

THE WEED SOCIETY  
OF NEW SOUTH WALES

PROCEEDINGS  
OF THE SYMPOSIUM ON

THE CHEMIST'S ROLE  
IN WEED CONTROL

Friday 24 November 1989

(AM) CIBA-GEIGY Australia Limited  
140-150 Bungaree Road:  
PENDLE HILL

(PM) BIOLOGICAL & CHEMICAL RESEARCH INSTITUTE  
Cnr Pemberton Street & Victoria Road  
RYDALMERE



THE WEED SOCIETY  
OF NEW SOUTH WALES

Proceedings of Symposium

"The Chemist's Role in Weed Control"

- CIBA-GEIGY Australia Limited, 140-150 Bungaree Road, Pendle Hill, NSW,  
and

Biological and Chemical Research Institute, Victoria Road, Rydalmere, NSW

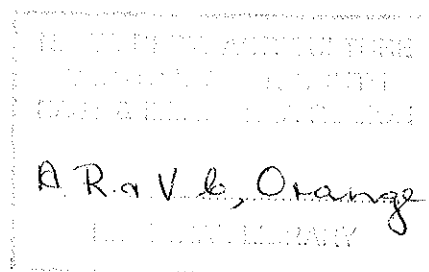
24th November 1989

Organising Committee: J. Burke, J. Toth, K. Watson

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FOREWORD

Statistics compiled by AVCA on behalf of its member companies, which hold about 85% of the market, show Australian herbicide sales for the year ending 30 June 1989, as \$A247 million of a total of \$A332 million for all agricultural chemicals, excluding animal health products. Herbicides sales grew by 15% while other agricultural chemicals had a nil growth compared to the previous year. These figures show the ever increasing importance of herbicides in Australian agriculture.

Today we start with the synthesis chemist inventing new active molecules. We then skip past the patent chemist and focus on the acceptance of the chemical name and generic or common name.

As the the research-development schedule continues the test compound is produced in larger batches and formulations are prepared for glasshouse and limited field plots evaluations. In parallel the toxicokinetic and metabolic studies in selected mammals and plants, plus the toxicological studies commence. Analytical methods for the active ingredient and by-product determinations lead to specifications for the technical active material. Chemical and physical properties of the technical and pure materials are established. Meanwhile in the ecochemistry laboratory hydrolysis, photolysis, metabolism in soil and water under aerobic/anaerobic conditions, leaching, adsorption/ desorption, volatility and dissipation are measured to forecast potential accumulation in the environment.

Some three to four years after discovery, the biological data from field stations, strategically placed around the globe, give indications if the new compound is capable of filling a worthwhile need. Provided results from the other parameters under investigation are also favourable, commitment is made to extend testing internationally. Normally at this point Australia sees the compound for the first time.

The local formulation and residue chemists work closely with the weeds agronomist, usually over two to four seasons, in evaluating and collecting the balance of the data package necessary to satisfy the company and the regulatory authorities on the efficacy and safety of the proposed product recommendations.

After commercial release the chemist concentrates mainly on product quality control and, to a lesser extent, residue monitoring. If improvements to the formulation or extended recommendations are needed later, the chemist is ready again to complement the agronomist.

I trust that the symposium will demonstrate how important is the chemist's role in weed control and that all participants will gain new insights into the term "herbicide".

Jack Burke  
President, Weed Society of New South Wales.

"The Chemist's Role in Weed Control"Programme/ContentsOFFICIAL OPENING*Herman Mami*Page No.

9.00 am Ray Chappell, MHR, Armidale, NSW.

SYNTHESIS AND NOMENCLATURE

Chairperson John Phillips, Principal Research Scientist,  
Division of Plant Industry, CSIRO, Canberra

Biochemical targets of herbicide action

9.15 am John Huppertz, Principal Research Scientist  
Division of Plant Industry, CSIRO, Canberra 1-5

Pesticide common names

9.55 am Jim Walker, Senior Science Officer, Agricultural  
& Veterinary Chemicals Section, Department of  
Primary Industries & Energy, Canberra 6-23

10.15 am Morning Tea

FORMULATION AND SAFETY

Chairperson Margaret Teleki, Laboratory Manager, CIBA-GEIGY  
Australia Limited, Pendle Hill, NSW

Principles of formulation

10.45 am Ross Brownscombe, Development Chemist, CIBA-GEIGY  
Australia Limited, Pendle Hill, NSW 24-53

Chairperson Roland Churches, Health, Safety and Environment  
Manager, CIBA-GEIGY Australia Limited,  
Pendle Hill, NSW

Material Safety Data Sheets

11.30 am Stephen Holland, Chemicals Section, Worksafe  
Australia, Sydney 54-61

12.00 Lunch

RESIDUES IN WATER AND SOIL

Chairperson Ross Higginson, Director of Chemistry, BCRI,  
Rydalmere, NSW

Herbicides in water : Economics or environment

1.25 pm Kath Bowmer, Senior Principal Research Scientist, 62-79  
Division of Water Resources, CSIRO, Griffith,  
NSW

A short history of herbicide persistence research

2.05 pm Ian Ferris, Pesticide Chemist, Agricultural 80-94  
Research Centre, Tamworth, NSW

3.00 pm Afternoon tea (simultaneously with inspections)

Glasshouse Inspection

John Toth, Senior Research Agronomist (Weeds)  
BCRI, Rydalmere, NSW

Laboratory Inspection

Paul Milham, Supervising Chemist, Agricultural  
& Veterinary Chemicals, BCRI, Rydalmere, NSW

RESIDUES IN FOODSTUFFS

Chairperson Doreen Clark, Analchem Consultants Pty. Ltd.,  
Lilyfield NSW

Pesticide residues in fodder forage and agricultural commodities

4.00 pm Denis Hamilton, Assistant Director, Agricultural 95-101  
Chemistry Branch, Department of Primary Industries,  
Brisbane, Qld.

FINALEClosing of symposium

4.40 pm Jack Burke, President - Weed Society of New South  
Wales.

## BIOCHEMICAL TARGETS OF HERBICIDE ACTION

John L. Huppatz

CSIRO Division of Plant Industry, G.P.O. Box 1600,  
Canberra, A.C.T. 2601.

### Introduction

The past twenty years has seen profound changes in the technology of chemical weed control. The emergence of compounds of greatly increased activity, efficacy and safety has led to increased use of herbicides, particularly in the developed countries. However, in the face of increasing public concern over pesticide usage generally, the strategies traditionally used for herbicide discovery and development are rapidly evolving to meet the rising demand for even greater effectiveness, lower cost and, most importantly, negligible environmental impact.

All herbicides in current use were discovered by the screening of large numbers of candidate compounds. This approach is becoming increasingly ineffective; novel structures with new, useful activities are harder to find, the cost of maintaining large screening facilities is escalating and the stringency of current regulatory and registration requirements is imposing severe restrictions on product development. Accordingly, interest in alternative methods of herbicide discovery is gathering momentum. Considerable effort has been directed towards the identification of specific herbicide targets in plant metabolic pathways. A greater insight into the interaction of phytotoxic molecules and plant biochemical systems should provide the basis for a more rational and directed approach to herbicide design.

Most major herbicides can now be classified according to their site of action. In a number of cases, a detailed knowledge of the nature and topography of the particular target site is beginning to emerge. A more cogent understanding of herbicide binding at the molecular level should facilitate the design of new active molecules, particularly when linked to the sophisticated computer modelling techniques now available.

This paper will consider a number of herbicide binding sites in detail and identify the chemical classes targetting these sites. The discussion will by no means be exhaustive, but will serve to illustrate recent advances in our understanding of the biochemical mode of action of different herbicide types.

## PLANT SPECIFIC TARGET SITES

Photosynthesis and essential amino acid biosynthesis are particularly attractive herbicide targets since these processes have no counterpart in mammalian physiology. A compound with the ability to selectively block plant specific biochemical pathways might be expected to have negligible mammalian toxicity. It is not surprising then, that efforts to discover new classes of compounds affecting photosynthesis or essential amino acid biosynthesis and attempts to maximise the activity of known herbicide classes blocking these pathways, have dominated herbicide research in recent years.

### *Photosynthesis*

Herbicide can block the photosynthesis pathway in plants by a number of different mechanisms, but by far the largest group of photosynthetic herbicides inhibit photosynthetic electron transport near photosystem II (PSII) (1). Generally characterised by low toxicity, though in some cases, unacceptable persistence, these compounds include the established urea (diuron, linuron, fluometuron), triazine (atrazine, simazine, terbutryn), triazinone (metribuzin, metamintron) and uracil (bromacil, terbacil) classes, generally referred to as amide-type PSII herbicides. Certain phenolic compounds (ioxynil, dinoseb) also exert their herbicidal effects by interfering with electron transport at the PSII level. Recent research has shown that the amide-type compounds, despite profound differences in their chemistry, all bind to a 32 kD polypeptide (the D1 or Q<sub>B</sub> protein) in the PSII complex in chloroplasts (1). They exert their herbicidal effect by displacing the native plastoquinone, Q<sub>B</sub>, from its binding site, thereby inhibiting photosynthetic electron flow.

An X-ray crystallographic structure of the photosynthetic reaction centre in bacteria has recently become available (2), allowing a detailed model of the corresponding system in higher plants to be proposed (3). A tentative picture of the three-dimensional architecture of the herbicide binding niche in the D1 protein can now be deduced. This type of detail should ultimately resolve the dilemma which has confronted the herbicide chemist for many years, viz., that compounds of such widely differing chemical type all bind to the same target site. Present indications are that the different classes bind to the site with different orientations, i.e., the binding domain is sufficiently large to accommodate

many chemical types with diverse substituent groups all capable of competing, either directly or indirectly, with the native quinone  $Q_B$  for its binding site.

#### *Essential amino acid biosynthesis*

The important broad spectrum herbicide, glyphosate, inhibits 5-enolpyruvylshikimate-3-phosphate (EPSP) synthase (4), the sixth enzyme in the shikimic acid pathway to the aromatic amino acids, tryptophan, tyrosine and phenylalanine. The mechanism of this enzyme reaction and its inhibition by glyphosate has been studied extensively but the design of new inhibitors of EPSP synthase has proved extraordinarily difficult. However, the enzyme from bacteria has now been obtained crystalline (5) and analysis of the X-ray crystallographic data should add significantly to our understanding of the nature and architecture of the active site.

The introduction of the sulfonylurea herbicides proved a significant breakthrough in the search for low dose, low toxicity herbicides. These compounds (chlorsulfuron, sulfometuron methyl, thiameturon methyl) exert their potent herbicidal effect by inhibiting acetohydroxy acid synthase (AHAS; also known as acetolactate synthase, ALS), the first common enzyme in the biosynthesis of the branched chain amino acids, valine, leucine and isoleucine (6). This enzyme assumed even greater significance when it was recognised as the primary target of a second, chemically distinct, herbicide class, the imidazolinones (imazapyr, imazaquin, imazamethabenz-methyl) (7). Like the PSII binding site, AHAS appears susceptible to a wide range of structurally dissimilar compounds capable of occupying overlapping binding sites on the enzyme. Unfortunately, AHAS has so far resisted crystallisation so that the X-ray data which would more precisely define the binding site is not yet available.

#### OTHER HERBICIDE TARGETS

Recently, herbicide targets have been identified in metabolic pathways not unique to plants. For example, phytotoxic effects can be produced by the inhibition of particular enzyme sites in lipid biosynthesis and the pathway to tetrapyrrolic pigments. Despite being ubiquitous, these sites are affected by compounds which are acceptable commercial herbicides with minimal toxicological problems. This fortunate circumstance could be due to a number of factors, including different enzyme properties and susceptibility in the plant and animal metabolic systems. The use of such compounds as probes has accelerated biochemical studies aimed at characterizing these enzymes.



### *Lipid biosynthesis*

Two major classes of grass herbicide, the cyclohexanediones (sethoxydim, tralkoxydim, clethodim) and the aryloxyphenoxy-propionates (haloxyfop, fluazifop, diclofop-methyl) block acetyl coenzyme A carboxylase (ACC), a critical enzyme in lipid biosynthesis (8). These compounds owe their specificity for graminaceous species to the fact that ACC derived from monocotyledonous species is sensitive whereas that from dicotyledons is not. This unique basis for herbicidal action implies a difference in structure between the two enzyme types, a property not suspected in previous biochemical studies. Purification and complete characterisation of ACC has not yet been achieved and an understanding of the inhibition of ACC by two such disparate chemical types is still to be realised.

### *Tetrapyrrole biosynthesis*

An enzyme involved in chlorophyll biosynthesis in plants has recently been implicated in the phytotoxic action of the diphenyl ether (bifenox, fomesafen, oxyfluorfen) class of herbicides (9). Protoporphyrinogen oxidase (PROTOX) catalyses the conversion of protoporphyrinogen to protoporphyrin IX, the tetrapyrrolic precursor of chlorophyll in plants. Apart from diphenyl ethers, a number of other compounds of widely divergent chemical type are potent inhibitors of PROTOX. These include the commercial herbicide, oxadiazon, and several experimental compounds based on heterocyclic ring systems. The herbicides also inhibit PROTOX from other sources, including mammals, where the enzyme is involved in haeme biosynthesis. Despite this potential source of toxicological problems, the number of herbicides of this type on the market or undergoing development attest to the selectivity of the compounds *in vivo*. Characteristics of the enzyme inhibition and whether these molecules have identical binding sites has still to be determined.

## CONCLUSION

The above discussion illustrates the diversity of herbicide targets so far discovered in plant metabolic systems. The list could be extended to include phytoene desaturase, an enzyme involved in carotenoid biosynthesis, which appears to be the primary target of certain bleaching herbicides (fluridone, norflurazon) and glutamine synthetase, inhibited by the herbicide phosphinothricin. This latter compound, like glyphosate, is an active site directed inhibitor and the structure appears to be unique in blocking glutamine synthetase. In many other examples discussed above, however, the particular enzyme is susceptible to a multitude of different structural types. Such enzymes offer the most attractive targets in the search for new phytotoxic molecules.

Despite the classification of most herbicide types into groupings according to mode of action, the precise targets of a number of important herbicide classes, most notably the auxin (2,4-D, MCPA, triclopyr) thiocarbamate (EPTC, vernolate, triallate) and anilide (propachlor, metalachlor, alachlor) groups, remain obscure. Recent work (11) suggests the latter group inhibits fatty acid biosynthesis without identifying the precise enzyme target.

Nevertheless, elucidation of so many primary target sites has profoundly affected strategies for herbicide design. *In vitro* assays designed to detect activity against known targets, particularly plant specific processes such as photosynthesis and essential amino acid biosynthesis, have become an integral part of many screening programs. Attention has also been directed to the *de novo* design of inhibitors for these and other key enzymes in plant metabolic pathways, though such efforts have as yet failed to produce a commercial herbicide. However, an increasing knowledge of the nature and properties of particular enzyme targets will lead to a better understanding of herbicide mode of action and greatly assist the chemist in designing more effective weed control agents.

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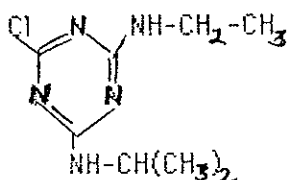
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## PESTICIDE COMMON NAMES

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### INTRODUCTION

Pesticide common names are the familiar names by which pesticides are known. For example, the name atrazine is familiar to all workers involved in weed control activities. Atrazine is the common name for the herbicide (by definition a pesticide) which is 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, and has the structure



Other typical common names are asulam, bromocil, butralin, diquat, dicamba, -all herbicides; insecticides diazinon, DDT, chlorpyrifos, fenthion, permethrin; fungicides captan, dodine, fentin, mancozeb, and so on.

The chemical name above and the structural representation both define the herbicide unambiguously, but is is clearly inconvenient - to say the least - to have to use either form in ordinary everyday transactions. It would be ludicrous to have to give an operator instructions using the unwieldy chemical name as an identifier. Inevitably, abbreviations or code numbers would be used, and these might vary from place to place. The sensible alternative is to invent a simple but unique name which if standardised internationally could be used everywhere to mean the same chemical. This is what is done, and the common name is that alternative.

But who decides what is a suitable name and how is it made internationally acceptable? that is, how is the selected name standardised? This paper attempts to outline some of the answers.

### SELECTION OF COMMON NAMES FOR PESTICIDES

The manufacturer of the pesticide coins its common name - at least in the first instance. This is as it should be, of course. In the same way that human parents in our society select the name for their child so it seems natural that the originator of the chemical should name the chemical. But this is as far as the analogy goes. The selected child's name may be the same as that of some other child. There is nothing in force legally or bureaucratically to prevent or obstruct this choice, at least on the ground that it may produce duplication, commercial confusion, and possibly dangerous or disastrous consequences if it is not unique. No doubt some confusion is caused at school and elsewhere if several children have the same name, but it is not thought serious enough to be disallowed or to be subject to examination for suitability by committees and other elements of the bureaucratic apparatus.

The position is different with proposed pesticide common names. Proposed common names must be unique. They must also conform to other criteria if they are to be deemed acceptable by the

committees which decide their suitability. They may not be the names of marketed products: trade names are not allowed. The proposed names must not be easily mistaken for registered trade marks. They should be (relatively) short, quite distinctive, easily pronounced, and be constructed - wherever possible - from a set of syllables which indicate their family groups (carbamates, triazines, etc) or other characteristic structural features.

This set of recommended syllables is on p7 of the attached 'APPENDIX 1: Pesticides and other agrochemicals - Principles for the Selection of Common Names' (ISO/DIS 257), a document put out by the International Organisation of Standards (ISO).

The Principles give guidelines for dealing with salts, esters, isomers in the general case, and they suggest (item 4.5.4, p3) the use of common root syllables for a pesticide which 'is closely related both chemically and in use to an already-named compound'. Hence the prevalence of groups of closely related common names, such as the insecticides permethrin, cypermethrin, alphamethrin, deltamethrin; and the herbicide names atraton and atrazine.

The recommended syllables set is not exhaustive; a perusal of any index of pesticide names will show frequent use of 'met' (=methyl), 'prop' (=propyl), 'fen'/'phen' (=phenyl), 'sulf'/'sulph' or thio/thia (= combined sulphur), chlor (=chloro), and so on. The overriding principle seems to be that any syllable can be used if it is an abbreviation for some function or part of the chemical name.

The APPENDIX 1 list (p4) also recommends some not obvious syllables, such as 'alin' for 2,6-dinitroanilines and 'tryn' for methylthio-substituted 1,3,5-triazines.

The coined names therefore have syllables in common, and an index of modern pesticides has the appearance of a permutations list of the abbreviations where repeats are not allowed in any name. The days of complete freedom in choice of a name are apparently gone; and splendid names like antu, barban, jasmoline, folpet, ovex, quassia, and even dieldrin, are unlikely to be coined again. Also, it should be noted, the use of numbers, acronyms, and constructions from consonants only (as capital letters) is unlikely to be approved; new names resembling 245-T or DDT would not be considered.

However, modern common names do give some indication of the structure or family of the pesticide, though this may be only apparent to those who spend a lot of time assessing the names. Incidentally, pesticides with simple chemical names do not need coined common names. For example, potassium chlorate and aluminium phosphide are regarded as adequately simple, unambiguous, and distinctive identifying names for the pesticides they describe.

There are difficulties in selecting suitable names for some pesticides and as differences between closely related ones become more refined the difficulties increase.

Examples of this tendency are the isomers of pyrethroids. None of this family are herbicides, but they illustrate nicely a sort of complexity which may occur in pesticide families, irrespective of use pattern, if the first named and marketed one is a mixture of all isomers and later developments produce commercial products based on selected isomers (or perhaps the one isomer) which constitute the actual active entity. For example, the pyrethroid cypermethrin, has 8 enantiomers (4 pairs) and it is understood - without being explicitly stated - that it is a racemic mixture. In recent years a commercial product has been marketed which comprises a sub-set of these enantiomers and which is said to have about twice the efficacy of cypermethrin. It is clearly a closely related but different pesticide to cypermethrin, and so a unique common name is required. Alphamethrin is the common name selected, and it is constructed from a set of rules specially devised to deal with the problem of pyrethroid isomers. The set of rules specific to the naming of pyrethroids is given in APPENDIX 2.

Complicated as it may be the pyrethroid isomers problem is likely to be simpler than that of the similar issue of multiple isomers associated with mould-produced pesticides where the number of enantiomers and other isomers may be relatively large. Either the set of pyrethroid rules suitably modified or a new set of rules may be necessary in future to deal with these compounds.

FIG.1 Examples of the SAA & ISO Standards defining Pesticides Common Names

SAA. AS 1719 p18

Recommended common name (with pronunciation)	Chemical name	Chemical formula	Remarks
chlorpyrifos (klor-pi-ri-fôs)	O,O-diethyl O-3,5,6-trichloropyrid-2-yl phosphorothioate		
chlorpyrifos-methyl (klor-pi-ri-fôs mē-thil)	O,O-dimethyl O-3,5,6-trichloropyrid-2-yl phosphorothioate		
chlorthal-dimethyl (klor-thäl-dí-mē-thil)	dimethyl tetrachloroterephthalate		
chlorthiamid (klor-thi-a-mid)	2,6-dichlorothiobenzamide		
coumachlor (koo-ma-klor)	3-(α-acetyl-4-chlorobenzyl)-4-hydroxycoumarin		

ISO. 1750-1981 p21

chlorpyrifos (IE)	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (IE)		C <sub>9</sub> H <sub>11</sub> Cl <sub>3</sub> NO <sub>3</sub> PS
chlorpyrifos <sup>2)</sup> (FI)	Thiophosphate de O,O-diéthyle et de O-trichloro-3,5,6-pyridyle-2) (FI)		
хлорпирифос (RI)	O,O-diethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (CI)		
chlorpyrifos-methyl (IE)	O,O-dimethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (IE)		C <sub>7</sub> H <sub>7</sub> Cl <sub>3</sub> NO <sub>3</sub> PS
chlorpyrifos-méthyl (FI)	Thiophosphate de O,O-diméthyle et de O-trichloro-3,5,6-pyridyle-2) (FI)		
хлорпирифос-метил (RI)	O,O-dimethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate (CI)		
chlorpyrifos (FI)	See: Voir chlorpyrifos (IE)		
chlorpyrifos-méthyl (FI)	See: Voir chlorpyrifos-méthyl (IE)		
chlorquinox (IE)	5,6,7,8-tetrachloro-quinoline (IE, CI)		C <sub>8</sub> H <sub>2</sub> Cl <sub>4</sub> N <sub>2</sub>
chlorquinox (FI)			
хлорквинокс (RI)	Tétrachloro-5,6,7,8-quinoline (FI)		
chlorthal <sup>3)</sup> (IE)	tetrachloroterephthalic acid (IE, CI)		C <sub>8</sub> H <sub>2</sub> Cl <sub>4</sub> O <sub>4</sub>
chlorthal <sup>3)</sup> (FI)			
хлортал <sup>3)</sup> (RI)	Acide tétrachloroterephthalique (FI)		

1) In USSR, chlor IFC (хлор ИФК) has been accepted as the common name. En URSS, chlor IFC (хлор ИФК) a été accepté comme nom commun.  
 2) In France, the common name chlorpyrifos-ethyl has been accepted. En France, le nom commun chlorpyrifos-ethyl a été accepté.  
 3) It should be stated which ester is present, for example chlorthal-methyl. Il convient de préciser quel est l'ester présent, par exemple chlorthal-méthyl.  
 4) The name "chlorthal" is not acceptable for use in USA, owing to the possibly misleading chemical significance of the syllable "al". Le nom "chlorthal" n'est pas acceptable pour l'emploi aux Etats-Unis, en raison de la signification éventuellement trompeuse de la syllabe "al".

## APPROVAL SYSTEM FOR PROPOSED COMMON NAMES

The approved pesticide common names for use in Australia are those recommended by the Standards Association of Australia (SAA). They are documented in SAA's AS 1719-1981 (& Addenda), 'Recommended Common Names for Pesticides'.

In cases where the SAA has not been asked to consider a proposed name and therefore has not made a recommendation, but one is needed quickly, the listing of ISO's approved common names is consulted (ISO is the International Organisation for Standardisation). It is presently acceptable to Australian registration authorities that ISO approved common names may be used provisionally in the absence of SAA names. It is expected that the SAA would later endorse the ISO name. As it is SAA policy to harmonise wherever possible with ISO this is what usually happens.

It may be asked why when there are ISO-approved common names there are no SAA ones. This is a reflection of Australia's position in the pesticide manufacturing world. Almost all pesticides are invented and manufactured overseas, and the manufacturers apply to ISO for approval of their proposed common names. This may happen before the chemical has been tested in Australia for possible application here. Also, some local subsidiaries of the manufacturers are often slow to apply to SAA for local acceptance of the common names proposed to ISO.

Harmonisation with ISO makes good practical sense. A single standard is clearly desirable internationally, for both scientific and trade reasons. Nationalistic individualism is reduced to a minimum, and the same name may be used across national boundaries without further translation being required.

National systems do exist and differ to varying degrees from each other and from the ISO one. Even the SAA standard has differences from ISO's, but these are not with the common name (except in one importance case: maldison against ISO's malathion). On the whole, most pesticide common names are the same everywhere though spellings may differ slightly when Roman script is used as seen in FIG 1 for the ISO entries.

SAA and ISO have somewhat similar procedural mechanisms for dealing with proposed common names. The SAA system is simpler and so will be outlined. It operates as a series of steps:

- (i) The originator coins a name and proposes it for adoption to SAA.  
SAA secretariat circulates the proposal among its Committee CH15\7 members for comment on acceptability. APPENDIX 4 shows the membership representation on this Committee.
- (ii) Members examine the proposed name for compliance with selection criteria, i.e. suitable name, distinguishable from other names, no conflict or close similarity with existing names or trade names/marks, correct chemical names and structural diagrams, correspondence with ISO approved names. After examination, member's comments are returned to the secretariat.
- (iii) If satisfactory, the proposed name is advertised as an SAA-approved name for inclusion in the Standard eventually.  
If not satisfactory, the proposer is told by SAA secretariat why the name has been rejected, and that a new proposal is needed.  
In fact, by the time proposals are put to SAA the names are usually well advanced in the ISO procedure, and there are few rejections.

If the proposed names have reached draft status in the ISO procedure they are usually suitable in Australia.

The ISO procedure (APPENDIX 3) is made more complicated by the necessity to send first proposals and national comments on them to all members; and as members are national representatives in several countries the procedure tends to be slow. ISO's secretariat collates responses to the circulated information and if comments are favourable the proposals are

circulated as draft standards for members to vote acceptance (or otherwise) in a letter ballot. ISO's secretariat decides borderline or split vote issues.

ISO has approved over 750 common names, though many are now redundant as the named pesticides are no longer manufactured. Several new proposal names are going through the procedural preliminary steps.

SAA has about 340 common names in its standard with over 80 either approved or awaiting approval to be added.

## PRESENT DIFFICULTIES

On the whole, the naming of pesticides does not present too many difficulties. Eventually there will be insufficient approved syllables with which to make distinctive arrangements into pronounceable names, and different acceptable syllables may need to be invented. Present difficulties arise in administrative 'processing' of proposals and in the construction of names for certain types of pesticide.

Difficulties due to 'processing' the proposals stem from the length of time usually taken to reach approval from the time the proposed name is first lodged with the Standards secretariat. Under-resourcing in both SAA and ISO is clearly a factor in the time taken; delayed replies from committee members and other consultants add to it; and applicants are not always prompt in producing proposals, for example, at the time experimental trials for use of the pesticide are planned to proceed. ISO's 'processing' procedure is slow because of the necessity to reach international consensus, and there are many players on the field.

Technical difficulties originate in the application of naming principles; as these are general rules there will usually be exceptions to them. The matter of pyrethroid isomers has been mentioned earlier and it is a case study for future, more complex, problems such as those of the macrocyclic pesticides of the next generation pesticides and possibly bio-engineered structures of the protein/polypeptide type. Of the many isomers some will be expectedly more biologically active than others.

'Biological activity' has been a source of some difficulty when used as a criterion for selecting pesticide common names. It has been a naming principle for some time (APPENDIX 1, item 4.2.2) that the 'biologically active' entity of the compound - if it could be identified in a detachable part of the compound, e.g. the acidic or basic moiety of a salt - would be given the common name in simple cases. With simple alkyl or phenyl complements to the biologically active entity there is no difficulty, such as the esters or salts of 2,4-D in which the 2,4-dichlorophenoxyacetic entity is deemed the (sole) biologically active part of the compound and is called 2,4-D. The complements are exchangeable without affecting the intrinsic herbicidal property of the pesticide. But with more complex compounds, such as the pyrethroids which are esters, the common name applies to the whole compound because the activity is considered to be a property of the whole molecule in its completeness. There have been borderline cases where the division of activity was not clear-cut, such as fosetyl-aluminium, and these have given difficulty in interpretation, and particularly in bureaucratic treatment of the names.

In earlier times, the first-named compound was given the common name irrespective of the complement if it was an ester and the common name applied to the whole compound. Subsequent variations in which the complementary moiety was changed were given names which had the new complement appended to the first name as a hyphenated suffix; for example, bromophos was given to the original dimethyl ester of the biologically active phosphorothioic entity, and the diethyl variant was called bromophos-ethyl.

Recently, ISO has advanced names such as tolclofos-methyl even though there is no predecessor called simply tolclofos. This may be a new policy, but it presents a problem to SAA as it is seemingly without precedent and the guiding principle has yet to be seen.

#### CONCLUSION

The work of establishing pesticide common names will continue as it is done now through established procedures. Possibly the process may become quicker, but it almost certainly will become more complicated with the development of the next generation pesticides such as macrocyclic and bio-engineered compounds.

#### ATTACHMENTS

- . APPENDIX 1. Pesticides and other agrochemicals: Principles for the selection of common names.
- . APPENDIX 2. System for constructing common names for isomers and isomer mixtures of pyrethroids and related compounds.
- . APPENDIX 3. Procedure for the establishment of common names for pesticides and other agrochemicals.
- . APPENDIX 4. Representation on SAA Committee CH/5/7.



# Pesticides and other agrochemicals — Principles for the selection of common names

## 1 Scope and field of application

This International Standard lays down principles for coining common names for pesticides and other agrochemicals. These principles are defined for the guidance of proposers of such common names and for the operation of ISO Technical Committee 81, *Common names for pesticides and other agrochemicals*.

NOTE — The procedure for the establishment of common names is given in annex B.

## 2 Definition

For the purpose of this International Standard, the following definition applies :

**common name** : A name freely available for common use in identifying a chemical substance without recourse to its scientific name.

## 3 Purpose

**3.1** The purpose of a common name is to provide a short, distinctive, easily pronounced name for a substance, the full chemical name of which is too complex for convenient use in science, commerce and official regulations.

**3.2** Because a common name has to be freely available for use in describing the substance for which it has been coined, it should not be permitted to become a privately owned trade mark in respect of those or similar goods.

**3.3** In order to achieve the desired goal of creating a common name that is generally acceptable internationally, rejection of any proposed common name by individual ISO member bodies [see B.2.1.3 and B.3.1.1 e)] should only be based on serious grounds and then only after every possible effort has been made to overcome the impediment to local acceptability.

## 4 Principles for selection

### 4.1 General

**4.1.1** No substance should be given a common name if its chemical name is reasonably short and distinctive (for example metaaldehyde, carbon tetrachloride).

**4.1.2** The identify of a common name should be maintained in all languages, subject to necessary linguistic variations.

**4.1.3** Common names should be as short as is practicable, but should not include single letters and/or numerals except as structural qualifiers.

NOTE — While the formation of common names from initials and numerals is no longer acceptable, exceptions (for example MCPA, 2,4,5-T) have been made for substances which had become so well known by that name that to use another name would have caused confusion.

**4.1.4** Common names should be distinctive in sound and spelling and should not be either difficult to pronounce or liable to confusion with existing names (see 4.5.1).

**4.1.5** To facilitate international spelling and translation, "f" instead of "ph" should be used in common names; the suffix "-phenyl" in the names of esters should, however, retain its normal spelling.

## 4.2 Salts and esters

### 4.2.1 Simple salts

The common name for a simple salt should be given to the parent acid or base. In the case of an acid, the complementary cation may be given as a hyphenated suffix and, in the case of a base, the complementary anion stated. A quaternary ammonium or phosphonium salt should be treated as a salt of a base, for example :

alloxydim-sodium  
imazalil nitrate  
chlormequat chloride

### 4.2.2 Simple esters

The common name for a simple ester whose biological activity depends upon the parent acid or hydroxy compound should be given to that parent. The complementary esterifying radical may be indicated as follows :

mecoprop-methyl  
dinoseb acetate

### 4.2.3 Complex esters and salts

If neither moiety of an ester or salt is simple, the common name should be given to the whole molecule, for example :

bupirimate  
decafentin

### 4.3 Purity of chemicals

Although common names should be given to chemical entities of known structure, in exceptional cases they may be given to mixtures the composition of which is constant for all practical purposes and of which the concentrations of active components can be specified.

Such exceptional cases may include :

- a) a reaction product mixture, provided that the concentrations of the main active components fall within acceptable limits about specified proportions;
- b) a polymeric reaction mixture, provided that the concentrations of the main active component polymers (the repeating units of which are specified) in the reaction mixture are known and are constant to within acceptable limits;
- c) an extract or derivative of a natural product (from animal, plant, fungal or bacterial sources) the composition of which is constant to within acceptable limits.

### 4.4 Isomers and isomeric mixtures

The following special considerations should be taken into account when coining names for mixtures of isomers.

4.4.1 The common name for a substance that can exist in enantiomeric (optically isomeric) forms owing to a single asymmetric centre should be assigned, without affixes, either to the racemate or to one of the enantiomorphs, depending on the form for which the common name is first required. If a common name is required subsequently for another stereochemical variant, it should be the original common name with the appended suffix "-MP", "-M" or "-P", for the racemate, the (-)-isomer or the (+)-isomer, respectively.

If more than one chiral centre is present, it may be necessary to adopt special measures such as a system based on the use of suffixes, for example that developed for the synthetic pyrethroids (see annex A).

4.4.2 The common name of a substance which consists of complementary geometrical isomers should indicate the essential familial features (see 4.6). A specific isomer or subgroup of isomers of such a substance may be assigned a common name [which may include a syllable or letter(s) implying either a *cis*-, *trans*-, (*E*)- or (*Z*)- form] only if the substance is produced commercially in a substantially pure form.

If a normal commercial product consists of a mixture of a single pair of isomers, the common name should apply to any mixture of the two. Individual isomers should be identified by suitable qualifiers, for example *cis* and *trans* or (*E*) and (*Z*).

NOTE — If it is commercially possible to produce mixtures with different ratios of isomers, the ratio should be stated on the commercial product, for example "60 : 40". The ratios will not form part of the common name.

4.4.3 The common name for a substance which consists of a mixture of optical and geometric isomers, for example some of the synthetic pyrethroids, should be one that is appropriate to the mixture and should be modified by qualifiers, if required, to specify subgroups or individual isomers.

4.4.4 If a substance consists of a mixture of structural isomers, only one of which is pesticidally active, the common name should be assigned only to the active isomer. However, if the substance consists of a mixture of pesticidally active isomers, and if the isomerism consists of variations in chain branching or position of substituents, the common name should be assigned to the mixture, which should be defined as "an isomeric reaction mixture of A + B...". In ISO 1750<sup>1)</sup>, footnotes giving indications of the usual proportions are included. If necessary, names for individual isomers may be derived by modifying the common name applied to the mixture.

### 4.5 Additional requirements

4.5.1 A common name should not be liable to confusion with :

- a) established chemical names;
- b) common names already either officially authorized or in well-recognized use for other pharmaceutical, pesticidal or related substances;
- c) trade marks considered as possibly similar to and enjoying legal protection in respect of pharmaceutical, pesticidal or related substances, unless the prior consent in writing of the trade mark owner has been secured.

4.5.2 In accordance with its definition and purpose (clauses 2 and 3), a common name cannot be a proprietary name in respect of goods broadly of the same category. However, in some cases, circumstances may exist during an interim period which make it desirable for proprietary rights to be maintained as, for example, where the proposer has agreed to surrender his proprietary rights subject to final acceptance of the name as an official common name. In such cases the proprietor should first agree in writing to discontinue the use of the name as a trade mark as soon as official recognition as a common name is given by ISO and thus :

- a) to permit the use of the name as the accepted common name by any party whatsoever who is properly using it;
- b) to surrender all proprietary rights as soon as the special circumstances justifying their retention have ceased to exist.

1) ISO 1750, *Pesticides and other agrochemicals — Common names.*

Table 1 — Recommended syllables<sup>1)</sup>

Type of compound	Recommended syllable	Position in name	Examples
2,6-dinitroanilines	-alin	Suffix	trifluralin $\alpha, \alpha, \alpha$ -trifluoro-2,6-dinitro - <i>N, N</i> -dipropyl- <i>p</i> -toluidine
1,3,5-triazines Chloro-substituted	-azine	Suffix	atrazine 6-chloro- <i>N</i> <sup>2</sup> -ethyl- <i>N</i> <sup>4</sup> -isopropyl-1,3,5- triazine-2,4-diamine
Carbamates	carb- or -carb- or -carb	Any position	carbofuran 2,3-dihydro-2,2-dimethylbenzofuran-7-yl methylcarbamate
Coumarins	coum- or -coum	Prefix or suffix	coumatetralyl 4-hydroxy-3-(1,2,3,4-tetrahydro-1-naphthyl)- coumarin
Antifungal compounds based on imidazole or 1,2,4-triazole and containing a chlorinated phenyl group	-conazole	Suffix	penconazole 1-(2,4-dichloro- $\beta$ -propylphenethyl)- 1 <i>H</i> -1,2,4-triazole
Dinitrophenols and their esters	din-	Prefix	dinoterb 2- <i>tert</i> -butyl-4,6-dinitrophenol
Phenoxypropionic acids of the fluzifop type	-fop	Suffix	fluzifop ( <i>RS</i> )-2-[4-(5-trifluoromethyl-2-pyridyloxy)phenoxy]propionic acid
Organophosphorus compounds	fos- or -fos- or -fos	Any position	quintofos <i>O</i> -ethyl <i>O</i> -quinolin-8-yl phenyl- phosphonothioate
1,3,5-triazines Methoxy-substituted	-meton	Suffix	methometon 6-methoxy- <i>N</i> <sup>2</sup> , <i>N</i> <sup>4</sup> -bis(3-methoxypropyl)- 1,3,5-triazine-2,4-diamine
Ethylenebis(dithiocarbamates)	-(n)eb	Suffix	maneb manganese ethylenebisdithiocarbamate (polymeric)
Quaternary nitrogen compounds	-quat	Suffix	paraquat 1,1'-dimethyl-4,4'-bipyridinium
Cyclopropanecarboxylic acid esters (pyrethroids)	-thrin	Suffix	permethrin 3-phenoxybenzyl (1 <i>RS</i> , 3 <i>RS</i> ; 1 <i>RS</i> , 3 <i>SR</i> )-3-(2,2-dichlorovinyl)- 2,2-dimethylcyclopropanecarboxylate
1,3,5-triazines Methylthio-substituted	-tryn <sup>2)</sup>	Suffix	simetryn <i>N</i> <sup>2</sup> , <i>N</i> <sup>4</sup> -6-methylthio- 1,3,5-triazine-2,4-diamine
Ureas	-uron	Suffix	linuron 3-(3,4-dichlorophenyl)-1- methoxy-1-methylurea

1) The recommendations are based on the chemical structures of the compound.

2) In English, the ending -tryne was originally recommended, but was abandoned because the ending might be thought to indicate the presence of a C=C grouping (see 4.6.2).

(CONTINUED)

4.5.3 A common name should not be included in a national standard until it is considered that conflicts with legally protected trade marks are unlikely and that the name is likely to be internationally acceptable.

4.5.4 In the common name proposed for a substance which is closely related both chemically and in use to an already-named compound, it is preferred but not required that the proposal should reflect the similarity by using a common root (which may or may not be a recommended syllable : see 4.6) in conjunction with syllables suggestive of the variation.

Examples :

ethirimol	dimethirimol
chlorotoluron	chloreturon
carbofuran	decarbofuran
formetanate	formparanate
permethrin	cypermethrin

#### 4.6 Recommended syllables

4.6.1 A common name should, if appropriate, include a syllable indicative of the types of compound listed in table 1.

The recommended syllable should be used in the name at the position specified. Judicious use of other non-chemical rather than chemical syllables in a common name provides greater flexibility and reduces the possibility of conflict with existing names.

4.6.2 The use of syllables with misleading chemical significance should be avoided. For example, a name ending in "-ol" or "-one" is not acceptable for a compound that is not an alcohol (or phenol) or a ketone.

### 5 Style of writing or printing common names

Common names should be treated as common nouns and should not, therefore, be capitalized except where required by national usage. Some common names which were coined before these principles were elaborated consist of initials and/or numerals. If such names consist only of initials, they should be written in capitals without intervening full-stops (for example, **MCPA**). If numerals and letters both occur, the numerals should be separated from one another by commas and from letters by a hyphen (for example, **2,4,5-T**).

## APPENDIX 2

## System for constructing common names for isomers and isomer mixtures of pyrethroids and related compounds

(This annex forms an integral part of this International Standard.)

### A.1 Designation of stereochemistry in the chemical name

The possible chiral centres involved are indicated by asterisks in the diagram below.

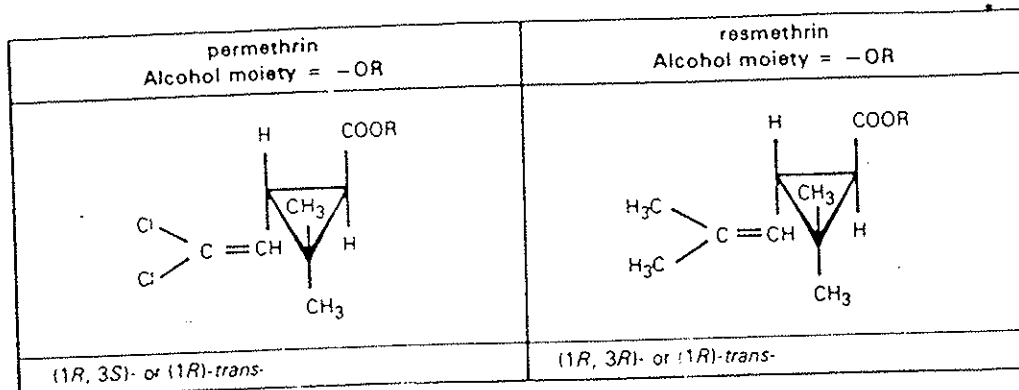
The absolute configuration at chiral centres can be designated by the use of the Sequence Rule, and geometrical isomerism by the *E* and *Z* descriptors. Both systems are described in the IUPAC *Rules for the nomenclature of organic chemistry*, Section E: Stereochemistry. However, the rigorous application of the Sequence Rule to the two chiral centres of the cyclopropane ring would lead to a description in which the relationship between biological activity and chemical structure is obscured. This is particularly unfortunate insofar as it would hinder discussion among workers in the pyrethroid field. In this document the relationship of these two chiral centres is described by the use of *cis*- and *trans*-, in conjunction with the

designation of the absolute configuration at C1, following a proposed system (*J. Chem. Soc. Perkin 1*, 1974, 2470). An example is shown in the diagram overleaf.

In these diagrams the stereochemistry of the cyclopropane ring is shown by means of a "Haworth" representation wherein the ring is considered as being planar and nearly perpendicular to the plane of the paper, with attached groups lying above or below the plane of the ring and represented by vertical lines. Carbon atom number two is closest to the observer and depicted by two wedges tapering into the distance, linking up to carbon atoms one and three. This representation also confers a clockwise notation to the cyclopropane ring.

IUPAC does not sanction the use of a combination of "absolute" and "relative" descriptors to describe a stereochemical situation but such a procedure has clear advantages in the description of the stereoisomeric mixtures which are to be found in the specialized field of pyrethroids.

Ester RCO-R'	
Alcohol moiety RO-	Acid moiety R'CO-



## A.2 Designation of stereochemistry in the common name

If a common name has already been assigned it shall continue to apply to the isomer mixture described in the ISO list. If necessary, ratios of *cis* to *trans* and (*R*) to (*S*) isomers in mixtures shall be shown on the label, but not as part of the common name. Preceding cases, especially permethrin, have already established this practice.

A future compound with a novel structure, irrespective of whether it is a single isomer or a mixture of isomers, should receive a new root name without a suffix.

However, a future compound related to a basic structure to which a common name had already been assigned should be given the same common name, but with a suffix (linked to the stem name by a hyphen) determined by reference to table 2.

Table 2 -- Stereochemical designations

Type	I	II	III	IV	V
Examples	terallethrin	fenvaleate	permethrin resmethrin	allethrin cypermethrin	cyhalothrin tralomethrin
Centres involved <sup>1)</sup>	Alc	Alc; Acid	Acid 1,3	Alc; Acid 1,3	Alc; Acid 1,3; Acid (substituent on 3)
Suffix					
A	( <i>RS</i> )	( <i>RS</i> ); ( <i>RS</i> )	(1 <i>RS</i> )- <i>cis-trans</i> -	( <i>RS</i> ); (1 <i>RS</i> )- <i>cis-trans</i> -	( <i>RS</i> ); (1 <i>RS</i> )- <i>cis-trans</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )
B		( <i>RS</i> ); ( <i>S</i> )	(1 <i>R</i> )- <i>trans</i> -	( <i>RS</i> ); (1 <i>R</i> )- <i>trans</i> -	( <i>RS</i> ); (1 <i>R</i> )- <i>trans</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )
D			(1 <i>R</i> )- <i>cis</i> -	( <i>RS</i> ); (1 <i>R</i> )- <i>cis</i> -	( <i>RS</i> ); (1 <i>R</i> )- <i>cis</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )
F			(1 <i>R</i> )- <i>cis-trans</i> -	( <i>RS</i> ); (1 <i>R</i> )- <i>cis-trans</i> -	( <i>RS</i> ); (1 <i>R</i> )- <i>cis-trans</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )
G			(1 <i>RS</i> )- <i>trans</i> -	( <i>RS</i> ); (1 <i>RS</i> )- <i>trans</i> -	( <i>RS</i> ); (1 <i>RS</i> )- <i>trans</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )
J			(1 <i>RS</i> )- <i>cis</i> -	( <i>RS</i> ); (1 <i>RS</i> )- <i>cis</i> -	( <i>RS</i> ); (1 <i>RS</i> )- <i>cis</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )
K		( <i>R</i> ); ( <i>R</i> ) plus ( <i>S</i> ); ( <i>S</i> )		( <i>S</i> ); (1 <i>R</i> )- <i>trans</i> - plus ( <i>R</i> ); (1 <i>S</i> )- <i>trans</i> -	
L				( <i>S</i> ); (1 <i>R</i> )- <i>cis</i> - plus ( <i>R</i> ); (1 <i>S</i> )- <i>cis</i> -	
N					( <i>RS</i> ); (1 <i>RS</i> )- <i>trans</i> -; ( <i>Z</i> )
T					( <i>RS</i> ); (1 <i>RS</i> )- <i>cis</i> -; ( <i>Z</i> )
U	( <i>S</i> )	( <i>S</i> ); ( <i>S</i> )		( <i>S</i> ); (1 <i>R</i> )- <i>trans</i> -	( <i>S</i> ); (1 <i>R</i> )- <i>trans</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )
V				( <i>S</i> ); (1 <i>R</i> )- <i>cis</i> -	( <i>S</i> ); (1 <i>R</i> )- <i>cis</i> -; ( <i>RS</i> ) or ( <i>ZE</i> )

1) Alc = Alcohol; Acid 1 and 3 being on the cyclopropane ring.

Table 3 — Summary of compounds for which common names have been proposed (to May 1982)

Proposed common name (in chronological order)	Structural type (for isomerism)	Isomer mixture	What name would have been, using proposed system
allethrin	IV	A	No change
dimethrin	III	A	No change
tetramethrin	III	A	No change
resmethrin	III	A	No change
bioresmethrin	III	B	resmethrin-B
pyresmethrin	III plus (ZE)	B	No change
bioallethrin	IV	B	allethrin-B
cismethrin	III	D	resmethrin-D
biopermethrin	III	B	permethrin-B
permethrin	III	A	No change
transpermethrin	III	G	permethrin-G
phenothrin	III	A	No change
cypermethrin	IV	A	No change
deltamethrin	IV	V	No change
fenpropathrin	I	A	No change
fenvalerate	II	A	No change
esdepallethrin	IV	U	allethrin-U
cyhalothrin	V	T	No change
terallethrin	I	A	No change
esfenvalerate	II	U	fenvalerate-U
cyphenothrin	IV	A	No change
flucythrinate	II	B	No change
tralomethrin	V	V	No change
fenfluthrin	III	B	No change
fenpirithrin	IV	A	No change
fluvalinate	II	A	No change
cycloprothrin	II	A	No change

## Procedure for the establishment of common names for pesticides and other agrochemicals

(This annex forms an integral part of this International Standard.)

### B.0 Introductory note

This annex has been prepared for the information of the ISO member bodies and of sponsors and originators of common names.

#### Glossary of the English (and French) terms and definitions

**B.0.1** proposed common name [proposition de nom commun] : Name submitted by the sponsor.

**B.0.2** draft proposal for a common name [avant-projet de nom commun] : Name circulated for preliminary enquiry to ISO/TC 81.

**B.0.3** draft common name [projet de nom commun] : Name circulated to ISO in a draft addendum to ISO 1750.

**B.0.4** accepted common name [nom commun accepté] : Name that has successfully passed the ISO voting stage, but has not yet been published in ISO 1750 or one of its addenda.

**B.0.5** published common name [nom commun publié] : Name that has been published in ISO 1750 or one of its addenda.

**B.0.6** national common name [nom commun national] : Name that has been published in a national standard of a particular country (the country to be stated).

### B.1 Stage 1 — Proposed common name

#### B.1.1 Submission

**B.1.1.1** Proposed common names are submitted to the ISO/TC 81 Secretariat for consideration with a view to adoption by ISO, normally through the national standards body of the country concerned. Submissions by other routes, for example from the manufacturers direct to the Secretariat or by the distributors in a country other than that in which the product is manufactured or originates, are permissible.

**B.1.1.2** Proposed common names submitted for letter ballot to the USA National Committee or conveyed to the Secretariat by any other national committee which wishes to do so, are assumed to have been submitted to the Secretariat for consideration and adoption by ISO/TC 81 without a specific request to this effect being necessary, unless a definite statement

is made by the sponsor that he does not wish the name to be considered by ISO.

NOTE — As a matter of principle, such statements can only be deprecated, because adoption of common names, which are used throughout the world, on a purely national level, without knowledge of their international acceptability, is certain to give rise to problems. The main such problem is the eventual use of different common names in different geographical contexts, which defeats the object of standardization.

#### B.1.2 Information required

##### B.1.2.1 Basic data

The following information is required to accompany a proposal for a new common name :

- a) the proposed common name, alternatives being allowed;
- b) the systematic chemical name for the compound to which the common name is to be applied, including :
  - 1) stereochemical identifiers, in the case of compounds that exist in different stereochemical forms, and, if appropriate, the proportions of the various isomers;
  - 2) in the case of compounds of uncertain composition, as much information on the chemical constitution as possible;
  - 3) the Chemical Abstracts Service Registry Number, or Numbers if appropriate;

NOTE — Three systematic chemical names will be included in ISO 1750, namely those corresponding to :

- the English interpretation of the IUPAC rules,
- the French interpretation of the UICPA rules, and
- that used by Chemical Abstracts.

These three names are provided by the recognized authorities in the United Kingdom and France and by the Chemical Abstracts Service, respectively.

- c) the molecular formula;
- d) the structure of the compound or compounds to which the common name is to be applied, indicating the stereochemistry if appropriate [see B.1.2.1 b)];

NOTE — The structures will, if necessary, be re-drawn to ensure self-consistency within ISO 1750.



e) the name and address of the sponsor, together with any proprietary names, including trade marks, for the product;

f) any other trivial names, code numbers or abbreviations for the compound;

g) the use of the product;

NOTE — At present, the most common uses, for which abbreviations (in parentheses) have been established by ISO/TC 81, are:

acaricides (A)

bactericides (B)

fungicides (F)

herbicides (H)

insecticides (I)

molluscicides (M)

nematicides (N)

plant-growth regulators (P)

safeners (S)

avicides (V)

synergists (Y)

h) a statement indicating whether the sponsor will himself arrange for a search for internationally registered trade marks or will request a search by WIPO (see B.1.2.2 and B.2.1.3).

### B.1.2.2 Trade mark reports

It is a principle [see 4.5.1c)] that common names shall not be liable to confusion with commercial trade marks. To check this as far as is practicable, sponsors of common names are required by ISO/TC 81 to obtain, pay for and submit to the ISO/TC 81 Secretariat reports of trade mark searches in classes 1 and 5 of the registers of:

- the World Intellectual Property Organization;
- the United States of America;
- the United Kingdom;
- the sponsor's country.

NOTE — It is permissible for the name that is being proposed as a common name to be registered as a trade mark in order to protect it until the common name has been adopted by ISO. All such rights have, however, to be relinquished as soon as the common name has been so adopted.

These reports should be provided at as early a stage as possible, preferably with the submission of the proposed common name, but certainly before the closing date of the preliminary enquiry (see B.1.3.1). It should be noted, however, that if a proposed common name be unacceptable at any stage for any reason, and a replacement common name considered, it is usually necessary for further trade mark reports to be submitted.

The reports are not required for common name proposals formed by attaching suffixes to common names for which trade mark reports have previously been submitted.

### B.1.3 Secretariat examination

B.1.3.1 The Secretariat examines all proposed common names, as soon as possible (usually within four weeks) after receipt. Unless there are strong reasons not to do so, the proposals proceed to the next stage (preliminary enquiry), after a careful check on the information supplied (see note under B.1.2.1b)) and re-drawing of the structure (see note under B.1.2.1d)). The submitters are informed of the action taken.

B.1.3.2 The Secretariat examination at this stage is on "absolute grounds", by which is meant compliance with the principles set out in ISO 257. The most common reasons for a proposed common name not being acceptable at this stage are

- misleading chemical significance, for example ending in the syllable "-ol" if the compound is not an alcohol;
- the compound concerned being an ester or salt, when the name should be coined for the active moiety (see 4.2);
- misleading similarity to an adopted common name
- likelihood of confusion with an adopted common name, with relevant trade marks or with other non-proprietary names, notably WHO International Non-proprietary Names (for pharmaceuticals);
- presence of a syllable recommended for inclusion in classes of compounds of which that proposed is not a member, or absence of an appropriate recommended syllable (see table 1).

These reasons are not exhaustive and are not necessarily in order of importance. In such cases if the objections are strong enough, the reasons are given to the originator with a request for a replacement proposal. In certain cases, the Secretariat may make suitable suggestions.

## B.2 Stage 2 — Draft proposal for a common name

### B.2.1 Preliminary enquiry (corresponding to ISO draft proposals)

B.2.1.1 After having been satisfied that Stage 1 has been completed, the Secretariat circulates the proposed names for preliminary enquiry to the participating ("P") and observer ("O") members of ISO/TC 81 and to international organizations in liaison with ISO/TC 81, notably the World Intellectual Property Organization (WIPO) and the World Health Organization (WHO), allowing a four-month period for reply.

B.2.1.2 Acceptance or objections should be lodged with the Secretariat within four months, that is before the closing date on the preliminary enquiry concerned.

**B.2.1.3** The object of this preliminary enquiry is to allow all the members of ISO/TC 81 (which are assumed to be those with an interest in the subject of pesticides, etc.) the opportunity to consider the acceptability of the proposed common name on "absolute grounds" (see B.1.3.2) and also to check for possibly conflicting nationally protected marks that present a barrier. In such cases, clearance from the trade mark owner for the use of the proposed common name needs to be obtained.

NOTE — A suitable form of words to obtain such clearance is given in B.6. for information.

If this clearance cannot be obtained, or the barrier otherwise overcome, the common name has to be identified in ISO 1750 as unacceptable in the country concerned, bearing in mind the principle embodied in 3.3.

If not already done at step B.1.2.2, the originator of the proposal arranges for a search to be carried out among the international registrations of trade marks effected under the Madrid Agreements (Marks<sup>1)</sup> for internationally registered trade marks identical with or similar to the proposed common names and submits the results (in full) to the Secretariat, if possible by the closing date on the preliminary enquiry concerned. This search shall be carried out in relation to classes 1 and 5 of the international classification established under the Nice Agreement<sup>2)</sup> and may be arranged either through the competent services of WIPO itself or through any suitable agency. All members of ISO/TC 81 are required to conduct a corresponding search for trade marks registered nationally.

The object of these searches is to avoid the possibility of dangerous confusion in sound or spelling with other products, especially those for foods or pharmaceutical products. In their replies to the preliminary enquiry notifying such conflicts, delay is avoided if the names and addresses of the owners of the trade mark with which confusion may arise are given, together with the type of product for which the trade mark has been registered. Failure to meet the closing date for replies to preliminary enquiries, or to notify that the reply will be delayed until a stated date, will inevitably result in considerable delays at later stages.

**B.2.1.4** In their replies to preliminary enquiries, France and the USA provide two additional items of information, if not already supplied. These are :

- a) France : the spelling, if different, and gender of the common name in French, and the French (UICPA) systematic chemical name;
- b) USA : the systematic chemical name preferred by the Chemical Abstracts Service.

## B.2.2 Secretariat examination

**B.2.2.1** The Secretariat examines the replies to the preliminary enquiries as soon as possible (usually within four weeks) after the closing date and either :

- a) approves the name for inclusion in a list for letter ballot by all ISO member bodies as a draft addendum to ISO 1750 (in this case, only one of any given alternatives is selected and, if necessary, any countries with conflicting nationally protected trade marks are noted); or
- b) decides that one or more comments make the name(s) unacceptable, in which case discussions are re-opened with the sponsors to obtain more acceptable replacements. These replacements are then submitted for second or subsequent preliminary enquiry, with an explanatory note in the remarks section of the data sheet, and so on, until an acceptable name is obtained.

**B.2.2.2** A summary of replies to preliminary enquiries, together with the proposed Secretariat action, is circulated to members of ISO/TC 81 as soon as possible after consideration. National standards bodies are expected to inform originators of successful proposals; in other cases, the direct negotiations mentioned in B.2.2.1b) take place.

**B.2.2.3** As specifically resolved by ISO/TC 81, acceptance of any proposed name on a national level should be withheld at least until the results of the preliminary enquiry are known.

**B.2.2.4** Names for compounds on which it seems unlikely that agreement can be reached by postal consultation are referred for discussion at a plenary meeting of ISO/TC 81.

## B.3 Stage 3 — Draft common name

### B.3.1 Draft addendum to ISO 1750

**B.3.1.1** The ISO/TC 81 Secretariat prepares a bilingual English and French version of a list of proposed names as soon as they have passed the draft proposal stage (B.2).

These lists contain :

- a) the proposed common names with English, French and Russian spellings, together with footnotes giving local spelling variations and countries where the ISO name is not acceptable, giving the reasons and, if known, the common names that are used in those countries;

NOTE — A distinction is made between a common name

- not being *acceptable*, for whatever reason, and
- not having been *adopted*.

1) The Madrid Agreement Concerning the International Registration of Marks (of 14 April 1891 as revised 14 December 1900, 2 June 1911, 6 November 1925, 2 June 1944, 15 June 1957 and 14 July 1967).

2) The Nice Agreement Concerning the International Classification of Goods and Services for the Purposes of the Registration of Marks (of 15 June 1957, as revised 14 July 1967).

Both of these Agreements are available from : World Intellectual Property Organization (WIPO), 34 chemin des Colombettes (Place des Nations), 1211 GENEVA 20, SWITZERLAND

A common name can be *acceptable* in any country without its having been *adopted* in that country. The means of promulgation of common names on a national level varies from country to country. Some (for example, the United Kingdom) automatically implement ISO common names in their national standard or in some other publication. Some (for example, USA) only adopt common names in their national standard if a specific national submission for that name is made.

b) the systematic chemical names, in English (IUPAC), French (UIPAC) and according to Chemical Abstracts usage, in that order;

c) the structure of the compounds or, in the case of reaction products or mixtures of isomers, etc, their compositions;

NOTE - Compounds of uncertain composition are given in an annex

d) the molecular formula;

e) the use(s) of the compounds, classified according to the list in the note to B.1.2.1g);

f) the countries where the names are not acceptable, referring to footnotes giving the reasons and, if known, the names which have been adopted or are proposed for adoption in the countries concerned;

g) annexes in which the corresponding information is given for compounds of uncertain composition.

**B.3.1.2** These lists are circulated as draft International Standards by the ISO Central Secretariat to all member bodies of ISO for letter ballot.

The remaining procedure follows precisely that of ISO in general, as laid down in the ISO Directives, and need not be dealt with in detail here

**B.4 Stage 4 - Accepted common name**

The name has not yet been published in ISO 1750 or one of its addenda.

**B.5 Stage 5 - Published common name**

The name has been published in ISO 1750 or one of its addenda.

**B.6 Standard letter of approach to trade mark owners concerning clearance for use of a proposed common name**

"Dear ...

The International Committee (ISO/TC 81) concerned with the coining of common names for pesticides is considering a proposal that the name... should become the ISO common name for the chemical... which is intended for use as a...

The Committee is always greatly concerned to respect the reasonable rights of prior trade marks owners and users, and to this end had conducted a search which has revealed your *prima facie* rights in the trade mark (No.)... (Mark)...

It is extremely difficult and expensive to select a common name acceptable throughout the greater part of the world and we are sure you will realise that it is to the general advantage of all those concerned with the safe and efficient use of pesticides to do all they can to contribute towards a successful process of selection in this field.

Common names are not, of course, trade marks and are not intended to perform the function of trade marks. Their function is simply to designate unambiguously the specific substance or compound for which they have been coined, without the necessity of recourse to the often complex systematic name

If your trade mark is in use upon a product which could be affected detrimentally by the adoption of the proposed common name by ISO we shall take this into the most serious consideration. Should this be the case, would you please be kind enough to let us know the product in question and, if possible, the principal territories in which it circulates. If, however, it is not in use (at all or upon a product likely to be affected), then we should appreciate your formal confirmation in order to clear the way to final adoption as soon as possible.

Your assistance to the Committee would be very greatly appreciated.

Yours sincerely ..."

PROPOSED RESTRUCTURE OF  
SUBCOMMITTEE CH/5/7 - COMMON NAMES FOR PESTICIDES

TERMS OF REFERENCE:

To maintain a list of recommended common names for pesticide chemicals used in Australia. The object of a common name is to provide a short, easily pronounced name for a pesticide when the full chemical name is too long and complicated for use in commerce and in official regulations.

PROPOSED MEMBERSHIP

<u>Interest</u>	<u>Number of Representatives</u>
<u>Public Health</u>	
National Health and Medical Research Council	1
<u>Research</u>	
CSIRO, Division of Applied Organic Chemistry	1
<u>Commonwealth Pesticide Registration Authority</u>	
Department of Primary Industries & Energy	1
<u>State Pesticide Registration Authorities</u>	
Department of Agriculture NSW	1
Department of Agriculture SA	1
Department of Agriculture & Rural Affairs Vic	1
Department of Health WA	1
Department of Health Services Tas	1
Department of Primary Industries Qld	1
<u>Manufacturers</u>	
Agriculture & Veterinary Chemicals Association of Australia	1
Australian Chemical Specialties Manufacturers Association	1
Aerosols Association of Australia	1

PRINCIPLES OF FORMULATION

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ABSTRACT

The important types of Pesticide Formulations are, Wettable Powders (WP's), Emulsifiable Concentrates (EC's) and Suspension Concentrates or Flowables (SC's). Other types currently in the initial phases of development and production are Water Dispersible Granules (WG's) Capsule Suspensions (CS's), Microemulsions (ME's) and oil-in-water emulsions (EW's).

WP's and EC's are easy to develop and produce, but in progressing from flowables to granules to capsule suspensions, there is an increasing level of complexity both in development and in production. The more difficult-to-make formulations have attracted wide interest and support within the industry because they offer greater safety and health properties.

Each of the formulation types is constructed from a "standard" recipe, the ingredients of which can be manipulated to achieve the desired goals of safety to all concerned, least impact on the environment, high quality, lowest cost and ease of production.

A discussion of the technology of each formulation type is included.

Each formulation that passes initial trials is subjected to a suite of conditions designed to seek out weak points of physical and/or chemical stability.

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In most cases, an active ingredient, in its raw state, is, unsuitable for direct application, so it must be converted into a form that delivers it to the target organism in the safest, most efficient way.

Figure 1 shows the main formulation types now either available or under active development.

<u>Liquids</u>	<u>Solids</u>
Suspension Concentrates (Flowables) (SC's)	Wettable Powders (WP's)
Emulsifiable Concentrates (EC's)	Granules
Ultra-Low Volume Sprays (ULV's)	Water dispersible Granules (WDG's)
Microemulsions (ME's)	
Oil in water emulsions (EW's)	
Capsule suspensions (CS's)	

Figure 1 Main formulation types.

Figures 2a and 2b shows the main constituents of each formulation type.

#### SUSPENSION CONCENTRATES

Suspension concentrates are liquid formulations based almost exclusively on water as the carrier. They most usually contain from 500 to 600 g per litre of active ingredient. This can be one or two or even three actives, depending on the application. Although the actives in suspension concentrates are almost always powders, some SC's are combinations of powder and liquid actives.

The actives, whether powder or liquid must have a low solubility in water to prevent crystallisation in the formulations. (In some instances specialist applications require the use of an active with quite high water solubility. If this active is present in low concentrations say 50 - 150 g/L it is sometimes possible to incorporate a water-miscible co-solvent to increase the solubility of this particular active and dissolve that portion of it which would otherwise crystallise in the formulation.)

In order to make a physically and chemically stable formulation a

large number of other ingredients must be added to improve the product's shelf life.

Wetting agents - are used to lower the surface tension of the water to enable the powder active(s) to wet out in a short time.

Dispersing agents - are added to prevent the individual particles of active ingredient from adhering to one another and prevent the formation of a non-redispersible cake. However, like wetting agents, the dispersing agents have a role in production. If attempts are made at the size reduction - which I'll come to later - in a wet milling operation without dispersing agents, a free-flowing liquid going into the mill without dispersing agent could very well come out a high viscosity non-pourable, non-manageable paste.

If left to stand the active will still settle out quite rapidly. Two means in tandem are employed to prevent this. The active - as mentioned above - is wet-milled. The slurry containing the active, wetting and dispersing agents is pumped through a size-reduction mill. On this site, size reduction is achieved by a Dyno-mill (Figure 3) which is essentially a large stainless steel chamber, 3/4 full of a mass of small glass beads which are kept in motion by uniformly spaced discs attached to a central spindle rotating at about 1900 - 3300 rpm. The slurry with the powdered active is pumped into the mill, the active is ground between the glass beads and exits through a sieve at the opposite end of the chamber. The flowable milled in this way usually ends up with a particle size distribution of 100% less than 20 microns. Particles of this size when added to water take a long time to settle under their own weight.

However, in the neat formulation, despite the size reduction, if left, these particles will still eventually settle out. To prevent this, after the milling operation a structuring agent or thickener is added as a gel which, when stirred into the liquid milled slurry, sets up an intricate lattice-like structure which holds the active particles in suspension. Such a thickener will also raise the viscosity of the formulation, and the trick is to balance the minimum viscosity increase with the maximum amount of suspending capacity.

A humectant is added to prevent drying out and flaking. When a container of flowable is transported around the countryside the liquid splashes around the inside of the keg. If left in a hot place, without humectant those splashes will dry out and crack into flakes, so that when next disturbed, the flakes wash into the formulation. They don't redispense and when diluted, in water, don't break-up so that when the farmer tips the keg into his mixing chamber and turns on the pump, the flakes will block his sieve if he has one, or even worse, the nozzles on his sprayer.

Antifoam is added both to prevent foaming during manufacture and

to a lesser extent, when the farmer is mixing the product. Bacteriostat is added to prevent spoilage during storage. Our experience has shown that flowable formulations with insufficient bacteriostat, can balloon out of shape with the production of CO<sub>2</sub> inside the keg.

Weather conditions in Australia can fall below freezing, i.e. 0°C, so we incorporate an antifreeze in our flowable formulations.

Not every suspension concentrate formulation contains the same combination of wetting and dispersing agents and thickeners and other components. Each active or combination of actives, and thus each formulation is tailor-made to enhance the physical properties and stability.

#### EMULSIFIABLE CONCENTRATES

Emulsifiable concentrates are generally a mixture of one or more water-insoluble actives (solid or liquid) dissolved together with a surfactant system in a (mostly) aromatic solvent system.

They are clear, mainly honey-coloured to dark brown liquids that when added to water form an opaque, white emulsion.

Emulsifiable concentrates are formulated by selecting, partly by trial and error and partly by experience, the combination of surfactants necessary to achieve the best quality emulsion with the greatest stability at the lowest price. Usually the surfactant system will range from 5-10% of the formulation. Their method of manufacture is the simplest we have - add the ingredients, stir to homogeneity, allow any crystalline material to dissolve, filter and pack.

#### WETTABLE POWDERS

In much the same way that EC's represent the easiest and least costly way of putting the liquid (and some crystalline) active ingredient in an easily usable liquid form, so wettable powders are the easiest way of getting powder actives and some crystalline actives into a solid form.

The active is blended with wetting and dispersing agents and a filler and then dry milled to reduce the particle size, so that when added to water, the active remains suspended for relatively long periods of time. For non-liquid actives, the filler can be a simple clay powder, but in some instances it is desirable to incorporate liquid actives within a WP formulation. In these instances the filler has to be a powder with a high oil absorption capacity. Some of those currently available have the ability to absorb many times their own weight in oil. If a liquid active is incorporated in this way, it almost invariably becomes



necessary to also add liquid surfactants chosen specially to emulsify the liquid active when the formulation is added to water. This does impose an upper limit on the amount of liquid active that can be incorporated into such a formulation.

Size reduction in WP's can be achieved either by a hammer mill (Figure 4), or if smaller particle size is required, by a jet-air mill (Figure 5).

Flowables, EC's and WP's represent the 3 classical formulations and up to now one or other of them have been the formulation type of choice.

However, things are changing. We are now under great pressure - both from governments and legislative bodies who can and do prohibit use of certain chemicals - and the public who are imposing other demands, such as an end to the use of the plastic kegs in which we pack our flowables. In this new world of heightened environmental awareness, there is a sincere effort being made to minimise the environmental insult that pesticides represent. For many years now development has been proceeding in just that direction. Many companies have been undertaking extensive work on alternative formulation technologies.

WATER DISPERSIBLE GRANULES

In proceeding from EC's to FW's there is as already mentioned, an increase in the level of complexity, more in the nature of the actual formulation, but also in its production. In progressing from WP's to WDG's there is almost no change in the complexity of the formulation, i.e. we still have active(s) + dispersing + wetting agents + filler, but there is a quantum leap in the level of production complexity.

PAN GRANULATION

The shallow pan disc pelletizer shown in Figure 6a is probably the most versatile of the agitation type agglomeration devices. It consists basically of a tilted, variable speed, rotating shallow pan with a rim that retains the agglomerating mass. Solids are fed continuously from above onto the disc - moisture and other binding agents can be added at various locations on the plate by means of sprays. Adjustable scrapers and ploughs maintain a uniform protective layer of product over the surface and also help control the flow pattern of material on the disc.

Manipulation of each of the variables - speed, and angle of rotation, location of powder and liquid feed points, and use of ploughs - gives the formulator great leverage when it comes to manipulating the quality of the finished product.

The important thing to note about the pan granulator is that

while it has great flexibility for manipulating operating parameters, such flexibility does ensure, that in both development and pilot and full scale production, great care - and time - must be taken to establish the correct parameters - for while being flexible it is also temperamental.

Possibly the most important feature of the tilted pan is that it is also a sizing device. The smaller nuclei of the feed material once deposited on the pan, gradually sift to the bottom edge of the pan and the tumbling load, from where they are, by virtue of their greater friction, carried to the top of the disc before falling once again to the bottom. As they become larger, by picking up the powder around them, the nuclei travels progressively small paths - see Figure 6b - and eventually cascade over the lip. By adjusting the various parameters, e.g. speed and angle, granules of a particular size can be built up and discharged over the lip when they reach the desired size - this removes the need for sieving and returning oversize and undersize granules for reworking.

Size of the agglomerates is controlled by the amount of liquid binder, by the location of the feed material inlet and liquid inlet and to a lesser extent by the retention time in the pan.

#### PIN GRANULATOR

Another agitative agglomerator, used mainly for agglomeration of coal dusts, carbon black and smelter dusts, but gaining wider use in the agglomeration of herbicides, is the pin mixer (Figure 7).

A pin-mixer is a horizontal stationary shell with a rotating agitator or rotor. The rotor is a shaft extending the length of the shell with pins spaced in a helical pattern along its length which serves to move the material along the shell.

The powder blend is metered into one end at the mixing zone where it is mixed with binder liquid. As the material begins its path down the shell it is spinning around the shell collecting fines and binder and becomes denser and larger, moves into the pelletising zone where most of the small particles of material are already agglomerated and proceeds to the densifying zone and thence to the discharge.

This mixer too, is quite versatile in that several parameters - speed and placement of the pins, rate of addition of the powder, and amount of binder can be manipulated to influence the size of the granule. It does have the major drawback of a quite large size distribution of the discharge which necessitates sieving and return of undersize and oversize granules.

I have concentrated on the pan granulator and pin mixer because these are two we have had most experience with in formulating WDG's. However, it must be said - and this is probably the main reason why granulation has not yet taken off as dramatically as one might expect - that the actual granulation step is just the guts of the process, in front of it and behind it is a great deal of other technology just as important. Whether the granulating device is a pin mixer or pan-granulator or some combination of these as shown in Figure 8, there is great complexity to the total process of WDG manufacture.

Technical and other ingredients are blended, hammer milled - in some cases such as formulations that might be an explosion hazard if milled dry the powder ingredients are wet milled and dried - blended with water and fed either directly into the pan granulator, or, if necessary through a pre-granulation step such as a pin-mixer, thence to the pan. The granules are then dried - this could be a fluid bed drier or micro-wave, depending on the active - screened, over and undersize being returned to the beginning via the hammer mill, and the material within spec. is packed.

It is the great number of steps and finicky nature of the actual granulator whether it be pin or pan that makes the WDG production process such a complex and intimidating process.

FLUIDIZED BED

The other major type of agglomerator is the fluidized-bed (Figure 9). In a fluidized bed granulator, agglomeration is achieved by doing the mixing, granulation and drying stages in one vessel. The granulating liquid, i.e. binder, can be sprayed either onto the surface of or within the vibrating fluid bed. In either case the nuclei catch the powdered fines which stick to the newly moistured surface of the nuclei. The body of the material is kept in fluid motion by the injection of the fluidizing gas through a perforated plate in the bottom of the vessel.

Another granulation system is the disc atomization or drop generator wherein a liquid is atomized by spraying through a nozzle or by being flung off a rapidly rotating disc at the top of a high sealed chamber into which is blown hot air. As the droplet falls through the hot air, the liquid portion is evaporated leaving behind the solids.

EXTRUDED GRANULES

As shown in Figure 10 the powdered material is mixed in a number of zones of increasing intensity to form an intimately mixed plastic mass which is pushed through a perforated end-plate.

These spaghetti like extrusions are dried and broken. Our most recent Plant Protection product - LOGRAN - is made this way.

MICROEMULSIONS

EC's generally contain from 40-70% solvent and one of the new formulation types currently undergoing development are the microemulsions. These are clear liquid formulations, in which the aromatic solvent has been replaced - mostly by water and to a lesser extent, by surfactants. A microemulsion will typically have from 5-25% active ingredient and similar levels of surfactant. The benefits of these formulations are that (some) toxic solvents are being phased out, flammability is greatly reduced, obviating the need for flammable labelling and warehousing and that only the active ingredient is left at the application point - the water and surfactants, washing away.

MICROENCAPSULATION

Mostly microcapsules are about 2-5 u in size and appear as a flowable-like product, i.e. an opaque, medium viscosity, easily pourable liquid. Each small capsule is a very thin walled shell, the wall being constructed of a polymer. Inside this shell is a minute reservoir of active ingredient.

The manufacture is relatively simple. As shown in Figure 11, a water insoluble liquid active - it is best also that the active not be susceptible to hydrolysis - is emulsified in water with one or more surfactants and one part of the polymer system then vigorously agitated to reduce the oil droplet size to the desired dimensions. When this is achieved the second part of the polymer system is added. Almost instantaneously the polymer shell forms around the liquid active droplet, sealing it in the shell. If necessary other ingredients are added, e.g. thickening agents and the product is then packed.

The process has the advantage that the product is manufactured in situ and requires little in the way of expensive or high tech equipment, but as usual there are drawbacks.

The first and most obvious is that the polymer-forming synthesis is non-returnable; once done, it is done and if done incorrectly, for example if the droplet particle size of the active is too large or too small - and there are quite fine tolerances for suitable capsules - the whole batch is lost (unlike WDG's where the over and undersize can be recycled). The second drawback is that only a few actives can be encapsulated in this way.

STABILITY TESTING

Whatever type of formulation is finally chosen, as soon as a likely candidate emerges, tests begin to determine its stability profile. Figure 12 shows the range of tests each formulation type will undergo.

In order that unsuitable formulations be picked up early, nearly every one is subjected to 2 weeks @ 54°C. This is a quick and easy way to eliminate poor candidates of nearly every formulation type: FW's will settle or phase, EC's will lose emulsion stability, ULV's will thicken or gel up, ME's and EW's will phase, and WP's and WDG's may go lumpy or sticky or lose suspensibility and in each type the active ingredient may degrade. For FW's and EC's and ME's and EW's, a parallel study at 0°C will find out those that crystallise or turn opaque.

Once past this hurdle, a formulation then has to last, with little or no diminution of quality in any of the applicable parameters, through 3 to 6 months at ambient and 40°C. If it can do this, samples are generally sent for field trials, and during this phase, its performance is assessed - both in application and in biological control. A ULV for example may fail because of phytotoxicity, a WDG may be unsuitable because of problems with wetting out and dispersibility and a flowable may fail because of flake formation. These last two are examples of weaknesses that can only be detected when large quantities of product are used.

After a formulation has lasted 6 months at 40°C and 2 (in some cases 3) years at ambient, and provided registration is ok, the product becomes available for sale.

Figure 2(a)

FORMULATION CONSTITUENTS

*examples:  
polyglycol*

1. SUSPENSION CONCENTRATES [FLOWABLES]:

- ACTIVE[S] - A SOLID, MELTING POINT > 70°C, LOW WATER SOLUBILITY < 200 ppm.
- SURFACTANTS - WETTING AND DISPERSING AGENTS.
- DYE - COLOURING FOR IDENTIFICATION PURPOSES.
- INERT CARRIER - ALMOST ALWAYS WATER, RARELY IN COMBINATION WITH ORGANIC SOLVENT.
- OTHERS - HUMECTANT, ANTIFREEZE, ANTIFOAM, BACTERIOSTAT, THICKENER.

*keeps active up in suspension*

2. EMULSIFIABLE CONCENTRATES:

- ACTIVE[S] - WATER INSOLUBLE.
- SURFACTANTS - EMULSION SYSTEM.
- SOLVENTS - ONE OR MORE.
- OTHER - e.g. STABILISER.

3. WETTABLE POWDER:

- ACTIVE[S] - MAY BE LIQUID OR POWDER.
- SURFACTANTS - WETTING AND DISPERSING AGENTS.
- FILLER - IF ONE OR THE ACTIVES IS A LIQUID, THE FILLER MUST HAVE HIGH OIL ABSORPTION CAPACITY.
- OTHER - DYES, ANTIFOAM.

4. ULTRA-LOW VOLUME LIQUIDS:

- ACTIVE[S] - WATER INSOLUBLE LIQUID.
- CARRIER - WATER-INSOLUBLE LIQUID, LOW VOLATILITY, LOW PHYTOTOXICITY
- OTHER - STABILISER [IF NECESSARY].

Figure 2(b)

1. CAPSULE SUSPENSIONS:

- ACTIVE[S] - WATER INSOLUBLE LIQUID OR POWDER.
- SHELL MATERIAL - POLYMER e.g. ISOCYANATE plus AMINE.
- CARRIER - WATER.
- SURFACTANT SYSTEM - WETTING AND DISPERSING AGENTS.

2. MICROEMULSIONS:

*as far  
EC's*

- ACTIVE[S] - WATER INSOLUBLE. *5-25%*
- SURFACTANTS - WETTING AGENT AND EMULSIFIERS. *5-25%*
- COSOLVENT - \_\_\_\_\_
- WATER

*active-dependent*

*active sensitive to variation in dose*

3. WATER DISPERSIBLE GRANULES:

- ACTIVE[S] - WATER INSOLUBLE.
- SURFACTANTS - WETTING AND DISPERSING AGENTS.
- FILLER

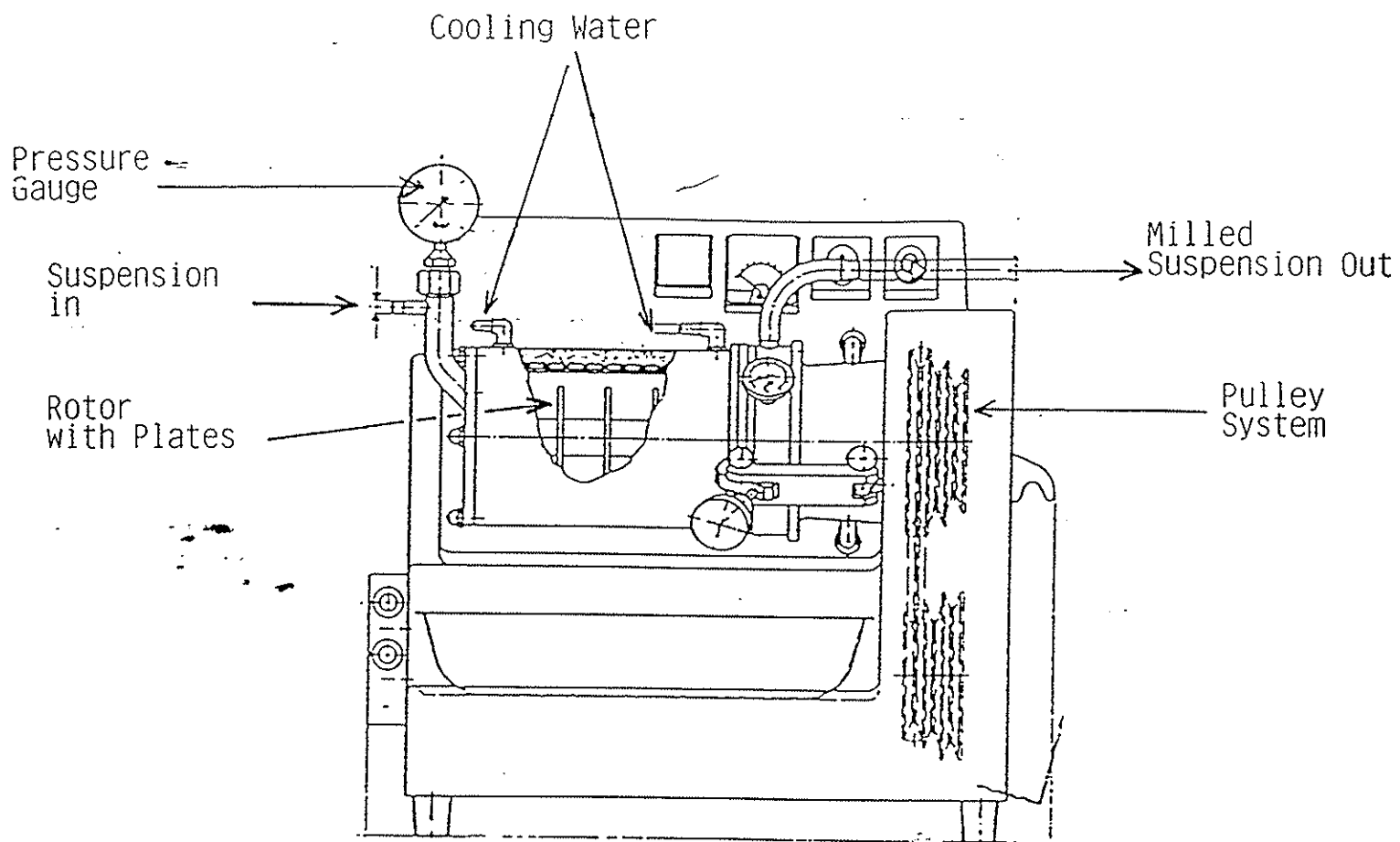


Figure 3 - DYNO MILL for Wet-milling of Suspension Concentrates.



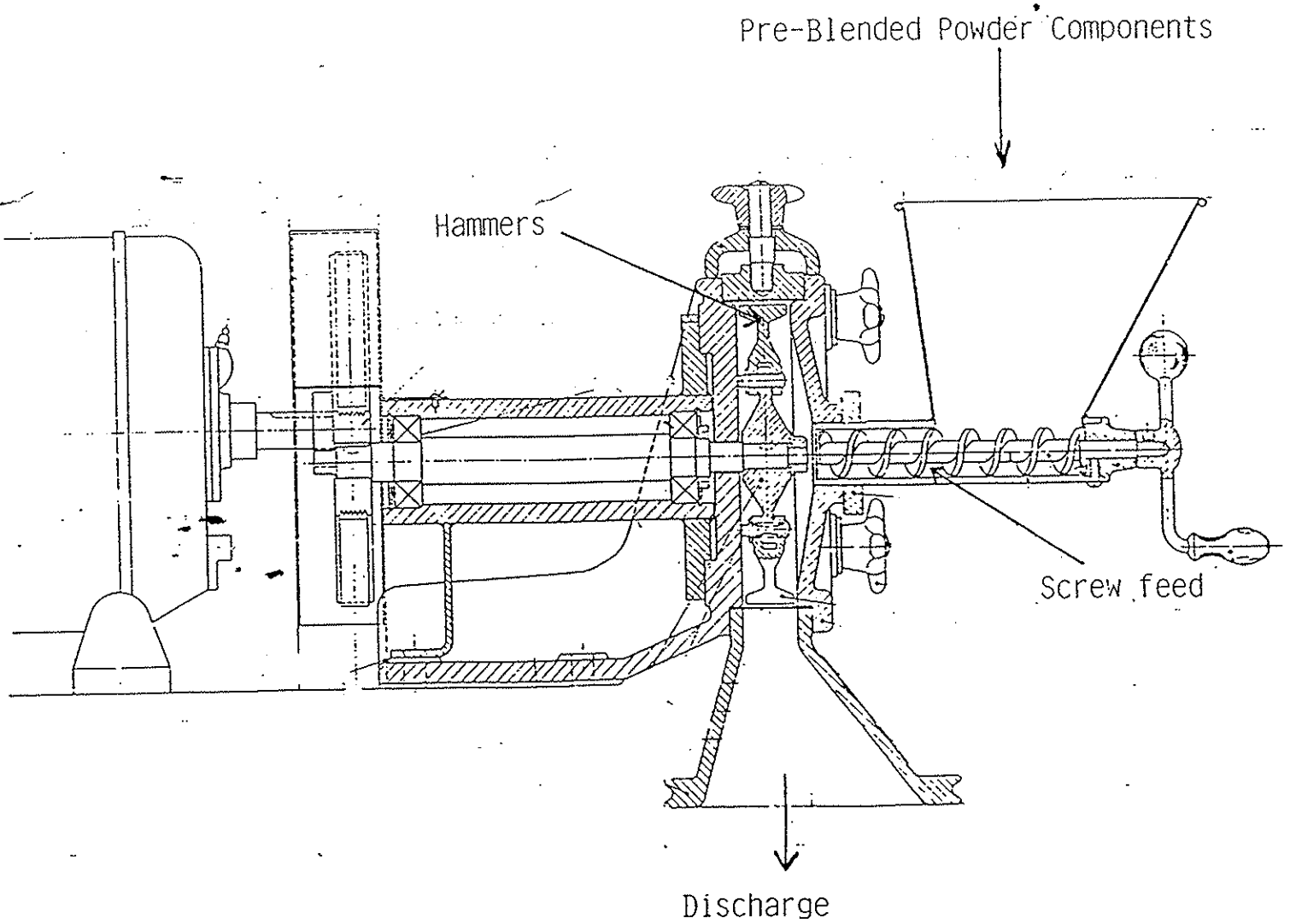


Figure 4 - Laboratory Hammer mill for dry-milling of wetttable powder formulations.

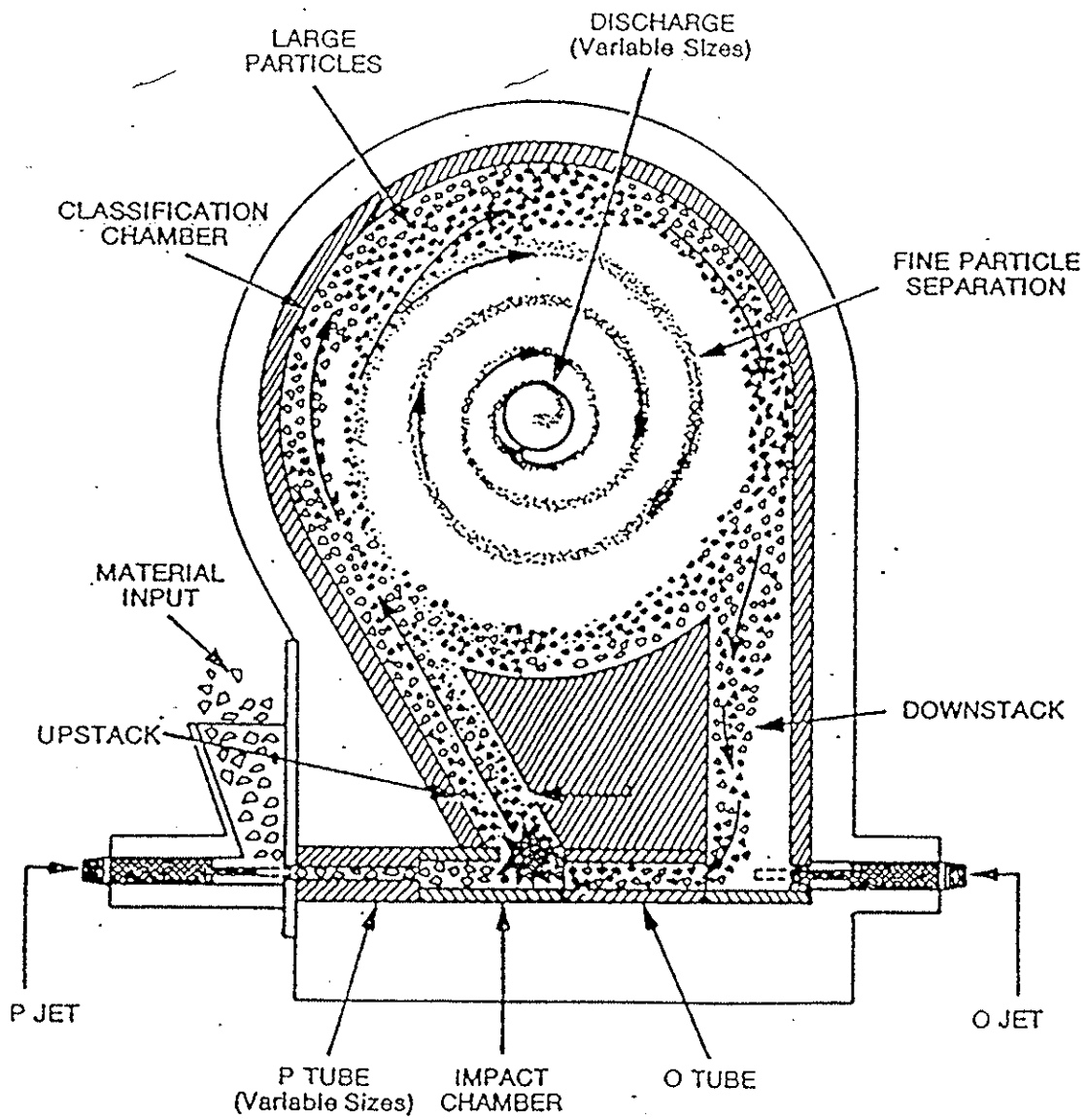


Figure 5 - Jet-air mill for dry-milling of wetttable powder formulations.

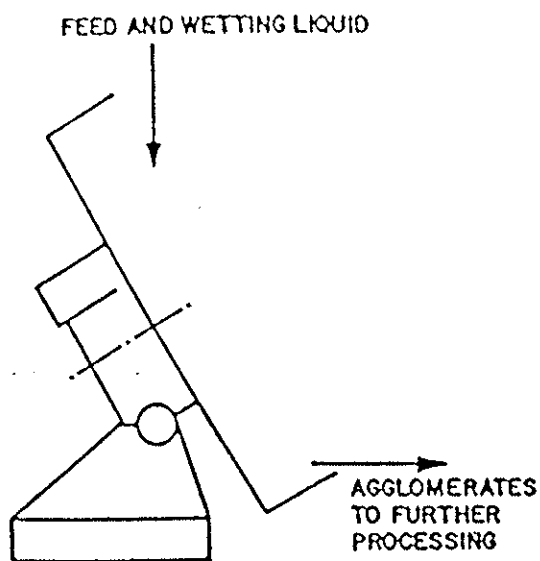


Figure 6(a) - Pan Granulator for production of water-dispersible granules.

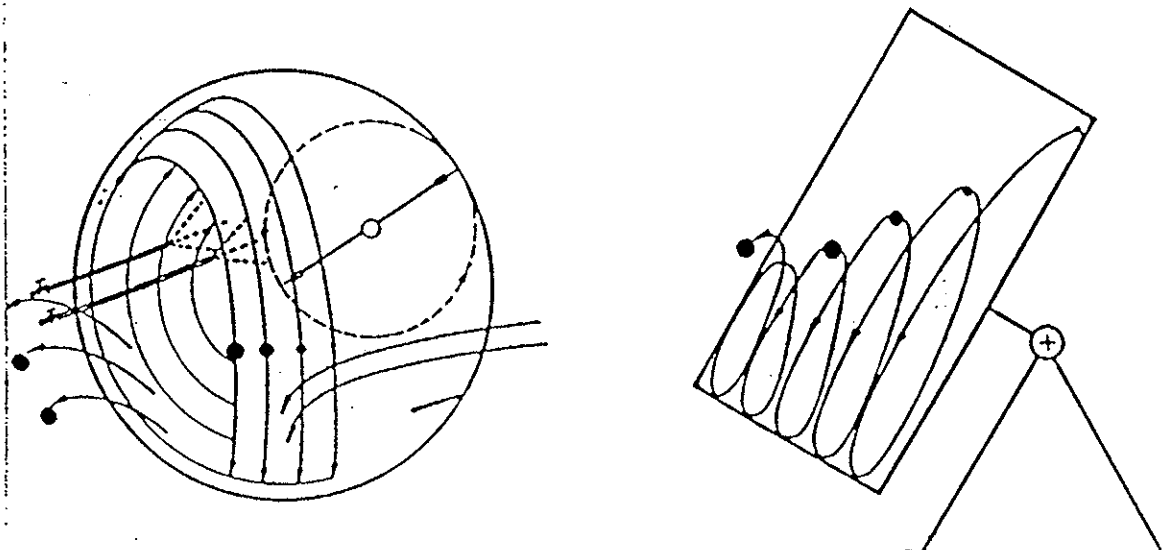


Figure 6(b) - Flow of material in a Pan Granulator.

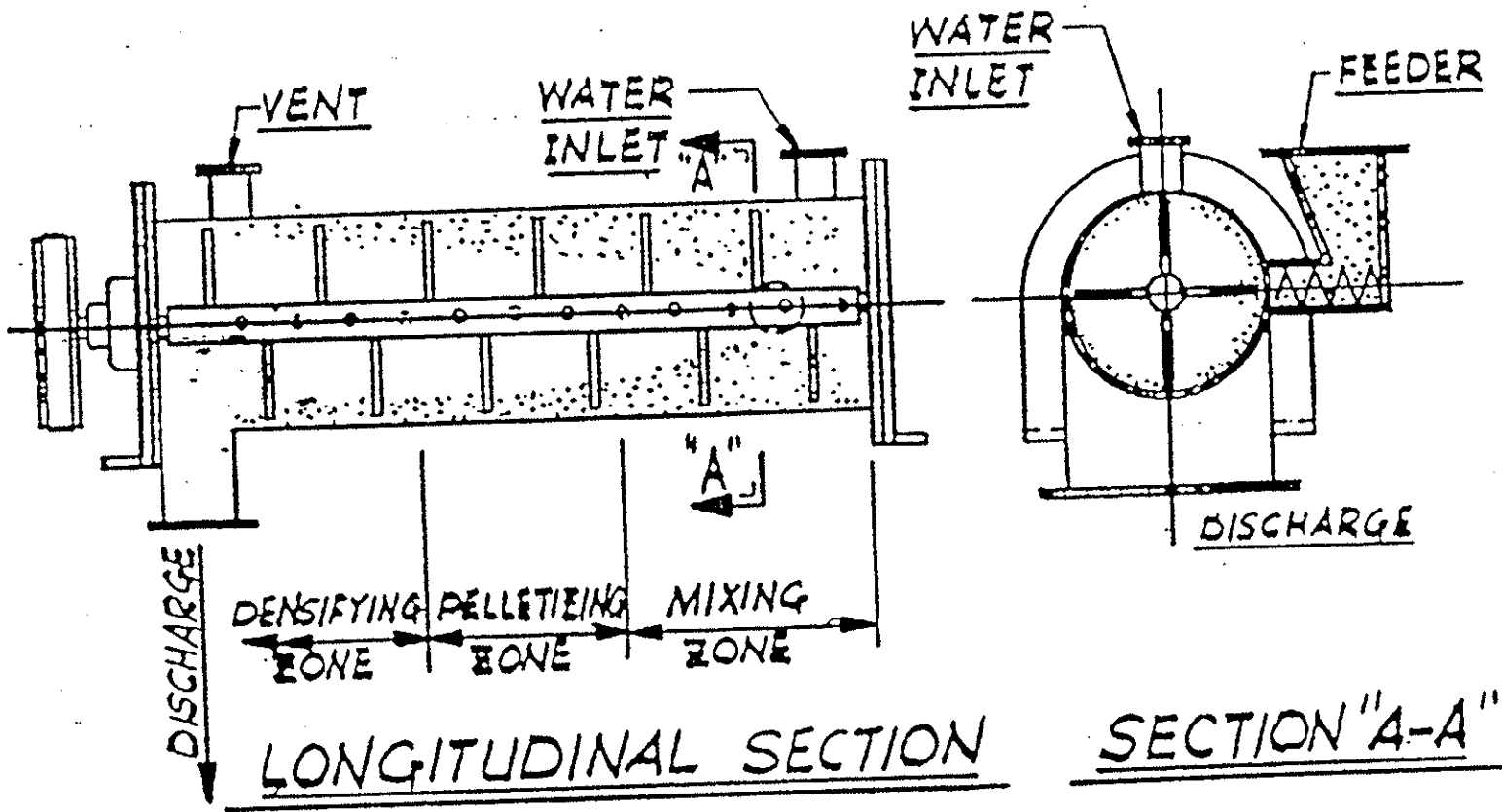
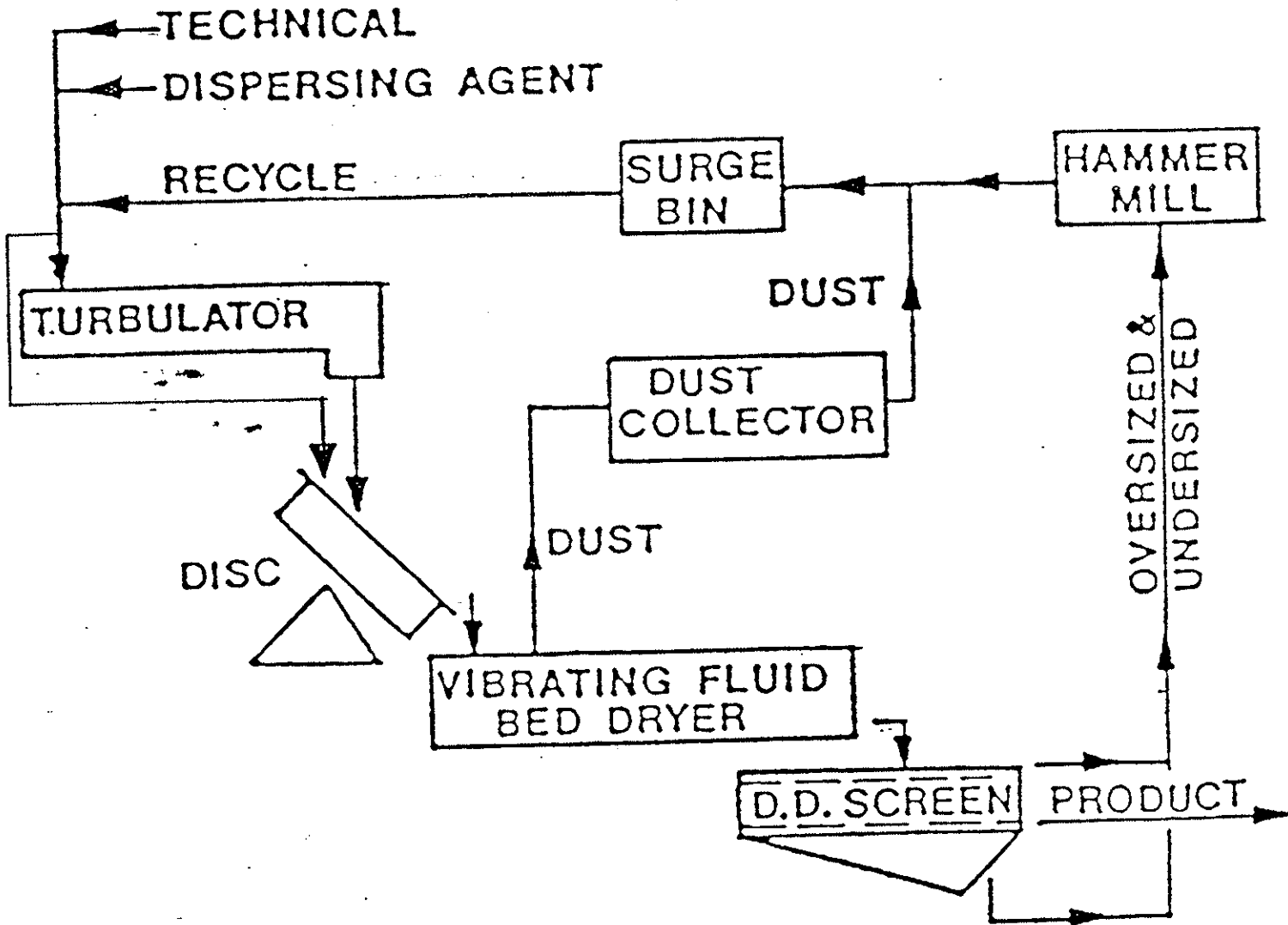


Figure 7 - Pin-mixer for production of water-dispersible granules.



FLOW DIAGRAM  
TURBULATOR/DISC PELLETIZER

Figure 8 - Total system for production of water-dispersible granules.

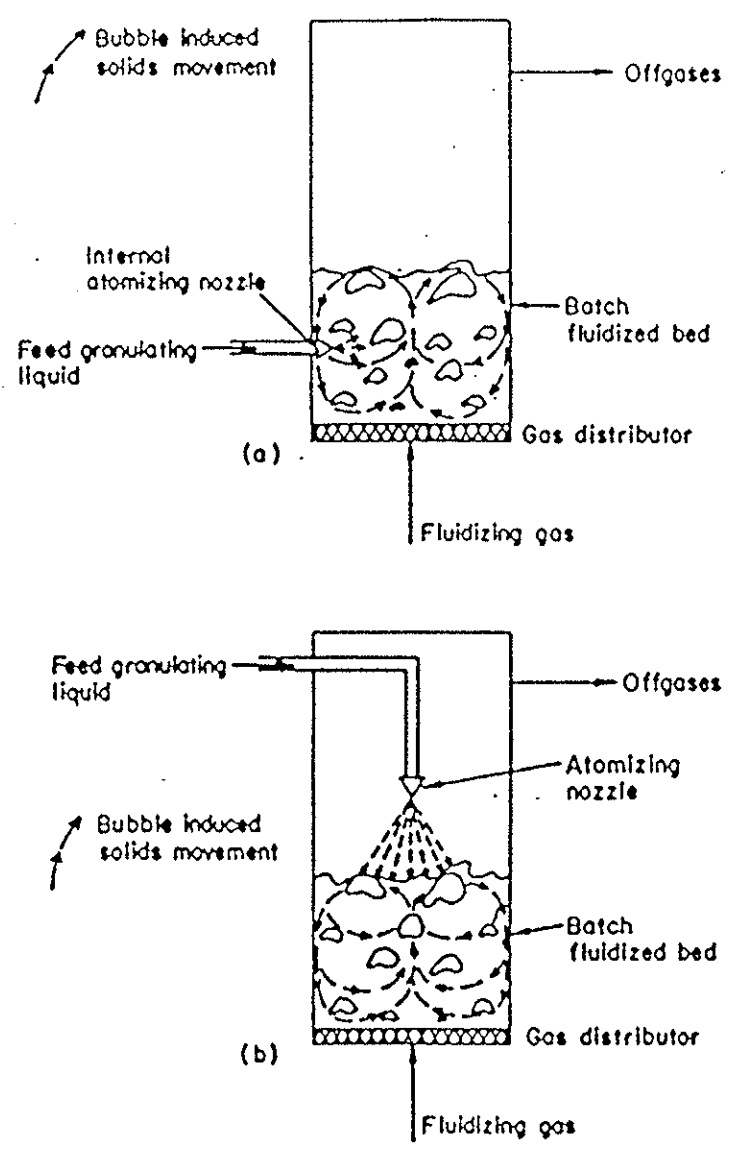


Figure 9 - Fluidized bed granulation.

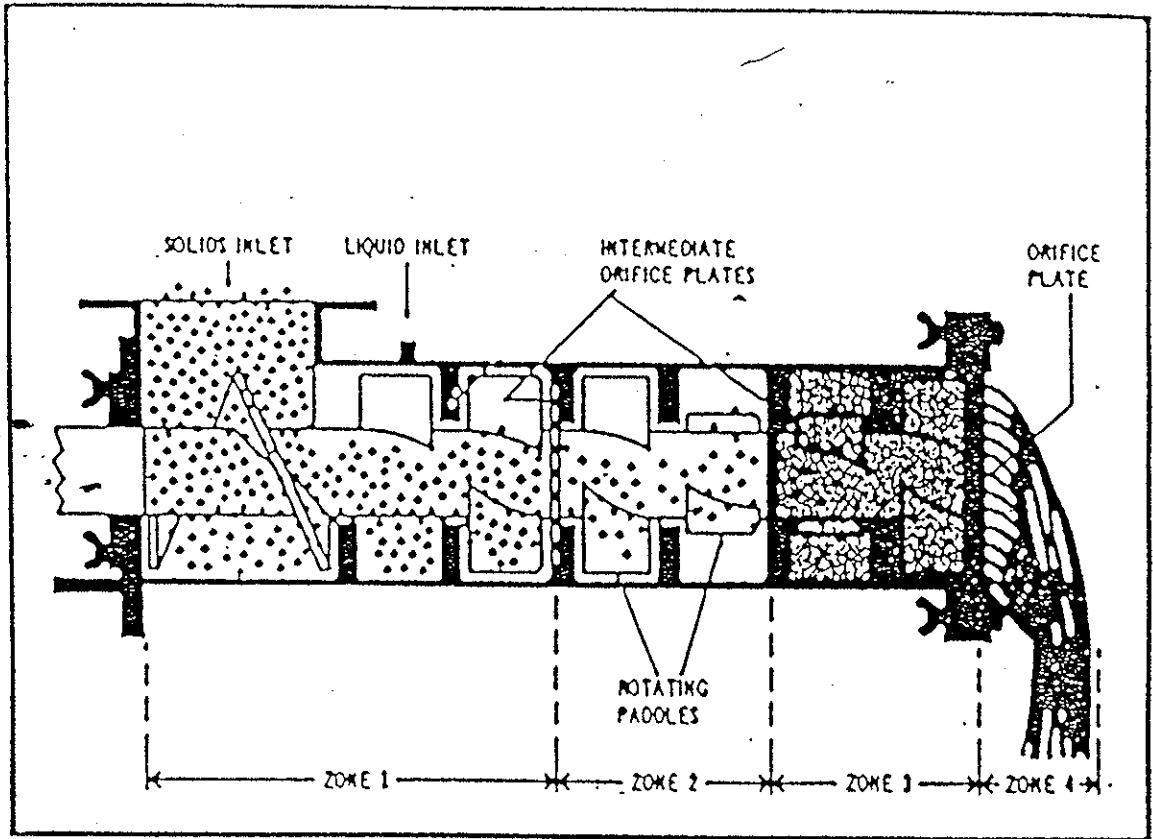


Figure 10 - Extrusion granulator.

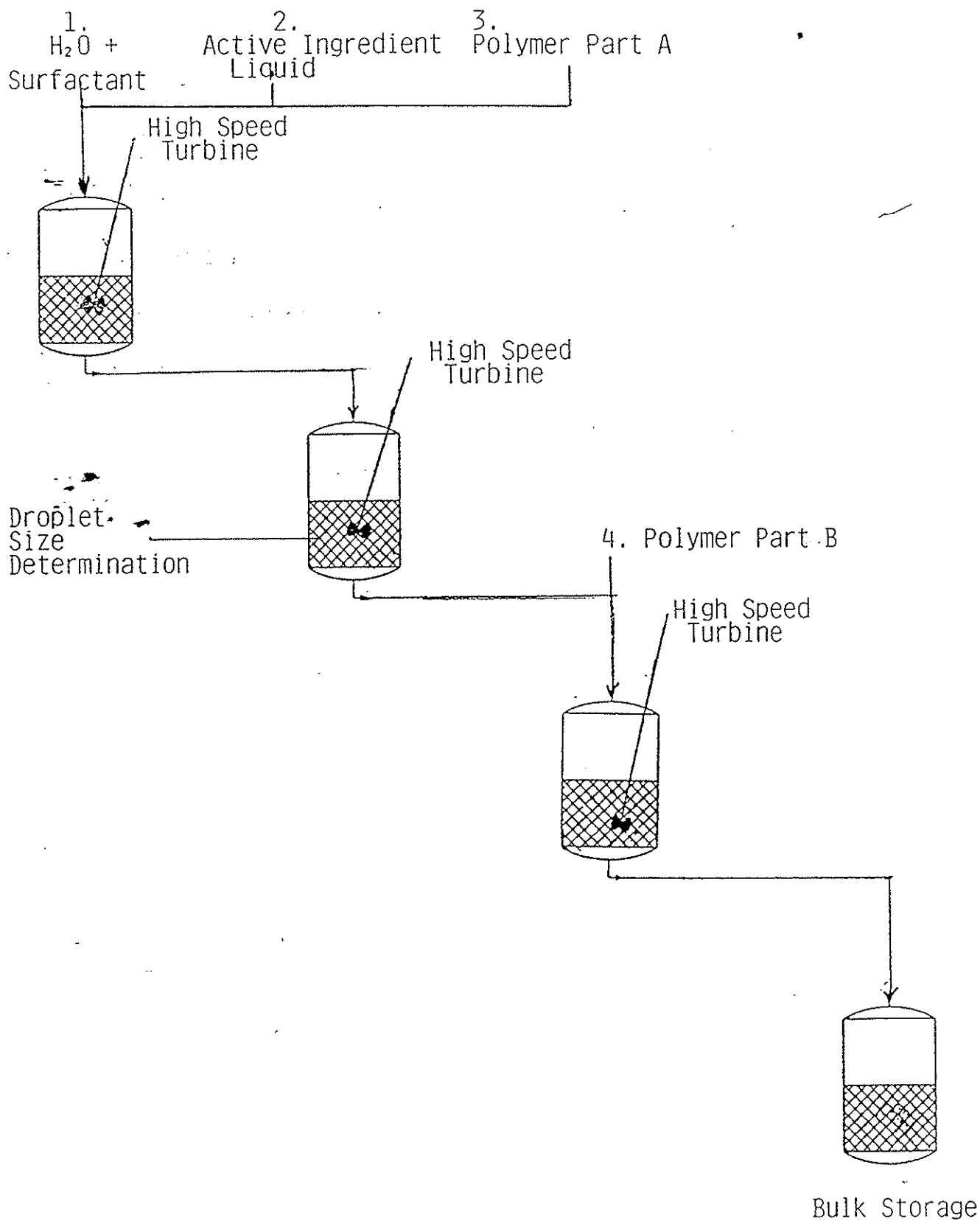


Figure 11 - Microencapsulation Procedure



	SC	EC	ULV	MB	EW	WP	WDG
ASPECT	✓	✓	✓	✓	✓	✓	✓
SG	✓	✓	✓	✓	✓	—	—
BULK DENSITY	—	—	—	—	—	✓	✓
VISCOSITY	✓	—	✓	—	—	—	—
% H <sub>2</sub> O	—	✓	✓	—	—	—	*
pH 5% (or 1%)	✓	✓	—	✓	✓	✓	✓
SUSPENSIBILITY Tap and Hard	✓	—	—	—	—	✓	✓
EMULSIONS Tap and Hard	—	✓	—	✓	✓	—	—
ATTRITION	—	—	—	—	—	—	✓
PARTICLE SIZE	✓	—	—	—	—	✓	—
SIEVE TEST	—	—	—	—	—	—	✓

\* If the active is sensitive to moisture

FIGURE 12 Testing parameters for each formulation type.

In January 1984 GIFAP (the international group of national associations of manufacturers of agrochemical products) issued in ten languages the second edition of its two letter abbreviations of formulation types. The first edition issued in 1978 has already be adopted by some official bodies including FAO and CIPAC.

The objective behind the code is to establish standard abbreviations in documentation, literature and correspondence worldwide, irrespective of the language used.

INDEX

46.

CODE	TERM	PAGE
AB	Grain bait	5
AE	Aerosol dispenser	4
AI	Active ingredient	1
AL	Other liquids to be applied undiluted	3
BB	Block bait	5
BR	Briquette	2
CB	Bait concentrate	4
CG	Encapsulated granule	3
CS	Capsule suspension	1
DP	Dustable powder	3
DS	Powder for dry seed treatment	4
EC	Emulsifiable concentrates	1
ED	Electrochargeable liquid	3
EO	Emulsion, water in oil	1
EW	Emulsion, oil in water	1
FD	Smoke tin	4
FG	Fine granule	3
FK	Smoke candle	4
FP	Smoke cartridge	4
FR	Smoke rodlet	4
FS	Flowable concentrate for seed treatment	4
FT	Smoke tablet	5
FU	Smoke generator	4
FW	Smoke pellet	5
GA	Gas	5
GB	Granular bait	5
GE	Gas generating product	5
GG	Macrogranule	3
GP	Flo-dust	3
GR	Granule	3
GS	Grease	5
HN	Hot fogging concentrate	5
KN	Cold fogging concentrate	5
LA	Lacquer	5
LS	Solution for seed treatment	4
MG	Microgranule	3
OF	Oil miscible flowable concentrate (oil miscible suspension)	2
OL	Oil miscible liquid	2
OP	Oil dispersible powder	2
PA	Paste	5
PB	Plate bait	5
PO	Pour-on	6
PR	Plant rodlet	5
PS	Seed coated with a pesticide	4
RB	Bait (ready for use)	5
SA	Spot-on	6
SB	Scrap bait	5
SC	Suspension concentrate (= flowable concentrate)	1
SG	Water soluble granules	2
SL	Soluble concentrate	1
SO	Spreading oil	3
SP	Water soluble powder	2
SS	Water soluble powder for seed treatment	4
SU	Ultra-low volume (ULV) suspension	3

CODE	TERM	PAGE
TB	Tablet	2
TC	Technical material	1
TK	Technical concentrate	1
TP	Tracking powder	3
UL	Ultra-low volume (ULV) liquid	3
VP	Vapour releasing product	6
WG	Water dispersible granules	2
WP	Wettable powder	2
WS	Water dispersible powder for slurry treatment	4

CODE	TERM	DEFINITIONS
	<u>1. Active ingredients and concentrates</u>	
AI	Active ingredient	Active ingredient as defined by common name.
TC	Technical material	A material resulting from a manufacturing process comprising the a.i. together with associated impurities. This may contain small amounts of necessary additives.
TK	Technical concentrate	A technical material either in solution or diluted with solid adjuvants for use only in the preparation of formulations.
	<u>2. Concentrates for dilution with water</u>	
EC	Emulsifiable concentrate	A liquid, homogeneous formulation to be applied as an emulsion after dilution in water.
EO	Emulsion, water in oil	A fluid, heterogeneous formulation consisting of a dispersion of fine globules of pesticide in water in a continuous organic liquid phase.
EW	Emulsion, oil in water	A fluid, heterogeneous formulation consisting of a dispersion of fine globules of pesticide in an organic liquid in a continuous water phase.
SC	Suspension concentrate (= flowable concentrate)	A stable suspension of active ingredients in a fluid intended for dilution with water before use.
CS	Capsule suspension	A stable suspension of capsules in a fluid (normally intended for dilution with water before use).
SL	Soluble concentrate	A liquid, homogeneous formulation to be applied as a true solution of the active ingredient after dilution in water.

CODE	TERM	DEFINITIONS
	2. <u>Concentrates for dilution with water</u>	Cont'd
SP	Water soluble powder	A powder formulation to be applied as a true solution of the active ingredient after solution in water but which may contain insoluble inert ingredients.
SG	Water soluble granules (Sometimes recognised as "dry flowable". However, the use of this term is not recommended).	A formulation consisting of granules to be applied as a true solution of the active ingredient after dissolving in water but which may contain insoluble inert ingredients.
TB	Tablet	Solid formulation in the form small, flat plates.
BR	Briquette	Solid block designed for controlled release of active ingredient.
WP	Wettable powder	A powder formulation to be applied as a suspension after dispersion in water.
WG	Water dispersible granules (Sometimes recognised as "dry flowable". However, the use of this term is not recommended).	A formulation consisting of granules to be applied after disintegration and dispersion in water.
	3. <u>Concentrates for dilution with organic solvents</u>	
OL	Oil miscible liquid	A liquid, homogeneous formulation to be applied as a homogeneous liquid after dilution in an organic liquid.
OF	Oil miscible flowable concentrate (oil miscible suspension)	A stable suspension of active ingredients in a fluid intended for dilution in an organic liquid before use.
OP	Oil dispersible powder (Can be confusing since the abbreviation 'OP' is sometimes used for Organo-phosphorous compounds.)	A powder formulation to be applied as a suspension after dispersion in an organic liquid.

CODE	TERM	DEFINITIONS
4. <u>Products to be applied undiluted</u>		
DP	Dustable powder	A free-flowing powder, suitable for dusting.
GF	Flo-dust	Very fine dustable powder for pneumatic application in greenhouses.
GR	Granule	A free-flowing solid product of a defined granule size range ready for use.
FG	Fine granule	A granule in the particle size range from 300 to 2500 um.
CG	Encapsulated granule	A granule with a protective or release controlling coating.
GG	Macrogranule	A granule in the particle size range from 2000 to 6000 um.
MG	Microgranule	A granule in the particle size range from 100 to 600 um.
ED	Electrochargeable liquid	Special liquid formulation for electrostatic (electrodynamic) spraying.
SO	Spreading oil	Formulation designed to form a surface layer on application to water.
AL	Other liquids to be applied undiluted	Self defining.
TP	Tracking powder	A rodenticide contact formulation in powder form.
UL	Ultra-low volume (ULV) liquid	A homogeneous liquid ready for use through ULV equipment.
SU	Ultra-low volume (ULV) suspension	A suspension ready for use through ULV equipment.

CODE	TERM	DEFINITIONS
5. <u>Products for seed treatment</u>		
DS	Powder for dry seed treatment	A powder for application in the dry state directly to the seed.
FS	Flowable concentrate for seed treatment	A stable suspension for application to the seed either directly or after dilution.
LS	Solution for seed treatment	A solution for application to the seed either directly or after dilution.
PS	Seed coated with a pesticide	Self defining.
SS	Water soluble powder for seed treatment	A powder to be dissolved in water before application to the seed.
WS	Water dispersible powder for slurry treatment	A powder to be dispersed at high concentration in water before application as a slurry to the seed.
6. <u>Miscellaneous formulations for special purposes</u>		
AE	Aerosol dispenser	A container from which the active ingredient(s) is (are) dispersed generally by a propellant as fine droplets/particles upon the actuation of a valve.
CB	Bait concentrate	A solid or liquid intended for dilution before use as a bait.
FU	Smoke generator	A combustible formulation, generally solid, which upon ignition releases the active ingredient(s) in the form of smoke.
FD	Smoke tin	Special forms of smoke generators.
FK	Smoke candle	Special forms of smoke generators.
FP	Smoke cartridge	Special forms of smoke generators.



CODE	TERM	DEFINITIONS
6. <u>Miscellaneous formulations for special purposes</u> Cont'd		
FR	Smoke rodlet	Special forms of smoke generators.
FT	Smoke tablet	Special forms of smoke generators.
FW	Smoke pellet	Special forms of smoke generators.
GA	Gas	A gas packed in pressure bottles or pressure tanks.
GE	Gas generating product	A product which generates a gas by chemical reaction.
HN	Hot fogging concentrate	A formulation suitable for application by hot fogging equipment.
KN	Cold fogging concentrate	A formulation suitable for application by cold fogging equipment.
GS	Grease	Very viscous formulation based on oil or fat.
LA	Lacquer	Solvent-based, film-forming composition.
PA	Paste	Water based film forming composition.
PR	Plant rodlet	A small rodlet, usually a few centimeters in length, a few millimeters in diameter containing an active ingredient.
RB	Bait (ready for use)	A formulation designed to attract and be eaten by the target pests.
SB	Scrap bait	Special form of baits.
GB	Granular bait	
AB	Grain bait	
PB	Plate bait	Special forms of bait.
BB	Block bait	

CODE	TERM	DEFINITIONS
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6. Miscellaneous formulations for special purposes Cont'd

VP	Vapour releasing product	A formulated product containing one or more volatile ingredients, the vapours of which are released into the air. Evaporation rate normally is controlled by using suitable formulations and/or dispensers.
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7. Animal Health products

PO	Pour-on	Solution for pouring on the skin of animals in a high volume (normally more than 100 mL per animal).
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SA	Spot-on	Solution for spot application on the skin of animals in a low volume (normally less than 100 mL per animal).
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Mr Stephen Holland  
Chemicals Section  
Worksafe Australia

TALK TO THE WEED SOCIETY OF NEW SOUTH WALES  
FRIDAY 24 NOVEMBER 1989

MATERIAL SAFETY DATA SHEETS

INTRODUCTION - WHAT IS WORKSAFE?

Worksafe Australia is the corporate title of the National Occupational Health and Safety Commission, a Federal Statutory body established under the National Occupational Health and Safety Act 1985.

Our task is to lead national efforts to provide healthy, safe and productive working environments, and to reduce the incidence and severity of occupational injury and disease.

This is achieved through the cooperative efforts of State, Territory and Commonwealth Governments and peak union and employer organisations. The National Commission is a tripartite body comprising representatives from these organisations.

The Chemicals Section of Worksafe is responsible for the development of:

- specific national strategies relating to standards development and to chemical hazards
- legislative provisions for adoption by the States/Territories; and
- non legislative guidance to promote occupational health and safety.

It is in this last group that we find the Worksafe Guidance Note for the Completion of a Material Safety Data Sheet.

WORKSAFE GUIDANCE NOTE FOR THE COMPLETION OF A MSDS

The first edition of the Guidance Note was published in 1986. The Guidance Note provided advice on how to compile a Material Safety Data Sheet to a minimum standard, and provided a format with which to work.

Since its introduction in 1986, the Guidance Note and proposed format has gained wide acceptance in this country. Many of the major chemical manufacturers and users have now converted their information sheets to the Worksafe format MSDS.

The Guidance Note was, of course, only a recommendation for the States to consider. However, to reinforce the impact of this and

other Worksafe recommendations, Worksafe has developed a Model Hazardous Substances Regulation. One component of which relates to the provision of information, and requires the production of a Worksafe format MSDS for all hazardous substances in the workplace.

Again, the Model Regulation is only a recommendation. However, it is known that specific hazardous substances legislation is currently being drafted in NSW, Victoria, WA, and SA, which is largely based on the Worksafe Model Regulation. It is known this State legislation will follow the Model with regard to information provision, namely, including a requirement to provide a MSDS in the Worksafe format for all hazardous substances, to the user of the such products. Queensland decided to preempt the Model Regulation, and in July this year proclaimed the Workplace Health and Safety Act, which specifies a requirement to provide the MSDS in the Worksafe format.

We are confident Tasmania, the NT, and the ACT will fall into line shortly. Both the NT and the ACT have indicated favour with the proposed Model Regulation.

Therefore, after three years, the Worksafe Material Safety Data Sheet will find its way into State legislation.

The proposed legislation is quite timely as it will serve as a platform for the issue of the second edition of the Guidance Note which has been developed this year.

The decision to produce a second edition was based largely on the information 'explosion' of the last few years, together with numerous comments received on the first edition, since its publication.

#### WHAT DOES A MATERIAL SAFETY DATA SHEET DO?

A Material Safety Data Sheet provides information and hazards of a substance so that an operator or user may understand and minimise risks in the use of the chemical in normal operations and may implement appropriate procedures in an emergency.

It is divided into four sections:

- . identification
- . health hazard information
- . precautions for use
- . safe handling information.

The MSDS format may be:

- . Two sided A4 pro forma

or

- . flexible format with sections expanded or contracted according to available information.

The preferred lay out features are:

- . information should be contained on two sides of an A4 sheet

. no boxes.

### PURPOSE OF MSDS

The information in an MSDS should assist in:

- . defining a hazard (physical, biological, environmental)
- . controlling a hazard
- . increasing effectiveness of action in emergencies
- . choice of correct clean up procedures.

Copious details are unnecessary in the MSDS as confusion may occur and the important points lost. However, sufficient detail is necessary to give clear instructions.

### IDENTIFICATION SECTION

This, first of all, establishes what product the MSDS applies to. MSDS apply to mixtures of chemicals, i.e., product formulations, substances as sold and supplied, not individual chemicals, unless of course an individual chemical is what is in use.

Identity data should give the name of the product, beginning with the name as it appears on the label, to establish the link between the MSDS and the container, so that the users are sure they are looking at the correct MSDS.

The MSDS should include major uses of a product and also the method of application, e.g., spray, mist, soak, is it a paint stripper, solvent degreaser?

Physical properties will give a preliminary indication of the profile of the chemical and some information on the hazards. Much of this will be stated more specifically in other sections of the MSDS - precautions for use, safe handling.

The section on ingredients should include all chemicals and specify exactly all the hazardous chemicals contained in the product. It should be completed even if there is only a single chemical entity in the product, e.g., pure methanol. The information should be included is the common chemical name, the Chemical Abstracts Services (CAS) number and the concentration (or the proportion at least within a range) should be stated.

### HEALTH HAZARD INFORMATION

The Health Hazard Information section on the material safety data sheet is where to find information on the adverse effects of substances on the body either on short term or long term exposure.

The health hazards described in this section of the MSDS are addressed further on the section on Precautions for Use. If a substance is listed as an eye irritant and there is any potential for it to splash in or make contact with the eye, then safety glasses, goggles or full face shields should be recommend. If there is an inhalation hazard, check for a recommendation in the engineering controls section.

## PRECAUTIONS FOR USE

The National Occupational Health and Safety Commission has developed a set of exposure standards for airborne contaminants in the workplace. The relevant Australian exposure limits should be listed in this section.

### Engineering Controls

Complete segregation of workers from chemicals is rarely achieved. Engineering control measures have the proven capacity to reduce exposure to chemicals if properly designed, implemented and maintained. These include :

- . process modification to eliminate hazardous chemical(s);
- . segregation of processes from personnel by partition and/or distance;
- . vessel containment controls;
- . enclosure of sources of chemicals to the maximum extent possible;
- . mechanical handling to reduce human contact with chemicals;
- . capture of chemicals at source and their safe disposal with a local exhaust ventilation system;
- . dilution ventilation of the workplace for chemicals of low toxicity.

The general belief these days is that where practicable, engineering solutions should be the aim in preference to requiring protective clothing. This part of the concept of making the workplace the worker, not the worker fit the workplace. Nevertheless, not always feasible or even possible to come up with engineering solutions to problems posed by the use of some chemicals. The protective clothing section should show clearly what is required. What type of respirator? Full face? Half? Gloves? What length, what material, neoprene, nitrile?

All equipment used should comply with an Australian standard equivalent local standard, e.g., State (if a Standard applies).

The last subsection of precautions gives specific information on flammability and the need to control ignition sources.

## SAFE HANDLING INFORMATION

The last section of the MSDS deals with Safe Handling Information. It gives all the storage and transport requirements. Most of the listings are straightforward. The MSDS should give location conditions and temperature of storage, the type of drum, although this should be used only to check that it is in a correct container and should not be interpreted as a direction for permission decant into another "suitable" container.

## SUMMARY

Overall, there is a large amount of information included on a material safety data sheet.

It can be used to predict fire and explosion hazards, and to determine:

- . what precautions may be used to prevent them
- . how a disaster should be handled if it occurs.

It can be used amongst other things to see:

- . whether a chemical has a significant inhalation hazard
- . whether an exposure limit has been determined
- . whether special ventilation is required
- . if a respirator must be worn and what type
- . whether skin exposure contributes to toxicity; and
- . whether specific types of protective clothing are required.

The Material Safety Data Sheet is not a cure for all ills, on its own it will not protect you from the hazards of a chemical. It will however, give you readily usable information which, used in conjunction with other information such as the label, will enable you to make a decision on a safe working practice to be adopted.

Company  
Address  
Telephone Number  
Emergency Telephone Number

## Material Safety Data Sheet

### IDENTIFICATION

Product Name	U.N. Number
Other Names	Hazchem Code
Manufacturer's Product Code	Dangerous Goods Class & Sub Risk
Use	Poisons Schedule

### Physical Description/Properties

Appearance	Flash Point (°C)
Boiling Point/Melting Point (°C)	Flammability limits (%)
Vapour Pressure (pascals or mm of Hg at 25°C)	Solubility in Water (g/L)
Specific Gravity	
Other Properties	

### Ingredients

Chemical entity	CAS No.	Proportion
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### HEALTH HAZARD INFORMATION

#### HEALTH EFFECTS

Acute Swallowed

Eye

Skin

Inhaled

Chronic

FIRST AID Swallowed

Eye

Skin

Inhaled

ADVICE TO DOCTOR



## PRECAUTIONS FOR USE

Exposure Standards

Engineering Controls

Personal Protection

Flammability

## SAFE HANDLING INFORMATION

Storage and Transport

Spills and Disposal

Fire/Explosion Hazard

---

Other Information

---

Contact Point

---

EXPERIMENTAL PESTICIDE  
SAFETY INFORMATION SHEET  
(for experimental pesticides in NSW)

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1. Identity of pesticide
  - 1.1 Code number/trade name:
  - 1.2 Active constituent(s): content in formulation; formulation type:
  - 1.3 Manufacturer/Supplier
  
2. Summary of toxicology of active constituent; and formulation product, if applicable.  
(All data are applicable to the active constituent)
  
3. RECOMMENDED SAFETY DIRECTIONS FOR OPERATORS
  
4. RECOMMENDED FIRST AID TREATMENT
  
5. PRECAUTIONS FOR PROTECTION OF THE ENVIRONMENT
  
6. RECOMMENDATIONS FOR DEALING WITH SPILLAGE AND UNWANTED PRODUCT
  
7. DATE OF COMPILATION OF THIS FORM

HERBICIDES IN WATER

Kathleen H. Bowner

CSIRO Division of Water Resources  
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Griffith NSW 2680

The Chemists Role in Weed Control

Weed Society of New South Wales  
Seminar

Sydney 24 November 1989



*"The corn is as high as an elephant's eye.  
But the weeds are over his head."*

HERBICIDES IN WATER: ECONOMICS OR ENVIRONMENT?

Kathleen H. Bowmer

CSIRO Division of Water Resources, Griffith, NSW 2680

The Debate: Conflict or Compatibility

Issues of environmental protection and conservation have been hitting the headlines lately. In my opinion it is a pity that the press and politics seems to polarise the community into "the developers" and "the conservationists", because this will inevitably lead to a prolonged battle and little progress for either side. No doubt CSIRO will be called in again to provide the "unbiased scientific truth"; as was expected in the Wesley Vale debate. Here, CSIRO was embarrassed by the opposing views of its scientists and has taken steps to try to ensure a united front on environmental issues in the future.

I am a scientist involved in one of the hottest environmental issues today, namely water pollution, specifically pollution with herbicides. What can I hope to achieve in providing "scientific truth" and how will it influence the debate?

It seems to me that there are several main problems:

Firstly, we have to accept as myth, the idea that science yields the truth. As pointed out by Professor Peter Cullen, in a recent address on the turbulent boundary between science and management (Cullen, 1989): "Scientists may seek truth, but rarely do they believe that any accepted truth of the moment is beyond challenge. Creative science normally involves demolishing what had previously been seen as truth."

Secondly, we need to recognise that scientific evidence is only the starting point. The final advice or decision will need to balance the benefits of any activity against the costs, taking into account economics, social effects and environmental consequences, and particularly the views of all concerned. An appreciation of resource economics and of processes for reaching consensus is important for any environmental scientist today.

For herbicides, specifically, we have a complication in the simple debate between economic benefits and environmental protection, because of some potentially beneficial effects of herbicides in protecting soil and water resources. Taking three general areas as examples:

Firstly, there is an increasing use of herbicides for selective weed control in crops, and in minimum or zero tillage agriculture.

These techniques are important for the conservation of energy, fertiliser and water, in turn helping to avoid the ravages of soil degradation and erosion, and the pollution of water with suspended sediment, nutrients and salt. Unfortunately, on the debit side, we have very little information on the potential costs of surface and ground water pollution in Australia.

Secondly, we use herbicides for the management of thousands of kilometres of irrigation distribution system, and, to a lesser extent, for coastal flood mitigation channels; sometimes with environmental benefits, compared with mechanical methods of control.

Thirdly, we are being faced with the problem of invasion of our wetlands and river systems with alien aquatic plants. Here judicious use of chemical control early in the invasion may be useful in eliminating the problem, or in maintaining it in manageable proportions until biological methods can be developed.

Each of these topics raise quite different economic and environmental issues and it is difficult, even undesirable to generalise. However, before proceeding onto the specific problems of herbicide use and water pollution in Australia it may be useful to consider the current residue limits in water, because this will highlight the importance of the aquatic environment as a stakeholder in water quality criteria.

#### Water Quality Criteria

Maximum herbicide concentrations permitted are described in Table 1. Values for potable water are set by the National Health and Medical Research Council. Figures for irrigation re-use are derived from work on clovers and pasture grasses in Victoria, nearly two decades ago (Bill and Graham, 1970), and include a substantial margin of safety. Residue limits for aquatic life are derived from the Environmental Protection Authority of Victoria (1983) and are threshold concentrations beyond which significant adverse effects for aquatic organisms can be expected.

There are many problems with this information:

- there is very little data available on the effect of herbicides for irrigated crops, although this will become important as water is increasingly recycled on a regional and local scale.
- many herbicides are unlisted; these include not only herbicides used on crop land which might reach water by runoff and leaching, but also those used in rice culture (bensulfuron, molinate, thiobencarb, propanil, MCPA), for aquatic weed control (TCA, aromatic solvents) and on ditch banks, near streams, and close to water courses (metsulfuron-methyl, triclopyr, tebuthiuron, and atrazine).

- there is a concern that breakdown products may be more ,  
problematical than the parent compound.
- there is a concern about subtle medical effects, especially  
for people with suppressed immune systems.
- the derivation of the data is sometimes suspect. For example,  
with identical algal test species and toxins, estimates of  
concentration required to inhibit algal biomass or growth rate  
can vary by up to 1000-fold between different laboratories  
(Nyholm, 1986).
- aquatic macrophytes and seagrasses are not included in the  
test protocol, although they may be more sensitive to some  
herbicides than fish and invertebrates, and are also central  
to the survival of aquatic ecosystems. Duckweeds are being  
investigated as additional test species (Eskdale and Buckney,  
1989).
- the problem with aquatic ecosystems is that the community  
response may be much more complicated so that the value of  
assays with single species is questionable. The critical  
balance between macrophytes and algal dominance in lakes has  
been described in an elegant series of papers from the  
University of East Anglia (Phillips et al., 1978; Balls et  
al., 1989; Irvine et al., 1989; Stansfield et al., 1989). The  
balance is determined by the competition between macrophytes,  
algal epiphytes, phytoplankton and zooplankton grazers, any  
component of which can be suppressed by a herbicide or  
pesticide. Once macrophyte dominance is overturned,  
re-establishment may be extremely difficult and expensive.  
This problem will be recognised by weed managers who have used  
herbicides such as diquat or dichlobenil for suppression of  
submerged macrophytes, with the subsequent development of  
algal blooms, as nutrients released by the macrophytes are  
captured by the phytoplankton.
- other aspects of water quality can profoundly affect the  
biological activity of given residues; for example  
inactivation of diquat by adsorption in many Australian turbid  
waters; and chelation of copper by dissolved organic matter.
- the use of concentration as a criterion is not particularly  
useful for most pollution incidents involving flowing water,  
such as return of irrigation tail water to a river where there  
may be a trace of herbicide for a short time. This has  
implications for design of monitoring programs since pulses of  
contamination might be missed by routine sampling at  
sparsely-spaced time intervals.
- information on the pattern of concentration and time required  
to damage non-target aquatic plants with herbicides is very  
limited (Fig. 1). Submerged aquatic plants seem to be able to  
withstand exposure to the photosynthetic inhibitor herbicide,

terbutryne, for at least a week at concentrations of several milligrams per litre providing there is transfer to freshwater later. Conversely, much lower concentrations of atrazine, of the order of 0.003 mg/L damaged Vallisneria americana in Chesapeake Bay, an estuary in USA. (For a review, see Bowmer, 1986). The interaction between concentration and time of exposure is being studied by the US Army Corps of Engineers. So far some information has been reported for the response of Myriophyllum spicatum (Watermilfoil) and Hydrilla verticillata (Hydrilla) to fluridone, diquat, endothal and 2,4-D (Table 2). This work is limited to the intentional use of aquatic herbicides for control of undesirable species in USA; but may give an indication of problems that might be encountered by low level residues for desirable plants also. For example, the two species tested here are extremely sensitive to fluridone, Watermilfoil biomass being reduced by 95% by only 0.0015 mg/L during an exposure time of 20 days.

- we also need to temper the concentration criteria with information about the persistence of the compound, to discover whether a pollution incident would have a strictly local or widely dispersed effect downstream.
- finally we may need to consider the interaction of herbicides with other toxicants, and consider whether there may be antagonistic or synergistic effects.

At this point you may be wondering whether there is any value in the figures given in Table 1, and whether this is really science.

The whole process of risk assessment from bioassay data have been elegantly debated, amongst other by Gehring (1987). The standard estimate, the margin of safety, is derived from the difference between the minimum concentration required to affect the subject organism or community, and the actual concentration anticipated in the water. Mount (1979), in a thoughtful and readable review, argues that the uncertainty associated with both these measurements is much more a feature of judgement and site-specific considerations than of the inherent properties of the molecule, or its fate or effect determined in laboratory experiments.

It is certainly true that in Australia the situations in which water may be accidentally or intentionally polluted with herbicides, are vastly different, with a wide geographic spread. Perhaps this helps to explain the lack of any national co-ordinated monitoring program for herbicides in water.



Fig. 1. Concentration-time relationship showing threshold values of concentration ( $C_R$ ) and time ( $T_R$ ) with damage or lethal effects in the hatched area.

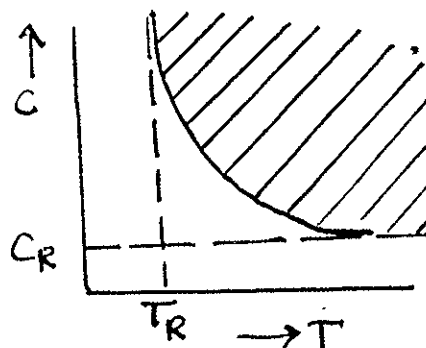


Table 1. Herbicides used in or near water in Australia and limits for residues (Australian Water Resources Council, 1985).

Herbicide	Use	Residue limit (mg L <sup>-1</sup> )		
		Potable	Irrigation	Aquatic life
Acrolein	Flowing water	*	0.1	*
Amitrole	Emergent plants	0.001	0.002	0.3
Asulam	Rumex spp.	0.3	*	*
Bromacil	Banks and bare beds	0.6	*	*
Copper	Algae	1.5	*	0.01
2,4-D	Emergent and banks	0.1	*	0.004
Dicamba	Broad-leaved spp. on banks	0.3	*	0.2
Dichlobenil	Submerged, bare beds	0.02	*	0.037
Diquat	Submerged, static water	0.05	*	0.0005
Diuron	Bare soil, beds and banks	0.04	0.002	0.0016
Dalapon	Emergent on banks	0.5	0.004	0.11
Fosamine	Woody spp. on banks	3.0	*	*
Fluometuron	Bare soil on banks	0.1	*	*
Glyphosate	Emergent and banks	0.2	*	*
Paraquat	Emergent, rice	0.04	*	*
Picloram	Woody spp. on banks	1.0	*	*
Simazine	Bare Beds	*	*	0.01
2,4,5-T	Woody spp. on banks	0.002	*	*
Triclopyr	Woody spp. on banks	0.02	*	*

Table 2. Threshold values of concentration ( $C_R$ ) and time ( $T_R$ ), extrapolated from Westerdahl (1985). [See Fig. 1 for explanation of  $C_R$  and  $T_R$ ]

Herbicide	Plant	$C_R$ (mg/L)	$T_R$ (h)
Diquat	Hydrilla	0.2	<12
2,4-D	Watermilfoil	0.3	<0.5
Endothal	Hydrilla	1.5	24
Fluridone	Hydrilla	0.02	120

Turning now to the benefits and costs of herbicide use, both economic and environmental. In particular, what scientific information is available on herbicides in water, and how is the data being interpreted?

1. Use of herbicides in cropping systems

Australian farmers spent some \$850m on agricultural chemicals in 1988 to capture a benefit of \$3 to 5 billion (ASTECC, 1989). About \$368m was spent on herbicides.

The advantages and disadvantages of herbicides for weed control have been reviewed recently by Combellach (1989). Advantages of the newer herbicides to control weeds, reduce pathogens, conserve moisture, save energy, protect soil structure, and reduce erosion are comprehensively described in a book on "Tillage, New Directions in Australian Agriculture" (Cornish and Pratley, 1987).

There are many complex issues. Direct drilling and reduced tillage techniques are not always beneficial, particularly for obtaining the highest yield. But many reports describe massive reductions in soil loss amounting to savings of the order of tonnes per hectare of soil (e.g. Ralph, 1986).

What are the potential benefits and costs for water pollution, arising from this increasing use of herbicides in the landscape?

*Surface water quality:*

Unfortunately, very little information is available for Australia so far, as illustrated in the review on environmental effects of herbicides used in conservation cropping systems (Wardrop, 1986).

Surface water monitoring for herbicides is generally not co-ordinated on any national, state or even regional basis. There

have been only a few isolated studies so far, and data is sometimes difficult to obtain, for both bureaucratic and political reasons.

Pesticide monitoring data for the River Murray between 1971 and 1986, for a total of 737 analysis gave only one sample positive for 2,4-D, and that at less than 0.01 micrograms per litre. Other herbicides were not listed.

Also in the River Murray some distortion of the mouth parts of Chironomid larvae was observed at two stations downstream of irrigation return flows, and by implication, attributed to stress from pesticide residues (Murray-Darling Basin Ministerial Council, 1987). The role of herbicides has not been investigated, except that chlorthal-dimethyl was implicated in causing distortion in the second generation of Chironomids (Madden, 1989).

Thoma and Nicholson (1989), working in the Onkaparinga catchment in the central Mt Lofty Ranges east of Adelaide, monitored water from a hilly horticultural catchment in the Picadilly Valley for various pesticides, chlorthal-dimethyl and propyzamide, with the objective of assessing the decline in drinking water quality for metropolitan Adelaide. In thunderstorms, concentrations of chlorthal-dimethyl and propyzamide reached 0.088 and 0.036 mg/L respectively, but further downstream residue concentrations declined. The concentration was less than 0.002 mg/L at the entrance to Mount Bold Reservoir.

Bowmer and Weerts (1987) measured bromacil, atrazine, diuron and glyphosate in irrigation surface waters in the main distribution systems of the Murrumbidgee Irrigation Areas, NSW. Glyphosate did not occur in any samples (<0.1 mg/L). Bromacil and atrazine were hardly ever found (at 0.0005 mg/L) but traces of diuron were present in all surface drainage waters. Bromacil was found in 9 out of 11 samples of subsurface water being pumped out of tile drainage pumps in citrus orchards. Atrazine was monitored in tail-water from two farms where it had been used in maize, irrigated using bed or hill and furrow systems. The load of atrazine carried off in the run-off water of the first irrigation event was only about 0.3-1.6% of that applied, giving an average concentration of up to about 0.15 mg/L. We feel that these concentrations may be sufficient to damage soyabeans or other sensitive crops if the water is recycled without dilution.

Intuitively it might be expected that the increasing usage of herbicides and potential for water pollution, may be countered by the increasing stability of the landscape. This would be expected particularly for these compounds which are extensively adsorbed, such as glyphosate, diquat, paraquat and perhaps atrazine; and (for all herbicides) because reduction in soil erosion is often coincident with better infiltration and water storage in the soil.

Avoidance of soil erosion is an obvious benefit of herbicide use in minimum tillage conservation farming. Another related benefit might be the reduction in transport of fine particles from the

landscape into watercourses, even though the loads involved may be quite small.

The impact of suspended particulate matter in scattering and absorbing light profoundly changes the ecology of rivers and reservoirs. Also, transport of nutrients, particularly phosphorus, along with the particles can stimulate the growth of algae and cyanobacteria. Water quality may deteriorate due to the production of odours such as geosmin and methylisoborneol (Hayes and Burch, 1989). Toxins are also produced by cyanobacteria. For example, *Microcystis*, a problem for reservoirs in South Australia produces a hepatotoxin; while *Anabaena*, a problem in the lower Murrumbidgee, sometimes produces a neurotoxin. The production of disinfection by-products is also related to the problems of water pollution with organic matter, including senescence of algal blooms (Hine and Bursill, 1987).

My hypothesis is that the use of herbicides in cropping might actually give substantial indirect benefits for water quality, due to the potential reduction in surface runoff of particles and nutrients. The effects of nutrients once they reach the water, including the extent of spiralling in streams, is being researched by several groups. There seems to be much less information on the contribution of diffuse agricultural nutrient sources, and the influence of new herbicide-based tillage methods in reducing the problem of nutrient-enrichment.

#### *Groundwater quality*

The prospects of groundwater pollution is a matter of increasing public concern, particularly in Europe and North America where groundwater is the most important source of drinking water. The occurrence of herbicides, notably 2,4-D, atrazine, alachlor and metribuzin in well water, although at extremely low concentrations, was reviewed by Hance (1987).

In Australia there are similar concerns for several areas where intensive horticulture is practised on sandy soils, particularly in Western Australia. Singh *et al.* (1988) obtained data for herbicide adsorption onto selected soils, and used a simple model (Jury *et al.*, 1987) to predict that the risk of groundwater contamination from linuron and diquat was low. However, in soils of low organic matter and high drainage rate, the risk of pollution from simazine was high.

In a study of leaching of herbicides in three Victorian soils Hatton (1988) concluded that in light soils and seasons of high rainfall, there was a risk of groundwater contamination with diclofop-methyl.

## 2. Irrigated crops, and water distribution and drainage systems

This subject has been reviewed in more detail by many authors, particularly Sainty and Jacobs (1981), Bowmer (1987) and Reinert and Rodgers (1987).

The largest pollution of water with herbicides must arise from the intentional application of herbicides for aquatic weed control.

Chemical methods are used because the logistics of maintaining thousands of kilometres of supply and drainage channels preclude a reliance on mechanical methods, particularly when the distribution system is operating at maximum capacity. In the irrigation systems of south-eastern Australia the return to growers exceeds 1000 million dollars, so the relative cost for treatment and application of about 6 million dollars is small.

The main herbicide used for submerged weeds in flowing water is acrolein, particularly for management of Elodea canadensis. The main advantages of acrolein are that it is cheap and has a rapid effect in restoring flow when injected for a short time, and also that it dissipates rapidly from flowing water, with a first order half life of about 4 hours, leaving no phytotoxic residue. A disadvantage is that it is toxic to fish at very low concentrations.

Ditchbank weeds which obstruct flow include Phragmites australis, Typha spp, and the grasses Paspalum distichum and Paspalum dilatatum. The main herbicides used for foliage application are glyphosate, dalapon and amitrole. Herbicides applied to the sediment surface after draining of water - the soil-residual compounds - include TCA and diuron, the latter being used mainly by farmers.

Residue levels can be minimised for foliage sprays by preventative management, so that the weeds are controlled before they spread from the channel margins into the water course; by control of drop size and drift and, for glyphosate, by use of rope-wick or other wiping methods. Channel draining before spraying can also minimise residue levels when water is subsequently introduced into the channels, as demonstrated experimentally for glyphosate; and already practised for dalapon.

The main concerns about the possible contamination of rivers and wetlands are in northern Victoria and southern New South Wales, and in the flood mitigation schemes of northern New South Wales which drain into the coastal rivers.

In the Murrumbidgee Irrigation Areas and Districts water is re-used in the region, giving inherent protection for rivers and wetlands. Local on farm re-use is already widely practised on the cotton farms of the Namoi River, and is increasingly being adopted in the Murray and Murrumbidgee irrigation systems. There are many advantages in local recycling of water, but there may be a decline in water quality eventually, particularly where salinity increases to concentrations which could damage the structure of the soil. Superimposed on this problem is the possibility that, in mixed cropping systems, herbicides used for selective weed control in one crop could damage another. Preliminary investigations were reported by Bowmer and Weerts (1986).

In irrigation distribution systems chemical control has several advantages compared with mechanical methods, apart from obvious differences in speed and cost.

Prevention of weed control by using soil-residual compounds, or early intervention with foliage acting sprays will help to avoid the accumulation of silt. Also mechanical methods disturb the channel lining, increasing seepage and infiltration of water, and easily giving low spots through over-excavation which are difficult to drain, and which will add to the dramatic problems of rising water-tables, and salinisation and waterlogging of the landscape of the Riverine Plain. For example, in the Murrumbidgee Irrigation Areas and Districts about 140,000 ha of land have developed water tables which can reach within 2 m of the surface, and which threaten the viability of irrigated agriculture, apart from rice growing. Canal seepage is reputed to contribute about 25% of accessions to groundwater, so it is important to avoid exacerbating the leakiness of earthen canals by mechanical disturbance.

#### Alien invaders

Several alien aquatic plants are a potential threat to Australia's wetlands and river systems in Australia, mainly because they can be extremely aggressive and out-compete native species.

Some, such as Salvinia molesta are amenable to biological control with insects, particularly in the warmer climates. For others, biological control methods have not yet been developed, and herbicides are being used either to eliminate the infestations at an early stage, or to limit the spread of the weeds until a biological control agent can be developed. In the case of Elodea canadensis herbicides are widely used for continuing management.

#### *Elodea canadensis*:

A native of North America, this plant is mainly a problem of irrigation distribution systems in Australia where it coexists with native plants especially Potamogeton spp. (Pondweeds) and Vallisneria spp. (Ribbonweed). The management of this weed was reviewed recently by Bowmer and Sainty (1989). Acrolein is used by State Authorities for routine, short-term management in flowing water. Other aquatic herbicides (e.g. fluridone, endothal-amine and terbutryne) require long contact time for effective control, making management difficult. Some other compounds (e.g. diquat and endothal-potassium salt) seem to be ineffective.

Draining and drying by exposure of sediments to high summer temperatures or winter frosts are an aid to management, and can be integrated with the maintenance of the systems and with the use of soil-residual herbicides mainly for other weedy species, such as Typha (cumbungi). We are currently investigating the potential for use of bensulfuron applied to the sediment, and left for about one week before introducing water. Advantages over acrolein could

include less hazard to fish and aquatic life, and more systemic action, giving better management of the weed.

The use of fish, particularly sterile grass carp (Ctenopharyngodon idella) has been researched intensively, particularly in the United States. There are logistical problems in herding and harvesting the fish in irrigation systems especially if an annual drawdown of water is required; the fisheries agencies are concerned about importation of disease, and possibility of escape; and there is a concern that in communities of several plant species the effect of the carp may be merely to increase the biomass of unpalatable species, such as Myriophyllum, Ceratophyllum demersum, Potamogeton and Egeria.

Currently this plant is still the main aquatic weed problem in southern New South Wales and Northern Victoria. Its spread in the Murrumbidgee systems has not been as extensive as expected, and generally it may be declining, perhaps as a result of the effects of European carp in dramatically increasing the turbidity of the water.

*Water hyacinth:*

This floating plant is currently a potential problem in tropical and coastal areas of Australia, where it blocks flow and is a potential habitat for aquatic stages of disease-carrying organisms particularly mosquitoes. Biological control with the weevils Neochetina bruchi and N. eichhorniae has been helpful in many situations. Occasional plants found in the Murray River have been removed by hand or sprayed with 2,4-D.

The most spectacular and disturbing infestation occurred in the Gingham watercourse near Moree, NSW, where some 20,000 hectares of dense plants spread in the wetlands created behind a log jam in the Gwydir River (Mitchell, 1977). An extensive draining program, a lucky period of drought, and limited use of amitrole and 2,4-D combined to bring the problem under control (New South Wales State Pollution Control Commission, 1978).

*Alligator Weed:*

A native of South America, Alternanthera philoxeroides (Alligator Weed) was first recorded in 1946 near Newcastle, NSW, and has spread through the lower Hunter Valley to river systems west of Sydney, to Woomargama near Albury and to south-eastern Queensland (Julien and Bourne, 1988). It is currently infesting several thousand hectares of damp pasture land near Williamstown, NSW and is regarded as a threat to inland river systems, wetlands and irrigated crops should it escape.

Biological control with a flea beetle, Agasicles hygrophila, have reduced the problem of the floating mats which form on large permanent waterways, but not on small waterways, swamps, or low-lying pasture land.

Glyphosate and metsulfuron-methyl are the main herbicides used by Local Government to try to maintain drainage channels for flood mitigation in low lying areas, but regrowth occurs rapidly. We are currently exploring the potential for other chemical controls which must be integrated with pasture establishment. After screening some hundreds of compounds for activity, only dichlobenil is giving any long term control so far (Bowmer et al. 1989). Some other herbicides being investigated at present include glyphosate, fluoxypyr, imazapyr, triclopyr, metsulfuron-methyl, bensulfuron and tebuthiuron; several are being used in combination with repeat treatments of diquat in an attempt to gradually reduce the plant's vigour.

*Mimosa pigra:*

A tall, prickly, leguminous shrub from Central America is invading the wetlands of northern Australia, with devastating implications for the majestic *Melaleuca* paper bark trees, native sedges and grasses, many native animals, waterbirds and lizards (Lonsdale and Braithwaite, 1988).

Infestations were largely confined to the city of Darwin until about 1950 when plants were scattered over about 4000 hectares; now an estimated 450 square kilometres are affected; including a floodplain perilously close to Kakadu National Park.

Several insects have been released and two fungi are being studied for potential biological control, but the prolific longevity and production of seeds, up to 12000 per square metre, reduces the chances of success. At best biological control cannot be expected for several years.

Meanwhile, the Australian National Parks and Wildlife service is spending about \$250,000 p.a. to monitor the spread of the shrub, and treat isolated outbreaks by hand.

Ian Miller of the Northern Territory's Department of Primary Industries and Fisheries has investigated the use of herbicides, finding tebuthiuron most useful. However, there are concerns about the persistence of the herbicide in soil, and its movement into water, as well as the prospects of soil erosion should *Mimosa* be chemically controlled. The problem here seems to be that if we wait to find all of the answers, much of the Top End may have fallen victim to this alien plant invasion.

Summary - The chemist's role in weed control

Traditionally the chemist's role in weed control will cover the detection of herbicide residues, the development of analytical methods, the design of new compounds, and determination of the fate and distribution of herbicides in the environment.

In writing this review about herbicides in water I have become painfully aware of the many other issues involved; in particular, of the need to understand the biological and ecological significance of



chemical measurements; and of the interaction between weed control, land use, and other aspects of water quality. I have tried to describe the benefits and costs of herbicide use, both direct and indirect; and to give a view which is neither developer nor conservationist. In doing this I have trespassed on the territory of many branches of science, and may have offended people whose view of science or chemistry is strongly based on traditional disciplines.

I listed some of the limitations of herbicide concentration as a criterion for water quality. The list of limitations was long, indicating that there can be no hard and fast rules; that we can expect the truth of science to remain elusive in this area.

I described three types of herbicide use, where water might be polluted either intentionally or indirectly. In all of these uses, to a greater or lesser extent, it became clear that the use of herbicides can help protect our soil and water resources.

In particular, there seems to be a great opportunity to increase conservation farming practices above the current area of about 20% of cropped land. Except for one experiment in the Onkaparinga catchment of South Australia, and one planned for the Douglas River area, Northern Territory, there seems to have been no attempt to investigate the benefits of terrestrial herbicide use in safeguarding water from extensive problems of nutrient enrichment. We may need to trade off the risk of herbicide pollution (small?) against the benefits of reduced eutrophication (very large?).

Also, we need to trade off the risks against the benefits of preventing alien aquatic plants from overtaking our rivers, wetlands and crops. Here the risk decreases as newer safer compounds, such as triclopyr, fluridone, imazapyr and the sulfonyl ureas become available for use near water.

Unfortunately, with very few exceptions, the debit side of surface and groundwater pollution has been poorly researched in Australia. In order to counter the inevitable press and community concern, we will need to be much better informed if we are to capture the potential environmental benefits of herbicide use.

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## A SHORT HISTORY OF HERBICIDE PERSISTENCE RESEARCH

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### INTRODUCTION

This paper outlines the evolution of herbicide persistence research and some of the problems and opportunities for agriculture. Herbicides cover a broad range of inorganic and organic compounds which control weeds. Classification is generally by the type of herbicide treatment or according to chemical properties of the herbicide.

Historically, herbicide persistence research has been published in weed science (WS) or plant physiology journals. In recent years, articles have appeared under environmental toxicology (ET). The choice often depends on the motivation for the investigations, i.e.

1. Modification of existing herbicides or herbicide formulations (WS)
2. Improving performance and safety (WS)
3. Regulatory requirements (WS or ET)
4. Accessing and prediction of environmental impact (ET).

Herbicide persistence research is often defined as any investigation into the fate and behaviour of herbicides in soil, air, water, plants, and/or animals. The emphasis has shifted from measurement of minute concentrations of herbicides in the components of the environment to the determination of no observable effect levels (NOELs) and the processes which control the distribution of herbicides. With around 200 active ingredients, numerous formulations and environments, it is not difficult to understand the reason for this approach.

### HERBICIDES IN AGRICULTURE

Urbanization and the decline in traditional labour-intensive methods of weed control, based on fixed crop rotations and livestock grazing, provided opportunities for herbicides and markets for cash crops (Elliot et al. 1968). By the end of the 19th century, inorganic herbicides had been discovered which provided a measure of selectivity, but these had disadvantages of high mammalian toxicity and/or were not degraded (Table 1). By the 1930s, research had been initiated in Britain to overcome these problems. The work came to fruition during World War II with the discovery of 2,4-D in England and the USA. 2,4-D was discovered by directed synthesis following the identification of the structure of the plant hormone indolacetic acid. While 2,4-D mimicked the action of indolacetic acid, only recently has a plausible mode of action been proposed (Fitzsimons et al. 1988). 2,4-D is a strong acid with 50% as the negatively charged anion and 50% as the neutral molecule at pH 2.6 (the so-called pKa). Thus at low pH, preferential absorption occurs of the neutral form, while in the alkaline plant phloem the equilibrium favours the anion which is subsequently trapped. This property confers remarkable systemic activity in plants and mobility in most soils. The activity against many emerged broadleaf weeds was a spectacular advance over the inorganic herbicides, with unprecedented selectivity towards winter cereals. Initially, pre-emergence activity was valued, but this property varied considerably between soils. The efficacy of 2,4-D coupled with food and labour shortages during and after World War II were factors in the rapid adoption of the new herbicide technology. However, the success of 2,4-D was to create other problems. In the

1950s, herbicides undermined the concept of rotation by altering the "fouling" crops into "clean" crops (Elliot et al. 1968). The same authors also noted "a high level of efficiency in weed control was reached on mixed and arable farms in the late 1940s when the rotations of the 19th and 20th centuries were still in use and farmers were in addition obtaining the benefits of fertilizers and the newly developed herbicides".

In the 1950s, potent inhibitors of plant photosynthesis were discovered: the substituted ureas and the triazines. The first urea, monuron, was developed by Du Pont in 1952. Monuron was developed for non-selective weed control at rates from 10 to 30 kg ha<sup>-1</sup>. However, diuron, another early urea, found a niche in the horticultural area as a selective herbicide at lower rates: 0.25 to 3 kg ha<sup>-1</sup>. More significant was the discovery of simazine by Geigy in Switzerland in 1957 (Knusli 1970). The discovery of herbicidal activity was to lead to the development of more than 20 triazines including atrazine. These herbicides enabled selective residual weed control in the lucrative corn and sorghum markets at rates of 0.5 to 4 kg ha<sup>-1</sup>. Atrazine was more water soluble than simazine and proved more reliable under conditions of low rainfall. The success of atrazine led to the realization that herbicides might eventually replace cultivation as the primary means for weed control. The ureas and triazines were neutral or weak bases. Hence adsorption onto soil constituents, organic matter and to a lesser extent clay, could modify their activity and persistence. The factors controlling the activity and persistence of these new herbicides were the subject of intense scrutiny in the 1960s. In Australia, it was another 20 years before these findings could be put into commercial practice.

The discovery of the contact action of the bipyridyl herbicides in 1958 provided non-selective weed control without the risk of injury to subsequent crops. The bipyridyls were strong bases. Thus at typical soil pHs, they existed primarily in the cationic form which reacted with negatively-charged clay particles and organic matter (Best et al. 1972). While absorbed into the clay matrix, the bipyridyls do not retain their phytotoxicity. However, the unchanged parent compound may be released under some circumstances (Singh et al. 1988). The broad spectrum activity and low residual phytotoxicity of the bipyridyls were key factors in the development of direct drilling. This concept was successfully promoted by ICI in Western Australia where acreage expanded from 10,000 ha in 1971 to 835,000 in 1982 (Jarvis 1983).

Simple plant bioassays (Gerber 1975), random screening and chemical synthesis had played a key role in the discovery of new herbicides. However, random screening techniques were neither infallible nor efficient, with success rates around 1 in 10,000. The inhibition of seedling emergence by trifluralin was not discovered in initial screens by Stauffer. The herbicidal activity of trifluralin was later discovered by Eli Lilly in the USA. Trifluralin gave residual weed control of grasses, especially in vegetable and horticultural crops. Trifluralin had an unusual set of physical and chemical properties: exceptionally strong affinity for organic matter, high volatility, and susceptibility to UV degradation. In the north-west, this had two disadvantages: (1) the requirement for mechanical incorporation, which encouraged excessive cultivation, and (2) it fostered a continuous cereal monoculture with control of 2,4-D-tolerant grass weeds.

The 1970s saw the discovery of two groups of herbicides with entirely new modes of action. These herbicides inhibited enzymes involved in the production of amino acids. Being unique to plants and a few microorganisms, these herbicides had low toxicity to mammals. Glyphosate is currently one of the most widely used herbicides world wide. The mode of action is believed to involve the inhibition of the enzyme 5-enolpyruvylshikimate-3-phosphate and the subsequent reduction in aromatic amino acid levels. In moist soil, degradation by soil microorganism is rapid. Consequently, carryover or release of phytotoxic residues is unlikely. Glyphosate is a systemic foliar applied herbicide, effective against a wide range of grass and broadleaf weeds. In north-western NSW, glyphosate and atrazine are important ingredients in the success of no-tillage sorghum.

In 1975 George Levitt of Du Pont discovered a new class of herbicides, the sulfonylureas. Key properties of this group include their low mammalian toxicity and their suitability for the newer no-tillage cropping systems. With use rates as low as 2 g a.i. ha<sup>-1</sup>, the sulfonylureas represent a quantum advance in herbicide chemistry. Interestingly, the first sulfonylurea developed, chlorsulfuron, was to lead to a resurgence of interest in the factors affecting herbicidal persistence and leaching (Beyer et al. 1988). The sulfonylureas have been shown to inhibit the enzyme acetolactate synthase (ALS), a key enzyme in the biosynthesis of branched amino acids in bacteria, fungi and higher plants. The general structure of the sulfonylureas consists of an aryl group, a sulfonylurea bridge and a nitrogen-containing heterocycle. Numerous structural modifications are possible to this basic toxiphore, many of which retain high activity. However, even minor structural modifications radically alter crop selectivity and soil residual properties. Thus, while the first sulfonylureas had selective residual activity, later Du Pont sulfonylureas were chosen for selective translocated activity with low soil residual activity.

## HERBICIDE PERSISTENCE INVESTIGATIONS

Initial herbicide persistence investigations were directed at providing a scientific explanation for field problems -- typically, poor reliability. Loss of highly valued residual activity of 2,4-D was an early example. Audus (1949) was able to demonstrate the crucial role of microorganisms in this process and recognised its importance "in the ability of the soil to "recover" from its toxic action". At typical concentrations resulting from agricultural use, soil microorganisms are able to metabolize herbicides to their inorganic constituents. However, other processes may be involved in the loss of herbicide activity, including volatilization (Spencer and Cliath 1980), photo-decomposition (Matthew et al. 1980, Zabik and Ruzo 1980), adsorption (Boesten and Van Der Pas 1983), absorption (Raupach et al. 1979), chemical hydrolysis (Armstrong et al. 1967) and leaching.

While the discovery and registration of herbicides has taken place primarily within the chemical industry, herbicide persistence research has been successful in the public sector. Table 2 shows the major groups co-operating with Australian researchers. The National Horticultural Research Station at Wellesborne and Rothamsted (UK) have active herbicide persistence programs which successfully integrated persistence in conjunction with efficacy and crop injury. Dr Allan Walker and Dr Peter Nicholls provided the source code for their herbicide simulation models and degradation parameters for many herbicides. The closure of the the Weed Research Organisation in 1986 was a serious loss to herbicide research internationally. Fortunately, Dr Ray Hance and several senior scientists who were transferred to Long Ashton have maintained contact with herbicide researchers in Australia, albeit in a private capacity. The Netherlands has perhaps the most intensive agricultural production systems in Europe. Dr M. Leistra and Dr Jos Boesten of the Pesticide Institute have been at the forefront in the development of dynamic mechanistic herbicide simulation models and contributed to the understanding of herbicide adsorption. Recent emphasis has been on the modelling of herbicide movement into groundwater. Both The Netherlands and Denmark have recently enacted legislation to reduce herbicide use. Dr Jens Streibig has been instrumental in developing statistical tests to identify with greater precision the interaction between herbicides and other agricultural chemicals. The goal is to reduce the intensity of herbicide use without lowering existing levels of weed control. The unique position of agriculture and the recreational value of land have ensured a continued commitment to herbicide persistence research in Federal Republic of Germany. Co-operation with the Weeds Research Institute has been fruitful. Existing plant bioassays to establish NOELs and methodology for the prediction of re-cropping intervals originated from Dr Wilfried Pestemer. The ability to attract research funding and Ph.D. candidates are important ingredients in the success of the programs. Like its former counterpart in England, the Weeds Research Institute integrates all aspects of weed

control and herbicide persistence with a strong focus on the development of practical recommendations for growers. In North America, herbicide contamination of surface and groundwater are issues of public concern. Investigation into the processes controlling herbicide persistence and movement are well advanced. In Washington Dr Michael Barrett heads a major groundwater program which attempts to classify and define the extent of groundwater contamination from both point source (depot spills, disposal) and non point source. Nearby at the USDA laboratories at Maryland, Drs Phillip Kearney and Donald Kaufman were early contributors to the identification of the pathways of herbicide loss. More recently this knowledge is being applied to the development of safe methods of disposal of concentrated wastes using both photochemical and microbiological procedures. The University of Wisconsin, Madison, was one of the first to offer graduate level programs in environmental toxicology. Former Professors E.P. Lichtenstein, F. Matsumura, J.E. Casida, W.C. Dauterman, and K.P. Buchholtz were responsible for establishing a sound basis for the newly emerging discipline. Drs W.F. Spencer, W.J. Farmer, M.M. Cliath and W.A. Jury of the University of California-Riverside contributed in like manner to the understanding of pesticide volatilization. Newly-appointed scientists have extended the scope of herbicide persistence studies with more emphasis on simulation modelling and statistical procedures. In Canada, the Forestry Pest Management Institute and the Chemistry and Biology Research Institute have been valuable sources of information on the fate of aerial applied pesticides and atrazine degradation, respectively. In New Zealand there is the MAF herbicide persistence program lead by Dr Anis Rahman. This program has been productive and highly successful in the application of research findings.

According to Saltzman and Yaron (1986) three quarters of the leading scientific contributions to the understanding about the fate of herbicides in soil were made in the 1960s and '70s. By contrast, little activity occurred in Australia during this period. Herbicide persistence research was initially a component of weeds research, often limited to a minor component of herbicide screening programs and fragmented. Reeves (1976) proposed a more co-ordinated approach to the whole area of weeds research and its funding. However, it was not until these suggestions were implemented by Wheat Research Council in the early 1980s that herbicide persistence research was established in its own right. The recommendations of four workshops helped shape and define priority areas (Table 4). Weeds research is now classified in three general areas: ecological, herbicide resistance, and persistence, with each area having a national co-ordinator and a set of priority areas for research funding. Information summarized in Table 4 lists herbicide areas currently under investigation in the herbicide persistence sub-section. Most areas involving the effect and fate of herbicides are being addressed. In Queensland, investigations have centred on weed control, persistence, and fate of widely-used commodity herbicides -- out-of-patent chemicals. Classification of soil types in terms of a persistence index is a new initiative which extends early research on residual herbicides (Marley 1980). The aim is two-fold: to validate existing models and to improve herbicide recommendations for specific localities. Although not strictly within the realm of herbicide persistence research, fundamental research is being undertaken by CSIRO Division of Soils, Townsville, into the development of numerical models of water infiltration into clay soils. The modification of the CREAMS model for Australian conditions to predict runoff, and stream sediment loading is another valuable contribution from the Department of Primary Industries, Queensland. Known as the PERFECT model, the pesticide subroutines are yet to be developed. However, it has been written in FORTRAN 77, the standard language for development in herbicide persistence programs. Modification to incorporate the herbicide component would involve two to three months of programming. Validation would require a longer period, although experiments have been proposed which may be used for this purpose.

Universities not only provide training in environmental toxicology and related disciplines, but also research into areas impinging directly on herbicide research. The University of New England has programs in environmental science (modelling), and there are two research programs: agronomy seed pelleting (Scott, 1989), which promises to more selectively utilize herbicides, and herbicide transport. The University of Sydney has



research programs in the application of molecular biology and biochemistry, in addition to a weeds program in agricultural chemistry. Two programs are being undertaken by the NSW Department of Agriculture and Fisheries. At Tamworth, modelling herbicide persistence and re-cropping have been emphasised. At Wagga, long running programs have been maintained into varietal tolerances to herbicides and the effect of environmental factors.

Victoria has the greatest concentration of herbicide persistence programs. The State Chemistry Laboratory in Melbourne supports a large field program in co-operation with regional research centres. The program assessed the long-term effects of three important herbicides under a range of environments typical of the Australian wheat belt (Johnstone et al. 1986). Soil sampling and chemical analyses were used to assess herbicide persistence and crop growth, primary yield, and to assess the impact of herbicide residues. In addition, problems regarding soil sampling variation, herbicide leaching, persistence, and effects on weed populations were examined. The analytical group is particularly strong, having developed classical analytical procedures and new immunoassays for the sulfonylurea herbicides at the ppt level. Research is now being directed towards the development of predictive tests and the use of GIS (Geo Information Systems) to link several layers of information in addressing district and regional problems. Strong regional groups have also been developed. At Horsham in western Victoria, a major research program is under way into controlled-release formulations.

Wheat production is small in Tasmania (Hyde-Wyatt 1986). However, herbicide carryover from high value crops can occur. Because of the diversity of subsequent crops, bioassay techniques are being developed to indicate potential problems.

South Australian soils are light textured and subject to erosion. Priority is given to stubble retention and reducing cultivation. However, with 1.2 million hectares of alkaline loams and sands, carryover of herbicide residues could adversely effect susceptible crops and more importantly the clover leys (Fawcett 1988). Extensive field trials have been undertaken by the South Australia Department of Agriculture on the effect of tillage regimes and the phytotoxicity of herbicides residues. The apparent low incidence of herbicide carryover is an interesting finding. This is the subject of more basic research being undertaken by the CSIRO Division of Soils. Preliminary results hold promise for the development of a more objective means of classifying soil according to persistence category. The approach has been to investigate the adsorption and degradation of herbicides on/in the principal soil components. The adjoining Waite Institute is the largest centre for herbicide resistance research in Australia. Close co-operation between herbicide persistence and resistance research is maintained by regular contact between individual researchers and more formally by presentation of papers at workshops and conferences.

Sandy soils, erosion, and vulnerable groundwater are features of Western Australia. Herbicide investigations have been undertaken to overcome problems with poor uniformity of application and optimizing herbicide application rates by developing a strategy of herbicide top-up with herbicides such as simazine. The University of Western Australia supports the largest program on the movement of herbicides into groundwater. The research seeks to identify the factors influencing movement and modelling herbicide leaching. The management of herbicides in vulnerable aquifers requires consideration of herbicide inputs from agriculture and forestry and this is currently under investigation.

The Department of Conservation in the Northern Territories in conjunction with the University is currently undertaking an environmental impact of herbicides in the Douglas River basin. Investigations propose large scale sites of several hectares with frequent monitoring of rainfall, runoff, sediment, nutrient and pesticide transfer.

While the programs are long-term, information has already been made available for public discussion. Some of the practical benefits are evident in the area of problem definition and prevention (Bowmer and Weerts 1987). The development of a sensitive immunoassay test for sulfonylureas (Rothnie 1988) at DARA is an important breakthrough. In the ELISA (Enzyme Linked Immuno Sorbant Assay) format, the test is rapid and able to detect sulfonylureas at physiologically-significant concentrations (parts per trillion). The objective is now to translate the ELISA protocol to a "dip stick" format capable of field use. New methods of analysis using GLC (Johnstone et al. 1985) and HPLC (Ferris and Haigh 1987) have improved the ability to monitor residual herbicides. The ability to monitor residual herbicides would provide growers with a means to optimize weed control and minimise re-cropping and environmental problems. The development of a means to optimize the timing of herbicide applications for local conditions (Ferris et al. 1985) has also been significant. The ability to enumerate herbicide-degrading microorganisms is an equally exciting development (Duxbury 1988). The development of a national clearance protocol and assessment acceptable to each state registration authority is an important step forward in simplifying herbicide registration. The extensive application instructions/restrictions on labels supported by use legislation has helped address the problems arising from careless and irresponsible spraying. Finally, the level of co-operation between research groups, industry, growers, and consumer groups has been excellent. Not only has this prevented unnecessary duplication of effort and the efficient use of scarce resources, but also the sharing of information has developed an environment where common goals can be identified and targeted.

In Australia, the range of skills and resources in the herbicide persistence area has improved over the last decade. However, inadequate resources were available to develop public sector research programs satisfactorily. In comparison with the State Chemistry Laboratories in Victoria (DARA), deficiencies were apparent in all herbicide investigations. The most obvious difference was the number of herbicide chemists working in the public sector. More subtle is the dearth of younger scientists with tenure and programs to develop the necessary analytical and numerical skills. At Toowoomba, the field based program involving out-of-patent herbicides is gradually overcoming a problem concerning inadequate access to analytical facilities. This is a common problem which has been aggravated by demands upon residue chemists from the so called "Beef Crisis" (Ferris 1988). Steps are being taken to re-allocate resources from banned organochlorine insecticides to herbicides of current agricultural significance. However, the process is likely to be slow because of the long persistence of the organochlorine insecticides in soil and the problem of illegal disposal. Insufficient trained staff to process the samples and operate the equipment efficiently is a problem at the CSIRO Centre for Irrigation Research at Griffith. In South Australia, where the most extensive field trials are being conducted, bioassay has been the only tool available to investigate the persistence and movement of herbicides. In the short term, provision of analytical services through DARA would be helpful. However, in the long term, a strengthening of existing units is required to meet the demands for information being placed on them by the agricultural community and the general public.

Community perceptions about herbicides leave little room for complacency. They often reflect poorly on the grower ("grim reaper"), chemical industry ("irresponsible"), regulatory controls ("ineffective"), universities and research institutions ("isolated"). A lack of understanding about the difficulties facing the primary producer, misconceptions about agricultural chemicals, and unrealistic demands are part of the problem (Siech 1980). However, the importance of individual responsibility in areas such as minimizing non-target exposure cannot be over-emphasised. Initiatives such as dealer certification and applicator training currently being sponsored by the agricultural chemical industry will help overcome these issues, particularly with support from government and semi-government organisations. The comments by the Director-General FAO address another problem of equal concern: "the growing disarray of the scientific infrastructure which now limits planning of crop protection to "management by crisis". He supported a global

vision of agriculture and co-operation among all scientists to solve major national and international problems. I believe that part of the collective responsibility of the herbicide persistence research groups is to assist in the development of such a vision.

## CONCLUSIONS

The chemical industry has developed a powerful array of herbicides over the last four decades. The trend is now towards post-emergence herbicides with lower mammalian toxicity and lower use rates. However, there is no panacea for all weed problems. For major crops a range of residual and non-residual herbicides are now available, which are economic and can underpin more sustainable systems of agriculture. The diversity of modes of action and chemical properties are sufficient to manage most weed and environmental problems when used in conjunction with good agricultural practice. Unfortunately, "understanding lags behind practice" (Sagar et al. 1968). The world's resources to tackle all weed/crop/environment interactions are limited. In Australia, herbicide persistence programs have been established recently throughout the major cropping areas. With support from the international community, industry, and grower organisations, the expertise and equipment have been assembled to measure and predict the persistence of herbicides. Data have been gathered over the last decade to develop safe and efficient usage of herbicides in the major wheat growing areas.

In the areas characterised by winter dominant rainfall, the use of direct drilling techniques and rotations such as wheat/legume (lupins, field peas, or clover) have been adopted rapidly to maintain soil fertility and reduce erosion. Residual herbicides such as simazine/atrazine and chlorsulfuron/triasulfuron have a role in reducing the cost of managing weed populations and reducing the total herbicide input into soil. In this system, the yield of the alternate susceptible crop (wheat in the case of simazine) can be used to assess possible carryover of phytotoxic residues or any long-term impact on the ability of the soil to produce crops (Greaves 1985).

The success of the direct drilling systems of the winter dominant rainfall areas is yet to be emulated in areas which require a fallow. In the northern summer dominant rainfall areas. A rotation based on wheat/sorghum/chickpeas or lucerne is considered promising by some growers in northern NSW and southern Queensland. Such a system has several advantages:

- weed and disease suppression
- cost-effective herbicides
- nitrogen fixation -- symbiotic and free-living nitrogen fixation
- rotation of herbicides with differing modes of action
- alternating susceptible crops whose yield may be used to monitor herbicide persistence.

The success of herbicide persistence research in the public sector could be evaluated in terms of:

- Productivity per unit input, especially per unit area of land and energy
- Reduction in off-target movement of soil, as a measure of cultivation, as determined by sediment loadings in rivers and waterways.
- Herbicides residues levels in drainage water from agricultural regions and vulnerable aquifers.
- Herbicide levels in food
- The level of herbicide exposure to "high risk" groups -- manufacturers and applicators-- and the results of prospective epidemiological studies.

These goals need not necessarily conflict with the pursuit of excellence in science, rather they could provide direction and purpose and a more objective means to evaluate the benefits of the herbicide technology and research to growers and the general community.

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**Table 1** Important herbicide developments

			Rate (kg ha <sup>-1</sup> )	Toxicity (rat)	Persistence (soil)
1896	France	Copper sulfate used for selective weed control in cereals	10 - 50	M	H
1901-1919	Europe and USA	Ferrous sulfate, sulfuric acid, sodium chlorate used as herbicides	4 - 50	M-H	L-H
1932-33	France	Dinitro-phenols and cresols patented and used as herbicides	1 - 10	H	L
1941-42	England	Discovery and development of 2,4-D for selective weed control in cereals	0.3 - 2	M	L-M
1957	Switzerland	Simazine and atrazine for selective residual weed control in corn	1 - 4	L	H
1958	England	Diquat developed as a contact herbicide	0.5 - 2	H	H
1961	USA	Picloram developed for woody weed control	1 - 5	L	H
1975	USA	Glyphosate developed as a contact herbicide	0.1 - 10	L	L
1978	USA	Chlorsulfuron and metsulfuron-methyl for residual weed control in winter cereals	0.003-0.025	L	L-H
1986	USA	Activity of aminolevulinic acid discovered	1 - 4	L	L

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L = low  
M = medium  
H = high

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Source: Elliot et al. (1968)

**Table 2** Overseas public sector contact groups in herbicide persistence

<b>USA</b>		
EPA	Washington	M.R. Barrett
USDA	Beltsville (Maryland)	P.C. Kearney, D. Kaufman, C. Hellings
University of Wisconsin	Madison	E.P. Lichtenstein
University of California	Riverside	W.F. Spencer, M.M. Cliath, W.J. Farmer, W.A. Jury, S.R. Yates
<b>Canada</b>		
Forestry Pest Management Institute	Ontario	K. Sundaram
Freshwater Institute	Manitoba	A. Smith
Chemistry and Biology Research Institute	Ottawa (Ontario)	D. Gamble
<b>England</b>		
Institute of Horticultural Research (National Vegetable Research Station)	Wellesbourne	A. Walker
Rothamsted	Harpenden	P. Nicholls, T. Addiscott
Long Ashton	Bristol	M. Greaves
<b>The Netherlands</b>		
Pesticide Institute	Wageningen	M. Leistra, J. Boesten
<b>Federal Republic of Germany</b>		
Weeds Research Institute	Braunschweig	W. Pestemer
<b>Denmark</b>		
Royal Vet. Agric. Univ.	Frederiksberg	J. Striebig
Ministry of the Environment	Copenhagen	E.H. Jensen
<b>Israel</b>		
The Volani Centre	Bet Dagan	N. Aharonson
<b>New Zealand</b>		
Ministry of Agriculture	Hamilton	A. Rahman



**Table 3** National workshop recommendations on herbicide persistence research in Australia

**Roseworthy (1981)** National Workshop on Tillage Systems for Crop Production

Residual herbicide effects, herbicide x cultivar interactions.

**Horsham (1983)** Weeds in Reduced Tillage Cropping Systems

Establish principles, co-ordination and standardization of techniques, prevention of adverse herbicide effects.

**Rutherglen (1986)** Persistence of herbicides in soil in wheat cropping systems in Australia (I)

Persistence

Long-term effects of repeated herbicides applications on residue levels in soil.

Movement in soil

Investigation of the effect of runoff and leaching on herbicide loss and distribution in soil.

The influence of tillage systems on the contamination of groundwater by herbicides.

Application

Identification of the factor(s) responsible for accelerated herbicide loss from plant stubble and soil.

Environmental impact

Interactions between different herbicide residues, and between herbicide residues and other agricultural chemicals, and their effect on non-target crops.

The effect of herbicide residues on soil flora and fauna, with emphasis on nitrogen fixation

Methodology

Investigation of the sources of sampling variability and the development of improved soil sampling procedures.

Development of a rapid and sensitive immunoassay for the analysis of chlorsulfuron residues in soil.

Development of simple bioassay procedures for the detection of phytotoxic herbicide residues in soil.

Modelling

The development of regional and/or common soil-type herbicide simulation models to predict the influence of climate on the persistence and distribution of herbicides in soil.

**Melbourne (1988)** Persistence of herbicide residues in wheat cropping systems in Australia (II)

Disposal of herbicides.

Integration of weed biology data.

Registration -- achieving uniformity between States, access, and data retrieval.

Herbicide bioassays	Mr K. Young	Tas. Dept. Agric. Mt. Pleasant Labs. PO Box 46 Launceston South Tasmania 7249	--
Residual herbicides for reduced tillage systems and crop production	Dr R.G. Fawcett	SA Dept. Agric. Northfield Labs. GPO Box 1671 Adelaide, SA 5001.	The SA Wheat Research Committee
Herbicide clay interactions	Dr M. Raupach	CSIRO Division of Soils, PMB No. 2 Glen Osmond SA 5064	Wheat Research Council
Residual levels of simazine on wheat growth Herbicide top-up	Dr T. Piper	Agric. Res. Serv. Jarrah Road South Perth, WA 6151	Wheat Research Council
Contamination of groundwater by pesticides	Dr R. Gerritse	CSIRO Div. of Groundwater Res. Wembley, WA 6014	
	Dr R. Alyward	Univ. of WA Nedlands, WA 6009	
	Dr R. Singh	Univ. of WA Nedlands, WA 6009	Aust. Development and Assistance Bureau
The development of a water/herbicide infiltration model for cracking clay soils	Dr P. Ross Dr K. Bristow	CSIRO Div. of Soils P.M.B. P.O. Aitkenvale Qld., 4814	--
Herbicide movement in the Douglas River Basin	Mr M. Dilshad	Land Conserv. Unit Cons. Commiss. NT P.O. Box 496 Palmerston, NT 0831	Aust. Water Research Advisory Council

## Pesticide Residues in Fodder, Forage and Animal Commodities

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When a pesticide is used on a crop or pasture it is important to know the level of any residue which may result in the feed of a food-producing animal. Residues in the feed may lead to residues in meat, eggs and milk. A series of scientific studies and evaluations are needed before standards for permitted residue limits can be set.

### Principles for setting standards

Standards should be based on reliable scientific data, but also require logic and practical judgements.

1. The scientific data should be obtained using fully documented methods and be subject to a review system.
2. The principles and logic should be explained, and should be open to public scrutiny.
3. Analytical and test methods must be available to check compliance with the standards.

### Animal transfer studies

The relationships between residues in the feed and residues in animal commodities are determined in animal transfer studies.

In a typical study feed containing a measured level of residue is administered to the test animals for 21 days. During this time residues are measured in milk (dairy cow study) or eggs (poultry study) and tissues (muscle, offal, fat) from some animals slaughtered at intervals during the study. At the end of 21 days the remaining animals are returned to a residue-free diet for a further 7 days to see how quickly residues deplete.

The results of animal metabolism studies should be available when animal transfer studies are evaluated.

The studies must answer the following critical questions:

- \* does the residue accumulate in a particular tissue?
- \* has the residue level reached a plateau within the duration of the feeding trial?
- \* how quickly does the residue deplete after withdrawal of treated feed?

### Maximum residue limit

The MRL is the maximum residue which should result when the agricultural chemical is used according to good agricultural practices. These legal MRL values are established as a measure to reassure consumers and offer a division between food which is legally (though not necessarily scientifically) considered fit or unfit to eat.

Before MRLs can be established, the agricultural chemical must have been evaluated fully for its toxicological properties and found to be satisfactory. Health authorities can then estimate an acceptable daily intake (ADI).

### Use pattern

The use pattern is summarised in the use instructions on the label, which include directions for application rates, timing, mode of application, etc. The use pattern must be based on experiments. Good agricultural practice implies that the desired effect, pest control, will be achieved without leaving behind more residues than are necessary.

### Residue trials

Residue trials should be conducted with the herbicide used according to the label or proposed label instructions. Where the label allows a range of application rates and timing those conditions which will lead to the highest residue within the label recommendations are to be chosen for the trial. This is because the residue data are needed to set the maximum level of residues.

It is wise to consult an experienced pesticide residue chemist before planning a residue trial.

### Residue analytical methods and residue definition

A residue analytical method suitable for use by regulatory authorities must be available. There must be evidence that it is valid for the commodities in question.

If residue samples have been stored in a freezer for extended periods evidence should be available to prove that residue concentrations are stable under the storage conditions.

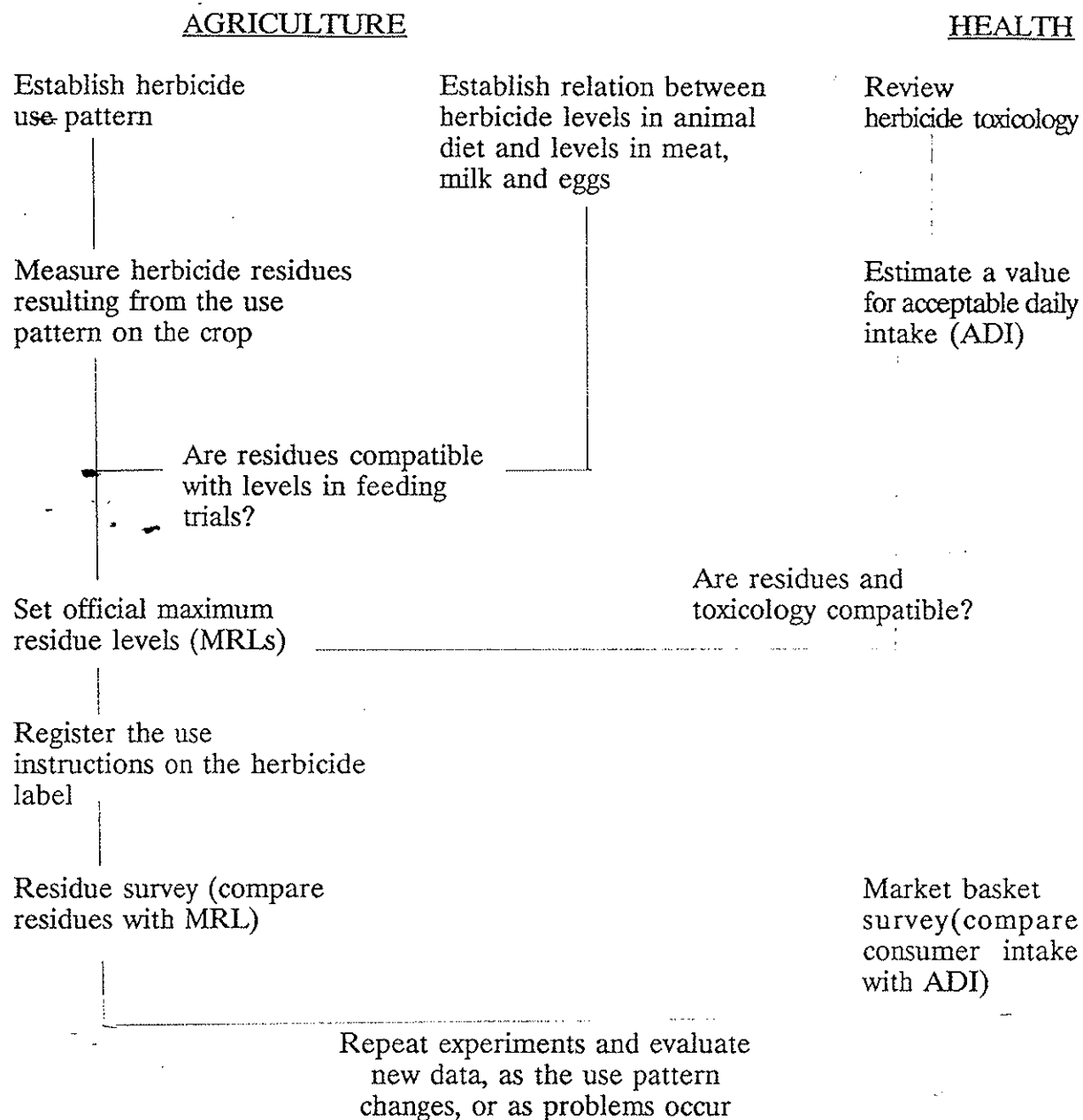
The residue definition is the statement of what compounds are included in the residue, and how it is to be expressed. For most pesticides it is parent pesticide only, but for some, metabolites with biological and chemical properties similar to those of the parent are included.

An experienced pesticide chemist will be able to provide reliable advice on residue methods and definitions.

### Evaluation of herbicide residues

The evaluation process for herbicide residues is summarised in Fig 1.

**Fig 1.** Evaluation of herbicide residues in animal feeds and animal commodities.



## Codex Classification of Foods and Animal Feeds

This classification describes and classifies foods and feeds moving in trade. Australia is moving to adopt this system for commodity descriptions in the MRL Standard.

The Classification is intended to be as complete a listing of food commodities in trade as possible, classified into groups on the basis of the commodity's similar potential for pesticide residues. The Classification provides a precise description of the food or animal feed commodity and for groups of foods and feedstuffs.

The Classification also describes which part of the commodity is to be analysed and how the residues are to be expressed (dry-weight or fresh weight).

### Primary Feed Commodities

"Primary feed Commodity" means the product in or nearly in its natural state intended for sale to the stock farmer as feed or to the animal feed industry as a raw material.

Primary feed commodities of plant origin are classified into: legume animal feeds; straw, fodder and forage of cereal grains and grasses, except grasses for sugar production; and miscellaneous fodder and forage crops.

**Table 1** Examples of commodities within feed commodity classifications.

Classification Code number	Commodity
<b>Legume animal feeds</b>	
AL 0157	Legume animal feeds
AL 0061	Bean fodder
AL 0072	Pea hay or Pea fodder (dry)
AL 1020	Alfalfa fodder
AL 1021	Alfalfa forage (green)
AL 0697	Peanut fodder
AL 0541	Soya bean fodder
<b>Straw, fodder (dry) and hay of cereal grains and grasses, except grasses for sugar production</b>	
AS 0161	Straw, fodder(dry) and hay of cereal grains and other grass-like plants
AS 0081	Straw and fodder (dry) of cereal grains
AS 0162	Hay or fodder (dry) of grasses
AS 0640	Barley straw and fodder (dry)
AF 0645	Maize forage
AS 0645	Maize fodder
AS 0651	Sorghum straw and fodder, dry
AS 0654	Wheat straw and fodder, dry

**Table 1 (continued)**

Classification Code number	Commodity
<b>Miscellaneous fodder and forage crops</b>	
AM 0165	Miscellaneous fodder and forage crops
AM 0691	Cotton fodder, dry
AM 0353	Pineapple fodder
AM 0659	Sugar cane fodder
AV 0659	Sugar cane forage

The Classification distinguishes forage and fodder in the following way.

**Forage:** Crops grown exclusively for animal feed. These crops are either used for grazing or are prepared as silage or as dry fodder; e.g. maize forage: whole green plant, prior to maturity (including the immature or nearly mature cobs).

**Fodder:** Coarse feed for livestock animals, especially cattle, horses and sheep, such as straw, hay, maize; e.g. maize fodder: whole stalks (with ears removed) remaining after the harvest of the mature and sun-dried cobs.

#### MRLs for feed commodities on dry-weight basis

MRLs for food commodities are set on a "fresh-weight" basis.

In view of the wide range of moisture contents in most animal feeds, except straws, moving in commerce, the MRLs should preferably be set and expressed on a "dry-weight" basis.

A "dry-weight" basis implies that the commodity is analysed for pesticide residues as received, that the moisture content is determined, and the residue content is then calculated as if it were wholly contained in the dry matter.

For feed commodities the residues are expressed on a dry-weight basis if not otherwise stated.

#### MRL Standard

Table 3 of the NH&MRC MRL Standard is entitled "Recommended Maximum Residue Limits for Pesticides in Animal Feeds". The table lists substances which, when used as directed, may result in detectable residues in animal feeds and for which the stated maximum residue limits apply.

The list includes herbicides.

If animals consume feed containing residues within limits specified in Table 3, then residues in animal commodities (meat, milk, eggs) will be within the limits specified in Table 1 of the MRL Standard.

### Codex MRLs

The Codex Committee on Pesticide Residues (CCPR) has a responsibility to establish maximum limits for pesticides on specific food items or groups of food items. Harmonisation of these residue limits across national boundaries should aid international trade.

It is Australian policy to recognise Codex MRL values and every effort is made to achieve harmonisation. Australia actively contributes to the Codex system of pesticide evaluation and estimation of MRL values.

Unfortunately not very many herbicides have been evaluated in the Codex system. This is because many uses of herbicides do not leave detectable residues in crops, so do not pose problems of international trade. The present list of herbicides in the Codex system comprises: amitrole, 2,4-D, diquat, glyphosate, paraquat, 2,4,5-T.

Glyphosate has been recently evaluated in the Codex system and the MRLs reflect residues arising in American and European agriculture. The MRLs for glyphosate in Australia were set a number of years ago and reflect the data supplied to the NH&MRC. It is apparent that different use patterns lead to different residue limit requirements ( Table 2).



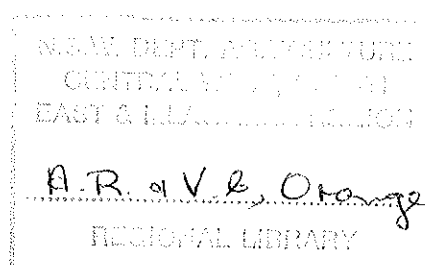
**Table 2** Glyphosate MRLs in feed commodities and animal commodities.

	Commodity	MRL, mg/kg
<b>Australia</b>	edible offal	0.5
	eggs	*0.05
	meat	*0.1
	milk	*0.1
	poultry	*0.1
	stockfood	0.3
<b>Codex</b>	MO 0812 Cattle, Edible offal of	2
	MM 0812 Cattle meat	0.05*
	ML 0812 Cattle Milk	0.05*
	PE 0112 Eggs	0.05*
	MO 0818 Pig, Edible offal of	1
	MM 0818 Pig meat	0.05*
	PM 0110 Poultry meat	0.05*
	AS 0162 Hay or fodder (dry) of grasses	50
	AL 0541 Soya bean fodder	20
	AL 1265 Soya bean forage(green)	5
	AS 0081 Straw and fodder (dry) of cereal grains	100

\* At or about the limit of determination

### Conclusion

The standards for permitted pesticide residues in food and feed commodities must be based on reliable scientific data, logic and professional judgement. Evaluation of herbicide residues is part of this system.

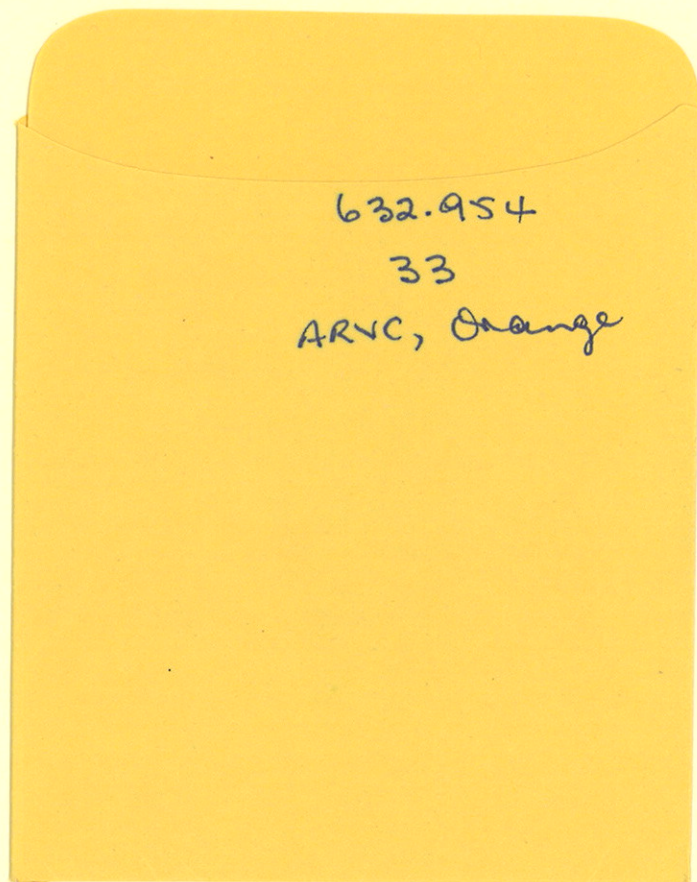


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