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Toxicology of the Herbicide Acrolein: Risk Assessment in Aquatic Environments

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1. Introduction

Submersed weeds on irrigation systems reduce water delivery capacity, clog pumps and structures, rupture canals, increase leakages and losses of water, increase water costs, etc. (U.S.EPA, 2007). Herbicide applications are a commonly used procedure to control submersed weeds in irrigation canals because of its practicability, efficacy and cost. Acrolein, currently registered under the trade name MAGNACIDE® H by Baker Petrolite Corporation, has been used for many years in the United States (U.S.EPA, 2007), Canada (MOE, 2005), Australia (Bowmer & Sainty, 1977), and Argentina (Caldironi et al., 2004).
Acrolein, also known as acraldehyde, acrylaldehyde, acrylic aldehyde, allylaldehyde, propenal, 2-propenal, prop-2-enal, prop-2-en-1-al, is a volatile, colourless, highly flammable liquid at ordinary temperature and pressure with a pungent odour. Its Chemical Abstract Service (CAS) number is 107-02-8. The chemical formula for acrolein is C_3H_4O and the molecular weight is 56.06. Fig. 1 illustrates its chemical structure. Acrolein has a density of 0.84 g/mL, a water solubility of 206 g/L, and a vapour pressure of (kPa) 29.3 at 20ºC. The log Kow (octanol/water partition coefficient) is -0.01 (high water solubility) and the log Koc (organic carbon/water partition coefficient) is 0.5 (low adsorption to soil) (WHO, 1991; U.S.EPA, 2003; ATSDR, 2007).

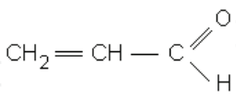

Fig. 1. Acrolein chemical structure

MAGNACIDE® H is an herbicide primarily used to remove submersed plants and algae from irrigation canals and ditches. Species of weeds such as *Potamogeton* spp., *Elodea* spp., *Najas* spp., *Zannichellia* spp., *Ceratophyllum* spp., *Zannichellia* spp. and algae such as *Anabaena* spp., *Chara* spp., *Cladophora* spp., *Selenastrum* spp., *Spirogyra* spp., are controlled by recommended label use rates of the product. According to the "Application and Safety Manual Acrolein" (Baker Petrolite, 2001), the chemical is applied by injection from the container with oxygen-free nitrogen gas into the flowing water, and travels downstream as a wave of treated water until, at some point, the chemical concentration drops to zero. Effective concentrations range from 1 mg/L to 15 mg/L and the treated area of canal is held at periods ranging from 30 minutes to 8 hours. Both the concentration and the treatment time may vary depending on the weed growth condition, water flow rate, temperature, and

application time desired. The label does stipulate that "water treated with MAGNACIDE® H herbicide must be used for irrigation of fields, either crop bearing, fallow or pasture, where the treated water remains on the field or held for 6 days before being released into fish bearing waters or where it will drain into them". MAGNACIDE® H is a restricted use pesticide for retail sail to, and use only by, certified applicators or persons under their direct supervision.

2. Mode of action

Acrolein is a cell toxicant that reacts with several molecules containing sulfhydryl groups, including proteins, exerting direct cytotoxic effects or interrupting cell signalling pathways. Acrolein reacts with glutathione (GSH) to produce the adduct glutathionyl propionaldehyde, and both induce oxygen radical formation in the presence of xantine oxidase and aldehyde dehydrogenase. The depletion of GSH decreases GSH peroxidase activity, resulting in a lower level of cellular protection against oxygen radical toxicity (Adams & Klaidman, 1993). Depletion of GSH inactivates multiple enzymes in the Calvin cycle affecting the photosynthetic reactions in chloroplasts isolated from *Spinacia oleracea* L. (Mano et al., 2009). In isolated rat hepatocytes, concentrations of 0.25 and 0.5 mM of acrolein decrease GSH with a concomitant lipid peroxidation that impairs the integrity of the cell membrane. Acrolein also induces apoptosis in the Chinese hamster (Tanel & Averill-Bates, 2007) and human bronchial epithelial cell, by depletion of GSH and generation of oxidants (Nardini et al., 2002). On the other hand, Luo et al. (2005) reported that acrolein induces death of PC12 cells, mainly by necrosis. These authors suggested that the ability of acrolein to induce cell death is closely related to mitochondrial ROS production and decreased cellular ATP levels. Further, acrolein conjugation with lysine residues of low density lipoproteins has been suggested as a factor in the development of atherosclerosis (Uchida et al., 1998)

3. Toxicity on non-target species

Non-target species that are principally exposed to acrolein include aquatic organisms inhabiting the irrigation canal. Potentially exposed organisms such as fish, invertebrates, amphibians, etc., are those inhabiting natural surface water that receive treated irrigation water. Terrestrial receptors that could be exposed to acrolein include mammals, birds, reptiles, and terrestrial-phase amphibians.

3.1 Aquatic organisms

Acrolein, the active ingredient of MAGNACIDE® H, is acutely toxic to aquatic organisms (Table 1). The tadpole of the frog *Xenopus laevis* is the most sensitive aquatic species tested, with a 96-h LC_{50} of 7 µg/L (Holcombe et al., 1987). The acute toxicity (LC_{50} or EC_{50} ug/L) reviewed by the U.S.EPA (2009) ranges between 14-320 µg/L and 57-180 µg/L for freshwater fish and crustacean, respectively. Insects seem to be more tolerant to acrolein with LC_{50} values between 600 to 2,800 ug/L (Venturino et al., 2007). Acrolein is also toxic to cyanobacteria. Several species from this group showed more than 95% of growth inhibition at a concentration of 1 mg/L of acrolein (Peterson et al., 1994).

Detoxification of [^{14}C] acrolein was studied in exposed fish (*Lepomis macrochirus* and *Ictalurus punctatus*) and shellfish (*Elliptio complanata* and *Orconectes virilis*). The mayor metabolites founded were glycidol, glycerol, 1,3-propanediol, and glyceric acid (Nordone et al., 1998).

Species	Group	Toxicity (LC_{50} ug/L) - exposure time	Reference
Xenopus laevis	Amphibia	7 – 96 hours	1
Catostomus commersoni	Fish	14 – 96 hours	1
Pimephales promelas	Fish	14 – 96 hours	1
Salmo gairdneri	Fish	16 – 96 hours	1
Rhinella arenarum	Amphibia	23 – 96 hours	2
Scenedesnus subspicatus	Algae*	26 – 72 hours	3
Lepomis macrochirus	Fish	33 – 96 hours	1
Oncorhynchus mykiss	Fish	38 – 96 hours	2
Daphnia magna	Crustacea	51 – 48 hours	1
Amia calva	Fish	62 – 24 hours	3
Oncorhynchus tshawytscha	Fish	80 – 24 hours	*3*
Carassius auratus	Fish	80 – 24 hours	*3*
Penaeus aztecus	Crustacea	100 – 48 hours	3
Cladophora glomerata	Alga*	100 - 24 hours	3
Rasbora heteromorpha	Fish	130 – 48 hours	3
Tanytarsus dissimilis	Insect	151 – 48hours	1
Aplexa hypnorum	Mollusc	>151 – 96 hours	1
Micropterus salmoides	Fish	160 – 96 hours	3
Heleobia parchappii	Mollusc	210 – 96 hours	2
Hyalella curvispina	Crustacea	240 – 96 hours	2
Fundulus similis	Fish	240 – 48 hours	3
Simulium spp.	Insect	600 – 246 hours	2
Anabaena	Algae*	690– 24 hours	3
Entosiphon sulcatum	Protozoa	850 – 72 hours	3
Chilomonas paramecium	Protozoa	1,700 – 48 hours	3
Balanus ebarneus	Crustacea	2,100 – 48 hours	3
Biomphalaria glabrata	Mollusc	2,500 - 24 hours	3
Chironomus spp.	Insect	2,830 – 24 hours	3

Table 1. Acute toxicity of acrolein in aquatic organisms. *reduction in photosynthes.
References: (1) Holcombe et al. (1987), (2) Venturino et al. (2007), (3) Cited in Eisler (1994)

3.2 Terrestrial organisms

According to the review by Eisler (1994), the adverse effects of acrolein depend on the mode and concentration or dose of administration, and duration of exposure. For example, single oral doses of 4 and 28 mg/Kg of body weight resulted lethal to guinea pigs and mice, respectively. The LC_{50} reported by inhaled acrolein (mg acrolein/L air) during 30 min and 6 hours exposure were 150 and 10.5 for dog and guinea pig, respectively. Adverse effects were also observed in birds. The oral LD_{50} of 3-5 months for the mallard, *Anas platyrhynchos*, was 9.1 mg/kg body weight. Auerbach et al. (2008) reported decreased survival and toxicity to the forestomach, squamous epithelial hyperplasia in rats and mice (both sexes) exposed 5 days a week during 3 months, by gavage, to 0–10 mg/kg acrolein and 0–20 mg/kg, respectively. Studies *in vitro* (mouse embryonic fibroblasts culture) showed formation of

DNA adducts, preferentially at specific nucleotide positions, moderately resistant to DNA repair. However, the results demonstrated that acrolein was not mutagenic to these cells at doses sufficient to produce DNA adducts (Kim et al., 2007). Further, rat embryo culture system treated with acrolein (200 and 250 μM) showed a drastic inhibition of growth differentiation without teratogenic potential (Schmid et al., 1981).

Conjugation with GSH is one of the two major detoxification pathways of acrolein. The 3-hydroxypropylmercapturic acid was the principal metabolite found in urine of male Wistar rats exposed to acrolein inhalation and intraperitoneal administration. To lesser extent, the metabolite 2-carboxyethylmercapturic acid was determined (Linhart et al., 1996).

Acrolein degrades quickly in soils and in plant tissues regardless of mode of administration. Most terrestrial crop plants can tolerate 15 mg of acrolein/L of irrigation water (Eisler, 1994). Nordone et al. (1997) evaluated the accumulation of acrolein in lettuce plants receiving either a single or multiple applications of 75 ppm [^{14}C]-acrolein in irrigation water. The results showed that both treatments leave almost no radioactive residues in leaves after 53 days. This study indicates that, under normal use scenarios, irrigation of crops with MAGNACIDE® H herbicide treated water is highly unlikely to result in the accumulation of biologically significant levels of acrolein in lettuce. Further, an experiment conducted in a greenhouse, where pepper plants were irrigated with water treated with 0.25 and 0.50 mM of acrolein, showed low values of chemical concentration in the extracts of the plants (2-18 ng/gr fresh tissue to undetectable levels within the few hours). The estimated half-life of acrolein in pepper plants was of 10.3 hours (Caldironi et al., 2004).

3.3 Humans

Liquid acrolein is absorbed by the skin, and is particularly irritating to the eyes. The vapor is highly toxic and a strong irritant (lachrymator) which acts principally on the mucous membranes of the eyes, nose, throat and lungs. The vapor concentration tolerable to humans is 0.1-1 ppm in air and can cause lung injury at 2-4 ppm (Baker Petrolite Corporation, 2001). The effects of long-term atmospheric exposure of humans to acrolein at tolerable levels are not known, but the concentrations likely to be found in the environment or workplace should not affect human reproduction (WHO, 1991). There is inadequate evidence in experimental animals for the carcinogenicity of acrolein (Group 3) (IARC, 1995).

4. Fate of acrolein after direct application into irrigation canals

The high reactivity of acrolein prevents its persistence in the environment, and its transportation over long distances (WHO, 2002; U.S.EPA, 2003). Dissipation of acrolein from aquatic ecosystems includes abiotic and biotic degradation, volatilization, absorption and dilution.

Acrolein is at equilibrium with the abiotic product 3-hydroxypropanal, and the presence of both compounds is transient (Nordone et al., 1996). The decay of acrolein and its hydration product is a first order process in agricultural canals when applied at the recommended concentrations. The half-life of acrolein in weedy irrigation canals from United States, Australia, and Argentina was 10.2, 4.3, and 9.63 hours, respectively (Bowmer & Sainty, 1977; Nordone et al., 1996; Venturino et al., 2007). The U.S.EPA (2007) also reported half-lives of acrolein between 2 to 20 hours in canals from Washington and Nebraska (U.S.A). Further, Eisler (1994) summarizes the half-time persistence of acrolein in freshwaters as usually less than 50 hours, and according to ATSDR (2007) acrolein may persist for up to 6 days. Bioassays

with fish and bacteria have demonstrated that acrolein losses its biocide activity in 120-180 days in different buffer systems at pH 7 and 22ºC (Kissel et al., 1978). Monitoring studies in United States (U.S.EPA, 2007) showed that the compound can be transported to distances of at least 61 miles beyond the initial site of application at concentrations that are still active.

At the application rate of 15 ppm acrolein into irrigation canals, the primary microbial degradation product was 3-hydroxypropanal. Other ephemeral products such as acrlylic acid, allyl alcohol, propionic acid, propanol, and 3-hydroxipropionic acid were also identified (Smith et al., 1995).

The high water solubility of acrolein and low estimated Koc suggests that acrolein does not significantly adsorb to suspended solids and sediment (HSDB, 2010; U.S.EPA, 2007). Volatilization from water surfaces is expected to be an important fate process based upon the compound's Henry's Law constant (1.0×10^1 mol $atm^{-1}dm^{-3}$). Estimated volatilization half-lives for a model river and lake (1 m deep) were 7.6 hours and 4.6 days, respectively (HSDB, 2010). In the atmosphere, the primary removal mechanism for acrolein is through the reaction with hydroxyl radicals with a half-life between 15–20 hours (Faroon et al., 2008).

It is unlikely that acrolein bioaccumulate or bioconcentrate significantly in aquatic organisms (WHO, 1991). Acrolein was not detected in the tissues of fish (*Lepomis macrochirus* and *Ictalurus punctatus*) and shellfish (*Elliptio complanata* and *Orconectes virilis*) exposed separately to [^{14}C]-acrolein in water (0.02 and 0.1 mg/L for fish and shellfish, respectively), over a 1-week period, and sampled 1 day after a second exposure. The presence of metabolites indicated that these species were able to rapidly metabolize acrolein (Nordone et al., 1998). An estimated Bioconcentration Factor of 3.2 suggests that the potential for bioconcentration in aquatic organisms is low ((HSDB, 2010).

5. Risk assessment of acrolein application as an herbicide in irrigation canals

We developed a risk evaluation of the use of acrolein in an irrigated valley, where applications of this compound (MAGNACIDE® H) had been currently performed for more than 20 years during the spring-summer seasons. The area of study was located in the Río Colorado valley (Argentina) between 39º10' to 39º55'S and 62º05' to 63º55'W. The irrigation of the area, controlled by the CORFO-Río Colorado cooperative, consists of 331 km of main canals, 3738 km of both secondary and tertiary canals, and 397 km of drainage canals which discharge directly to the Argentinean sea. The herbicide had been applied at different target concentrations and durations. The application scheme of 15 mg/L for 1 hour was used principally during the first years of use. Afterwards, it was applied at a target concentration of 4 mg/L for 12 hours. The temperature in water canals ranged from 15 to 22.5ºC during the application seasons. Water flow rates were regulated currently between 0.20-0.50 m/s, according to weed proliferation status.

Keeping a tiered approach recommended by ECOFRAM (1999), we divided the ecological assessment into four tiers: (a) Literature-based screening level ecological risk assessment, (b) risk assessment with site-specific information, (c) risk assessment with native species, (d) impact of acrolein on benthic invertebrates (field study).

At tier 1, we compared the maximum predicted peak concentration in the CORFO canals with acute endpoints such as effective or lethal concentration, from the most sensitive species of freshwater fish, amphibian, molluscs and crustacean from Table 1. Even though it has been suggested that LC_5 or LC_{10} may be a more appropriate parameter (EU, 2002), EC_{50} or LC_{50} is the data generally available in the literature. Only freshwater organisms were

selected to assess the aquatic risk since they are the principal ecological receptors. Hazard Quotients (HQ) were calculated using the target concentrations of acrolein in the two different application schemes. The calculated acute HQ were compared with criteria used for risk characterization in tier 1 (Urban & Cooke, 1986). The acute HQ estimated for both application schemes highly exceeded the risk criteria for all groups of organisms evaluated (Table 2). The tadpole *Xenopus laevis* and the mollusc *Aplexa hyponorum* were the most sensitive and the most tolerant species to acute exposure of acrolein, respectively.

Species	Group	Acute endpoint[a] (mg/L)	HQ[b]	
			Scheme 1	Scheme 2
Daphnia magna	Crustacea	48-h EC_{50} (0.051)	78.43	235.29
Pimephales promelas	Fish	96-h LC_{50} (0.014)	285.71	857.13
Xenopus laevis	Amphibia	96-h LC_{50} (0.0070)	571.43	1714.29
Aplexa hypnorum	Mollusc	96-h LC_{50} (0.15)	26.67	80.00
Tanytarsus dissimilis	Insect	48-h LC_{50} (0.15)	26.67	80.00

Table 2. Hazard quotients (HQ) for the most susceptible species from representative groups. HQ were calculated from endpoints and target concentrations of acrolein in two different application schemes: Scheme 1, 15 mg/L for 1 hour; Scheme 2, 4 mg/L for 12 hour. [a]Acute toxicity data cited in Holcombe et al. (1987)], [b]HQ 0.5 or greater indicates a higher risk category.

Chronic toxicity data were not used in this study because of the limited information available and the rapid dissipation of acrolein in treated canals. The risk criteria were highly exceeded for all of the species analyzed implying that progress to tier 2 was indispensable.
The environmental fate behavior of acrolein was incorporated in tier 2, to provide probabilistic expressions of the potential risk associated with its use as an herbicide. First, effects of acrolein on aquatic freshwater organisms were characterized by distribution sensitivity curves (ECOFRAM, 1999). The acute toxicity data obtained from scientific literature (Holcombe et al., 1987; WHO, 1992; Eisler, 1994) included 10 species of fish, 1 species of amphibian, 3 species of crustacean, 2 species of molluscs, 1 species of insect, 2 species of protozoan, and 3 species of algae (Table 1). According to the Guidance Document on Aquatic Ecotoxicology (EU, 2002), two algae species from different taxonomic groups should be included for herbicide risk assessment. Even though photosynthesis inhibition is not an equivalent endpoint, it was included into the list to compare algae toxicity. The species were ranked by decreasing sensitivity and the rank was transformed to a percentile [$i/(n+1)$], where i is the species rank, and n is the total number of species listed. The probit analysis was performed to obtain the regression lines and to determine the 10th percentiles. Figure 2 represents the LC_{50} log-transformed and the percentiles converted to probabilities from the data set and the distribution profile of toxicities to organisms. From the fitted line of the distribution for all species the 10th percentile was 0.011 mg/L which means that 10% of the species have LC_{50} values lower than this concentration. On the other hand, the 10th percentile from the distribution of sensitivities to acrolein in animals, excluding the values from algae and weeds, was 0.0094 mg/L. This analysis suggests that a significant number of aquatic species may be seriously and unacceptably affected by acrolein concentrations in the canals.

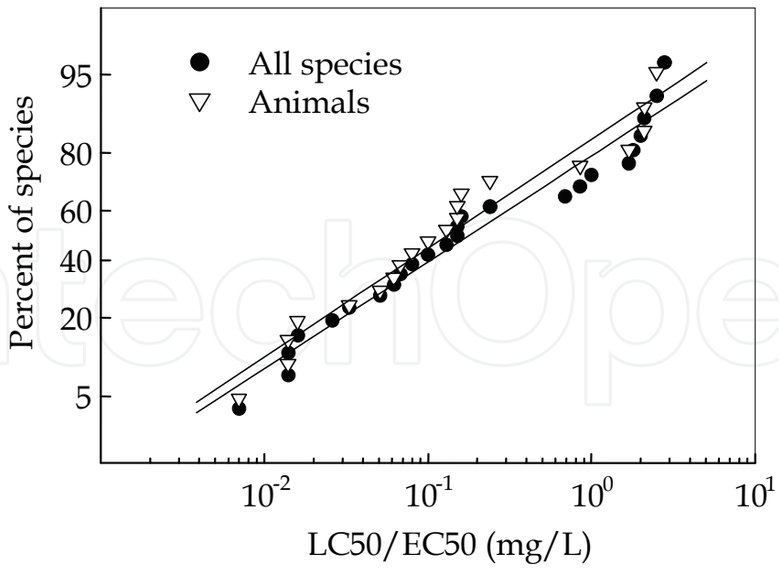

Fig. 2. Distribution of acute toxicity values for different taxonomic groups of organisms. Percentile probabilities were calculated from acrolein LC_{50} or EC_{50} values for freshwater organisms (•) (probit regression line Y = 0.8128 + 1.0861X, R=0.9783, N=25; 10^{th} percentile 0.0118 mg/L), or animal freshwater species (∇) (probit regression line Y = 0.9794 + 1.1107X, R=0.9758, N=20; 10^{th} percentile 0.00938 mg/L).

Next, an estimation of acrolein levels along the canals was considered for risk evaluation. On the basis of CORFO application data during several application seasons, we estimated the dissipation of acrolein in the canals. The model applied takes into account the time-space variability of acrolein concentrations within the canals, applying an exponential equation (1) that predicts the exposure at different distances from the application site:

$$[\text{Acrolein}]_d = [\text{Initial acrolein}] \times e^{-[\ln 2 / t_{1/2} \times d\ (\text{km}) / v\ (\text{km/h})]} \quad (1)$$

where:
$[\text{Acrolein}]_d$ = Concentration of acrolein at distance *d* from the application point.
[Initial acrolein] = Concentration of acrolein at the application point.
$t_{1/2}$ = 9.63 h according to dissipation studies performed on the canals.
v (km/h) = water flow velocity in the canal.
The pulse of acrolein passing through the canal may be visualized as a block with side heights exponentially decreasing as it is moves by water flux, and length depending on the application schedules (Fig. 3).
According to this model, the predicted concentrations were calculated at several distances from the application point in order to analyze theoretical exposures within the water body. The maximum distance calculated from the application point was 20 km since it is the approximate span wherein weed control is still effective. The predicted concentration of acrolein at different distances and the percentage of species whose LC_{50}/EC_{50} were exceeded at each concentration is summarized in Table 3. These results showed that a high percentage of the species are likely to be affected by the herbicide despite the distance from the application point in the treated canal.

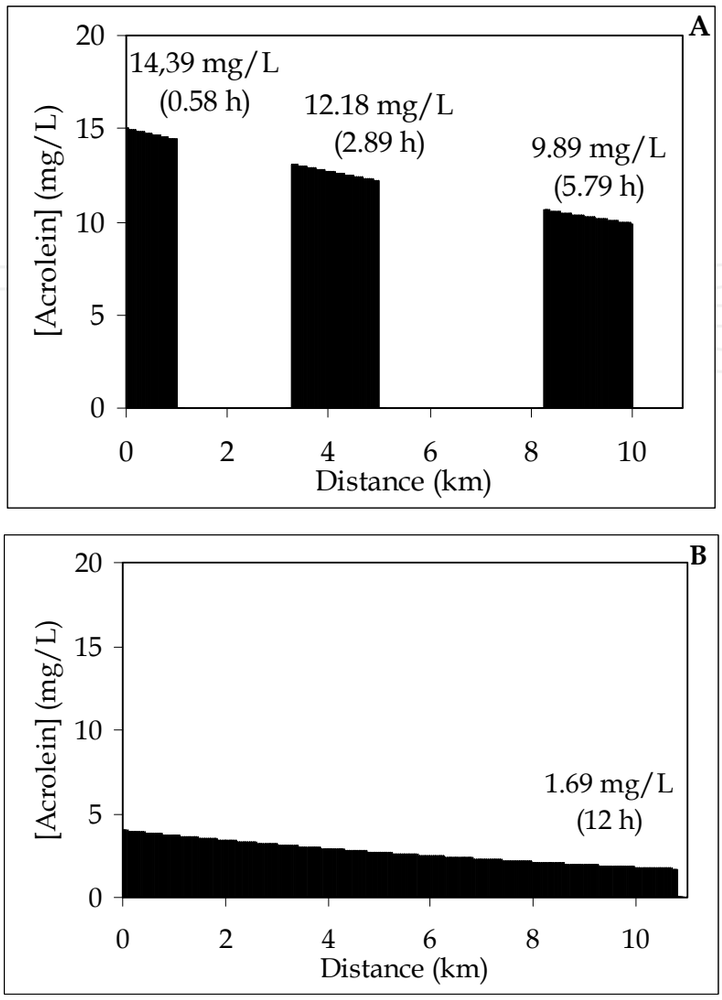

Fig. 3. Exponential dissipation model.
The exponential dissipation of acrolein was simulated for a model canal with a half-life of 9.63 h and: (A) scheme 1, flow velocity 0.48 m/s, 15 mg/L of the compound applied continuously during 1 h, or (B) scheme 2, flow velocity 0.25 m/s, 4 mg/L of the compound applied continuously during 12 hours.

Distance from the application point (km)	Predicted concentration (mg/L)	Percent of species with LC_{50}/EC_{50} exceeded
0	4.00	100
5	2.68	100
10	1.80	88.91
15	1.21	84.46
20	0.81	78.24

Table 3. Predicted concentration of acrolein and percent of species affected. Concentrations following application of acrolein were estimated for a target concentration of 4 mg/L during 12 hours at the application point and at different points along a canal with water velocity of 0.25 m/sec.

To increase the environmental realism of the tier 2 scenario, different application patterns of acrolein over six years at CORFO-Río Colorado (N=165 applications) were incorporated to the analysis. According with the dissipation model, the expected concentrations at the application point, at 10 km and at 20 km downstream were estimated. The environmental expected concentration as a cumulative exceedence curve at the above three distances, and the distribution profile of toxicities is presented in Fig. 4.

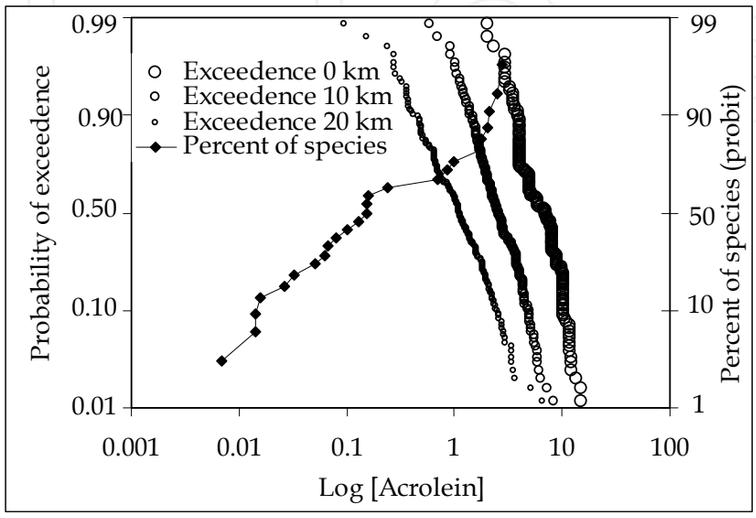

Fig. 4. Concentration exceedence probabilities and toxicity distribution profile for acrolein applications at CORFO-Río Colorado canals.

For each concentration on the X axis, this curve indicates the frequency that concentration was exceeded during the period of time analyzed, and the percentage of species affected. Therefore, each pair of points (probability and percentage of species) can be associated to a concentration. For example, during that period, the concentration causing mortality to 73% of the species (1 mg/L) was exceeded in 55%, 95% and 100% of the applications at 20, 10 and 0 km from the application point, respectively. On the basis of the results here depicted, it may be concluded that acrolein poses sufficient risk as an herbicide to require a higher level of assessment. Some of the studies proposed by ECOFRAM (1999) in tier 3 of aquatic risk assessment are: (a) Acute toxicity studies with additional species, (b) investigation of the toxicity associated with repeated exposures, (c) chronic toxicity studies, (d) sediment toxicity studies.

Additional acute toxicity studies with native species, collected nearby the potential site of exposure to acrolein or obtained from hatcheries, were then performed in tier 3. The last instar larvae of the insects *Chironomus* spp. and *Simulium* spp., the mollusc *Heleobia parchappii*, the crustacean *Hyalella curvispina*, tadpoles of the amphibia *Rhinella arenarum*, and juveniles of the fish *Oncorhynchus mykiss* were selected for the study. The different organisms were exposed to different concentrations of acrolein. The experimental conditions and the complete ecotoxicological data listing the LC_{95}, LC_{50}, Lowest Observed Effect Concentrations (LOEC), and No-Observed Effect Concentrations (NOEC) are published elsewhere (Venturino et al., 2007). The toad *R. arenarum* was the most sensitive species followed by the fish *Oncorhynchus myskiss*. However, toxicity in both species is almost three times lower (0.023 and 0.038 mg/L) than in their related counterparts *Xenopus leavis* and

Catostomus commersoni, (0.007 and 0.014 mg/L), respectively. The native species *Chironomus* spp. was the less sensitive to acrolein with the highest LC_{50} (2.83 mg/L). A probit analysis on percentile sensitivity distribution for the native species provides an estimation of 0.013 mg/L acrolein as the 10th percentile, which is the concentration eventually affecting 10 percent of native species (Fig. 5). This value is quite similar to the 10th percentile estimated from the sensitivity distribution using published data for other species (Fig. 2).

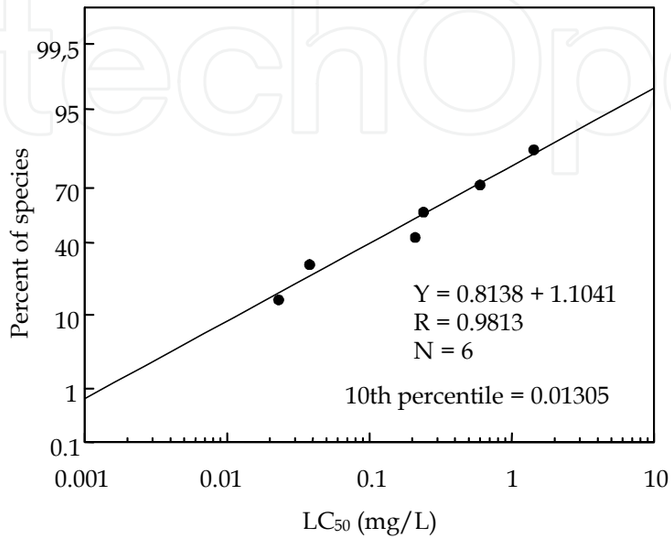

Fig. 5. Distribution of acute toxicity values for different taxonomic groups of native organisms. (Venturino et al. (2007), with permission of SETAC press).

To compare the ecotoxicological data with field predicted exposure concentrations, a first approach can be made using the percent mortality obtained at 24 hours with exposures to 0.5 and 1.0 mg/L of acrolein in laboratory tests. These levels were chosen considering the potential concentration of acrolein approaching 20 km from the application point in the low-concentration treatment schedule (0.8 mg/L), and the probable exposure time in the canals. The values obtained, shown in Table 4, indicate an unacceptable risk for fish, amphibians, and the amphipod *H. curvispina*, an intermediate risk for snails and black fly larvae, and no risk for midges.

Acrolein (mg/L)	Species (stage)					
	toad (larvae)	amphipod (adult)	snail (adult)	fish (juvenile)	black fly (larvae)	midge (larvae)
	% Death in 24 h					
0.5	100%	100%	20%	100%	36%	0%
1.0	100%	100%	n.d.	100%	98%	0%

Table 4. Percent of mortality at 24 hours of exposure to 0.5 mg/L and 1.0 mg/L acrolein in laboratory tests.

To improve the risk assessment, the sensitivity distribution along the distance from the application point was analyzed. From it, the exceedence probabilities could be assessed as

percentiles of native species affected by acrolein. The two extreme application schedules of 15 mg/L-1h (scheme 1) and 4 mg/L-12h (scheme 2) were chosen, spanning the most of the alternatives used at CORFO-Río Colorado (Fig. 6). From the probit analysis, it is inferred that the distances needed for acrolein dilution and degradation to a concentration affecting no more than a 10% of native species are not physically feasible (175 km for scheme 1; 74 km for scheme 2). On the other hand, it alerts on the risks posed by both application schemes: scheme 1 produces an acute exposure (1 h) that probably affects 95% and 90% of native species at about 11 km and 30 km respectively dowstream the application point. Scheme 2 affects 90% of native species just at the application point. In both cases, the risk probability decreases linearly with the distances from the application point.

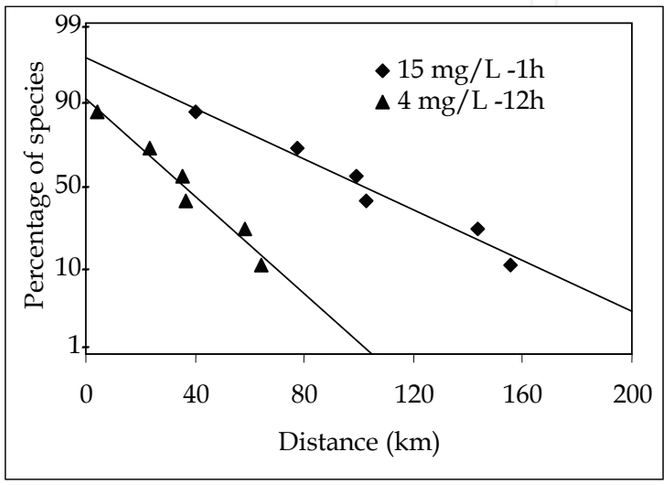

Fig. 6. Joint probability graph for native species

The use of acrolein as an herbicide against aquatic weeds currently requires periodical applications during spring-summer seasons. Acrolein exposure in aquatic ecosystems occurs in pulses, with peak concentrations in the water lasting few hours. Such pulses are applied periodically, typically every 20-30 days. Repeated exposure assays have been performed with two native species applying pulse-recovery schemes, simulating the application frequencies in CORFO-Río Colorado canals (Venturino et al., 2007). The effects were tested at 96h-LOLC and LC_{50} values for each species. *R. arenarum*, which was the most sensitive to acrolein, presented a significant increase in mortality after the first exposure-recovery cycle, and the effect was observed after acrolein removal, during the recovery period. According to this observation, a lower survival rate constant was significantly determined for acrolein treatments (Table 5). Latency effectively occurred because the onset of mortality was delayed, becoming evident during the recovery time. No cumulative effects for the repeated exposures were observed, and the final number of surviving larvae was statistically the same. Selection of tolerant individuals takes place during the first exposure, then the remaining sub-population is similar in number for both treated and control groups. Moreover, *R. arenarum* tadpoles surviving the three pulses of acrolein arrived to metamorphosis at the same time and proportion as controls. The intermediate-sensitive crustacean, *H. curvispina*, was also subjected to acrolein pulses of 1day-exposure followed by recovery. No effects were observed on this species, concluding that the short exposures did

not cause cumulative damage or that the recovery time between repeated exposures (6 days) was enough to overcome the deleterious effects. So, the acute effects of acrolein on *H. curvispina* are related to peak duration since the LC_{50} determined at 96 hours of exposure (0.24 mg/L) does not cause mortality at the repeated short term exposure of 24 hours.

Treatment group	Control	LOLC	LC_{50}
		(0.010 mg/L)	(0.023 mg/L)
% Survival:			
1st Exposure-Recovery	64.2 ± 4.4	59.2 ± 4.4	53.3 ± 4.2
2nd Exposure-Recovery	58.3 ± 4.4	54.2 ± 3.0	46.7 ± 5.1
3rd Exposure-Recovery	49.2 ± 3.0	50.0 ± 5.2	41.7 ± 6.0
Latency effects		YES	YES
Mortality rate constant (d)	13.9 ± 0.1	6.8 ± 1.3*	6.9 ± 2.7*
% Metamorphosis	19.0 ± 0.2	20.1 ± 0.2	23.9 ± 5.4

Table 5. Repeated exposure effects of acrolein in *R. arenarum*. Three cycles of 1 day-exposure followed by 13 days-recovery in acrolein-free media were evaluated. LOLC: Lowest-Observed-Lethal Concentration; LC_{50}: Lethal Concentration-fifty. * denotes significant differences vs. control group, p= 0.018. Data obtained from Venturino et al. (2007), with permission of SETAC press.

The acute toxicity tests and risk assessment on native species lead to a concern about acrolein effects in the irrigation canals. Repeated exposure tests showed no cumulative effects, as population survival remained unchanged with respect to controls after the third exposure. Other studies at this stage of the evaluation are not recommended for the use of acrolein as an herbicide. The physical and chemical properties of the compound such as its high reactivity, its low tendency to partitionate to organic matter, and its low persistence in the environment do not require sediment toxicity studies as a priority. At this step, the risk evaluation needs to include field studies to broaden the analysis towards community and population levels. This category of approach in tier 4 lets the determination of effects on a variety of organisms in the ecosystem, including the interaction among species and indirect effects. In the case of the use of acrolein as an aquatic herbicide, a field study on benthic invertebrates has been designed to establish the safety of the exposure regime of MAGNACIDE® H at the CORFO-Río Colorado canals (Albariño et al., 2007). These organisms are prone to human perturbation of the ecosystem, and relatively sedentary if compared to other organisms such as fish or amphibian. A total of 34 benthic macroinvertebrates were identified in CORFO-Río Colorado canals. From the study, spanning two years, it was determined that acrolein was able to reduce community diversity and abundance during the application seasons. However, the benthic community was able to recover its ecological attributes two months after ceasing canal treatments with acrolein. Thus, the use of acrolein as an herbicide would be ecologically acceptable, taking into account that its toxic effects are reverted in a reasonable time (Campbell et al., 1999). The directional flux in the lotic systems under study probably allow the recolonization of the areas where a local perturbation has been introduced, such as the application of the herbicide, by flowing organisms from upstream sites (Winterbourn & Townsed, 1998).

6. Conclusions

There are no generally accepted quantitative criteria for evaluating ecological significance and expert judgement is always required. We have shown here evidences from literature data and from risk assessment with native species that acrolein used for weed control in irrigation canals is extremely toxic for most of the living organisms at the recommended treatment concentrations and conditions. Nevertheless, its presence in the canals is transient and it has been observed a natural recovery process, mainly operating through the introduction of species from outside the treated area that minimizes the ecological risk. Populations of species with a high intrinsic growth rate, such as zooplankton, may rapidly recover after an acute toxicity event. Species with lower intrinsic growth rate, such as amphibians and fish, will require longer periods for population recovery. One advantage in the protection of higher organisms such as birds and mammals is the irritating odour of the herbicide. The odour prevents them from getting close to the treated area, so these species are not endangered by the compound.

Taking into account the fact that most population effects derived from the use of acrolein as an aquatic herbicide are temporary, we conclude that its use is ecologically acceptable because recovery occurs within a reasonable period of time. In order to minimize the risk on the ecological receptors, a strict control on the treatment regime, concentration applied, timing and frequency of application must be ensured. Treated canals must be controlled during the applications, water release must be prevented until the product has dissipated, and it must be ensured that water is used only for irrigation purposes.

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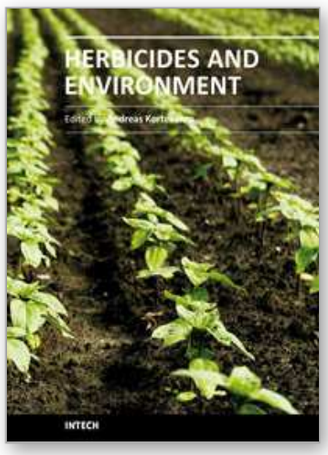

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Herbicides are much more than just weed killers. They may exhibit beneficial or adverse effects on other organisms. Given their toxicological, environmental but also agricultural relevance, herbicides are an interesting field of activity not only for scientists working in the field of agriculture. It seems that the investigation of herbicide-induced effects on weeds, crop plants, ecosystems, microorganisms, and higher organism requires a multidisciplinary approach. Some important aspects regarding the multisided impacts of herbicides on the living world are highlighted in this book. I am sure that the readers will find a lot of helpful information, even if they are only slightly interested in the topic.

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