute 7-day EC ₅₀ , biomass (mg/L)	0.0128	<i>Lemna gibba</i>	Moderate
Algae - Acute 72-hour EC ₅₀ , growth (mg/L)	0.012	<i>Pseudokirchneriella subcapitata</i>	Moderate

HC5 = 1895 (408–8811) µg/L derived from LC₅₀ of aquatic animals exposed up to 4 days.

6.3.4. Environmental standards/regulations

Water standards and criteria

Australian Drinking Water Guideline: 10 µg/L

Regulations

Registered for use in: Nine countries (including AU, NZ, SA, US).

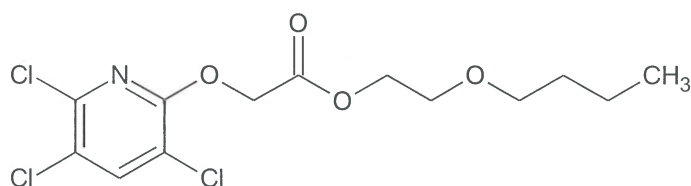
6.3.5. Important user information

Users should pay attention to

- the protection of groundwater, when the active substance is applied in regions with vulnerable soil and/or climatic conditions;
- the long-term risk and the risk from secondary poisoning for mammals and the risk for earthworms.

Conditions of use shall include risk mitigation measures and monitoring programmes should be initiated to verify potential groundwater contamination in vulnerable zones, where appropriate.

6.4. Triclopyr butoxyethyl ester (TBEE)



6.4.1. Physico-chemical properties

	Triclopyr butoxyethyl ester (TBEE)	Triclopyr acid
Cas number	64700-56-7	55335-06-3
Name (IUPAC)	2-butoxyethyl 3,5,6-trichloro-2-pyridyloxyacetate	3,5,6-trichloro-2-pyridyloxyacetic acid
Use class	Herbicide	
Chemical class	Pyridine compound	
Mode of action	Systemic, Synthetic auxin growth regulator taken up via leaves and roots and induces an epinastic ⁸ response leading to chlorosis, cessation of normal growth and death.	
Appearance	Clear liquid	
Vapour pressure	0.48×10^{-3} Pa (25 °C)	0.17×10^{-3} Pa (25 °C) ToxNet: 1.26×10^{-6} mmHg
Henry's law constant	2.47×10^{-7} atm.m ³ /mole	ToxNet: 9.7×10^{-10} atm.m ³ /mole EU: 2.9×10^{-3} Pa.m ³ /mol (25 °C)
Solubility in water (at 20 °C)	6.81 mg/L PAN: 7 mg/L	ToxNet: 440 mg/L EU/PAN: 8.1 g/L
Dissociation constants (pKa)	n/a	EU: 3.97
Partition coefficient (log K_{ow})	4.75 (pH5), 4.62 (pH 7), 4.31 (pH 9) at 22 °C	EU: 4.62
Adsorption coefficient (K_{oc})	780 PAN: 62	EU: 27 PAN: 48 ToxNet: 1.5–134
Hydrolytic stability (DT₅₀)	PAN: 7 d	84 d (pH 5), PAN: 8.7 d (pH 7), 0.3 d (pH 9) at 25 °C
Photostability in water (DT₅₀)	Predicted 3.1 h (40°N, 25 °C)	0.1 d

⁸ Differential growth of the upper surface of parts of the plant.

	Triclopyr butoxyethyl ester (TBEE)	Triclopyr acid
	Triclopyr butoxyethyl ester (TBEE)	Triclopyr acid
Aerobic soil half-life	PAN: 13 d	PAN: 39d EU: lab studies DT ₅₀ range 13-52 days, DT ₉₀ range 44-171 days; field studies DT ₅₀ range 6.9-53.9 days ToxNet: 1.5 to 134 d
Anaerobic soil half-life	PAN: 27 d	1300 d

6.4.2. Environmental fate⁹

TBEE has low vapour pressures and thus volatilisation occurs only to a minor extent. Low Henry's law constant indicates little tendency for escaping an aqueous solution. With the exception of spray drift which can be avoided with proper application techniques, triclopyr is not expected to be found in air.

TBEE rapidly converts to triclopyr acid by hydrolysis in both natural water and soil in less than a day. In sunny conditions, photolysis of TBEE may occur more quickly than hydrolysis and microbial degradation occurs as well. Since the conversion of TBEE to triclopyr is rapid, only triclopyr needs to be considered for environmental impact studies. Unlike TBEE, triclopyr has little tendency to hydrolyse (DT₅₀ = 270 days), and photolysis is the main degradation pathway in natural water. In river water, the half-life of triclopyr was determined to be 1.3 days in artificial and natural light. In natural water, oxamic acid is the main photodegradation product with low molecular-weight organic acids as minor products.

In lentic systems, the estimated half-life for total triclopyr (ester plus acid) in water at 3 kg of active ingredient per hectare was 4.3 days with more than 95% dissipated within 15 days.¹⁰

In lotic systems, concentrations of triclopyr in waters and associated sediment over sprayed with triclopyr BEE were transient, presumably because of rapid dilution and photolysis. TBEE was aerielly applied by helicopter to an 8-km reach of the Ahuriri River upstream of Lake Benmore. Triclopyr was not detected in the river water samples subsequently collected.

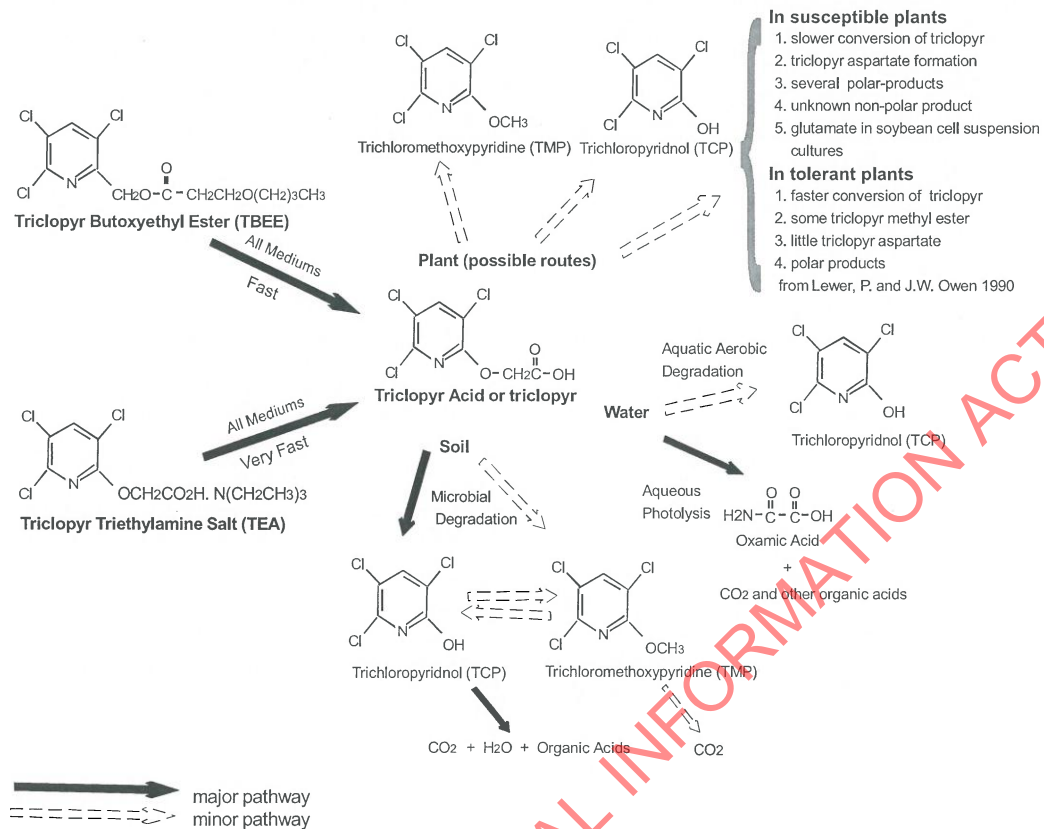
⁹ <http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/triclopyr.pdf>

¹⁰ Cessna AJ, Grover R, Waite DT 2002. Environmental fate of triclopyr. In: Ware GW ed. Reviews of Environmental Contamination and Toxicology: Continuation of Residue Reviews. New York, NY, Springer New York. Pp. 19-48.

In soil, TBEE rapidly hydrolyses to triclopyr acid with a half-life of three hours (Bidlack 1978). The major route of triclopyr dissipation in soil is microbial degradation. Increases in temperature and moisture, cause microbial activity and degradation to increase. Aerobic degradation in soil produces the metabolites 3,5,6-trichloro-2-pyridinol (TCP), 3,5,6-trichloro-2-methoxypyridine (TMP) and CO_2 . The relative amounts of these products in a lab soil-column study at 54 days were 4% triclopyr, 88%TCP, and 15%TMP for triclopyr acid-treated soil, and 6% triclopyr, 88% TCP and 7%TMP for TBEE treated soil. Unlike microbial degradation, soil photolysis is a minor route of dissipation. Another study performed in anaerobic soil conditions found that TBEE hydrolysed to triclopyr within one day and then slowly converted to TCP. Both TCP and TMP eventually convert to CO_2 .

TBEE tends to adsorb to organic matter and is relatively immobile. It was found to have a K_{oc} of 6,000 cm^3/g . The K_{oc} of triclopyr ranged from 19–78 cm^3/g with an average of 27 cm^3/g . It was noted that triclopyr has a similar mobility as 2,4-D and should be classified as mobile in the Helling classification system. Triclopyr sorption to soil increases with time, decreasing the potential for leaching. This may be the reason why studies indicate that triclopyr has low mobility. When 2.5 cm of simulated precipitation was leached every two days through soil columns treated with triclopyr, the application stayed within the top 10 cm of the soil column and was not found in the eluates. Triclopyr is only somewhat prone to lateral movement. In a runoff study, samples from a treated plot contained less than 1 ppb triclopyr from one to 105 days after application at 300 g active ingredient/ m^2 . Furthermore, adsorption of triclopyr was found to increase as the amount of organic matter increases in soil. The breakdown products are also not mobile. TMP is listed as 'very slightly mobile' and TCP is listed as 'slightly mobile'. Most of the TCP is expected to stay in the top 3 to 5 cm of soil.

Triclopyr is listed as 'fairly degradable' in soil at reported half-lives ranging from 12 to 27 days. TCP is listed as 'slightly degradable' with half-lives ranging between 12 and 229 days, and TMP as 'very slightly degradable' at 50 to 450 days.

Figure A1.2. Triclopyr degradation pathway¹¹¹¹ <http://www.cdpr.ca.gov/docs/emon/pubs/fatememo/triclopyr.pdf>

6.4.3. Toxicology and ecotoxicology

TBEE rapidly transforms into triclopyr or triclopyr acid. For this reason, the assessment is carried out on triclopyr.

Toxicity information toward humans

- acute toxicity: slight
- carcinogenicity: unclassifiable
- endocrine disruption: not listed
- reproductive and developmental toxicity: not listed
- ground water contaminant: potential (TBEE).

Toxicity information toward other organisms

Terrestrial organisms

Organisms - Endpoint	Concentration	Species	Toxicity level
Mammals - Acute oral LD ₅₀ (mg/kg) (TBEE)	577	Rat	Moderate
Mammals - Short term dietary NOEL (mg/kg)	3	Rat, 2 year	High
Birds - Acute LD ₅₀ (mg/kg)	1698	<i>Anas platyrhynchos</i>	Moderate
Birds - Short term dietary LC ₅₀ /LD ₅₀ (mg/kg feed)	> 5620	<i>Anas platyrhynchos</i>	-
Honeybees – Contact Acute 48 hour LD ₅₀ (µg/bee)	> 100	<i>Apis mellifera</i>	
Earthworms - Acute 14 day LC ₅₀ (mg/kg)	> 521	<i>Eisenia fetida</i>	

Aquatic organisms

Organism group	Acute toxicity range
Fish	Moderately to high toxicity
Insects	Not acutely toxic to high toxicity
Zooplankton	Moderately toxic

Organisms – Endpoint	Concentration	Species
Fish		
Acute 96-hour LC ₅₀ (mg/L)	117	<i>Oncorhynchus mykiss</i>
Chronic 21-day NOEC (mg/L)	46.3	Unknown species
Aquatic invertebrates		
Acute 48-hour EC ₅₀ (mg/L)	> 131	<i>Daphnia magna</i>
Acute 96-hour LC ₅₀ (mg/L)	0.01	<i>Deleatidium</i> spp
Chronic 21-day NOEC (mg/L)	48.5	Unknown species
Sediment dwelling organisms - Chronic 28-day NOEC, static, water (mg/L)	23.0	<i>Chironomus riparius</i>
Aquatic plants and algae		
Acute 7-day EC ₅₀ , biomass (mg/L)	0.8	<i>Lemna gibba</i>
Acute 72-hour EC ₅₀ , growth (mg/L)	75.8	<i>Raphidocelis subcapitata</i>
Chronic 96-hour NOEC, growth (mg/L)	8	Unknown species

HC5= 238 (142–399) µg/L derived from freshwater plants and animals (IC₅₀, EC₅₀ and LC₅₀) exposed to triclopyr (TBEE) for 1 h to 14 days.

6.4.4. Environmental standards/regulations

Water standards and criteria

France – Water quality guideline for the protection of aquatic life – PNEC: 5.8 µg/L.