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A review on formulations used for aerial basal bark applications (ABBA) for control of isolated, wilding conifers

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Report information sheet

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Executive summary

In May 2017, the National Programme for Wilding Conifer Control hosted a consultation workshop 'Good Practice for Aerial Wanding of Wilding Conifers'. The objective of the workshop was to obtain the views of the industry, and other agencies, on the practice of controlling wilding conifers through the use of Aerial Basal Bark Application or ABBA. At the meeting it was evident that there was wide variation in the solvents (oils) and products being used for ABBA as well as questions pertaining to their impact on human and environmental health. Formulations included triclopyr applied as 20% Grazon (600 g L^{-1} triclopyr (BEE), Dow AgroSciences), or similar generic products, in a mineral (diesel, used engine transformer oils, Jet-A1 or kerosene) or vegetable oil (biodiesel, Ethy-NZ) or as the formulated product X-Tree® Wet & Dry (120 g L^{-1} triclopyr BEE in a biodiesel, Etec Crop Solutions Ltd).

Objectives

As an outcome of the consultation workshop it was decided that a more in-depth review of the human and environmental impacts of the variety of mixes in use for ABBA, and their effect on efficacy, be conducted. The aim of this review was to support the development of good practice for ABBA and to ensure that practices endorsed by the National Programme for Wilding Conifer Control achieve minimal impacts on human health and the environment.

Key results

- Triclopyr (as 20% Grazon®) is applied in a range of oils (diesel, biodiesel, Jet A-1, recycled transformer oils), or as X-tree Wet & Dry (triclopyr in biodiesel), for control of wilding conifers using ABBA. It is a directed spray, targeted at the upper crown and bark of isolated trees. A variety of methods are used by different operators.
- Most operators report that all mixes are effective. However, there is no actual data on the comparative effects of oils on the efficacy of triclopyr applied as an ABBA. Studies on the uptake of triclopyr into foliage indicate that modified seed oils could provide better uptake (including in bark) than the mineral oils due to better solubility of triclopyr (applied as Grazon®) in the vegetable rather than mineral oils and thus better stability of the spray formulation.
- The mineral oils (diesel, Jet-A1, kerosene, transformer oils) are more toxic and eco-toxic than the vegetable oils with the potential for high variation in their toxicity profiles depending on the type and source of diesel. Further, they are more flammable (kerosene in particular) than vegetable oils and are not readily biodegradable. Unlike petroleum oils, biodiesels are renewable, have a very low mammalian toxicity and are rapidly degraded in soil and water by microorganisms. For blends of biodiesel of 2%, 5% and 20% the highest rate of biodegradation occurs with the highest concentration of biodiesel.
- Most oils, and also triclopyr, have high aquatic toxicity which is reflected in the hazard rating. Further, kerosene has been found to increase toxicity of triclopyr to fish. Existing guidelines recommend that ABBA operations must not be used within 10 m of a river or wetland area.
- Triclopyr undergoes hydrolysis in the human body and is rapidly excreted in the urine. In the studies reported in this review no adverse effects were reported as a result of exposure to triclopyr at the respective rates tested. However, most studies on applicator exposure to triclopyr have been conducted with knapsacks, hand-guns and ground sprayers (tractor-mounted booms). USEPA exposure assessments indicate that applicators using either paint-brusher rollers or mixing, loading and spraying with backpacks or using manually pressurised hand-wands have the highest levels of exposure to triclopyr. Use of a single or double layer of clothing, gloves and respirator significantly reduced the risk of exposure.
- X-Tree® Wet & Dry is a stable mix of triclopyr and biodiesel and removes the need for operators to mix chemical on site.

Gaps in our knowledge

- The effect of different oils on the efficacy of triclopyr applied as ABBA and the pathway of uptake (significance of bark versus foliar uptake) is unknown.

- The diversity of wand configurations and application methods in use is not well documented. Method of application and wand configuration could have a big impact on efficacy, human exposure and environmental impact.
- The potential for dearomatised fluids to be used as a solvent for triclopyr is unknown. These products offer reduced human health and environmental concerns in comparison to the conventional middle distillates (diesel, kerosene, transformer oils). Whether hydro-treated light petroleum products would offer an advantage over biodiesels would essentially come down to cost and availability (and effect on efficacy).
- No information is available on exposure to triclopyr (dermal or inhalation) of an applicator using a wand from an open helicopter cockpit. Exposure of the operator in the cockpit to fines produced in the spray operation is therefore unknown. This especially for the formulations containing diesel and used engine oils that have an aspiration hazard classification. This lack of knowledge limits our ability to recommend health and safety practices and personal protective equipment that may be required over and above that already on the label/MSDS of products used – particularly the need to include a respirator as part of the protective gear. *Use of personal protective equipment should therefore be reviewed in light of these findings.*
- The amount of herbicide and oil that persist in the soil and litter following ABBA and whether residues can be transferred over time to nearby water bodies is unknown. While targeted, spot control of isolated individuals is likely to pose a low risk to water sources it must be noted that most oils and triclopyr trigger an aquatic toxicity hazard rating.
- There is almost no information on the human and environmental toxicity of oils and triclopyr when used in combination as most of the available information is on the individual components. Whether the mixes alter the toxicity and eco-toxicity profile of the individual components is unknown.

Recommendations

The role of cost and method of application (wand configuration, aircraft etc.) on choice of operational activities and formulation have not been considered in this report.

While all of the oil carriers currently used in ABBA will likely perform effectively in promoting triclopyr efficacy, there is substantial evidence to suggest that the petroleum based oils (aviation fuels, diesel, used engine oils) are likely to have a greater negative impact than the vegetable oils on human health and the environment. Aside from the hazards associated with triclopyr alone, concerns associated with the petroleum based oils include flammability (aviation fuels), potential toxicity to aquatic life, irritation to the respiratory tract, skin and mucous membranes, possible carcinogenicity (and the presence of polyaromatic hydrocarbons) and slow biodegradation. Further, toxicity and eco-toxicity can vary by orders of magnitude depending on the source and type of diesel fuel. In contrast, the biodiesels, or vegetable oils, have lower mammalian toxicity, are not flammable and are rapidly degraded in the environment. These are also renewable fuels. The high flash point of biodiesel also enables safer storage, transportation, and application of the formulation.

Therefore, taking a precautionary approach and on the basis of the health and environmental profiles of petroleum based oils, we do not recommend the use of diesel, aviation fuels and used engine oils as solvents for triclopyr in ABBA operations. As a minimum first step biodiesel blends (5%, 20% etc) should be endorsed as good practice for ABBA operations, with 100% biodiesel the preferred solvent.

On the basis of the information presented in this report there is a need for the National Programme, and operators, to take a look at the full range of PPE options when using triclopyr in oils.

A review on formulations for aerial basal bark applications (ABBA) for control of isolated wilding conifers

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Introduction

The concept of using low volumes of herbicide, applied aerially to bark, to control wilding pines in New Zealand is based on herbicide mixtures of triclopyr butoxyethyl ester (BEE) in an oil carrier (Raal 2014). The spray is applied (typically as a solid stream) from a helicopter using a wand (1.5 m- 4 m) operated manually from the aircraft cockpit by a second person in the helicopter, to target the crown trunk (bark) and upper stem branches in sufficient volume to run spray down the tree to the ground. The technique is widely used because placement on upper crown bark and triclopyr selectivity achieves high mortality rates of wilding pines with very little damage to surrounding vegetation and minimal off-target contamination of the environment. The premise for the success of this basal bark application in killing wilding pines is that the oil carrier facilitates uptake of the highly oil soluble (lipophilic) herbicide through the bark and its loading into the adjacent vascular tissue, thereby promoting movement of the herbicide throughout the plant. It is deemed critical to completely encircle the stem during the spray operation because of the limited lateral movement of compounds in the plant tissue; translocation via vascular tissue occurs only vertically in plants.

In May 2017, the National Programme for Wilding Conifer Control hosted a consultation workshop ‘Good Practice for Aerial Wanding of Wilding Conifers’. The objective of the workshop was to obtain the views of the industry, and other agencies, about the practice of controlling wilding conifers through the use of Aerial Basal Bark Application or ABBA. A number of topics relating to aerial wanding were discussed at this meeting including planning, operations, health and safety, monitoring and chemicals/herbicide mixes used. With respect to use of chemicals it was clear that while the mixes in use were generally successful, there was wide variation in the solvents (oils) and products being used as well as questions pertaining to their impact on human and environmental health. Formulations being used in ABBA operations included triclopyr applied as 20% Grazon® (600 g L^{-1} triclopyr (BEE), Dow AgroSciences), or similar generic products, in a mineral (diesel, used engine transformer oils, Jet-A1 or kerosene) or vegetable oil (biodiesel, Ethy-NZ) or as the formulated product X-Tree® Wet & Dry (120 g L^{-1} triclopyr BEE in a biodiesel, Etec Crop Solutions Ltd.). The use of triclopyr in oil for aerial woody weed control is well documented in the Department of Conservation (DOC) good practice guideline for woody weed control (Raal, 2014). Outlined in this guide are also health and environmental concerns associated with the different oil mixes and recommendations on safe handling procedures.

As an outcome of the consultation workshop it was decided that a more in-depth review of the human and environmental impacts of the variety of mixes in use, and their effect on efficacy, be conducted. The aim of this review was to support the development of good practice for ABBA operations and to ensure that practices endorsed by the National Programme for Wilding Conifer Control achieve minimal impacts on human health and the environment. As such, the specific objectives of this report were to:

1. Based on available literature, review the environmental (eco-toxic) and human health effects of triclopyr and oils currently being used for ABBA.
2. Based on available evidence, provide an indication of the effect on biological efficacy of different oils used as carriers in combination with triclopyr for ABBA.
3. Identify gaps in knowledge that prevent a full assessment of human and/or environmental impacts as well as effects on biological efficacy.
4. Where there is sufficient evidence, identify those practices that should be retained and those could be potentially eliminated, modified or improved.

Objective 1. Review environmental and human health effects of triclopyr and oils currently being used for ABBA

1.1 The toxic and eco-toxic properties of triclopyr and oils currently being used in ABBA

The parameters defining the human toxicity and eco-toxicity of the active ingredient triclopyr and its co-formulants in the product Grazon®, as well as the range of oils used in ABBA operations, are shown in Tables 1-4 in Appendix A. Included in these tables are the human health and environmental hazard classifications for each compound, either that assigned by HSNO (Hazardous Substances and New Organisms Act, 1996), the New Zealand Hazard Classification System or, where no HSNO classification was found, that prescribed by the Globally Harmonised System (GHS) (Pratt, 2002). The GHS provides an internationally agreed system for hazard classification of chemical products and for communication of those hazards. An information sheet on the correlation between GHS and New Zealand HSNO Classes is available on the EPA Website. Recommendations, as taken from product labels or material safety data sheets, for protective equipment required when handling the active ingredient or oils have also been included in these tables.

The information in Tables 1-4, Appendix A, is comprehensive and key points to note from these tables include:

1. The active ingredient triclopyr is classified as being harmful if swallowed or inhaled and may cause organ damage through repeated exposure, the latter being the point to note;
2. Jet A1 fuel is classed as a flammable liquid and vapour;
3. All mineral, or petroleum based, oils (Jet A1, diesel, used engine oils) have an aspiration hazard classification (may cause allergic or asthmatic symptoms if inhaled), are potentially carcinogenic and are also classified as highly toxic to the aquatic environment;
4. Personal protective equipment when using triclopyr and all oils include the use of overalls (some recommend PVC, others cotton), chemical resistant gloves and protective eye and face wear;

5. Biodiesel: There are many grades of biodiesel – from 5% "bio" and the rest diesel, through to 100% biodiesel (100% Alkyl C14-C24 methyl esters) and hazard classifications will vary according to the exact composition of the product. We have included estimates on toxicity and ecotoxicity of a part biodiesel (5-20%) and full biodiesel. There are differences, for example:

   Z Diesel is considered a hazardous substance and a dangerous good.

   Z Bio D B5 (5% "bio") is a hazardous substance but NOT a dangerous good

   Z B100 Biodiesel is a non-hazardous substance and a non-dangerous good.

   Biodiesel has a lower mammalian and ecotoxicity profile than diesel. It may be an important point to consider whether operators are looking at 100% bio-diesel or not.

6. For some products there is conflicting information and for others no information, particularly the oils. This may be reflected in the Tables 1-4, Appendix A. Many of the parameters shown are derived from standard laboratory tests and variation can arise due to very slight changes in the test parameters. In reality, toxicity and ecotoxicity should also be assessed using these

parameters together with field experiments that are able to validate risk of harmful exposure in-field in specific relation to the herbicide application regime in question.

7. We have not included any information on the BioEster in this report, initially requested in the terms of the review. BioEster is a biodiesel. On contacting the manufacturer we found that they do not have an MSDS for this product and also that they have stopped manufacturing this product. The company has been pushed out of business by Etec's products (i.e. X-tree Wet & Dry).

The information in Tables 1-4 (Appendix A) reflects the toxicity and ecotoxicity properties (e.g. K_{ow}, solubility, pKa, ARfD, NOAEL, Drinking water standards, LD_{50}, ADI, WHO Toxicity standards, LC_{50} (trout, daphnia, earthworm, bee etc.), DT_{50} soil and water) of the listed chemicals (triclopyr, mineral and vegetable oils) which are typically values derived from standardised laboratory tests. While these, together with the hazard classification, provide some indication of the risk posed to human health or the environment during use, data collected from field trials or summarised in review papers can provide a further insight into the risks posed by their use in any particular spraying scenario. It is important to remember that any risk of exposure to a hazard posed by a chemical during spraying is particular to the operational use pattern or scenario being investigated.

The following sections are a basic review of the literature examining the impact on human health and the environment during spraying of similar kinds of oils (petroleum products and biodiesels) and the active ingredient triclopyr. This information supports data shown in Tables 1-4 (Appendix A).

1.2 Literature review of the impact on human health and the environment of oil carriers and triclopyr used in ABBA.

1.2.1 Toxicity and eco-toxicity of oil carriers used in ABBA

Petroleum Products *(diesel, kerosene, Jet-A1, used engine oils)*

All of the mineral oils currently used in ABBA operations, diesel, kerosene and aviation fuels, are generically known as the conventional middle distillates. Such products have been widely used as solvent carriers and adjuvants for oil-soluble active ingredients such as triclopyr. For example, they have been used with phenoxy herbicides for turf, right-of-way sprays, and other applications (Krevalis 2005), used in broadacre farming to carry herbicides (Nalewaja 2002), and used alone or with insecticides in horticulture (e.g. Gauvrit and Cabanne 1993, Sharma and Dogra 1986, Singh et al., 1986, Song 1988). Since about 1940 these petroleum oils have also been used to kill weeds, as non-selective contact herbicides (Klingman and Ashton, 1981). The toxicity of these oils to plants has been correlated with their chemical structure, with shorter-chain hydrocarbons generally having more toxicity than longer-chain compounds (Vaughn and Holser, 2007). Middle distillates have been used as adjuvants and solvents for a number of reasons, including acceptable solvency, ready availability, and relatively low cost.

In recent years, however, the use of middle distillates in these applications has come under pressure due to toxicity concerns (Krevalis 2005). The concerns around middle distillates primarily have to do with the toxicological and ecotoxicological properties of these materials (see Table 1 & 2, Appendix A). There is a significant amount of information available on the toxicology of middle distillates, which has been summarized in the Environmental Contaminants Encyclopaedia (Irwin et al., 1997) and by the World Health Organisation (Environmental Health Criteria 171). Concerns cited include potential toxicity to humans and aquatic life, irritation to the skin and mucous membranes, possible carcinogenicity and the presence of polyaromatic hydrocarbons (PAHs, also referred to as polynuclear aromatics, PNAs) (See Table 1 and 2, Appendix A). "One of the problems with diesel is that the composition, and the amount and type of PAHs present, varies with diesel type (Grade 1-D, Grade 2-D, Grade 4-D, Marine Diesel, etc.) and diesel sourcing (straight run, cat cracked, reformate based). Because of this, the environmental impacts of different diesel fuels can vary by more than an order of magnitude" (Irwin et al., 1997), (Krevalis 2005). These aromatic solvents have other disadvantages such as low flash-point, high volatility and unpleasant odours (as well as enhancing the unpleasant odour produced by the herbicide/pesticide active ingredient) (Chin et al., 2012). Dunkel and Richards (1998) found petroleum-based inert ingredients to be at least as toxic as the full formulation to non-target aquatic organisms, while Krevalis (2005) found that the mutagenicity of petroleum oils was proportional to the concentration of three- to seven-ring PAHs and that materials with these higher levels of PAHs lead to a greater degree of tumour formation in mice when applied to the skin, possibly due to genotoxic mechanisms. Middle distillates may be hazardous to the environment and beneficial species not only because of their toxicology characteristics but also due to not readily biodegrading (Chin et al., 2012).

A substitute to be used as a carrier should have low toxicity, low odour, low water solubility, low vapour pressure, excellent colour and effective spray ability (Chin et al., 2012).

Biodiesels

Biodiesels are also used as a solvent for triclopyr in ABBA operations, either pre-mixed in X-tree Wet & Dry or as a solution with 20% Grazon. Biodiesel is a *renewable fuel* comprised of the mono-alkyl esters of fatty acids primarily derived from vegetable oils (Schwab et al., 1987; Van Gerpen, 2005), but also animal fats (See Table 3, Appendix A). Biodiesel is typically produced by reacting vegetable oils with an alcohol such as methanol or ethanol in the presence of a catalyst to yield the mono-alkyl esters and glycerin. Unlike petroleum oils which are moderately toxic and slow to degrade in the environment, biodiesel has very low mammalian toxicity with LD_{50} values greater than 5000 mg/kg when administered orally to rats and is rapidly degraded in soil and water by microorganisms (Zhang et al., 1998; Peterson and Möller, 2005) (see Table 1, Appendix A; Biodiesals 5%, 20%, 100%, X-tree Wet & Dry, Hasten, Kwickin, Punch Penetrant).

Langroodi (2012) found that for biodiesel blends of 2%, 5% and 20%, the highest rate of biodegradation was with the high concentration of biodiesel. Biodiesel blends increased the biodegradation of the toxic polyaromatic hydrocarbons, possibly by making them more readily available for microorganisms by solubilising them. The high flash point of biodiesel enables safer storage, transportation, and application of the formulation.

Vaughn and Holser (2007) found that 2% biodiesel/water emulsions were phytotoxic to broadleaf weed species, whereas ≥ 5% biodiesel was phytotoxic to perennial ryegrass. They concluded that biodiesels in conjunction with certain surfactants can act as contact herbicides to kill broadleaf weeds (in turfgrass…note that they only studied up to 10% biodiesel in water!). Because biodiesels are chemically synthesised, they would not qualify as “organic” herbicides under the current USDA National Organic Program Standards.

Dearomatised Fluids

As an alternative to the use conventional middle distillates (diesel, kerosene and Jet-A1), which do not have a favourable human health and environmental profile, it has been proposed (Krevalis 2005) that dearomatised fluids could be used as (petroleum based) solvents in herbicide applications, potentially giving better performance. Note that none of the solvents currently used in ABBA operations are classified as dearomatised fluids.

Dearomatised fluids, such as Exxsol D110 Fluid (ExxonMobil Chemical Company), are produced from petroleum-based raw materials which are treated with hydrogen in the presence of a catalyst to produce a low odour, low aromatic hydrogen solvent. The major components include normal alkanes, isoalkanes, and cyclics. The lower volatility and lower phytotoxicity of the dearomatised fluid may promote enhanced uptake of the herbicide, resulting in improved performance.

Some of these materials, such as the Exxsol® D fluids, conform to the requirements of the U.S. Food and Drug Administration (FDA) for certain direct and indirect food contact applications. Compared to the middle distillates, these materials offer diminished human health/hygiene concerns. They also offer lower environmental concerns in terms of lower ecotoxicity and better biodegradation. Besides lower odour, the lower aromatic content also means less risk of causing dermatitis and less rubber swelling. The lower aromatic content is also reflected in the lower polynuclear aromatic (PNA) content of the dearomatised hydrocarbon fluids compared to diesel. A second difference between these materials is the much higher flash point of the dearomatised hydrocarbon fluids. This should translate into less concern from a fire safety viewpoint with these materials. Finally, although the boiling ranges overlap, the boiling ranges of the dearomatised hydrocarbon fluids are much narrower than those of kerosene or diesel, with much higher initial boiling points.

Compared to middle distillates such as diesel, the dearomatised hydrocarbon fluids offer diminished human health/hygiene concerns. This is most clearly reflected in the skin irritation data and the sub-chronic and carcinogenicity results (Table 1). In fact, the carcinogenicity results are such that in Europe, diesel is classified as a Category 3 Carcinogen, while in the U.S., many companies label diesel as being a potential human cancer hazard. The dearomatised hydrocarbon fluids also offer diminished environmental concerns in terms of lower toxicity to marine species (Table 1).

Table 1. Comparison of toxicological properties of dearomatised hydrocarbon fluid and diesel (from Krevalis 2005).

Parameter	**Dearomatised Hydrocarbon Fluids (DHF1)**	**Diesel**
Acute Oral	LD_{50} > 15 g/kg	LD_{50} > 5 g/kg
Acute Dermal	LD_{50} > 3.2 g/kg	LD_{50} > 4.1 g/kg
Skin Irritation	mild	moderate-severe
Genotoxicity	negative	positive/equivocal
Subchronic	low	moderate
Carcinogenicity	not expected to be carcinogenic	weak skin tumour promotion potential
AQUATIC TOXICITY		
Mysid shrimp 96 h LC_{50} of water soluble fraction	> 1 000 000 ppm	< 50 000 ppm 2000 ppm typical
Rainbow trout 96 h LC_{50}	> 1 000 000 ppm	6.6 ppm
Fathead minnow 96 h LC_{50}	> 755 ppm	57 ppm

Biodegradation of the dearomatised hydrocarbon fluids is also better. The dearomatised hydrocarbon fluids are readily biodegradable (> 60 %) in stringent standard tests while the middle distillates typically do not pass ready biodegradability test conditions. Lower molecular weight compounds may be expected to be degraded relatively quickly in aerobic conditions, while higher molecular weight compounds, particularly polycyclic aromatics, will degrade slower". Half-lives for some of the PNAs that can be present in middle distillates have been calculated to be 2 years in soils and up to 6 years in sediments

Dearomatised hydrocarbon fluids as solvent and adjuvant for 2,4-D Ester resulted in equivalent performance when compared to a formulation using kerosene as solvent and diesel as adjuvant. Although not shown in this paper, Krevalis (2005) stated that work with other herbicides, specifically triclopyr ester and picloram + 2,4-D amine, gave similar results - equivalent performance compared to diesel when the dearomatised hydrocarbon fluid was used as adjuvant.

With regards to petroleum based products, Ebbon (2002) stated "Ideally it would be preferable to use a safer alternative to a product manufactured from components regarded as carcinogenic"

1.2.2 Toxicity and eco-toxicity of triclopyr butoxyethyl ester (BEE)

Spray Applicator Exposure

The active ingredient in Grazon® is triclopyr butoxyethyl ester (BEE), which undergoes hydrolysis in the human body to form triclopyr acid, which is rapidly excreted almost completely in urine (Feldman and Maibach, 1974) with a first order excretion half-life of 16.8 h (dermal) for triclopyr (Carmichael et al., 1989). Over 80% of triclopyr (Carmichael et al., 1989) is eliminated as acid, thereby facilitating urine biomonitoring (Zhang et al., 2011). Triclopyr BEE is of low acute toxicity to humans and is placed by the US Environmental Protection Agency (EPA) in Category III slightly toxic (in New Zealand HSNO Classification of 6.1D-harmful) (Table 1 & 2, Appendix A). Triclopyr has been reported to damage neurons (Reddy et al., 2011). Immunofluorescence analysis of primary neurons (of mice) revealed decreased neuronal branching and degenerating neurons in neurons treated with triclopyr (and picloram).

Applicators may contact the chemicals by inhalation, ingestion, and dermal absorption. However, for most applications of triclopyr the first two routes are considered of minor importance compared to dermal exposure, which is the most important route of entry (Spencer et al., 2000; Abbott et al., 1987). Triclopyr is absorbed in humans through the skin, the most common route of exposure. Inhalation exposure to triclopyr is much lower than dermal exposure due to the low volatility triclopyr BEE.

The oral reference dose (RfD) determined by the EPA (based on a study using rats) that is not likely to cause harmful effects during a lifetime for both adults and children is 0.05 mg/kg-day (US EPA, 1998). This is equivalent to 4 mg day^{-1} for an adult human of approximately 80 kg.

Gosselin et al. (2005) studied the urine of forestry workers applying Garlon 4 (triclopyr BEE) in Quebec, Canada. Their urine was monitored on the final day of a five-day work week. Eight workers were applying dilute 20 percent Garlon 4 and 80 percent mineral oil with a backpack unit directly on the stumps of recently cut trees, and two workers were applying 12.6 liters of Garlon 4 mixed in 1,800 liters of water under high voltage transmission lines from a tractor-mounted boom.

The workers collected all their urine from the start of their workday until the first urination the following morning. The average amount of triclopyr found in urine was 0.0564 mg/kg of body weight ranging from 1.04 to 12.98 mg/day in the eight backpack sprayers, and 3.61 to 5.97 mg/day in the two boom sprayers. A mathematical model was developed to estimate the absorbed dose from triclopyr exposure using the amount excreted in the urine by each worker. The mean estimated daily absorbed dose based on a simulated fraction recovered in the urine was 11.92 mg (34.9%) in the backpack sprayers and 14.4 mg (31.4%) in the boom sprayers. *This dose would result in a cumulative urinary excretion of triclopyr equal to 1.45 mg/kg b.w. for a 24 h collection, 2.63 mg/kg b.w. for a 48 h collection and 2.83 mg/kg b.w. for a 72 h collection.* Comparisons between the estimated daily doses absorbed by the workers in this study and the RfD show that there is a potential health risk for these workers under the current conditions. Since there is no observed effect in humans exposed to triclopyr, there is no proof that the NOEL established for rats corresponds to a safe dose for humans.

The results of the study were reported to the managers supervising these workers so that tighter security measures could be implemented during manipulations of the product in order to minimise worker contact with the product. Worker education and serious supervision were also recommended to ensure that neoprene gloves and rubber boots or boot covers are worn at all times.

Zhang et al. (2011) monitored a crew of 8 backpack sprayer applicators, a mixer/loader, and a field supervisor employed in a conifer release program in northern California during the summer of 2002. Two herbicides, 2,4-D and triclopyr esters (1.6:1 acid equivalents) were applied as a tank mix. The absorbed dosages of 2,4-D and triclopyr were calculated based upon both cotton whole body suits and biomonitoring (urine, 24 h). Dosages based upon accumulation of the herbicides on body suits averaged 42.6 μg (a.e.) 2,4-D/kg-d and 8.0 μg (a.e.) triclopyr/kg-d. Six consecutive days of concurrent urine collections showed that backpack applicators excreted an average of 11.0 μg (a.e.) 2,4-D/kg-d and 18.9 μg (a.e.) triclopyr/kg-d. Estimates based upon curve fitting were 17.1 and 29.3 μg (a.e.)/kg-d (0.0171 and 0.0293 mg/kg-d), respectively. *The mixer/loader and the field supervisor had less contact with spray mix and treated foliage and 3- to 5-fold lower adsorbed daily dosage than the backpack applicators.* Results from that study suggest that passive dosimetry for 2,4-D consistently overestimated the dosage measured using biomonitoring by a factor of 2-3 fold, while for triclopyr, passive dosimetry underestimated the absorbed dose based on biomonitoring by a factor of 2-4 fold. No adverse health effects were reported or observed during the conifer release programme.

A two-day biomonitoring study of skin and inhalation exposure to Garlon 4 was conducted in California in 1995 (Spencer et al., 2000) of ten forestry workers applying Garlon 4 (containing 61.6% (5.56 lb/gal) of the formulated product) using backpack sprayers and spray wands) (Spencer et al., 2000). Twenty-four-hour urine samples were collected to estimate absorbed dose.

Dermal exposure was monitored by measuring residues on work clothing worn next to the skin (long sleeved cotton T-shirts and knee-length socks) and wipe samples of the hand, face, and neck. Upper body exposure accounted for 45 percent of exposure, legs 33 percent, hands 19 percent and face/neck three percent. Mean measured dermal triclopyr exposure of 18.67 mg per person accounted for 98 percent of the estimated daily absorbed dose for the two days.

Triclopyr has a low vapor pressure (0.2 mPa at 25 °C), and inhalation is generally not a major route of exposure. Inhalation accounted for approximately 0.3-5% of a workers' measured dose. Inhalation doses of triclopyr BEE measured using personal air monitors ranged from 32.6 to 71.7 μg per day, accounting for 1.89 percent of the mean daily absorbed dose for the two days.

Urine samples were collected at 24h to obtain an estimate of absorbed dose (EAD). Overall EAD from urinary triclopyr (0.058 mg/kg bw) was significantly greater than that estimated from dermal plus inhalation monitoring (0.013 mg/kg bw) $p < 0.01$, suggesting (and in agreement with Zhang et al., 2011) that the methodology used to assess exposure did not provide a comprehensive assessment (Marin Municipal Water District, 2010).

A study was conducted (Middendorf et al., 1994) of sixteen forestry worker volunteers at three different sites, applying Garlon 4 using backpack sprayers and hand guns. Four to six pounds (1.82 to 2.72 kg) of triclopyr were applied per day. Dermal exposure was monitored by applying body surface patches and use of hand rinses. Inhalation exposure was monitored by personal air concentration in the breathing zone. All urine was collected over a five-day period—the day before, the day of, and three days after application—to obtain the amount of triclopyr excreted in order to estimate absorbed dose.

The mean exposure rate was 0.004 (0.00035–0.01428) mg/kg per kg a.e. handled. Neither of two workers with the highest exposure rates (0.01428 and 0.01176) wore gloves. The mean exposure rate of 0.00221 (0.0015–0.00506) mg/kg per kg a.e. was much lower when including only the fourteen workers who wore gloves. The mean dermal absorption rate was 0.046 mg/hour (0.0163–0.0873). Personal air levels ranged from 5 to 15 µg/m (Middendorf et al., 1994, as reported in the Marin Municipal Draft 2010).

None of these studies considered aerial application. However, from the literature, there are various database and modelling techniques that have been used for exposure assessment, which may be used to assess the level of protection and the type of preventive measures necessary to ensure minimum hazard during application. Numerous generic databases, including the Pesticide Handlers Exposure Database (PHED), the European Predictive Operator Exposure Model (EUROPOEM), the Agricultural Re-entry Exposure Task Force (ARETF), the Agricultural Handlers Exposure Task Force (AHETF), the Outdoor Residential Exposure Task Force (ORETF) and EUROPOEM II, have been developed (Gao et al., 2014, Franklin and Worgan, 2005; Soutar et al., 2000; Guidelines for Exposure Assessment; PHED Exposure Surrogate Reference Table; Li et al., 2010; Krieger, 1995).

As an example, Table 2 is an excerpt from the USEPA/Office of Pesticide Programs / Health Effects Division Occupational Pesticide Handler Unit Exposure Surrogate Reference Table (PHED). The Exposure Surrogate Reference Table provides pesticide exposure information for risk assessment based on exposure scenarios, exposure routes and applicable personal protective equipment. *Note that the use of gloves significantly reduces dermal exposure*. Of the activities chosen to show in Table 2, the level of dermal exposure is in the order of: Applicator/Paintbrush/roller > Mixer/loader/applicator, manually pressurized handwand > Mixer/loader/applicator, Backpack sprayer > Mixing/loading liquids > Applicator, open cab groundboom > Flagger > Applicator, Aerial, Fixed wing (enclosed cockpit).

While dermal exposure by an applicator in a fixed-wing aircraft is low, as expected, there is no information on dermal exposure to an applicator using a wand from an open helicopter cockpit! Note: The actual exposure dose is determined by environmental conditions and other factors such as wind velocity and direction, relative humidity, crop height, area and method of pesticide application (Calumpang 1996). The exposure dose also depends on the droplet size, which may vary with the spray volume rate. This effect of droplet size can be accounted for when sufficient replicates of the specific spray volume rate are available for measurement. Another challenge in determining exposure relates to the standardisation of application duration, because the time of observation strongly influences the estimation of exposure. Many other factors can also affect the exposure dose: the type of equipment used (e.g. open or closed systems), the frequency, duration and rate of application, the use of personal protective equipment such as gloves and garments and the type of job performed (Gao et al. 2014, Calumpang 1996, Nuyttens et al. 2009, Choi et al. 2006).

Table 2: Excerpt from the Occupational Pesticide Handler Unit Exposure Surrogate Reference Table.

USEPA / Office of Pesticide Programs / Health Effects Division Occupational Pesticide Handler Unit Exposure Surrogate Reference Table					
Exposure Scenario (Activity, Equipment, Formulation, Site, etc.)[1]	**Exposure Route**	**Personal Protective Equipment (PPE) Level[2]**	**Data Source[3,4,5]**	**Statistic**	**Unit Exposure (µg/lb ai)**
Mixing / Loading Liquids	Dermal	Single layer, no gloves (A)	AHETF (MEA)	Mean	220
		Single layer, gloves	AHETF (MEA)	Mean	37.6
		Double layer, gloves (B)	AHETF (MEA)	Mean	29.1
		Engineering control (closed loading system)	PHED	“Best fit”	8.6
	Inhalation	No Respirator	AHETF	Mean	0.219
		PF5 (C)	AHETF	Mean	0.044
		PF10 (D)	AHETF	Mean	0.022
		Engineering control (closed loading system)	PHED	“Best fit”	0.083
Applicator, Aerial, Fixed-Wing/Liquids	Dermal	Engineering control (Enclosed cockpit)	AHETF (MEA)	Mean	2.08
	Inhalation	Engineering control (Enclosed cockpit)	AHETF (MEA)	Mean	0.0049
Applicator, Open Cab Groundboom	Dermal	Single layer, no gloves (A)	AHETF (MEA)	Mean	78.6
		Single layer, gloves	AHETF (MEA)	Mean	16.1
		Double layer, gloves (B)	AHETF (MEA)	Mean	12.6
		Engineering control (Enclosed Cab)	PHED	“Best fit”	5.1
	Inhalation	No Respirator	AHETF	Mean	0.34
		PF5 (C)	AHETF	Mean	0.07
		PF10 (D)	AHETF	Mean	0.03
		Engineering control (Enclosed Cab)	PHED	“Best fit”	0.043
Applicator, Paintbrush/roller	Dermal	Single layer, no gloves	PHED	“Best fit”	180000
		Single layer, gloves (E)	PHED	“Best fit”	24000
		Double layer, gloves (B, E)	PHED	“Best fit”	22000
	Inhalation	No Respirator	PHED	“Best fit”	280
		PF5 (C)	PHED	“Best fit”	56
		PF10 (D)	PHED	“Best fit”	28

USEPA / Office of Pesticide Programs / Health Effects Division
Occupational Pesticide Handler Unit Exposure Surrogate Reference Table

Exposure Scenario (Activity, Equipment, Formulation, Site, etc.)[1]			**Exposure Route**	**Personal Protective Equipment (PPE) Level[2]**	**Data Source[3,4,5]**	**Statistic**	**Unit Exposure (µg/lb ai)**
Flagger		Liquids	Dermal	Single layer, no gloves	PHED	“Best fit”	11
				Single layer, gloves	PHED	“Best fit”	12
				Double layer, gloves (B)	PHED	“Best fit”	10.6
			Inhalation	No Respirator	PHED	“Best fit”	0.35
				PF5 (C)	PHED	“Best fit”	0.07
				PF10 (D)	PHED	“Best fit”	0.04
Mixer / Loader / Applicator, Backpack Sprayer	General Broadcast/Foliar Applications	Nurseries, Christmas Tree Farms, Wildlife management, Rights-of-way, Forestry, Landscaping (turf/plants/bushes/trees),	Dermal	Single layer, no gloves (A)	AHETF (MEA, *f*RA)	Mean	58400
				Single layer, gloves	AHETF (MEA, *f*RA)	Mean	30500
				Double layer, gloves (B)	AHETF (MEA, *f*RA)	Mean	16900
			Inhalation	No Respirator	AHETF	Mean	69.1
				PF5 (C)	AHETF	Mean	13.8
				PF10 (D)	AHETF	Mean	6.9
Mixer / Loader / Applicator, Manually-pressurized Handwand		Greenhouses, Wildlife management, Nurseries, Landscaping, Industrial/Commercial areas, Poultry/livestock houses, Animal treatments, Outdoor residential areas, Interior landscaping, Aquatic areas, Structural, Mushroom houses, Christmas Tree Farms	Dermal	Single layer, no gloves	PHED	“Best fit”	100000
				Single layer, gloves	PHED	“Best fit”	430
				Double layer, gloves (B)	PHED	“Best fit”	365
			Inhalation	No Respirator	PHED	“Best fit”	30
				PF5 (C)	PHED	“Best fit”	6.0
				PF10 (D)	PHED	“Best fit”	3.0

USEPA / Office of Pesticide Programs / Health Effects Division
Occupational Pesticide Handler Unit Exposure Surrogate Reference Table

Exposure Scenario (Activity, Equipment, Formulation, Site, etc.)[1]	Exposure Route	Personal Protective Equipment (PPE) Level[2]	Data Source[3,4,5]	Statistic	Unit Exposure (μg/lb ai)

[1] If the description of the scenario is silent on specific equipment, sites, formulations, etc., the data is applicable to all potential applications for that scenario.

[2] Single layer = long-sleeve shirt, long pants, shoes plus socks. Double layer = “coveralls” in addition to single layer.

Exposure monitoring data representing all levels of PPE for all scenarios is unavailable. In order to represent different PPE levels, exposure values are calculated using assumptions for the protection afforded by additional layers of clothing, chemical-resistant gloves, or respirators. Exposure assessors should be mindful of the uncertainties that this convention introduces into the overall calculations. In all cases, estimates based on direct measurements representing the PPE-level specified are the most reliable. If a scenario uses PPE calculation assumptions, they are identified in the table with one or more of the following notations:

(A) “No glove” hand exposure back-calculated from available “gloved hand” exposure data by multiplying by 10 (i.e., chemical-resistant gloves are assumed to reduce hand exposure by 90%).
(B) ”Double layer” body exposure calculated from available “single layer” body exposure data by dividing by 2 (i.e., an additional layer of clothing is assumed to reduce body exposure by 50%).
(C) “PF5” respirator exposure calculated from available “no respirator” exposure data by dividing by 5 (i.e., a PF5 respirator is assumed to reduce inhalation exposure by 80%).
(D) “PF10” respirator exposure calculated from available “no respirator” exposure data by dividing by 10 (i.e., a PF10 respirator is assumed to reduce inhalation exposure by 90%).
(E) “Gloved” hand exposure calculated from available “no glove” hand exposure data by dividing by 10 (i.e., chemical-resistant gloves are assumed to reduce hand exposure by 90%).
(F) “Single layer” body exposure calculated from available “total deposition” body exposure data by dividing by 2 (i.e., an additional layer of clothing is assumed to reduce body exposure by 50%).
(G) “Double layer” body exposure calculated from available “total deposition” body exposure data by dividing by 4 (i.e., two layers of clothing are assumed to reduce body exposure by 75%).

If a scenario does not have one of these notations, the data underlying the recommended values is a direct match for the indicated level of PPE.

[3] PHED = Pesticide Handler Exposure Database; AHETF = Agricultural Handler Exposure Task Force; ORETF = Outdoor Residential Exposure Task Force; MRID = Master Record Identification (#).

[4] Where applicable, the notation “MEA” is added to signify that the default values reflect an (upward) adjustment by the U.S. EPA for potential inefficiency of the hand wash and face/neck wipe exposure monitoring methods. MEA = Method Efficiency Adjustment.

[5] Where applicable, the notation “*f*RA” is added to signify that the default value reflects an (upward) adjustment by the U.S. EPA to reflect that the underlying data did not meet benchmark accuracy objectives. *f*RA = fold Relative Accuracy.

[6] Due to the effect that the back-calculation from “gloved hands” to represent “non-gloved hands” has on distributional variability and parametric estimates, no adjustment was made to hand measurements to represent unit exposures for “single layer, no gloves”. That is, the unit exposure for “single layer, gloves” is also assigned to “single layer, no gloves”.

https://www.epa.gov/sites/production/files/2016-11/documents/handler-exposure-table-2016.pdf

Ecotoxicity of triclopyr BEE in New Zealand

There have been no studies conducted on the environmental impacts and persistence of triclopyr in soil and water when applied in ABBA operations. Based on toxic and eco-toxic profile (Tables 1 and 2, Appendix A) triclopyr is considered very ecotoxic to aquatic life with low to moderate persistence in soil. An evaluation of the international literature pertaining to the ecotoxicity of triclopyr BEE is beyond scope of this review. An outline of studies on ecotoxicity conducted in New Zealand are highlighted below.

New Zealand aquatic benthic macroinvertebrate composition.

Maloney (1995) studied the effect of triclopyr BEE (Grazon) on the abundance and species composition of benthic aquatic macroinvertebrates in the Ahuriri river, New Zealand, following a standard large-scale herbicide spray operation.

The abundance and species composition of aquatic benthic macroinvertebrates were compared between an area aerially sprayed with the herbicide Grazon at 3 L ha^{-1} (active ingredient triclopyr) and an upstream control site (no triclopyr). Spray nozzles were chosen that emitted a large drop size to reduce drift. A 1-2 m buffer strip was left around all water edges to minimise contamination of water. No triclopyr was found in water samples taken prior to spraying, and none was detected at the control site and any time during the experiment. However 1, 3.4, 1.3 and 1.5 µg L^{-1} triclopyr was detected in the treatment area within 1, 2.5, 4.5 and 6.5 hours after application, respectively. Aquatic invertebrate species composition was similar in treatment and control sites, and did not change over time.

Concentrations of triclopyr recorded in water samples were extremely low, and well below concentrations required to harm any taxa tested in laboratory studies to date. For example, *Deleatidium* spp. has a 96 h LC$_{50}$ value (i.e., the concentration of triclopyr required to kill 50% of individuals over a 96 h exposure period) of 10 µg L^{-1} and is the most sensitive of three laboratory-tested taxa (Hickey & Martin 1993). *Deleatidium* spp. are also known to be very sensitive to the presence of other toxins (e.g., heavy metals: Hickey & Vickers 1992), yet numbers in the Ahuriri River did not respond to the inputs of triclopyr recorded in concurrent water sampling. Tests on another invertebrate (*Daphnia magna*) show greater tolerance to triclopyr, with 96 h LC$_{50}$ levels of 133 000 µg L^{-1} (Dow Elanco unpubl. data). Similarly, tests on rainbow trout (*Oncorhynchus mykiss*) with an acute oral toxicity LD50 of 117 000 µg L^{-1}, and mallard (*Anas platyrhynchos*) with an LD$_{50}$ of > 5600 g L^{-1} indicate that these species are very insensitive to the presence of triclopyr. The application of herbicide in this study produced triclopyr concentrations in the Ahuriri River that were far below those published for invertebrate, fish, or avian taxonomic groups; therefore on this basis alone it is very unlikely that changes in numbers of any of these taxonomic groups could be attributed to the presence of triclopyr in the river.

Note on non-NZ study: Guilherme et al. (2014) studied the genotoxicity of Garlon (triclopyr BEE) and kerosene to fish. They found both genotoxic, with the formulation having a higher genotoxic potential than the active ingredient alone. They therefore thought that the kerosene increased the toxic nature of the active ingredient triclopyr. They were unsure whether the effect was additive or synergistic. This outcome was in agreement with Lohani et al. (2000) who found that kerosene could elevate the genotoxic potential of Chrysotile asbestos in hamster embryo fibroblasts. While Grazon doesn’t contain kerosene, this aspect should be considered when spraying triclopyr BEE using kerosene (e.g. Jet fuel A1) as the carrier.

New Zealand Reptiles

More than 50% of native New Zealand reptiles are declining or threatened (Hitchmough et al., 2013). Chemical contaminants are an additional stressor that may be contributing to reptile decline

(Gibbons et al., 2000). Therefore, Weir et al. (2016) characterised the toxicity of several rodenticides and herbicides (including triclopyr) to reptiles to provide a screening-level risk assessment of these chemicals applicable to native reptiles of New Zealand using the western fence lizard, *Sceloporus occidentalis*, as a surrogate organism. Of the five herbicides tested (glyphosate, clopyralid, triclopyr, metsulfuron-methyl and haloxyfop-methyl) and one common adjuvant in glyphosate formulations (polyethoxylated tallowamine or POEA), only triclopyr was toxic to fence lizards below 1750 µg g^{-1} (LD50 = 550 µg g^{-1}). However, Weir et al. (2016) considered the LD_{50}'s to be very high for all herbicides (including triclopyr), with risk estimates for field applications very low (<0.02 for triclopyr, <0.002 for other herbicides), and therefore lizard toxicity to triclopyr would probably be environmentally unrealistic under normal application scenarios. For example, in order to achieve exposure levels that would create even moderate risk of acute toxicity, application rates would need to be more than 50-times greater than the assumed application rate (1.12 kg ha^{-1}).

New Zealand Spiders

The endangered New Zealand spider, *Latrodectus katipo,* is restricted to coastal habitats around New Zealand, which are being invaded by lupins. Evans et al. (2009) tested the effect of two herbicides used to control lupins, Grazon (triclopyr) and Versatill (clopyralid) and the surfactant Boost (an organosilicone) on the survival of an exotic surrogate spider species (*Steotoda capensis*). Laboratory tests of mortality of the spiders indicated that spider survival was unaffected when treated with the herbicides Grazon and Versatill at both full and half application rates but treatment with the surfactant alone (Boost), applied at the lowest levels recommended for use in NZ (Goodwin and McBrydie 2000), significantly reduced spider survival by about 30% when compared with spiders in the control group. The Department of Conservation took a precautionary approach and avoided the use of surfactants when aerially spraying tree lupin on Kaitorete Spit in 2007. The authors recommended, pending further research, that Boost not be used when applying herbicide in habitats occupied by endangered invertebrates.

Stream run-off losses and soil and grass residues from triclopyr applied to hillside gorse

In a 1991 New Zealand study triclopyr levels were measured in stream runoff after a helicopter aerial application to a hillside area of gorse and pasture grass treated with about 3.97 kg a.i./ha of triclopyr BEE (140 L volume water sprayed; Wilcox et al., 1991). Samples were collected continuously for six months after treatment. The highest concentration of triclopyr was detected on the third sampling event following the first major rainstorm (about 200 mm rain) since the application, at 41 to 46 days after treatment. Samples collected after that time yielded no detections, suggesting that the first substantial rainfall caused runoff of most of the available triclopyr. The total mass of the triclopyr in the stream water was calculated to be about 103 g or equal to about 2.9% of the total triclopyr applied. Adsorption of triclopyr to stream sediments and uptake by aquatic plants may have removed some of the herbicide from the water, suggesting that actual runoff rates might be higher. Triclopyr was not detected at the catchment outlet 400 m downstream of the sampling point.

Soil and grass samples from the treated site were also analysed seven times over eight months; half-lives for soil of 107 days in sheltered sites and 97 days in exposed sites were determined; the grass concentrations declined exponentially to yield half-lives of 30 days for the period 2 – 249 days after spraying. Concentrations of triclopyr in grass and soil samples taken from sites below large gorse bushes increased over the first 32 days but declined similarly to samples from exposed sites after the first significant rainfall of the study. The persistence in grass was much longer than reported elsewhere, but concentrations were well below those considered to be acutely toxic to grazing animals. The researchers also noted that soil temperature and the amount and type of organic matter affect the persistence of triclopyr.

Objective 2. The effects of oils on the efficacy of triclopyr

2.1 Use of oils in ABBA on efficacy of triclopyr

The technique of ABBA, using a wand, for control of wildings was first reported in 2014 by Raal, in an excellent DOC Guideline (Raal, 2014). Raal described the herbicide mix used as one part triclopyr BEE (600 g/L formulation) in four parts oil. The carrier oils listed were predominantly mineral oils, with only one vegetable-based oil described, plus a recommendation for a commercial premix based on biodiesel (Table 3). There was no preferential recommendation for oil to use based on efficacy, but X-Tree Basal (pre-mixed) was recommended because it removed the need for operators to mix herbicide and oils on site. Raal listed 47 woody weed species known to be controlled by the basal bark herbicide mixture, using 20-30% triclopyr formulation in an oil carrier.

Table 3. Carrier oils used in ABBA to control wilding pines (Raal 2014)

Oil	**class**	**source**	**Herbicide mix**	**notes**
diesel	mineral	fuel pump	+Grazon	User and environmentally unfriendly
Jet A-1	mineral	aviation	+Grazon	As above, plus corrosive to helicopters
Paraffin oil	mineral	retail	+Grazon	
Syntol oil	mineral	recycled	+Grazon	Carcinogenicity unknown
Genera oil	mineral	refined paraffin	+Grazon	expensive
Kerosene	mineral	retail	+Grazon	flammable
Biosafe	vegetable	retail	+Grazon	Endorsed by Dow AgroSciences
X-Tree Basal	biodiesel	Etec Crop Solutions	Triclopyr BEE 1:4 pre-mix	Includes penetrant in oil

Following on from this, Briden, Raal & Gous (2014) described ABBA using a wand, with a herbicide mix of one part triclopyr BEE (600 g/L formulation) in four parts oil (e.g. canola based biodiesel). They reported the technique readily controlled *P. contorta* under 10 m in height, but would kill trees of any size if sufficient herbicide was applied.

There have been virtually no direct comparisons reported, of effects of different oils on triclopyr efficacy from ABBA, all other things being equal. Gous *et al* (2014) used paraffinic oil carriers to test the efficacy of ABBA of six triclopyr-based herbicides on *P. contorta* and *P. nigra*. They noted a significant difference between two mineral oils on triclopyr efficacy on *P. contorta*, but did not disclose the oil specs or make a preferential recommendation of oil use based on efficacy. The use of oil extended the period over which trees could be treated and the method was effective in controlling trees up to 8 m tall with low volume applications (0.5 – 1 L spray/tree). Additionally, they concluded that the ABBA technique was far more rapid and safe than the existing practice of skid hopping.

Gous *et al* (2015) tested three triclopyr-based treatments, using ABBA, for efficacy on four wilding conifer species ranging in size from 0.5-16 m tall. They used a single paraffinic oil (identity not disclosed) as the carrier, applying 1 L of spray per tree. Use of the most effective herbicide treatment allowed successful control of all four species up to a height of 8-10 m and use of oil as the carrier allowed treatment time to be extended throughout the year.

Rolando and Gaskin have been conducting studies to compare the uptake and translocation of triclopyr formulations in *P. contorta* through 2016-17 in an MBIE funded project. These studies primarily investigated triclopyr performance as in aerial boom sprays applied to **foliage**, but some data (unpublished) has been generated for treatments using oils as carriers. Grazon (Dow AgroSciences) applied in a mineral oil carrier (BP Dothi oil) was shown to approximately double the uptake of triclopyr (at 18 kg/ha) into *P.contorta* foliage relative to Grazon alone, or the TDPA brew (brew used for control of dense *P. contorta* stands), by seven days after treatment. The uptake of triclopyr into foliage using a methylated seed oil (MSO; Punch, Etec Ltd) as the carrier was increased even more, by a factor of 2.4 (to approx. 80%), similar to the uptake measured with X-Tree Wet & Dry (Etec Ltd) into *P. contorta* foliage. X-Tree Wet & Dry contains triclopyr BEE (18.8%), methylated vegetable oil (80.7%) and undisclosed surfactant (0.5%) in a pre-mixed formulation, removing both the safety concerns of mixing oils and herbicide in the field, and any environmental concerns with respect to petroleum distillates. Grazon was totally solubilised in the MSO (Punch) and remained stable for many weeks, whereas it is relatively insoluble in diesel (Fig 1) and Dothi oil (not shown). This is likely a function of Grazon itself containing no petroleum distillates (it is composed primarily of triclopyr BEE (~72%) and diethylene glycol monoethyl ether (~20%)).

Fig 1. Stability of triclopyr in mineral oil & MSO carriers
Left: Grazon (18 kg triclopyr/ha) + diesel (100 L/ha), Right: Grazon (18 kg triclopyr/ha) + MSO (100 L/ha)

Translocation of triclopyr dose away from the foliar uptake site, when applied in oil carriers (mineral and MSO), was generally greater than for the TDPA brew (an aqueous brew used in boom spraying of wilding conifers), as was the observed phytotoxicity to foliage at seven days after treatment. These results suggest use of the modified seed oils may benefit efficacy of triclopyr more than mineral oils, in both basal and foliar applications, in addition to the MSOs having a lower environmental impact and being safer to use. They also indicate that **foliar** uptake may contribute substantially to triclopyr efficacy on wilding pines in ABBA. Uptake of triclopyr into basal bark of NZ *P. contorta*, applied in an undisclosed MSO carrier, was determined to be approximately 35% at 48 h, progressing to 63% at seven days, after treatment (Gaskin, unpublished data).

In conclusion, there is no published data on the comparative effects of oils on the efficacy of triclopyr, as an aerial basal bark application, on wilding conifers in New Zealand. It is likely that all the oil carriers currently used in ABBA perform effectively in promoting triclopyr efficacy, but there is some evidence to suggest that modified seed oils could be more beneficial in this respect than mineral oils, in addition to their environmental and human health advantages. MSO will also provide better solubility of triclopyr (Grazon) than mineral oil carriers and more stable spray formulations. For these reasons, the pre-mixed, MSO-containing formulation (X-Tree Wet & Dry), is currently the favoured and safest option for wilding conifer control.

2.2 Use of oils with triclopyr to improve control of woody weeds

Oil adjuvants are used with herbicides because of their ability to increase absorption of the herbicide through waxy cuticles (Nalewaja 2002), and because they increase spray retention and coverage on difficult-to-wet target plants (Holloway *et al* 2000). Diesel oil has been used to increase herbicide efficacy (e.g. 2,4,5-T) since the 1950s. Petroleum-derived oils were introduced as adjuvants for selective herbicides in 1964 (Jones & Andersen 1964) and soon after, vegetable oils also were found to be effective adjuvants for herbicides. In 1985 methylated seed oils (MSO) were reported as herbicide adjuvants (Nalewaja *et al* 1985) and esterified vegetable oils are also now used extensively to improve herbicide efficacy. Oils can enhance the efficacy of many classes of herbicides, but the difference between seed and mineral oils varies with herbicides and weed species (Gauvrit & Cabanne 1993). Little attention has been given to understanding the mode of action of oils in enhancing herbicide efficacy (Wang & Liu 2007); it is believed this is primarily related to increasing the penetration of active ingredient (AI), but absorption data do not always relate to efficacy (Nalewaja 2002). The penetration of vegetable oils themselves into plants is extensive (Mercier et al 1997) and that of mineral oils has been demonstrated (Tan *et al* 2005).

Triclopyr efficacy is enhanced by oils, both in high-volume aqueous (boom) spray applications targeting foliage, where oils are used in low concentrations as adjuvants, and in low-volume basal bark applications, where oils are used as spray carriers for the herbicide. Published research on basal bark applications with triclopyr is limited and comparative effects of oils on triclopyr uptake, translocation and efficacy on woody weeds via basal bark application even more so. Schneider (1991) examined triclopyr uptake, translocation and efficacy with four oils, from basal bark applications to four woody species in the US, including Virginia pine. Pine was the most difficult species to control. The oils used were kerosene, an MSO and two refined petroleum distillates. The MSO, kerosene and one mineral oil gave excellent control and mortality of all species at the concentrations and doses used. Herbicide uptake and translocation of triclopyr to inner bark, wood and leaves was greatest with the MSO. On the basis of these findings, a US patent was granted to DowElanco (Keeney & Troth 1995) relating to novel triclopyr BEE compositions using MSOs as carriers, to control undesirable vegetation by basal bark applications.

The efficacy of an MSO versus diesel as a triclopyr carrier for basal bark treatment, was compared on nine American hardwood species (Rhodenbaugh & Yeiser 1994). Three rates of triclopyr were tested with both oils. The MSO provided equal or greater efficacy across all nine species and for all herbicide rates, with either dormant or growing season application. These researchers concluded that MSO was a viable alternative to diesel oil carriers for basal bark control of hardwood weeds with triclopyr.

Rathfon (2006) reported a factorial study of triclopyr treatments and oil diluents (diesel, two paraffin oils and an MSO) in basal bark applications to control Amur honeysuckle. Triclopyr consistently controlled 94-95% of shrubs, across all shrub sizes and months of application over two growing seasons. The type of oil had no effect on herbicide efficacy.

Triclopyr application timing and concentration influenced basal bark efficacy on Chinese privet (Enloe *et al* 2016), but there were no efficacy differences between an aliphatic mineral oil carrier (Bark Oil Blue, Loveland USA) and a ready-to-use formulation, Pathfinder II (Dow AgroSciences, USA). The oil type in the latter is not disclosed.

New Zealand researchers, Raal and Gous (refer Part 1), have pioneered **aerial** basal bark application (ABBA) of triclopyr to control wilding pines. There are no references to similar control techniques anywhere else in the world. ABBA is a proven effective tool to manage emerging wilding conifer infestations at an early stage using triclopyr in a variety of mineral or plant oil carriers. There has been no reported systematic investigation of the influence of these oils on efficacy, but the preferred option should be MSO; MSO can provide equal efficacy relative to mineral oil and it is both environmentally and toxicologically more benign than using petroleum oils.

Research on the use of oils as adjuvants to enhance the efficacy of herbicides applied in aqueous carrier is well documented in numerous papers and in comprehensive reviews (Nalewaja 2002, Gauvrit & Cabanne 1993, Hamilton 1993). Holloway *et al* (2000) showed that an MSO consistently increased spray retention and surface coverage on waxy, difficult-to-wet leaf surfaces more than a mineral oil. Only one study was found in the current review of literature which compared the effects of MSO and mineral oil adjuvants on the uptake and translocation of triclopyr BEE in aqueous sprays (Downs 2009). In that study, MSO was the more effective adjuvant for promoting uptake and (dose) translocation of triclopyr in the woody shrub, Salal. Recent studies by Gaskin & Horgan (2016, unpublished) have determined that the uptake of triclopyr (18 kg/400 L/ha) into *P. contorta* with the addition of an MSO (0.5% Punch) was significantly increased, and was approx. double that with a mineral oil adjuvant (0.5% Uptake Oil). The oil effects on translocation of triclopyr were not determined.

The only other research relating to triclopyr uptake with oil was reported by Tse-Seng *et al* (2009). A mineral oil (Agridex) was found to maximise the control of *Hedyotis verticillate* with triclopyr (+metsulfuron) relative to a nonionic surfactant and an organosilicone surfactant.

The documented effects of oils as adjuvants for herbicides are: improving spray retention, improving droplet spread and spray contact with leaf surface, solubilising epicuticular waxes and enhancing herbicide penetration (Nalewaja 2002). Those effects differ with the oil, herbicide, target species and environment, indicating the complexity of optimising herbicide efficacy. It appears that oil adjuvants improve the control of wilding conifer species with triclopyr for any, or all, of the above reasons, but the relative effects of mineral versus MSO on triclopyr efficacy are not established at this time. For that reason the preferred option should be MSO, because of its likely equivalent or improved effects on efficacy, and its lower environmental impact and toxicity to spray applicators.

Objective 3. Knowledge gaps

Currently, there is no single, easily available, online good practice guide for aerial wanding of wilding conifers. A manual developed by the Department of Conservation (Raal, 2014) is the most comprehensive guide available. The DOC manual is excellent and provides a detailed breakdown of how to apply the herbicide in ABBA operations, the equipment required, pro’s and cons of different aircraft, limitations to use of the technique, equipment maintenance, health and safety requirements and potential environmental impacts of the chemicals used. However, no single formulation, wand configuration or method of application is endorsed as good practice, with much choice left to the discretion of the pilot or operator. Further, there is no referencing to support the effect of different methods of application on efficiency and efficacy with cost possibly one of the bigger drivers of chemical/formulation selection. As a result there remain a variety of methods used operationally with questions pertaining to the human and environmental impacts of the different mixes, and possibly also application methods, and their impact on efficacy. The variation in practice across the industry was a concern captured at the ABBA consultation meeting held in May 2017 and was a basis for the commissioning of the current report. It is reassuring that much of the independent information collected in this review supports that already noted in the DOC manual, but with more depth in the detail.

3.1 What we know (summary)

Using the DOC good practice guideline for ABBA, the information supplied in this report and the outcome of the consultation workshop we know that:

- Triclopyr (as 20% Grazon®) is applied in a range of oils (diesel, biodiesel, Jet A-1, recycled transformer oils), or as X-tree Wet & Dry (triclopyr in biodiesel), for control of wilding conifers using ABBA. It is a directed spray, targeted at the upper crown and bark of selected trees. A variety of wanding methods are used by different operators.
- Most operators report that all mixes are effective. However, as noted in the review on efficacy, there is no actual data on the comparative effects of oils on the efficacy of triclopyr applied as an ABBA. Studies on the uptake of triclopyr into foliage indicate that modified seed oils, or biodiesels, could provide better uptake (including in bark) than the mineral oils due to better solubility of triclopyr (applied as Grazon) in the vegetable rather than mineral oils and thus better stability of the spray formulation.
- The mineral oils (or conventional middle distillates; diesel, Jet-A1, kerosene) are more toxic and eco-toxic than the vegetable oils with the potential for high variation in their toxicity profiles depending on the type and source of diesel. Further, they are more flammable than vegetable oils and are not readily biodegradable. Unlike petroleum oils, biodiesels are renewable, have a very low mammalian toxicity and are rapidly degraded in soil and water by microorganisms. For blends of biodiesel of 2%, 5% and 20% the highest rate of biodegradation occurs with the highest concentration of biodiesel.
- Most oils, and also triclopyr, have high/acute aquatic toxicity with associated hazard rating. Further, kerosene has been found to increase toxicity of triclopyr to fish. The DOC manual recommends that the ABBA operation must not be used within 10 m of a river or wetland area.
- Triclopyr undergoes hydrolysis in the human body and is rapidly excreted in the urine. In the studies reported in this review no adverse effects were reported as a result of exposure to triclopyr at the respective rates tested (these were all at label recommended rates). Most studies on applicator exposure to triclopyr have been conducted with knapsacks, hand-guns and ground sprayers (tractor-mounted booms). The USEPA exposure assessments shown in Table 2 indicate that applicators using either paint-brusher rollers or mixing, loading and spraying with backpacks or using manually pressurised hand-wands have the highest levels of exposure to triclopyr. Use of a single or double layer of clothing, gloves and respirator significantly reduced the risk of exposure (see Table 2).
- X-Tree Wet & Dry is a stable mix of triclopyr and biodiesel and removes the need for operators to mix chemical on site.

3.2 Gaps in our knowledge

The following bullets highlight the gaps in our knowledge which limit our ability to evaluate some of the potential environmental and health impacts of herbicides and oils used in ABBA operations.

- The effect of different oils on the efficacy of triclopyr applied as ABBA and the pathway of uptake (the significance of bark versus foliar uptake) is unknown. This limits our abilities to make recommendations based on efficacy.
- The diversity of wand configurations and application methods in use (in combination with aircraft used) is not well documented. Method of application and wand configuration could have an impact on efficiency, efficacy, human exposure and environmental impact.
- The potential for dearomatised fluids to be used as a solvent for triclopyr is unknown. As discussed in the review, these products offer reduced human health and environmental concerns in comparison to the conventional middle distillates (diesel, kerosene and aviation fuels). Whether hydro-treated light petroleum products would offer an advantage over biodiesels would essentially come down to cost and availability (and effect on efficacy). The cost and availability of such products would need to be determined before any further work was conducted on efficacy.
- **No information is available on exposure to triclopyr (dermal or inhalation) of an applicator using a wand from an open helicopter cockpit.** Therefore, exposure of the operator in the cockpit to fines produced in the spray operation, and the effect of different formulations, wand configurations and aircraft on the production of fine droplets is unknown. This especially for the formulations containing diesel, aviation fuels and transformer oils which have an aspiration hazard classification. This lack of knowledge limits our ability to recommend health and safety practices and personal protective equipment that may be required over and above that already on the label/MSDS of products used – particularly the need to include a respirator as part of the protective gear. *Use of personal protective equipment should therefore be a high priority for the ABBA operation and also reviewed until the exposure risks have been quantified.*

  Note that the DOC manual states that “rubber gloves, full body, cotton (not disposable plastic) overalls, and eye protection must be worn”. There is no mention of use of a respirator even though both diesel and transformer oils trigger an aspiration hazard. A better understanding of whether spray is being captured in the rotor vortices and recirculated to the operators in fine droplets, particularly when using petroleum based oils, would assist in clarifying this point and enable appropriate safety gear recommendations.
- The amount of herbicide and oil that persist in the soil and litter following ABBA operations, if any, and whether residues can be transferred over time to nearby water bodies is unknown. While the DOC manual recommended a 10 m buffer, we do not know whether this standard is stringently adhered to and whether the proposed distance is sufficient to eliminate risk of contamination. The risk of contamination of water sources during ABBA operations is therefore unknown. As all active ingredients are rated as highly toxic to aquatic organisms this should be at least noted even though spot control of isolated individuals in ABBA operations is likely to pose a low risk to water sources, provided the mixes are used only to manage low density, isolated trees and dose is targeted to tree size.
- There is almost no information on the human and environmental toxicity of the oils and triclopyr when used in combination as most of the available information is on the individual components. Whether the mixes alter the toxicity and eco-toxicity profile of the individual components is unknown.

Objective 4. Recommendations

The role of cost and method of application (wand configuration, aircraft etc.) on choice of operational activities and formulation have not been considered in this report.

While all of the oil carriers currently used in ABBA operations will likely perform effectively in promoting triclopyr efficacy, there is substantial evidence to suggest that the petroleum based oils (aviation fuels, diesel, used engine oils) are likely to have a greater negative impact than the vegetable oils on human health and the environment. Aside from the hazards associated with triclopyr alone, concerns associated with the petroleum based oils include flammability (aviation fuels), potential toxicity to aquatic life, irritation to the respiratory tract, skin and mucous membranes, possible carcinogenicity (and the presence of polyaromatic hydrocarbons) and slow biodegradation. Further, toxicity and eco-toxicity can vary by orders of magnitude depending on the source and type of diesel fuel. In contrast, the biodiesels, or vegetable oils, have lower mammalian toxicity, are not flammable and are rapidly degraded in the environment. These are also renewable fuels. The high flash point of biodiesel also enables safer storage, transportation, and application of the formulation.

Therefore, taking a precautionary approach and on the basis of the health and environmental profiles of petroleum based oils, we do not recommend the use of diesel, aviation fuels and used engine oils as solvents for triclopyr in ABBA operations. As a minimum first step biodiesel blends (5%, 20% etc) should be endorsed as good practice for ABBA operations, with 100% biodiesel the preferred solvent. Our recommendations do not take into consideration the implications to cost, operations and method of application for ABBA operations.

On the basis of the information presented in this report there is a need for the National Programme, and operators, to take a look at the full range of PPE options when using triclopyr in oils.

In the Winning against Wildings programme we will be investigating some gaps in knowledge around efficacy (such as the significance of dose and foliage versus bark uptake pathways). However, many of the gaps in knowledge highlighted above will not be directly addressed by our current research programme, notably that of operator exposure during the wanding operation.

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Appendix A

Table 1. Summary of information on toxicology of triclopyr (as active ingredient and in formulation) as well as a range of oils used in ABBA applications.

Name	**NOEL or NOAEL (mg/kg/d)**	**AOEL (mg/m^3) TWA**	**LD$_{50}$ Acute Oral (mg/kg bw)**	**LD$_{50}$ - Dermal (mg/kg bw)**	**LD$_{50}$ Inhalation (mg/L air)**	**ADI (mg/kg/d)**	**Health concerns/GHS Class**	**Handling**	**Ref.**
Triclopyr butoxyethyl ester (active ingredient of Grazon and X-tree Wet & Dry)	5 (general) 35.7 (mice) 100 (rat) 30 (rabbit)	0.05 (rat) 2 (general)	577 (rat) 1698 (duck) >2000 (rat) 500- 2000 (birds) > 100 µg (bee) >2000 (general)	>2000 (rabbit,) 521 (earthworm) > 100µg/bee	>2.6 (general) > 4.8 (rat)	0.005 (Aus) 0.03 (EC)	May cause allergic skin reactions. Possible blood, kidney & liver toxicant. Harmful if swallowed.	Wear overalls, chemical resistant gloves, protective eyewear	1-8
Grazon*	See triclopyr	See triclopyr	>2000 (rat)	>2000 (rabbit)	> 0.025 (rat, LC$_0$)	See triclopyr	Harmful if swallowed or inhaled. Causes mild skin irritation. May cause an allergic skin reaction Causes eye irritation. May cause damage to organs through prolonged or repeated exposure.	Do not breathe dust/ fume/ gas/ mist/ vapours/ spray. Wear protective gloves/ protective clothing / eye and face protection.	9-15
Diethylene glycol monoethyl ether	37 ppm (worker inhalation)	25 ppm	5900-6100 (rat) 3600 (rabbit)	8500 (rabbit) 500 (rabbit) >32 (guinea pig)	>5240 (rat)		Irritant effects, cough, shortness of breath, dizziness, narcosis, diarrhoea, nausea, vomiting	Use respirators (Filter A (acc. to DIN 3181)), gloves and safety glasses	16-18
X-Tree Wet & Dry	See triclopyr	See triclopyr	>2000 See triclopyr	>1000 See triclopyr	See triclopyr	See triclopyr	May be harmful if swallowed. May cause eye irritation. May cause an allergic skin reaction. May cause damage to kidneys through prolonged or repeated oral exposure.	Wear PVC overalls, chemical resistant gloves, facemask or goggles	19-26
Hasten ESO			>5000	>5000			No adverse effects expected	Avoid skin and eye contact.	27

Name	NOEL or NOAEL (mg/kg/d)	AOEL (mg/m^3) TWA	LD$_{50}$ Acute Oral (mg/kg bw)	LD$_{50}$ - Dermal (mg/kg bw)	LD$_{50}$ Inhalation (mg/L air)	ADI (mg/kg/d)	Health concerns/GHS Class	Handling	Ref.
(methylated seed oil)								Wear safety glasses or goggles, impermeable gloves (PVC or neoprene) and overalls	
Jet fuel A1	494 (kerosene)	50-2000 TWA 200 (absorbed through skin)	5000 (rat) 2835 (rabbit) TDLo oral for man 3570 LDLo oral for man 500	2000 (rabbit)	5.2 (rat)		Flammable liquid and vapour. Causes mild skin irritation. May be fatal if swallowed and enters airways.	Wear protective nitrile gloves. Wear eye or face protection. If ventilation is inadequate, use respirator that will protect against organic vapour and dust/mist. Keep away from ignition sources Take precautionary measures against static discharge. The product should not be allowed to enter drains, water courses or the soil.	28-33
Bio Diesel (5%-20%) e.g. Z Bio D B5; B 20		TWA 5 (aerosol) 100 (vapour)	>5000	>2000	>5		May cause allergic or asthmathic symptoms if inhaled May be fatal if swallowed and enters airways. Causes mild skin irritation. Suspected of causing cancer. GHS ASPIRATION HAZARD:1 SKIN CORROSION/IRRITATION: 3 CARCINOGENICITY: 2B	Wear protective gloves and eye/face protection	34-35
Bio Diesel 100% e.g. Z B100		TWA 5 (oil Mist, mineral)	*17 400 (species not identified) 5000 – 15000 (Rat)	2000-20 000 (Rabbit)	+No data		May be harmful if swallowed. Prolonged skin contact may cause temporary irritation. Causes eye irritation.	Wear protective cotton overalls, gloves (nitrile or neoprene) and eye/face protection as appropriate. If engineering controls are	36-38

Name	**NOEL or NOAEL (mg/kg/d)**	**AOEL (mg/m^3) TWA**	**LD$_{50}$ Acute Oral (mg/kg bw)**	**LD$_{50}$ - Dermal (mg/kg bw)**	**LD$_{50}$ Inhalation (mg/L air)**	**ADI (mg/kg/d)**	**Health concerns/GHS Class**	**Handling**	**Ref.**
							Prolonged inhalation may be harmful.	not effective in controlling airborne exposure then an approved respirator should be used	
Diesel e.g. Z Diesel		TWA 5 (aerosol) 200 (vapour) 100 (skin)	>5000 (rat)	>5000 (rabbit)	>4100, rat)		Vapour is irritating to the eyes and the respiratory tract (nose, throat, lungs). Diesel fuel: Carcinogenic in animal tests. Caused mutations in-vitro. May be fatal if swallowed and enters airways GHS ASPIRATION HAZARD: 1 SKIN IRRITATION: 3 CARCINOGENICITY: 2B	Wear protective gloves and eye/face protection	39-40
Used engine or transformer oil			>2000 (oils, rat) 984 (iron, rat) 2700 (pyrene, rat)	>4480 (rabbit)			May cause allergic or asthmathic symptoms if inhaled May cause genetic defects May cause cancer May damage fertility Causes damage to organs following single exposure GHS CLASS SKIN CORROSION / IRRITATION: 2 EYE DAMAGE / IRRITATION: 2B SENSITIZATION – RESPIRATORY: 1 SENSITIZATION – SKIN: 1 GERM CELL MUTAGENICITY: 1B CARCINOGENICITY: 1B TOXIC TO REPRODUCTION: 1B SPECIFIC TARGET ORGAN TOXICITY - SINGLE EXPOSURE: 1 (KIDNEYS,	Personal protection not required but protective clothing, gloves and eye protection recommended	41-44

Name	NOEL or NOAEL (mg/kg/d)	AOEL (mg/m^3) TWA	LD$_{50}$ Acute Oral (mg/kg bw)	LD$_{50}$ - Dermal (mg/kg bw)	LD$_{50}$ Inhalation (mg/L air)	ADI (mg/kg/d)	Health concerns/GHS Class	Handling	Ref.
							CENTRAL NERVOUS SYSTEM, LUNGS) SPECIFIC TARGET ORGAN TOXICITY - SINGLE EXPOSURE: 3 (CENTRAL NERVOUS SYSTEM AND RESPIRATORY TRACT) ASPIRATION HAZARD: 1		
Kwickin (methylated seed oil)		No data	No data	No data	No data	No data	Causes serious eye irritation. GHS CLASS Eye damage/irritation: 2	Wear overalls, rubber gloves, goggles or disposable face shield.	45-46
Punch Penetrant (methylated seed oil)			>5000	>5000	No data	No data	No adverse effects expected	Protective clothing, gloves and glasses	47-48

+ Because essentially no vapours are generated at normal temperatures, pure or neat biodiesel should not pose an inhalation hazard (DOT, 2000).

* https://ntp.niehs.nih.gov/ntp/htdocs/chem_background/exsumpdf/methylsoyate_508.pdf ^Stephan Bio-diesel (same CAS # but may be only 95%

Where multiple values are quoted, they have been taken from different sources and may be due to differences in testing methodology and/or product formulation. Where information wasn't available on Triclopyr butoxyethyl ester, toxicology data has been based on Triclopyr or is sometimes quoted based upon the breakdown product triclopyr ion which is more toxic. NOAEL = No observed adverse effect level; AOEL = acceptable operator exposure level; LD$_{50}$ = Lethal dose that kills half (50%) of the animals tested by body weight (bw); ADI = The acceptable daily intake; WHO = world health organisation, OEL = occupational exposure limits;, MOE = margin of exposure, TDL$_0$lowest dose resulting in a toxic effect; LDL$_0$=lowest lethal dose

Table 2: Summary of information on ecotoxicology of triclopyr (as pure active ingredient and in formulation) as well as a range of oils used in aerial basal bark applications**.**

Name	**HazChem code**	**Transport /packing group Class.**	**HSNO Class.**	**Drinking water standards MAV (mg/L)**	**LC_{50} (mg/L)**	**DT_{50} (days)**	**Summary toxicity/ecotoxicity (derived from GHS, HSNO and NFPA hazard scales)**
Triclopyr butoxyethyl ester (active ingredient of Grazon and X-tree Wet and Dry)				0.1 (triclopyr)	117 (rainbow trout) 148 (bluegill sunfish) 2.9-133 (daphnia) 45 (algae, 5d) 6 (caddisfly) 0.36 (Bluegill sunfish) 0.1-3.0 (algae)	30-90 (in soil) 3-10 (plants) 7 (water) 13 (aerobic soil) 27 (anaerobic soil) 46 (in soil) 8.7 (in water) 1.5-6.6 0.6-208 (water, pH 5 water gave 208)	Birds (slightly) Mammals (none to low) Fish (Moderate to High) Insects (none to High) Zooplankton (Moderate)
Grazon*	2X	9/III	6.1D Health-harmful, 6.3B Health-irritating to skin, 6.4A Health-irritating to eye, 6.5B Health-contact sensitisers, 6.9B Health-harmful to human target organs or systems, 9.1A Environment-very ecotoxic aquatic, 9.2A Environment-very ecotoxic soil, 9.3C Environment-harmful terrestrial	See triclopyr	See triclopyr See diethylene glycol monoethyl ether Balance (no data)	See triclopyr See diethylene glycol monoethyl ether Balance (no data)	See triclopyr Very toxic to aquatic life with long lasting effects. Very toxic to the soil environment. Harmful to terrestrial vertebrates
Diethylene glycol monoethyl ether (Grazon carrier)		14.1-14.6 Not dangerous			6010(catfish) >100 (most aquatic organisms) 1982 (daphnia)	90% in 28 days	
X-Tree Wet & Dry	2X or 3Y	9/III	6.1E Health-may be harmful aspiration, 6.4A Health-irritating to eye, 6.5B health-contact sensitisers,	See triclopyr	See triclopyr	See triclopyr	See triclopyr Very toxic to aquatic organisms. Very toxic to the soil environment

Name	**HazChem code**	**Transport /packing group Class.**	**HSNO Class.**	**Drinking water standards MAV (mg/L)**	**LC$_{50}$ (mg/L)**	**DT$_{50}$ (days)**	**Summary toxicity/ecotoxicity (derived from GHS, HSNO and NFPA hazard scales)**
			6.9B Health-harmful to human target organs or systems, 9.1A Environment-very ecotoxic aquatic, 9.2A Environment-very ecotoxic soils				
Hasten ESO (methylated seed oil)	Not classified	Not classified	Not classified		>100 LC50 (48h) (Daphnia) >100 LC50 (96h) (Fish)	Biodegradable	Fish (Moderate to High Toxicity) Insects (Not Acutely Toxic to High Toxicity) Zooplankton (Moderate Toxicity) Eye irritation
Jet fuel A1	3Y	3/III	3.1C physical-flammable liquid low hazard, 6.3B Health-mildly irritating eye, 6.1E Health-harmful, 9.1B Environment-ecotoxic aquatic	~0.001(odour)* < .001 (taste)*	2-5 (rainbow trout) 3.2 (fathead minnow) 2.16 (daphnia) 1-3 (algae)		Toxic to aquatic life with long-lasting effects Can be ignited under most ambient conditions
Bio Diesel (5-20%)	3[Z]	9/III	3.1D Physical-flammable liquid low hazard, 6.1E Health-may be harmful aspiration, 6.3B Health-mildly irritating to skin, 6.7B Health-suspected human mutagen, 9.1B Environment-ecotoxic aquatic	~0.001(odour)* < .001 (taste)*	1-10 (toxic)	biodegradable	Toxic to aquatic life with long last effects
Bio Diesel 100%	Non-Hazardous	Not a Dangerous Good	Non-Hazardous		>1000 mg/L, 96 hours (fish)	*Biodegradable, 4x faster than petroleum 28 days ≥ 85% degraded	

Name	**HazChem code**	**Transport /packing group Class.**	**HSNO Class.**	**Drinking water standards MAV (mg/L)**	**LC_{50} (mg/L)**	**DT_{50} (days)**	**Summary toxicity/ecotoxicity (derived from GHS, HSNO and NFPA hazard scales)**
Diesel	3[Z]	9/III	3.1D Physical-flammable liquid low hazard, 6.1E Health-may be harmful aspiration (Aspiration toxicant: Category 1), 6.3B Health-mildly irritating to skin, 6.7B Health-suspected human mutagen, 9.1B Environment-ecotoxic aquatic	~0.001(odour)* < .001 (taste)*	1-1000 (daphnia) 1-100 (fish) 1-100 (algae)	28 days in Water <60% (biodegradable)	Toxic to aquatic life with long lasting effects
Used engine or transformer oil	3[Y]				May contain toxic compounds 0.139 - 0.908 (zinc, daphnia) 0.24 (rainbow trout) 3.5 (bluegill sunfish) 0.09 - 0.125 (zinc, algae)	Inherently biodegradable	Where present, components such as polychlorinated biphenyls and terpenyls (PCB's and PCT's) are harmful to aquatic organisms and may cause long term adverse effects in the aquatic environment
Kwickin (methylated seed oil		Not classified			No data	No data	
Punch penetrant (methylated seed oil)	2[X] or 2[Z]	NA, II	6.1E1 Health-may be harmful aspiration, 6.3B Health-mildly irritating to skin, 6.4A Health-irritating to eye		No data	Readily biodegradable	

EC= European council; HASCHEM = Hazardous chemical; HSNO = Hazardous Substances and New Organisms (Act; New Zealand); MAV = Maximum acceptable value; WHO = World health organisation; NFPA= National Fire Protection Association (United States); GHS = Globally harmonized system. *Petroleum products: These are the levels at which the products can be tasted or smelled. WHO does not establish drinking water standards for petroleum products because taste and odour will in most cases be detectable at concentrations below those of health concern, particularly with short‑term exposure. This is below the drinking water standard. LC_{50} = Lethal concentration that kills half (50%) of animals tested; DT_{50} = The rate of degradation of chemicals in soils (half-life); MAV = Maximum acceptable value

Table 3. Physical chemistry**.**

Name	**Ingredients**	**K_{OW} / Log P (pH 7, 20ºC)**	**K_{OC}**	**K_d (ml/g)**	**pH**	**Solubility 20ºC (g/L)**
Triclopyr butoxyethyl ester (active ingredient of Grazon and X-tree Wet and Dry)	2-butoxyethyl 2 –[3,5,6-trchloro-2-pyridinyl)-oxy]-acetate	[1]4.01 [4]4.62 4.09	[4]0-50 59 41-59 [2]62	87 (unaged soil) 225 (aged soil)		[2]0.007 (Triclopyr butotyl) [3,4]0.023 (triclopyr butoxyethyl ester)
Grazon	Triclopyr butoxyethyl ester (71.7%) Diethylene glycol monoethyl ether (20 %)					Emulsifiable
Diethylene glycol monoethyl ether (Grazon carrier)	Diethylene glycol monoethyl ether	-0.54 (ether)	20 (very high, ether)		pH 6.7	Soluble
X-Tree Wet & Dry (carrier)	Triclopyr as the butoxy ethyl ester Ethyl Esters of Fatty Acids derived from Canola Oil					Emulsifiable
Hasten (methylated seed oil)	Ethyl and Methyl esters of Canola Oil (>60%) Nonionic surfactants (10-30%)					Emulsifiable
Jet fuel A1	Kerosene (petroleum), hydrodesulfurised and /or Kerosene (petroleum),	2-6				Very slightly
Bio Diesel 5-20%%	hydrocarbons C9-20, average C15	3-6				Negligible
Bio-Diesel 100%	Alkyl C14 – C24 Methyl Esters (methyl soyate; soybean oil)	Not Available			Not available	Insoluble
Diesel		> 3.5				Negligible
Used engine or transformer oil	Mixture of paraffinic, naphthenic and aromatic petroleum hydrocarbons that may contain one or more of the following: carbon deposits, sludge, aromatic and non-aromatic solvents, water (as a water-in-oil emulsion),					Slight <0.1%

	glycols, wear metals and metallic salts, silicon-based antifoaming compounds, fuels, polycyclic aromatic hydrocarbons (PCAH's) and miscellaneous lubricating oil additive materials. In the unlikely event that used transformer oils are mixed with other waste oil then polychlorinated biphenyls and terpenyls (PCB's/PCT's) may also be present.					
Kwickin oil (methylated seed oil)	Methyl and Ethyl esters of refined canola oil (60-90%) Non- ionic surfactants (10-40%)				pH 6-8 (1% aq. sol.)	dispersable
Punch Penetrant oil (methylated seed oil)	Ethyl and Methyl Esters of Fatty Acids produced from Refined Oil Seed Rape (Esterified Seed Oil [ESO])				pH 6-8	disperses

Where multiple values are quoted, they have been taken from different sources and may be due to differences in testing methodology and/or product formulation. K_{OW} = The octanol-water partition coefficient; K_{OC} = the soil organic carbon (OC) affinity coefficient; Kd = coefficient normalised for soil organic carbon content

[1] PPDB: Pesticide Properties DataBase. University of Hertfordshire. http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/2398.htm

[2] http://www.pesticideinfo.org/Detail_Chemical.jsp?Rec_Id=PC34645

[3] http://npic.orst.edu/ingred/ppdmove.htm

[4] Dow Agro SDS for Triclopyr BEE (technical)

Table 4. HSNO classification codes

Code	Description
	Physical hazards
1.1	Substances and articles that have a mass explosion hazard
1.2	Substances and articles that have a projection hazard but not a mass explosion
1.3	Substances and articles that have a fire hazard and either a minor blast hazard
1.4	Substances and articles that present no significant explosive hazard
1.5	Very insensitive substances that have a mass explosion hazard
1.6	Extremely insensitive articles that do not have a mass explosion hazard
2.1.1A	Flammable gas- high hazard
2.1.1B	Flammable gas - medium hazard
2.1.2A	Flammable aerosol
3.1A	Flammable liquid - very high hazard
3.1B	Flammable liquid - high hazard
3.1C	Flammable liquid - medium hazard
3.1D	Flammable liquid - low hazard
4.1.1A	Readily combustible solids and solids that may cause fire through friction:
4.1.1B	Readily combustible solids and solids that may cause fire through friction: low
4.1.2A	Self-reactive substances: type A
4.1.2B	Self-reactive substances: type B
4.1.2C	Self-reactive substances: type C
4.1.2D	Self-reactive substances: type D
4.1.2E	Self-reactive substances: type E
4.1.2F	Self-reactive substances: type F
4.1.2G	Self-reactive substances: type G
4.1.3A	Solid desensitised explosives: high hazard
4.1.3B	Solid desensitised explosives: medium hazard
4.1.3C	Solid desensitised explosives: low hazard
4.2A	Spontaneously combustible substances: pyrophoric substances: high hazard
4.2B	Spontaneously combustible substances: self-heating substances: medium
4.2C	Spontaneously combustible substances: self-heating substances: low hazard
4.3A	Solids that emit flammable gas when in contact with water: high hazard
4.3B	Solids that emit flammable gas when in contact with water: medium hazard
4.3C	Solids that emit flammable gas when in contact with water: low hazard
5.1.1A	Oxidising substances that are liquids or solids: high hazard
5.1.1B	Oxidising substances that are liquids or solids: medium hazard
5.1.1C	Oxidising substances that are liquids or solids: low hazard
5.1.2A	Oxidising substances that are gases
5.2A	Organic peroxides: type A
5.2B	Organic peroxides: type B
5.2C	Organic peroxides: type C
5.2D	Organic peroxides: type D
5.2E	Organic peroxides: type E
5.2F	Organic peroxides: type F
5.2G	Organic peroxides: type G
	Health hazards
6.1A	Substances that are acutely toxic - Fatal
6.1B	Substances that are acutely toxic - Fatal
6.1C	Substances that are acutely toxic- Toxic

6.1D	Substances that are acutely toxic - Harmful
6.1E	Substances that are acutely toxic –May be harmful, Aspiration hazard
6.3A	Substances that are irritating to the skin
6.3B	Substances that are mildly irritating to the skin
6.4A	Substances that are irritating to the eye
6.5A	Substances that are respiratory sensitisers
6.5B	Substances that are contact sensitisers
6.6A	Substances that are known or presumed human mutagens
6.6B	Substances that are suspected human mutagens
6.7A	Substances that are known or presumed human carcinogens
6.7B	Substances that are suspected human carcinogens
6.8A	Substances that are known or presumed human reproductive or developmental
6.8B	Substances that are suspected human reproductive or developmental toxicants
6.8C	Substances that produce toxic human reproductive or developmental effects on
6.9A	Substances that are toxic to human target organs or systems
6.9B	Substances that are harmful to human target organs or systems
8.1A	Substances that are corrosive to metals
8.2A	Substances that are corrosive to dermal tissue UN PGI
8.2B	Substances that are corrosive to dermal tissue UN PGII
8.2C	Substances that are corrosive to dermal tissue UN PGIII
8.3A	Substances that are corrosive to ocular tissue
	Environmental hazards
9.1A	Substances that are very ecotoxic in the aquatic environment
9.1B	Substances that are ecotoxic in the aquatic environment
9.1C	Substances that are harmful in the aquatic environment
9.1D	Substances that are slightly harmful to the aquatic environment or are
9.2A	Substances that are very ecotoxic in the soil environment
9.2B	Substances that are ecotoxic in the soil environment
9.2C	Substances that are harmful in the soil environment
9.2D	Substances that are slightly harmful in the soil environment
9.3A	Substances that are very ecotoxic to terrestrial vertebrates
9.3B	Substances that are ecotoxic to terrestrial vertebrates
9.3C	Substances that are harmful to terrestrial vertebrates
9.4A	Substances that are very ecotoxic to terrestrial invertebrates
9.4B	Substances that are ecotoxic to terrestrial invertebrates
9.4C	Substances that are harmful to terrestrial invertebrates

NB: Refer to the classification User Guide for further details on the criteria for each classification

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