

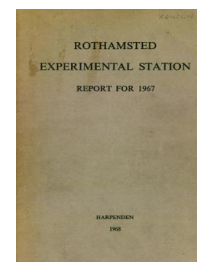
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D. C. Griffiths (1968) *Substitutes for Organochlorine Insecticides to Control Soil Insects That Attack Cereals* ; Rothamsted Report For 1967, pp 332 - 349 - DOI:

<https://doi.org/10.23637/ERADOC-1-120>

SUBSTITUTES FOR ORGANOCHLORINE INSECTICIDES TO CONTROL SOIL INSECTS THAT ATTACK CEREALS

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The important cereal pests, wireworms, wheat-bulb fly, leatherjackets and frit fly, can be controlled by organochlorine insecticides, but these insecticides have some disadvantages in practice. For example, the chlorinated cyclodienes aldrin and dieldrin are toxic to birds [123] and, in the United Kingdom, were voluntarily withdrawn from use as seed-dressings on spring-sown cereals in December 1961. Organochlorine insecticides are stable compounds, and when applied to soil they persist for many years [124]. Their residues can harm some beneficial insects in amounts too small to affect pests [125], but some pests that have been exposed to organochlorine insecticides for long periods have developed resistance. Resistance to organochlorine insecticides has not yet occurred in soil pests of cereals in the United Kingdom (U.K.), but has occurred in species of wireworms that attack potatoes and sugar beet in the United States of America (U.S.A.) [15, 126, 127, 128]. The increasing use of organochlorines led to small amounts of them occurring in the body fat of people not occupationally exposed to organochlorines, and in some birds and their eggs. Such effects were reviewed in 1964 by the Advisory Committee on Poisonous Substances Used in Agriculture and Food Storage. Their report [129] placed no restriction on the use of BHC, but recommended that uses of DDT should be reviewed after 3 years and that immediate restrictions be placed on the more toxic compounds, aldrin and dieldrin. There has been much work to find replacements among compounds that are more easily metabolised in the soil, in plants and animals, and without unwanted long-term effects. The results of the search, mainly among organophosphorus and carbamate insecticides, are summarised and discussed here.

The same materials have been tested under different names or numbers by various authors, but in this article references to the same compound are put together under the name adopted by the British Standards Institution (Recommended Common Names for Pesticides [130] and supplements), or by the Entomological Society of America [131]. Where no name exists, the manufacturer's code number is given. To aid identification, recently adopted names are listed also by the previously used name or code number. The lists of synonyms given by Warry [132] and Kenaga [133] are useful for reference.

Wireworms (Elateridae)

Wireworms are larvae of certain Elaterid beetles, mainly *Agriotes* spp. in the U.K. They inhabit old grassland and damage susceptible crops, for example, cereals and root crops, in the first few seasons after ploughing the old grass. Seed-dressings of γ -BHC are used extensively in the U.K. to

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protect cereals from attack, but there is little evidence that such dressings applied at the recommended rates to autumn-sown cereals kill many wireworms or protect subsequent crops from attack [134, 135]. The use of aldrinated fertiliser was discontinued as a result of the 1964 M.A.F.F. Report [129], which recommended also that aldrin and dieldrin soil treatments against wireworms should be used only on potato crops for the next 3 years, when this use should be reviewed again.

Most tests in the laboratory have been made with *Agriotes* spp. in the U.K. and *Conoderus falli* Lane and *Melanotus communis* (Gyll.) in the U.S.A. However, non-organochlorine insecticides have been tried against several other species of wireworms in the field, and Table 1 lists more than a hundred such compounds tested against several types of wireworms on various crops.

Compounds that worked well in laboratory tests in different parts of the world include the organophosphorus insecticides B 29952, B 30237, B 30468, B 30911, "Dursban", fenitrothion, fenthion, Hercules 3004, Murphy P1973 and P2188, and the carbamate Hercules 5727. In most laboratory tests [1, 2, 3, 4, 5, 6, 15, 21, 42] wireworms have been confined in containers with soil that has been mixed with the insecticide. The insecticide is more thoroughly mixed with the soil than it would be in the field, and it cannot leach from the containers. The soils are not subjected to weathering, the watering regime differs from conditions in the field, and confined, wet soils may become acid. Therefore, materials that do well in the laboratory may not necessarily perform well in field conditions.

Materials with some field effectiveness. Parathion is the most extensively tested organophosphorus insecticide, and only tests that compared it with other organophosphates have been included here. It was effective or moderately effective in field use against more than 10 species of wireworms on various crops in different parts of the world, but in the U.K. parathion has been less effective than aldrin when applied in a similar way. Other organophosphorus compounds reported to be effective in the field are Bayer 38156 and Stauffer N2790 ("Dyfonate"), two related insecticides; the former has been tested against species of *Agriotes* in the U.K. and species of *Conoderus* in the U.S.A., and the latter against these and other types of wireworms. Diazinon and fensulfothion were moderately effective against species of *Conoderus*, *Limonius* and other wireworms in the U.S.A. and Canada, but were not very effective against *Agriotes* in the U.K. Methidathion (GS 13005) was twice reported effective against wireworms in the U.S.A., but did not work well against *Dalopius pallidus* and *Agriotes mancus* in Canada. Phorate has been tested extensively abroad and, like parathion, is one of the best organophosphorus compounds tried against wireworms in potatoes in the U.K. Thionazin is very toxic to wireworms in laboratory tests, but field results vary. Trichloronate (B 37289) gave some good results against wireworms in the U.S.A. and Canada: it had some effectiveness against *Agriotes* spp. in the U.K., but less than aldrin in the quantities tested.

Methods of applying insecticides. Common methods of applying insecticide are to spread granules or to spray the soil, and then harrow or disc the

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TABLE 1

Possible substitutes for organochlorine insecticides tested against wireworms

(Numbers following the ; refer to papers in the list of references)

American Cyanamid	Dursban; 5
AC 12008; 18	Dyfonate <i>see</i> : Stauffer N 2790
18706 <i>see</i> : ethoate methyl	EPN; 19, 24, 33, 37, 43
43064; 5, 6, 42	ethion; 1, 4, 6
47031; 42	ethoate methyl; 1, 5
Allied Chemicals	Ethyl Guthion <i>see</i> : azinphos ethyl
GC 3561; 2	fenchlorphos; 29, 54
3562; 1	fenitrothion; 2, 4, 7, 53, 154
3583; 2	fensulfothion; 2, 5, 6, 8, 10, 34, 36, 42, 45
3661; 1	fenthion; 2, 3
4072 <i>see</i> : chlorofenvinphos	fentin acetate; 4
6506; 36	Fitios <i>see</i> : ethoate methyl
aminocarb; 10	Folthion <i>see</i> : fenitrothion
Aphidan; 5	Geigy GS 12968 <i>see</i> : lythidathion
arprocarb; 2, 27, 34, 36	13005 <i>see</i> : methidathion
azinphos ethyl; 5, 18, 34	30493; 2
azinphos methyl; 1, 6, 18, 29, 42	30494; 2
Bayer 22408; 2	Guthion <i>see</i> : azinphos methyl
22684; 2	Hercules 3004; 1
23453; 1	3895; 2
24498; 2	5727; 2, 11, 34
25141 <i>see</i> : fensulfothion	Imidan; 2
25198; 2	Isolan; 3
29952; 2	lythidathion; 45
30237; 2	malathion; 1, 6, 10
30468; 2	mecarbam; 5, 29, 54
30554; 2	methidathion; 32, 34, 45
30911; 2	methiocarb; 2
34042; 2	mevinphos; 1, 6
34098; 2	Monsanto CP 7769; 1
37289 <i>see</i> : trichloronate	9533; 2
37344 <i>see</i> : methiocarb	10502; 1
38156; 3, 6, 7, 10, 28, 29, 30, 32, 54,	10516; 1
137	10561; 2
39007 <i>see</i> : arprocarb	10878; 2
44646 <i>see</i> : aminocarb	11549; 2
Baygon <i>see</i> : arprocarb	11903; 2
Bidrin; 1, 5, 6	12432; 2
Birlane <i>see</i> : chlorofenvinphos	Murphy P 1973; 5
Bomyl; 1, 6	2188; 5
Boots RD 14526; 4	naled; 1, 6
14639; 4	Niagara 9203; 34
14838; 4, 137	9205; 6
14977; 4	10242; 34, 36, 44
14984; 4	NC 1721; 4, 31
14991; 4	1531; 31
15038; 4	2107; 31
18242; 4	2108; 31
bromophos; 4, 137	parathion; 1, 5, 6, 8, 9, 10, 14, 15, 16, 17, 19,
a carbamate; 5	20, 21, 22, 23, 24, 25, 28, 32, 33, 34, 36,
carbaryl; 1, 3, 6, 10, 154	37, 38, 40, 41, 42, 46, 48, 52, 53, 54, 59, 154
carbophenothion; 1, 3, 6, 55	parathion methyl; 1, 33
chlorfenvinphos; 2, 5, 6, 10, 29, 36, 45, 54	phorate; 1, 3, 6, 8, 9, 12, 16, 18, 28, 32, 36,
Chlorthion; 1	38, 41, 42, 47, 48, 49, 51, 54, 154
Ciodrin; 2, 10	Phosdrin <i>see</i> : mevinphos
Cidial; 31	phosphamidon; 1
Delnav <i>see</i> : dioxathion	Plant Protection R 30569; 38
demeton; 6, 19, 21, 22, 33, 56	Pyrazothion; 2
diazinon; 1, 4, 6, 8, 9, 10, 16, 26, 29, 30, 31,	Ronnel <i>see</i> : fenchlorphos
32, 34, 35, 36, 38, 39, 40, 41, 42, 44, 45,	Shell 8530; 6, 32
46, 54, 154	
dichlofenthion; 1, 4, 9, 10	
dichlorvos; 1, 3, 10	
dimethoate; 3, 6, 58	
dioxathion; 1, 6	
disulfoton; 1, 3, 6, 8, 13, 28, 32, 34, 36,	
38, 41, 42, 48, 54, 56, 57, 154	
Du Pont 691; 2	

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TABLE 1 (Continued)

Shell SD 4092; 1	Thiocron; 36
4239; 1	thionazin; 1, 3, 6, 7, 9, 10, 11, 12, 16, 28, 29,
4457; 2	30, 34, 36, 41, 44, 47, 54
5532; 2	trichloronate; 7, 8, 13, 32, 38, 44, 45
5539; 2	trichlorphon; 1, 6, 154
9098; 42	Trithion <i>see</i> : carbophenothion
Stauffer N2790; 4, 6, 7, 8, 32, 34, 38, 39, 42,	UC 8305; 1, 6, 41
44, 45, 46, 50, 53, 54, 55	10854 <i>see</i> : Hercules 5727
3055; 6	21149; 36, 42
5092; 6	Vapam; 59
R1448; 2	VC 13 <i>see</i> : dichlofenthion
1505; 2	Zectran; 10
Sumithion <i>see</i> : fenitrothion	Zinophos <i>see</i> : thionazin
Temik <i>see</i> : UC 21149	

insecticides in before planting the crop. With organochlorine insecticides many workers favoured applying the insecticide early so that they had time to take effect before a crop was planted. With the shorter-lived organophosphates and carbamates early applications have given variable results. In the U.S.A. Day *et al.* [9] and Cuthbert *et al.* [17] protected potatoes against *Conoderus falli* by applying insecticides to the previous cover crop, but in Quebec, Lafrance [45] found re-invasion of potatoes by second-year larvae of *Dalopius* and *Agriotes* in plots treated with diazinon the previous year. A very late application of diazinon in July protected sweet potatoes from species of *Conoderus* in tests by Brett *et al.* [39].

Several workers have applied granular organophosphates in a concentrated band to the planting furrow [9, 12, 14, 48, 49, 52, 54]. With one exception [9], granules placed in the furrow have protected potatoes better against wireworms than when broadcast. Similarly, insecticides applied in the drill row of corn crops [19, 32] have given good results.

Tobacco plants have been protected from wireworm attack in the U.S.A. and Russia by adding organophosphorus insecticides to the transplanting water used to moisten the soil around the plants [10, 33, 47, 59]. Baits have been used to estimate wireworm populations [136], and a bait of diazinon on corn grits was effective against *Conoderus* and *Melanotus* [40]; the value of such insecticidal baits merits more study.

The organophosphorus insecticides AC 12008 [18], azinphos ethyl [18], azinphos methyl [18], Bayer 38156 [7], demeton [22, 56], diazinon [26], disulfoton [56], ethion [4], parathion [21, 22, 23, 25], Stauffer N2790 [55] and trichloronate [7, 13] have all been tried as seed-dressings, but results have usually been inconclusive or less good than with standard γ -BHC seed-dressings. γ -BHC rapidly stops wireworms from feeding, a property not shared by many other insecticides, for whereas wireworms did not bite nutrient-soaked paper discs treated with γ -BHC they readily bit similar discs treated with some other insecticides [137].

Wheat-bulb fly (*Leptohylemyia coarctata* Fall.)

Adult female wheat-bulb flies lay eggs during July and August in bare soil, either of fallow fields or under crops lifted early or that do not cover the soil completely during the egg-laying period. Eggs hatch the following year in late January to early March, and the larvae burrow into and destroy

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the shoots of winter wheat, barley and rye, and some grasses. Oats are not susceptible, and spring cereals usually escape attack because they are sown after the eggs have hatched. The pest can be controlled by applying insecticides to the soil, to the seed or to the growing crop in spring. Treating soil requires several pounds of insecticide per acre and is more likely to harm other soil fauna than are seed-dressings, which use only 2–3 oz insecticide/acre. Although seed-dressings are slightly less efficient than soil treatments in killing wheat-bulb fly larvae or in protecting plants from attack, they cost less and are easier for the farmer to use because he can buy his seed already dressed. Seed-dressings of γ -BHC, aldrin and dieldrin have therefore been extensively used for several years, but, because of the hazard to birds, seed treated with aldrin or dieldrin should not be sown later than 31 December, and their use in the U.K. is to be reviewed again shortly. Spraying with organophosphorus insecticides in spring is usually practised only when other measures of control were ineffective or omitted, and recent experiments have mainly studied how to time the sprays correctly.

Tables 2a and 2b list the non-organochlorine insecticides that have been tested against wheat-bulb fly as seed-dressings, granules or spring sprays; they include some arsenical and fluorine compounds which Bardner [61] compared with organophosphorus and carbamate insecticides in early tests.

Seed-dressings. Candidate insecticides are tested by applying them to seeds, sowing the seeds during autumn either in boxes to which wheat-bulb fly eggs are introduced [61] or in infested field soils [60] and examining the plants for damage next spring. These methods do not show whether a material that fails to protect plants does so because it lacks persistence or lacks toxicity to wheat-bulb fly larvae.

Of the 65 non-organochlorine materials tried as seed-dressings, 49 were ineffective and 12 were moderately effective, i.e. they gave better plant stands than untreated seeds but did not equal the organochlorines, or were less consistent than the organochlorines on a range of soil types. These moderately effective materials were the organophosphorus insecticides "Aspon", azinphos ethyl, AC 43064, B 38156, bromophos, diazinon, dichlofenthion, dioxathion, parathion, Stauffer N2790, trichloronate and VC 3-759. Of the remaining four insecticides, chlorfenvinphos and ethion have now been tested extensively in field trials with very good results: carbophenothion has also worked well, and "Dursban", so far tested only in single-row trials, was sufficiently promising to be included in larger trials for 1967/8.

Granules. Materials tested as granules are the organophosphorus insecticides AC 43064, AC 47470, chlorfenvinphos, B 38156, diazinon, dichlofenthion, disulfoton, mecarbam, menazon, parathion, phorate, Plant Protection R 30472, R 30569, Stauffer N2790, thionazin and trichloronate.

Where comparisons can be made, materials effective as seed-dressings are effective also as granules: because more insecticide is used, granules of

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TABLE 2

Possible substitutes for organochlorines tested against wheat-bulb fly

(a) as soil treatments or seed-dressings, (b) as sprays

(Numbers following the ; refer to papers in the list of references)

<p>(a)</p> <p>Allied Chemicals GC 4072 <i>see</i>: chlor-fenvinphos</p> <p>American Cyanamid AC 43064; 60, 66</p> <p>American Cyanamid AC 47031; 60</p> <p>American Cyanamid AC 47470; 66</p> <p>Aphidan; 80, 85</p> <p>Aspon; 80</p> <p>azinphos ethyl; 60</p> <p>barium silicofluoride; 61</p> <p>Bayer 37289 <i>see</i>: trichloronate</p> <p>Bayer 38156; 4, 65, 66, 75, 76, 77</p> <p>Bidrin; 60</p> <p>Birlane <i>see</i>: chlorfenvinphos</p> <p>Boots RD 14639; 4</p> <p>Boots RD 14838; 4</p> <p>Boots RD 14984; 4</p> <p>Boots RD 15721; 60</p> <p>bromophos; 60, 68</p> <p>calcium arsenate; 61</p> <p>a carbamate; 80</p> <p>carbaryl; 63</p> <p>carbophenothion; 55, 60, 63, 82</p> <p>chlorfenvinphos; 65, 66, 69, 72, 82, 84</p> <p>Chlorthion; 61</p> <p>coumaphos; 80</p> <p>Dazomet; 4</p> <p>Delnav <i>see</i>: dioxathion</p> <p>demeton; 61</p> <p>demeton methyl; 61</p> <p>diazinon; 61, 64, 65, 66, 69, 71</p> <p>dichlofenthion; 4, 64, 65, 66, 69</p> <p>dimethoate; 63, 64, 71</p> <p>dioxathion; 80</p> <p>disulfoton; 60, 63, 66, 74</p> <p>Dursban; 80</p> <p>Dyfonate <i>see</i>: Stauffer N2790</p> <p>ethion; 60, 65, 66, 69, 79, 80, 81, 82, 83, 87</p> <p>ethoate methyl; 80, 85</p> <p>Ethyl Guthion <i>see</i>: azinphos ethyl</p> <p>fenchlorphos; 69, 77</p> <p>fenitrothion; 4</p> <p>fenthion; 76</p> <p>Fentin acetate; 60</p> <p>Fitios <i>see</i>: ethoate methyl</p> <p>fluoroacetanilide; 61</p> <p>Folithion <i>see</i>: fenitrothion</p> <p>Geigy GS 12968 <i>see</i>: lythidathion</p> <p>Geigy GS 13005 <i>see</i>: methidathion</p> <p>lead arsenate; 61</p> <p>lythidathion; 71</p> <p>malathion; 61</p> <p>mecarbam; 4, 66</p> <p>menazon; 65</p> <p>methidathion; 60, 71</p> <p>mevinphos; 63</p> <p>Murphy P 1973; 80</p>	<p>Paraoxon; 61</p> <p>parathion; 61, 64, 66</p> <p>phorate; 61, 63, 66</p> <p>Phosdrin <i>see</i>: mevinphos</p> <p>Plant Protection R 30472; 60, 66</p> <p>Plant Protection R 30569; 60, 66</p> <p>Pyrolan; 61</p> <p>Ronnel <i>see</i>: fenchlorphos</p> <p>Shell SD 8211; 60</p> <p>Shell SD 8447; 60</p> <p>sodium fluoroacetate; 61</p> <p>Stauffer N2790; 55, 60, 65, 66, 68, 69</p> <p>Sumithion <i>see</i>: fenitrothion</p> <p>thionazin; 4, 66</p> <p>Tributyltin oxide; 60</p> <p>trichloronate; 4, 13, 65, 66, 67, 69, 74, 75, 76, 77</p> <p>trichlorphos; 61</p> <p>Trithion <i>see</i>: carbophenothion</p> <p>vamidothion; 60</p> <p>VC 13 <i>see</i>: dichlofenthion</p> <p>VC 3-759; 60</p> <p>VC 3-670; 60</p> <p>VC 3-764; 60</p> <p>VC 3-768; 60</p> <p>VC 9-85; 60</p> <p>Zectran; 4</p> <p>zinc fluoroacetate; 61</p> <p>Zinophos <i>see</i>: thionazin</p> <p>(b)</p> <p>American Cyanamid AC 43064; 66</p> <p>azinphos methyl; 67, 86</p> <p>Bayer 38156; 74</p> <p>Bidrin; 66, 74</p> <p>demeton; 62</p> <p>demeton methyl; 78</p> <p>diazinon; 87</p> <p>dimethoate; 4, 66, 67, 70, 74, 78, 86, 87</p> <p>ethion; 86</p> <p>endothion; 87</p> <p>ethoate methyl; 85</p> <p>fenthion; 78</p> <p>formothion; 66, 73, 86</p> <p>menazon; 74</p> <p>mevinphos; 78, 87</p> <p>parathion; 62, 78</p> <p>phosalone; 86</p> <p>phorate; 62</p> <p>thionazin; 66, 70</p> <p>trichlorphos; 62, 66, 78</p> <p>trichloronate; 70, 74</p> <p>vamidothion; 86</p>
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some compounds (e.g. phorate and disulfoton) have been active against wheat-bulb fly where seed-dressings have not. As already explained, however, granules cost more than seed-dressings and are less selective in their action. Some good results have been obtained in experiments with granules spread over the crop during spring [13, 67, 74, 75, 85], and this method, like spring sprays, might be useful when earlier measures have not been taken or have failed.

Sprays. The effectiveness of spring sprays depends on when they are applied in relation to the stage of development of both the plant and the larvae [66, 70, 78]. Spraying with dimethoate increased yields most when the larvae were young and the plants had unattacked side buds that could replace the damaged central shoots [70]. Early sowing is itself a considerable safeguard, for early sown crops usually have enough unattacked shoots to withstand moderate infestations of wheat-bulb fly larvae. A disadvantage of sprays is that it is often too wet for a ground sprayer to be used early enough to give the best results. Non-organochlorine insecticides tested as sprays are listed in Table 2b, but no materials have any special advantage over dimethoate or formothion, the ones commercially used.

Leatherjackets (*Tipula* spp.)

Leatherjackets are larvae of crane flies, of which *Tipula paludosa* Meig. is the most common species damaging cereals in the U.K. Adult flies lay eggs in grassland during summer and autumn, the eggs hatch in about 10 days, and the larvae feed just below the soil surface on the roots and underground stems of grass throughout the winter and the following spring. When the grass is ploughed the larvae feed on the newly planted crop,

TABLE 3
Possible substitutes for organochlorine insecticides tested against leatherjackets as sprays, granules or baits

(Numbers following the ; refer to papers in the list of references)	
azinphos methyl; 92	lythidathion; 91
Bayer 37289 <i>see</i> : trichloronate	malathion; 88, 91, 95
Birlane <i>see</i> : chlorfenvinphos	mecarbam; 88
carbaryl; 88, 92, 94, 95	mevinphos; 92
Carbamate A; 92	naled; 95
Carbamate B; 92	an organophosphorus compound; 92
chlorfenvinphos; 91, 94	parathion; 89, 90, 91, 92, 94
Chlorthion; 92	phorate; 94
demeton methyl; 88	Phosdrin <i>see</i> : mevinphos
diazinon; 88, 92, 94	phosphamidon; 88, 92
dichlorvos; 92	Sumithion <i>see</i> : fenitrothion
dimethoate; 88, 92	trichloronate; 94
Dipterex <i>see</i> : trichlorphon	trichlorphon; 88, 91, 92
fenitrothion; 91, 93, 94	thionazin; 91
fenthion; 92	Zinophos <i>see</i> : thionazin
Folithion <i>see</i> : fenitrothion	
GC 4072 <i>see</i> : chlorfenvinphos	
GS 12968 <i>see</i> : lythidathion	
Guthion <i>see</i> : azinphos methyl	

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whether cereals, root crops or vegetables. In warm, damp weather leather-jackets can feed on the surface, cutting off the plants at ground level. Chemical control is by baits of Paris Green (copper aceto-arsenite), or by sprays or baits of the organochlorine insecticides γ -BHC or DDT. However, some varieties of barley are sensitive to DDT, and BHC can taint subsequent root crops. Some work has therefore been done on control with non-organochlorine compounds. Table 3 lists the insecticides tested. Baits containing the organophosphorus compounds fenitrothion, parathion and thionazin worked well in tests by Golightly [91], and an unnamed carbamate (A) in tests by Lange [92]. Sprays used with some success include fenthion, fenitrothion, an unnamed organophosphate, thionazin, chlorfenvinphos and parathion. The last three materials also worked as granules, as did trichloronate and phorate. Fenitrothion as a spring spray has lived up to its earlier promise in recent field trials in England [93], but in Scotland was effective only at 2 lb a.i./acre, whereas parathion was very effective at 3 oz a.i./acre [94].

Frit fly (*Oscinella frit* (L))

Oscinella frit has three generations a year in most parts of the British Isles. Damage to cereals is most serious in spring oats and in maize. Adult flies lay eggs on and at the bases of young plants, and the larvae that emerge bore into the young shoots and destroy the growing points. Young plants are killed, and slightly older plants produce many weak tillers. A second generation of larvae, which arises from eggs laid in summer, damages oat grains. The third generation of larvae overwinters in grasses, but if the grass is ploughed the larvae may damage a following cereal crop (autumn-sown wheat, barley or rye).

Chemical control of frit fly on late-sown oats is by two DDT sprays, one just before or at the time frit flies lay their eggs on young plants, the second about a fortnight later. Several organophosphorus sprays have been tried (Table 4a), and parathion and dimethoate were promising on late-sown oats [98] and on maize [116], even when applied as single "late" sprays, i.e. about a fortnight after egg laying, when symptoms of attack were conspicuous. The late sprays have the advantage that they avoid treating crops that will not be attacked, but correct timing is important [110]. The beneficial effects of sprays, especially of non-persistent materials, against the first generation of frit fly may be offset by second-generation frit invading the crop and attacking the grain, as Jepson [100] found with parathion sprays.

Table 4b lists non-organochlorine insecticides tested as soil or seed treatments against frit fly. Trials of granules by Walker [96] showed that phorate was more effective than thionazin in protecting silage maize, and worked better applied in the furrow than broadcast. Jepson and Mathias [104] also obtained good results with phorate used in this way to protect sweet corn. However, in other trials Walker [102] found that the relative control given by broadcasting granules over young plants or by applying granules to the furrow at sowing depended on the time of attack; his studies with radioactive phorate showed that broadcasting phorate gave

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an intense concentration of up to 17 ppm phorate equivalent in the plants after 1–3 weeks, whereas placing it in the furrow produced less activity for 9 weeks. A disadvantage of placing phorate in the furrow is that it sometimes damages young plants [103, 138].

TABLE 4

Possible substitutes for organochlorines tested against frit fly

(a) *sprayed on to plant*, (b) *applied to seed or soil*

(Numbers following the ; refer to papers in the list of references)

(a)	(b)
aziphos methyl; 116	demeton; 56
demeton; 113, 118	dimethoate; 98, 122
demeton methyl; 97, 109	disulfoton; 56, 57, 103, 115, 119
diazinon; 116	ethion; 107
dimefox; 111	methyl parathion (+parathion); 117
dimethoate; 98, 116	OMPA <i>see</i> : schradan
Dipterex <i>see</i> : trichlorphon	parathion; 98, 112, 115, 117
DNOC; 118	Pestox III <i>see</i> : schradan
Ethyl Guthion <i>see</i> : aziphos methyl	phorate; 96, 97, 102, 103, 104, 105, 107, 115, 121
methyl parathion (+parathion); 117	schradan; 101, 108, 111, 117
OMPA <i>see</i> : schradan	thionazin; 96
parathion; 97, 98, 100, 106, 110, 112, 113, 116, 117, 118, 120	Zinophos <i>see</i> : thionazin
Pestox III <i>see</i> : schradan	
schradan; 111	
thionazin; 114	
trichlorphon; 97	
Zinophos <i>see</i> : thionazin	

Seed-dressings of demeton, disulfoton, parathion, phorate and schradan have been reported to have some effect, but seed-dressings have limitations because some frit fly eggs are laid on the plant, and larvae from these may enter the plants above soil level [99]. Organophosphorus insecticides that are active as seed-dressings against wheat-bulb fly are therefore less likely to work against frit fly because they owe much of their success to action in the soil. To control frit fly adequately the advantage would seem to lie with moderately persistent, very systemic materials.

The present status of the pests and the insecticides

The pests. Progress in control of wireworms with non-organochlorine insecticides has been disappointing considering the many materials tested. In the U.K., soil treatments with aldrin are still superior to soil treatments with other types of insecticide, and no non-organochlorine insecticide of acceptable mammalian toxicity rivals γ -BHC as a seed-dressing. In the U.S.A. the organophosphorus insecticides diazinon, parathion and phorate are recommended against species of wireworms that are resistant to organochlorines, but, before resistance developed, organophosphorus compounds like parathion did not compare favourably with organochlorine insecticides [20, 21, 24]. Therefore in the U.K., where wireworms

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have not developed resistance to organochlorines, it is not surprising that aldrin still gives the best results. However, some organophosphorus compounds are quite effective when put in the furrow and may be profitable in protecting potatoes, but are too costly to use for cereals.

Of the cereal pests discussed, the search for substitutes to replace the persistent organochlorine insecticides has probably met most success with wheat-bulb fly. Chlorfenvinphos and ethion seed-dressings have been adequately tested and are very effective against this pest. Liquid seed-dressings of chlorfenvinphos and powder seed-dressings of ethion are now available commercially. Carbophenothion and "Dursban" have also given promising results as seed-dressings in experiments. Granules of chlorfenvinphos, N2790 and trichloronate are effective, but insecticides are more difficult to apply in this form, and the cost would probably be justified only when growing special varieties for seed. Correctly timed spring sprays of parathion, dimethoate and formothion have given reasonable results in experiments, and the last two, being less toxic than parathion to mammals, are used commercially.

Against leatherjackets, several organophosphorus compounds are effective as baits, but these are difficult to prepare and to apply evenly. Of the sprays, fenitrothion is less toxic to mammals than the other organophosphorus insecticides tried, but it is not marketed in the U.K. for agricultural use. Granular formulations are more suitable than sprays with the more toxic materials.

Experiments on chemical control of frit fly have decreased with the decline in the acreage of oats in the U.K. Of the non-organochlorine sprays, parathion has given good results, but is very toxic to mammals. The less toxic organophosphate dimethoate gave promising results in experiments [98, 116], but requires further testing. Should the acreage of oats increase again to the point where frit fly is troublesome, suitable organophosphorus insecticides might provide acceptable alternatives to DDT. For treating soil or seed, the need for systemic insecticides has already been explained. With insecticides that are very toxic to mammals, granular formulations with a small percentage of active ingredient are preferable to seed-dressings because they are less hazardous to handle, but oats can be sown early to reach a non-susceptible stage of growth by the time frit fly lay their eggs, and the use of expensive granular treatments is probably not justified: with sweet corn the optimal sowing date is in May, and phorate granules are recommended for this crop.

The insecticides. Sprays can be applied to the aerial parts of plants to kill shoot-boring stages of wheat-bulb fly and frit fly, but the four pests discussed in this paper spend part of their lives in soil, and their control often involves putting insecticide in soil to kill insects directly, or to be taken up by the plants, and so to kill insects living in the shoots. Placing insecticides in soil brings special problems. Not only must the insecticide be toxic to the pest but it must resist leaching enough to remain in the root zone, it must not be lost by volatilisation, or degraded chemically or microbially before it has done its job, and it must not be so strongly adsorbed by soil that it is inactive biologically.

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Except for two references [111, 139], there is no information about the toxicity of non-organochlorine insecticides as stomach, contact or fumigant poisons to larvae of wheat-bulb fly, frit fly, leatherjackets or wireworms. Most testing has been done in soil, and when an insecticide fails, it is not known whether this is because it is not toxic to the insect or because it lacks some other property mentioned above. The importance of microbial decomposition, leaching and volatilisation of soil insecticides was discussed by Edwards [124], but most work so far has been done on organochlorine insecticides, and few organophosphorus materials have been studied in detail. Adsorption of insecticides in soil is of key importance, because it affects the extent of leaching and decomposition, and the concentrations available for killing insects by contact or fumigant action. For example, Harris and Mazurek [143] showed that, of 10 insecticides deposited on a metal surface, all except DDT volatilised and killed crickets held on a screen $\frac{1}{4}$ in. above the treated surface. In contrast, when the insects were held above the same insecticides incorporated in a moist sandy loam, aldrin, heptachlor, chlordane, trichlorphon and mevinphos were still moderately volatile, but diazinon, parathion and dieldrin were only slightly volatile, and DDT and Zectran were not volatile and killed no insects in 24 hours. This loss of fumigant activity was attributed to adsorption of insecticide in soil, and the processes of adsorption are discussed below. The fate in soil of few non-organochlorine insecticides has been studied in detail, but enough materials have now been tested against soil pests of cereals to try to discuss why some insecticides work better than others.

Adsorption. Several authors have shown [125, 140, 141, 142, 149] that insecticides in soil are more active in moist than in dry conditions. To explain why dieldrin-treated mud blocks were more toxic to mosquitoes at high than at low humidities, Barlow and Hadaway [140] suggested that water was adsorbed preferentially on the active sites of soil particles, so displacing insecticide and resulting in increased mobility of insecticide molecules. Harris [143, 144, 145, 146, 147, 148] developed the idea that the initial activity of an insecticide in a mineral soil depends upon the degree to which it is adsorbed on the active sites of soil particles and how well it can compete with water for these sites. By measuring in a Potter spray tower the contact activity of a range of insecticides to crickets and flies, and comparing these values with their activity in moist and dry soil, he concluded that some insecticides, e.g. the organochlorines isobenzan, HRS 1671, aldrin and lindane, and the organophosphorus compounds phorate, UC 8305 and trichloronate, were not strongly adsorbed by dry soil and did not compete with water for active sites on the soil particles, and so would be expected to give consistently good initial control of soil insects in mineral soils. In contrast, other organophosphorus insecticides like Bomyl and azinphos methyl, although toxic to the test insects in spray-tower tests, worked poorly in soil, because they were strongly adsorbed, even in moist soil. Another group, including the organophosphates thionazin, diazinon, dichlofenthion, SD 9098 and GS 12968, were strongly adsorbed by dry mineral soil, but competed so little with water for active sites on the soil particles that they were very toxic in moist mineral soil, and so would be

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expected to give inconsistent results in the field. A fourth class of materials, including the organophosphates fenitrothion, methyl parathion, GS 13002 and the carbamates Niagara 10242 and UC 21149 ("Temik"), were moderately to strongly adsorbed by dry soil but only moderately competitive with water for the active sites, and in Harris's view would be expected to give consistent results in mineral soils provided they were used at greater concentrations than their contact-toxicity figures would suggest.

These suggestions may help to explain the activity of trichloronate and phorate against cereal pests and the inconsistent performance of thionazin against wireworms, and diazinon against wheat-bulb fly. A difficulty is that deductions about adsorption, based on an indirect measurement such as the number of insects killed, can mislead if a change in soil conditions affects the behaviour of the insects. Further, Gerolt [150] showed that insects took up more dieldrin from glass in moist than in dry air, and he suggested that the mobility of insecticide molecules is affected by R.H. and that the effect of humidity is not restricted to specific substrates. Ebeling and Wagner [170] showed that the displacement of insecticides from a substrate by water depended on the insecticide itself and on its formulation, but took place on hydrophilic substrates and not on hydrophobic substrates. When they eliminated the effect of the substrate by suspending flour beetles above layers of insecticide 1 cm thick more insects were killed at 80% R.H. than at 20% R.H. with some formulations of diazinon, and they concluded that some explanation other than displacement of insecticide from a substrate by water was needed.

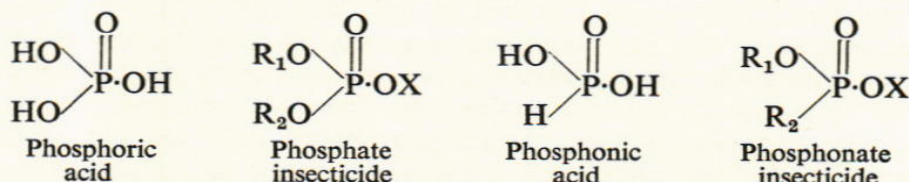
Adsorption of insecticides on the organic matter of soils is also very important. Several authors [142, 151, 152] have shown that organochlorine insecticides are relatively inactive in soils with much organic matter. Other types of insecticide are similarly affected: in tests with the organochlorines heptachlor and DDT and the organophosphorus materials dichlofenthion, diazinon and parathion in 10 types of soil, Harris [153] concluded that heptachlor, DDT and dichlofenthion were adsorbed by the clay fraction, the three organophosphorus materials by the sand or silt fraction and all five materials by the organic matter. His lists [144] showed that many insecticides, organochlorines, organophosphates and carbamates were much less active in a moist muck soil than in a moist sandy loam. He also studied how soil moisture affected the insecticidal activity of diazinon, parathion, DDT and heptachlor [148] in sandy loam (1.44% organic matter, mineral fraction = 76.6% sand:21.06% silt:2.34% clay), a clay soil (9.09% organic matter, mineral fraction = 17.02% sand:31.32% silt:51.66% clay) and a muck soil (64.6% organic matter, mineral fraction = 14.47% sand:38.82% silt:46.71% clay). The influence of soil moisture on insecticidal activity depended on the soil type: it was greatest in the sandy loam, but in the clay with 9.09% organic matter the insecticides also became more active as moisture content increased, whereas in the muck soil the insecticides were relatively inactive at all moisture contents. Similarly, these four insecticides, and dichlofenthion, were not very toxic to crickets in dry or moist muck soil containing 39.76% organic matter [153].

Not all insecticides are equally strongly adsorbed by organic matter.

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Direct chemical measurements by Graham-Bryce [155, 156] showed that phorate and disulfoton were strongly adsorbed in soils with much organic matter, but in the three soils so far studied dimethoate and menazon were much less strongly adsorbed. Possibly many organochlorines and some relatively lipophilic organophosphates like phorate are adsorbed mainly on the organic matter of soils, whereas relatively hydrophilic insecticides are adsorbed mainly on the mineral fraction. However, it is not yet certain what physical properties of insecticides or what features of their chemical structures influence adsorption on organic matter as opposed to adsorption on clay, silt and sand. Many more direct measurements of adsorption are needed, especially with series of insecticides whose substituents are varied systematically.

Decomposition. More persistent insecticides are required to control some cereal soil pests than others. Short-lived materials may control leather-jackets if they are applied when the insects are feeding at or near the soil surface. In contrast, insecticides applied in the autumn to protect plants against wheat-bulb fly must persist until the following spring when the larvae attack. Moderate persistence may be necessary also for insecticides used against wireworms, because insecticide and soil cannot be thoroughly mixed in the field, so control may depend partly on insects moving into zones of insecticide, and the probability of this happening increases with extended persistence of the insecticide. Moderate persistence may also be an advantage in soil insecticides used against frit fly, but systemic properties are also very important. Of the non-organochlorine insecticides so far tested, organophosphorus compounds have proved best when applied to soil against the cereal pests discussed. These compounds are esters of phosphoric acid, phosphonic acid and related acids, in which the hydrogen atoms have been replaced by other groups.



R_1 and R_2 are commonly methyl (CH_3), ethyl (C_2H_5) or propyl (C_3H_7); the doubly bound O and/or the O of the OX group is replaced by S in phosphorothioates or phosphorodithioates; variations in X among organophosphorus insecticides are many.

The best results against wheat-bulb fly were obtained with carbo-phenthion, chlorfenvinphos, ethion, "Dursban" and the moderately effective compounds listed on p. 336. All except chlorfenvinphos have the doubly bound O and/or the O of the OX group replaced by S, and nearly all are diethyl phosphates and phosphonates (R_1 and $R_2 = \text{C}_2\text{H}_5$), whereas ineffective organophosphorus compounds tried against wheat-bulb fly included diethyl compounds, dimethyl compounds and some methyl/propyl and methyl/butyl compounds. Against wireworms several dimethyl organophosphates, like fenthion and fenitrothion, have done well in

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laboratory tests, and two dimethyl compounds methidathion [32, 34] and Niagara 9203 [34] were reported effective in the field. Most reports of field effectiveness, however, refer to diethyl phosphates and phosphonates, and it is the diethyl compounds phorate, parathion and diazinon that have gained acceptance in the U.S.A. for field use. Against frit fly the systemic phorate is the only non-organochlorine recommended. Therefore, in those situations where soil insecticides need moderate persistence to control cereal pests the most successful of the organophosphorus insecticides are mostly diethyl, S-substituted phosphates and phosphonates.

One possible reason may be hydrolysis rates. The phosphorus atom of organophosphorus insecticides has a partial positive charge, and this site is susceptible to attack by hydroxyl ions (OH^-) during alkaline hydrolysis. The size of the positive charge depends on whether the substituents of the molecule tend to draw electrons away from the phosphorus atom or to donate electrons to it. The $=\text{O}$ atom has a greater electron-withdrawing effect than the $=\text{S}$ atom, so series of organophosphorus insecticides containing the latter are less easily hydrolysed [157, 158, 169]. Similarly, methyl groups donate less electrons to the phosphorus atom than do ethyl groups, which in turn donate less electrons than isopropyl groups, and holding one alkyl group constant and increasing the size of the other showed that the order of ease of hydrolysis is methyl > ethyl > isopropyl [159]. Hydrolysis destroys the insecticidal activity of organophosphorus compounds and has been shown to be a path of breakdown in soil of parathion [160], Imidan [161], diazinon and thionazin [162]. The rate of hydrolysis would be expected to depend on pH and temperature, but in equivalent conditions should happen faster with dimethyl phosphates than with corresponding S-substituted diethyl compounds, and may therefore help to explain the persistence and effectiveness of the latter. Mulla's results [163, 164] support this, for in laboratory tests which compared many organophosphorus compounds and carbamates, certain of the diethyl phosphorothioates and phosphonothioates remained active longest in soil. Also, some dimethyl compounds, active against wireworms in laboratory tests where conditions are sometimes acid, have failed in the field. The variable results of thionazin in wireworm trials could also be explained in terms of relative persistence in field soils of different pH, and in one trial [7] residues of this insecticide were greater in the more acid than in the less acid areas of the same field.

In the present state of knowledge, however, there is need to be wary of taking any particular argument too far. Variations in the part X of the molecule greatly affect hydrolysis rates of organophosphates [171]. This may be why certain dimethyl compounds persist in soil, e.g. fenthion and B 37342 [167], dimethoate applied in usual amounts [165] and large amounts [166], and why some diethyl compounds are short lived. For some compounds, if leaching, microbial attack or volatilisation occur very rapidly, rates of hydrolysis may be relatively unimportant.

Volatility, solubility. Diethyl organophosphorus compounds are likely to be less volatile than their corresponding dimethyl analogues, but adsorption in soil affects the vapour toxicity of insecticides, and the stated vapour

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pressure of an insecticide is not a good indication of its fumigant activity in soil. Diethyl S-substituted organophosphates would be expected to be less polar, and so less soluble in water than corresponding dimethyl phosphates, and where diethyl and dimethyl analogues can be compared (e.g. demeton S, parathion, demeton O, carbophenothion and their methyl analogues) this is true. Most of the compounds effective against wheat-bulb fly and wireworms are very slightly soluble in water (150 $\mu\text{g}/\text{l}$ or less) but it is not clear whether slight solubility *per se* is a useful characteristic of soil insecticides, and the relationship between solubility, adsorption and leaching, for molecules of widely differing chemical structure, is far from clear.

Conclusions

At least three things may contribute to the success of an organochlorine insecticide like aldrin in the soil. It is toxic to many insect pests; it is less readily inactivated than many other insecticides by adsorption on the mineral fraction of soil; it has great persistence.

The factors that govern persistence and adsorption of insecticides in soil are not fully understood. Most work has been done with insecticides of widely differing structures, and further studies are needed on how adsorption and decomposition are affected by altering a single substituent of a molecule at a time.

Until now, the testing of soil insecticides has largely been empirical. In such tests diethyl organophosphorus compounds seem to have given better results than dimethyl organophosphates or carbamates against wheat-bulb fly, wireworms and possibly frit fly. By analogy with Harris's work this may be because these materials, like aldrin, are not strongly inactivated by the mineral fraction of soil, but there is no reason to think they would not be adsorbed by organic matter. Diethyl organophosphorus compounds are likely to be less soluble and less volatile than their dimethyl analogues: they may also be less easily hydrolysed, and so have some advantage where moderate persistence in soil is required. Although individual ones differ widely in their toxicity to mammals, diethyl organophosphorus compounds are more toxic to mammals than their corresponding dimethyl analogues [168], but if they work better than dimethyl compounds in soil this disadvantage may have to be tolerated to control certain soil-borne pests.

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