Herbicides for Use in or Near the Aquatic Environment: Priorities for Environmental Quality Standard Development

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Statement of Use
This report reviews the available environmental data on the nine herbicides currently approved for use in or near water. It prioritises the chemicals for EQS development and will be of value to Agency staff in assessing the potential effects of these substances on water quality.

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EXECUTIVE SUMMARY

The Environment Agency are concerned with the impact of nine herbicides approved for use in or near water: asulam, dalapon, dichlobenil, diquat, 2,4-D amine, fosamine ammonium, glyphosate, maleic hydrazide and terbutryn. The purpose of this report is to review the available environmental data on those herbicides approved for use in England and Wales and, where necessary, make recommendations for the development of Environmental Quality Standards (EQSs).

The review comprises an effects and exposure assessment of these herbicides relating to the aquatic environment. The effects assessment derives from a review of their toxicity, persistence and bioaccumulation while the exposure assessment is based on an evaluation of the fate and behaviour of these chemicals in aquatic habitats combined with information concerning their production and usage in the UK.

None of the nine herbicides are given high priority for EQS development. Four of the herbicides were, however, classified as medium priority for EQS development. These were terbutryn, dichlobenil, glyphosate and asulam.

KEY WORDS

Environmental Quality Standards; aquatic toxicity; persistence, bioaccumulation, herbicides.

1. INTRODUCTION

This report reviews the aquatic toxicity, bioaccumulation and persistence of nine herbicides which are approved for use in or near water. The latter includes areas immediately adjacent to drainage channels, streams, rivers, ponds, reservoirs, canals, boreholes, dry ditches and areas designated for water storage and will, in most cases, include areas within flood banks. Section 2 comprises chemical profiles for each of the herbicides which incorporate data on: use, fate and behaviour, routes of entry to the aquatic environment and toxicity to aquatic organisms. The prioritisation of the herbicides for EQS development and discussion are set out in Section 3 and the main conclusions arising from this report are set out in Section 4. Tables summarising their freshwater and saltwater toxicity are located in Appendices A and B respectively and potable water standards are outlined in Section 1.5.

1.1 The use of herbicides in or near water

The use of herbicides in or near the aquatic environment is necessary to control weeds which interfere with activities such as irrigation, drainage, angling and other recreational activities or are damaging to the habitat. The prolific growth of three non-native weed species in particular; Japanese Knotweed, Giant Hogweed and Himalayan Balsam can be detrimental to populations of native species. These invasive plants cause problems because they grow rapidly, out-compete native species provide a poor habitat for insects, birds and mammals, increase the risk of river bank erosion when they die back in the autumn, and create potential flood hazards if dead stems fall into watercourses. Human health effects are also a problem with Giant Hogweed which can cause skin blistering on contact. The main users of aquatic herbicides are the Drainage Boards because herbicides approved for use near or in water provide effective control of weeds which reduce the efficiency of drainage channels.

Herbicides have the advantage that they can selectively remove undesirable species whilst leaving non-target species which may constitute an important part of the ecosystem. Areas of weed provide shelter for fish fry and invertebrates and often selective weed control, through the use of herbicides, is the preferred option since it results in only partial removal of the habitat. The approved herbicides in this review, though not particularly selective compared to other terrestrial herbicides can be used to achieve selective control by careful timing of application. If treatment is correctly targeted then habitat diversity can be improved by removing unwanted weeds to encourage growth of more desirable species (NRA 1995).

The major concerns, however, regarding the use of herbicides in or near the aquatic environment are the contamination of surface and ground waters extracted for potable supply, the ecotoxicological effects these herbicides may have on aquatic flora and fauna and the effects on the habitat and food sources of terrestrial animals. Due to the modes of action of the various active ingredients in herbicides on plant metabolic processes (e.g. photosynthesis inhibitors, growth regulators), it is to be expected that some non-target plants and algae, in particular, will be affected in and around the area of application. These may include primary producers such as cyanobacteria, algae and higher aquatic plants important to the functioning of the ecosystem. Application of herbicides into or near watercourses is therefore strictly controlled.

1.2 Herbicides approved for use in or near water

Products which are approved for use in or near water in England and Wales are listed in Pesticides 1995 (HMSO 1995). The legislative framework governing the use of these pesticides is summarised by NRA (1995). Aquatic weeds can broadly be divided into five groups: emergent weeds, floating weeds, submerged weeds, algae and waterside plants.

Partial treatment of emergent or floating leaves is achieved through using herbicides which can be applied directly to the leaves (2,4-D amine, glyphosate, and diquat). Submerged weeds should ideally be controlled by granular formulations such as dichlobenil and terbutryn which are adsorbed through plant roots. Herbicides approved for use in or near water are used on banks primarily to control three main species of invasive plants; Japanese Knotweed, Giant Hogweed and Himalayan Balsam which have displaced native species. Other undesirable species such as bracken are also effectively controlled through the use of these herbicides. There are 9 herbicides approved for use near water, these are shown in Table 1.1. It is important to note that there may be other formulations available which contain the above active ingredients, however, only the products shown in Table 1.1 are approved for use in or near water.

Table 1.1 Herbicides approved for use in or near water

Herbicide	Approved formulations	Control of aquatic weeds	Control of weeds on banks
Asulam	Asulox		x
Dalapon + dichlobenil	Fydulan		x
Dichlobenil	Casoron G, Casoron GSR	x	
Diquat	Reglone (liquid) Midstream (alginate)	x	
2,4-D amine	Dormone, Atlas 2,4-D	x	x
Fosamine Ammonium	Krenite		x
Glyphosate	Barcaly Gallup amenity, Glyphogan, Glyfonex, Clayton Swath, Helosate, Roundup, Roundup Pro, Roundup Biactive, Roundup Pro Biactive, Roundup Biactive Dry, Spasor, Stetson	x	x
Maleic hydrazide	Regulox K, Royal MH 180		x
Terbutryn	Clarosan 1FG, Algae Kit, Blanc Kit	x	

Only five herbicides are approved for application directly onto weeds in the water: glyphosate, dichlobenil, terbutryn, diquat and 2,4-D amine. The largest users of these herbicides are the Drainage Boards and farmers who use them to clear drainage ditches and channels. The quantities used in England and Wales in 1994 have recently been collated by the Centre for Aquatic Plant Management. The results are shown in Table 1.2. These are likely to represent only a small proportion (approximately 5-10%) of the total quantity of herbicides used for control of aquatic weeds. Whilst the figures are incomplete, they do provide an approximate indication of the relative usage of the nine herbicides used in aquatic situations. During 1994, adverse weather conditions resulted in a reduction in the amounts applied compared with previous years. In terms of amounts of actual active ingredient, dichlobenil, glyphosate, asulam and diquat appear to be the most heavily used aquatic herbicides in 1994. Dichlobenil and terbutryn are applied to the water as slow release granules and are the more persistent of the approved herbicides. Of the herbicides which are not approved for use in water but which can be used near water, asulam is the most heavily used with maleic hydrazide also having a significant usage. The two herbicides, dalapon and fosamine ammonium appear to be used in negligible quantities near water.

Table 1.2 Results from an aquatic herbicide usage survey, summarising responses received from 38 people (data from the Centre for aquatic Plant Management)

Herbicide	Total active ingredient (kg or l)	Maximum Area (ha)[4]	Minimum Area (ha)[4]	Total Product
Asulam	1610.40	366.00	-	4026
2,4-D amine	519.49	245.62	116.35	1105.3
Dalapon	92.50	6.25	1.89	125
Dalapon/ dichlobenil	16.75 (10.00)[1] (6.75)[2]	0.56	-	100
Dichlobenil G	1175.45	386.98	116.09	17414
Dichlobenil GSR	1293.18 (2468.63)[3]	230.93	129.32	6465.9
Diquat	1012.00	202.40	101.20	5060
Diquat alginate	57.95	5.80	-	579.5
Fosamine ammonium	0	0	-	0
Glyphosate	1614.43	322.89	-	4484.54
Maleic hydrazide MH180	0.00	0.00	-	0
Maleic hydrazide Regulox K	741.25	370.63	185.31	2965
Terbutryn	57.79	115.58	57.79	5779

Notes:
[1] Weight of dalapon
[2] Weight of dichlobenil
[3] Total weight of dichlobenil combined
[4] Dependent on application rate

An indication of the risk to the aquatic environment associated with the use of aquatic herbicides can be estimated by comparing the concentrations likely to cause ecotoxicological effects with the predicted exposure concentrations to aquatic organisms. The following two sections briefly summarise the effects of using herbicides in or near water and their likely routes of exposure to aquatic life.

1.3 Effects of applying herbicides onto or near water

Ecological effects from the use of herbicides applied in or near water can be divided into those which are direct and those which occur indirectly, mainly resulting from the depletion in oxygen. In the short term, effects on the dissolved oxygen levels resulting from the decaying plant material and the displacement of fauna which feed on macrophyte vegetation are likely to be most important. In addition, the release of nutrients from dying plants and the biomass of plant residues available for decomposition can lead to growth of micro-organisms and so increase the biochemical oxygen demand of the system. In the longer term, ecological effects may arise from the alteration in community structure and abundance of flora caused by the use of these herbicides.

In this review, the assessment of the effects of these herbicides on aquatic life is largely restricted to their direct toxic effects on freshwater organisms due to both the paucity and uncertainty of data relating to the effects resulting from deoxygenation. Where data of this nature are available for a particular herbicide, these have been included in the substance profile in Section 2. However, the need to have comparative effects data for each substance in order to standardise the classification for EQS development has necessitated the use of direct toxicity data for prioritisation purposes.

1.4 Exposure of herbicides to aquatic life

The exposure of these herbicides to aquatic organisms, deriving from their use in or near water courses, will depend on the application rate, the method of application, the number and location of the sites treated, as well as the fate and behaviour characteristics of the herbicides in water. These include such factors as their persistence and bioavailability to aquatic organisms. The relative risk resulting from exposure to herbicides used in or near water compared with the risk arising through other uses of these herbicides also requires consideration.

Aside from their use in or near water, these herbicides can also enter water (including groundwaters) from other sources associated with their use in terrestrial situations e.g. agriculture and non-agriculture use, and these inputs could far outweigh those resulting from the use of herbicides in aquatic situations. Entry to water from the use of these herbicides in terrestrial situations can occur via a number of pathways such as spray drift and surface run-off. These additional inputs will be particularly significant for herbicides such as asulam which are frequently applied from the air. Under these conditions it may be difficult to identify and avoid over-spraying small streams which may easily be hidden from view by overgrowing vegetation. Surface run-off and drainage from fields may also represent a significant route of entry for herbicides such as 2,4 D-amine and maleic hydrazide which are potentially mobile in soils. In addition, glyphosate/diuron mixtures are widely used by Local Authorities for weed

control on hard surfaces. The tendency for herbicides to be lost from treated areas will depend on a number of environmental factors including the application rate, the stage of development of the crop and weed cover, the soil type and the amount of rainfall. The physico-chemical properties of the substance in soil, in particular the adsorptive properties and biodegradability will also affect the amounts found in surface run-off and drainage waters from such applications.

The exposure of these herbicides to aquatic life can be reduced to some extent through good agricultural practice. There are several publications which provide guidance on the safe application and disposal of pesticides. In particular, the recently updated guidelines which are specifically aimed at users of aquatic herbicides entitled *Guidelines for the use of herbicides in or near watercourses and lakes* (MAFF 1995a) and *Control of Invasive Plants Near Watercourses* (NRA 1994). The MAFF guidelines advise on the correct usage of herbicides which have been approved for safe use in or near water under *The Control of Pesticides Regulations (1986) (COPR)* made under *The Food and Environment Protection Act, 1985 (FEPA)*. This document also lists the available guidelines for the use of pesticides in various situations.

Selection of the most appropriate herbicide, correct timing of application and partial clearance rather than total removal should all minimise the risk to aquatic life. It is recommended that small areas of weed (20-25%) are left as shelter for fish fry and as substrata for primary and secondary producers (Hellawell and Bryan 1982). It should also be noted that only a few of the available formulations containing the nine active ingredients are approved for use near or in water and care should be taken to ensure that the correct formulation is applied. Similarly, application of the pesticide should be made in accordance with the manufacturer's instructions and recommended procedures for proposed applications should be adhered to. Furthermore, other methods of control should also be considered, e.g. mechanical removal, biological, etc. for particularly sensitive areas. Deoxygenation of the water, resulting from the use of herbicides can be reduced by applying the herbicides early in the year when plant biomass is small and by removing cut weed from the water. Timing of applications can also be co-ordinated to avoid certain times of the year and certain areas (such as gravel beds) which are important for fish fry and egg survival. Methods which minimise the inputs of these herbicide to the aquatic environment are described in more detail in the *Guidelines for use of herbicides on weeds in or near water courses and lakes* (MAFF 1995a).

1.5 Potable water standards

The use of herbicides in or near potable water supplies is monitored by legislation and guideline levels that may or may not be derived on a health basis as shown in Table 1.3. The UK Water Supply (Water Quality) Regulations 1989 (HMSO 1989), the Surface Water Directive (CEC 1975) and the USEPA MCLs currently provide mandatory standards. The other health advisories and guidelines are not mandatory and are based on health effects.

Table 1.3 Potable Water Standards

Herbicide	UK Water Supply (Water Quality) Regulations (1989)[1] ($\mu g\ l^{-1}$)	DoE Advisory Value[1] ($\mu g\ l^{-1}$)	Surface Water directive (A1)[6] ($\mu g\ l^{-1}$)	Surface Water directive (A2)[6] ($\mu g\ l^{-1}$)	Surface Water directive (A3)[6] ($\mu g\ l^{-1}$)	WHO[2] ($\mu g\ l^{-1}$)	EPA standard (MCL)[3] ($\mu g\ l^{-1}$)	EPA Health Advisory[4] ($\mu g\ l^{-1}$)	Canadian Guidelines ($\mu g\ l^{-1}$)
Asulam	0.1	-	1	2.5	5	-	-	-	-
Dalapon	0.1	-	1	2.5	5	-	200	200	-
Dichlobenil	0.1	-		2.5	5	-	-	-	-
Diquat	0.1	-	1	2.5	5	-	20	20	70 (MAC)
2,4 D-amine	0.1	-	1	2.5	5	30	70	70	100 (IMAC)[5]
Fosamine ammonium	0.1	-	1	2.5	5	-	-	-	-
Glyphosate	0.1	1000	1	2.5	5	-	700	700	280 (IMAC)[5]
Maleic hydrazide	0.1	-	1	2.5	5	-	-	4000	-
Terbutryn	0.1	-	1	2.5	5	-	-	-	-

Notes to Table 1.3:

1. The UK Water Supply (Water Quality) Regulations 1989 gives a Prescribed Concentration Value of individual pesticides and related products as 0.1 $\mu g\ l^{-1}$ in drinking water. In addition, the sum of the detected concentrations of individual substances cannot exceed 0.5 $\mu g\ l^{-1}$. These values are not necessarily based on adverse health effects that may occur if the value is exceeded but may be based on other parameters such as aesthetics. The DoE, under certain circumstances may issue a Health advisory, as is the case with glyphosate which is based on health effects.
2. The World Health Organisation did not examine the majority of the herbicides mentioned in this report and therefore no guidelines were set for them. However, a guideline of 30 $\mu g\ l^{-1}$ was set for 2,4 D although this was not expressed as the amine itself.
3. Maximum Contaminant Level. Maximum permissible level of a contaminant in water which is delivered to any user of a public water system.
4. Lifetime Health advisory: The concentration of a chemical in drinking water that is not accepted to cause any adverse non-carcinogenic effects over a lifetime of exposure, with a margin of safety.
5. IMAC - Interim Maximum Acceptable Concentration. Recommendations for those substances for which there are insufficient toxicological data to derive a MAC (Maximum Acceptable Concentration) with reasonable certainty. These take into account the available health-related data, but employ a larger safety factor to compensate for the additional uncertainties involved.
6. Refers to the category of surface water defined in the Directive

* Form of 2,4-D not specified

2. CHEMICAL PROFILES

2.1 Asulam CAS: 3337-71-1

Asulam acid CAS: 2302-17-2

Molecular formula	$C_8H_{10}N_2O_4S$
Molecular weight	230.24
Vapour pressure	<1 m Pa at 20 °C
Solubility	4-5 g l^{-1} at 20-25 °C
Log K_{ow}	<1
Log K_{oc}	2.48 (K_{oc} of 302)
Stability	stable in water for >4 years at room temperature at pH 8.5

(RSC 1994; BCPC 1991; Kenyai 1980; WSSA 1989)

Asulam sodium

Molecular formula	$C_8H_9N_2NaO_4S$
Molecular weight	252.2
Vapour pressure	<1 x 10^{-7} mm Hg at 25 °C
Solubility	> 500 g l^{-1}
Log K_{ow}	1.01
Stability	can be hydrolysed to sulphanilamide, sulfanilic acid and 4-hydroxybenzene sulfonic acid under acid conditions with a half-life of >2 months at pH 3, 25 °C

(Confidential data 1995)

2.1.1 Production and use

Asulam is a selective systemic herbicide, absorbed by leaves and shoots, and is used for the control of bracken and docks (MAFF 1995a). It cannot be applied directly to the water surface, though some limited overspray may occur during aerial application of the herbicide to bracken though this can be reduced with careful mapping. The product is applied as a coarse spray to the foliage of terrestrial and riparian plants in the UK. It is recommended that asulam is applied to docks between April and September when the plants are in full leaf but before flower stems are present (MAFF 1995a). Quantities used to treat bracken and docks on river banks have been collated by the Centre for Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994, asulam can be considered on the most heavily used of those herbicides approved for use in water.

In the UK, its main use is for the control of bracken. The control of bracken is necessary to allow the regeneration of heather on moorlands to protect grassland and sheep from bracken invasion in upland areas. Bracken is an important vector of sheep ticks, and the bracken spores themselves are known to be carcinogenic. Data relating to quantities of asulam used in aerial applications show that in 1994, asulam was used on 167 occasions to treat an area of 8556 ha. The areas receiving the highest treatment are, in descending order; Northern England, Scotland, Wales and Midlands and Western (MAFF 1995b). It is manufactured at one site in the UK by Rhone-Poulenc.

2.1.2 Fate and behaviour in the aquatic environment

Asulam is likely to be moderately persistent in the aquatic environment. RSC (1994) report that it is stable for more than four years in water at pH 8.5, though it can be hydrolysed to some extent under acidic conditions (half-life of >2 months at pH 3, 25 °C). In the presence of sunlight, however, asulam is expected to degrade rapidly though no half-lives are reported. It will also biodegrade (Confidential data 1995).

Despite its low octanol-water partition coefficient (log K_{OW} of 1.01) and high solubility (>500 g l^{-1}) the following study suggests that, in the aquatic environment asulam will become associated with suspended solids. In an aerobic system consisting of a flooded soil, an asulam formulation "X" was observed to adsorb onto soil components and particulate matter suspended in the water. The herbicide was also conjugated as a result of microbial activity (Confidential data 1995).

However, the effects from spraying asulam (asulox containing 40% WV/V asulam sodium) onto bracken at 4.5 kg ha^{-1} (4 lb ai/acre) on local surface water and groundwater concentrations were investigated by Ball and Pink (1974). The highest concentration was 0.5 ppm (after one hour) found at the junction of two streams flowing through the sprayed area. Concentrations were <0.05 ppm after 72 hours. Concentrations in groundwater rose briefly to 0.23 ppm but were below the level of detection two weeks after spraying. The results suggest that asulam may be mobile in soils, as its physical-chemical properties suggest.

2.1.3 Other routes of entry into the aquatic environment

The principal use of asulam in the UK is for the control of bracken (8556 ha treated in 1994 by aerial application), mainly in upland areas of northern England and Scotland. Run-off from treated areas of bracken may therefore constitute larger loads into the aquatic environment than other practices. Due to the rough terrain found in areas where bracken control is necessary, asulam is frequently applied by helicopter. Spraying is undertaken by professional contractors who visit the sites and map watercourses and other areas which need protection and fall within the zones of high bracken density. Despite these measures some spray may not be intercepted by the bracken strands. Hence, the major potential route of entry for asulam into the aquatic environment is expected to be spray drift to water courses, particularly small streams which are not easily seen from the air, during aerial application of the herbicide to upland areas. Treatment of vegetation occurs between April and September, hence the maximum levels in waterways can be expected to occur in July and August. Given its relatively

low adsorptive properties (log K_{ow} of 1.01), it is also possible that the herbicide may run-off into waterways from treated land, especially if there is a heavy rainfall shortly after application. However, its low persistence in soils (see below) and rapid photodegradation on the foliage will reduce concentrations found in run-off.

In soil, asulam is not persistent with a half-life of approximately 6-14 days (RSC 1988). Tooby *et al.* (1980) reported that the maximum concentration of asulam likely to be measured at the point where it would enter water, if applied at the application rate recommended for use near water, to water 1 m deep, would be 1.0 mg l^{-1}. However, this would subsequently be diluted.

2.1.4 Toxicity and bioaccumulation in aquatic organisms

The toxic effects of asulam on aquatic organisms are shown in Table A1. Fish appear to be tolerant to asulam as acute and chronic effect concentrations are generally above 5000 mg l^{-1}. Freshwater invertebrates are more sensitive with an 48 hour EC50 and NOEC of 63.4 mg l^{-1} and 8.96 mg l^{-1} respectively reported for *Daphnia magna* (using formulation "X") (Confidential data 1995). However, macrophytes and algae appear to be the most sensitive group though sensitivity varies according to species (Table A1). Asulam sodium salt was reported to be of high toxicity to duckweed (*Lemna gibba)*, *Selanastrum costatum* and *anabaena flos-aqua* with EC50 and NOEC values ranging from 0.19 - 0.3 mg l^{-1} and 0.02 - 0.37 mg l^{-1} (not included in Table A1) (Confidential data 1995).

Only limited data are available relating to the effects of asulam on saltwater organisms. These are presented in Table B1. These data suggest that asulam is of low toxicity to saltwater crustaceans with effect concentrations reported to be above 100 mg l^{-1} (96 hour LC50 of >100 mg l^{-1} for both the Fiddler crab and Grass shrimp). The toxicity of an asulam formulation "X" to marine invertebrates ranges from 91 - 4455 mg l^{-1} (not included in Table B1) suggesting that it is of low acute toxicity to marine invertebrates. Again algae appear to be more susceptible; asulam sodium salt solution was reported to be highly toxic to the marine diatom *Skeletonema costatum* in a 120 hour study with effect concentrations occurring at concentrations between 0.04 - 4.6 mg l^{-1} (Confidential data 1995). There are no data available relating to the toxicity of asulam to saltwater fish. However, given the low toxicity of asulam to freshwater species it seems unlikely that asulam will have toxic effects on saltwater fish at the very low concentrations expected in sea water.

The low octanol-water partition coefficient (log K_{OW} of approximately 1) indicates that asulam will not bioaccumulate in aquatic organisms. The low propensity to bioaccumulate is confirmed by an experimental study using an asulam formulation "X", which reports a BCF <1 for the bluegill sunfish (*Lepomis macrochirus*). After 14 days depuration, the compound was undetectable, in whole fish or when divided into edible and non-edible portions (Confidential data 1995).

2.1.5 Analysis

Methods for the analysis of asulam in waters are briefly outlined below.

The sample is extracted using octadecyl-bonded silica solid phase cartridges (C18-SPE). The asulam in the resulting extract is determined by high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector; LOD = 0.2 $\mu g\ l^{-1}$ (HMSO 1987a)

or

The acidified sample is extracted into dichloromethane. The dried extract is concentrated using Kuderna-Danish apparatus and finally evaporated to dryness. The residue is re-dissolved in trimethylpentane (with 2% propan-2-ol) and any asulam present is determined by high performance liquid chromatography (HPLC) with an ultraviolet (UV) detector; LOD = Not given (HMSO 1987a).

2.2 Dalapon CAS: 75-99-0

Molecular formula	$C_3H_4Cl_2O_2$
Molecular weight	143.0
Vapour pressure	0.01 m Pa
Henrys Law constant	6.43 x 10^{-8} $atm.m^3/mole$
Solubility	900 g l^{-1} (25 °C) (dalapon-sodium) 502 g l^{-1} (25 °C) (dalapon)
Log K_{OW}	0.78
Log K_{OC}	0.48 (K_{OC} of 3)
BCF	2.2 (Log BCF of 0.35)
Stability	readily decomposed by soil organisms, slowly hydrolysed in aqueous solutions at 25 °C

(RSC 1994; BCPC 1991; Hansch and Leo 1981; Kenega 1980; SRC 1988)

2.2.1 Production and use

Dalapon is used as a mixture with dichlobenil mixture (the only available formulated product being Fydulan) as a broad spectrum herbicide. It is a granular formulation used for the control of annual weeds, seedling perennials and most perennial grass species. It may be applied to the water edge, but may not be applied directly to the water surface (MAFF 1995a). In terrestrial situations, dalapon-sodium is used to control annual and perennial grasses at <37 kg ha^{-1} on non-crop areas and at various rates on many other crops including citrus, coffee, rubber and sugar-cane.

It usually formulated as the sodium salt. The two salts (magnesium and sodium) are very soluble in water (BCPC 1991). The formulation Fydulan is manufactured by Zeneca.

2.2.2 Fate and behaviour in the aquatic environment

Dalapon is not excessively persistent in the aquatic environment with biodegradation being the predominant removal mechanism. In freshwater bodies, dalapon is degraded by micro-organisms with a half-life ranging from 9 - 60 days. Tooby *et al.* (1980) reported that the maximum concentration of dalapon likely to enter water, if applied at the application rate recommended for use near water, to water 1 m deep, would be 3.0 mg l^{-1}.

In field experiments, the decay of dalapon in aquatic sediments followed the classical pattern for a microbially mediated degradation, with a slow lag-phase (10-20 days) followed by a rapid phase of decline (<8 days). A first order half-life of 9 days was reported (Bowmer 1987).

2.2.3 Other routes of entry into the aquatic environment

Since usage of dalapon in riparian weed control appears low (see Section 1.2) it is likely that if dalapon is detected in the aquatic environment it is likely to have originated from terrestrial applications. In soil, degradation occurs over 4-6 months (Eglite *et al.* 1979; Kearney *et al.* 1969) with moist, damp conditions increasing the rate of break down (Kearney *et al.* 1969). Kaufman (1966) reported 100% degradation in seven days in a soil system in which the water was constantly recirculated and 100% degradation in three days in acclimated soil. Leaching of dalapon from soil may be significant particularly in dry sandy soils where microbial degradation is likely to be minimal. Eglite *et al.* (1979) found that dalapon leached to a depth of 40 cm though highest concentrations were recorded in the top 10 cm. Dalapon was classified as being highly mobile in soil using a soil TLC method (R_F of 0.69, Class 5) (Helling 1971).

2.2.4 Toxicity to aquatic organisms

The toxic effects of dalapon on freshwater organisms are shown in Table A2. with respect to acute toxicity, algae appear to be the most sensitive organisms tested. The lowest acute effect concentration was an EC50 of 2 mg l^{-1} for *Hormidium stoechidium* (Cullimore 1975). Invertebrates appear to be less sensitive to acute effects with a 48 hour LC50 for *Daphnia pulex* of 17 mg l^{-1} suggesting that dalapon is only moderately toxic to invertebrates (MAFF 1985) although only a few data are available for invertebrate tests. Chronic effects in invertebrates, however, appear to occur at relatively low concentrations. The copepod *Heliodiaptomus vidus* has a 315 hour LC50 of 0.1 mg l^{-1} (George and Hingorani 1982). Dalapon is of low toxicity to fish with toxic effects occurring at concentrations typically above 100 mg l^{-1}. However, few data are available concerning the toxicity of the formulated product Fydulan (containing a dalapon/dichlobenil mixture) which is the formulation approved for application to the water's edge, but these suggest that it is more toxic than dalapon alone. A 48 hour LC50 value of 8.1 mg l^{-1} was reported for rainbow trout (NRA 1995).

Table B2 summarises the toxicity of dalapon to saltwater organisms. Data were only available for algae. These suggest that marine algae are less sensitive to dalapon than freshwater species; the lowest acute and chronic effect concentrations were 25 mg l^{-1} and 20 mg l^{-1} respectively (Walsh 1972).

Dalapon has a low log K_{OW} (0.78) which indicates that it is unlikely to bioaccumulate in aquatic organisms. No experimental data are available.

2.2.5 Analysis

A method for the analysis of dalapon in waters is outlined below.

The acidified sample is extracted into diethyl ether. The dried extract is concentrated by Kuderna-Danish apparatus and hydrolysed with alkali. Impurities are removed from the extract by back washing with hexane. The remaining aqueous sample is acidified and further extracted into dichloromethane. The dried extract is concentrated as above and derivatised with acidified butan-1-ol. Dalapon is extracted into hexane and determined by gas chromatography (GC) using an electron capture detector (ECD); LOD ~ 0.024 $\mu g\ l^{-1}$ (HMSO 1985).

2.3 Dichlobenil CAS: 1194-65-6

Molecular formula	$C_7H_3Cl_2N$
Molecular weight	172.0
Vapour pressure	0.073 m Pa at 20 °C
Solubility	18 mg l^{-1} at 20 °C
Log K_{OW}	2.65
BCF	13
Stability	stable to sunlight and acids but rapidly hydrolysed by alkali to 2,6-dichlorobenzamide

(RSC 1994; BCPC 1991; Eadsforth and Moser 1983)

2.3.1 Production and use

Dichlobenil is a selective herbicide which is used for post- and pre-emergence control of annual and perennial weeds at the seedling and later stages of growth in fruit and other crops at 2.5-10 kg ha^{-1} (MAFF 1995a, BCPC 1991). Dichlobenil formulations Casoron G and Casoron GSR can be applied directly to the water and are used to control some floating and submerged leaves. They comprised slow release granules which are applied to the surface of still and slow flowing water (MAFF 1995a). Also, a dalapon + dichlobenil mixture (Fydulan) is applied as a granular formulation in non-crop areas near water courses in early Spring (4.5-12 kg ha^{-1} for control of aquatic weeds and at >20 kg ha^{-1} for total weed control) but this product is not approved for application directly to the water surface (MAFF 1995a). Data relating to the quantities used in or near water have been collated by the Centre for Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994 dichlobenil is one of the major herbicides used for weed control in water. Dichlobenil is manufactured by Duphar, PBI Gordon and Shell (RSC 1994). Fydulan is manufactured by Zeneca Agrochemicals.

2.3.2 Fate and behaviour in the aquatic environment

Due to its low solubility and moderate octanol-water partition coefficient (log Kow = 2.65), dichlobenil is likely to be adsorbed onto soil and to sediments in the aquatic environment. Tooby *et al.* (1980) reported that the maximum concentration of dichlobenil likely to enter water, if applied at the application rate recommended for use near or in water to water 1 m deep, would be 1.0 mg l^{-1}. Treatment of a farm pond (at pH 8.5) in New York State with dichlobenil (5.25 kg ha^{-1}) resulted in maximum concentrations of 1.4 and 8 ppm in the water and aquatic sediments respectively, seven days after treatment. After seven weeks, these maximum levels had decreased by 85 and 78% respectively. The concentration of dichlobenil had decreased to 0.002 ppm in the water and 0.13 ppm in the hydrosoil after 140 days (Rice *et al.* 1974).

A similar study was carried out by Lay *et al.* (1984) which monitored dichlobenil residues in a pond following application at 4.3 mg l^{-1}. The maximum concentration detected in water was 4.2 mg l^{-1} on day 3-5 after dosing. After 55 days the concentration had decreased to 1.5 mg l^{-1}. Another study carried out in Oklahoma reported rapid disappearance of dichlobenil (applied at 40, 20 and 10 ppm) from a pond, with only 3% remaining after 11 days, whilst an identical study in Denver reported that dichlobenil was persistent for more than 189 days (Cope *et al.* 1969).

In the aquatic environment, degradation of dichlobenil occurs through hydrolysis, volatilisation and biodegradation to 2,6-dichlorobenzamide (BAM). Miyazaki *et al.* (1975) reported that dichlobenil was biodegraded to BAM and other unknown metabolites in a pond study using labelled dichlobenil. More than 75% of the added dichlobenil was initially removed through volatilisation over the period of a month. The remainder was degraded to CO_2 via 2,6-dichlorobenzamide by micro-organisms. When a suspension of *Arthrobacter* was incubated with [^{14}C]dichlobenil, the herbicide was rapidly metabolised with 70% of the initially added [^{14}C], present in the form of BAM after 6 days (Miyazaki *et al.* 1975).

BAM is persistent in aquatic systems and is soluble in water. It could have effects on organisms within the water column, though it appears to be less toxic than the parent compound (see Section 2.3.4).

2.3.3 Other routes of entry into the aquatic environment

In soil, dichlobenil is unlikely to leach due to its relatively low solubility and moderate adsorptive properties (log K_{ow} of 2.65). It was classified as being of low mobility in soil using a soil TLC method (R_F of 0.22, Class 2) (Helling 1971). Degradation occurs via microbial breakdown to 2,6-dichlorobenzamide (BAM) which is slowly broken down to 2,6-dichlorobenzoic acid. The half-life of dichlobenil in soil is approximately 1-12 months depending on soil type (RSC 1994).

The limited mobility of dichlobenil suggests that run-off into water courses is unlikely. Furthermore, given that it is mainly applied as a granular formulation, contamination of the aquatic environment with dichlobenil is less likely.

2.3.4 Toxicity to aquatic organisms

The acute toxic effects of dichlobenil shown in Table A3, suggest that dichlobenil is of moderate toxicity to fish with effect concentrations of 8.1 - 20.0 mg l^{-1}. Invertebrates appear to be similarly sensitive with effect concentrations of 3.7 - 11 mg l^{-1} respectively. The two available algae studies indicate that the herbicide is also moderately toxic to algae with effect concentrations of 6 mg l^{-1} and 17.2 mg l^{-1} for *Hormidium barlowi* and *Chlamydomonas* species respectively. There are no available data on the toxicity to macrophytes.

The main degradation product of dichlobenil, 2,6-dichlorobenzamide (BAM) was not found to be toxic (survival and reproduction) to *Daphnia magna* at concentrations of up 320 mg l^{-1}. A concentration of 18 mg l^{-1} was, however, reported to significantly reduce the survival and growth of embryos and larvae of rainbow trout (considered sensitive life stages) (Van Leeuwen and Maas 1985).

Lay *et al.* (1984) investigated the effects of dichlobenil on physico-chemical properties and phytoplankton density in a pond resulting from an application of 4.3 mg l^{-1}. O_2^- and H^+ concentrations were significantly lower for 35 and 30 days respectively in the treated water compared to the controls (which is consistent with depressed photosynthesis as a result of plant damage or death.). The conductivity was also reported to be higher for 65 days following treatment. The diversity of phytoplankton species in the pond treated with dichlobenil, as indicated by the Shannon-Weaver diversity index, was significantly reduced.

The toxicity of dichlobenil to saltwater species is summarised in Table B3. Marine algae appear to be more tolerant to dichlobenil than freshwater species. Walsh (1972) reports acute and chronic effect concentrations which range from 90 - 150 mg l^{-1} and 25 - 60 mg l^{-1} respectively for four species (see Table B4). The harpaticoid *Nitocra spinipes* is more sensitive with a reported 96 hour LC50 of 0.27 mg l^{-1} for the formulated product Casoron G (Linden *et al.* 1979). There do not appear to be any data available for other saltwater invertebrates or fish.

Dichlobenil is not readily accumulated by aquatic organisms with a reported BCF of 13 for rainbow trout (RSC 1994). Moreover, the octanol/water partition coefficient for BAM is 120 (log K_{ow} of 2.08) implying a lower propensity to bioaccumulate than dichlobenil (Van Leeuwen and Maas 1985).

2.3.5 Analysis

A method for the analysis of dichlobenil is outlined below.

The sample is extracted with dichloromethane. The dried extract is concentrated by Kuderna-Danish apparatus and the dichlobenil is determined by negative ion chemical ionisation gas chromatography mass spectrometry (GCMS); LOD = Unknown

2.4 Diquat CAS: 2764-72-9

CAS: 85-00-7 diquat dibromide
CAS: 6385-62-2 diquat dibromide monohydrate

Molecular formula	$C_{12}H_{12}N_2$
Molecular weight	184.2
Vapour pressure	<0.013 m Pa
Solubility	700 g l^{-1} at 20 °C
Log K_{ow}	<0.1
Stability	DT50 of 74 days in simulated sunlight. Stable at pH 5- 7, 10% loss at pH 9 in 30 days (25 °C) in dark, degradation increases above pH 9

(RSC 1994; BCPC 1991)

2.4.1 Production and use

Diquat is a contact, bipyridylium desiccant and herbicide with some systemic properties. It is used for the control of some floating and submerged weeds and algae. It is available in a viscous gel formulation and can be used for localised control in still and fast-flowing water (MAFF 1995a). Diquat, supplied as the alginate formulation (Midstream) is suitable for partial treatment of submerged weeds and non-rooted plants. The alginate sticks to the plants and restricts movement of the active ingredient into the surrounding water. Control of aquatic weed represents one of its major uses though it is also used for potato haulm destruction, control of broad-leaved weeds and seed crop desiccation. Where grasses predominate, a diquat-paraquat formulation is used. Data relating to the quantities used in or near water have been collated by the Centre for Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994 diquat (particularly Reglone, an aqueous solution of the dibromide salt), is one of the major herbicides used for weed control in water. The above physico-chemical properties therefore refer to those of diquat dibromide. It is manufactured in the UK by Zeneca.

2.4.2 Fate and behaviour in the aquatic environment

Adsorption to sediment, particularly in turbid waters, uptake by plant material and photo-degradation are likely to be the major removal processes for diquat in the aquatic environment. The toxic mode of action of diquat is inactivated by turbid conditions through adsorption onto suspended solids. It is also rapidly photo-degraded in freshwater bodies (Funderburk and Bozarth 1967). Approximately 50% of the 14C from diquat was lost over 48 hours and more than 75% after 96 hours (Funderburk et al. 1966). In static water (laboratory test), initial concentrations of 0.5 - 1.0 mg l-1 decreased to 0.1 - 0.3 mg l-1 over 4 - 7 days Calderbank 1972 and Calderbank and Slade 1976, cited in WHO 1984) . Similarly in pond water treated

with diquat at 2.5 mg l^{-1}, residues of 0.01 - 0.08 mg l^{-1} were measured after 7 - 9 days. After 14 - 30 days no residues were found (Grzenda *et al* 1966 cited in WHO 1984).

Diquat is also biodegraded. Simsiman and Chesters (1976) reported a rapid degradation of ^{14}C-diquat sorbed to plant material. After 22 days, 32% had been degraded to water-soluble products and 19% was bound to the sediments. In a weed free system, however, most of the diquat was adsorbed to the sediments and persisted for much longer (180 days), suggesting that studies carried out in systems containing no plant material may over-estimate persistence and toxicity. Slow microbial degradation was favoured by aerobic conditions. The principal degradation products are picolinic acid, picolinamide and 1,2,3,4-tetrahydro-1-oxopyrido(1,2-a)-5-pyrazinium salt (TOPPS) (Cable *et al.* 1993).

Persistence of diquat in aquatic sediments has been shown to be long-term. Tuyen and Bhagava (1991) reported that four years after an application of diquat at 0.35 kg ha^{-1} (0.31 lb/surface acre), diquat was detected at 1.7 ppm. The extent to which diquat bound to sediments is bioavailable to benthic organisms is unclear.

2.4.3 Other routes of entry into the aquatic environment

Diquat is also applied as a herbicide to potato crops though its major use (and hence the application through which the major input of diquat into watercourses occurs) is as an aquatic herbicide. Diquat dibromide is strongly adsorbed to soils and run-off from soils therefore seems unlikely. In a soil TLC test, diquat was classified as being immobile in soil (R_F of 0.06, Class 1) (Helling 1971). Moreover, the adsorption process inactivates the herbicidal activity of diquat. Similarly, in the aquatic environment diquat is rendered ineffective under turbid and alkaline conditions. Biodegradation of free diquat can occur although microbial degradation of the adsorbed form is much slower. The major degradation process for diquat in the terrestrial environment is through photo-degradation on leaf surfaces (WHO 1984). Tooby *et al.* (1980) reported that the maximum concentration of diquat likely to enter water, if applied at the application rate recommended for use near or in water, to water 1 m deep, would be 2.0 mg l^{-1}.

2.4.4 Toxicity to aquatic organisms

Diquat is rapidly degraded by light and inactivated by adsorption onto particulate matter reducing the probability of toxic effects occurring in the field. However, the mode of action of diquat as a competitive inhibitor of photosynthetic electron transport does mean that it may have toxic effects on a wide range of phytoplankton and algae (Dodge 1971). The freshwater toxicity of diquat is shown in Table A4. As expected, algae are the most sensitive to diquat with the lowest EC50 value of 0.019 mg l^{-1} for *Navicula* sp. (Phlips *et al.* 1992). However, no macrophyte data could be located.

Diquat is of moderate toxicity to invertebrates with effect concentrations ranging from 1.0 - 7.1 mg l^{-1}. The lowest observed effect concentration refers to an eight day LC50 for *Daphnia pulex* (Crosby and Tucker 1966). The available data suggest that toxic effects of diquat on fish are also moderately low with LC50s typically above 4 mg l^{-1}. Sub-acute effects from diquat, however, have been reported in goldfish (*Carassius auratus*) at 1.10 mg l^{-1} (Berry

1984). In natural water bodies, toxic effects on fish are unlikely due to the adsorption of diquat onto aquatic weeds and sediment. However, the application of diquat to areas of water with prolific weed growth may result in a depleted oxygen supply due to the decay of plant matter. The lowest avoidance concentration for mayfly nymphs was reported as 1 mg l^{-1} (Verschueren 1983). The decay of the macrophytic community has also been reported to cause an increase in the conductivity and reduce the pH as well as deplete dissolved oxygen levels (Draxl *et al.* 1991).

Melendez *et al.* (1993) reported effects on a microbial community structure (comprising bacteria, algae, fungi, protozoa and micrometazoa) in a static microcosm at concentrations greater than 0.3 mg l^{-1} over a 21 day exposure period. Exposure of diquat within the microcosm, however, was maximised by the absence of sinks such as plant material and sediment. The effects observed may therefore not be indicative of those expected to occur in the field.

In a pond study, Hilsenhoff (1966) found that an application of 1 mg l^{-1} of diquat resulted in significant changes in the numbers of organisms, particularly in four species of snails and some arthropods (*Amphipoda talitridae*), collected from the shoreline vegetation due to the destruction of their habitat. Populations of bottom fauna remained relatively constant throughout the one month study. Fungi play an important role in conditioning of leaves which represent a primary energy source in ponds and streams, as well as being a significant part of the diet of benthic invertebrates. Fronda and Kendrick (1986) investigated the inhibition of feeding by the gastropod mollusc, *Lymnaea elodes*, a principal detritus feeder in ponds by exposing various fungi, on which the gastropod fed or which conditioned leaves on which the gastropod fed, to diquat. When the fungi were grown in a media containing 1 mg l^{-1} diquat there was a 54.5% reduction in survival of the gastropod mollusc when these were fed to the snails. In addition, the snails stopped grazing on leaves conditioned by fungi (*Beverwykella pulmonaria*, *Hormiactis ontariensis* and *Helicon elegans)* at diquat concentrations greater than 0.005 mg l^{-1} (thought to be because the fungi were inhibited at this concentration and therefore the leaves were not adequately conditioned for the snails). However one species of fungi, *Pseudoagerita matsushimae* appeared to be resistant to the diquat and snails fed on this species had the highest survival rate (Fronda and Kendrick 1986).

A microcosm study by Pratt *et al.* (1989) investigated the effect of sediment on estimates of diquat toxicity found that microbial communities were sensitive in the range of common application rates in the absence of sediment (effect levels ranged from 0.04 - 21.9 mg l^{-1} diquat) over three weeks. In sediment-amended microcosms, the toxic effects of diquat were eliminated and communities recovered completely within two weeks.

The dominant algal groups changed and total phytoplankton densities increased when a single dose of 1 mg l^{-1} was added to both an outdoor freshwater system and a laboratory multi-species system. A long term application of 0.3 mg l^{-1} over eight weeks had similar effects. The rise in phytoplankton biomass was due to an increase in the numbers of conjugatophytes and chlorophytes. Cladoceran populations were the most affected group (Draxl *et al.* 1991). However, the results should only be treated with caution as only limited controls were carried out and the data do not clearly show if effects on various organisms were due to direct effects of the herbicide or indirect effects, e.g. reduction in food sources.

There is some indication that residual phytotoxicity resulting from the release of diquat from sediments, may occur in sheltered and enclosed bodies of water depending on the type of bottom sediment. Birmingham and Colman (1982) found that adsorbed diquat could become desorbed and cause phytotoxic effects at 7% of the diquat adsorption capacity. They estimated that ten applications of diquat at 22.5 l ha^{-1} (the recommended application rate) to a 1 ha pond would result in sediment levels at which the residual phytotoxicity would become apparent, based on the assumption that all of the diquat became evenly bound in the top 3 cm of sediment.

The bioaccumulation of diquat in trout was investigated by Calderbank (1972) who measured concentrations of 0.3-0.4 mg kg^{-1} in the gut, liver and kidney in fish which had been exposed to 1 mg l^{-1} over seven days. Trout exposed to the same concentration over 16 days contained residues of 0.5-0.6 mg kg^{-1} but these levels decreased below the level of detection when the fish were transferred to fresh water. The bioaccumulation factor was not calculated.

Reish *et al.* (1979) reviewed the toxicity and bioaccumulation of diquat in marine and estuarine organisms. Diquat was found to have a low toxicity and was not bioaccumulated by any of the species tested.

The saltwater toxicity data relating to diquat are summarised in Table B4. The only available study suggests that acute toxicity to algae is apparent only at concentrations above 5000 mg l^{-1}. However, chronic effects have been observed at much lower concentrations (ten day EC50 = 15 - 200 mg l^{-1}) (Walsh 1972). There are no data available relating to the toxicity of diquat to saltwater species of fish. Given that inputs to the marine environment will primarily originate from rivers, it is probable that the rapid degradation and removal to sediments in rivers would preclude chronic effects occurring in the marine environment.

2.4.5 Analysis

A method for the analysis of diquat in waters is outlined below.

The sample is concentrated using an ion-exchange resin. The concentrated sample is derivatised using alkaline sodium dithionate. Diquat is determined by visible light spectroscopy; LOD = 0.01 µg l^{-1} (HMSO 1987b).

2.5 2,4-D amine CAS: 94-82-6

WRc has recently reviewed 2,4-D, including 2,4-D amine, for the Environment Agency (Lewis *et al.* 1996). Environmental quality standards (EQSs) of 200 µg l^{-1} and 40 µg l^{-1} (to be expressed as a maximum allowable concentration (MAC) and an annual average (AA) respectively) have been proposed for non-ester forms of 2,4-D for the protection of freshwater life. For ester forms of 2,4-D, EQSs of 1 and 1 µg l^{-1} (to be expressed as a MAC and AA respectively) have been proposed. An outlined of the available data are given below.

Molecular formula	$C_{10}H_{10}C_{12}O_3$
Molecular weight	249.10
Vapour pressure	negligible
Solubility	46 mg l^{-1} at 25 °C
Stability	The acid salts are very stable.

(RSC 1994)

2.5.1 Production and use

2,4-D amine is a selective herbicide used for the control of many terrestrial annual and perennial broadleaf plants. It can affect submerged weeds but is not approved for their control in the UK. The product is applied as a coarse spray to the foliage of target species from early summer to September (MAFF 1995a). The principal use of 2,4-D is in agriculture (for the control of broad-leaved weeds in cereals, turf, grassland, orchards, non-crop land, in forestry) but substantial quantities are also sold in formulations available to the amateur gardener. Data relating to the quantities used in or near water have been collated by the Centre for Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994, the use of 2,4-D amine, although significant, is much less than for other herbicides such as diquat and dichlobenil. It is manufactured by Agrolinz, Compania, Marks, Rhone-Poulenc, Universal Crop Protection and Vertac (RSC 1994). It is a strong acid and often formulated as the salt or ester derivative. Only the salt formulation, 2,4-D amine, is approved for use in water.

2.5.2 Fate and behaviour in the aquatic environment

In natural waters 2,4-D amine dissociates to form the 2,4-D carboxylate anion and does not seem to be persistent in water. An application of 4.48 kg ha^{-1} resulted in water concentrations of 189 and 4 ppb after 1 and 29 days respectively. In a confined water body where 4.49 kg ha^{-1} had been applied, the concentration of 2,4-D decreased from 689 ppb to 11 ppb after 1 and 39 days respectively (Tuyen and Bhargava 1991). Tooby *et al.* (1980) reported that the maximum concentration of 2,4-D likely to enter water if applied at the recommended rate to water 1 m deep would be 0.4 mg l^{-1}. A study by Schultz and Harman (1974) determined half-lives of 2 to 5 days at 30 °C for 2,4-D in water at initial concentrations of 0.17 and 1.6 mg l^{-1}. Boyle (1980) reported a half-life of 15 days at 20-25 °C. Degradation appears to be much slower at lower temperatures with a reported half-life of 45 days at 10 °C.

2.5.3 Other routes of entry into the aquatic environment

It is estimated that approximately 48 tonnes of 2,4-D are applied annually to terrestrial crops.

Monitoring data for Environment Agency Regions for 1992 and 1993 (TAPS 1995) indicate some peaks in 2,4-D concentrations in surface waters. The data indicate a maximum of 1.55 µg l^{-1} (average 0.015 µg l^{-1}, number of samples =212) and 1 µg l^{-1} (average 0.3 µg l^{-1}, number of samples = 149) reported for freshwater in Anglian and Severn Trent regions.

Monitoring was also undertaken for surface waters in the Thames regions, however, all samples were below the limit of detection. Monitoring data for 1993 show some high concentrations of 2,4-D were detected in freshwater in Wessex and Yorkshire regions (13.4 and 28 $\mu g\ l^{-1}$ respectively). However, there is no information on the source of these peaks.

In soil, 2,4-D is degraded rapidly by aerobic bacteria to methyl(methylaminomethyl)-dithiocarbamic acid which then undergoes further degradation to methyl isothiocyanate (which is volatile and evaporates), formaldehyde, hydrogen sulphide and methylamine (RSC 1994).

Leaching of 2,4-D is unlikely to occur due to its rapid biodegradation, although as an anion it is mobile in soil (under the soil TLC method it has an R_F of 0.69, Class 4) due to repulsion from the negatively charged soil particles.

2.5.4 Toxicity to aquatic organisms

The acute toxic effects of 2,4-D on freshwater organisms are shown in Table A5. The herbicide appears to be only moderately toxic to non-target species of algae. 2,4-D was found to enhance the growth rate of the freshwater unicellular green alga (*Chlamydomonas reinhardtii*) at 1 mg l^{-1}. Inhibitory effects were only detected at concentrations above 5 mg l^{-1} (Wong and Chang 1988). Toxicity to aquatic macrophytes, however, occurs at concentrations of <1 mg l^{-1} (Lewis *et al.* 1996). Frond production in the duckweed (*Lemna gibba*) was inhibited at <1 mg l^{-1}. 2,4-D is also moderately toxic to freshwater invertebrates. The lowest reported acute effect concentration was a 48 hour LC50 of 4 mg l^{-1} for *Daphnia magna* (Sanders 1970). 2,4,-D appears to be of moderately low toxicity to fish with the majority of effect concentrations occurring above 100 mg l^{-1} (see Table A5). One study by Birge *et al.* (1979), however, reports a 23 day and 27 day LC50 of 4.2 mg l^{-1} for rainbow trout. However, the toxicity data produced by Birge *e al.* for other substances have been criticised (Jones *et al.* 1992) and should therefore be treated with caution.

The saltwater toxicity of 2,4-D is summarised in Table B5. 2,4-D is moderately toxic to marine algae in both acute and chronic studies with reported EC50s of 50 - 60 mg l^{-1} (over 1.5 hours) and 50 - 75 mg l^{-1} (over 10 days) respectively (Walsh 1972).

2,4-D amine can taint and colour water at concentrations as low as 0.001 mg l^{-1} after chlorination. Therefore, it is not permitted for use where there is any risk to water abstracted for potable supply.

2.5.5 Analysis

A method for the analysis of 2,4-D amine in waters is outlined below.

The acidified sample is extracted into diethyl ether. The dried extract is concentrated using Kuderna-Danish apparatus and subsequently methylated with freshly prepared diazomethane. The methylated 2,4-D is determined using positive ion electron impact ionisation (EI) - gas chromatography mass spectrometry (GCMS); LOD = 0.025 $\mu g\ l^{-1}$.

Other analytical methods are given in Lewis *et al* (1996).

2.8.1 Production and use .

Maleic hydrazide is a growth regulator which is used to inhibit the sprouting of potatoes and onions and to retard the growth of grasses, hedges and trees. Its major use in the UK is as a sprouting suppressant of stored vegetables. In terms of its approved use near water, it is used to control the growth of grass on banks. It is not applied directly to the water. For growth retardation, maleic hydrazide is applied in aqueous solution as a coarse spray to the foliage of target species between March and September. Only one or two applications per season are required (MAFF 1995a). Data relating to the quantities used in or near water have been collated by the Centre for Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994, the use of maleic hydrazide, although significant, is much less than for other herbicides such as diquat and dichlobenil. Maleic hydrazide is manufactured by Uniroyal Chemical Limited.

2.8.2 Fate and behaviour in the aquatic environment

Maleic hydrazide is unlikely to persist in the aquatic environment as it is rapidly degraded by photolysis to form nitric acid, formic acid, succinic acid, maleic acid, fumaric acid and 12 other non-volatile products. The photolytic half-life is 15.9 - 34 days at pH 9. The major degradation product of photolysis is maleic acid. It can also be biodegraded (Howard 1991). The low log K_{ow} value (-3.67) and high solubility of maleic hydrazide indicates that it will not adsorb onto sediments.

2.8.3 Other routes of entry into the aquatic environment

In clay soils, maleic hydrazide is generally expected to be mobile although this is dependent on pH (Howard 1991). It does not appear to be persistent in soils with 87-100%, 86-100% and 47-67% degradation occurring over 40 days in sand, muck and clay respectively (Hoffman *et al.* 1962). Aerobic microbial degradation appears to be the major route of degradation. A half-life of 11 hours has been reported for a 90 day aerobic metabolism study carried out in loamy sand soil. In this study [^{14}C]- maleic hydrazide degraded readily with CO_2 as the principal degradation product. Other degradation products included: maleic acid, maleimide and five unidentified minor components (Confidential data 1995).

2.8.4 Toxicity to aquatic organisms

The acute toxic effects of maleic hydrazide to freshwater organisms are shown in Table A8. It appears to be of low toxicity to fish and invertebrates with the majority of effect concentrations typically above 100 mg l^{-1}. The lowest toxic concentration reported was a 48 hour LC50 of 56 mg l^{-1} for rainbow trout (Howard 1991). Few plant studies have been conducted, but effects in *Lemna* occur at about half the concentration they do for trout, and *Selenastrum* an order of magnitude less.

2.6.4 Toxicity to aquatic organisms

The acute toxic effects of fosamine ammonium are shown in Table A6. Fosamine ammonium appears to be of low toxicity to aquatic organisms with 96 hour LC50s of 278 mg l^{-1} and >415 mg l^{-1} for bluegill sunfish and rainbow trout respectively for the formulated product Krenite (concentration of active ingredient was not reported). However, there are no available data on its toxicity to freshwater plants. In addition, there are no available data concerning the toxicity of fosamine ammonium to saltwater organisms.

2.6.5 Analysis

A method for the analysis of fosamine-ammonium in waters is outlined below.

The sample is evaporated to dryness using a rotary evaporator. The residue is re-dissolved into mobile phase (acidic 0.02 M potassium dihydrogen phosphate) and the fosamine-ammonium is determined by high performance liquid chromatography (HPLC) using an ultraviolet (UV) detector; LOD = Unknown.

2.7 Glyphosate CAS: 38641-94-0

Molecular formula	$C_3H_8NO_5P$
Molecular weight	169.1
Vapour pressure	0.04 m Pa
Volatility	Negligible 1.94 x 10^{-7} mm Hg at 45 °C
Solubility	12 g l^{-1}
Log K_{OW}	0.0017 at 20 mg l^{-1}
Log K_{OC}	3.42 (K_{oc} of 2630)
Stability	trimesium cation DT50 >30 days in aqueous solution when exposed to light (25 °C, pH 9)

(RSC 1994; BCPC 1991; Kenega 1980; Environment Canada 1990)

2.7.1 Production and use

Glyphosate is a non-selective, non-residual post-emergence herbicide used on a wide range of grasses, sedges and broad leaved weeds applied at rates of 1.68-2.24 kg ha^{-1} for perennial species and 0.34-1.12 kg ha^{-1} for annual species. It has been approved for use on lilies, reeds and emergent weeds in or near watercourses and lakes and is applied in aqueous solution as a coarse spray to the foliage of target species typically between June and October (MAFF 1995a). Data relating to the quantities used in or near water have been collated by the Centre for Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994, glyphosate is one of the major herbicides. Glyphosate is manufactured by Monsanto. Pure glyphosate has a zwitterion structure and forms the following salts: glyphosate iospropylamine, glyphosate-

ammonium, glyphosate-sesquisodium and glyphosate-trimesium. These salts are acidic (BCPC 1991). In the water soluble herbicides such as Roundup and the newer formulation Roundup Pro Biactive, the isopropylamine salt of glyphosate is the active ingredient. There are no available data on the amounts of Roundup or Roundup Pro bioactive currently used or estimated for future use for the control of aquatic weeds.

2.7.2 Fate and behaviour in the aquatic environment

In freshwater, glyphosate is rapidly degraded by photo-degradation and biodegradation with a half-life of four days reported for a laboratory photolysis study. Under normal field conditions, however, biodegradation is likely to be the predominant removal process due to the high turbidity of natural waters (Hoie and Freistad 1986). Adsorption to sediments is also expected to occur and thus biodegradation under anaerobic conditions in sediments is likely to be the most important removal process (Tooby and Spencer-James 1978; Wan 1986).

The principal degradation product is aminomethylphosphonic acid (AMPA) for which a half-life of 10 weeks in pond water was reported (Environment Canada 1990). Sacher (1978) reports a half-life of 12 days in a non-flowing pond for glyphosate. In flowing water, maximum residues of glyphosate which could be expected at 1 and 5 miles downstream from banks initially treated with 150 ppb were only 10 and 3 ppb respectively.

In a pond study by Goldsborough and Brown (1993), it was found that glyphosate disappeared rapidly from the surface of water (half-life ranging from 3.5-11.2 days) following an application of 2.1 kg ha^{-1}. AMPA residues were detected in the water during the first 14 days after treatment. The concentrations of glyphosate and AMPA in the sediment increased for up to 36 days indicating that the sediment was the major sink for the herbicide.

Similar observations were made by Zaranyika and Nyandoro (1993) in a 72 day study where 38 ml of Roundup (395 g l^{-1} glyphosate) was added to tanks containing river water and sediment to give a solution containing 150 ppm glyphosate (15 g of glyphosate added to the tanks). An immediate loss of 35% from solution to sediment was demonstrated using HPLC analysis. On Day 0, 5.26 g of the 15.0 g of glyphosate added to the non-sterile tank was in the sediment leaving 97.5 ppm in solution. No appreciable degradation was observed in distilled water controls, while rapid degradation was observed in the river water/sediment systems. The results suggest that degradation is primarily microbial, but that adsorption is also a primary method of initially removing this herbicide from the water column.

2.7.3 Other routes of entry into the aquatic environment

Glyphosate can enter the aquatic environment through direct use near water courses or by surface run-off from terrestrial applications (Tooby 1980). It has a high affinity for particulate matter and is unlikely to leach into ground water or to run-off from soils (Environment Canada 1990; Reuppel *et al.* 1977). Both glyphosate and its major degradation product AMPA are biodegraded rapidly in the soil under aerobic and anaerobic conditions, further minimising the risk of contaminating the aquatic environment (Rueppel *et al.* 1977). Tooby *et al.* (1980) reported that the maximum concentration of glyphosate likely to enter water if applied at the

application rate recommended for use near or in water, to water 1 m deep, would be 0.18 mg l^{-1}.

In soil, the main route of degradation is through microbial break down. It has a reported soil half-life of less than 60 days (WSSA 1989). Microbial breakdown has been shown to be a co-metabolic process and can occur under both aerobic and anaerobic conditions (Environment Canada 1990).

2.7.4 Toxicity to aquatic organisms

The data relating to the freshwater toxicity of glyphosate, and two of its formulations, Roundup and Roundup Pro Biactive (360 g l^{-1} present as 480 g l^{-1} isopropylamine salt) are shown in Table A7. Glyphosate appears to be of moderate to low acute toxicity to fish and invertebrates with respective effect concentrations ranging from 86 - 97 mg l^{-1} and 3.2 - >780 mg l^{-1} respectively. The formulation Roundup is more toxic by an order of magnitude than the pure compound and the newer formulation Roundup Pro Biactive to some aquatic algae due to the use of the surfactant MONO818 which has a higher toxicity than glyphosate itself. Toxicity data for the newer formulation Roundup Pro biactive also shows acute toxicity to other aquatic organisms to be over an order of magnitude lower than the older formulation (Garnett, in Press). Elevated temperatures have also been found to increase the toxicity of glyphosate (Folmer *et al.* 1979).

The toxic effects on algae due to glyphosate occur in the range of 1 - 8.5 mg l^{-1} (Environment Canada 1990). For Roundup only a 72 hour EC50 = 7.9 mg l^{-1} for an unknown algae species is available. Given the higher toxicity of the formulated product, Roundup to freshwater organisms and the limited data available for algae, toxic effects due to this formulation could occur at concentrations less than 1 mg l^{-1}. It is possible therefore that glyphosate, or more specifically the formulation Roundup, may exhibit toxic effects on non-target algae and invertebrates in the field.

Lockhart *et al.* (1989) measured growth inhibition in the floating aquatic plant, *Lemna minor* resulting from applications of Roundup. Plant growth was relatively insensitive to glyphosate dissolved in the culture medium (threshold for toxicity between 16.9 - 169.1 mg l^{-1} but the plants were killed by application of glyphosate as a spray (water concentrations of 3.9 mg l^{-1}). The inhibited growth of the plants appeared to result mainly from the arrival of spray droplets onto the leaves rather than from uptake from the water suggesting that glyphosate would have little tendency to partition from water to plants. Non-target vegetation which is submerged below the water surface is therefore unlikely to be adversely affected by glyphosate applications. However, aquatic plants growing above the water surface could be affected by overspray or irresponsible disposal.

In a series of field studies, Hilderbrand *et al.* (1982) reported that concentrations of Roundup above the 96 hour LC50 value (52.0 mg l^{-1} in this case) did not adversely affect rainbow trout held in pens placed in a shallow moderately fast-flowing stream. Even concentrations up to 220 kg ai ha^{-1} (corresponding water concentration not given) had no effect suggesting that Roundup concentrations in the water column fall very rapidly through degradation and adsorption onto suspended matter. Furthermore, fish were reportedly demonstrating avoidance

reactions at concentrations >40 mg l^{-1} suggesting that in the field lower mortalities would be observed than suggested by laboratory data. However, results from another study investigating the toxic effects on safflower (*Carthamus tinctorius*), indicated that only a minor proportion of glyphosate was adsorbed onto suspended solids and sediments even in turbid irrigation water and that phytotoxicity was not significantly reduced.

The only effect concentration observed for Roundup in seawater was a 96 hour LC50 of 22 mg l^{-1} for *Nitocra spinipes* (Linden 1980 shown in Table B6). For glyphosate available data for marine invertebrates indicate low toxicity with reported LC50s in the range >10 - >1000 mg l^{-1}. There are no data available relating to the toxicity of the principal degradation product, AMPA to marine organisms.

The available data suggest that glyphosate is unlikely to bioaccumulate in aquatic organisms. A maximum BCF of 1.6 was reported for bluegill sunfish exposed to 0.6 mg l^{-1} glyphosate over 28 days (Environment Canada 1990). Bioaccumulation factors of less than 0.18 have been reported for channel catfish, largemouth bass and rainbow trout (Sacher 1978).

2.7.5 Analysis

A method for the analysis of glyphosate in waters is outlined below.

The sample is concentrated by rotary evaporation and a cation-exchange cleanup is carried out on the subsequent extract. The glyphosate is separated using High Performance Liquid Chromatography (HPLC), made fluorogenic and the fluorescence produced is measured using a fluorimeter; LOD = 0.08 µg l^{-1} (HMSO 1985).

2.8 Maleic hydrazide CAS: 123-33-1

CAS: 123-33-1	1,2-dihydropyridazine-3,6-dione
CAS: 1007-13-3	6-hydroxy-2H-pyridazin-3-one
CAS: 51542-52-0	Potassium salt
CAS: 28330-26-9	Sodium salt

Molecular formula	$C_4H_4N_2O_2$
Molecular weight	112.1
Vapour pressure	non volatile
Solubility	6 g l^{-1} at 25 °C
Log K_{ow}	-3.67 at pH 7
Log K_{oc}	1.6 (K_{oc} of 40)
BCF	5 (log BCF of 0.7)
Stability	degraded in light (25 °C) DT50 58 days at pH 5 and 7, 34 days at pH 9. Stable to hydrolysis. Rapidly degraded by soil and sewage treatment micro-organisms.

(RSC 1994; BCPC 1991; USEPA 1987; Kenega 1980)

2.8.1 Production and use .

Maleic hydrazide is a growth regulator which is used to inhibit the sprouting of potatoes and onions and to retard the growth of grasses, hedges and trees. Its major use in the UK is as a sprouting suppressant of stored vegetables. In terms of its approved use near water, it is used to control the growth of grass on banks. It is not applied directly to the water. For growth retardation, maleic hydrazide is applied in aqueous solution as a coarse spray to the foliage of target species between March and September. Only one or two applications per season are required (MAFF 1995a). Data relating to the quantities used in or near water have been collated by the Centre for Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994, the use of maleic hydrazide, although significant, is much less than for other herbicides such as diquat and dichlobenil. Maleic hydrazide is manufactured by Uniroyal Chemical Limited.

2.8.2 Fate and behaviour in the aquatic environment

Maleic hydrazide is unlikely to persist in the aquatic environment as it is rapidly degraded by photolysis to form nitric acid, formic acid, succinic acid, maleic acid, fumaric acid and 12 other non-volatile products. The photolytic half-life is 15.9 - 34 days at pH 9. The major degradation product of photolysis is maleic acid. It can also be biodegraded (Howard 1991). The low log K_{ow} value (-3.67) and high solubility of maleic hydrazide indicates that it will not adsorb onto sediments.

2.8.3 Other routes of entry into the aquatic environment

In clay soils, maleic hydrazide is generally expected to be mobile although this is dependent on pH (Howard 1991). It does not appear to be persistent in soils with 87-100%, 86-100% and 47-67% degradation occurring over 40 days in sand, muck and clay respectively (Hoffman *et al.* 1962). Aerobic microbial degradation appears to be the major route of degradation. A half-life of 11 hours has been reported for a 90 day aerobic metabolism study carried out in loamy sand soil. In this study [^{14}C]- maleic hydrazide degraded readily with CO_2 as the principal degradation product. Other degradation products included: maleic acid, maleimide and five unidentified minor components (Confidential data 1995).

2.8.4 Toxicity to aquatic organisms

The acute toxic effects of maleic hydrazide to freshwater organisms are shown in Table A8. It appears to be of low toxicity to fish and invertebrates with the majority of effect concentrations typically above 100 mg l^{-1}. The lowest toxic concentration reported was a 48 hour LC50 of 56 mg l^{-1} for rainbow trout (Howard 1991). Few plant studies have been conducted, but effects in *Lemna* occur at about half the concentration they do for trout, and *Selenastrum* an order of magnitude less.

Toxic effects on saltwater organisms appear to occur in the same range as to freshwater species with 96 hour EC50 and LC50s of >111 and >103 mg l^{-1} for Eastern oyster and mysid shrimp respectively (see Table B7). There were no toxicity data available for saltwater fish.

2.8.5 Analysis

A method for the analysis of maleic hydrazide in waters is outlined below.

The sample is reacted with 2,4-dinitrophenylhydrazine to form a hydrazone. The hydrazone is extracted with dichloromethane and the extract dried. The dried extract is gently evaporated to dryness and the residue re-dissolved in acetonitrile. The hydrazone produced is determined by high performance liquid chromatography (HPLC) using an ultra violet (UV) detector; LOD ~ few µg l^{-1} (HMSO 1988).

2.9 Terbutryn CAS: 886-50-0

Molecular formula	$C_{10}H_{19}N_5S$
Molecular weight	241.4
Vapour pressure	0.128 m Pa at 20 °C
	0.225 m Pa at 25 °C
Solubility	25 mg l^{-1} at 20 °C
	22 mg l^{-1} at 20 °C
Log K_{ow}	3.49
	3.65
BCF	90
Log K_{oc}	2.85 (K_{oc} of 708)
	2.39-3.16 (K_{oc} of 247-1450 corresponding to five soil types)
Log K_{om}	2.16-2.93 (K_{om} values of 145-852 corresponding to five soil types)
Stability	no significant hydrolysis at pH 5, 7 or 9 soil, DT50 14-15 days

(RSC 1994; BCPC 1991; Kenega 1980; Lockhart *et al.* 1983; Confidential data 1995)

2.9.1 Production and use

Terbutryn is a triazine herbicide used in the control of grasses in winter cereals applied in the Autumn at a rate of approximately 1.5 kg ha^{-1}, and also as a co-formulated mixture for pre-emergent weed control for peas and potatoes. As an aquatic herbicide, it is authorised for use in and or near watercourses for the control of floating and submerged weeds. Terbutryn is applied as a granular, slow release formulation once per season, in April or May before a heavy growth of weed has developed to reduce the risk of water de-oxygenation (MAFF 1995a). It is applied to still or slow moving waters (<1 m per 3 minutes) only, at a rate of 0.05 - 0.1 ppm. Data relating to the quantities used in or near water have been collated by the Centre for

Aquatic Plant Management. The available data are presented in Table 1.2 and further discussed in Section 1.2. These indicate that in terms of relative use in 1994, the use of terbutryn, is quite small compared with other aquatic herbicides. Terbutryn is not manufactured in the UK (only in the USA) and is sold in the UK as Prebane 500 SC (a herbicide which is used in *winter* cereals) and Clarosan 1FG, the aquatic herbicide. Clarosan is formulated in the UK at a plant in Huddersfield. Prebane 500 SC is imported as a ready formulated product which is packaged at a site in Cambridgeshire.

2.9.2 Fate and behaviour in the aquatic environment

In the aquatic environment, aerobic microbial degradation is the primary removal mechanism for terbutryn. Photolysis and hydrolysis may also occur though these processes will not be significant degradation pathways compared to biodegradation. The photolysis product hydrido terbutryn has not been found in aquatic systems (Confidential data 1995). The half-life of terbutryn in natural water bodies ranges from 2 weeks to two months. Half-lives in sediments are considerably higher, up to 8 months in pond sediment. From the low vapour pressure, the relatively high water solubility and strong adsorptive properties, terbutryn can essentially be regarded as being non-volatile from water. The principal degradation products are hydroxyterbutryn, N-deethylhydroxyterbutryn and terbutryn sulphoxide (Cable *et al.* 1993).

In water, the main breakdown product is hydroxy terbutryn, though de-ethyl terbutryn also occurs to some extent. Given the higher biological activity of the de-alkylated triazine herbicides as compared to the hydroxy metabolites, de-ethyl terbutryn, in addition to the parent compound, will be of concern as regards environmental effects (Confidential data 1995).

Biodegradation of terbutryn in the aquatic environment varies according to the temperature. A pond with approximately 3000 m^3 water was treated with 100 g terbutryn. After the first application in July, terbutryn was degraded with a half-life of 6-10 days, with water temperatures of 2 - 25 °C. After the second application at the end of August, the degradation was rapid initially then flattened out with temperatures decreasing from 20 °C to 10 °C (Confidential data 1995).

Adsorption to sediments is also likely to play a role in reducing water concentrations, particularly in shallow waters. After 1-2 months, adsorption constants of 10, 5, 3 and 6 l kg^{-1} were reported for terbutryn, hydroxy terbutryn, hydroxy de-ethyl terbutryn and de-ethyl terbutryn respectively in a river system after 73 days. In a pond system, these were 78, 19, 9 and 31 l kg^{-1}. The reversibly adsorbed, i.e. extractable residues accounted for 50-70% of the total sediment residues (Confidential data 1995).

Once bound to sediments, biodegradation of terbutryn takes considerably longer than in the water column. In a laboratory study, terbutryn was found to degrade slowly in static culture flask incubators with a reported half-life of 240 days in pond sediment and 180 days in river sediment. Hydroxy terbutryn was the major degradation product though n-deethylhydroxytebutryn and terbutryn sulphoxide were also present in significant amounts (Muir *et al.* 1982).

Mackenzie *et al.* (1983) applied 0.05-0.4 mg l^{-1} of terbutryn to ponds in Ontario, Canada and reported that about half this remained in the water column while half partitioned into the sediment. Persistence varied from little or no disappearance after 41 days to rapid disappearance in a few days. Low residue levels were identified in sediments 12 months after treatment.

The predicted environmental concentration (PEC) in surface waters, in the short term, which could occur under reasonable worst case conditions from the use of terbutryn was estimated to be 6 µg l^{-1}, relating to its main use as a herbicide when applied at 1.5 kg ha^{-1} to annual crops. The long term PEC in surface waters is estimated as <0.1 µg l^{-1} for terbutryn and <0.01 µg l^{-1} for de-ethyl terbutryn (Confidential data 1995). Indirect exposure of water bodies from overspray of fields results in an estimated maximum local concentration of 0.006 mg l^{-1}, assuming an application rate of 1.5 kg ha^{-1}, 1% drift to water and subsequent distribution throughout 25 cm of water (Confidential data 1995). A rapid dilution and degradation would, however, reduce this level considerably in a short amount of time. Drift to stagnant water or by run-off from treated fields would result in an estimated 0.0001-0.001 mg l^{-1} occurring only locally and on a seasonal basis (Confidential data 1995). The PEC for de-ethyl terbutryn is estimated to be one tenth that of terbutryn. Its PEC would therefore be below 0.01 µg l^{-1} (Confidential data 1995).

2.9.3 Other routes of entry into the aquatic environment

In soil, biodegradation is probably the major degradation process for terbutryn, with a reported half-life of 14 - 28 days (RSC 1994). The half life of terbutryn in biologically active soils is around two weeks after spring application and about six weeks after autumn application. However, persistence of terbutryn in soils is dependent on soil type with aerobic half-lives varying from 38 days in a loamy sand to two weeks in fresh field soil (silt). The main metabolite is hydroxy terbutryn (25% after six months in silt). Degradation of terbutryn under anaerobic and sterile conditions was observed to be very limited suggesting that microbial degradation is the dominant degradative mechanism. The degradation pathways involve cleavage of methylthio- group under formation of the hydroxy derivative and de-ethylation. Since hydroxylation is the fastest reaction the major metabolite is likely to be hydroxy terbutryn (Confidential data 1995).

Soil leaching studies indicate that terbutryn does not readily leach. A column leaching study, carried out to EPA Guidelines, showed only 0.1-3.8% of the applied terbutryn in the leachate of soils with an organic matter content of above 0.9%. In a sandy soil with an organic matter content above 0.9%, 9.7% of the applied terbutryn was found in the leachate. Bis-dealkylated terbutryn and more polar metabolites such as dealkylated hydroxy triazines are more mobile, though they occur only as minor soil degradation products (Confidential data 1995).

2.9.4 Toxicity to aquatic organisms

The toxic effects of terbutryn to freshwater organisms are shown in Table A9. Terbutryn is highly toxic to aquatic organisms with effect concentrations ranging from 0.0034 mg l^{-1} to 4 mg l^{-1}. As expected algae appear to be particularly sensitive with growth inhibition occurring

at concentrations as low as 0.0009 mg l^{-1}. Freshwater invertebrates and fish are also sensitive to terbutryn with respective acute effect concentrations ranging from 1.4 - 2.66 mg l^{-1} and 1.1 - >4 mg l^{-1}. Effects from terbutryn appear to be mainly acute since chronic exposure studies report similar effect concentrations. To give an indication of the probability of toxic effects arising in the aquatic environment (under reasonable worst case conditions), the reported No Observable Effect Concentrations (NOECs) are compared with the Predicted Environmental Concentration (PEC).

The lowest EC50 found in freshwater algae growth inhibition tests was 0.0034 mg l^{-1}. With a short term PEC of 6 µg l^{-1}, growth inhibition of some algae species could occur (therefore the NOEC/PEC ratio is lower than 1 for the blue-green algae *Anabaena flos-aquae*). The lowest response for freshwater crustacean species was an EC50 of 1.4 mg l^{-1}, for *Daphnia magna* (though a more recent study reports a slightly higher 48 hour EC50 of 2.66). The NOEC/PEC ratio (PEC = 6 µg l^{-1}) for *Daphnia magna* is 217, based on a NOEC of 1.3 mg l^{-1}.

The most acutely sensitive fish species was rainbow trout with a reported 96 hour LC50 of 1.1 mg l^{-1}. Chronic effects on fathead minnows were examined during a 34 day exposure of embryos and larvae to concentrations ranging from 0.21 - 3.4 mg l^{-1}, the NOEC (for growth) was 0.84 mg l^{-1}. Given a short term PEC of 6 µg l^{-1}, the NOEC/PEC ratio is 140.

Since the PECs of de-ethyl terbutryn are lower by a factor of 10, NOEC/PEC ratios of this metabolite are greater than for the parent compound. Toxicity of terbutryn will therefore be the primary concern for aquatic organisms.

In addition to the direct toxic effects of terbutryn to aquatic organisms, effects may also occur due to changes in the physico-chemical properties of the water. For instance, reductions in dissolved oxygen following terbutryn treatments have been observed by a number of authors (Robson *et al.* 1974, Crossland and Elgar 1974 and Wingfield and Johnson 1981). Murphy *et al.* (1981) also noted effects due to increases in dissolved CO_2, BOD, NH_4-N and PO_4P in canals which had been treated with terbutryn at 0.01 g l^{-1} and <0.02 g l^{-1}. At 0.09 g l^{-1}, both filamentous plants algae and submerged vascular plants were severely suppressed for 3-12 months. No phytoplankton blooms were noted at any of the sites. In a separate study, the same authors reported pronounced macrophyte destruction in treated canals. Loss of groups previously associated with the plants was accompanied by an increase in the abundance of certain taxa of benthic fauna, particularly *Lumbriculidae* and *Nematoda*. However, at another site where filamentous algae had survived following less severe treatment, fauna recovered in parallel with submerged flora (Hanbury *et al.* 1981).

Changes in community structure were also observed by Tyson (1974) who reported changes in dominance from epiphytic "high oxygen" animal species to benthic "low oxygen" species in ponds and ditches following treatment with terbutryn. Longer-term effects have been investigated by Robson *et al.* (1978). Temporary reductions in the dominant *Cladocera* and *Copepoda* populations were observed after each treatment but there was little overall effect on size, diversity or seasonal development of the zooplankton community.

The effects of terbutryn (0.05 mg l^{-1}) and diquat (1 mg l^{-1}) on small microcosms containing water, sediment and *Elodea canadensis* were investigated by Cragg *et al.* (1984). Total numbers of planktonic bacteria were found to increase significantly by 3-11 fold and

heterotroph counts also rose by 3-23 fold. This was accompanied by a decrease in pH and dissolved oxygen content and an increase in alkalinity and free CO_2 concentrations.

The toxicity of terbutryn to saltwater organisms appears to be greater than to freshwater species, especially to algae. A nine-day EC50 of 0.0009 mg l^{-1} has been reported for the marine diatom, *Skeletonema costatum*, see Table B8. The most sensitive invertebrate tested was the Mysid shrimp with a 96 hour EC50 of 0.74 mg l^{-1}. Marine molluscs are also sensitive, though to a lesser extent, with an 48 hour EC50 of 5.6 mg l^{-1} reported for the Quahog clam (Confidential data 1995).

Terbutryn has a log Kow of 3.65 suggesting a propensity to bioaccumulate. However, the available experimental data, suggests that bioaccumulation will not occur to any great extent in aquatic organisms. In a flow-through bioaccumulation study with bluegill sunfish (*Lepomis macrochirus*) a steady state was reached after 10 days, with a BCF of 100 for the edible parts, 240 for the non-edibles, 160 for the whole fish. In a 14 day depuration period, 60% and 88% of the uptake amount was eliminated from the edible and non-edible parts, respectively.

2.9.5 Analysis

A method for the analysis of terbutryne in waters is outlined below.

The alkaline sample is extracted into dichloromethane and the dried extract concentrated by Kuderna-Danish apparatus. The terbutryne in the extract is determined by gas chromatography using a nitrogen selective detector; LOD ~ 0.15 µg l^{-1} (HMSO 1985).

3. DISCUSSION AND PRIORITISATION FOR EQS DEVELOPMENT

In assessing the potential risk of substances to the aquatic environment, a number of areas require consideration such as toxicity, bioaccumulation, persistence and usage. Many schemes of varying complexity are available in the literature which prioritise chemicals. This review has adopted a scheme similar to those used to prioritise timber treatment chemicals and the chemicals used in fire fighting foams (Williams 1994, Wilkinson 1994), based on a prioritisation scheme developed for the Department of the Environment (DoE) for the selection of candidate I substances that are potentially dangerous to aquatic life (Hedgecott and Cooper 1991).

The scheme follows a "Decision Tree" method in which chemicals are assigned to a final priority category (e.g. high, medium, low or not a priority). Substances are selected for EQS development on the basis of a combination of their toxicity, bioaccumulation, persistence and quantities used, see Figure 3.1. The categorisation of values as high, medium or low, although simplistic, avoids problems associated with other more complex prioritisation schemes where the various parameters are scored and these are then combined. Since the amounts used refers to quantities used in or near water, the priority scheme classifies the substances according to their present use as aquatic herbicides. Any significant change in the amounts used over time will therefore alter the classification and it may be necessary to re-classify these substances should there be a large increase in the usage. Similarly the extent to which these herbicides are used on weeds growing in farming areas and upland areas, e.g. bracken, are not taken into account by the scheme, for the sake of simplicity. Inputs arising from these applications are considered separately in the discussion below.

Owing to the paucity of public data relating to actual quantities used for this purpose in the UK it is not possible to categorise substances used as aquatic herbicides on an accurate quantitative basis (see Section 1.2). It is, however, possible to use descriptors e.g. high or low usage based on the limited data on usage in Table 1.2 with an arbitrary 'cut off' point of approximately >500 = high. The criteria for classifying substances based on their toxicity, bioaccumulation and persistence in aquatic ecosystems are shown in Table 3.1. A summary of the effects and likely exposure of aquatic organisms to each of the herbicides is shown in Table 3.2. The behaviour of the substances in soil and the Predicted Environmental Concentration (PEC) in water resulting from their use on arable crops (Tooby 1980) are also given where data are available. Table 3.3 summarises the toxicity, bioaccumulation and persistence of the reviewed substances and assigns them to low, medium and high priority bands as described in Table 3.1. The toxicity classifications are based on the most sensitive species for which data are available. Once each chemical has been classified as either high, medium or low for each parameter it is then possible to classify it as either a low, medium or high priority candidate by use of the selection scheme shown in Figure 3.1.

Table 3.1 Criteria for classifying chemicals

Hazard	Descriptor	Effect	Range
Aquatic toxicity	high	lowest toxic concentration	<1 mg l^{-1}
	medium		1-10 mg l^{-1}
	low		>10 mg l^{-1}
Bioaccumulation	high	BCF	>1000
	medium		100-1000
	low		<100
Persistence	high	half-life in water	>100 days
	medium		10-100 days
	low		<10 days

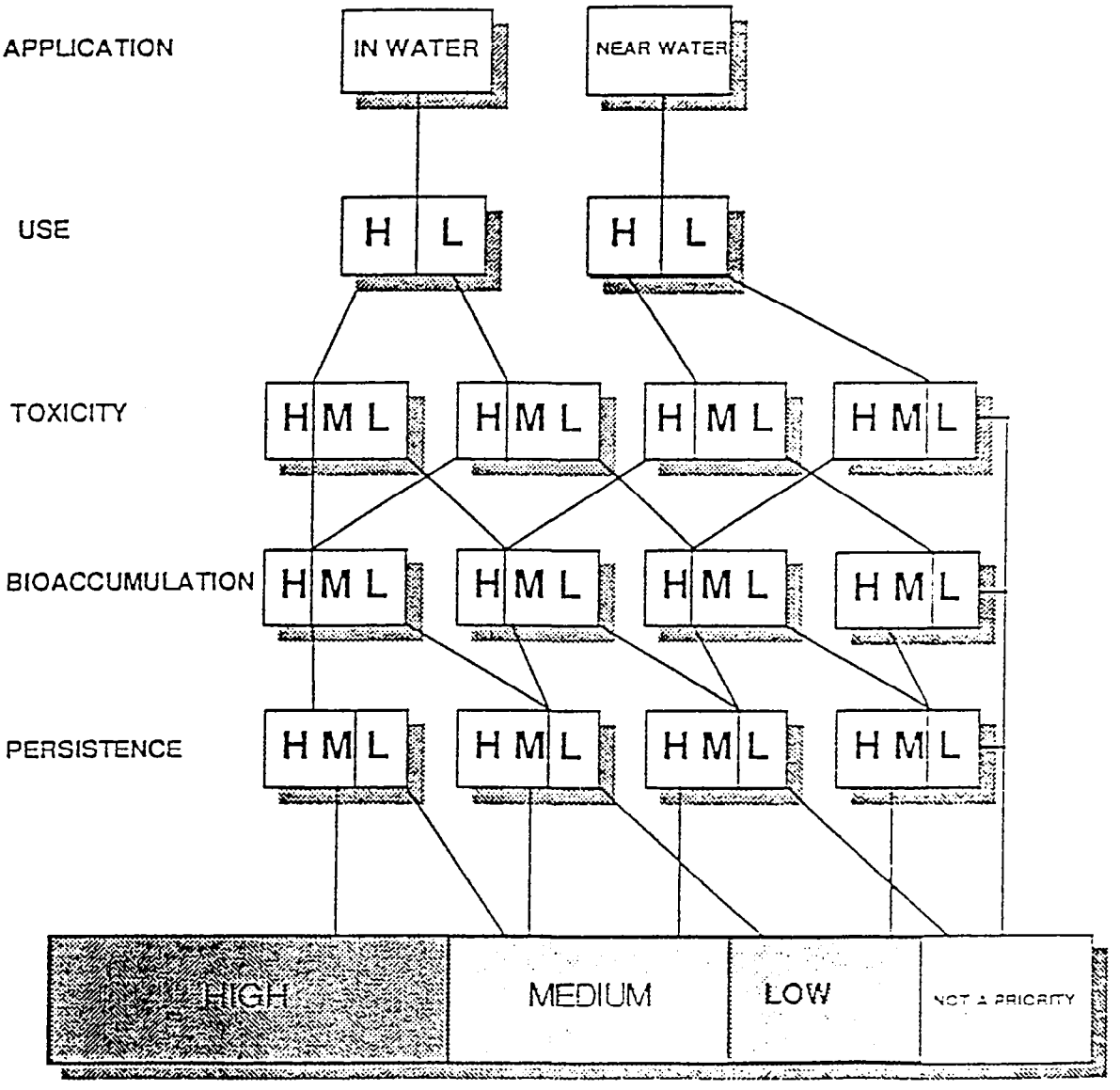

Figure 3.1 Prioritisation scheme for aquatic herbicides

Table 3.2 Summary of the effects and likely exposure of aquatic herbicides to freshwater organisms

Substance	Amounts Used H/L		EFFECTS					EXPOSURE			
			Toxicity (in mg l^{-1})			Bioaccumulation		Persistence			
	In or near water	Terrestrial situation	fish	invertebrates	algae	log Kow	BCF	Half-life in water and main removal route	Half-life in soil	Tendency to Leach	PEC range (mg l^{-1}) in water resulting from use on arable crops
Asulam	H[1]	H	> 5000 96 h LC50 *O mykiss*	63.4 - > 17000 48 h LC50 *D magna*	0.19 - >1000 EC50 (NOEC 0.02)	<1	<1	> 2 months pH 3 4 years at pH 8.5 Adsorption	6 - 14d	Possibly	1.0 (Tooby 1980)
Dalapon	only used as a mixture with dichlobenil[1]		8.1 > 30000 48 h LC50 *O mykiss*	0.1 - 6 315 h LC50 *H vidus*	2 - 10 EC50 *H stoechidium*	0.78	2.2	9 - 60d Biodegradation	100% in 7d	Y Highly mobile	3.0 (Tooby 1980)
Dichlobenil	H		8.1 - 20 48 h LC50 *O mykiss*	3.7 - 11 48 h LC50 *D pulex*	6 - 17.2 EC50 (growth) *Hormidium barlowi*	2.65	13	Moderately persistent Volatilisation Hydrolysis Biodegradation Adsorption Degradation product BAM also persistent	1 - 12 months	N Low mobility	1.0 (Tooby 1980)
Diquat	H	L	7.8 - 35.0 96 h LC50 largemouth bass	1.0 - 7.1 8d LC50 *D magna*	0.019 - 0.073 EC50 *C vulgaris*	<0.1		2 days Photodegradation Adsorption Biodegradation Uptake		N Immobile	2.0 (Tooby 1980)
2,4-D amine	L	H	4.2 - 4200 23d LC50 *O mykiss*	4 - >100 48h LC50 *D magna*	<1 - 5 growth inhib *L gibba*			45d at 10 °C		Y but degradation is rapid	

Substance	Amounts Used H/L		EFFECTS					EXPOSURE			
			Toxicity (in mg l^{-1})			Bioaccumulation		Persistence			
	In or near water	Terrestrial situation	fish	invertebrates	algae	log Kow	BCF	Half-life in water and main removal route	Half-life in soil	Tendency to Leach	PEC range (mg l^{-1}) in water resulting from use on arable crops
Fosamine ammonium	L[1]	L	278->1000 96h LC50 *O mykiss*	No data	No data			Adsorption	7 - 10d		
Glyphosate	H		1.3 - 1000 96h LC50 *O mykiss* (Roundup)	3.0 - >780 48h EC50 *D magna* (Roundup)	1 - 8.5 Oxygen evol inhib *E gracilus* (Roundup)	<0.01	1.6	4 - 11d 10 weeks in sediments Photolysis Biodegradation Adsorption Degradation product is AMPA	< 60d	N	0.18 (Tooby 1980)
Maleic hydrazide	H[1]	L	56 - 1608 48h LC50 *O mykiss*	107 96h LC50 *D magna*	9.84 5 day NOEC *Selanastrum capricornutum*	<0.01	5	Rapid photolysis	2 - 6d		
Terbutryn	L		1.1 - >100 96h LC50 *O mykiss* 34d (NOEC 0.84 *P.promelas)*	1.4 - 2.66 48h LC50 *D magna*	0.0034 - 0.1 9d EC50 *A flos-aquae*	3.65	160	2 - 8 weeks up to 8 months in sediments Biodegradation Adsorption	14 - 28d	N	6 µg l^{-1} (Confidential data 1995)

Notes: 1. Not applied directly to water
L = Low
M = Medium
H = High
where L, M and H are used under the Amounts Used column, they refer to relative quantities only.

As can be seen from Table 3.3 none of the nine herbicides are classified as a high priority for EQS development. However, five substances are classified as a medium priority: 2,4-D, dichlobenil, glyphosate, asulam and terbutryn. This was based mainly on their high toxicity to non-target species of algae, though some also have relatively high toxicities to invertebrates, e.g. a 48 hour LC50 of 1.4 mg terbutryn l^{-1} for *Daphnia magna*. 2,4-D has been reviewed by WRc and EQSs proposed (Lewis *et al* 1996) thus obviating the need to discuss it any further in this section.

In general, the chemicals reviewed in this report are of low toxicity to fish and are not bioaccumulated by aquatic organisms with the result that none of them are considered a high priority for EQS development. Most of the herbicides, as expected, are toxic to non-target species of algae and some species of invertebrates, though adsorption to suspended solids and uptake by plant material reduces the bioavailability of most of these herbicides to aquatic organisms in the field. Persistence varies from hours to months depending on the physico-chemical properties and the environmental conditions. However, most of the herbicides are likely to partition out of the water column onto plant matter or suspended solids with degradation taking place in sediments over a period of months. Toxic effects on benthic organisms could therefore occur if residues accumulate to significant levels.

Table 3.3 Priority list of herbicides used in or near water in the UK

Substance	Use in water	Use	Freshwater toxicity			Bioacc.	Persistence	Priority
			Fish	Invert.	Algae			
Asulam	No	H	L	L	H	L	M	M
Dalapon	No	L	M	H	M	L	M	L
Dichlobenil	Y	H	M	M	M	L	M[4]	M
Diquat[1]	Y	H	M	M	H	L	L	L
2,4-D amine	Y	L	M	M	H	L	M	M
Fosamine ammonium	N	L	L	ND	ND	L	L[2]	No
Glyphosate	Y	H	M	M	M	L	M[3]	M
Maleic hydrazide	N	H	L	L	ND	L	M	No
Terbutryn	Y	L	M	M	H	M	M	M

Footnotes:
1. Diquat is inactivated (in terms of its toxic mode of action) under turbid conditions through adsorption onto suspended solids
2. Based on persistence in soil
3. Degradation product AMPA appears to be persistent in water
4. Degradation product BMA appears to be persistent in water

ND = No data
H = High
M = Medium
L = Low
Y = Yes

Dichlobenil is used to control floating and submerged leaves. It is applied as a granular formulation which provides a slow release of the herbicide into the water over a period of time and is one of the more persistent herbicides used in water with degradation occurring over a period of weeks rather than days. Adsorption onto suspended solids and plant matter are the primary removal mechanisms. The main degradation product, BAM, also appears to be persistent in aquatic systems. Dichlobenil in its pure and formulated form is moderately toxic to freshwater fish and invertebrates with effect concentrations ranging from 8.1 - 20.0 mg l^{-1} and 3.7 - 11 mg l^{-1} respectively. The risk to the aquatic environment associated with its use in terrestrial applications appears to be limited by its high affinity for soil particles and its mode of application as a granular formulation. The major inputs of dichlobenil into water will therefore, mostly derive from its use as an aquatic herbicide. Since it is applied as granules directly to the water and is moderately persistent, exposure of aquatic organisms to dichlobenil is likely to occur over a significant length of time. Given that it has moderate acute toxicity to invertebrates (the lowest effect concentration is a 48 hour LC50 of 3.7 mg l^{-1} for *Daphnia pulex*) and the absence of any chronic toxicity data, dichlobenil is considered to be the most important substance requiring EQS development within the medium priority band of substances.

Terbutryn is a triazine herbicide which is used to control floating and submerged weeds and algae. As with dichlobenil, it is applied to the water as slow release granules. It is persistent in the aquatic environment with half-lives ranging from 1 week to 2 months depending on environmental factors such as temperature. One of the major removal pathways is adsorption onto suspended solids with subsequent settling out on the sediments where the half-life is considerably longer (up to 8 months). Biodegradation is the predominant removal mechanism. Terbutryn appears to be the most toxic of the nine herbicides particularly to freshwater algae with toxic effects occurring at concentrations as low as 0.0131 mg l^{-1} (nine day EC50 for *Selanastrum capricornutum)* and 0.0034 mg l^{-1} (nine day EC50 for *Anabaena flos-aquae*). Invertebrates and fish are also sensitive to terbutryn with effect concentrations of 1.4 - 2.66 mg l^{-1} and 1.1 - 4.0 mg l^{-1} respectively.

Quantities used in agriculture and horticulture are not accurately known but, the low tendency to leach from soils and its granular application suggest that inputs of terbutryn from run-off, leaching and overspray will be small compared with those arising from its use to control aquatic weeds. The high toxicity of terbutryn to aquatic organisms and its moderate persistence combined with its direct application to water as granules contribute to its classification as a medium priority for EQS development. However, since the results from the aquatic herbicide usage survey (Table 1.2) indicate that usage of terbutryn is small compared to dichlobenil, it is recommended that it is given slightly lower priority than dichlobenil.

Glyphosate is a widely used non-selective, non-residual post-emergence herbicide used on lilies, reeds and emergent weeds in or near watercourses and lakes. In freshwater, adsorption to sediments is expected to occur and thus biodegradation under anaerobic conditions in sediments is likely to be the most important removal process. The main degradation product of glyphosate, AMPA (aminomethylphosphonic acid), is however, slightly more persistent with a reported half-life of ten weeks in pond water. Glyphosate appears to be of low acute toxicity to

fish and invertebrates with respective effect concentrations ranging from 86 - 97 mg l^{-1} and 3.2 - >780 mg l^{-1}. However, the formulation Roundup is more toxic by an order of magnitude than the pure compound due to the use of the surfactant MONO818 which has a higher toxicity than glyphosate itself. The available data suggest that glyphosate is unlikely to bioaccumulate in aquatic organisms with a BCF of 1.6 reported for bluegill sunfish exposed to 0.6 mg l^{-1} glyphosate over 28 days. The absence of any toxicity data on AMPA and the paucity of data relating to the fate and behaviour of the glyphosate formulation Roundup which is 10 times more toxic than glyphosate in the aquatic environment gives more cause for concern. In addition, while the toxicity of the newer formulation, Roundup Pro bioactive, to aquatic organisms is less than Roundup, there are no available information on the relative or expected use of these two formulations. Data relating to the effects of glyphosate and AMPA on benthic organisms are also scarce. Glyphosate is therefore given medium priority for EQS development. However, it is likely that exposure to aquatic organisms will be much less compared with the granular formulations terbutryn and dichlobenil because glyphosate is applied directly onto the plant foliage. Uptake and adsorption processes will therefore limit the amount entering the water although some overspray onto the water surface could occur during treatment. For this reason glyphosate is given a lower priority than dichlobenil and terbutryn within the medium priority band. The level of usage of glyphosate in non aquatic situations is not accurately known although it is widely used on set-aside land. Its low tendency to leach and rapid breakdown in soil would, however, preclude large quantities entering the aquatic environment through leaching and surface run-off, though some overspray could occur during treatment of arable crops close to water courses.

Asulam is a selective systemic herbicide which is used in the control of bracken and docks on river banks. It is likely to be persistent in the aquatic environment though it can undergo photodegradation in the presence of sunlight. Since the principal use of asulam is for the control of bracken, run-off from treated areas of bracken and overspray of small steams during aerial application will probably constitute larger loads into the aquatic environment than bankside weed control practices. However, its low persistence in soils and rapid photodegradation on the foliage will reduce concentrations found in run-off. Freshwater invertebrates are moderately sensitive to asulam with a 48 hour EC50 and NOEC of 63.4 mg l^{-1} and 8.96 mg l^{-1} respectively reported for *Daphnia magna* though algae appear to be the most sensitive group with EC50 values ranging from 0.19 - 0.3 mg l^{-1} (see Section 2.1.4). Its inclusion in the medium priority band results mainly from its high usage and the possibility that contamination of watercourses could occur through overspray during aerial application to areas of bracken. The sensitivity of some non-target species of plants to asulam and its moderate persistence in aquatic systems also contribute to its classification as a medium priority for EQS development. Since it is not applied directly to the water it is intentionally given a lower priority than dichlobenil, terbutryn and glyphosate.

In summary, since terbutryn and dichlobenil are applied directly to water as slow release granules, the exposure to aquatic life from dichlobenil and terbutryn, on a site specific basis, can be regarded as significantly higher than the exposure to asulam, which is not applied directly to the water, and glyphosate which is sprayed onto floating foliage. Given also, their higher toxicity to invertebrates and non target algae, the risk to aquatic life associated with the use of dichlobenil and terbutryn can be considered higher than that associated with asulam.

Dichlobenil and terbutryn are therefore given higher priority for EQS development than asulam. Similarly, glyphosate is accordingly given higher priority than asulam for EQS development due to its higher toxicity to invertebrates and its greater exposure to aquatic life resulting from its direct application to the water.

4. CONCLUSIONS

1. The toxicity, bioaccumulation and persistence of nine herbicides, asulam, dalapon, dichlobenil, diquat, 2,4-D amine, fosamine ammonium, glyphosate, maleic hydrazide and terbutryn. approved for use in or near water have been reviewed for prioritised for the development of Environmental Quality Standards EQSs.

2. 2,4-D has already been reviewed and EQSs proposed to the Environment Agency (Lewis *et al* 1996) thus obviating the need for prioritisation.

3. None of the herbicides are considered a high priority for EQS development. Terbutryn, dichlobenil, glyphosate and asulam, however, are classified as medium priorities for EQS development. Classification was based on their mode of application, the amounts used, their toxicity, bioaccumulation and persistence in the aquatic environment. The medium priority rating arose largely from high toxicity to invertebrates and non-target species of algae and persistence in sediments.

4. It is recommended that dichlobenil be given highest priority within the group of four medium priority herbicides based its high toxicity to aquatic organisms, its relatively large usage as an aquatic herbicide and its granular application method. The remaining three herbicides are ranked in order of decreasing priority for EQS development as follows: terbutryn, glyphosate and asulam.

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APPENDIX A FRESHWATER TOXICITY OF HERBICIDES APPROVED FOR USE IN OR NEAR WATER

Table A1 Freshwater toxicity of asulam

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Chlorella pyrenoidosa (green alga)	5-72	50% inhib. in pop. growth	6	2
Dunaliella bioculata (green alga)	48	55% inhib. in pop. growth	23	3
Invertebrates				
Gammarus pulex (shrimp)	8 days	LC50	>17 000	4
Limnaea peregra (snail)	8 days	LC50	>17 000	4
Daphnia magna (water flea)	48	LC50	63.4	6
Daphnia magna (water flea)	48	NOEC	8.96	6
Fish				
Oncorhynchus mykiss (rainbow trout)	96	LC50	>5000	1
Lepomis macrochirus (bluegill sunfish)	96	LC50	>5000	6

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Carassius auratus (goldfish)	96	LC50	>5000	1
Ctenopharygodon idella Val (Grass carp)	96	TLm	>10 000	5

Notes: Additional confidential data expressed as a range are given in Section 2.1.4

References:
1. BCPC (1991)
2. Wright (1972)
3. DoE (1972a)
4. DoE (1972b)
5. Tooby *et al.* (1980)
6. Confidential data (1995)

Table A2 Freshwater toxicity of dalapon

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Anabaena sp. (blue-green algae)		growth[c]	10[b]	8
Hormidium stoechidium		EC50 (growth)	2	9
Chlamydomonas agloeformis		EC50 (growth)	10	9
Invertebrates				
Daphnia magna (water flea)		LD50	6[a]	7
Daphnia pulex	48	LC50	17	2
Heliodiaptomus vidus (planktonic copepod)	315	LC50	0.1	6
Fish				
Gambusia affinis (mosquito fish)	96	TL50	19 100[c]	5
Oncorhynchus mykiss (rainbow trout)	96	LC50	>100	1
Oncorhynchus mykiss (rainbow trout)	48	LC50	8.1[d]	10
Rasbora heteromorpha (harlequin fish)	48	TLm	210-325	4

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Carassius auratus (goldfish)	96	LC50	>100	1
Ctenopharygodon idella Val (Grass carp)	96	TLm	>30 000	3

Notes:
a Dalapon acid
b Maximum concentration permitting growth
c TL50 = Median Tolerance Limit
d dalapon/dichlobenil mixture (Fydulan)

References:
1. BCPC (1991)
2. MAFF (1985)
3. Tooby *et al.* (1980)
4. Alabaster (1969)
5. Johnson (1978)
6. George and Hingorani (1982)
7. Frear and Boyd (1967)
8. Venkataraman and Rajyalakshmi (1972)
9. Cullimore (1975)
10. NRA (1995)

Table A3 Freshwater toxicity of dichlobenil

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Hormidium barlowi		EC50 (growth)	6[a]	7
Chlamydomonas spp.	48	signif inhib of growth	17.2 (1×10^{-4} M)[b]	6
Invertebrates				
Daphnia magna (water flea)	26	LC50	9.8[b]	1
Daphnia pulex	48	LC50	3.7[b]	1
Gammarus lacustris	96	LC50	11[a]	3
Fish				
Oncorhynchus mykiss (rainbow trout)	48	LC50	8.1[b]	2
Rasbora heteromorpha (harlequin fish)	48	TLm	11[a]	5
Ctenopharygodon idella Val (Grass carp)	48	TLm	12[a]	4
Ctenopharygodon idella Val (Grass carp)	96	TLm	9.4[a]	4
Rasbora heteromorpha (harlequin fish)	96	LC50	16[b]	2
Poecilia reticulata guppy	48	LC50	>18[b]	1

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Lepomis macrochirus (bluegill sunfish)	48	LC50	20[b]	2

Notes: a Analytical grade
b No data on formulation used

References:
1. BCPC (1991)
2. MAFF (1985)
3. Miyazaki (1975)
4. Tooby *et al.* (1980)
5. Alabaster (1969)
6. Hess (1980)
7. Cullimore (1975)

Table A4 Freshwater toxicity of diquat

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Bacteria				
Microcystis aeruginosa (cyanobacteria)	3 days	EC50 (growth)	0.065	4
Anabaena flos-aquae (cyanobacteria)		inhib. of growth for Reglone	33.3	6
Microbial community	7 days	MATC (species richness and proportion of producers) in microcosms with no sediment	0.11	5
Microbial community	7 days	MATC (species richness and proportion of producers) in microcosms with sediment	2.70	5
Algae				
Chlorella vulgaris		EC50 (growth)	0.1	7
Ochromonas danica (crysophyte)	3 days	EC50 (growth)	0.023	4
Navicula sp (diatom)	3 days	EC50 (growth)	0.019	4
Cryptomonas ozolini	3 days	EC50 (growth)	0.035	4
Selanastrum capricornutum (chlorophyte)	3 days	EC50 (growth)	0.073	4
Invertebrates				
Daphnia magna (water flea)	26	LC50	7.1	2
Daphnia pulex	8 day	LC50	1.0	3
Hyalella azeteca (amphipod)	48	LC50	3.4	10

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Fish				
Oncorhynchus mykiss (rainbow trout)	96	LC50	8.0	1
Lepomis macrochirus (bluegill sunfish)	96	LC50	35.0	1
Micropterus salmoides (largemouth bass)	96	LC50	7.8	1
Rasbora heteromorpha (harlequin fish)	48	TLm	70[a]	8
Cirrhina mrigaia Hamilton (major carp) fingerlings	-	LD50[a]	400-440	9

Notes: a diquat-dibromide

References:
1. Verschueren (1983)
2. Crosby and Tucker (1966)
3. WHO (1984)
4. Phlips *et al.* (1992)
5. Pratt *et al.* (1990)
6. Birmingham and Colman (1977)
7. Cullimore (1975)
8. Alabaster (1969)
9. Ashton and Crafts (1973)
10. Williams *et al.* (1984)

Table A5 Freshwater toxicity of 2,4-D

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Invertebrates				
Daphnia magna (water flea)	48	LC50	4	5
Daphnia magna (water flea)	26	LC50	>100	4
Fish				
Oncorhynchus mykiss (rainbow trout)	23 days	LC50	4.2	6
Oncorhynchus mykiss (rainbow trout)	27 days	LC50	4.2	6
Ctenopharygodon idella Val (Grass carp)	96	TLm	1313	1
Rasbora heteromorpha (harlequin fish)	24	TLm	3400-4200[a]	2
Rasbora heteromorpha (harlequin fish)	48	TLm	2400-3100[a]	2
Cirrhina mrigaia Hamilton (major carp) fingerlings	-	LD50[b]	300-100	3

Notes: a Shell 2,4-D SR Pellets
b acute oral LD50 in mg kg^{-1}

References:
1. Tooby *et al.* (1980)
2. Alabaster (1969)
3. Ashton and Crafts (1973)
4. Crosby and Tucker (1966)
5. Sanders (1970)
6. Birge *et al.* (1979)

Table A6 Freshwater toxicity of fosamine ammonium

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Fish				
Oncorhynchus mykiss (rainbow trout)	96	LC50	>415	1
Lepomis macrochirus (bluegill sunfish)	96	LC50	278	1
Pimephales promelas (fathead minnow)	96	LC50	>1000	1

Note: Above data refer to the effects of the formulated product, Krenite.

References: 1. BCPC (1991)

Table A7 Freshwater toxicity of glyphosate

Species		Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae					
Cyanobacteria sp.	glyphosate	-	EC50 (growth)	2	6
Euglena. gracilus	glyphosate	100 minutes	inhib of O_2 evolution	1	6
Algae (species not given)	Roundup Pro biactive	72	EC50 (biomass)	150	7
Algae (species not given)	Roundup	72	EC50 (no further info. available)	7.9	7
Macrophytes					
Lemna sp. (duckweed)	glyphosate	7 days	37% reduction in growth	8.5	6
Lemna minor (duckweed)	glyphosate	14 days	ED50	2.0	6
Invertebrates					
Daphnia magna (water flea)	glyphosate	96	LC50	>780	1
Daphnia magna (water flea)	glyphosate	21 days	NOEL	100	7
Daphnia magna (water flea)	Roundup	96	IC50	25.5	4
Daphnia magna (water flea)	Roundup	48	EC50 (immobilisa-tion)	3.0	5

Species		Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Daphnia pulex (water flea)	glyphosate	48	EC50	3.2[a]	6
Daphnia pulex (water flea)	glyphosate	48	EC50	7.9[b]	6
Daphnia magna (water flea)	Roundup	96	IC50	3.0	5
Daphnia magna	Roundup Pro biactive	48	LC50	676	8/7
Daphnia sp	Roundup	48	LC50	5.3	8
Fish					
Oncorhynchus mykiss (rainbow trout)	glyphosate	96	LC50	86	1
Oncorhynchus mykiss (rainbow trout)	glyphosate	21 days	NOEL	52	7
Oncorhynchus mykiss (rainbow trout)	Roundup	96	LC50	8.3	6
Oncorhynchus mykiss (rainbow trout) fingerling	Roundup	96	LC50	1.3	5
Oncorhynchus mykiss (rainbow trout)	surfactant (Roundup MONO8181)	96	LC50	2.0	6
Pimephales promelas (fathead minnow)	glyphosate	96	LC50	97	5
Pimephales promelas (fathead minnow)	glyphosate	chronic	NOEL (repro)	>25.7	7
Pimephales promelas (fathead minnow)	Roundup	96	LC50	9.4	6

Species		Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Pimephales promelas (fathead minnow)	Roundup	96	LC50	2.3	5
Pimephales promelas (fathead minnow)	surfactant (Roundup MONO8181)	96	LC50	1.0	6
Carp (species not given)	Roundup	96	LC50	3.9	6
Trout (species not given)	Roundup Pro biactive	96	LC50	>989	8
Trout (species not given)	Roundup	96	LC50	8.2	8
Carp (species not given)	Roundup Pro biactive	96	LC50	>895	9/7
Carp (species not given)	Roundup Pro biactive	96	LC50	>895	9

Notes: ED50 Effective dose at which glyphosate was toxic to 50% of plants
a with suspended sediment present
b without suspended sediment present

References:
1. BCPC (1991)
2. Mitchell *et al.* (1987)
3. WSSA (1989)
4. Servizi *et al.* (1987)
5. Folmer *et al.* (1979)
6. Environment Canada (1990)
7. Monsanto (1996)
8. Clemence and Merritt (1993)
9. Garnett (in Press)

Table A8 Freshwater toxicity of maleic hydrazide

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Selenastrum capricornutum green alga	5 days	NOEC	9.84	5
Macrophytes				
Lemna gibba Duckweed	14 days	IC50	110	5
Lemna gibba Duckweed	14 days	NOEC	23.7	5
Invertebrates				
Daphnia magna (water flea)	48	LC50	>1000	5
Daphnia magna (water flea)	96	LC50	107	1
Nitzchia palea diatom	5 days	IC50	>97.8	5
Fish				
Oncorhynchus mykiss (rainbow trout)	24	LC50	85	3
Oncorhynchus mykiss (rainbow trout)	48	LC50	56	3
Lepomis macrochirus (bluegill sunfish)	96	LC50	1608	1
Cyprinodon variegatus sheepshead minnow	96	LC50	104	5
Rasbora heteromorpha (Harlequin fish)	96	LC50	125	2

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Rasbora heteromorpha (harlequin fish)	48	TLm	880[a]	4

Notes: a maleic hydrazide/2,4-D as triethanol amine salt

References: 1. BCPC (1991)
2. Verschueren (1981)
3. Howard (1991)
4. Alabaster (1969)
5. Confidential data (1995)

Table A9 Freshwater toxicity of terbutryn

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Anabaena flos-aquae (cyanobacteria)	9 days	EC50 (growth inhib)	0.0034	5
Selanastrum capricornutum (green algae)	9 days	EC50 (growth inhib)	0.0131	5
Stichococcus sp. (green algae)	7 days	population growth	0.1	4
Macrophytes				
Lemna minor (duckweed)	12 days	inhib of growth	0.02	3
Invertebrates				
Daphnia magna (water flea)	48	LC50	1.4	2
Daphnia magna (water flea)	48	EC50	2.66	5
Daphnia magna (water flea)	21 days	NOEC (survival and offspring production)	1.3	5
Fish				
Oncorhynchus mykiss (rainbow trout)	96	LC50	1.1 - 3.0	5
Oncorhynchus mykiss (rainbow trout)	96	LC50	1.8 - 3.0	1
Pomephales promelas (fathead minnow)	34 days	NOEC	0.84	5
embryos and larvae (crucian carp)	96	LC50	1.4 - 4.0	1

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Lepomis macrochirus (bluegill sunfish)	96	LC50	4.0	1
Lepomis macrochirus (bluegill sunfish)	96	LC50	1.3 - 4.0	5
Pimephales promelas (fathead minnow)	34 days	NOEC	0.84	5

References:
1. BCPC (1991)
2. Tyson (1974)
3. Bahadir and Pfister (1985)
4. Wingfield and Johnson (1981)
5. Confidential data (1995)

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APPENDIX B SALT WATER TOXICITY OF HERBICIDES APPROVED FOR USE IN OR NEAR WATER

Table B1 Saltwater toxicity of asulam

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Invertebrates				
Uca pugnax (Fiddler crab)	96	LC50	>100	1
Palaemonetes vulgaris (Grass shrimp)	96	LC50	>100	1

References 1. Confidential data (1995)

Table B2 Saltwater toxicity of dalapon

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Chlorococcum sp (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	25	1
Dunaliella tertiolecta (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	25	1
Isochrysis galbana (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	40	1
Phaeodactylum tricornutum (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	25	1
Chlorococcum sp (unicellular algae)	10 days	EC50[a] growth	50	1
Dunaliella tertiolecta (unicellular algae)	10 days	EC50[a] growth	100	1
Isochrysis galbana (unicellular algae)	10 days	EC50[a] growth	20	1
Phaeodactylum tricornutum (unicellular algae)	10 days	EC50[a] growth	25	1

Notes: a technical acid

References: 1. Walsh (1972)

Table B3 Saltwater toxicity of dichlobenil

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Chlorococcum sp (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	90	1
Dunaliella tertiolecta (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	125	1
Isochrysis galbana (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	100	1
Phaeodactylum tricornutum (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	150	1
Chlorococcum sp (unicellular algae)	10 days	EC50[a] growth	60	1
Dunaliella tertiolecta (unicellular algae)	10 days	EC50[a] growth	60	1
Isochrysis galbana (unicellular algae)	10 days	EC50[a] growth	60	1
Phaeodactylum tricornutum (unicellular algae)	10 days	EC50[a] growth	25	1
Invertebrates				
Nitocra spinipes (harpaticoid)	96	LC50	0.27[b]	2

Notes: a technical acid
b Casoron G

References: 1. Walsh (1972)
2. Linden *et al.* (1979)

Table B4 Saltwater toxicity of diquat

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Chlorococcum sp (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	>5000	1
Dunaliella tertiolecta (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	>5000	1
Isochrysis galbana (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	>5000	1
Phaeodactylum tricornutum (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	>5000	1
Chlorococcum sp (unicellular algae)*p*	10 days	EC50[a] growth	200	1
Dunaliella tertiolecta (unicellular algae)	10 days	EC50[a] growth	30	1
Isochrysis galbana (unicellular algae)	10 days	EC50[a] growth	15	1
Phaeodactylum tricornutum (unicellular algae)	10 days	EC50[a] growth	15	1

Notes: a diquat dibromide

References: 1. Walsh (1972)

Table B5 Saltwater toxicity of 2,4-D

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Chlorococcum sp (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	60	1
Dunaliella tertiolecta (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	50	1
Isochrysis galbana (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	60	1
Phaeodactylum tricornutum (unicellular algae)	1.5	EC50[a] decreased oxygen evolution	60	1
Chlorococcum sp (unicellular algae)	10 days	EC50[a] growth	50	1
Dunaliella tertiolecta (unicellular algae)	10 days	EC50[a] growth	75	1
Isochrysis galbana (unicellular algae)	10 days	EC50[a] growth	50	1
Phaeodactylum tricornutum (unicellular algae)	10 days	EC50[a] growth	50	1

Notes: a technical acid

References: 1. Walsh (1972)

Table B6 Saltwater toxicity of glyphosate

Species	Formulation	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Nitocra spinipes (harpaticoid)	Roundup	96	LC50	22	1
Palaemonetes sp (Grass shrimp)	Glyphosate	nd	LC50	281	2
Uca pugilator (Fiddler crab)	Glyphosate	nd	LC50	934	2
Mysidopsis bahia (Mysid shrimp)	Glyphosate	nd	LC50	>1000	2
Atlantic oyster	Glyphosate	nd	LC50	>10	2
Echinus sp. (Sea urchin)	Glyphosate	nd	LC50	>1000	2

Notes: nd - no data

References: 1. Linden *et al.* (1979)
2. Monsanto

Table B7 Saltwater toxicity of maleic hydrazide

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Skeletonema costatum (diatom)	5 days	IC50	>102	1
Invertebrates				
Crassostea virginica (Eastern oyster)	96	EC50	>111	1
Mysidopsis bahia (mysid shrimp)	96	LC50	>103	1

References: 1. Confidential data (1995)

Table B8 Saltwater toxicity of terbutryn

Species	Exposure (hours)	Effect	Conc. mg l^{-1}	Ref
Algae				
Skeletonoma costatum (marine diatom)	9 days	EC50 (growth inhib)	0.0009	1
Invertebrates				
Mysidopsis bahia (mysid shrimp)	96	EC50	0.74	1
Mercenaria mercenaria (Quahog clam)	48	EC50	5.6	1
Penus duorarum (Pink shrimp)	48	EC50	1.0	1

References: 1. Confidential data (1995)

REFERENCES TO APPENDIX B

Linden, E., Bengtsson, B.E., Svanberg, O. and Sundstrom, G. (1979) The acute toxicity of 78 chemicals and pesticide formulations against two brackish water organisms, the bleak (*Alburnus alburnus*) and the harpaticoid *Nitocra spinipes*. *Chemosphere*, **11/12,** 843-851.

Walsh (1972) Effects of herbicides on photosynthesis and growth of marine unicellular algae. *Hyacinth Control*, **10,** 45-48.

APPENDIX C GLOSSARY OF TERMS

AMPA	Aminomethylphosphonic acid
BAM	2,6-Dichlorobenzamide
BCF	Bioaccumulation Factor
EQS	Environmental Quality Standard
TLC	Thin Layer Chromatography
TLm	Median Toxic Lethal Threshold