# ASPECTS OF THE CHEMICAL AND PHYSICAL CONTROL OF PERSISTENCE WITH SPECIAL REFERENCE TO THE USE OF POLYMERS

Richard M. Wilkins*

May & Baker Ltd., Ongar Research Station, Ongar, Essex.

Summary The persistence of a pesticide in the environment depends on its chemical and physical properties and also upon its immediate environment. By combining the pesticide with a polymer both its intrinsic properties and its molecular environment can be altered. Two general approaches to achieving this are possible: physical entrapment within a polymeric matrix or chemical bonding to a macromolecule.

The preparation of a range of controlled release combinations, of 2,4-D as a pendant substituent, with synthetic and natural polymers was carried out. The polymer backbones included polyvinyl, polysaccharide and polyphenolic types carrying the 2,4-D as an ester or amide side group. The biological persistence of these combinations was studied in soil by means of a lettuce seed germination test to determine factors influencing the release rates of the active ingredient. The most important variable appeared to be hydrophobicity of the macromolecule which increased persistence and depressed the release rate.

## INTRODUCTION

As a result of long years of research into the discovery and use of pesticides, the environmental characteristics required of such biologically active materials are finally becoming identified. An ideal pesticide can be defined as one that persists at the site of action as long as control is needed and thereafter rapidly degrades. Not only would this "ideal" pesticide provide the desired control but no residue would persist to be ultimately disseminated in the environment.

However, in practice, pesticides start to suffer losses immediately after conventional application as a result of degradation, leaching, volatilisation and binding to soil particles. The propensity of a particular pesticide to suffer from any of these losses will depend on its chemical and physical properties and these may not bear any relationship to its activity against the target organism. Often, those pesticides that appear the most effective in the field are the more persistent.

* Present address: Department of Agricultural Biology, University of Newcastle upon Tyne, Newcastle upon Tyne. NE1 7RU

Other factors, such as the need to reduce repeat applications, also tend to give importance to long persistence as opposed to intrinsic pesticidal activity.

On the other hand, long persistence makes a pesticide undesirable due to the possibility of carryover and damage to follow-on crops or of wide-spread ecological effects such as exemplified by the organochlorine insecticides. Such dangers to the environment have been well documented (Allan et al, 1973 b) and an "ideal" pesticide would have minimal movement in, and interaction with, the biosphere.

## The value of the control of persistence

As mentioned previously, pesticides of short persistence, require repeat applications to maintain control and prevent pest damage to, for example, a crop. Extended periods of protection can be achieved by application of dose rates higher than that theoretically necessary to offset this disadvantage of a short-persisting pesticide. In these situations (which, in practice, include most conventionally spray applied treatments) a large concentration of pesticide is available whose only function is to maintain a lethal dose at the target organism. This 'reservoir' of pesticide, as well as the effective concentration at the target organism is subject to environmental losses from the moment of application. If these losses are assumed to be the results of a unimolecular reaction, then the greater the 'reservoir' the faster the rate of loss will be. In fact, the rate of loss will increase logarithmically; doubling the dose rate will increase the duration of persistence by an amount equal to the half-life of the pesticide (Allan et al, 1973 b).

This contrasts with the much lower loss rate that would be involved if the ambient concentration of pesticide is maintained at the minimum necessary for very short-term control. If this minimum concentration is maintained continuously by a controlled release mechanism then the amount of pesticide saved, compared to conventional spray methods, would be considerable and would increase approximately logarithmically for every multiple of the pesticide half-life that control is needed (Allan et al, 1973 b).

In terms of application techniques and to effectively extend the persistence of non-persistent biocides, the preceding discussion implies two requirements of a controlled release formulation. The first requires that the biocide is protected from the environment while, secondly, it is released at a rate appropriate to maintain the minimum lethal dose at the target species. In theoretical terms it is possible to reduce the amount, compared to conventional techniques, of pesticide applied and yet obtain equivalent control for a long predetermined period. It can be said that the efficiency of use of a pesticide is thus increased with corresponding benefits in reduced expense of materials and curtailment of hazards to wildlife (Allan et al, 1971 a).

## Application of the controlled release approach

In the past few years the application of the controlled release method to modify the persistence of pesticides has been the subject of much effort, particularly in the U.S.A. This technique is based upon a formulation that isolates the active agent from the environment and with a single application delivers it to the target organism continuously, usually obviating the need for spraying (Allan et al, 1974). This approach has found applications in drug delivery systems, in anti-fouling paints and in fertilizers and shows good potential for plant protection using systemic insecticides, herbicides, fungicides etc. Transport of the active agent from the controlled release source to the target organism can exploit the air (pheromones and vapour-acting insecticides, e.g. dichlorvos), water (aquatic molluscicides for Bilharzia control) or soil (systemic insecticides).

In general, the mechanisms for protection and release of the pesticide can be categorized as chemical or physical (Allan et al, 1971 a). Physical methods range from dispersing or dissolving the active agent in an inert matrix, to encapsulation and to maintaining it within a bottle (Baker and Lonsdale, 1975). The release rate of the agent into the environment is achieved by physical processes (Baker and Lonsdale, 1974). When dispersed or dissolved in a suitable matrix (usually polymeric) the release of the pesticide is determined by diffusion through the matrix (Neogi and Allan, 1974). Diffusion is also the usual rate controlling step of release in the case of encapsulation, although, depending on the material of the capsule, leaching also occurs. If the wall of the capsule permits selective entry of water the resulting osmotic effect can be used to pump a biologically active material from an impermeable container (e.g. bottle) through a rate restricting orifice. Alternatively, this can be achieved by diffusion or evaporation from a wick (Baker and Lonsdale, 1975).

Because there are fewer restrictions upon the chemical nature of the pesticide in the case of physical controlled release combinations these have been more developed than the chemical combinations and some have reached commercial exploitation. However, this paper will be confined to the chemical approach to modification of pesticide persistence.

## Chemical methods

In contrast to physical methods which actually separate the pesticide from the environment, and can be likened conceptually to a microscopic spray tank, the chemical approach relies upon the formation of derivatives of the pesticide. The pesticide molecule is, in this case, protected from environmental losses such as degradation, leaching and evaporation by forming an integral part of an insoluble macromolecule. The chemical approach is less widely applicable compared to the physical method as it is limited to pesticides possessing functional groups capable of forming bonds to polymer substrates. Release of the bonded pesticide is achieved by degradation of the polymer in the environment.

In the case where the pesticide does not possess a suitable functional group it can be trapped within a polymer matrix and released as the polymer decomposes, or is eroded away. This may appear to be a physical method but if the rate of decomposition exceeds the rate of diffusion then the release will be chemically controlled.

Where the pesticide is directly attached to the polymeric substrate the method of preparation is likely to be the reverse of its decomposition in the environment (Allan et al, 1971 c). Two basic approaches to synthesis are possible (Allan et al, 1973 b). First, the pesticide could be bonded by a suitable labile link to the polymer substrate and form a pendant side-group. Second, the pesticide could be part of the polymeric backbone, which therefore contains the labile bonds. These basic alternatives could then be built into a more complex three dimensional or branched polymer. Such a polymer could undergo breakdown in the environment (e.g. in the soil) until the molecular weight is reduced ultimately to the point of volatility or water solubility.

When the pesticide forms part of the backbone, either alone or copolymerised with other biologically inert or active monomers, it must of necessity possess at least two chemically functional groups. Examples of pesticides that can be condensation polymerised in this way are amiben (3-amino-2,5-dichlorobenzoic acid) and picloram (4-amino-3,5,6-trichloropicolinic acid).

Short-lived systemic pesticides are the most suitable for controlled release plant protection as these possess a means of transport from the polymer (after release) to the target enzyme system, with limited effect outside of the treatment zone.

### Evaluation of chemical combinations

Although no chemically controlled release formulation is yet in regular use a number of such pesticide-polymer combinations have been made and tested and some have demonstrated field potential. The difficulties in synthesis referred to above have limited the choice to simple herbicides and fungicides. Few of these have been evaluated under practical conditions.

A number of pesticides have been incorporated into vinyl monomers and then polymerized. This has recently been reviewed (Feld et al, 1975) and a subsequent report (Harris et al, 1975) disclosed limited evaluation. The synthetic derivatives prepared included poly (vinyl 2,4-dichlorophenoxyacetate), poly (2-acryloyloxyethyl 2,4-dichlorophenoxyacetate), poly (1-methyl-2-acryloyloxyethyl 2,4-dichlorophenoxy acetate), poly (acryloyloxybutyl 2,4-dichlorophenoxyacetate) and a copolymer of 2-acryloyloxyethyl 2,4-dichlorophenoxyacetate and 1,1-dimethyl-2-hydroxypropylamine methacrylamide. However, rates of release of 2,4-D in neutral water at 30°C were very slow with the exception of the last copolymer.

Modification of synthetic polymers has also been used to prepare herbicide-polymer combinations. 2,4-D and MCPA have been covalently bonded to poly (vinyl alcohol) (PVA) and also to a divinylbenzene-styrene copolymer (Jakubke and Busch, 1973). Some of the resulting combinations have shown activity in a limited test (Neogi and Allan, 1974).

Similarly, esters of a range of starch and modified starches and 2,4-D were evaluated in aqueous buffer solutions at pH6 and 8 and ambient temperatures (Mehltretter et al, 1974). Fairly rapid release rates were found under these conditions.

The largest amount of research has been carried out on modification of natural wood waste polymers (Allan et al, 1971 c). Bioassays carried out on a combination of 2,4-DB with Douglas fir bark indicated good long-term selectivity between conifers and deciduous brush (Allan et al, 1972). This was followed with results of field trials that showed that the combination (containing 47% 2,4-DB) released sufficient herbicide during two growing seasons to suppress deciduous brush (Allan et al, 1973 a) and give treated Douglas fir seedlings a permanent advantage compared to the untreated in reforestation (Allan et al, 1975).

The purpose of the work described in this report is to explore the characteristics required of a pesticide-polymer combination under soil conditions and define some general principles in its design. This study has been carried out with a simple herbicide, 2,4-D, chosen because of its functional group (carboxylic acid) and as it contains no labile bonds in its structure. Thus, a series of polymeric derivatives of 2,4-D were synthesized and their release rates determined in soil by a seed germination bioassay.

## MATERIALS AND METHODS

### (a) Synthesis of the herbicide-polymer combinations

#### Materials and analytical methods

Acrylic acid, as supplied by Rohm and Haas, contained 200 p.p.m. hydroquinone monomethyl ether inhibitor. Vinyl 2,4-dichlorophenoxyacetate monomer was distilled twice under vacuum before polymerization. The petroleum ether used was the fraction boiling 30-60°. Other starting materials and solvents were standard reagent grade unless otherwise specified. Melting points were uncorrected.

Elemental analyses were carried out by the Industrial Research Institute, Osaka, Japan. Viscosities were measured with an Ostwald capillary viscometer, maintained at 25.00 ± 0.05° and plotted to zero concentration to obtain the intrinsic viscosity. The synthetic polymer derivatives were purified by dissolution and precipitation with specific solvents and non-solvents.

To determine purity of the monomers thin layer chromatography (tlc) (precoated silica gel plates, supplied by E. Merck A.G.) was used and generally eluted with ethyl acetate or methanol-benzene mixtures. Saponification of the polymers was carried out by refluxing a known weight of the dried polymer in alcoholic potassium hydroxide for 4-6 hr. Titration of the reaction mixture with standard hydrochloric acid using phenolphthalein indicator gave an estimate of the amount of base consumed in hydrolyzing the polymeric ester and thus of its saponification equivalent.

The nitrogen contents were established by means of the standard Kjeldahl method. The chlorine contents were found by neutron activation in a nuclear reactor. Samples were irradicated for 2 min in a neutron flux of about $1.8 \times 10^{12}$ neutrons/cm$^2$ sec, cooled and counted by integrating the 1.60 MeV photopeak of $^{38}Cl$ using a 3" x 3" NaI (Tl) crystal and multichannel analyzer. The half-life of $^{38}Cl$ (37.3 min) allowed one standard ($NH_4Cl$ solution) to be irradiated with three unknowns and the count of each corrected to that for a constant time by allowance of the amount of decay. The chlorine content was then calculated by simple proportion to the standard.

## A - Homopolymer of vinyl 2,4-dichlorophenoxyacetate

### (i) Vinyl 2,4-dichlorophenoxyacetate

2,4-dichlorophenoxyacetic acid (66g, 0.3 mol), mercuric acetate (1.2g, 0.0037 mol) and vinyl acetate (300g, 3.5 mol) were stirred and heated. Fuming sulphuric acid (containing 20% $SO_3$, 0.24g, 0.002 mol) was added dropwise. The resulting light brown solution was refluxed for 4 hr, cooled, filtered and sodium acetate (1.0g) added to the filtrate. This was concentrated at reduced pressure, taken up in ether, shaken twice with 10% sodium carbonate solution (300 ml), then water, dried with anhydrous magnesium sulphate, filtered and the filtrate concentrated at reduced pressure. Vacuum distillation of the residue yielded ethylidene diacetate at 80-85°/2mm (2.0g) and the vinyl ester monomer (31.5g) at 142-150°/2mm. Crystallization from petroleum ether gave colourless crystals (25g, 0.1 mol, 33% of theoretical yield), melting at 40-41°. (Found: C, 48.82; H, 3.28. Calc. for $C_{10}H_8O_3Cl_2$: C,48.57; H, 3.26%).

### (ii) Polymerisation of vinyl 2,4-dichlorophenoxyacetate

A surfactant mixture of sodium alkylaryl polyether sulphonate (Rohm and Haas' Triton X-200, 1.8g) and sodium alkylaryl polyether sulphate (Rohm and Haas' Triton X301, 2.8g) a total of 1.16g solids, was added to distilled water (80 ml). When dissolved vinyl 2,4-dichlorophenoxyacetate (29.2g), potassium persulphate (0.2g) and 0.7 ml of a fresh solution of ferrous sulphate heptahydrate (0.3g) in distilled water (200 ml), were added and the mixture was stirred at 50° to form an emulsion. Nitrogen was passed into the liquid for 15 min, then sodium metabisulphite (0.2g) was added. The mixture was stirred at 65° under an atmosphere of nitrogen for 1 hr, cooled and poured into an ice-cold solution of sodium chloride in a Waring Blendor. The precipitate was filtered off, resuspended in the Blendor with fresh water and well washed. This was repeated several times with water, air-dried and then repeated twice with ether, filtered and air-dried to yield a white granular solid (26.5g). The softening point was 90-100°. (Found: Cl, 30.12%. $(C_{10}H_8O_3Cl_2)_n$ required: Cl, 30.0%). The ether washings gave unpolymerized vinyl 2,4-dichlorophenoxyacetate (3g). The conversion to polymer was 90%.

### B - Copolymer of vinyl 2,4-dichlorophenoxyacetate and acrylic acid

Vinyl 2,4-dichlorophenoxyacetate (10.0g), Triton X-200 (0.6g), Triton X-301 (0.8g) and distilled water (40 ml, dissolved gasses removed by prior boiling) were stirred at 50° under an atmosphere of nitrogen to form an emulsion. Acrylic acid (2.0g), potassium persulphate (0.8g), ferrous sulphate solution (0.3 ml of a fresh 0.15% solution of $FeSO_4.7H_2O$ in distilled water) and sodium metabisulphite (0.08g) were added. The emulsion was stirred at 65° for 2 hr, and then poured into a salt/ice/water mixture stirred in a Waring Blendor to precipitate the white sticky polymer. The salt solution was decanted and the polymer washed with fresh water and in the same way with methanol. The residue was air- and vacuum-dried at room temperature to yield a dry white powder (3.4g). Analysis for chlorine gave 20.2%, corresponding to a molar ratio of acrylic acid: vinyl 2,4-dichlorophenoxyacetate of 3:2 and 63% available 2,4-D.

The methanol washings, after drying with anhydrous magnesium sulphate gave a white solid on evaporation. Extraction of this with boiling ether (three times with 50 ml) yielded vinyl 2,4-dichlorophenoxyacetate (5.9g). The residue (3.0g) was almost entirely homopolymer of vinyl 2,4-dichlorophenoxyacetate. The conversion, based on the proportion of vinyl 2,4-dichlorophenoxyacetate consumed was 34%.

## THE COMBINATION OF 2,4-D WITH NATURAL POLYMERS

### C - The combination of 2,4-D with Douglas Fir bark

Douglas Fir bark (obtained from Weyerhaeuser, Longview, Wa USA) was dried at 105° for several days, powdered and passed through a No.20 sieve. The bark (48.0g) was suspended in sodium-dried benzene (500 ml) and a fraction of the benzene (100 ml) distilled off. To the cooled suspension were added pyridine (5 ml), and 2,4-dichlorophenoxyacetyl chloride (20g, 0.083 mol) over 10 min. The mixture was refluxed for 1 hr and stirred at room temperature overnight. The bark was filtered off and washed several times with benzene and methanol, and air- and vacuum-dried to yield the combination (50g), similar in appearance to the starting material apart from a slightly darker colour. Analysis for chlorine found 4.07% compared to 0.11% for the starting material, which gave a 2,4-D content of 12.3% by weight.

### D - The combination of 2,4-D with alpha-cellulose

Alpha-cellulose sheet was broken down in a Waring Blendor and dried at 105° for several days. The cellulose (15g, 0.15 mol based on glucose) was suspended in sodium-dried benzene. Pyridine (KOH-dried, 2 ml) was added followed by 2,4-dichlorophenoxyacetyl chloride (6g, 0.025 mol) dropwise. The suspension was agitated at room temperature overnight, filtered off, well washed with benzene, methanol and water and vacuum-dried. Analysis for chlorine found 2.36% which corresponded to a 2,4-D content of 7.32% by weight.

## THE COMBINATION OF 2,4-D WITH SYNTHETIC POLYMERS

### E - Esterification of poly(vinyl alcohol) with 2,4-dichlorophenoxyacetyl chloride

Poly(vinyl alcohol) (44g, DuPont's Elvanol 52-22 medium molecular weight) was dissolved in distilled water (100 ml). Sodium hydroxide (16g, 0.4 mol) in water (100 ml) was added, followed by butanone (100 ml) and the clear solution stirred at -5°. A cooled solution of 2,4-dichlorophenoxyacetyl chloride (29g, 0.12 mol) in butanone (116 ml) and toluene (25 ml) was added dropwise and the mixture stirred for 1.5 hr at -5°. The emulsion formed was broken down after standing for 24 hr and the esterified poly(vinyl alcohol) was filtered off, washed with water and dried as a clean white powder (22g). Analysis for chlorine found 14.88% which corresponded to 46.3% of 2,4-D by weight.

F - Acylation of poly (ethylenimine) with 2,4-dichlorophenoxyacetic acid

Low molecular weight poly(ethylenimine) (10g, 0.23 mol, Montrek 18, Dow Chem. Co.) was boiled with benzene (250 ml) to dry the polymer by azeotropic distillation of the water. 2,4-dichlorophenoxyacetic acid (39g, 0.18 mol) in the minimum volume of hot methanol was added. The mixture was refluxed for 4 hr with a fraction of the condensate continually removed and with the addition of fresh benzene. The mixture was cooled and the benzene decanted from the polymer which was washed with additional benzene and dried under vacuum to yield a light yellow solid (46g), with a softening point about 20° and a nitrogen content of 6.96%. Hydrolysis with potassium hydroxide indicated 87% of 2,4-D by weight.

G - Acylation of poly(ethylenimine) with methyl 2,4-dichlorophenoxyacetate

Medium molecular weight poly(ethylenimine) (30g, Montrek 600, Dow Chem.Co., 33% aqueous solution) was dried by distillation with benzene until the azeotrope of water and benzene ceased to distil. The benzene was decanted and the residue dissolved in methanol (150 ml). Methyl 2,4-dichlorophenoxyacetate (38g) was added to the methanol solution which was refluxed for 3 hr, stood overnight at room temperature and reduce to a small volume. The residual viscous solution was poured into a stirred, ice-cold solution of sodium chloride to precipitate the amide of poly (ethylenimine) as a white powder. This was washed with water, boiled with benzene to azeotrope off the water, the benzene decanted and the residue dried under vacuum to yield the polymer as an off-white solid (20g). The benzene solution contained unreacted methyl 2,4-dichlorophenoxyacetate (24g). Analysis of the polymer for nitrogen found 7.70%. Hydrolysis with alcoholic potassium hydroxide indicated a 2,4-D content of 85%.

H - The above procedure was followed, using lower ratios of the methyl ester to the poly(ethylenimine), except that the amide was precipitated from the methanol solution by addition of benzene and hexane. This gave resins with a softening point of about 20° and with nitrogen contents of 8.72, 11.14 and 12.52%. 2,4-D contents as determined by hydrolysis with potassium hydroxide, varied correspondingly and the combination containing 68% by weight was selected for evaluation of release rates.

(b) Evaluation of release rates of the herbicide-polymer combinations

Bioassay in the soil environment

The herbicide-polymer combinations were used without further purification than that described in the synthetic section. 2,4-D was technical grade, recrystallized 2-3 times from benzene (m.p. 140-1°).

A friable sandy-loam with a high organic content (pH 5.8) was used for the study of release rates. Non-sterile sieved dry soil (200g) was placed in plastic pots (with a drainage hole) and the powdered polymer combinations were either evenly sprinkled upon the soil surface and then covered with a little more soil or, for the higher amounts, were stirred into the surface layer. A range of dose rates from 5 to 1000 mg per pot of the polymers were applied. Soil surface area was 150 $cm^2$. The treatments were maintained either (i) as near as possible to 60% of soil water capacity by frequent watering or (ii) were left exposed to natural precipitation and not watered. No pot replicates were used.

At the start of each experiment and at weekly intervals approximately 20 seeds of lettuce (Lactuca sativa L.) were placed in each pot. The following week germination of the seeds in the treated pots was determined and compared to the germination count in the untreated pots. In general, it was noted that the germination count of treated pots was either 0% compared to the controls or 100%.

This indicated that the range of sensitivity of the lettuce germination bioassay was narrow compared with the range of dose rates of extant 2,4-D. Thus, the time when the germination rate for each treated pot rose to this upper level was considered as the termination of effective release.

The release rates were studied over a period of three months during March to May 1969 in a sheltered position in the open in Seattle, Washington, U.S.A. (Wilkins, 1969). Natural rainfall during this period totalled 400mm. Free drainage of the pots prevented souring of the soil but leaching occurred in the pots exposed to rain.

## Standardization of the lettuce seed germination bioassay

The sensitivity of germination of lettuce seeds to free 2,4-D acid was determined over a range of concentrations. Lettuce seeds were exposed to solutions of different concentrations of 2,4-D on a layer of filter-paper in a covered Petri dish in the dark and at a constant temperature of 20°. After 4 days (to allow for any retardation of germination as a result of 2,4-D) a germination count was made and the resulting dose-response relationship is expressed in Fig.1. From this graph it can be seen that high percentages of germination were observed when the concentration of released (or residual) 2,4-D dropped to about 1 ppm.

Table 1

Properties of the herbicide-polymer combinations evaluated

| Designation | Method of preparation | Linkage | Saponification equivalent (g. of polymer) | Maximum[1] releasable 2,4-D % w/w | Approx. Half-life in soil (days) | Persistence of 10 mg/pot 2,4-D (days) |
|---|---|---|---|---|---|---|
| A | Homopolymerization of 2,4-D vinyl ester | -COO- | 246[2] | 89 | - | - |
| B | Copolymerization of 2,4-D vinyl ester and acrylic acid | -COO- | - | 63[3] | 10 | 32 |
| C | Esterfied bark[4] | -COO- | - | 12 | 24 | 83 |
| D | Esterfied cellulose[4] | -COO- | - | 7 | 13 | 50 |
| E | Esterfied PVA[4,5] | -COO- | 1956 | 45 | 19 | 64 |
| F | Acylation[6] of low molecular weight PEI[7] | -CONH- | - | 87 | 18 | 60 |
| G | Acylation[8] of medium molecular weight PEI | -CONH- | - | 85 | 15 | 50 |
| H | Acylation[8] of medium molecular weight PEI | -CONH- | - | 68 | 7 | 25 |
| J | 2,4-D acid | - | - | 100 | 11 | 47 |
| L | 2,4-D acid exposed to rainfall | - | - | 100 | 7 | 22 |

1/ determined by hydrolysis with alcoholic potassium hydroxide. This is slightly less than that calculated from Cl or N elemental analysis, due to side reactions during synthesis.

2/ Intrinsic viscosity: 0.21

3/ equivalent to a molar ratio of 3 carboxylic acid to 2 2,4-D ester pendant groups.

4/ Using 2,4-D acid chloride.

5/ PVA : polyvinyl alcohol.

6/ Using 2,4-D acid.

7/ PEI : polyethylenimine

8/ Using 2,4-D methyl ester.

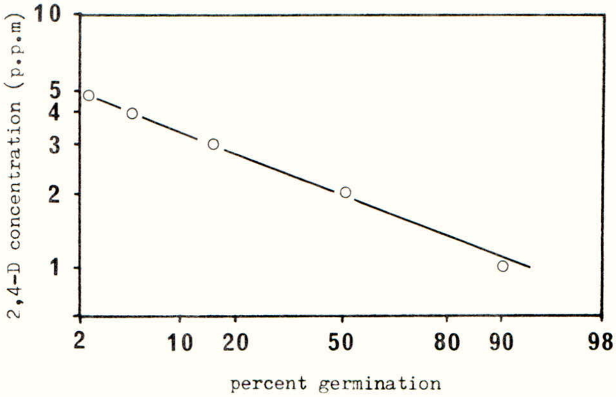

Fig. 1 The effect of 2,4-D on germination of lettuce seed.

## RESULTS

The herbicide-polymer combinations evaluated are given in Table 1. In this selection of ester and amide derivatives of 2,4-D the following characteristics are varied: degrees of substitution, molecular weight, nature of substrate or backbone and of pendant groups adjacent to the herbicide moiety. To correlate the bioassay results with those of the extensive trials carried out on herbicide-bark combinations (Allan et al, 1973 a) a 2,4-D ester of bark has been included.

The results of the outdoor pot evaluation of this range of 2,4-D combinations are shown in Fig.2. This represents the period over which each dose rate inhibited the germination of lettuce seeds placed weekly in the soil. Results from the dose-response studies (Fig.1) indicate that this period of inhibition of germination terminated when the concentration of released 2,4-D dropped below about 1 p.p.m. As the initial polymers were well washed after preparation to remove any free 2,4-D and as these insoluble polymeric derivatives would not be expected to possess any biological activity, then inhibition of seed germination under the conditions of the experiment implies release of the 2,4-D or of water-soluble derivatives.

The pot treatments were all established with similar dose rates of approximately 5, 10, 25, 50, 100, 500 and 1000mg per pot of herbicide-polymer combinations. As the different combinations contained various proportions of 2,4-D, the dose rates in terms of the active ingredient become as expressed in Fig.2 (e.g. 25mg/pot of the 2,4-D bark combination 'C' (12%) is equivalent to 3mg/pot available 2,4-D).

All of the polymers showed biological activity with the exception of the homopolymer of vinyl 2,4-dichlorophenoxyacetate. In general, at similar dose rates of the active ingredient, the combined form of 2,4-D persisted, as long or longer, than the free acid in soil.

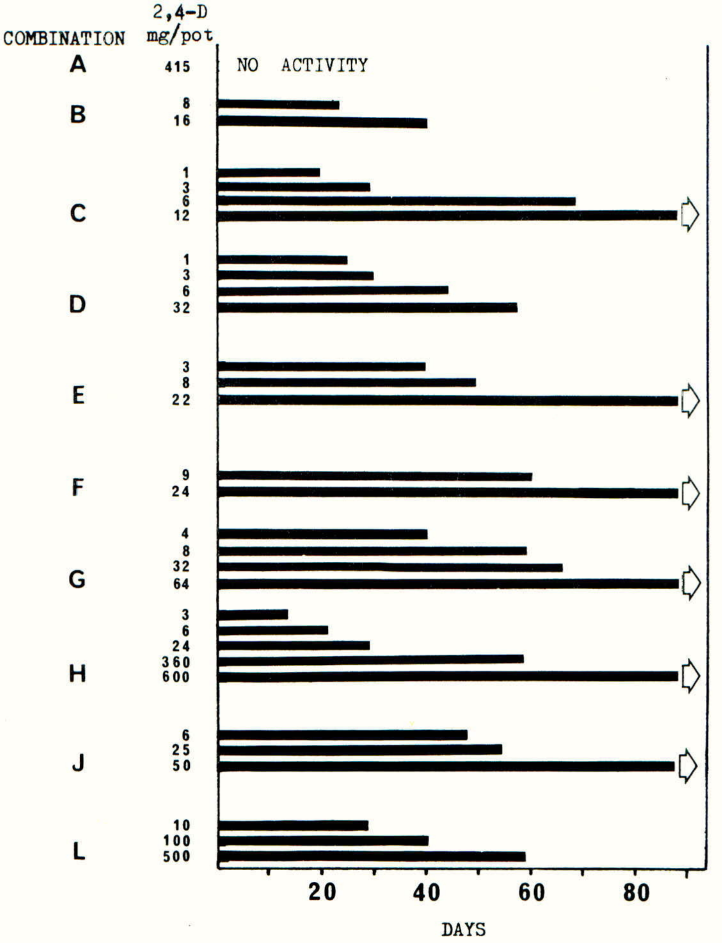

Fig. 2 The duration of activity of the herbicide-polymer combinations.

⇨ activity still apparent at termination of experiment

**L** application of uncombined 2,4-D acid to soil exposed to rainfall

# DISCUSSION

## Design of polymers containing herbicides as pendant substituents

The process of controlled release is illustrated in Fig.3 for a combination containing a pesticide as a side-group. In this figure the active ingredient is represented as P-P, to emphasize the most labile bond within the pesticide molecule itself. If the combination resulting from the pesticide; P-P, and the polymer chain; -M-M-M-M- is considered, then it is possible to have many modes of degradation in the soil environment. These degradative pathways are summarized by Reactions 5 and 6 in Fig.3. For successful release, Reaction 5 should proceed at a faster rate than Reaction 6, under environmental conditions. This indicates that the bond linking the pesticide to the macromolecule should be more labile than the weakest part of the structure of the pesticide itself. This leads to a very real problem, especially with most systemic insecticides as these depend on a weak bond for their activity. There are no reports of chemically bonded insecticides to date. However, it may be possible to overcome this by means of alternative hydrolysis mechanisms (Neogi and Allan, 1974). In this respect there is a case for pesticides selected specifically for use as controlled release agents and to exploit modes of biological action not available to conventionally applied materials, e.g. chronicity (Janes, 1974).

For the above reasons and because of the ease of forming linkages with a wide range of polymers, 2,4-D was chosen as the pesticide in this present study.

## Preparation of the herbicide-polymer combinations

The possible routes to polymers containing a pesticide as a pendant substituent are illustrated in Fig.3. Of the two basic approaches, the first (Reaction 2), reacting a pesticide with a preformed polymer (synthetic or natural) has the advantages of the availability of a range of such substrates with varying molecular weights and the choice of degrees of substitution obtainable by varying the reaction conditions. The second approach utilizes the reaction of the pesticide with a suitable monomer (Reaction 3) to form a derivative which can undergo condensation or addition polymerization (with or without other monomers) to yield the pesticide-polymer combination (via Reaction 4). Unless reaction conditions are mild, there is the possibility of breakdown of the pesticide as represented by Reaction 9 in Fig.3. Both approaches can be modified by the use of bridging moieties between the pesticide and polymer to give an increased range of linkages and of distances between the pesticide and polymer (Feld et al, 1975).

In this present study the first synthetic approach was used to prepare polymeric derivatives of 2,4-D with poly(vinyl alcohol) (PVA), polyethylenimine (PEI) cellulose and bark. The methods used were based on that of Tsuda (1964) for poly (vinyl alcohol) and of Hollyday (1958) for polyethylenimine.

The second approach was employed to synthesize homopolymers of vinyl 2,4-dichlorophenoxyacetate. The vinyl monomer was prepared by transvinylation from vinyl acetate (Hopff and Osman, 1968) and emulsion polymerized (Rohm and Haas Bulletin, 1967) to give the homopolymer. This had previously been synthesized by Dovlatyan and Kostanyan (1965) but their method of bulk polymerization had yielded very low molecular weights. A copolymer of vinyl 2,4-dichlorophenoxyacetate with acrylic acid was also prepared by emulsion polymerization. The inclusion of this combination was prompted from the observations of Morawetz and Gaetjens (1958), who noted that a copolymer of acrylic acid and p-nitrophenyl acrylate hydrolyzed much faster than the homopolymer of the latter. It was considered that the adjacent pendant carboxylic acid group would catalyze hydrolysis of the ester and increase the rate of release of the 2,4-D.

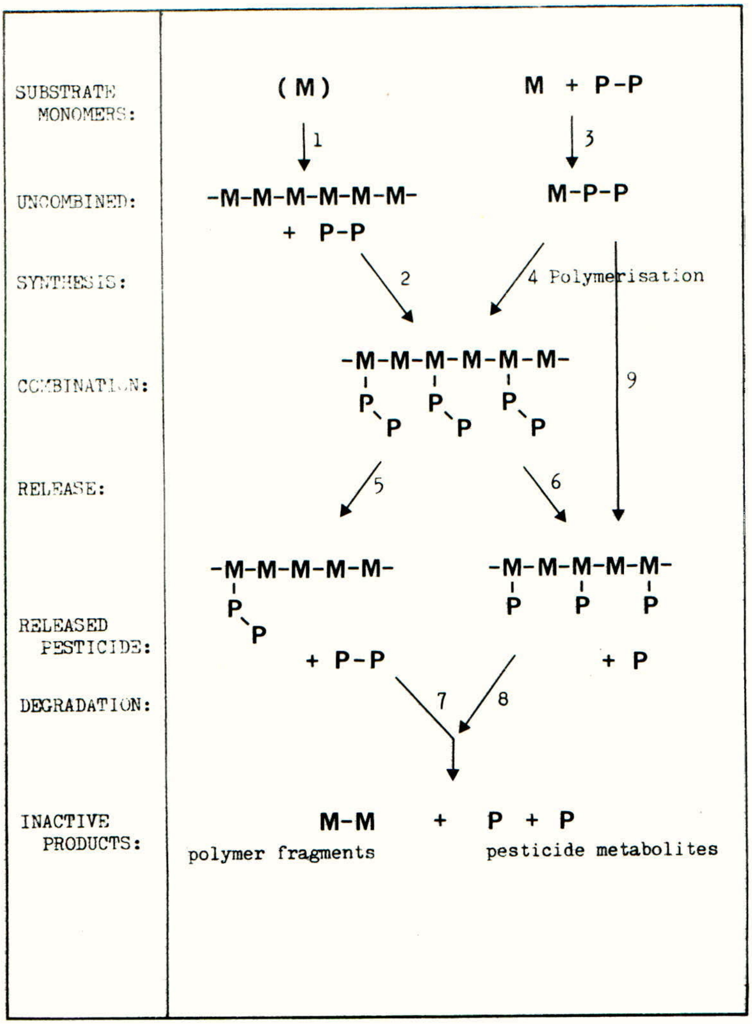

Fig. 3 Synthetic and degradative routes for a controlled release combination containing a pesticide (P - P) as a side-group.

The range of polymer derivatives as listed in Table 1 were designed to determine the effect of these structural variables, as well as secondary characteristics such as physical state and hydrophobicity, on the rate of release of the herbicide.

## Rates of Release

The previous approach to evaluation of herbicides chemically bonded to macromolecules has been predominantly to immerse the combination in non-sterile water and to measure the aqueous concentration of the herbicide at various intervals (Mehltretter et al, 1974). In the case of studies on aquatic herbicides (Harris et al, 1975) this method has a limited validity for providing expected information under natural conditions, such as exist in ditches, lakes etc. But the utilization of soil in pots placed outside with a bioassay carried out in the same soil, as described here, was considered to be more representative of field conditions and indicative of the period of control to be expected.

The theoretical determination of the release rates from side-chain degradation of pesticide-polymer combinations has been described (Baker and Lonsdale, 1975; Neogi and Allan, 1974). If diffusion and surface barrier effects are ignored then the persistence will depend on the logarithm of the initial concentration of the pesticide. This relationship has been confirmed for 2,4-D combined with bark and lignin, both water insoluble polymers (Neogi and Allan, 1974). Thus, in order to compare the herbicidal effectiveness of the different polymer combinations prepared here, the half-life of each was determined from a plot of the persistence (from the bioassay) against the logarithm of the 2,4-D content per pot at each polymer dose rate. This provided an approximately linear plot for polymers derived from water-soluble and insoluble substrates. The relationship for some of the combinations studied is given in Fig.4. The approximate relative persistences were thus determined and are provided in Table 1 for all the materials tested (in terms of both half-life and persistence of a fixed amount of 2,4-D).

No activity was observed in the case of the homopolymer of vinyl 2,4-dichlorophenoxyacetate ('A'). This confirms the results of Dovlatyan and Kostanyan (1965) who applied this polymer derivative in the form of a foliar spray and found no herbicidal effect. The most likely explanation of the lack of activity of this polymer lies in the high proportion (89% by weight) of 2,4-D giving a hydrophobic character and thus resistance to microbial attack and degradation. By reducing the concentration of 2,4-D in the macromolecule, i.e. by replacing the ester with hydroxyl groups, as in 'C', activity was shown and was somewhat longer in duration than 2,4-D alone.

When carboxylic acid groups are carried on the polymer backbone as well as the 2,4-D ester, as in 'B', the half-life was reduced to about the same as for the uncombined 2,4-D. This result could be explained on the basis that the carboxylic acid groups increase the hydrophilicity of the macromolecule (more so than in the case of hydroxyl) and help to solubilize it, especially in later stages of degradation when the chain length may be reduced by fission. In addition, there may be hydrolysis of the ester linkage, catalysed by the adjacent carboxylic acid groups, which continues without the presence of hydrolytic enzyme systems (Jakubke and Busch, 1973).

The uncombined 2,4-D as used for reference in the bioassays was in the form of the powdered acid. The parent acid was used in place of an ester or salt formulation, as it was considered that the released 2,4-D would be the free acid, and therefore it was preferable for comparison with the combinations. However, the powdered acid may have functioned, to a small extent, as a controlled release formulation due to the limited solubility of 2,4-D in water (620 p.p.m.).

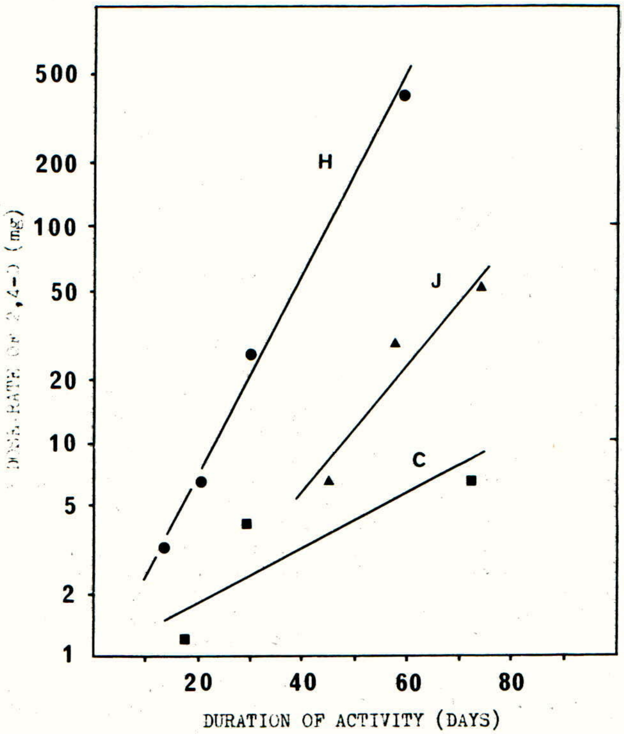

Fig. 4 Relationship between the duration of herbicidal activity and the initial dose rate in terms of the 2,4-D component for some of the herbicide-polymer combinations. ▲ 2,4-D alone (J) ■ combined with bark (C) and ● combined with PEI (H)

The release rates of the amide derivatives ('F', 'G' and 'H') show a wide range with no correlation with molecular weight. It would appear that, with this limited evidence, the degree of substitution by 2,4-D is more important, giving greater release rates at lower values. This effect has been noted elsewhere (Neogi and Allan, 1974). It is thus likely that accessibility of hydrolytic enzymes to the linking bond is more important than the energy of bonding (Allan et al, 1973 b) in overall release rates. In comparing the amide bonded herbicides with the corresponding ester bonded formulation ('E') it would appear that the former release the 2,4-D at a higher rate or, in other words, give better release rates at comparatively greater degrees of substitution.

Combinations based on natural polymers gave a wide range of release rates. Cellulose esterified to a small 2,4-D loading (7% by weight, which is equivalent to one 2,4-D molecule to every 7-8 glucose residues) showed herbicidal activity but no greater persistence than 2,4-D alone. This could be the result of fragmentation and liberation of soluble 2,4-D derivatives. High rates of release were also found for combinations of 2,4-D with starches (Mehltretter et al, 1974) under mild conditions in the laboratory. These latter materials in soil would also, probably, give short persistence.

These polysaccharide derivatives can be contrasted with the bark combination ('C') which with a low percentage of 2,4-D (12%) gave a considerable increase in persistence. This material demonstrated appreciable release rates in the laboratory only when exposed to water at higher temperatures. The method used, that of continuous extraction of the combination in a Soxhlet apparatus, provides a convenient rapid assessment of the potential of a formulation for effective controlled release in the environment (Chopra, 1972). Lignin, a polyphenolic macromolecule, being in effect less hydrophilic than bark, offers herbicide combinations with even longer persistences and makes an excellent substrate for controlled release (Neogi & Allan, 1974).

## Acknowledgments

The author gratefully acknowledges the guidance of Prof.G. Graham Allan, College of Forest Resources, University of Washington, Seattle, Washington, U.S.A. during the experimental work. Appreciation is also given to Mr. R.J.Cole and Dr. D.L.Colinese of May & Baker Ltd for reviewing the manuscript.

## References

ALLAN, G.G., CHOPRA, C.S., NEOGI, A.N. and WILKINS, R.M. (1971 a) Design and synthesis of controlled release pesticide-polymer combinations, Nature, 234, 349-351

ALLAN, G.G., CHOPRA, C.S., NEOGI, A.N. and WILKINS, R.M. (1971 b) Concept of chemical combination of pesticides with solid waste macromolecules, International Pest Control, 13, 10-15

ALLAN, G.G., CHOPRA, C.S., NEOGI, A.N. and WILKINS, R.M. (1971 c) The synthesis of herbicide-forest solid waste combinations, Tappi, 54, 1293-1294

ALLAN, G.G., CHOPRA, C.S. and RUSSELL, R.M. (1972) Selective suppression of weeds and deciduous brush in the presence of conifers, International Pest Control, 14, 15-20

ALLAN, G.G., CHOPRA, C.S., MAGGI, M.W., NEOGI, A.N. and WILKINS, R.M. (1973 a) Growth enhancement of a juvenile conifer forest by a controlled release herbicide, International Pest Control, 15, 8-13

ALLAN, G.G., CHOPRA, C.S., FRIEDHOFF, J.F., GARA, R.I., MAGGI, M.W., NEOGI, A.N., ROBERTS, S.C. and WILKINS, R.M. (1973 b) Pesticides, pollution and polymers, Chem. Tech. 4, 171-178

ALLAN, G.G., GARA, R.I. and WILKINS, R.M. (1974) Field testing of insecticide-polymer combinations for the long-term control of the mahogany shootborer. International Pest Control, 16, 4-12

ALLAN, G.G., FRIEDHOFF, J.F. and POWELL, J.C. (1975) Growth enhancement of a juvenile conifer forest four years after application of a controlled release herbicide. International Pest Control, 17, 4-9

BAKER, R.W. and LONSDALE, H.K. (1975) Fundamentals of controlled release. Proceedings 1975 International Controlled Release Pesticide Symposium (Dayton, Ohio, U.S.A.) 9-39

CHOPRA, C.S.,(1972) Private communication

DOVLATYAN, V.V. and KOSTANYAN, D.A. (1965) Polyvinyl esters of aryloxyacetic acids. Izv. Akad. Nauk. Arm. SSR. Khim. Nauk., 18(3), 325-327 (Russ.).

FELD, W.A., POST, L.K. and HARRIS, F.W. (1975) Polymers containing pesticides as pendent substituents, Proceedings 1975 International Controlled Release Pesticide Symposium (Dayton, Ohio, U.S.A.) 113-122

HARRIS, F.W., FELD, W.A. and BOWEN, B.K. (1975) Polymers containing pendent herbicide substituents, Proceedings 1975 International Controlled Release Pesticide Symposium. (Dayton, Ohio, U.S.A.), 334-348

HOLLYDAY, W.C. (1958) Pour-point depressants for lubricants. U.S. Patent 2,852,467, Sept 16 1958.

HOPFF, H and OSMAN, M.A. (1968) The vinyl exchange reaction II. Vinyl acetate with carboxylic acids weaker than acetic acid. Tetrahedron, 24(10), 3887-3890.

JAKUBKE, H.D. and BUSCH, E. (1973), Synthesis of low molecular weight active substances covalently bonded to polymeric supports and investigations of enzymatic reactivation. Z. Chem, 13(3), 105-106 (German)

JANES, G.A. (1974) Chronicity phenomenon, Proceedings Controlled Release Pesticide Symposium, September 16-18, 1974, University of Akron, Akron, Ohio, U.S.A. N.Cardarelli (Ed).

MEHLTRETTER, C.L., ROTH, W.B., WEAKLEY, F.B., McGUIRE, T.A. and RUSSELL, C.R. (1974) Potential controlled - release herbicides from 2,4-D esters of starches. Weed Science, 22, 415-418.

MORAWETZ, H. and GAETJENS, E. (1958) A kinetic approach to the characterization of the microtacticity of a polymer chain. Journal of Polymer Science, 32, 526-528

NEOGI, A.N. and ALLAN, G.G. (1974) Controlled release pesticides : concepts and realization, in Controlled Release of Biologically active Agents. A.G.Tanquary and R.E.Lacey (Eds.), Plenum Press, New York.

ROHM and HAAS CO. (1967) Emulsion polymerization of acrylic monomers, Bulletin SP-154, Special Products Dept., Philadelphia, U.S.A.

TSUDA, M. (1964). Schotten-Baumann esterification of poly(vinyl alcohol). Makromol. Chem. 72, 174-182.

WILKINS, R.M. (1969) Design of polymers for the sustained release of selected herbicides, M.S. Thesis, University of Washington, Seattle, Washington, U.S.A.