Management Of Aquatic Plants With Acrolein

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ABSTRACT

Acrylaldehyde (acrolein) is widely used by state government authorities in Australia to control submersed aquatic plants, particularly elodea (*Elodea canadensis* Rich.) in flowing water in irrigation canals. Theoretically the herbicide may be mixed with the water in a single upstream application or added at two or more equi-distant stations downstream. It is proposed that the quantity of acrolein required and the economy of multiple additions may be conveniently calculated by water managers, providing the time for the treated water to travel through the weed-infested stretch is known. It is assumed that acrolein dissipation from the water is a first order process with a rate constant (K) of 0.16 per hr, and that the dosage required for weed control at the downstream limit of the intended treatment (E_L) is known. The value of K was derived from observations in six irrigation channels in Australia and from data for two trials supplied by the United States Bureau of Reclamation. E_L was obtained by calculating the residual dosage at the downstream limit of seven successful treatments in canals containing various submersed species including elodea and some ribbonweed (*Vallisneria spiralis* L.). These observations suggest that within limits (concentration > 0.1 ppm; contact time > 2 hr), E_L may be largely independent of the separate values of concentration and time, providing that the product exceeds a minimum value of about 2 ppm for 1 hr. In tank experiments 80% control of ribbonweed was obtained with 3.7 ppm for 1 hr; floating pondweed (*Potamogeton tricarinatus* F. Muell & A. Benn.) required relatively large dosages—about 2 ppm for 12 hr or 15 ppm for 1.7 hr, and this is confirmed by practical experience in routine weed control operations.

INTRODUCTION

In the irrigation systems of southeast Australia the efficiency of water supply and drainage is often reduced by the rapid growth of submersed aquatic plants. Elodea, a native plant of North America and previously showing explosive colonization in northwest Europe, is now widespread in the Murray Valley Irrigation Districts of southern New South Wales and northern Victoria. As a result, about 1500 km of channels in these districts require maintenance with herbicides. New infestations of elodea appeared in the Coleambally and Murrumbidgee Irrigation Areas (MIA) in 1973 (19), and severe effects on the efficiency of water distribution were anticipated. Other important species are reported by Bill and Graham (6) and Sainty (18).

Acrolein is widely used by government authorities to control submersed aquatic plants in flowing water. About 66,000 kg of herbicide are used annually to treat about 4000 km of channels. Acrolein is a general biocide. It destroys vital enzyme systems on contact with plant cells, causing the tissues to disintegrate (3), and is also extremely toxic to fish (7, 12). Since some of the treated water may eventually reach natural watercourses, and in some situations may even be used for domestic supply, it is important to minimize the addition of the herbicide while maintaining adequate weed control.

The standard method for acrolein addition is based on commercial recommendations.[1] The herbicide is mixed with the water at a convenient point upstream and allowed to flow over the weed beds. In Australia, a concentration maximum of 15 ppm is imposed to safeguard irrigated crops and the time for addition is adjusted accordingly. In the United States of America addition is greatly prolonged in larger canals so that concentrations of about 0.1 ppm may be used (2, 4, 5). In an unpublished report[2] the effectiveness of the latter approach was disputed for Australian situations. It was also suggested that the efficiency of acrolein use should be increased in long canals by application in smaller quantities at several points downstream.

The strategy of multiple additions is based on the concept that in any given length of canal, effective weed con-

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[1] The recommended dosage is equivalent to 1.2 to 3.6 kg of acrolein per unit discharge measured in megaliters per day. 1.0 kg of acrolein per megaliter per day is equivalent to 24 ppm acrolein for 1 hr.

[2] J. A. Todd. 1974. Personal Communication.

trol is achieved by maintaining the product of concentration and contact time above the minimum lethal dose. An addition above this minimum is required to compensate for the dissipation of acrolein from the water. Theoretically the addition can be made in a single dose at the upstream limit of the weed infestation or in two or more applications at equi-distant stations downstream. This paper describes a method for calculating the quantity of acrolein required in different situations, and summarizes the progress being made towards rationalizing the use of acrolein with regard to economy and safety.

THEORY

Acrolein dissipates from water by processes of volatilization, adsorption and degradation, and is diluted by mixing as it flows downstream. For long injection times and at distances close to the injection point a plateau exists in the concentration-time curve, and as long as the plateau persists the peak concentration is determined by the rate of loss of the herbicide. Observations by the United States Bureau of Reclamation (USBR) which have been reported previously (16) suggest that acrolein dissipation from flowing water is a first order process as described in equation (1), where K is the first order rate constant of decay, C_a and C_b are the concentrations observed in the plateau region as the mass of treated water passes through stations at distances x_a and x_b downstream from the injection point, and U is the average mean velocity of flow.

$$K = \frac{U}{\Delta x} \ln(C_a/C_b) \tag{1}$$

The rate of loss of acrolein is also described by equation (2) where E is the dosage of acrolein at each station, obtained by measuring the area underneath the concentration-time curve during the passage of the treated water (16).

$$K = \frac{U}{\Delta x} \ln(E_a/E_b) \tag{2}$$

Further downstream from the injection point longitudinal dispersion contributes to the attenuation of maximum concentration by rounding off the plateau and equation (1) is no longer applicable. Equation (2) is applicable whether or not a plateau is present, and dosage (the product of concentration and contact time) is independent of dispersion effects.

The theoretical dosage required at the injection point (E_o) may be calculated for any situation by rearrangement, using equation (3), where E_L is the minimum lethal dosage which must be maintained in the water at the downstream limit and t is the time taken for the herbicide to travel through the weed infested stretch.

$$E_o = E_L \exp(Kt) \tag{3}$$

Solution of equation (3) requires that a value of travel time should be available for each situation; estimates may be obtained conveniently in the field by using a colorimetric test to track the progress of the treated water, or by marker dye techniques. Assessment of K and E_L, which are also required, are described in the following sections.

ASSESSMENT OF THE RATE OF DISSIPATION

The first order rate constant of decay (K) has been computed from observations of the dissipation of acrolein from flowing water.

Data collected by the USBR for two treatments (A, B) in the Columbia Basin Project (2) are described in Tables 1 and 2, together with data for three Australian channels which we have presented previously (9, 16). These channels (C, D, E) were located in the Murray Valley Irrigation Districts and contained moderate to dense infestations of elodea.

Three further sets of data (F, G, H) are reported here for selected irrigation channels containing dense populations of aquatic weeds of contrasting physical characteristics. In two of the channels the sampling procedure was designed to investigate the possibility that dense weed growth could impede the mixing of acrolein with the water.

The dominant species were elodea in Finley Berrigan, and curly pondweed (*Potamogeton crispus* L.) in Griffith Lake View Channel. A heavy infestation of floating pondweed occurred in Benerembah Lateral, together with a mixed population of ribbonweed and sago, curly, blunt, and perfoliate pondweeds (*Potamogeton pectinatus* L., *P. crispus* L., *P. ochreatus* Raoul, and *P. perfoliatus* L.). Channel descriptions are given in Table 1.

Acrolein was injected into the water at a point midstream at constant flow during time τ to give a concentration C_0 (Table 2).

In Finley Berrigan Channel centreline samples were

TABLE 1. DESCRIPTION OF CANALS AND LOCATION OF SAMPLING STATIONS DOWNSTREAM FROM THE INJECTION POINT. DATA FROM THE UNITED STATES BUREAU OF RECLAMATION (A, B); THE WATER RESOURCES COMMISSION, NEW SOUTH WALES (C, D, F, G, H); AND THE STATE RIVERS AND WATER SUPPLY COMMISSION, VICTORIA (E).

	Canal	Velocity (km/hr)	Discharge (Ml/Day)	Temp. (C)	Location	
					Station 1 (km)	Station 2 (km)
A	Potholes June	2.5	3957	19	—	—
B	Potholes July	2.5	3920	23	—	—
C	Finley Main Blighty	0.31	110	20	0.9	2.1
D	Finley Berrigan 6C	0.09	11	22	0.6	1.0
E	Cobram 4	0.28	40	24	0.7	2.1
F	Finley Berrigan 1	1.21	735	21	2.3	—
G	Griffith Lake View	0.45	29	16	1.5	—
H	Benerembah Lateral 32	0.33	na	23	1.5	—

TABLE 2. FIRST ORDER RATE CONSTANT (K) FOR DISSIPATION OF ACROLEIN FROM FLOWING WATER IN IRRIGATION CANALS. FOR DESCRIPTION OF CANALS, SEE TABLE 1.

	Injection conditions		Dosage (ppm x hr)			K(1/hr)				
			Station			Equation (1)		Equation (2)		
Canal	τ(hr)	C_0(ppm)	0	1	2	Station 0-1	Station 1-2	Station 0-1	Station 1-2	Mean
A	48.0	0.1[a]	4.8[a]	—	—	0.208		—		0.208
B	48.0	0.1[a]	4.8[a]	—	—	0.172		—		0.172
C	0.95	17.0	16.2	9.8	5.7	—	—	0.232	0.138	0.168
D	2.0	21.8	43.6	22.2	19.8	—	—	0.133	0.031[b]	0.133
E	5.0	11.1	55.5	41.9	17.9	0.116	0.151	0.262	0.160	0.211[c]
F	1.5	2.0	3.0	1.8	—	—	—	0.180	—	0.180
G	1.2	12.0	14.4	9.1	—	0.173	—	0.126	—	0.126[c]
H	8.0	12.0	96.0	—	—	0.104	—	—	—	0.104
									Mean	0.163
									Standard Deviation	0.039

[a] Target exposure, not necessarily achieved.
[b] Suspect data, see text.
[c] Equation (2) used in preference to (1), see text.

collected at recorded intervals as the treated water passed through the sampling station. In Lake View and Benerembah Lateral Channels a manually-operated peristaltic pump was used to collect water simultaneously from six points fixed in the cross section. Acrolein was separated from non-toxic reaction products and determined by colorimetric reaction with dinitrophenylhydrazine as previously described (10). Results for Lake View Channel are plotted in Figure 1.

Values of K (Table 2) were computed using equations (1) and (2). Equation (1) was applicable to Benerembah Lateral and Lake View Channels where plateau concentrations were defined, but not to Finley Berrigan Channel. For application of equation (2) the upstream dosage (E_a) was calculated from the product of known concentration and time of injection, and the exposure at the downstream station (E_b) was obtained by integrating the area under the concentration-time curve. Equation (2) was applicable to all the channels and was used in preference to equation (1) to derive a mean value for K (Table 2); equation (2) gives a more reliable estimate because fluctuations in plateau concentration are smoothed in the integration process. It is believed that changes in channel geometry and incomplete mixing below Station 1 invalidated the sampling procedures in Finley Berrigan 6C and this result has been disregarded.

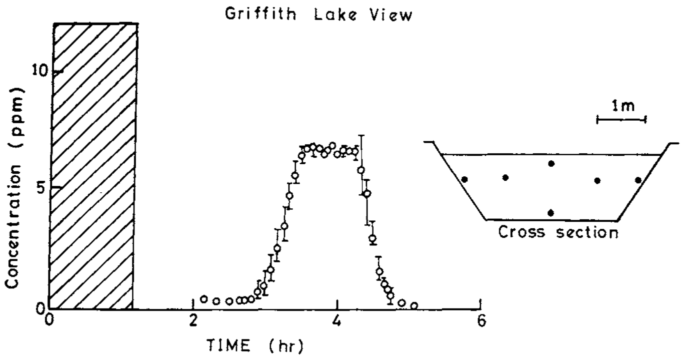

Figure 1. Acrolein concentrations (mean and range for six points in the section) at times from the start of injection at a station 1.5 km downstream. The cross section shows the location of sampling points. The hatched zone represents injection conditions.

Results show that the eight values of K obtained agree quite closely, with a mean of 0.163 per hr, corresponding to a half life of 4.3 hr.

ASSESSMENT OF THE MINIMUM LETHAL DOSAGE

Tank Experiments

Some limited information on E_L was obtained by exposing mature plants of floating pondweed or ribbonweed to known dosages of acrolein. In assays using floating pondweed a range of dosages was obtained by varying the contact time at a fixed concentration (nominally 2 or 15 ppm); in assays using ribbonweed the contact time was constant (1 hr) and the concentration varied. The plants were well-established in buckets of mud; they were immersed in treated water (500 liters) in open tanks, washed, then returned to clean water for 7 days before visual assessment. Turbulence was achieved during treatment in some of the tanks by bubbling with nitrogen gas. The concentrations of acrolein were determined by chemical analysis and corrected as necessary for dissipation during exposure.

Experimental conditions and results are given in Table 3. For ribbonweed in turbulent water, the data fitted a curve of the form

$$y/100 = 1 - \exp(-0.430x)$$

where y is lethality (%) and x is dosage (the product of concentration in ppm and contact time in hr). Data obtained for floating pondweed fitted the relationship

$$\text{probit}\, y = a + b \log x.$$

Regression lines were fitted to calculate the dosages required for 50 and 80% control.

The results (Table 3) suggest that floating pondweed is about seven to ten times more tolerant of acrolein than ribbonweed and this is confirmed by experience in routine weed control operations. For floating pondweed similar dosages were required for control, whether treated at 2 or 15 ppm, suggesting that E_L may be largely independent of the separate values of concentration and time (within the limits of concentration imposed) providing that the *product* is maintained above a minimum. For 80% control within 7 days of treatment, the dosage required

TABLE 3. THE EFFECT OF ACROLEIN ON AQUATIC PLANTS. CONCENTRATION (C) AND TIME (τ) OF EXPOSURE, AND DOSAGES ($C\tau$) REQUIRED FOR 50 (LC_{50}) AND 80 (LC_{80}) PERCENT CONTROL.

Species	Exposure		Turbulence	$C\tau$(ppm x hr)	
	C(ppm)	τ(hr)		LC_{50}	LC_{80}
Ribbonweed	V[a]	1	+	1.6(1.3 — 2.0)[b]	3.7(3.2 — 4.6)[b]
Floating pondweed	15	V[a]	—	9[c](8 — 13)	26[c](23 — 38)
	15		—	14[c]	26[c]
	2		+	10[c]	26[c]
	2		+	15(11 — 22)	22(16 — 39)

[a] Variable.
[b] Estimated dosages for control and 95% confidence limits.
[c] Regression lines are not significantly different; 95% confidence limits are calculated from their common line.

was about 4 and 26 ppm x hr for ribbonweed and floating pondweed respectively.

Irrigation Channels

Additional information on E_L was obtained by calculating the residual dosage at the downstream limits of the treated lengths of several irrigation channels (Table 4), assuming a decay constant of 0.16 per hr.

In Wah Wah Main, Barren Box Outfall and Finley Berrigan Canals the extent of satisfactory weed control was assessed by inspection. Wah Wah Main contained a light infestation of ribbonweed, Barren Box Outfall contained ribbonweed and several species of pondweed in early growth stages, and Finley Berrigan was very densely infested with elodea. Data for West and Potholes Canals were calculated from information supplied by the USBR (2) for travel times between successive "booster" injections.

The criterion for satisfactory weed control may differ in each situation. However, with the exception of Wah Wah Main, where low temperatures and sparsity of weeds may invalidate this approach, the dosages needed to achieve control at the downstream limit were similar. Dosages at the injection point represented extreme combinations of high concentration-short time and low concentration-long time additions, which varied by an order of magnitude. The relative consistency of calculated downstream dosages suggests that E_L is largely independent of the separate values of concentration and time (within the limits of Table 4) providing the product of concentration and time is maintained at approximately 2 ppm x hr.

This estimate of E_L, derived from observations in irrigation channels (Table 4), is about 50% of the dosage for control observed for ribbonweed and an order of magnitude lower than the dosage required for 80% control of floating pondweed (Table 3). Floating pondweed was not represented in the irrigation channels described in Table 4, and the evidence suggests that the derived value for E_L of 2 ppm x hr may grossly underestimate the quantity of acrolein required for control of this species.

DISCUSSION

Optimizing the Use of Acrolein

Until further information is available, and excepting for the moment situations infested with floating pondweed, it is suggested that values of K or 0.16 per hr and E_L of 2 ppm x hr may be substituted in equation (3) to give a conservative estimate of the quantity of acrolein required providing that the travel time is known. (Tables are available from the authors on request).

For multiple additions at the second and subsequent injections the dosage of acrolein required must be corrected for the lethal dosage (2 ppm x hr) residual from the previous upstream injection. In practice, particularly for short injection times, it may be difficult to achieve the

TABLE 4. ACROLEIN TREATMENTS IN IRRIGATION CANALS.[a] CALCULATION OF THE MINIMUM LETHAL DOSAGE (E_L) AT THE DOWNSTREAM LIMIT OF EFFECTIVE CONTROL USING EQUATION (3) WHERE E_0 IS THE DOSAGE AT THE INJECTION POINT AND ASSUMING A FIRST ORDER RATE CONSTANT FOR DISSIPATION (K) OF 0.16 PER HR. DATA COLLECTED BY THE WATER RESOURCES COMMISSION, NEW SOUTH WALES (A TO C) AND THE UNITED STATES BUREAU OF RECLAMATION (DTO G).

	Canal	Injection conditions C_0 (ppm)	τ (hr)	Distance treated (km)	Velocity (km/hr)	Temp. (C)	Dosage (ppm x hr)	
							E_0	E_L
A	Wah Wah Main	19.0	1.0	~30	0.8	13	19.0	0.06
B	Barren Box Outfall	0.85	40.9	15.3	0.86	27	34.7	2.0
C	Finley Berrigan	2.0	1.5	3.0	0.54	21	3.0	1.2
D	West May 1970	0.1	48	>24	1.9	18	4.8	0.63
E	Potholes June 1970	0.1	48	>20	2.5	19	4.8	1.33
F	West June 1970	0.1	48	>41	2.8	19	4.8	0.48
G	Potholes July 1970	0.1	48	>20	2.5	23	4.8	1.33

[a] Some of this data has been presented previously (8) but E_L was calculated using the best available value of K of 0.17 per hour.

coincidence of a downstream injection on the mass of residual acrolein. The evidence presented previously suggests that the minimum lethal dosage is represented by the area underneath the concentration-time curve, so superposition should not be critical. However, it may be advantageous to attempt some overlap and this should be achieved more readily by injecting sequentially in progression downstream.

The total dosage of acrolein required for one, two or ten additions is shown in Figure 2 as a function of travel time. The economy of two or ten additions compared with one addition is shown in Figure 3. As travel time approaches 15 hr, for example, the additional costs and inconvenience of two additions are balanced by a 50% saving in acrolein; more than two additions would probably not be warranted since the further economy of ten additions is only 17%.

Boundary Conditions

Some evidence has been presented to suggest that, within limits, lethal dosage is largely independent of the separate values of acrolein concentration and time of exposure. Consequently, the time for addition may be adjusted at the convenience of the operator or to maintain the concentration at a selected level. However, the lethality of a given dosage of many toxic substances is often reduced at very low concentrations or short exposure times (13) and in an analogous fashion practical experience suggests that limitations must be imposed on injection conditions to ensure satisfactory weed control with acrolein. The limitations also reflect concern for the safety of irrigated crops and non-target organisms:

concentration (C) ppm $0.1 < C < 15$
time of exposure (τ) hr $2 < \tau$

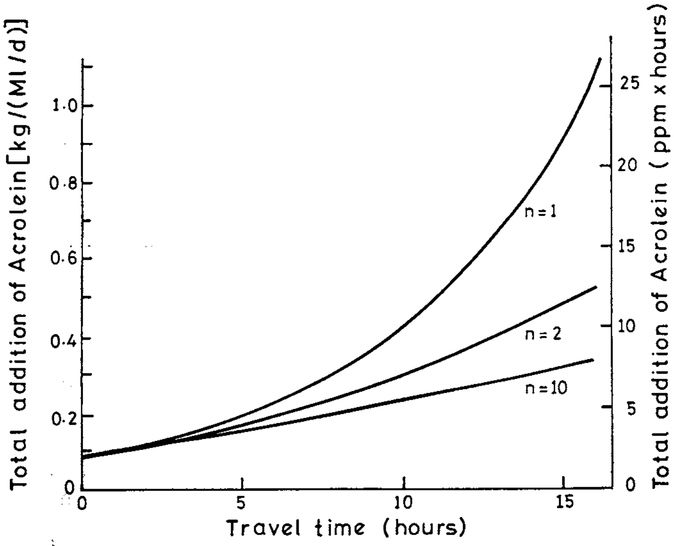

Figure 2. The total quantity of acrolein required for one, two, and ten additions to achieve control of aquatic weeds in irrigation canals.

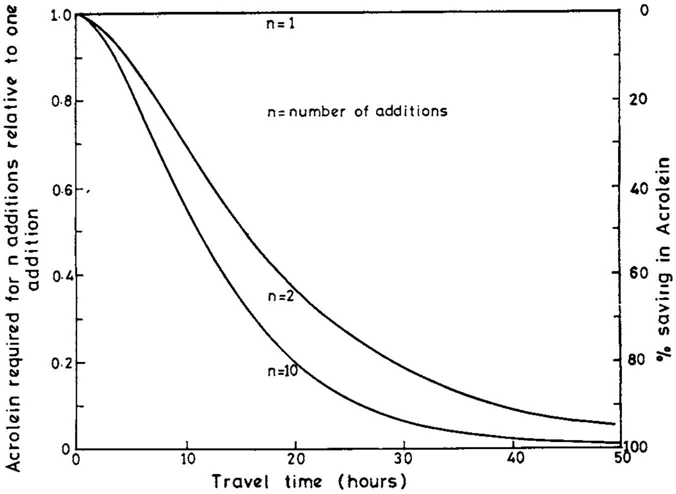

Figure 3. The economy of n additions of acrolein relative to one addition. (Travel time extends from the first addition to the downstream limit of the intended treatment.)

The minimum acceptable concentration was selected by reference to Table 4, and the minimum time for addition from the practical experience of personnel of the Water Resources Commission.[3] Imposition of a concentration maximum ensures the safety of irrigated crops (1, 4, 6) and, as a further precaution, government authorities restrict the use of water for 48 hours after treatment to allow dissipation to proceed. Fish life in irrigation channels is considered of secondary importance, but where water drains into natural watercourses or where water is ultimately used for domestic supply more severe restrictions on maximum concentration may be required. Taking 0.1 ppm as the downstream permissible level[4] a conservative estimate, from the safety viewpoint, of the permissible injection concentration could be calculated using equation (1), providing travel time was known. However travel times may be difficult to determine in many drainage canals since discharges are often extremely irregular, and dilution with untreated water may often ensure that concentrations do not reach hazardous levels.

Transverse Mixing

One of the assumptions implicit in this approach has been that the acrolein is uniformly mixed with the water. Bowmer and O'Loughlin (11), reporting a typical result for natural waterways (20), suggested that in uniform flowing channels the mixing length needed to attain a concentration deviation of not more than 5% from its mean value in the cross section may be of the order of 200 channel widths downstream. It was suspected that in Australian conditions dense weed growth may further impede the rate of herbicide mixing with the flow, with the consequence that plants at the edge of the channel may not receive a lethal dosage for a much greater distance.

However, computation of the areas underneath the concentration-time curves for six points in the cross section of

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[3] J. A. Todd, G. Smith, and K. Shaw. 1975. Personal Communications.

[4] Pesticides Review Committee, Victoria; Clean Waters Act, New South Wales, 1970: Regulations, 1972.

Lake View Channel (Figure 1) showed that dosages experienced were very similar, with a deviation of less than 4% from the mean. In this situation weed infestations were severe and the sampling station was about 1.5 km or 260 channel diameters downstream from the injection point. In Benerembah Channel, where the sampling station was about 1.5 km or 115 channel diameters downstream, the deviation in dosage measured in the leading edge was less than 9% from the mean.

These results suggest that problems of transverse mixing would have little influence on the adequacy of weed control, in accord with recent calculations (15) that uniform dosage should be achieved at a comparitively short distance from the injection point. For a typical irrigation canal, and assuming a lateral mixing coefficient representative of narrower or weedy channels (14), O'Loughlin (15) calculated that the edge dose is 33% of the centre line dose at 16 channel diameters downstream, and 87% of the centre dose at three times this distance.

Apparently errors in one-dimensional prediction of required dosage (equation 3) are only significant in smaller irrigation channels at distances very close to the injection point. Furthermore, in multiple additions, at the second and subsequent injection point, short distances of non-uniform mixing will be blanketed by the effects of lethal or near-lethal dosage residual from upstream. It has not yet been determined whether these conclusions remain valid for large, low velocity flows.

THEORY AND PRACTICE

The quantities of acrolein used in practice in several supply channels in the MIA, where ribbonweeds and pondweeds predominate, are shown in Table 5. Theoretical dosages calculated using equation (3), assuming that $K = 0.16$ per hr and $E_L = 2$ ppm x hr are also shown for coincident injection points. Typical injection conditions are shown for one of the channels in Figure 4. In three of the channels the quantity of acrolein required for weed control was about three times greater than predicted, and in one channel, about eight times greater. As required for routine maintenance in these situations, weed control was achieved to the end of the canal, and some over-treatment was anticipated. However, two of the channels (Barren Box Outfall and Widgelli 2) contained some floating pondweed which may require a dosage an order of magnitude greater than the value of E_L used in theoretical predictions.

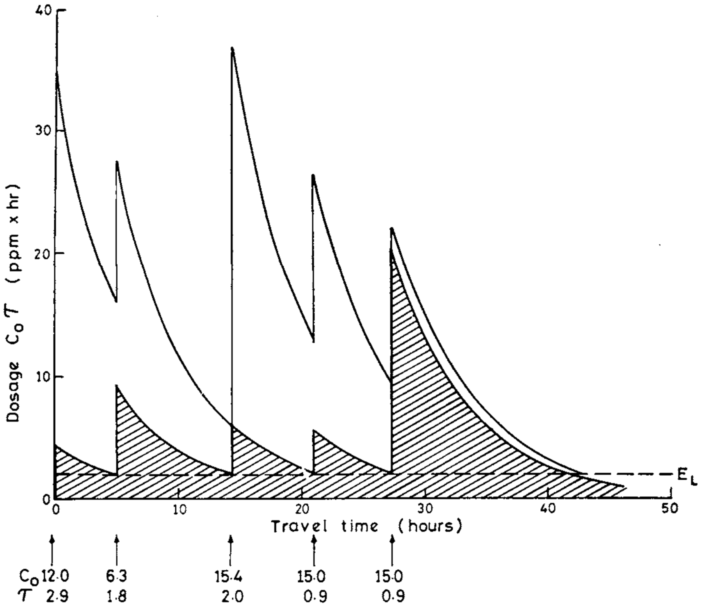

Figure 4. Acrolein additions used in practice in Barren Box Outfall Channel, and the dissipation of dosage with time assuming a value of K of 0.16 per hr. Actual dosage is derived from the product of concentration (C_0) and time (τ) for each addition. The hatched area shows theoretical requirements for coincident injection points (see also Table 5).

In contrast, in the Irrigation Districts of southern New South Wales, control of elodea is routinely achieved with dosages which are much smaller than predicted.[5] These differences may reflect the differences in weed species in the two areas. Some evidence from the literature (17) suggests that elodea is not particularly sensitive to acrolein, but the data is limited and may require re-consideration. Uncertainties in determining travel time may also be implicated, and may reflect the effects of different weed species and densities on the hydrological characteristics of the channels. This factor is now being investigated by comparing the behaviour of acrolein in weedy and clean channels.

In commercial recommendations (1) water velocity is included in factors affecting standard additions of acrolein, but the intended length of canal treatment is not considered. Consequently, although quite detailed records of acrolein use have been kept by government authorities,

TABLE 5. DOSAGES OF ACROLEIN USED IN PRACTICE[a] IN FOUR IRRIGATION CHANNELS IN THE MURRUMBIDGEE IRRIGATION AREAS, TOGETHER WITH THEORETICAL REQUIREMENTS FOR COINCIDENT INJECTION POINTS.

Channel	Date	Velocity (km/hr)	Discharge (Ml/day)	Distance treated[b] (km)	Number of additions	Dosage (ppm x hr)[c] Actual	Theoretical	Ratio
Barren Box Outfall	11/73	0.50	24	>20.9	5	104	38	2.7
Widgelli 2	12/73	0.54	73	>12.1	3	130	16	8.1
Lateral 58	12/73	0.25	15	>6.4	2	86	29	3.0
Widgelli 1	11/73	0.50	24	>8.1	1	69	27	2.6

[a] G. Smith. 1975. Personal Communication.
[b] Weed control effective to end of channel.
[c] A dosage of 24 ppm for 1 hr, or equivalent, corresponds to 1 kg of acrolein per megaliter/day.

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[5] J. A. Todd. 1975. Personal Communication.

travel times have not been included, and the data available for testing the usefulness of the approach presented here are rather limited. It is also recognised that several factors (e.g., weed species and density, temperature, and turbulence) have not been considered in theoretical predictions, and that experience and intuition are essential in assessing acrolein dosages appropriate for many irregular situations. This paper is presented not as an authoritative recommendation for the use of acrolein in practice, but as a simple and rational aid for management authorities, and as a basis for refinement and modification as further information becomes available.

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