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Ecological risk assessment of glyphosate, 2,4-D and acrolein used in Goulburn-Murray irrigation system

Fazlzadeh davil Mehdi[1], Mazloomi Sajad[1], Rahsepar Shokouh Alsadat[2]*, Sohaili Johan[2] and Moradi Birgani Payam[2]

[1]Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran.

[2]Department of Environmental Engineering, Faculty of Civil Engineering, Universiti Technologi Malaysia, 81310, Skudai, Johor, Malaysia.

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To control aquatic weeds grown in Goulborn-Murray irrigation channels and drains in Victoria, Australia, a number of herbicides namely glyphosate, 2,4-D amine and Acrolein are used so that, normal water flow can be maintained. The objective of the current study is to assess the impact of mentioned herbicides for the potential ecological risks to a range of receptors such as human, aquatic ecosystem (fishes, algae, Daphnia) and crops. Different exposure pathways has been considered in calculating Predicted Environmental Concentration (PEC) of herbicides in water; spraying directly in the water, on to plants and subsequent wash-off, onto the soil, embankments and spray drift (run off). Ecological Risk Assessment (ERA) methodology with tiered or phased approach (I and II) has been taken for different scenarios provided by Goulburn Murray Valley (G-MW) for all irrigation areas. To evaluate the risk of herbicide effects, Hazard Quotient (HQ) number has been calculated as a representative of risk. Final assessment, Tier II, with consideration of dilution, adsorption, biodegradation and half-life of herbicide in each compartment (water and plant) has indicated many scenarios. However, in case of channels no serious risk is posed, whereas the risk is manifest in drains. Moreover, the main source of exposure for each herbicide has been identified in each case and some recommendations both for management practice and for future research have been provided to prevent harm, especially to aquatic ecosystem and crops.

Key words: Glyphosate, 2,4-D amine, acrolein, predicted environmental concentration (PEC), ecological risk assessment (ERA), hazard quotient (HQ), tiered approach.

INTRODUCTION

Recently there is a doubt about possible detrimental impacts of herbicides on non-target receptors (Kookana et al., 2003). In one study in New South Wales a conservative fluorescent tracer was used to predict the glyphosate upper limit in flowing water in channels and the result showed that predicted concentration in channel exceeded irrigation and drinking water guideline (Bowmer, 1982).

This study had been taken in a simple way (Tier 1 assessment approach). Fish kills at the Goulburn Weir, Nagambie, Victoria in January 2004 have increased awareness of potential issues. The possible impacts on environment caused of elevated application rates of glyphosate and 2,4-D as used under special permits, also need to be examined. As a result of these concerns, the Goulburn River audit (EPA, Victoria) recommended an

*Corresponding author. E-mail: rshokouhalsadat2@live.utm.my. Tel: +60127426923.

assessment of the risk to non-target receptors that is posed by spraying of G-MW's drains, channels and natural carriers.

Goulburn-Murray region in Victoria covers 68,000 km^2 from the Great Dividing Range north to the River Murray and from Corryong down river to Nyah near Swan Hill and included several numbers of earth-lined channels and drains to distribute water to farms and cities and accumulate drainages.

Unfortunately in some seasons aquatic weeds chocked in irrigation channels and weeds prevent normal water flow. So that, some herbicides are used to eliminate them. Acrolein, glyphosate and 2,4-D amine are the main herbicides used in channels, drains and embankments to control theses aquatic weeds.

In this study the main receptors that are considered include the water flea (*Daphni*a spp.) representing aquatic invertebrates, rainbow trout *(Oncorhynchus mykiss)* representing fish, and a range of crops (including tomatoes) as well as drinking water guidelines and water quality guidelines for irrigation and wetlands. These receptors were chosen in consultation with G-MW to represent the various ways the water is used. Different exposure pathways which have been considered are: spray landing directly in the water, spraying on to plants in the channel and subsequent wash-off, spraying onto the soil in a channel or a drain, spraying on channel and drain embankments and then run off occurring into the channel or drain and spray drift. The principles have been illustrated by considering three herbicides with very different properties (glyphosate, 2, 4-D amine and Acrolein).

To assess the risk, a tiered or phased approach has been used in this study.In the Tier 1 a near worst case scenario is considered. In this phase, it is assumed that no losses of the herbicides occur either from degradation or absorption. In Tier 2 a more refined assessment of the expected environmental concentrations is used in the risk assessment. The first and second tier assessments both assess the exposure of each receptor organisms is likely to be exposed to the hazard (toxicity of herbicides).

The assessments indicated that many scenarios do not pose a serious risk, whereas the risk is manifest in others. In many cases the assessments were limited by the availability of suitable data. This information is used to make recommendations both for management practice and for future research.

In this study, risk assessment with tiered approach (I & II) has been used to evaluate harm to receptors. This approach is a process for a systematic, informed progression from the use of very simple assessments to increasingly more complex risk assessment methods. Usually higher Tier involves an increased level of effort and complexity of risk assessment. In this method problem formulation and basic information such as exposure pathways and various receptors needs to be defined before any quantitative assessment of the risk(s) in each Tier.

MATERIALS AND METHODS

The first approach (Tier I) is to make conservative simplifying approximations and often many scenarios can be seen as posing very little risk. Further assessment is required for those cases that do not pass the Tier 1 assessment and they would require to be considered in the second Tier which needs more complete information. In this paper Tier 2 assessment will be presented merely.

To evaluate the level of risk, the hazard quotient approach (HQ) which is the ratio of estimated site-specific exposure to a single chemical from a site over a specified period to the estimated daily exposure level, at which no adverse health effects are likely to occur, has been chosen.

The effect of exposure on receptors is defined by two ways. The better documented EC50, LD50 and LC50s; or by the more sensitive and probably more realistic measures of NOAEC (or NOAEL) which are more difficult to be obtained than the first way. Both approaches are used in this study. Due to sensitivity of this study and to be on safe side, NOAEC, NOAEL, EC50 and LC50 of the most sensitive receptors in each class have been collected from various literature and used in this assessment.

The maximum application rate is assumed in each case where the herbicide is applied to a channel or drain. The given application rates of herbicides will be multiplied by the fraction of active ingredient (a.i.) and converted to the active rate of application. The predicted environmental concentration (PEC) will be calculated for each herbicide using different assumptions involving channel depth or the drain depth together with the application rates for each scenario.

Moreover, in addition to allowing run off from embankment and application uncertainties, Tier 2 estimation of the PEC will include loss pathways of the toxicants such as dilutions, breakdown, volatilization and absorption. It may also include a safety factor (a factor of 10). Regarding different application methods used for applying glyphosate and 2,4-D amine, and Acrolein, two processes are considered to calculate PEC.

Determination method of PEC for Glyphosate and 2,4-D amine

In this step the factors which affect final herbicide concentration present in water are described and used in the calculation of PEC. Processes such as biodegradation and effective half-life of herbicide in each compartment (for example, water, soil and plant), 1 to 2% fraction run off from the bank, the fraction of herbicide applied to a plant and wash off from them after application time, when the channels and drains become full, are considered. These processes are described in Figure .

As it is mentioned in Figure 1, 10 to 50% of herbicides are accidentally sprayed into water and 50 to 80% of those intercepted by plants. Water is allowed to flow in channels and drain after 4 days so that, breakdown in this duration will be considered in calculation.

Determination method of PEC for acrolein

In contrast to the other two herbicides that have been considered, no Acrolein will be directly intercepted by the soil so only the water phase has to be considered.

To predict Acrolein concentration in channels, all the known pathways that lead to Acrolein loss are considered. These pathways include break down in water, loss to the air. Since the

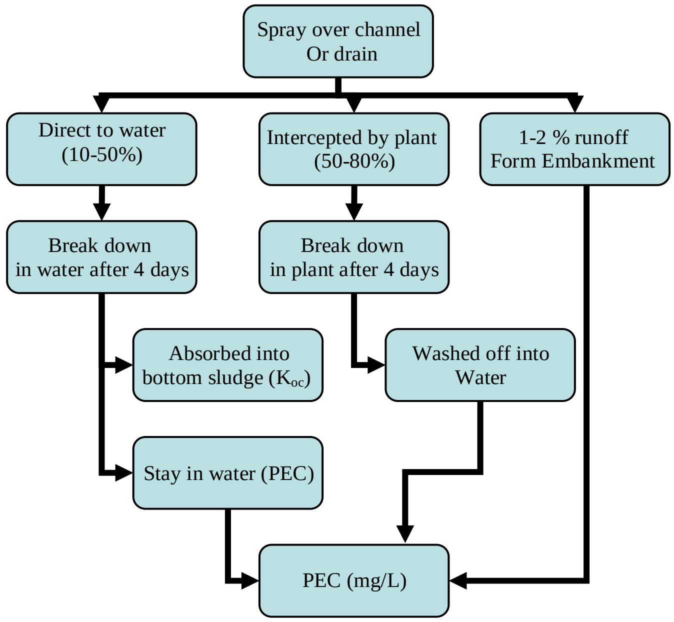

Figure 1. Method for assessing the concentration of pesticide in water following spraying with herbicide.

channels are full and flowing at the time of application, some other factors such as flow rate and channel width together with channel length (which is used as a surrogate for time) also will affect dispersion and are considered in the calculations. Moreover, duration of application rate is taken into account.

During the dispersion phase, the tracer behaves as a one-dimensional slug of material in the channel; the only significant concentration gradient is that in the direction of flow. The **Error! Reference source not found.** predicts the tracer behavior (O'Loughlin and Bowmer, 1975).

$$\frac{\partial c}{\partial t} + U\frac{\partial c}{\partial x} = D\frac{\partial^2 c}{\partial x^2} - Kc \qquad (1)$$

Where: D= longitudinal dispersion coefficient; *K*=the first order rate constant (tracer decay); *U*= velocity of water; and *t*= number of days since application *c*= concentration of component in certain time and location.

Their analytical solution of the formula for case of Acrolein (which is non-conservative material) and injected instantaneously gives:

$$\frac{C(x,t)}{C_0} = 0.5\exp\left(\frac{-Kx}{U}\right)\left\{\mathrm{erfc}\left[\frac{x-U(t+\tau)(1+H)}{\sqrt{4D(t+\tau)}}\right] - \mathrm{erfc}\left[\frac{x-Ut(1+H)}{\sqrt{4D(t+\tau)}}\right]\right\} \qquad (2)$$

Where: C*(x, t)* = concentration of herbicide in *x* m downstream after *t* hours; C_0 = initial applied rate (mg/L); and $H = 2KD/U^2$

There are some unknown parameters in the given formula such as *K*, *D*, and *H* which can be found in various ways, but estimates can be found for those parameters. *K* for herbicide depends on the half-life of herbicide in water and is estimated by dividing 0.693 to half life of the herbicide. The longitudinal dispersion coefficient *D* depends on the channel depth and the velocity of water and can be founded using the formula of Hutson and Roberts (1987):

$$D = 5.9 \times U \times \text{channel depth} \qquad (3)$$

Where *U* is the velocity of the water.

Irrigation areas' properties

There are six irrigation areas in Goulborn-Murray region. These areas are typically covered by Emergent weeds (Milfoil – Floating pondweed, Arrowhead, Cumbungi) and submerged weeds and algae (ribbonweed, pondweed, *Elodea*). Arrowhead is common weed which often occupy total channel and drains bed, while Cumbungi (bull rush) often occurs in small patches in channel. Milfoil and floating pondweed both occur in a few areas and they may cover up to 50% of the channel area.

The application rate of each herbicide in each channel and drain due to different type and plenty of weed coverage is varied. However, generally the more weed grown in channels and drains, the higher application rate of herbicide is sprayed to control weeds. Glyphosate and 2,4-D amine has to be applied in dry channel to have more effective impacts on weeds, so that the water will be lowered to 10 to 15 cm depth and to prevent expanding toxicant the water will be kept for 4 days, then the channel will be filled by water and will let to flow ; whilst in case of Acrolein, direct injection is preferred and the water may not be stopped in any stages. The summary of these data have been collected in **Error! Reference source not found.**.

2,4-D amine is just used in Murray Valley and Shepparton channels with 3-5 m width and 0.4-1 meter depth. Since arrowhead in totally covered the channel bed, 10 L/ha 2,4-D amine through boom spray is used to kill the weeds. But glyphosate is used in different areas in different channel sizes as it is shown in By contrast, Acrolein is injected into full channel to submerge the weeds. But it is just used in two irrigation areas within two different methods which have the same effect on the weeds. These two methods with application conditions and channel's properties which they are injected in are shown in Table 3.

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methods which have the same effect on the weeds. These two methods with application conditions and channel's properties which they are injected in are shown in Table 3.

Toxicity to receptors

The Toxicity of three herbicides to a range of receptors has been given in Table. Different endpoints (tolerance values) are needed for different receptors. Some, for example tomato, have an EC_{05} of

Table 1. Irrigation area's properties

Parameter	Glyphosate	2,4-D amine	Acrolein
Irrigation areas	MV, SH, CG, RC, PB,T	MV, SH	T, MV
Weed species	Emergent weeds: Milfoil – Floating pondweed, Arrowhead, Cumbungi	Emergent weeds : Arrowhead	Submerged weeds and algae : ribbonweed, pondweed , *Elodea*
Application method	Boom spray ,hand gun	handgun	Office plate or ADU
Application time	Dry channels and drains	Dry channels	Full channels
Application rate	40- 20- 9 (L/ha)	10 (L/ha)	0.3 ppm for 48 h - 3 ppm for 6 h
Holding time	4 day	0 day	0

MV: Murray Valley, Sh: Shepparton, CG: Central Goulborn , RC: Rochester Campaspe, TO: Torrumbarry.

Table 2. Data collected around channels and drains sprayed by glyphosate.

Scenario	Irrigation area	Width m)	Depth (m)	Weed species	Rate (L/ha)	Coverage
1	MV, Sh Channels	3-5	0.3-0.5	Arrowhead	20-40	Total
2				Cumbungi	9	0.1%
3	CG, RC channels			Arrowhead	40	0.5%
4				Cumbungi	9	0.1%
5	Pyramid channels	2-4	0.3-0.5	Cumbungi	9	0.1%
6				Water milfoil & floating pond weed	20	50%
7	TO channels	1.5	8	Water milfoil & floating pond weed	20	40%
8	Drains	1-2	0.1-0.3	Arrowhead	27	Total
9				General weeds	15	Total
10				Water milfoil and Alisma	20	70%

MV:Murray Valley, Sh: Shepparton, CG:Central Goulborn , RC:Rochester Campaspe, TO: Torrumbarryy.

Table 3. Data collected for Acrolein at application time.

Method	Irrigation channel	Flow rate (ml/d)	Width (m)	Depth (m)	Application rate (ppm)	Length of treatment (h)
1	MV	200	12-15	1.5	3	6
2	TO	10	3	0.8	0.3	48

MV:Murray Valleyl Goulborn , TO: Torrumbarry.

2.7 mg/L that has been deduced from the literature (Table) whereas others such as the maximum Acceptable level (MAL) in irrigation water are set by regulation.

Properties of herbicides used

2,4-D amine

2,4-D amine has K_{oc} of 20 and its behavior in water mainly depends on the pH of water. In low pH water, 2,4-D amine will remain in a neutral molecular form and its potential for adsorption to organic particles of water will increase therefore, its persistence will be increased. However, microorganisms of aquatic environment can degrade 2,4-D amine quickly. Degradation rate is increasing with increasing nutrients and dissolved organic carbon (EXTOXNET, 1996). Due to different environment circumstances, different half lives have been reported for 2,4-D amine. For instance, in natural water a range of 4 to 28 days has been estimated by the USEPA (2006), while this number has been specified for aerobic aquatic environment to 15 days (USEPA, 2005). Unfortunately there was no clear data available on half life of 2,4-D amine in weed foliage but the estimated half life of 2.5 days has been taken from GLEAMS.

Glyphosate

Glyphosate has K_{oc} of 24000. Glyphosate in water is strongly adsorbed to suspended organic and mineral matter and it becomes persistent. Moreover, as glyphosate is stable to breakdown by sunlight (USEPA, 1992), volatilization and photo-degradation losses are insignificant. However, glyphosate's interest to adsorb organic substances and inorganic clays results in rapid dissipation of herbicide from water and settling down to the soil through this adsorption. Several literatures have identified different half life for glyphosate in aquatic environment. The average half-life of 2 to 10 weeks has been reported by USEPA in 1992. The comparison of this range with other sources such as Ghassemi et al. (1981) reported half life of 7 to 10 weeks in non flow natural pond water resulted in taking 10 weeks (70 days) half life in this study.

Moreover, in case of glyphosate same as 2,4-D amine, there is not enough information about its breakdown in weed foliage and 9 days estimated half life in foliage by GLEAMS has been taken in this study.

Table 4. Toxicity of three herbicides to different receptor.

Receptors	Tolerance values (mg/L)		
	2,4-D amine	**Glyphosate**	**Acrolein**
Alga	NOEC: 26.4 (H2)	EC50: 48.5 (H3)	EC:50: 0.00005(T)
Lemna	NOEC: 2.029 (H2)	Physiology: 16.9 (O)	EC50: 0.07 (T)
Rainbow	NOEC: 0.0164 (X)	EC50 :8.2 (R)	LC50: 0.065 (B)
Crops	LOEL: 0.22 (Q)	NOEL: 2.2 (H)	MAL: 1.5 (A)
Tomatoes	No damage: 0.15 (F)	5%reduction: 2.7 (S1)	N/A
Irrigation water	MAL: 0.03 (A)	MAL: 0.1 (A)	N/A
Drinking water	MCL: 0.07 (U1)	MCL: 0.7 (U1)	MCL: 0.32 (U2)
Daphnia	NOEC : 19.7 (I)	Population reduction :1(H1)	LC50: 0.022(S2)
Aquatic life	95%protection: 0.28 (A)	95%protection: 1.2 (A)	Chronic effect: 0.001 (E)

A= ANZECC (2000), B= Bond et al. (1960), E=EPA (2005), F= Fagliari et al. (2005), H1= Hutson and Roberts (1987), H2= Hughes et al. (1990), H3= Herbicide manual, Inchem (1997), O= O'Brien et al. (1979), Q= Que et al. (1981), R= Renzo (2000), S1= Santos and Gilreath (2006), S2= Siemering et al. (2005), T = Tomlin (2000), U1=USEPA (2007), U2= USEPA (1987), X= Xie and Thrippleton (2005).

Acrolein

Due to high solubility of Acrolein in water and also having low K_{oc} of 0.5, whatever released into water would not adsorb to suspended solids and sediments (HSDB, 2003). But it does not mean that it would persistence in water so long. Surprisingly, Acrolein has been found with a short half-life in water in the field. Generally, its half-life in water depends on water temperature, turbidity, weed load, oxygen concentration, volatilization (regarding to high vapour pressure) and also the influence of micro-organisms (Bowmer and Sainty, 1991). The more the pH, the higher the rate of Acrolein reaction in water. Moreover, the rate of loss is much faster reflecting the influence of turbulence in increasing loss through volatilization (Hutson and Roberts, 1987).

USEPA Office of Pesticides Program calculated half-lives 3 to 7 h for Acrolein from degradation rate constants in irrigation canals (Turner and Erickson, 2003). In other study half-life of 4 to 10 h has been reported in literature in irrigation channels. The USEPA's toxicological review on Acrolein shows that the half-life of Acrolein in a model river can be as low as 4.4 h (HSDB, 2003). The most relevant data are the Australian studies by Bowmer and colleagues reviewed by Bowmer and Sainty (1991) on dissipation of Acrolein from irrigation channels under different flow conditions and temperature. That review showed the half-lives ranging from 3.3 to 6.7 h. Most half-life data in literature also falls within 3.3 to 10.2 h. For this study 5 h have been used for the half-life of Acrolein in channels as an average time.

General assumptions

In general 4 m width and 40 cm water depth has been assumed for channels in all irrigation areas. So that 1 ha channel will include 4 ML water after 4 days holding time. However, the big channels in Torrumbarry area with 1.5 m width and 8 m depth include 15 ML water in the same time. Drains are another concern in this study. In general 10 cm water depth and 2 m width is assumed for all irrigation areas.

The other issue is run off factor, with considering all uncertainties such as applicator inaccuracy and rain in application time and etc. and also extra investigation mentioned before, 2% runoff has been considered as the worst case.

RESULTS AND DISCUSSION

The study used simple mechanistic models to predict environmental concentrations of the herbicide residues and these are compared to some of the available monitoring data. The validity of the results is dependent on the quality of input data and the assumptions made in the assessments (including modelling assumptions and working approximations).

Tier 2 assessment of Glyphosate in channels

The worst case scenario in using herbicides would be spraying the highest rate (40 L/ha) in the smallest channel in Murray Valley and Shepparton areas. A heavy infestation of arrowhead covers almost the entire channel bed and severely restricts the flow of water. Spraying typically occurs when there is 60% cover and the water level is lowered to 10 and 15 cm of plant height. As a result since sides are not deliberately sprayed and no herbicide is directly applied to soil, it is assumed that 40% of the herbicide is sprayed onto water and none is intercepted directly by soil at the bottom of the channel. Moreover, during the four days between spraying and release of water there will be some decomposition, with the rates depending on whether the herbicide is in the

water or on the plant. The half-life in water is relatively long (70 days) so most (96%) would persist. By contrast the half-life is short (2.5 days) on the surface of the plant so only 33% persists after 4 days.

When the water returns, a fraction of that glyphosate will be removed as wash off. The exact amount is not known so several values have been used in this report. Initially following GLEAMS estimation 60% was assumed to be washed off, but this value from the authors' experience seems too high. On the other hand, the effect of sorption of the glyphosate (high K_{oc}) by the organic matter rich layer at the bottom of the channel plays an important role which decline glyphosate fraction in water (0.003). The released amount will be diluted in 4 ML water the maximum PEC will be 0.43 mg/L.

Considering two other wash off factors, 10 and 1%, different PEC of 0.076 and 0.012 mg/L are obtained. HQs for all three PEC number are calculated and shown in **Error! Reference source not found.**. The second worst case scenario is spraying glyphosate with half application rate (20 L/ha) with the same assumptions which results in halved PECs and HQs. In other cases, since weeds are grown in patches (just cover 1% of channels) and they are sprayed by hand gun, the PECs and HQs of glyphosate are much less than what is calculated for the worst case.

However, case No 7 is a different scenario (refer to **Error! Reference source not found.**). As shown in **Error! Reference source not found.**6, the PECs and as a result the HQs are approximately 10 times less than PECs and HQs derived from row No. 1. Since the plants are quite dense and cover 50% of channels, it is assumed that 50% of the applied herbicide is intercepted by foliage and the other 50% is divided between water (50%), but other estimations are same as the first case. Potential harm to any of receptors is unlikely in this scenario, although with the highest wash off factor of 60% the limit for the concentration of glyphosate in irrigation water is approached.

Tier 2 assessment of Glyphosate in drains

Arrowhead is controlled in drains with 1 ML water per ha by spraying with glyphosate at a rate of 27 L/ha (row No. 8 in By contrast, Acrolein is injected into full channel to submerge the weeds. But it is just used in two irrigation areas within two different methods which have the same effect on the weeds. These two methods with application conditions and channel's properties which they are injected in are shown in Table 3.

). Since the arrowhead is totally covered drains, 80% interception by foliage has been assumed in calculation and 20% of the rest is mixed into water. As it is mentioned before that the amount of wash off is not well known, so values of 60, 10 and 1% are used in prediction of glyphosate concentration in drains at the highest wash off rate of 60% there is the potential of harm to *Daphnia* and to aquatic ecosystems. The concentration of glyphosate in the water would exceed guidelines for both irrigation water and drinking water. Even at 1% wash off, the concentration still exceeds the guideline for irrigation water despite the HQ for algae being only 0.01 and that for irrigation water being 0.45. This would imply that the guideline value of 0.1 mg/L for

irrigation water is possibly too low and that the value should be reviewed.

Glyphosate is also sprayed to kill general aquatic weeds with rate of 15 L/ha (raw No. 9 in By contrast, Acrolein is injected into full channel to submerge the weeds. But it is just used in two irrigation areas within two different methods which have the same effect on the weeds. These two methods with application conditions and channel's properties which they are injected in are shown in Table 3.

) on the bottom and sides of drain. The calculations are similar to those for arrowhead but the PEC values are less due to the lower application rates. The HQs are also lower, and in case of 10% wash off, the only values exceeding 1 is the irrigation water and drinking water guideline (refer to **Error! Reference source not found.**7). In case of Water milfoil and *Alisma* weeds which cover 70% of channels, the application rate of 20 L/ha (between two application rates) glyphosate is used. This means that the PECs and HQs will not be very different.

Tier 2 assessment of 2,4-D amine in channels

2,4-D amine is sprayed by rate of 10 L/ha in Murray Valley and Shepparton channels to control the arrowhead. All estimations are same as previous cases and water body after 4 days will be 4 ML. The only difference occurs in assumption of runoff percentage. Due to strong absorption of 2,4-D amine to soil, run off from paths of access are not expected to exceed 1% so this proportion is taken as a near worst case. Same as glyphosate, with considering different wash off factor, different PEC values are calculated. 45% estimated by GLEAMS, 20 and 5% estimated by authors. Neither PECs nor HQs are changed through this 40% difference in wash off factor, notably. And 2,4-D amine seems to make harm for most of receptors in all three scenarios.

However, the effluent from the channels is likely to be diluted when it reaches a water body such as a natural carrier or wetland. If the dilution is 10-fold and the wash-off factor was 5%, rainbow trout and aquatic ecosystems are likely to be affected (refer to HQ'3 column).

Furthermore, the concentration of 2,4-D amine would still exceed the guidelines for irrigation water and drinking water. However, if the dilution was 100-fold (as it is shown in HQ"3 column) no harm would be expected from 2,4-D amine (**Error! Reference source not found.**).

Tier 2 assessment of Acrolein in channels

Such as previous herbicides, the worst case scenario means the smallest channel will be taken in this study. The channel with 12 m width, 1.5 m depth and channel with 3 m width, 0.8 depth are taken into assumption. As previously mentioned in addition to breakdown, dispersion coefficient of Acrolein also plays an important role to estimate its concentration in length of channel. To predict concentration of Acrolein, the **Error! Reference source not found.** will be used as shown below.

Table 5. Required elements used in Equation 4.

Irrigation area	C_0 (mg/L)	U (m/h)	τ (h)	D (m^2/h)	H
TO	0.258	173.61	48	819.44	0.0075
MV	2.58	462.97	6	4097.28	0.0053

TO: Torrumbarry, MV: Murray valley.

Table 6. PECs and HQs of glyphosate using various wash off factors.

Receptors	Tolerance (mg/L)	Wash off fraction					
		0.60	0.10	0.01	0.60	0.10	0.01
		Case No. 1 (Worst case)			Case No. 7		
		PEC (mg/L)					
		0.430	0.076	0.012	0.048	0.009	0.002
		HQ					
Irrigation water	0.1	4.30	0.76	0.12	0.48	0.09	0.02
Drinking water	0.7	0.61	0.11	0.02	0.07	0.01	0.00
Daphnia	1	0.43	0.08	0.01	0.05	0.01	0.00
Aquatic life	1.2	0.36	0.06	0.01	0.04	0.01	0.00
Crops	2.2	0.20	0.03	0.01	0.02	0.00	0.00
Tomatoes	2.7	0.16	0.03	0.00	0.02	0.00	0.00
Rainbow	8.2	0.05	0.01	0.00	0.01	0.00	0.00
Lemna	16.9	0.03	0.00	0.00	0.00	0.00	0.00
Alga	48.5	0.01	0.00	0.00	0.00	0.00	0.00

(Red colour in cells denote HQ > 1, orange HQ 0.1 – 1.0 and green HQ < 0.1).

Table 7. PECs and HQs of glyphosate in drains using parameters from Table 3 with various wash off factors.

Receptors	Tolerance (mg/L)	Wash off fraction					
		0.60	0.10	0.01	0.60	0.10	0.01
		Case No. 8			Case No. 9		
		PEC (mg/L)					
		1.545	0.262	0.318	0.858	0.146	0.018
		HQ					
Irrigation water	0.1	15.45	2.62	3.18	8.58	1.46	0.18
Drinking water	0.7	2.21	0.37	0.45	1.23	0.21	0.03
Daphnia	1	1.55	0.26	0.32	0.86	0.15	0.02
Aquatic life	1.2	1.29	0.22	0.27	0.72	0.12	0.02
Crops	2.2	0.70	0.12	0.14	0.39	0.07	0.01
Tomatoes	2.7	0.57	0.10	0.12	0.32	0.05	0.01
Rainbow	8.2	0.19	0.03	0.04	0.10	0.02	0.00
Lemna	16.9	0.09	0.02	0.02	0.05	0.01	0.00
Alga	48.5	0.03	0.01	0.01	0.02	0.00	0.00

(Red colour in cells denote HQ > 1, orange HQ 0.1 – 1.0 and green HQ < 0.1).

$$C(x,t) = 0.5 \times C_0 \times \exp\left(\frac{-Kx}{U}\right)\left\{\operatorname{erfc}\left[\frac{x - U(t+\tau)(1+H)}{\sqrt{4D(t+\tau)}}\right] - \operatorname{erfc}\left[\frac{x - Ut(1+H)}{\sqrt{4D(t+\tau)}}\right]\right\} \quad (4)$$

Considering half life of 5 h gives K of 0.1386. The other converted known parameters (U, C_0, τ) and also calculated unknown parameters (D, H) in this equation are given in Table 5.

Replacing all obtained data from Table 5 into **Error! Reference source not found.** gives two equations with two unknown quantities of x and t. analytical solution of these two equations results in two diagram shown in

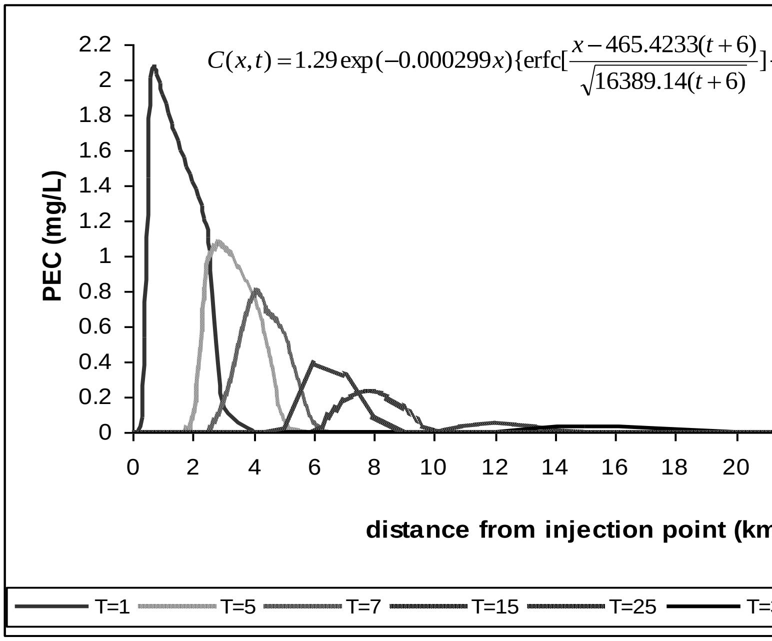

Figure2 and 3.

The environmental concentration depends on the initial injection concentration, the channel geometry and rates of flow. The predicted environmental concentration for the

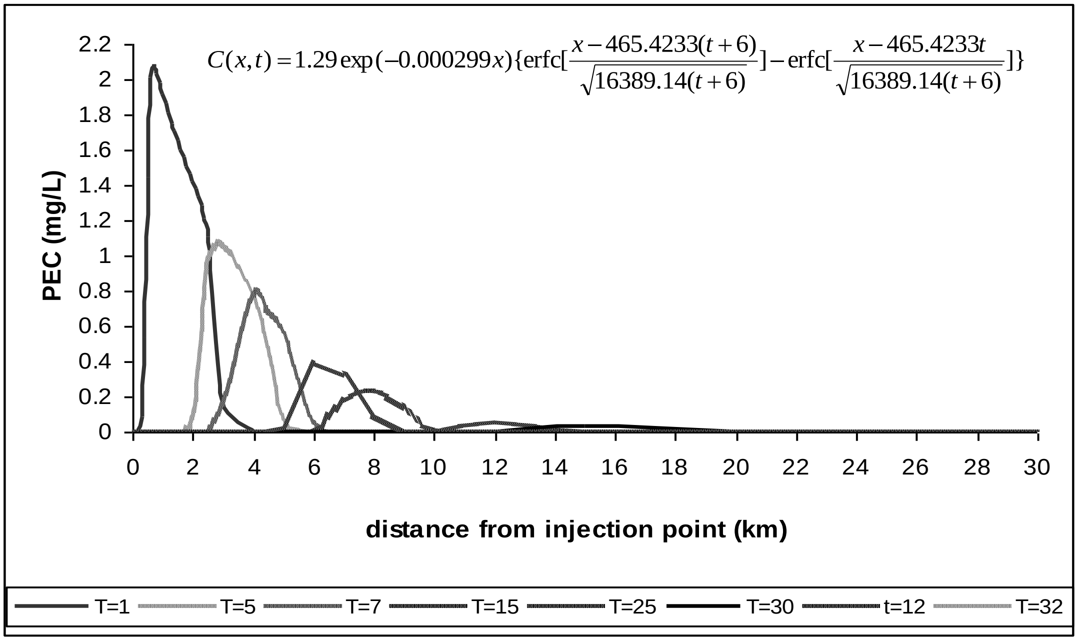

Figure 2. Estimated concentrations of Acrolein in Murray valley irrigation channel at different times and distances from the injection point following 3 ppm injection (using data collected in Table).

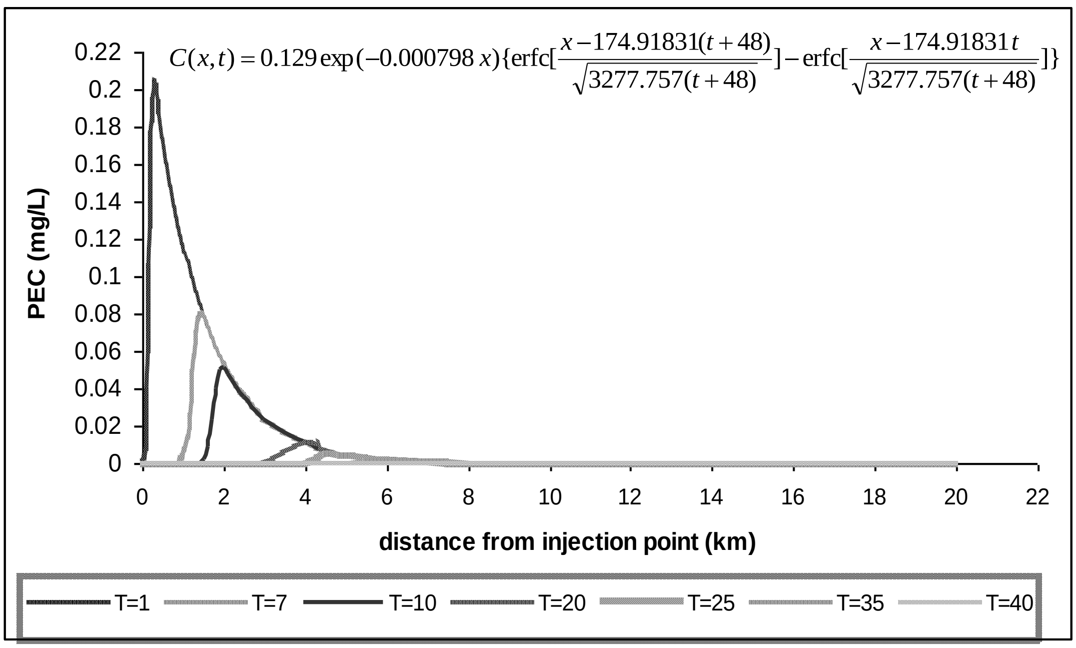

Figure 3. Estimated concentrations of Acrolein in Torrumbarry irrigation channel at different times and distances from the injection point following 0.3 ppm injection (using data collected in Table).

injection concentration of 2.58 mg/L would never reach 2.2 mg/L Acrolein in water and for the proposed injection rate of 0.258 mg/L this amount would not make 0.22 mg/L neither.

Figures 2 and 3 show that the concentration of Acrolein decreases with increasing distance away from the injection point through a combination of dilution and loss of the active ingredient. The estimated hazard quotients for Acrolein at the higher injection rate are shown in Table for the 3 ppm injection rate and in **Error! Reference source not found.** for injection rates of 0.3 ppm Acrolein.

At the higher injection rate of 3 ppm, concentration of

Table 8. PECs and HQs for 2,4-D considering different wash off factor and 60% plant coverage.

Receptor	Tolerance (mg/L)	Wash off				
		45%	20%	5%	10 time dilution	100 time dilution
		PEC (mg/L)				
		0.75	0.58	0.47	0.047	0.004
		HQ1	HQ2	HQ3	HQ'3	HQ"3
Rainbow Trout	0.0164	45.73	35.37	28.66	2.87	0.24
Aquatic Ecosystem	0.028	26.79	20.71	16.79	1.68	0.14
Irrigation value	0.03	25	19.33	15.67	1.57	0.13
Drinking Water	0.07	10.71	8.29	6.71	0.67	0.06
Tomato	0.15	5	3.87	3.13	0.31	0.03
Crops	0.22	3.41	2.64	2.14	0.21	0.02
Lemna	2.029	0.37	0.29	0.23	0.02	0
Daphnia	19.7	0.04	0.03	0.02	0	0
Alga	26.4	0.03	0.02	0.02	0	0

Red colour in cells denote HQ > 1, orange HQ 0.1 – 1.0 and green HQ < 0.1.

Table 9. HQ at different distances from source of application of 3.0 ppm Acrolein.

Species	Tolerance (mg/L)	Distance (km)								
		1 km	7 km	10 km	15 km	20 km	25 km	30 km	35 km	40 km
		PEC (mg/L)								
		1.91	0.32	0.13	0.03	0.006	0.001	7.2×10^{-5}	1.6×10^{-5}	3×10^{-6}
		HQ								
*Selenastrum capricorutum**	0.00005	38400	6400	2600	600	130	28	6.6	1.5	0.33
Aquatic life	0.001	1920	320	130	30	6.5	1.4	0.33	0.01	0
Goldfish	0.0114	168	28	11	3	0.57	0.12	0.03	0	0
Rabbit	0.05	38	6.4	2.6	0.6	0.13	0.03	0.01	0	0
*Lemna gibba**	0.07	27	4.6	1.9	0.43	0.09	0.02	0	0	0
Drink water	0.32	6	1	0.41	0.09	0.02	0	0	0	0
Dog	1	1.92	0.32	0.13	0.03	0.01	0	0	0	0
Toxic for crops-pasture	1.5	1.28	0.21	0.09	0.02	0	0	0	0	0
Soybean	15	0.13	0.02	0.01	0	0	0	0	0	0

Red colour in cells denote HQ > 1, orange HQ 0.1 – 1.0 and green HQ < 0.1; * values based on EC50, others are NOAEC.

Table 10. HQ at different distances from source of application of 0.3 ppm of Acrolein.

Species	Tolerance (mg/L)	Distance					
		1 km	3 km	5 km	6 km	10 km	12 km
		PEC (mg/L)					
		0.116	0.023	0.0048	0.0021	9×10^{-5}	1.8×10^{-5}
		HQ					
*Selenastrum capricorutum**	0.00005	2320	460	80	42	1.8	0.04
Aquatic life	0.001	116	23	4	2.1	0.09	0
Goldfish	0.0114	10.2	2.02	0.35	0.18	0.01	0
Rabbit	0.05	2.32	0.46	0.08	0.04	0	0
*Lemna gibba**	0.07	1.66	0.33	0.06	0.03	0	0
Drinking water	0.32	0.36	0.07	0.01	0.01	0	0
Dog	1	0.12	0.02	0	0	0	0
toxic for crops- pasture	1.5	0.08	0.02	0	0	0	0
Soybean	15	0.01	0	0	0	0	0

Red colour in cells denote HQ > 1, orange HQ 0.1 – 1.0 and green HQ < 0.1; * values based on EC50, others are NOAEC.

1 km downstream is almost 2 mg/L, and this would be expected to cause harm to all the receptors except soybean. There is a likelihood of potential for harm to algae up to 35 km downstream from the injection point

with the other receptors but for typical aquatic life no harm would be expected beyond 25 km from the injection point. Crops are generally more tolerant, with no harm expected to crops when water is taken beyond 3 km from the injection point. The concentration is expected to be sufficiently low beyond 10 km that they are likely to meet drinking water guidelines.

Injection of Acrolein at the lower concentration would produce much fewer HQs that exceed 1.0. In this method the Acrolein concentration in treated water beyond 1 km from the injection point is always under 0.2 mg/L which is less than the maximum acceptable level for drink water and irrigation. To be on safe side, for drinking water consumption 5.5 km downstream would be more appropriate as safe intake point. The water concentrations of Acrolein in this case are expected to be in the safe range for aquatic life 10 km downstream from injection point.

Conclusion

Comparison of herbicide effects

Glyphosate is widely used in the removal of weeds from waterways. It is used in a variety of ways including spraying when the water levels are low or in target spraying with a hand gun to remove potentially troublesome patches of weeds. There were few threats posed by the use of glyphosate, particularly when glyphosate was applied to weeds in a channel. The only threat posed by glyphosate was to irrigation water, and that threat occurred only when a high wash-off value was assumed.

There was a similar result for drains, where again the main threat posed was to irrigation water. There was a possibly threat to *Daphnia*, aquatic ecosystems and drinking water if a 60% wash-off occurred.

Further risk reduction has been achieved by using a hand gun to target patches of potentially troublesome weeds. Such a reduction in glyphosate application has the added beneficial effect of reducing the amount of carrier that is being applied.

2,4-D has the potential for causing more harm than glyphosate. It is more mobile and less sensitive to the wash-off fraction. In its undiluted form channel water treated with 2,4-D has the potential to affect tomatoes and other crops almost independent of the wash-off fraction. It is surprising that two of the plant indicators (alga and *Lemna*) had HQs below one and were therefore as not posing a risk.

Acrolein is a potent herbicide and has the potential to cause harm many kilometres from the injection point. If

applied at 3.0 ppm level, for general aquatic life this could be 25 km and for algae as much as 35 km. The position is much safer if Acrolein is injected at the lower rate of 0.3 ppm. Where Acrolein is to be applied to drains, there is the potential for longer half-life due to the lack of turbulence as well as the threat to its receiving water body. Acrolein should not be used in drains – as a G-MW policy.

The comparison between 2 methods - injection 3 ppm Acrolein for 6 h or 0.3 ppm for 48 h using HQs only gives part of the picture as the HQs do not consider the duration of the exposure. Much of the ecotoxicological data is based on a 48 h exposure, so the results for the low rate of injection should be realistic. However, the results for the 3.0 ppm injection rate for only 6 h may over-estimate the toxicity to Acrolein.

The use of a lower concentration of Acrolein for a longer creates a larger volume of water contains herbicide than when higher concentrations are used for shorter times. This may create a disposal problem for the larger volume of contaminated water.

Guideline values for irrigation water

A comparison of the tolerance values of plant receptors to the three herbicides is given in **Error! Reference source not found.**11. In each case, the irrigation guidelines are many times less than those of the other plants. This is particularly so for Amitrole, suggesting that the guideline value irrigation water is too low. For 2,4-D there is a factor of 5 between the tolerance value of tomatoes and that of irrigation water – such a difference is reasonable as some safety factor should be allowed. For glyphosate the minimum difference is a factor of 22. Because there is concern about the possible detrimental effects of the herbicides on non-target species, it is recommended that local data be obtained on the susceptibility of local crops to enable more reliable irrigation water limits to be obtained for these three herbicides.

Besides, this report has considered only the active herbicide component of the products that are applied. Typically the products contain some type of carrier and possibly a surfactant (adjuvant) with a result that the fraction of active ingredient may be significantly less than 1.

Acute versus chronic risks

This study has focused on acute risks which is appropriate for the assessment of local effects. There may also be a much lower threshold for chronic risks. Caution must therefore be applied not only to the acute levels but also to the chronic levels that could arise as the sum of many small effects upstream of the receiving water.

Table 11. Comparison of tolerance values across receptors.

Receptors	Tolerance values (mg/L)

	2,4-D amine	Glyphosate	Acrolein
Alga	26.4 (H1)	48.5 (T)	0.00005 (T)
Lemna	2.029 (H1)	16.9(O)	0.07 (T)
Crops	0.22 (Q)	2.2 (H2)	1.5 (A)
Tomatoes	0.15 (F)	2.7 (S)	N/A
Irrigation water	0.03 (A)	0.1 (A)	N/A

F= Fagliari et al. (2005), A= ANZECC (2000), H1= Hughes et al. (1990), H2= Hutson and Roberts (1987), O= O'Brien et al. (1979), Q= Que et al. (1981), S= Santos and Gilreath (2006), T= Tomlin (2000).

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