Guidance for Rivers on herbicide use

Introduction

Environment Canterbury has a role in managing river environments. Operationally, this work includes but is not limited to maintaining flood protection and drainage schemes in the region, managing biosecurity risks, and enhancing associated wetland and riverine environments. Agrichemical spraying is used for vegetation control in fairways and berms of larger rivers, as well as smaller drainage scheme waterways. Both terrestrial and aquatic vegetation is targeted as required, which may involve spraying over water in the case of macrophytes.

Rivers currently hold resource consent to use Glyphosate, Triclopyr and Diquat with associated surfactants. In the future Rivers would like to establish a pathway to use other agrichemicals when deemed appropriate. However, the use of alternative agrichemicals is envisaged to require an internal assessment of effects prior to use. Specific additional agrichemicals are not considered further in this document.

There is a large body of research on the fate and impacts of pesticides within the environment and yet there remains considerable controversy around the appropriateness or otherwise of the use of the multitude of different chemicals. There follows a brief review of human health and aquatic ecological risks associated with glyphosate, triclopyr and diquat use on or near rivers, lakes and wetlands.

Glyphosate

In the U.S a broad scale survey of Glyphosate in ground and surface waters, sediments and precipitation totalling 3732 samples concluded that Glyphosate and its breakdown product AMPA were mobile and occur widely in the environment (Battaglin et al. 2014). Glyphosate was detected in more than 50% of samples of sediments, water in ditches and drains, precipitation, large rivers and streams, but in less than 40% of samples of lakes, ponds and wetlands, soil water discharges and groundwater. Glyphosate was routinely detected alongside AMPA. Concentrations were typically less than toxicological levels of concern for humans and wildlife (Battaglin et al. 2014). A New Zealand wide survey of groundwater in 2018 found contamination by glyphosate in 1 well from 135 (Close and Humphries 2019). However, a Canterbury specific survey of stream bed sediments in 2019 found glyphosate and AMPA at 9 out of 13 sites (Authors obs.). An experiment to determine the persistence of glyphosate and AMPA in drains near Rangiora found there was a background presence of both chemicals and both chemicals remained present in the sediments 14 weeks after spraying (Collins and Harding 2017).

Acute and chronic toxicity to humans appears to be low although some formulations may cause greater irritation of the skin and eyes than the chemical itself. Glyphosate is poorly absorbed from the digestive tract and mostly excreted unchanged by mammals leaving only minute amounts in the body after 10 days (US-EPA 1987). Glyphosate is considered to have no significant potential to bioaccumulate in the environment, although elevated levels in manatee plasma have been found associated with chronic exposure (Maria et al. 2021). WHO (2005/2011/2017) states that because glyphosate in the environment occurs at concentrations well below those at which human toxic effects are observed, it is not considered necessary to derive a guideline value. WHO (2017) did develop a health-based value of 0.9 mg/L for AMPA alone or in combination with glyphosate. Because of their low toxicity, the health-based value derived for AMPA alone, or in combination with glyphosate, is orders of magnitude higher than concentrations of glyphosate or AMPA normally found in drinking-water. For this reason, a maximum acceptable value for NZ drinking water standards has not been derived.

The active chemical in Glyphosate is considered moderately persistent in soils with an estimated half-life of 47 days. The compound is strongly absorbed to soils so not considered a risk of leaching despite being highly soluble in water. In aquatic systems the chemical is strongly absorbed to particles and broken down by microorganisms. Half-lives range from 12 days to 10 weeks, although AMPA (the breakdown product) may persist much longer. AMPA is considered to have similar toxicity to glyphosate and elevated levels in soils have been linked to effects on earthworm populations (Dominguez et al. 2016). Glyphosate may be translocated extensively throughout a plant. However, while it is metabolised by some plants it remains intact in others (Kidd and James 1991)

Toxicological studies on birds, fish, bees and earthworms have found the specific glyphosate chemical to be slightly toxic to non-toxic. However, some formulations may be more toxic to due to differences in the salts and parent compound or the surfactants (Annettt, Habibi, and Hontela 2014). For example, while glyphosate was found to be not toxic to bumble bees an additional chemical found within Roundup Ready-to-use caused 90% mortality (Straw, Carpentier, and Brown 2021).

Most guidance on safe levels are based on toxicity bio-assays for single species that do not provide information on sub-lethal impacts, chronic effects and effects on ecosystems (Vera, Lagomarsino, and Sylvester 2010; Rodrigues, Oliviera, and Abe 2017). Although evidence is limited and piecemeal due to the complexity of ecological systems there exists a growing number of studies that have identified impacts of glyphosate based herbicide use on ecosystems (Kelly et al. 2010; Vera, Lagomarsino, and Sylvester 2010; Griesinger, Evans, and Rypstra 2011; Annettt, Habibi, and Hontela 2014). For example in lakes glyphosate exposure had species specific effects on diatom community development with the potential to impact benthic habitats and whole aquatic ecosystem function (Corrales, Meerhoff, and Antoniades 2021). Glyphosate has also been linked to the proliferation of cyanobacteria through the suppression of green algae and elevation of phosphorus concentrations which is a breakdown product (Vera, Lagomarsino, and Sylvester 2010; Berman et al. 2020). Lakes tended to shift from clear to turbid states and there was a general shift in the diatom/phytoplankton community. In another study soil mycorrhizal communities where significantly altered after glyphosate application and changes in earthworm behaviour changed general soil leaching rates (Zaller et al. 2014).

Glyphosate application has been regarded as a successful tool for the reduction of Grey Willow in New Zealand wetlands (Griffiths et al. 2018). Relative to equivalent triclopyr applications, glyphosate substantially reduced the dominance of tall Grey Willow and increased the cover of most native plant groups. However, the authors also noted that the effect was not enduring as Grey Willow seed from outside the sprayed area allowed the species to re-establish over time and the aerial spray method did result in non-target species impacts when the willow canopy cover was initially patchy. Terrestrial invertebrates in the Whangamarino wetland responded to the control of Grey Willow by glyphosate with a decline in all metrics after 27 days (Watts et al. 2015). However, this was attributed to changes in available habitat with the death of the grey willow canopy and after 1 year all metrics of invertebrate communities showed an increase over the starting point. A laboratory based study comparing glyphosate and triclopyr based herbicides on the growth of *Lemna minor*, a common floating pond weed, a green algae and on enzymatic activity in soil found that the triclopyr product had an order of magnitude greater inhibitory effect than glyphosate, but that all herbicides where toxic to non-target species (Tajnaiova et al. 2020)**.**

Triclopyr

Triclopyr comes in two available forms; an ester and an amine-based product. MSDS documents indicate that the ester-based product is highly toxic to fish and aquatic invertebrates and should not be used close to waterways or over shallow groundwater. The Garlon XRT MSDS describes the ester-based compound as a risk to groundwater contamination particularly in areas with shallow, permeable soils. These constraints are not considered to apply to the amine-based products which, based on toxicological test have been found to be only slightly-toxic to non-toxic to a range of non-target organisms.

Triclopyr amine and ester compounds are considered to have low toxicity to humans if swallowed in small quantities, although respiratory and eye irritation may occur with prolonged exposure. In general, the compound is not considered to be a single exposure toxicant, although some formulations cause significant eye irritation in rabbits according to the Extension Toxicological Network Pesticide Information Profile (EXTOXNET).

The NZ drinking water standards have set a provisional MAV of 0.1 mg/L triclopyr (MoH 2018).

Biodegradation is rapid under controlled laboratory conditions, but under OECD test guidelines the compound cannot be considered readily biodegradable. EXTOXNET states the half-life in soil ranges from 30-90 days, although a breakdown product, trichloropyridinol, had a half-life of 279 days. Triclopyr does not readily bind to soils so can be highly mobile. Reported half-lives in water are 2.8 to 14.1 hours, depending on season and depth of water.

The compound is readily translocated throughout plant tissues after uptake through foliage. Cowberries contained residues of 2.4 ppm at 6 days, 0.7 to 1.1 ppm at 30 to 36 days, and 0.2 to 0.3 ppm at 92 to 98 days after application. Half-life in above ground drying foliage is estimated to be 2-3 months (EXTOXNET). Bioaccumulation potential is considered low. Accordingly, while caution is advised for handlers of the chemical there does not appear to be a high risk of effects due to ingestion of plant or animal material subsequently collected from the sprayed area, provided a suitable period of time has elapsed for breakdown in soils or water. A Canadian study into the risk of bioaccumulation of triclopyr in browsing mammals found an acceptable level of risk for acute exposure (a single application). However, there was deemed to be an unacceptable level of risk for chronic toxicity in moose (Voinorosky and Stewart 2021). The study suggested site- and species-specific information was needed to determine the actual risks of bioaccumulation in browsing species.

Similar to the glyphosate suite of herbicides, results have been found whereby various formulations using triclopyr showed different degrees genotoxicity in a freshwater eel (Guilherme et al. 2015). However, DNA damage occurred in the presence of both the triclopyr and proprietary formulations. These results highlight the importance of keeping triclopyr out of water.

Aerial application of triclopyr (amine) was found to be ineffective at targeted grey willow control and resulted in a decrease in the dominance of non-target native species (Griffiths et al. 2018). In another study, applications of Garlon 360 (triclopyr amine) where found to be highly effective against alder, water celery and purple loosetrife, but grey willow showed regrowth after 1 year (Champion et al. 2011). A study overseas found that a cocktail of herbicides were more effective at controlling woody vegetation, including willow species and promoting a mosaic of herbaceous plants (Hutchinson and Langland 2010). Control of tamarisk in American Southwest rangelands has resulted in triclopyr residues in soils at levels that effect non-target species up to 89 days after application (Douglass et al. 2016). There was an interaction between herbicide degradation variability due to localised soil properties and the sensitivity of non-target species that influenced the overall trajectory of plant communities. These interactions could be exploited or should at least be understood to inform the design of long term weed control projects with the intent of restoring native vegetation or controlling infestations. Further evidence to support the need for carefully designed site and community specific herbicide regimes come from the differential effects of both glyphosate and triclopyr on lichens in North-eastern Ontario (McMullin, Bell, and Newmaster 2012).

A Canterbury specific survey of stream bed sediments in 2019 found Triclopyr at 1 out of 19 sites in water samples and at zero sites in sediment samples (Authors obs.). However, across 76 water samples collected between 1988 and 2001 triclopyr was detected on 37 occasions with a maximum concentration of 5.6 µg/L. Triclopyr was the third most commonly detected herbicide behind Simazine and Terbuthylazine.

Diquat

Diquat bromide is a non-selective, fast acting herbicide and plant growth regulator causing injury only to the part of the plant to which it is applied. EXTOXNET states it is considered moderately toxic via ingestion with cows being particularly sensitive. Diquat is also considered moderately toxic via exposure to the skin. Chronic effects include damage to the eyes and skin. Ingested and dermal doses of Diquat are rapidly excreted from the body with complete elimination after 4 days by rats.

The chemical is considered slightly to moderately toxic to birds and moderately to practically non-toxic to fish and aquatic invertebrates. However, certain fish species have been found to suffer significant respiratory stress at diquat concentrations in water similar to those used for aquatic vegetation control (Johnson and Finley 1980). The majority of toxicology studies on Diquat have been classical acute or chronic exposure mortality assays. However, this approach has been criticised as unrealistic given the very short periods of exposure wrought by rapid sorption to particles (Clayton 2021). Based on the application instructions for some Diquat based products for aquatic plants in water, exposure may take the form of multiple short term pulses (McCuaig, Martynuik, and Marlatt 2020). Bouetard et al. (2013) found results indicative of oxidative stress in the cosmopolitan water snail *Lymnea stagnalis* after a single short exposure. A subsequent study found that repeat doses of Diquat altered cellular level processes in juvenile Rainbow trout that had implications for growth rates (McCuaig, Martynuik, and Marlatt 2020). However, both these studies make that point that the effects on benthic macroinvertebrates and potentially fish have not been adequately assessed (Emmett 2002).

Field based studies on the negative effects of Diquat have typically found no response to the target organism (Breckles and Kilgour 2018). Neither aquatic invertebrate community structure nor amphibian growth and condition showed any effect in separate studies (Cooke 1977; Wilson 1968). A study in New Zealand examined the effects on Diquat exposed Shortfin Eel (*Anguilla australis*) in the Avon River, Christchurch, during the treatment of a weed infestation. Various measures of stress were taken and no response to herbicide application detected (Tremblay 2004).

It should be noted that Diquat was banned by the EU in 2019 based on concerns related to the exposure of bystanders, residents and birds. The use of diquat in the EU remains a topic of considerable controversy.

Diquat is considered to be highly persistent in soils because it binds so strongly to organic matter and clay particles. It may remain present for long periods of time (months), but it is considered biologically inactive whilst bound. When applied to water the chemical disappears rapidly due to particle binding. Diquat is rapidly absorbed into plant tissues, but kills the tissue immediately preventing further movement of the compound around the plant. While it would not be considered appropriate to swim or gather aquatic food source immediately after the application of diquat, the rapid sorption of the compound to particles and consequent non-mobility in the environment or bioaccumulation mean these activities will be safe after an elapsed period of time.

A Canterbury specific survey of stream bed sediments and water in 2019 found Diquat at zero out of 8 sites (Authors obs.).

Advice on the actual and potential effects due to the use of Glyphosate, Triclopyr and Diquat

1. The potential effects on water quality, aquatic and terrestrial fauna, flora and ecosystems;

Effects of herbicide use on water quality, fauna, flora and ecosytems will be variable between site types, receptor sensitivities, the chemical used, and the application regime; discrete or periodic. A review of the literature shows science is barely scratching the surface of understanding the range of effects herbicides have on the natural environment (Kohler and Triebskorn 2013). However, the information to hand suggests that each chemical or formulation has the potential for a range of deleterious effects. Thus, while effects on water quality, fauna, flora and ecosystems are very difficult to quantify, describe or predict, there remains the potential for many different effects to occur. Accordingly, a cautious approach should be taken to herbicide use alongside a strategy to reduce, minimise or avoid their use. The inappropriate use of herbicides could demonstrably result in a loss of ecological values and biodiversity. Therefore, each proposed use of herbicides should occur within a strategic framework or plan that outlines the measures taken to ensure the protection of biodiversity (through avoidance of effects on water quality, fauna, flora and ecosystems).

For example, many stable flowing waterways are prone to growth of nuisance levels of exotic macrophytes that, amongst other unfavourable outcomes, exacerbate flooding. Current practises may involve herbicide application to reduce or clear aquatic macrophyte growth. Clearance is an appropriate strategy for achieving eradication of pest macrophyte species (such as Egeria, Lagarosiphon, or Ceratophyllum). However, most other exotic macrophytes contribute significantly to the structure of aquatic ecosystems and need only to be prevented from reaching excessive or nuisance biomass levels. It is therefore important to have clear objectives of the purpose and outcome of herbicide application to aquatic macrophyte communities.

The excessive application of herbicides to waterways and riparian areas may cause impacts beyond the targeted objective, and exert effects on fauna and flora, and the die back and rotting of weeds may reduce dissolved oxygen in the water (Jewell 1971). Manual clearing or mechanical clearing may be a more appropriate method. As a further alternative to using agrichemicals, weed growth in narrow (<2m) waterways can be suppressed by shading from riparian vegetation. The ongoing, targeted use of a herbicide might be justified as a transitionary tool while riparian vegetation is established. However, the accumulative effects of routine herbicide management of the waterway in perpetuity would not appear to put the health of the waterway or wider environment first. An additional effect that should be considered in the context of riparian vegetation is the increased degree of runoff and bank erosion associated with denuded vegetation. At a time when there is growing emphasis on the planting of stream banks for a variety of reasons including water quality it would seem quite anachronistic to risk damage to riparian vegetation with a non-selective herbicide. Intact riparian buffers not only provide shading to waterways to naturally reduce weed growth but they also may form corridors of biodiversity along waterways (including drains) that sit within otherwise biodiversity depauperate farming systems.

I recommend that a strategic herbicide plan outline the pathway to decrease the reliance on herbicides (promoting non-chemical methods) or otherwise justify their continued use only when no viable alternatives exist. For example, fairway clearance on braided rivers frequently involves the use of herbicides to maintain a bare gravel or low stature vegetation community that doesn't impede flood flows, promote lateral erosion or impact negatively on the natural character and ecology of the braided river. The invasive woody vegetation causing the issues in the fairways are rapid growing and apparently ubiquitous in the seed bank of braided rivers. There is no obvious alternative control other than mechanical clearance, and considerable doubt about the possibility of eradicating these species from a catchment even with the use of conventional herbicides. Persistent herbicides that also prevent seed germination are not appropriate in these natural environments. In this situation the potential negative effects of herbicide use might be outweighed by both the benefits of maintaining river flood capacity and restoring riverbed habitats, unless alternatives such as a wider unrestricted fairway with less intensive vegetation control are possible. The strategic herbicide-use plan could consider a whole river regime to strategically minimise the seed bank. It is also important to note that herbicide application in this context may increase the potential for nesting success of braided river birds and maintain some of the natural bed movement erosional processes characteristic of braided river that would otherwise be lost to invasive woody weed invasion.

2. The potential effects on human and animal food sources;
   Glyphosate has been found to show variable degrees of metabolisation within plants, being broken down in some, but remaining present in others. In the absence of plant species specific information on breakdown of glyphosate or the environmental fate of additional chemicals mixed with the herbicide it would appear that there is a residual risk of ingestion of the chemical through the consumption of plants not otherwise killed by the herbicide. Glyphosate itself has a low potential

to bioaccumulate although may be present at elevated levels due to chronic exposure. Glyphosate is poorly absorbed by the human gut and mostly excreted leaving only trace amount in the body. Glyphosate is considered to have low chronic and acute toxicity to humans although this topic remains an area of active research and controversy. Provided application rates and any stand down periods stipulated by the New Zealand Environmental Protection Agency (NZ EPA) are followed, there should be an acceptably low risk to human or animal health through secondary ingestion.

A frequently voiced concern over Glyphosate levels in foodstuffs is the incorporation of genes for Glyphosate tolerance in cultivated plants. This has allowed regular spraying of such food crops with glyphosate throughout the growth phase from emergence through to harvest, essentially maximising levels of glyphosate within an otherwise unaffected crop. This issue is not present in New Zealand as we do not approve the use of such genetically modified organisms (GMO) that can lead to this issue. It does however, highlight that frequent regular spaying of plants likely to be consumed (i.e. watercress) should be actively avoided.

Triclopyr is similarly metabolised or excreted rapidly by humans and extensive testing by the US-EPA identified little to no concerns around human health from dietary exposure provided NZ EPA application rates and stand down periods are observed.

3. The potential effects on drinking water

Glyphosate binds rapidly to particles upon entering water and so is not considered likely to travel far in water. Therefore, the risks of the chemical getting into groundwater drinking water supplies are slim. In a national survey of pesticides in 135 groundwater wells glyphosate was only detected in 1. Drinking water sourced from surface water is at greater risk of contamination and applications should avoid proximity to community water supply intakes.

Triclopyr may travel much further in water and is consequently not recommended for use over water or shallow groundwater. This raises the question of the appropriateness of the use of triclopyr on river bed and berm where groundwater may be <1m below the surface of highly permeable gravels and thin soils. Although considered to have generally low toxicity to humans triclopyr may be long lasting in the environment and should not be used in proximity to community water supply intakes without careful and considerable caution.

4. Advise on testing for agrichemicals in surface and groundwater samples. Focusing on glyphosate and triclopyr.

Current spray operations undertaken by Rivers require monitoring of water quality for glyphosate and triclopyr. For glyphosate, water downstream of the spraying operation shall not exceed 0.1 g/m^3 and for triclopyr not more than 0.01g/m^3. It is assumed that these thresholds have been previously deemed appropriate (after reasonable mixing), but it is helpful to put them into context of guideline concentrations that are available.

The Australian and New Zealand Environment and Conservation Council (ANZECC) 2021 water quality guidelines include default trigger values for glyphosate in freshwater. The 99%, 95%, 90% and 80% species protection levels are 0.18 g/m^3, 0.32 g/m^3, 0.46 g/m^3 and 0.76 g/m^3, respectively. The currently consented maximum value downstream of spraying is ~50% of the 99% trigger level and is ~$1/3^{rd}$ of the 95% trigger level and so would appear suitably conservative. However, the ANZECC (2000) documents note that toxicity varies greatly between formulations suggesting that the trigger values for glyphosate should be divided by 40 if the common roundup formulation is used. Ideally, formulation specific trigger values would be available from the NZ EPA or ANZECC (2021) to inform monitoring. However, in the absence of product specific guidance from the NZ EPA or general literature a conservative approach should be taken. Therein, I would recommend that the current consent trigger values are retained, but that consideration be given to additional sampling of the stream bed sediments that are the ultimate receiving environment of glyphosate and its break down products. Although surveys to date suggest that glyphosate and AMPA are common in stream bed sediments additional data on the specific role of waterway maintenance as opposed to other sources will inform future consenting processes.

In addition, the use of sprays over large, swift rivers such as the Waitaki, Waimakariri and Rakaia is unlikely to produce any discernible impact on aquatic communities given the massive degrees of dilution unless significant quantities of chemical are discharged directly to water. Accordingly, I would recommend that water quality sampling focus on small rivers, streams and drainage networks rather than use in large braided rivers.

Triclopyr ester-based herbicides should not be used over or near water due to their toxicity to aquatic life. Accordingly, any detection of triclopyr ester-based formulations (above the detection limit) in water associated with this consent would indicate an inappropriate use of the chemical.

There are no aquatic life trigger values for Triclopyr formulations in the ANZECC guidelines. There is an ANZECC recreational bathing trigger of 0.02 g/m^3 that is double the current consented value. The current consented value would appear to include a degree of conservatism if it is deemed that the use of triclopyr amine-based formulations around water is unavoidable.

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