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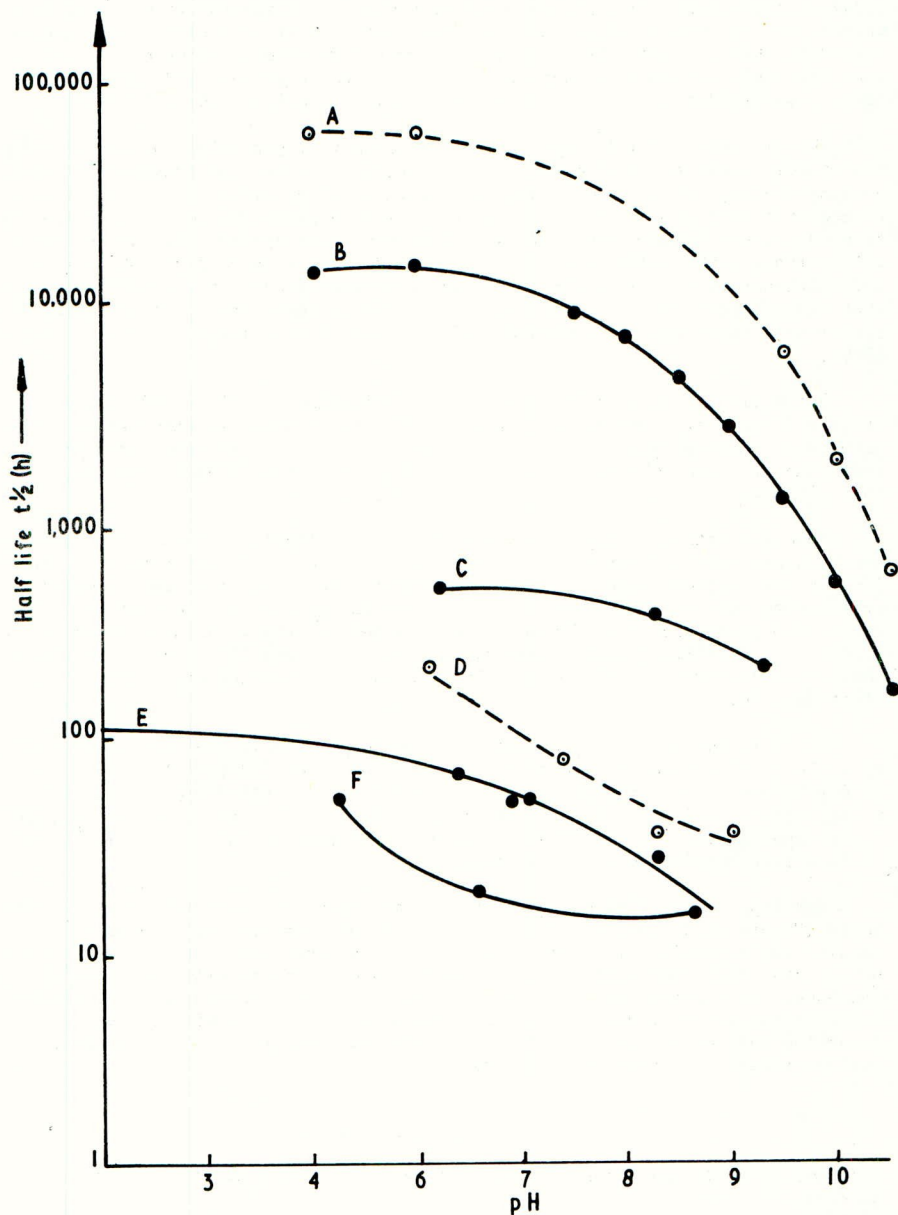
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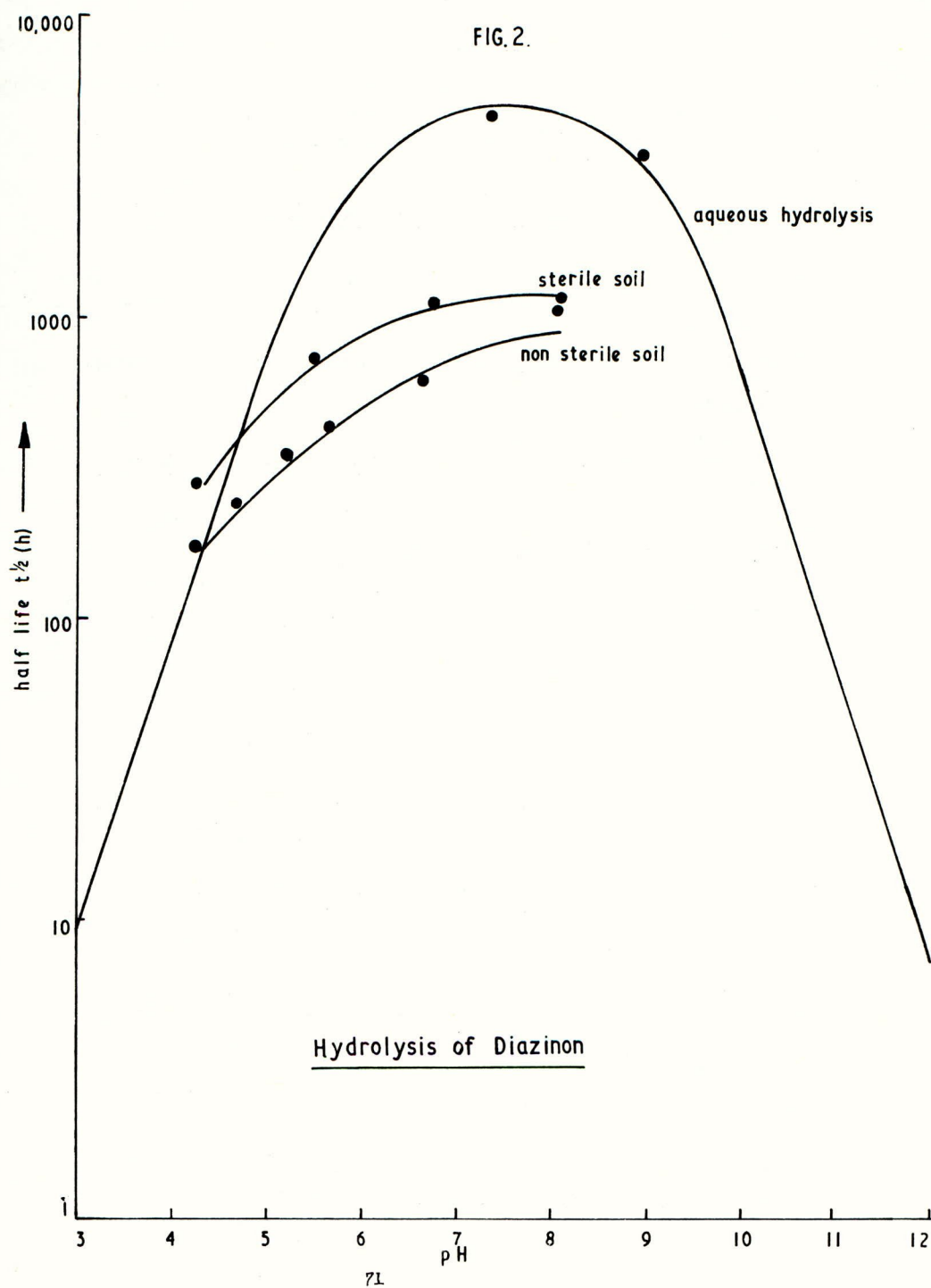
**FIG.1**

Hydrolysis of Methyl Parathion ●—● and Parathion ○—○



A and B, aqueous hydrolysis. C, hydrolysis on sterile soil.  
D and E, hydrolysis on non sterile soil  
F, hydrolysis on ion-exchange resin.

FIG. 2.



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ADSORPTION OF ORGANOPHOSPHORUS COMPOUNDS BY SOIL  
CONSTITUENTS AND BY SOILS

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Summary Isotherms are presented for the adsorption of dimefox by four soils, by humic acid, and by clays, and for the adsorption of menazon by preparations of montmorillonite. Three additional model compounds and a variety of techniques were used to investigate the mechanisms by which certain classes of organophosphorus compounds interact with clays. The practical implications of the results are briefly discussed.

Résumé On présente des isothermes pour l'adsorption du dimefox par quatre sols, par l'acide humique, et par des argiles, ainsi que pour l'adsorption du menazon par des préparations de montmorillonite. Trois autres substances modèles et une variété de techniques furent employées pour la recherche des mécanismes qui entrent en jeu dans l'interaction entre les argiles et certaines classes de composés organophosphorés. On discute brièvement les incidences pratiques de ces résultats.

INTRODUCTION

Adsorption and desorption are among the most important processes determining the effectiveness of soil applied pesticides. It is generally agreed that the organic and inorganic colloidal materials are the most active of the soil constituents for binding (and hence inactivating) such pesticides.

Although application of physico-chemical techniques can yield much information on the overall interactions between any particular soil and pesticide, they fail, because of the complexity of the soil system, to show clearly the adsorption mechanisms involved. The modern approach therefore studies interactions between pesticides and pure clay and extracted humic preparations. In extrapolating this approach to soil systems it should be remembered that soils contain a mixture of clays many of which are interstratified, often coated with humic materials and with oxides and hydroxides of iron and aluminium. Therefore increased emphasis is being placed on studies on soil clay (with and without associated coatings) - organic chemicals interactions.

Organophosphorus compound-soil interactions have not been extensively studied. However, data by Graham-Bryce (1967) on the adsorption of disulfoton by a wide range of soils, and by MacNamara and Toth (1970) for the adsorption of malathion on soils, clay minerals, and organic matter have significantly advanced understanding in this field and have provided many ideas for the research described here.

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This paper will describe the adsorption of dimefox ( $\text{N N N}'\text{N}'$ -tetramethylphosphorodiamidic fluoride) by selected soils, by clay isolated from one of these soils, by humic acid, and by well defined clay preparations. Data from a variety of techniques will give indications about the mechanisms of interactions between clays and menazon ( $\text{S}$ -[4,6-diamino-1,3,5-triazin-2-ylmethyl]dimethyl phosphorothiolothionate), three model compounds which are not used as pesticides, and, by inference, organophosphorus compounds in general.

## METHOD AND MATERIALS

Dimefox and menazon were supplied by the Murphy Chemical Co. Ltd., and by I.C.I., Plant Protection Ltd., respectively. The three model compounds used,  $\text{O,O}$ -diethylmethylphosphonate (I),  $\text{O}$ -ethyl- $\text{S}$ -ethyl methylphosphonothionate (II), and  $\text{O,O}$ -diethyl-2-(diethylamino) ethylphosphonate (III) are illustrated in Fig. 1.

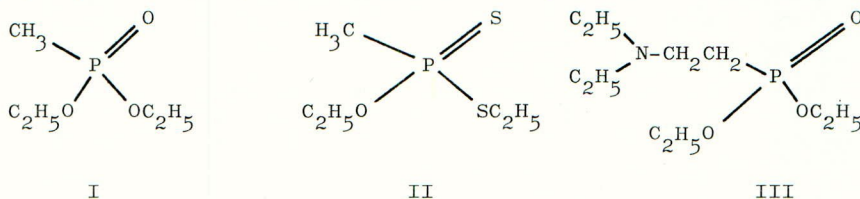


Fig. 1

Model organophosphorus compounds used in research.

### Soils and clay and humic acid preparations

Some characteristics of the soils used, as supplied by the Rothamsted Experimental Station, are presented in Table 1.

Table 1  
Soils used in adsorption studies

Soil	Clay Content (%)	Organic Carbon (%)	CEC (meq $100\text{g}^{-1}$ )	pH
Adventurers	28	40.0	170.0	7.3
Brome Pin	12	1.2	10.7	7.7
Prick Willow	68	13.7	85.4	6.5
YNYS	36	1.0	7.1	4.3

In cases of montmorillonite (No. 26, Clay Spur, Wyoming) and vermiculite (near Libby, Montana) clays, samples of  $<2\mu\text{m}$  equivalent spherical diameter were used. Homoionic clays were generally prepared by using the appropriate chloride salts, as described by Barshad (1969). Hydrogen ion saturated montmorillonite (hereafter called  $\text{H}^+/\text{Al}^{3+}$ -montmorillonite) was obtained by passing the ground clay suspension (20 g in 1.0l) down a column (160  $\text{cm}^3$ ) of Amberlite 1R-120 ( $\text{H}^+$ -form) resin. The eluate was freeze dried.

Humic acids were extracted with 0.5N sodium hydroxide from H<sup>+</sup>-saturated Fenland soil (80% organic matter), and precipitated by stepwise addition of concentrated HCl to pH 1.0. This precipitate was washed with distilled water, then dialyzed against distilled water at 4°C for five days, and the retentates were freeze-dried.

#### Adsorption experiments

Adsorption from aqueous solution was determined by the conventional slurry technique, or by the Continuous Flow (Diaflo) procedure described by Grice and Hayes (1972) and by Grice *et al.* (1973). Previously (Grice and Hayes, 1972), it had been noted that sedimentation of adsorbent on the membrane of the Continuous Flow cell caused some anomalies in the adsorption isotherms obtained from this technique. For the experiments described here, a very fine stainless steel wire mesh was placed over, and in intimate contact with, the Pellicon PSAC membrane [supplied by Millipore (U.K.) Ltd., Millipore House, Abbey Road, Park Royal, London, NW10 7SP], and the magnet which rested on this mesh was vigorously agitated to prevent adsorbent sedimentation and concentration polarisation at the membrane surface.

#### Analytical procedures

Aqueous solutions of dimefox (24  $\mu$ l aliquots) were analysed by gas liquid chromatography (g.l.c.). A 5ft x 0.25in glass column, packed with S.E. 30 (10%) liquid phase on a Universal Support material (60-85 mesh size), was used in a Perkin Elmer F11 Chromatograph equipped with a series 900, dual, flame ionisation/halogen - phosphorus specific detector. An oven temperature of 110°C was standardised and employed with the appropriate (Perkin-Elmer setting 2 $\frac{1}{2}$ ) injection block temperature. Hydrogen (17 lb in<sup>2</sup>) and air (25 lb in<sup>2</sup>) pressures were as recommended by the makers. There was a gradual variation in response of the detector, and this was overcome by taking into account the response for standard samples injected after every third application of unknown.

Polarography was used to measure the equilibrium solution concentrations of menazon. Samples (0.5 cm<sup>3</sup>), in Britton Robinson buffer (5.0 cm<sup>3</sup>, pH 6.0), gave a sharp peak at a reduction potential of 1.217 mV. In order to measure decomposition in solution, an aqueous menazon solution was monitored over a 16 day period and hydrolysis was estimated at less than 2% per day.

#### Thermoanalytical investigations

Adsorbate-clay complexes were formed by adsorbing the appropriate organophosphorus compound from the vapour phase or from solution in n-hexane. Thermogravimetry (TG) and derivative thermogravimetry (DTG) studies employed the Perkin-Elmer TGS-1 Thermobalance, and a Perkin-Elmer DSC-1B Calorimeter was used in differential scanning calorimetry (DSC) work. Experimental details are given by Lundie (1971), and will also be presented in later publications.

#### X-ray diffraction studies

Dimefox was adsorbed from aqueous solution on Na<sup>+</sup>-montmorillonite and the sample was then formed into an orientated disc. Compounds I, II, and III were adsorbed from the vapour phase or from solution in



n-hexane onto the appropriate montmorillonite preparations. Diffraction data were obtained by means of a Picker Powder Diffractometer with smoothed KV and mA stabilized CuK $\alpha$ -radiation (36KV and 20 mA).

#### Infrared spectroscopy

Spectra of liquid samples were obtained from thin films (between sodium chloride discs) by use of a Perkin-Elmer, Model 457, Infrared Spectrophotometer. For spectra of powdered samples (20mg, prepared by adsorbing compound I from solution in n-hexane onto the appropriate clay preparation) the Model TR 25 Multiple Attenuated Total Reflection (MATR) attachment was used. All spectra were scanned from 4000 - 600  $\text{cm}^{-1}$ .

#### Calorimetric studies

Adsorbents (250-1000mg) were suspended in 25  $\text{cm}^3$  of n-hexane at 30°C. Solutions of I, II, and III in n-hexane (0.5  $\text{cm}^3$  of ca.  $1 \times 10^{-1} \text{M}$  solution in each case) were sealed separately in 1.0  $\text{cm}^3$  glass vials. The separate reactions were initiated by breaking the vials, and allowing adsorbent and adsorbate to equilibrate in an LKB Precision Calorimeter. Experimental and calculation procedures, as described by Wadsö (1966), were followed. In separate experiments, the amounts of adsorbate adsorbed were measured by g.l.c. Enthalpy changes were expressed in terms of heat evolved  $\text{mole}^{-1}$  of compound adsorbed. An LKB Batch Microcalorimeter was used in some experiments, and the technique employed was similar to that of Hayes *et al.* (1972).

### RESULTS AND DISCUSSION

#### Adsorption of dimefox by humic acid, soils and montmorillonite clay

Isotherms for the adsorption of dimefox by nine adsorbents are presented in Fig. 2. Some of these data have been presented already (Grice and Hayes, 1972), but the new stirring procedure used in the Diaflow cell has made it possible to produce more accurate data for the isotherms in this instance. Isotherms 1,4,5,6,7,8, and 9 (Fig. 2) were obtained by the Diaflow procedure, and the solid lines are extrapolated, as broken lines, to the vertical axis. The procedure used to obtain the data involved the collection of 2 $\text{cm}^3$  fractions by means of a syphon device, and analysis of each fraction was carried out by g.l.c. Volumes of the fractions were not sufficiently reproducible to allow confident analysis of the data below an equilibrium solution concentration of 0.005g 100g $^{-1}$ . Taking into consideration the data available, and the errors inherent in it at the low concentrations, we feel that the extrapolations indicated (broken lines, Fig. 2) give a fair representation of the shapes of the isotherms for the adsorption of dimefox on the different adsorbents. Continuous monitoring of the eluent concentrations would largely offset the difficulties experienced. There is good reason to believe that the isotherms presented are of the high affinity type, except perhaps in the cases of 1,2, and 3 (isotherms 2 and 3 were obtained by slurry technique).

It can be seen that the most extensive adsorption took place on  $\text{H}^+$ -humic acid. Langmuir and inverse Langmuir plots, using the data available from the solid line of isotherm 9 (Fig. 2) gave adsorption capacities of 30.7 and 33.3g, respectively for monolayer coverage per 100g of humic acid. A Courtauld atomic model of the dimefox molecule indicated that it occupied a space with dimensions 5.75 x 6.76 x 8.50Å. The maximum area occupied by the dimefox molecule was thus 57.375Å $^2$ .

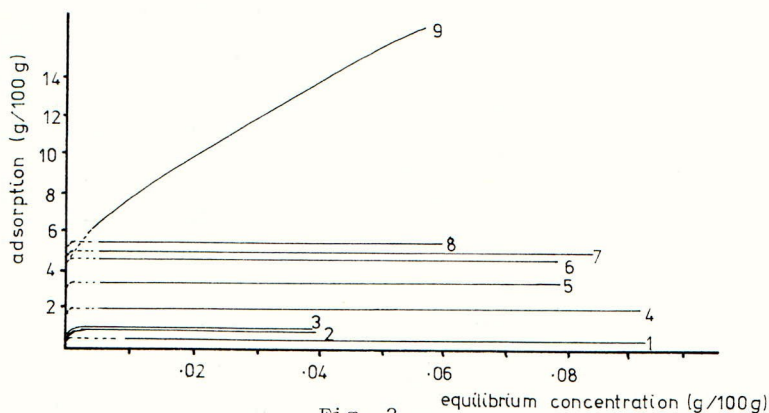


Fig. 2

Isotherms for the adsorption of dimefox by:

1, Brome Pin soil; 2,  $\text{Na}^+$ -kaolinite; 3,  $\text{Na}^+$ -illite; 4, Adventurers soil; 5, Prick Willow soil; 6, Clay extracted from YNYS soil; 7,  $\text{Na}^+$ -montmorillonite; 8, YNYS soil; 9,  $\text{H}^+$ -humic acid.

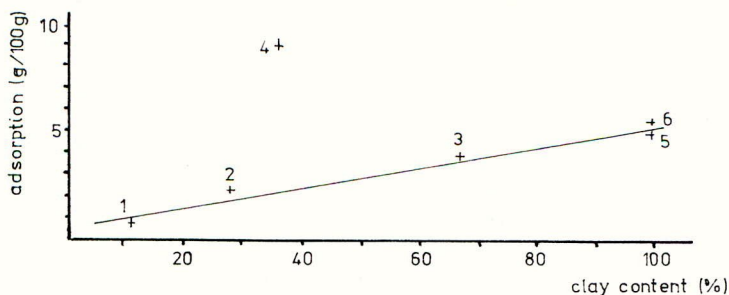


Fig. 3

Correlation with clay contents for the adsorption of dimefox on 1, Brome Pin; 2, Adventurers; 3, Prick Willow; 4, YNYS, 5, Clay extracted from YNYS; 6,  $\text{Na}^+$ -montmorillonite.

Combination of this value with that of  $33.3\text{g } 100\text{g}^{-1}$  gives a surface coverage area of  $747\text{m}^2\text{g}^{-1}$  for dimefox on  $\text{H}^+$ -humic acid. This agrees with quoted data for the surface area of such compounds. Because dimefox could be expected to be protonated at the pH of the medium (pH 3.5) it is reasonable to expect that ion-exchange was responsible for some of the adsorption observed. This aspect is being researched further.

There was, however, no correlation between adsorption of dimefox and the organic matter contents of the soils studied. Extents of adsorption, as shown in Fig. 3, correlated with soil clay contents (except in the case of YNYS), and also with adsorption by  $\text{Na}^+$ -montmorillonite.

It can be seen that the adsorption of dimefox by the clay extracted from the YNYS soil was of the order which might be predicted from the correlation data in Fig. 3. No satisfactory explanation is available at this time for the anomalous adsorption behaviour of the YNYS soil although the high adsorption capacity of this soil might be

attributable to the presence of colloidal amorphous materials such as allophanes.

DSC failed to differentiate between the desorption of water and dimefox adsorbed on  $\text{Na}^+$ -montmorillonite. From adsorption isotherm and microcalorimetry data the  $\Delta H$  of adsorption was estimated at  $-15.0$  to  $-17.5 \text{ KJ mole}^{-1}$  of dimefox adsorbed, and this range agreed well with the value of  $-14.6 \text{ KJ mole}^{-1}$  obtained from treatment of the isotherm data by the method of Joyner *et al.* (1947). These data point to the involvement of weak attraction forces, such as van der Waals forces, in the adsorption mechanisms.

#### Adsorption of menazon by montmorillonite preparations

Isotherms for the adsorption of menazon by  $\text{Na}^+$ -montmorillonite and by  $\text{H}^+/\text{Al}^{3+}$ -montmorillonite are presented in Fig. 4. It is clearly evident that the latter adsorbent had the higher affinity for the adsorbate.

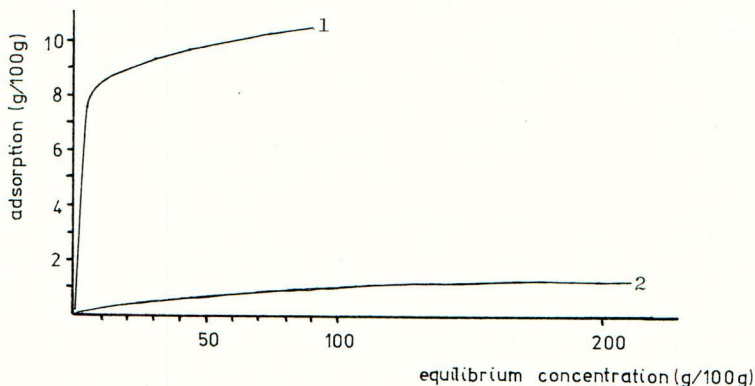


Fig. 4

Adsorption of menazon by: 1,  $\text{H}^+/\text{Al}^{3+}$ -montmorillonite; 2,  $\text{Na}^+$ -montmorillonite.

A  $\text{pK}_a$  value of 4.4 was determined polarographically for menazon, and the pH values for  $\text{Na}^+$ - and  $\text{H}^+/\text{Al}^{3+}$ -montmorillonite suspensions (0.1g in 25  $\text{cm}^3$  water) were 8.7 and 4.1, respectively. These data suggest that the triazine ring in the menazon molecule was protonated in the more acid medium, and was then adsorbed as the charged species.

Microcalorimetry studies gave  $\Delta H$  adsorption =  $-11.3 \text{ KJ mole}^{-1}$  adsorbed for the menazon- $\text{Na}^+$ -montmorillonite system. The enthalpy of adsorption was constant for all points on the isotherm. This indicates that the same mechanism of adsorption operated over the entire range, and points to the involvement of weak specific attraction forces, such as van der Waals forces, between adsorbent and adsorbate. In the case of the menazon- $\text{H}^+/\text{Al}^{3+}$ -montmorillonite system the enthalpy of adsorption was constant ( $\Delta H = -25.9 \text{ KJ mole}^{-1}$  adsorbed) for amounts of menazon adsorbed greater than  $2 \text{ g } 100 \text{ g}^{-1}$  of clay. However, the average enthalpy value  $\text{mole}^{-1}$  adsorbed for amounts less than  $1 \text{ g } 100 \text{ g}^{-1}$  was  $-81 \text{ KJ}$ . Thus highly energetic attraction forces were involved at



organophosphorus compound with iron and aluminium impurities, or chemical interaction with any iron and aluminium oxides and hydroxides deposited on the clay surface. The value  $\Delta H = -25.9 \text{ KJ mole}^{-1}$  adsorbed, for the higher levels of adsorption, suggests the involvement of processes such as ion exchange, hydrogen bonding, or non-specific charge-dipole interactions in the adsorption mechanism.

#### Interactions of model organophosphorus compounds with clays

Compound I was chosen because it is aliphatic, has a relatively low molecular weight, and because it does not contain readily ionizable functional groups. Compound II was chosen in order to examine the effects of the thiophosphoryl and ethylthio functional groups on adsorption, and compound III was chosen because it contains a triethylamine group instead of the methyl group in I.

DSC, TG, and DTG techniques were used to study the desorption of I from powdered glass,  $\text{K}^+$ -kaolinite, pyrophyllite,  $\text{Ca}^{2+}$ - and  $\text{H}^+/\text{Al}^{3+}$ -montmorillonite preparations. DTG indicated that desorption from glass powder was of zero-order, and that the attractive forces between glass and adsorbate were no stronger than the organophosphate-organophosphate interactions. Material desorbed at less than  $128^\circ\text{C}$  from  $\text{K}^+$ -kaolinite were held at energies approximately equivalent to that held by glass. This indicates that some multilayer adsorption had taken place. From results with DSC it was calculated that the energy required to desorb the surface layer of I from  $\text{K}^+$ -kaolinite was  $50 \text{ KJ mole}^{-1}$  adsorbed. By the same technique the activation energy for desorption of this compound from pyrophyllite was estimated at  $54 \text{ KJ mole}^{-1}$ .

Thermoanalytical analysis indicated the presence of three different sites for the adsorption on I on  $\text{Ca}^{2+}$ -montmorillonite. The energy required to desorb the compound from the external surface was the same as that for pyrophyllite, and an activation energy of  $67 \text{ KJ mole}^{-1}$  was calculated for desorption from the interlamellar surfaces. However, the strongest interaction was shown to take place between the phosphoryl group of I and the calcium ion located in the interlamellar spaces. From DTG analysis it was shown that the amount of I desorbed in the  $300\text{--}400^\circ\text{C}$  range corresponded to two molecules of organophosphate per interlamellar calcium ion, and the energy required to remove the adsorbate, co-ordinated in this way, amounted to  $137 \pm 10 \text{ KJ mole}^{-1}$ . A lowering, by  $25 \text{ cm}^{-1}$ , of the frequency of the infrared absorption band of the phosphoryl group (when I was adsorbed on clay) had indicated the involvement of dipole-charge interactions between this group and the exchangeable calcium ions on the clay. X-ray diffraction data had shown that adsorption of I caused an interlattice expansion of  $12.7\text{\AA}$ . This indicates that a bimolecular layer of adsorbate, "sandwiching"  $\text{Ca}^{2+}$  ions, was formed in the interlamellar regions.

The DTG curve for the  $\text{I-H}^+/\text{Al}^{3+}$ -montmorillonite complex had similar features to that for the  $\text{Ca}^{2+}$ -montmorillonite system.

Reaction calorimetry was used to compare the integral enthalpy ( $\Delta H_i$ ) values for the adsorption, from solution in *n*-hexane, of the three model compounds ( $5 \times 10^{-5}$  moles in each case) by  $\text{Ca}^{2+}$ -montmorillonite (0.5g, containing 19% by weight of water). The Gibbs free energy change was calculated from the equation  $\Delta G = -RT \ln C_s f_s / C_f$ , where  $C$  and  $C_s$  were the concentrations in solution and on the adsorbate surface, respectively, and  $f_1$  and  $f_s$  were the respective activity

coefficients, assumed to be unity. Entropy changes ( $\Delta S$ ) were obtained from:  $\Delta G = \Delta H_1 - T\Delta S$ ; where  $T$  is the absolute temperature.

Results are summarised in Table 2. It should be remembered that the integral enthalpy values take into account the total energy changes in the system, and the  $\Delta H$  value for the adsorption of the appropriate organophosphorus (OP) compound will be lowered by the amount of energy required to displace the water initially present on the adsorbent surface.

Table 2

$\Delta G$ ,  $\Delta H_1$  and  $\Delta S$  values for adsorption of model compounds by  $\text{Ca}^{2+}$ -montmorillonite

Compound Formula	No.	$\Delta H_1$ , KJ mole <sup>-1</sup>	$\Delta G$ , KJ mole <sup>-1</sup>	$\Delta S$ , j°K <sup>-1</sup>
(EtO) <sub>2</sub> P(O)CH <sub>3</sub>	I	-34.0	-23.5	-34.4
(EtO)(EtS)P(S)CH <sub>3</sub>	II	- 3.2	-13.4	+40.3
(EtO) <sub>2</sub> P(O)CH <sub>2</sub> CH <sub>2</sub> NEt <sub>2</sub>	III	-50.0	-23.5	-75.6
(EtO)(EtS)P(O)CH <sub>3</sub>	IV	-27.7	-10.1	-58.8

Compound IV is introduced in Table 2 because the thermodynamic data given for it, when compared with those for compound I, provide an evaluation of the effects on the thermodynamics of adsorption of substituting the -SEt for the -OEt group. It can be seen that the  $-\Delta H_1$  values for II and IV are less than that for I. The larger value for the phosphoryl (compared with the thiophosphoryl) compound can be attributed to the greater polarity of the phosphoryl group which allows stronger coordination between this compound and the interlamellar calcium ions. Similarly, the polarity of the phosphoryl group was lowered by substituting -OEt for -SEt (compare I and IV), and the effect of this is reflected in the appropriate  $-\Delta H_1$  values for adsorption.

Substitution of  $\text{>PS}$  for  $\text{>PO}$  and of one -SEt for one -OEt group gave striking differences between the  $\Delta S$  values for the adsorption of I and II by  $\text{Ca}^{2+}$ -montmorillonite. These changes reflect the differences in the interactions between the two compounds and the solvent, *n*-hexane. The less polar molecule will have the higher affinity for the solvent.

X-ray diffraction showed that monomolecular layers of compounds I, II and IV were interlamellarly adsorbed. In the case of III, however, three molecular layers were adsorbed in the interlamellar spaces of  $\text{Ca}^{2+}$ -montmorillonite. The increased reactivity of this compound can be attributed to the co-operative contribution to adsorption of the tertiary amine group. Co-ordination between the phosphoryl groups and interlamellar calcium ions is almost certainly involved in the adsorption mechanism. A simple model of the conformations adopted by this compound in the interlamellar spaces would have two of the three molecular layers lying on the internal surfaces of the clay lattice, and co-ordinated with calcium through the phosphoryl groups (pointing outwards into the interlamellar space). The middle layer need only share co-ordination with a calcium ion already co-ordinated with one of the surface adsorbed molecular layers.



## GENERAL CONCLUSIONS

H<sup>+</sup>-humic acid was shown to have a high affinity for dimefox, and the mechanisms of adsorption in this instance were thought to include a contribution from cation-exchange processes. At the pH of agricultural soils, however, the dimefox molecule would not be expected to be protonated, and clays were shown to have a greater affinity for this molecule than did the organic matter content of the soils used. In general it would appear that soil clays will have a higher affinity than soil organic matter for polar aliphatic OP compounds. However, the possibility of strong interactions between these compounds and mineral oxides and hydroxides in soils is recognised. Co-ordination of the >PO and >PS functional groups with interlattice mineral cations will provide the strongest binding mechanism for soil clay-OP interactions (in the absence of oxide and hydroxide coatings on the clay surfaces). S containing OP compounds will be less strongly bound by soil clays than their O containing analogues.

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## NOTES

A SIMPLE RELATIONSHIP BETWEEN SOIL ADSORPTION OF ORGANIC  
CHEMICALS AND THEIR OCTANOL/WATER PARTITION COEFFICIENTS

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Summary The adsorption of un-ionised organic chemical by four Rothamsted soils, expressed as soil organic matter/water partition coefficients ( $Q$ ), is related to their octanol/water partition coefficients ( $P$ ) by  $\log Q = 0.524 \log P + 0.618$ . A similar relationship exists between  $P$  and  $R_f$  values on soil thin layers. Good prediction of soil behaviour of organic chemicals can be obtained using mobility classes based on octanol/water partition coefficients.

Résumé L'adsorption des produits chimiques organiques non-ionisés par quatre sols de Rothamsted, exprimée par les coefficients de partage entre la matière organique du sol et l'eau ( $Q$ ), a rapport à leurs coefficients de partage entre l'octanol et l'eau ( $P$ ) par l'expression  $\log Q = 0.524 \log P + 0.618$ . Un rapport semblable existe entre  $P$  et les valeurs  $R_f$  sur des couches minces du sol. On peut obtenir une bonne prédiction du comportement des produits chimiques organiques dans le sol en utilisant des classes de mobilité fondées sur les coefficients de partage entre l'octanol et l'eau.

INTRODUCTION

The correlation between adsorption of un-ionised organic compounds by soil and the soil's organic matter content is well established. Several attempts have been made to predict adsorption by soils by relating the organic matter/water partition coefficient, ( $Q$ ), to the parachor (Lambert 1967, Hance 1969) or free energy substituent constants within related series of compounds (Briggs 1969). In practice, these relationships need to be determined for each series of compounds and they cannot be simply applied to a wide range of chemical structures. This paper reports a relationship between  $Q$  and octanol/water partition coefficients that can be easily and widely used.

Previous work has shown that adsorption by soils can be related systematically to chemical structure and supports the hypothesis that organic matter behaves like an organic 'solvent' (Lambert 1967). If it does then equation 1, found by Collander (1950), which relates partition between one organic solvent and water and a second organic solvent and water should hold, as Lambert (1968) has suggested, when organic matter/water is one of the solvent pairs.

$$\log P_1 = a \log P_2 + b \quad (1)$$



## RESULTS

This hypothesis was tested using average values of  $Q$  determined as previously described (Briggs 1969) on four Rothamsted soils for 30 chemicals with a wide range of polarities and values of  $P$ , the octanol/water partition coefficient, either taken from the literature (Leo *et al* 1971) or determined spectrophotometrically (Fujita *et al* 1964). Octanol/water was chosen because of its wide use as a model for biophases in correlations between biological activity and chemical structure. Equation 2 gave a good fit to the data ( $r^2 = 0.84$ ).

$$\log Q = 0.524 (\pm 0.048) \log P + 0.618 (\pm 0.113) \quad (2)$$

A similar test of the hypothesis can be applied to results obtained from soil thin-layer chromatography if it is assumed that relative mobility on the plates is governed only by adsorption on soil organic matter as the stationary phase. The Martin and Synge (1941) equation may then be written:

$$\log (1/R_f - 1) = \log Q + \log A_s / A_m \quad (3)$$

For a given soil  $A_s$  and  $A_m$ , the cross-sectional areas of the organic phase and water phase, are constants and substituting for  $\log Q$  from equation 1 gives equation 4 where  $P$  is again the octanol/water partition coefficient.

$$\log (1/R_f - 1) = a \log P + \text{constant} \quad (4)$$

Frontal  $R_f$  values for 25 un-ionised pesticides on Hagerstown soil from Maryland U.S.A. were taken from Helling and Turner (1968), Helling (1971 a,b,c) and Helling *et al* (1971). The regression line is:

$$\log (1/R_f - 1) = 0.517 (\pm 0.022) \log P - .951 (\pm 0.075) \quad (5)$$

The slope is almost the same as that in equation 2 as it should be if organic matter from different soils behaves relatively uniformly as an adsorbing surface. Where comparable values of  $Q$  are available they are similar for soils from England, Europe and North America despite obviously different origins and probable differences in the detailed chemical structure of the soil organic matter. The close similarity of the slopes of equations 2 and 5 indicates that  $\log P$  and equation 2 can be used to give an estimate of  $Q$  that is widely applicable. It is interesting that the slopes are similar to the average value (0.55) found by Leo *et al* (1971) in equations relating  $\log P$  to the partition of organic compounds onto a number of biological macromolecules.

## DISCUSSION

Helling and Turner (1968) divided pesticides into five mobility classes based on  $R_f$  values on Hagerstown soil (2.5 per cent organic matter) and Helling (1971c) concluded that this classification adequately described behaviour in 14 soils containing 1-8 per cent organic matter, a range common to most agricultural soils.  $R_f$  values for a given compound decreased as organic matter content increased; however the range of  $R_f$  used to define the mobility class on Hagerstown soil was wide enough to cover most of the soils examined. Using equation 5 these mobility classes can be defined in terms of  $\log P$  and  $Q$ .



Class	Rf	log P	Q
Immobile	0 - 0.09	> 3.78	> 398
Low	0.10 - 0.34	3.78 - 2.39	398 - 74
Intermediate	0.35 - 0.64	2.39 - 1.36	74 - 29
Mobile	0.65 - 0.89	1.36 - 0.08	29 - 4.5
Very mobile	0.90 - 1.00	< 0.08	< 4.5

The mobility class from the above table or the approximate values of Q from equation 2 can readily be obtained for new compounds or possible soil metabolites either using log P values from the review by Leo *et al* (1971), calculated using Hansch's  $\pi$  constant, (Fujita *et al* 1964) or a simple experimental determination. Many  $\pi$  constants in the literature are derived from the phenoxyacetic acid series where electronic effects of substituents are small; in a series such as the phenylureas where P is very sensitive to electronic effects, experimental values of P, which include these effects, predict Q much better than calculated values.

Three examples illustrate the use of the octanol/water partition coefficient to predict behaviour of three different types of compound in soil.

The herbicide 2,6-dichlorothiobenzamide is converted in soils to 2,6-dichlorobenzonitrile which in turn is hydrolysed to 2,6-dichlorobenzamide (Beynon and Wright, 1972). Using the value for an aliphatic amide (because of steric inhibition of resonance), calculated values of log P are 2.3, 3.0 and 1.3 and indicate mobility classes of 'intermediate', 'low' and 'mobile' for the thioamide, nitrile and amide. This agrees well with field observations. Calculated values of Q are 66, 155 and 20 and experimental values are 57, 135-165 and 5-15 (Beynon and Wright, 1972; Briggs 1968).

The oxime carbamate insecticide aldicarb is rapidly oxidised in soil to the sulphoxide. Experimental values of log P of 0.8 and -0.7 classify the parent compound as 'mobile' and the metabolite as 'very mobile' which is the leaching behaviour observed in practice (Goring, 1972).

The polychlorinated biphenyls, important environmental contaminants are a third example of a different structural type, whose behaviour in soil has not been closely examined. The experimental value (Leo *et al*, 1971) of log P for biphenyl itself is 4.0 so that it would be classed as immobile in soil. The bulk of the material in commercial PCB samples contains more than 3 chlorine atoms per molecule and has a calculated log P > 6. Extensive metabolism would have to occur before any leaching in soil would be expected.

Octanol/water partition coefficients provide a good prediction of soil behaviour using equation 2 and the mobility classes derived from it. Organic matter in soils has similar properties to the humic materials in lakes, streams and rivers so that a good indication of the likely redistribution in the environment by water transport of un-ionised compounds from any source can also be obtained from a single measurement or calculation.

#### Acknowledgements

I thank Drs. N. F. Janes, K. A. Lord and I. J. Graham-Bryce for helpful discussions and criticism.

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COMPUTATIONS ON SOIL FUMIGATION WITH METAM-SODIUM

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Summary Soil fumigation with metam-sodium was simulated with computer models. The influence of rate of conversion of metam-sodium on the dose pattern for methyl isothiocyanate was checked. Equations and solutions are given for simultaneous vapour diffusion and leaching. In a series of simulations, the effect on dose pattern was traced of a period of rainfall soon after fumigation.

Résumé La désinfection du sol avec du métam-sodium a été simulée à l'aide des modèles mathématiques. L'effet de la vitesse de transformation du métam-sodium sur les doses de methyl isothiocyanate obtenues a été vérifié. Des équations et des solutions adéquates décrivant le transport du composé par diffusion dans la phase gazeuse et par convection avec la phase liquide ont été données. Dans une série de calculs par ordinateur, l'effet de précipitation quelque jours après la fumigation a été simulé.

INTRODUCTION

In late years there is an increasing interest in metam-sodium, particularly for possible use in large-scale fumigation in arable farming against plant-parasitic nematodes. The desired characteristics of such applications are: effectiveness at low rates, low cost of the chemical, inexpensive techniques of application with the usual injection apparatus, only a short period with risk of after-effects and minimum consequences for the environment. In the past, results with metam-sodium were very variable and occasionally there were prolonged after-effects. This indicated that understanding of soil behaviour of the active compound was inadequate so that the selected soil conditions and application techniques were not optimum.

A detailed study on the behaviour of metam-sodium and the active conversion product methyl isothiocyanate was thus necessary. Data on the conversion rates and on the distribution of methyl isothiocyanate over the phases in soil were determined in the laboratory (Smelt and Leistra, 1973). Computation models were developed starting from those made for the behaviour of the isomers of 1,3-dichloropropene in soil (Leistra, 1971, 1972). Several modifications and extensions were made and assumptions had to be checked for the particular metam-sodium situation. The computation models were checked with detailed field experiments including measurement of soil physical characteristics and gas chromatography of methyl isothiocyanate concentrations (Leistra et al, 1973; Smelt et al, 1973). After testing, the combination of computation models and

basic data can be used to simulate soil fumigations. Suitable tools are then obtained to make quantitative predictions on effectiveness and after-effects under a wide variety of conditions (Leistra and Smelt, 1973; Leistra, 1973b).

On this occasion attention is concentrated on the lay-out of the computation models as adapted and extended for metam-sodium. Illustrations are given for some typical situations.

#### The standard computation model

By far the majority of farmers and contractors apply fumigant with horizontal-blade and plough injectors, so the initial distribution is in a plane. Injection depth is usually about 18 cm. The area density of methyl isothiocyanate formed ( $M_{init}, \mu\text{g cm}^{-2}$ ) is calculated from the volume of metam-sodium solution per area (recommended rate 400 l./ha), the concentration of metam-sodium (usually 0.38 kg/l.), the fraction that is converted to methyl isothiocyanate (about 0.92), and the molecular weights of precursor and fumigant. On the basis of measured soil physical characteristics, the profile is divided into, for example, 5 layers: 3 above and 2 below the injection level. The soil profile is further divided into computation compartments of, for example, 2 cm thickness and concentrations are computed for points in the middle of these compartments. Compartment thickness,  $\Delta x$ , is selected in such a way that a suitable arrangement over the layers is obtained, with which transitions between layers coincide with computation points. However, another selection of compartment arrangement is possible (Leistra, 1972).

Values are assigned to temperature-dependent quantities like the diffusion coefficient of methyl isothiocyanate in air,  $D_a$ , the water/gas phase distribution ratio,  $K_w/g$ , the decomposition rate constant,  $k_r$ , and for each of the soil layers the value of the soil/gas phase distribution ratio,  $K_s/g$  (Smelt and Leistra, 1973). Next the values of the soil physical characteristics for each layer are introduced including bulk density,  $\rho_b$ , volume fraction of the water phase,  $\epsilon_w$ , volume fraction of the gas phase,  $\epsilon_g$ , and the estimated quotient  $D_p/D_a$ , where  $D_p$  is the coefficient for diffusion of methyl isothiocyanate through the gas-filled pore system in soil. These estimates of  $D_p/D_a$  are obtained from literature data and from experience with dichloropropene (Leistra, 1972). A convenient quantity is the fumigant capacity factor,  $\phi$ , for the concentration in the gas phase,  $C_g$ , defined as  $\phi = \epsilon_g + \epsilon_w K_w/g + \rho_b K_s/g$ . This capacity factor connects the concentration of fumigant in the whole soil,  $Q$ , with  $C_g$ :  $Q = \phi C_g$ .

The differential equation for fumigant vapour diffusion in heterogeneous soil systems (Leistra, 1971) is

$$\partial(\phi C_g)/\partial t = \partial(D_p \partial C_g / \partial x) / \partial x \quad (1)$$

The change in soil conditions with position and time is expressed in the position and time dependence of the coefficients  $\phi$  and  $D_p$ .

To get a suitable distribution of methyl isothiocyanate concentrations over the grid points at the start of the numerical computations, an analytical solution for diffusion from an instantaneous plane source (Leistra, 1971) can be used, provided the rate of formation is not restrictive. The time,  $t_{anal}$ , for which this distribution is calculated is confined to the period in which only the two layers around the injection depth are important for the diffusion and is usually about a day. Because decomposition rates of methyl isothiocyanate in soils are rather high, the amount,  $M_{anal}$ , for which this distribution is calculated is obtained with:  $M_{anal} = M_{init} \exp(-k_r t_{anal})$ . The comparatively low resistance to upward diffusion, for example after injection with a blade injector results in a fraction of 2/3 to 3/4 that diffuses upwards in the initial period.



The numerical solution for Equation 1 is obtained by conversion into an explicit difference equation. The first-order forward difference in time is combined with the second-order central difference in space (Smith, 1969). For heterogeneous systems the following difference equation is obtained:

$$C_g(i,j+1) = r_{dm}(i) C_g(i-1,j) + r_d(i) C_g(i,j) + r_{dp}(i) C_g(i+1,j) \quad (2)$$

In this, the computation factors for diffusion alone,  $r_d$ , are:

$$\begin{aligned} r_{dm}(i) &= D_{pm}(i) \Delta t / (\phi(i) (\Delta x)^2) \\ r_{dp}(i) &= D_{pp}(i) \Delta t / (\phi(i) (\Delta x)^2) \\ r_d(i) &= 1 - r_{dm}(i) - r_{dp}(i) \end{aligned}$$

The subscript m refers to the range between  $x(i-1)$  and  $x(i)$  while p as second subscript refers to the range between  $x(i)$  and  $x(i+1)$ .

The numerical computations start with the assessment of the time step,  $\Delta t$ , that can be used. This time step is limited because the highest value for the quotient  $D_p(i) \Delta t / [\phi(i) (\Delta x)^2]$  in a soil profile should be smaller than 0.5. The value of  $\Delta t$  is strongly influenced by the prevailing soil conditions and usually a value in the range 0.1-0.5 day can be taken. The computed diffusion and capacity characteristics for the layers are arranged over the compartments. At the transitions between layers, average capacity factors are taken. For each period with constant conditions, the computation factors have to be computed only once, so the computations in the dynamic section are as simple as possible. The concentration at the soil surface is set at zero, the methyl isothiocyanate being immediately removed by wind. The lower boundary is mostly taken at about 50 cm depth and the nature of the condition here depends on the local situation. The ultimate value of  $C_g(i,j+1)$  at time  $t(j+1)$  is obtained by taking account of decomposition during  $\Delta t$  by multiplication by the factor  $\exp(-k_r \Delta t)$ .

One of the objects of the computations is to obtain the cumulative concentration-time product [dose,  $ct(i,j)$ ] for methyl isothiocyanate in the water phase at various depths. For this integration the trapezium rule can be used

$$ct(i,j+1) = ct(i,j) + 0.5 \Delta t K_{w/g} [C_g(i,j) + C_g(i,j+1)] \quad (3)$$

The computation of concentrations and doses are repeated until the time arranged for output, for example for comparison with measured concentrations of methyl isothiocyanate. If conditions are constant, computations can be continued with the same computation factors till concentrations are very low.

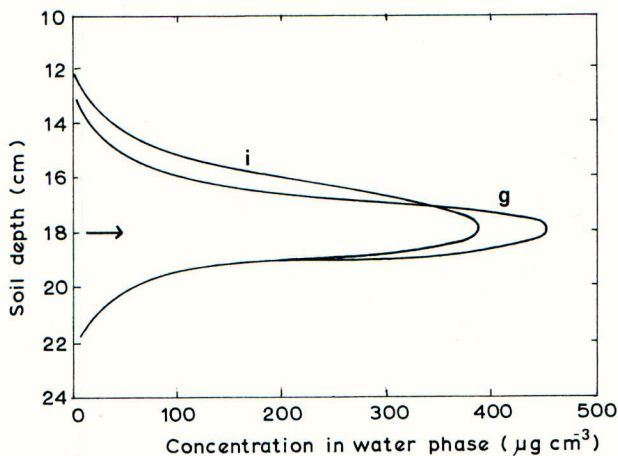
Changes in the conditions with time are introduced according to need and as far as available basic data permits. First the fumigant concentrations in whole soil are computed for each of the compartments. With changes in temperature, new values have to be set for a number of quantities:  $D_a$ ,  $K_{w/g}$ ,  $K_s/g$  and  $k_r$ . If soil moisture or structure change, new values should be set for  $\epsilon_w$ ,  $\epsilon_g$ , and the quotient  $D_p/D_a$ . New capacity factors,  $\phi(i)^{new}$  are calculated and if necessary a new time step taken. The computation factors,  $r_d$ , per point have to be calculated again. The concentrations with which the new period starts are:

$$C(i,j)^{new} = Q(i,j) / \phi(i)^{new}.$$

#### Effect of rate of formation of methyl isothiocyanate

Conversion of metam-sodium to methyl isothiocyanate takes some time and this may have some effect on diffusion patterns. In a modified computer model, the analytical starting solution was replaced by a section describing gradual formation of methyl isothiocyanate. A first-order rate equation was used:  $dM_p/dt = -k_{rp} M_p$ . The area density of precursor,  $M_p$ , is expressed in methyl isothiocyanate equivalent ( $\mu g \text{ cm}^{-2}$ ) and  $k_{rp}$  is the first-order conversion rate constant. It was assumed that the value of  $k_{rp}$  was  $3.0 \text{ day}^{-1}$ , which means that 95% of the metam-sodium applied was converted after one day, when the total amount of methyl isothiocyanate was formed. In the computations, the first day

Fig. 1 Computed distribution of methyl isothiocyanate in the profile one day after injection of metam-sodium into humic sand soil.  
i = instantaneous plane source;  
g = gradual formation.



was divided into ten time steps. The area density of methyl isothiocyanate,  $\Delta M$ , formed per time step,  $\Delta t$ , is:  $\Delta M = [1 - \exp(-k_{rp} \Delta t)] M_p$ , where  $M_p$  is the area density of precursor at the beginning of the time step. At each time step  $\Delta M$  was introduced in a computation compartment of 2 cm thickness around the injection depth.

The concentrations after one day computed for a moist humic sand soil (pF 2.0) at 15°C are given in Fig. 1. As could be expected, concentrations near the injection depth are higher with the gradual conversion than with the instantaneous source. Continuation of the computations with the two starting distributions showed that the position of the dose line (e.g. Fig. 2) near the soil surface was hardly 0.2 cm lower after the gradual formation. Because the conversion rate in the example was lower than found for most soils and conditions (Smelt and Leistra, 1973), both approaches for the initial period may be used. The introduction of gradual conversion might be more relevant with precursors like dazomet, with a slow conversion under some conditions.

Fig. 1 shows that after one day distribution in the profile of methyl isothiocyanate is still restricted. This illustrates the slow diffusion in the humic sand soil if at the wet side of the favourable range.

#### Diffusion and leaching

With many soils, more than half the amount of methyl isothiocyanate is present in the water phase (Smelt and Leistra, 1973). With rainfall, leaching may thus be an important process. With some extension and modification, leaching may be built into the computation model described.

A differential equation that can be used for the description of simultaneous diffusion and leaching of fumigants in soil is

$$\frac{\partial Q}{\partial t} = \frac{\partial}{\partial x} \left( D_p \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial x} \left( D_{disp} \frac{\partial C}{\partial x} \right) - v \frac{\partial C}{\partial x} \quad (4)$$



There is a convective transport caused by a water flux,  $v$ , resulting from the difference between precipitation and evaporation at the soil surface. An important associated spreading phenomenon is hydrodynamic dispersion represented by the coefficient  $D_{disp}$ . The equation is simplified by changing over to one dependent variable,  $C_g$ , and by combination of the coefficients for the spreading processes into one coefficient  $D_{spr}$ . With the relations  $Q = \phi C_g$  and  $C_w = K_w/g C_g$ , the equation becomes

$$\partial(\phi C_g)/\partial t = \partial(D_{spr} \partial C_g / \partial x) / \partial x - v K_w/g \partial C_g / \partial x \quad (5)$$

To approach the value for the coefficient of hydrodynamic dispersion for the fumigant in the water phase, the following relation can be used:  $D_{disp} = DISP \cdot v$ . The factor  $DISP$  is the dispersion distance which assumes a value of, for example, 1 cm for soils under leaching conditions (Frissel et al, 1970). The expression of the spreading coefficient in the considered system is:  $D_{spr} = D_p + DISP \cdot v K_w/g$ .

Conversion of Equation 5 into an explicit difference equation gives

$$C_g(i, j+1) = r_{dlm}(i) C_g(i-1, j) + r_{dl}(i) C_g(i, j) + r_{dlp}(i) C_g(i+1, j) \quad (6)$$

The computation factors for diffusion plus leaching,  $r_{dl}$ , are

$$\begin{aligned} r_{dlm}(i) &= D_{sprm}(i) \Delta t / [\phi(i) (\Delta x)^2] + v K_w/g \Delta t / (\phi(i) \Delta x) \\ r_{dlp}(i) &= D_{sprp}(i) \Delta t / [\phi(i) (\Delta x)^2] \\ r_{dl}(i) &= 1 - r_{dlm}(i) - r_{dlp}(i) \end{aligned}$$

With compartments in computations on convective transport, a pseudo-spreading is introduced. The value of the pseudo-spreading coefficient,  $D_{spr}^{pseudo}$ , with respect to the concentration in the water phase can be approached with:  $D_{spr}^{pseudo} = v \Delta x / 2$  (Goudriaan, 1973; Leistra, 1973a). In the computations, only a net spreading coefficient has to be added:  $D_{spr}^{net} = D_p + DISP \cdot v K_w/g - v K_w/g \Delta x / 2$ .

#### Effect of rainfall on dose pattern

One of the possible applications of the computation model involving vapour diffusion and leaching is to simulate the effect of rainfall on the dose pattern. In a series of computations, injection of 400 l. of metam-sodium solution (0.38 kg/l.) was simulated for a humic sandy soil. Soil moisture was on the wet side (pF about 2.0) of the favourable range. Details are given in Table 1. In the standard case, conditions were kept constant throughout fumigation. The computed dose pattern for methyl isothiocyanate in the water phase is given in Fig. 2. At 50  $\mu g \text{ cm}^{-3}$  day, nematode mortality is presumably high.

In the next run, injection under the same conditions was simulated but there was a total rainfall surplus of 20 mm on the second and third day. The situation was simulated by taking in this period a constant percolation rate and a higher moisture content in the layers 0-28 cm (pF about 1.5). After the third day, moisture content in the layers 0-28 cm was lowered to the original values and that of the layer 28-60 cm was set higher for three days. From the sixth day onwards, moisture condition in the entire profile corresponded again with pF 2.0. The two most significant phenomena, percolation and temporary increase in moisture content, were thus allowed for, though in a simplified way. In a third run, rainfall on the fifth and sixth day after injection was simulated in the same way.

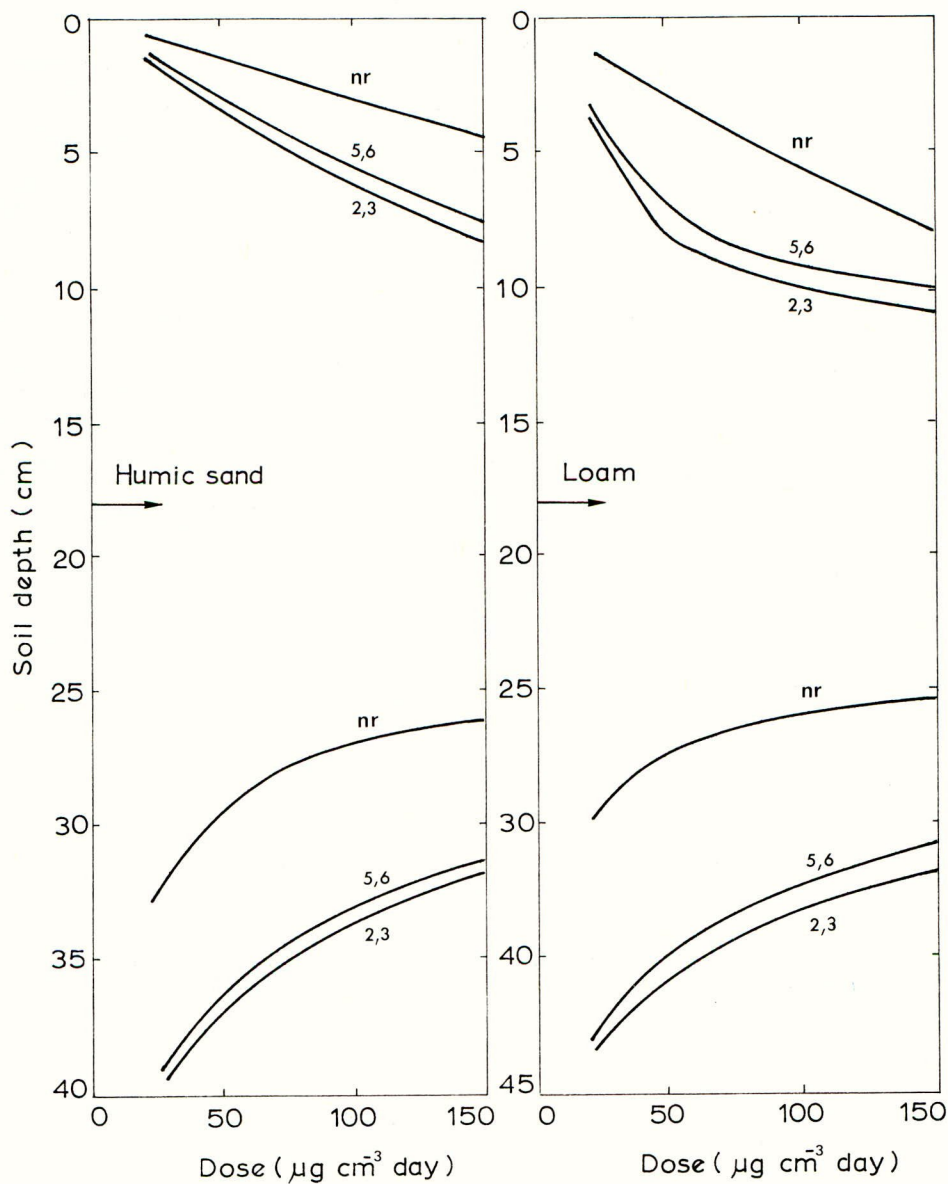
In Fig. 2, the dose patterns for the different situations are given. As a result of the rainfall, the dose patterns are clearly displaced downwards. The displacement shows most clearly at the lower end and amounts to about 7 cm for the most important range of concentration. At the top of the profile, displacement is somewhat less because the soil surface acts as a sort of turning-point

Table 1

Soil physical properties with diffusion and distribution characteristics for methyl isothiocyanate

Soil type, temperature, pF	Decomp. rate constant (day <sup>-1</sup> )	Layer (cm)	Organic matter content (g g <sup>-1</sup> )	Bulk density (g cm <sup>-3</sup> )	Water phase (cm <sup>3</sup> cm <sup>-3</sup> )	Gas phase (cm <sup>3</sup> cm <sup>-3</sup> )	D <sub>p</sub> /D <sub>a</sub>		K <sub>s</sub> /g	Capacity factor (cm <sup>3</sup> cm <sup>-3</sup> )
							approx. range	estim. value		
Humic sand, 15°C, pF 2.0	0.06	0- 8	0.050	1.25	0.31	0.20	0.02-0.06	0.040	42	120
		8-18	0.050	1.30	0.33	0.16	0.01-0.04	0.025	42	126
		18-28	0.040	1.45	0.33	0.10	0.01	0.007	34	121
		28-60	0.020	1.55	0.26	0.14	<0.03	0.015	17	83
Humic sand, 15°C, pF 1.5	0.06	0- 8	0.050	1.25	0.36	0.15	0.01-0.03	0.020	42	130
		8-18	0.050	1.30	0.38	0.11	0.01	0.010	42	137
		18-28	0.040	1.45	0.38	0.06	<0.01	0.004	34	131
		28-60	0.020	1.55	0.31	0.09	0.01	0.008	17	93
Loam, 15°C, pF 2.0	0.11	0- 8	0.023	1.10	0.30	0.25	0.04-0.10	0.070	9.5	76
		8-18	0.023	1.25	0.34	0.14	<0.03	0.020	9.5	85
		18-28	0.021	1.35	0.35	0.09	0.01	0.007	8.7	87
		28-60	0.021	1.30	0.34	0.12	<0.02	0.015	8.7	85
Loam, 15°C, pF 1.5	0.11	0- 8	0.023	1.10	0.33	0.21	0.02-0.07	0.045	9.5	82
		8-18	0.023	1.25	0.38	0.10	0.01	0.015	9.5	94
		18-28	0.021	1.35	0.39	0.05	<0.01	0.005	8.7	96
		28-60	0.021	1.30	0.38	0.08	0.01	0.010	8.7	93

Fig. 2 Dose pattern computed for methyl isothiocyanate in the water phase after injection of metam-sodium into humic sand soil and loam soil, respectively.  
 nr = no rainfall; 2,3 = rainfall on second and third day;  
 5,6 = rainfall on fifth and sixth day after injection.





for the dose pattern. The spreading of the concentration pattern after one day is rather limited, so leaching in the earlier period caused a large proportion of the fumigant to be leached into the denser layer below the level of injection.

The same series of simulations was carried out for a loam soil, with a lower adsorption and a higher decomposition rate (Smelt and Leistra, 1973). Details of soil properties and interaction characteristics are given in Table 1. The computed dose patterns are represented in Fig. 2. In the standard case, the top centimetres of the profile were badly disinfected and activity at 30 cm depth was very poor. Fumigation under somewhat drier conditions would have resulted in a much better dose pattern (Leistra and Smelt, 1973). With this soil type too, rainfall caused a substantial displacement of the dose pattern. The effect is even stronger with the loam soil than with the humic sand soil. As a result of the lower adsorption and the higher decomposition rate, the dose pattern at the top is even more unfavourable. The greater extent of leaching is partly offset at some decimetres depth by the greater part of the fumigant being decomposed near the injection depth.

### GENERAL DISCUSSION

A further step has been taken to describe fumigant behaviour in soil quantitatively with the development of computation models. Although a number of simplifying assumptions are made, the importance of various aspects of methyl isothiocyanate behaviour in soil can be traced. Differences in the rate of conversion of metam-sodium to methyl isothiocyanate in the practical range are not very important.

Under rather wet conditions, methyl isothiocyanate is easily leached over several centimetres and this will reduce its effectiveness. In practice, there are several other complicating factors. Under rather wet conditions, horizontal distribution of fumigant will be very irregular, so its effectiveness is less than the average dose line would indicate. Further, low concentrations presumably contribute little to the effective dose so that the flatter dose lines are even more unfavourable. A limited amount of rain after injection into a drier soil will be less unfavourable for the effect in the top layer, particularly if methyl isothiocyanate is spread to a considerable extent. A main effect is then the increase in moisture content in the top layer accompanied by a decrease in diffusion rate (Smelt et al, 1973).

The same computation model can be used to estimate leaching of fumigant residues in the winter season. Residues of methyl isothiocyanate can be leached over several decimetres and contamination of ground and surface water is thus possible. Only with application under somewhat drier conditions in the period up to early autumn is the risk of leaching out of the profile very small. The rather low diffusion rate and the high decomposition rate then favour elimination in the top of the profile.

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## NOTES



FUNGICIDAL CONTROL OF WINTER WHEAT FOLIAGE DISEASES

IN FRANCE

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Summary Trials started in 1970 showed that it is possible to control foliage diseases on winter wheat with fungicides such as benomyl, benomyl + mancozeb or methylthiophanate + maneb. The best results were obtained after treatments during stem extension and flowering or, more often, at both stages. The experimentation in progress will allow us to measure the risk for wheat in each region in order to know precisely the conditions in which fungicide application will be profitable.

Résumé L'expérimentation réalisée sur le blé tendre d'hiver depuis 1970 a mis en évidence la possibilité de limiter les dégâts provoqués sur cette culture par les maladies fongiques grâce à l'utilisation de produits fongicides tels que le benomyl et les mélanges mancozèbe + benomyl ou manèbe + méthylthiophanate. Les résultats les plus intéressants ont été observés à la suite d'applications réalisées, soit courant montaison soit en fin épiaison, soit, le plus souvent, successivement à ces deux époques. L'expérimentation en cours doit permettre d'étudier localement les risques encourus par la céréale, afin de préciser les conditions dans lesquelles il est opportun d'intervenir compte tenu du coût des traitements.

INTRODUCTION

Fungicidal control of cereal foliage diseases has been possible for a long time only with seed-dressing. This seems to be an excellent treatment against seedborne diseases such as damping-off, bunt and loose smut but it does not protect wheat from diseases which infect after seed germination. New systemic fungicides which can be sprayed onto the foliage appeared on the market in 1972 and made it possible for farmers to protect the plant during the whole growing season. These new chemicals can also be used as seed-dressings, but the yield advantage has appeared to be best following spray application.

The aim of the trials done by the "Institut Technique des Céréales et des Fourrages" since 1970 is : (a) to measure the importance of damage caused by foliage diseases on yield and on grain quality, (b) to compare the efficiency of treatments performed at different growth stages of wheat.

Treatment was carried out against many fungus diseases and not against one in particular. Many different diseases were generally found in the same plot and it was difficult to foresee which would be dominant in each case.

## METHODS AND MATERIALS

From 1970 to 1972, 103 trials have been carried out on winter wheat with the following chemicals (doses kg/ha a.i.) benomyl (0.3) ; benomyl (0.3) + mancozeb (2) ; methylthiophanate (1) + maneb (2) ; mancozeb (2). The materials were applied at the following stages (Feekes-Large scale) : erect (stage 5) ; stem extension, last leaf just visible (stage 8) ; flowering (stage 10.5) ; repeated applications in same plots at stages 5 and 8 ; 5 and 10.5 ; 8 and 10.5.

The main varieties used were : Capitole (27 trials) ; Hardi (13 trials) ; Champlain (12 trials) ; Joss (7 trials) ; 26-10 (3 trials). The trials were situated in the main region of wheat production in France.

The diseases observed were :

- Foot rot : eyespot (*Cercospora herpotricoides*) ; brown foot rot (*Fusarium* spp.)
- On leaves and heads : leaf spot (*Septoria* spp.) ; ear blight (*Fusarium* spp.) ; mildew (*Erysiphe graminis*) ; yellow and brown rust (*Puccinia* spp.).

## RESULTS

### 1. Effect of the treatments on yield and quality of wheat

Table 1

Overall yield increases obtained after two fungicide treatments  
growth stages 8 and 10.5 with benomyl + mancozeb

Year	No. of trials	Yield of control plot t/ha	Yield increase t/ha	% increase
1970	21	4.870	0.350	7
1971	42	4.800	0.510	11
1972	40	5.750	0.580	10

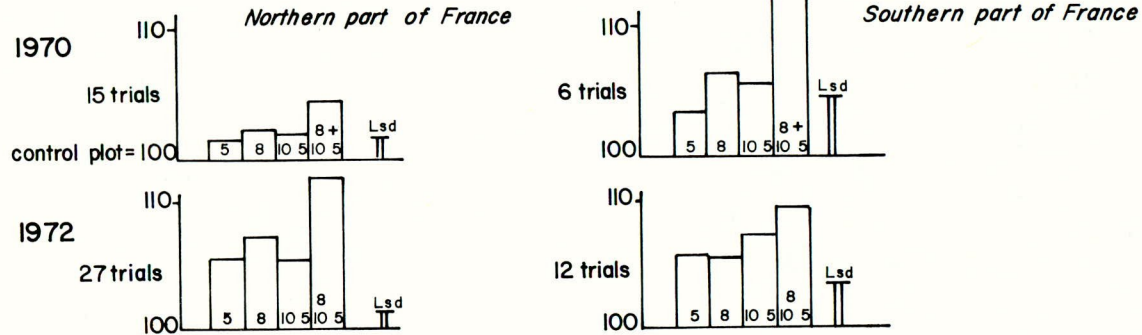
The overall yield increases shown in Table 1 following treatment with benomyl and mancozeb at growth stages 8 and 10.5, were due mainly to the increase of 1000 grains weight and, sometimes, in the number of heads. They show the favourable effect of fungicides on migration of dry matter in the host and give an idea of the minimum damage caused by the diseases.

These trials also made it possible to compare different kinds of fungicides. Benomyl used alone at flowering (stage 10.5) gave a yield increase of 180 kg/ha whereas the mixture benomyl + mancozeb gave 320

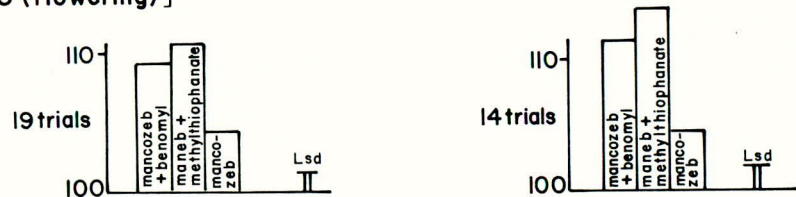
Fig.1

Winter wheat : effect on yield of different foliage treatments performed in 1970, 1971 and 1972 (% of control plots)

- 1) Comparison between benomyl + mancozeb applications at different wheat growth stages in 1970 and 1972 (Feekes-Large scale)



- 2) Comparison between chemicals [1971 applications at stages 8 (stem extension) and 10-5 (flowering)]





kg/ha increase (average of 40 trials in 1972). Mancozeb usually gave a lower yield gain than that obtained with systemic fungicides (Fig. 1-2°). The activity of systemic fungicides increases when they are mixed with chemicals such as mancozeb.

Comparison between treatments given at different stages of plant growth is shown in Fig. 1-1°. Two periods in particular seem to be favourable for treatment : (a) during stem extension, from the beginning of stem extension till the boot stage ; this treatment is effective against foot-rot and diseases of the first leaves ; (b) at flowering ; this treatment is successful against foliage and head diseases. Plant protection is well ensured with repeated applications at these two growth stages. Nevertheless it is possible to obtain partial protection using one of these treatments.

## 2. Profitability of treatments

An example of the cost of treatments is shown in Table 2

Table 2

### Costs of fungicide treatments

	1 treatment	2 treatments
Loss due to wheelings	25 F	25 F
Cost of chemicals	109 F	218 F
Cost of treatment	20 F	40 F
<hr/>		
Total cost	Francs 154 F	283 F
	Kg 310 kg	570 kg
	(100 kg = 50 F)	

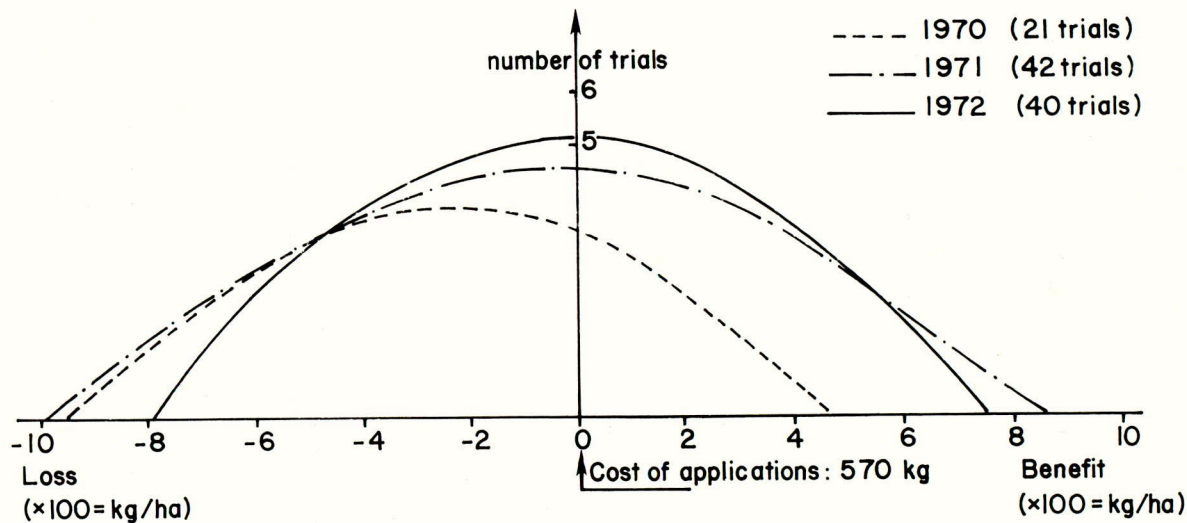
Fig. 2 shows that the yield increase may be important but that it is also variable. For the last three years the yield increase in many cases has not repaid the cost of treatment because of the present high cost of systemic fungicides. It is therefore necessary to specify the risk before deciding on the most suitable treatment. At present it is not possible to prove any precise correlation between yield loss and disease level. The risk can only be determined through investigation of the different factors which are favourable to the diseases.

### a) Influence of site and year

Fig. 1 shows that the yield increase after treatment differs according to site and climate. The benefit of treatment did not differ from year to year in the south part of France whereas, in the north, it was

Fig. 2

Profitability of treatments on winter wheat (benomyl + mancozeb)  
applied during stem extension (8) and at flowering (10-5)



ineffective in 1970 but beneficial in 1971 and 1972. The losses caused by disease in 1971 may be explained by the very dry and warm period in the beginning of July. In contrast, in 1972, the early attack of eyespot and brown foot-rot was favoured by a mild winter which seemed to be of great importance.

b) Influence of soil type

Table 3 shows that in 1971 and particularly in 1972, the yield increase was higher on light than on heavy soils.

Table 3

Yield increase on heavy and light soils following benomyl + mancozeb treatment at growth stages 8 and 10.5

Yield increase (kg/ha)		
Clay content	1971	1972
> 12.5 %	470 (16 trials)	530 (16 trials)
< 12.5 %	530 (16 trials)	660 (18 trials)

c) Influence of previous crop

In the same trials the yield increase was higher when the previous crop was wheat or maize than when it was not a cereal, eg. potatoes, beet or rape (Table 4).

Table 4

Influence of previous crop on yield increase following benomyl + mancozeb treatment at growth stages 8 and 10.5

Yield increase (kg/ha)		
Previous crop	1971	1972
Potatoes, beet, rape	450 (15 trials)	470 (11 trials)
Wheat or maize	580 (17 trials)	610 (26 trials)



#### d) Influence of varieties

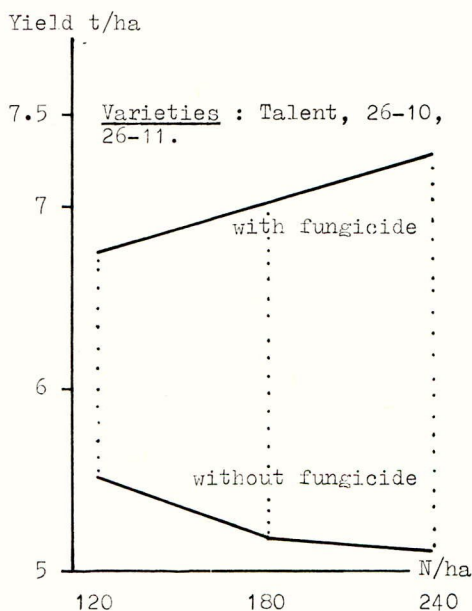
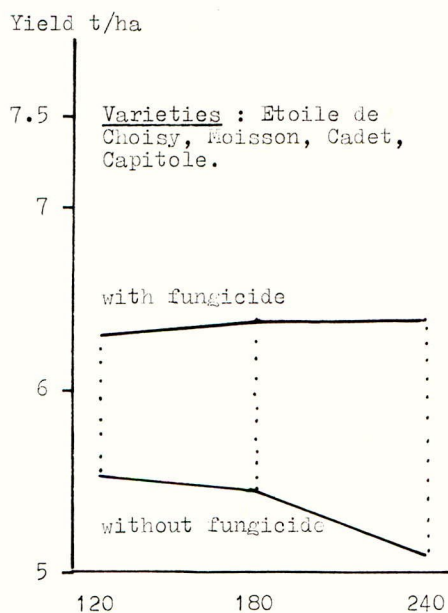
Trials on winter wheat in 1972 showed that certain varieties such as Joss, Talent, 26-10 and 26-11 gave a yield increase of 950 kg/ha to 1140 kg/ha, whereas varieties such as Hardi, Capitole and Champlain gave an increase of only 730 kg/ha to 860 kg/ha.

#### e) Influence of nitrogen

The incidence of fungicide treatments was studied in 1972 on 7 varieties with 3 different rates of nitrogen : 120, 180 and 240 units (Fig. 3). In these trials, the yield of each variety declined as the rate of nitrogen increased. In the presence of the fungicide, this phenomenon was not observed and it was possible to distinguish two groups of varieties : those which did not gain in yield with an increasing nitrogen rate (Etoile de Choisy, Moisson, Capitole, Cadet) and those which did increase in yield with an increasing nitrogen rate (Talent, 26-10 and 26-11).

Fig. 3

Influence of fungicide treatments with variable nitrogen rate on different varieties of winter wheat (average of 4 trials situated in the southern part of France)



## DISCUSSION

Fungicide treatments on wheat foliage promote yield increases and also have a favourable influence on grain quality. However, in the current economical situation such treatment cannot be advised as a matter of course and it is necessary to study the different factors which influence the gravity of diseases before deciding on treatment. The conditions most likely to cause a yield decrease seem to be the following : a dry climate at the end of the vegetative period (southern part of France and on light soils in the northern part) - poorly drained soils - mild winter (favourable for foot-rot spread) - when the previous crop is a cereal - when the variety is sensitive to the diseases - when nitrogen supply is at a high level - when minimum tillage is practised, leaving crop debris on the surface.

According to the risk, the grower has to choose between the four following possibilities : (a) no treatment ; (b) one treatment during stem extension which is mainly effective against foot-rot diseases ; (c) one treatment at flowering which protects the late leaves and the heads ; (d) two treatments, during stem extension and at flowering. These two treatments give the most regular and largest yield increases but, even when the risk is at its highest, one treatment only is more economical in many situations.

Fungicide treatment of wheat foliage should not be systematic but there are still many problems concerning specific recommendations in each situation (for example, the behaviour of each variety, the economical dosage of chemicals). Another problem is deciding whether to treat or not. At present it is difficult to foresee the benefit of treatment in each single case but the experimentation now in progress should allow us to draw up a map of the losses caused by disease.

If it does become possible to protect cereals against disease by the use of fungicides, this could raise many questions concerning crop rotation, cultivations, choice of varieties, sowing dates and fertilizer rates. Indeed, following the use of fungicides, it is not certain that current agricultural techniques will remain the most satisfactory, both from a technical as well as an economic point of view.

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THE EFFECT OF TRIDEMORPH ALONE AND IN MIXTURES WITH OTHER FUNGICIDES

ON DISEASES OTHER THAN ERYSIPIHE GRAMINIS

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Summary Tridemorph, in addition to controlling cereal powdery mildew, Erysiphe graminis, has a marked effect against certain other cereal pathogens. Tridemorph applied either alone or in mixture with metiram, has given good control of Puccinia striiformis (yellow rust) on wheat and barley. Treatment of wheat with a mixture of tridemorph and metiram reduced levels of Septoria nodorum (glume blotch).

Tridemorph applied to barley reduced levels of Rhynchosporium secalis (leaf blotch), while an improved effect was obtained with a mixture of tridemorph and carbendazim.

Résumé Les essais au champ ont montré qu'en plus du contrôle de l'oidium des céréales, Erysiphe graminis, le tridemorphe avait un effet marqué contre certains autres agents pathogènes des céréales. Le tridemorphe appliqué soit seul, soit en mélange avec le metiram, a donné un bon contrôle de Puccinia striiformis (rouille jaune) sur blé et sur orge. Le traitement du blé avec un mélange de tridemorphe et de metiram diminuait le taux de Septoria nodorum (septoriose sur glume).

Le tridemorphe appliqué sur orge diminuait le taux de Rhynchosporium secalis (rhynchosporiose sur feuille) et par ailleurs un meilleur effet a été obtenu avec le mélange de tridemorphe et de carbendazim.

INTRODUCTION

Since the detection of the fungicidal activity of tridemorph and other N-alkyl substituted 2,6-dimethylmorpholines, numerous experiments have been reported showing the effectiveness of tridemorph against cereal powdery mildew. Jung and Bedford (1971) and Evans and Hawkins (1971) have described work carried out in England with tridemorph against cereal powdery mildew.

During the course of some of these investigations, it was observed that tridemorph had an effect against diseases other than Erysiphe graminis i.e. Puccinia striiformis, Puccinia recondita, Septoria nodorum, Rhynchosporium secalis.

In 1972 and 1973 some of these effects have been investigated further.



## METHODS AND MATERIALS

In all trials a randomised block design with four replicates was used. Plots measured 4m x 12.5m or 15m. Treatments were applied with a Van der Weij knapsack sprayer fitted with cone nozzles. Tridemorph was applied at 0.52 kg a.i./ha. Carbendazim was applied at the rates stated. Metiram (Zineb-polyethylene thiuram-disulphide complex) was applied at 1.6 kg a.i./ha. All sprays were applied in 250 l/ha water.

### Formulations

- Tridemorph - 75% a.i. w/v emulsifiable concentrate
- Carbendazim - 50% wettable powder (BAS 3460F)
- Metiram - 80% wettable powder

Disease assessments were made using the appropriate key from the Guide for the Assessment of Cereal Diseases devised by the Plant Pathology Laboratories, Harpenden. Cereal growth stages are expressed using the Feekes-Large scale (Large, 1954).

Trials were harvested using a "Hege 125" small plot combine or Claas Compact 25 combine.

## RESULTS

### Wheat

#### Puccinia striiformis (yellow rust)

Results from a trial carried out in 1971 indicated that tridemorph had a marked effect against yellow rust (P. striiformis). The figures for disease control and the effect on grain weight are presented. (Table 1)

Table 1

The effect of tridemorph applied to winter wheat (cv. Joss Cambier)  
on levels of P. striiformis and grain weight

Treatment	% disease level on flag leaf		Thousand grain wt. (g)
	at GS 10.1	at GS 10.5	
Untreated	3.60	20.4	45.5
Tridemorph	0.42	5.8	47.4

Tridemorph was applied at GS 9 when infection was present on the lower leaves, but not on the flag leaf.

Observations indicated that the effect of tridemorph was mainly curative; pustules appeared to dry up within 5 days of application. In trials carried out in 1972 the effect of tridemorph was again recorded and yields following tridemorph application were significantly higher than in untreated plots (Table 2).

Table 2

The effect of tridemorph applied to winter wheat (cv. Joss Cambier)  
on levels of *P. striiformis* and yield at two sites (A and B)

Treatment	% disease level on flag leaf at GS 10.5		Yield kg/ha	
	A	B	A	B
Untreated	12.5	68	4167	3534
Tridemorph	2.5	47	<u>5071</u>	4067
Standard error <sup>+</sup>			96	408

In Trial A, application was made at G.S. 10 where the flag leaves were free of yellow rust, and in Trial B, application was at G.S. 10 with 10-15% infection on the flag leaf.

Septoria nodorum (glume blotch) and Puccinia recondita (brown rust)

In further trials carried out in 1973 with a mixture of tridemorph and metiram, effects against *S. nodorum* (glume blotch) and *P. recondita* (brown rust) were observed. (Tables 3 and 4)

Table 3

The effect of an application of tridemorph plus metiram on foliar and ear  
diseases and yield of winter wheat (cv. Maris Nimrod) at GS. 9 (25/5/73)

Assessment (% infection at GS. 10.5 - 26/6/73)		Untreated	Treated	s.e. <sup>+</sup>
Septoria nodorum	- ear	22.5	17.5	
Septoria nodorum	- flag leaf	21.0	11.0	
Puccinia striiformis	- flag leaf	5.0	1.75	
Puccinia recondita	- flag leaf	2.5	1.0	
Green tissue	- flag leaf	26.0	40.0	
Senescence *		45.5	46.25	
Yield (kg/ha)		5034	<u>5687</u>	209

\* Senescence which could not be directly related to any of the diseases present.

Table 4

The effect of an application of tridemorph plus metiram to  
winter wheat (cv. Maris Ranger) at GS 10.3 (8/6/73)

Assessment (% infection at GS 11.1 - 12/7/73	Untreated	Treated
Erysiphe graminis - ear	10.6	2.5
Erysiphe graminis - flag leaf	1.25	0.5
Erysiphe graminis - 2nd leaf	16.25	5.0
Septoria nodorum - flag leaf	4.37	1.5
Septoria nodorum - 2nd leaf	46.25	18.75

Barley

Puccinia striiformis (yellow rust)

In 1973, severe infections of yellow rust were recorded in some winter barley crops. Applications of tridemorph plus metiram gave marked reductions in disease levels. (Table 5)

Table 5

The effect of tridemorph plus metiram applied at two growth  
stages to winter barley (cv. Astrix) on levels of P. striiformis

Date of assessment GS at assessment	15/5 8	16/6 10.5	19/6 11.1				
GS and date at application	% infection on leaf *		% infection on leaf		% green tissue on leaf		
	3	4	1	2	1	2	
Untreated	2.0	14.0	14.4	33.7	20	20	
GS 6 - 28/4	2.0	3.5	5.0	20.8	25	30	
GS 8 - 14/5	-	-	4.7	11.8	40	55	
GS 6 + GS 8	-	-	2.0	7.5	50	60	

\* Leaves 1 and 2 free of infection at GS 8

Treated plots showed marked decreases in disease levels for a considerable period after application.

Rhynchosporium secalis (leaf blotch)

In 1973 trials were laid down to evaluate the effect of tridemorph, alone and in mixture with carbendazim, on infections of R. secalis on spring barley. One trial was laid down on the cultivar Deba Abed (seed treated with ethirimol)



and the second on plots of Maris Mink drilled at two different dates within the same field. In both trials no mildew was recorded.

Table 6

The effect of tridemorph, alone and in mixture with carbendazim, applied to spring barley (cv. Deba Abed) at GS 8-9 on levels of *R. secalis* and yield

Treatment	% disease level at GS 10.5		Yield kg/ha	Relative yield
	Leaf 1	Leaf 2		
Untreated	42.0	86.6	3565	100
Tridemorph	18.1	65.7	<u>3816</u>	107
Tridemorph + carbendazim 0.25 kg	5.7	45.0	<u>4318</u>	121
Tridemorph + carbendazim 0.5 kg	3.5	27.4	<u>4268</u>	120
Standard error $\pm$			184	
Disease levels at GS 8-9: Flag leaf - trace, leaf 2 - 1%, leaf 3 - 7.5%				

Tridemorph alone gave a marked reduction in disease level, while mixtures with carbendazim gave a greater degree of control.

Table 7

The effect of tridemorph, alone and in mixture with carbendazim, applied to spring barley (cv. Maris Mink) sown at two dates, on levels of *R. secalis* and yield

		Crop drilled 12/3			Crop drilled 28/3				
Treatment		% disease level (at GS 10.5) on leaf			Yield kg/ha	% disease level (at GS 10) on leaf			Yield kg/ha
		1	2	3		1	2	3	
	Untreated	21.2	40.1	44.5	4872	7.6	16.3	28.5	4961
(E)	Tridemorph	21.6	36.6	39.6	5014	8.9	12.2	19.7	<u>5468</u>
(E)	Tridemorph + carbendazim	4.3	14.8	15.8	<u>5486</u>	0.7	2.4	4.6	<u>5468</u>
	Untreated	11.5	20.6	23.1	<u>5312</u>	5.2	8.8	14.0	<u>5260</u>
(L)	Tridemorph	11.5	20.6	23.1	<u>5312</u>	5.2	8.8	14.0	<u>5260</u>
(L)	Tridemorph + carbendazim	3.4	9.2	16.8	<u>5618</u>	1.9	3.5	12.3	<u>5590</u>
Standard error $\pm$					299				206

(E) = application at GS 4-5 on late drilled crop and GS 5-6 on early drilled crop (24th May)

(L) = application at GS 8-9 on late drilled crop and GS 9-10 on early drilled crop (14th June)

Observations on grain surface microflora (Hill, personal communication) have shown that populations of Alternaria spp., Penicillium spp. and Aspergillus spp. were eliminated, and populations of Cladosporium spp. and Sporobolomyces reduced, by foliar applications of tridemorph.

## DISCUSSION

The results presented indicate that tridemorph has a marked curative effect against P. striiformis on wheat, resulting in significant yield increases (Table 2). Further trials with this mixture in 1973 again showed an effect against P. striiformis and in addition effects against S. nodorum. These results (Table 3) indicated that treatment gave an increase in yield, but it is not possible to relate this effect to individual disease levels. It would appear that an application of tridemorph plus metiram, after flag leaf emergence, markedly reduces levels of the important late season diseases of wheat.

The results presented on barley show that tridemorph plus metiram also has a marked effect against P. striiformis on this crop (Table 5). In addition, applications of tridemorph to barley gave considerable reductions in levels of R. secalis. The extent of this effect varied with time of application and levels of disease present in the crop, but in each instance yield was increased. The degree of the control and effect on yield was increased when a mixture of tridemorph and carbendazim was used (Tables 6 and 7). Foliar applications of tridemorph have also been shown to reduce levels of certain fungi in the grain microflora.

Previous work (Jung and Bedford, 1971 and Evans and Hawkins, 1971) has shown that tridemorph is an effective treatment for control of powdery mildew (E. graminis) on barley. Although mildew is the most widespread disease of barley (King, 1972) other diseases can also cause considerable yield loss (James, Jenkins and Jemmett, 1968). The effects of tridemorph on certain of these diseases, in particular P. striiformis and R. secalis may represent an added benefit from the use of this material for the routine treatment of mildew in barley.

## Acknowledgements

The authors wish to thank Mr. R. A. Hill of Rothamsted Experimental Station, for permission to quote his observations on the effect of tridemorph on grain microflora. Thanks are also due to their colleagues of BASF United Kingdom Ltd., and to the growers who kindly co-operated with the trials.

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THE TIMING OF APPLICATION OF BENODANIL (BAS 3170F)

FOR THE CONTROL OF CEREAL RUST DISEASES

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Summary BAS 3170F was tested against Puccinia striiformis on wheat and barley and against Puccinia hordei on barley. Good control of both diseases was obtained. For optimum yield benefit, however, timing of application was found to be important. For the control of P. striiformis in wheat and barley greatest yield benefit resulted when the flag leaf was protected from infection. Under conditions of early, continuous infection, two applications may be required.

For the control of P. hordei, best yield responses were obtained with applications made at or before the onset of the rapid phase of rust development. Under conditions of early and prolonged infections again two sprays may be necessary for maximum yield benefit.

Resume BAS 3170F a été essayé contre Puccinia striiformis sur blé et sur orge ainsi que contre Puccinia hordei sur orge. Un bon contrôle des deux maladies a été obtenu. Cependant pour obtenir un gain de rendement optimum, il est apparu que l'époque d'application était importante. Sur blé et sur orge dans la lutte contre Puccinia striiformis les plus gros gains de rendement ont été obtenus quand l'étendard était protégé de l'infestation. Deux applications peuvent être nécessaires dans des conditions d'infestation précoce et continue. Pour la lutte contre Puccinia hordei les meilleures réponses quant au rendement ont été obtenues avec des applications effectuées au moment où avant le début de la phase rapide de développement de la rouille. De même, dans des conditions d'infestation précoce et prolongée, deux pulvérisations peuvent être nécessaires pour obtenir un gain maximum de rendement.

INTRODUCTION

Benodanil - the proposed common chemical name for 2 iodo-benzanilide - is a related chemical to mebenil (Pommer and Kradel, 1969). Preliminary results showed benodanil to be more active than mebenil (Pommer and Zwick, 1971), and development of mebenil was discontinued. During the period 1971-73, benodanil has been evaluated for control of Puccinia striiformis Westend on wheat and barley, and Puccinia hordei Otth. on barley. At an early stage in the development of benodanil, it became apparent that timing of application is of prime importance. The trials presented are intended to show the optimal timing of a single application of benodanil for maximum yield benefit.



## METHOD AND MATERIALS

Benodanil was used as a wettable powder formulation containing 50% a.i. and is referred to by the code number BAS 3170F.

In the trials for control of *Puccinia striiformis* on wheat and *Puccinia hordei* on barley, BAS 3170F was applied at a rate of 1.5 kg/ha a.i. at various stages of growth of the crop. The modified Feekes Scale (Large, 1954) was used to assess the growth stages. In the trials for control of *P. striiformis* on barley, BAS 3170F was applied at 1.0 kg/ha a.i. Volume of application was 250 l/ha in all trials.

In the trial described in Table 1, the two varieties were included as split plots within a randomised block design. All trials were replicated four times. Plot size was 12.5 or 15 metres x 4 metres.

Leaf disease assessments were made by assessing percentage of leaf area infected, using a logarithmic scoring system (1-9) in the 1972 trials, the figures being converted to percentages for presentation. In the 1973 trial, percent infection of leaf area was scored directly. Where ear infection occurred, it was measured by counting the number of infected glumes on ten ears per plot, and expressing this figure as a percentage.

Trials were harvested using a Hege 125 combine or 'Claas Compact' combine harvester.

## RESULTS

Results are presented on the effect of timing of application on disease level and yield.

### Puccinia striiformis on Winter Wheat

Table 1  
The effect of application of BAS 3170F to two cultivars at  
various growth stages on disease levels and yield

Growth stage and date at application	% disease level at application <sup>1</sup>		% disease level at GS 10.5.32		Relative yield	
	A	B	A	B	A	B
Untreated	-	-	29.0	45.0	100	100
G.S 5 - 26.4.72	< 2.5	-	17.5	25.0	145*	145*
GS 6-7 - 15.5.72	< 5	< 2.5	16.0	21.0	146*	175*
GS 8-9 - 31.5.72	5	5	11.0	13.0	165*	183*
GS 9-10 - 15.6.72	15	20	17.5	19.0	146*	141*
GS 10.3 - 23.6.72	25	30	27.0	32.5	128*	138*
GS 6-7,9-10,10.3	-	-	7.5	10.0	183*	187*
Yield of untreated (kg/ha)					3,228	2,724
L.S.D. (P = 0.05)					36.8	29.0

Yellow rust was first seen in the crop at the end tillering.

Cultivar A - Maris Beacon

B - Joss Cambier

1 - on whole plant

2 - on flag leaf

In each case, an application at G.S. 8 gave the lowest disease levels on the flag leaf at G.S. 10.5.3 and resulted in the highest yield.

Table 2

Comparison of applications of BAS 3170F at growth stages 8 and 10 to cv. Joss Cambier in two trials (A and B)

Growth stage at application	% disease level at GS 10.5.1 <sup>1</sup>		% ear infection		Relative yield	
	A	B	A	B	A	B
Untreated	14.0	40.0	19.0	29.0	100	100
8	2.5	15.0	13.5	19.7	138***	127***
10	2.5	27.0	10.2	16.0	126***	115
Yield of untreated (kg/ha)					4,068	3,516
L.S.D. (P = 0.001)					19.8	13.2

Yellow rust first appeared in Trial A at G.S. 7, and in Trial B at G.S. 5-6.

1 = on flag leaf

In both trials, application at G.S. 8 gave a 12% higher yield response than did application at G.S. 10.

Table 3

The effect of application of BAS 3170F applied at three growth stages to plots of cv Joss Cambier in which yellow rust first appeared at early tillering

Growth stage at application	% disease level at application 1	% disease level at GS 10.5.1 <sup>2</sup>	Relative yield	Thousand grain wt (g)
Untreated	-	40 (85)	100	35.8
5	20	30 (51)	114***	34.3
7	16	30 (24)	115***	37.2
9	26	7.5 (51)	122***	37.8*
Yield of untreated (kg/ha)			2,916	

1 - mean of top three leaves

2 - flag leaf, with 2nd leaf in brackets

L.S.D. (P = 0.05)

(P = 0.001)

- 5.6  
11.8 -

Application at each growth stage gave an increase in yield, but only the later applications gave an increase in grain size.