

# EFFECT OF GRAIN MOISTURE ON THE BIOLOGICAL ACTIVITY OF PROTECTANTS ON MAIZE

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## Abstract

The biological activity of freshly-applied fenitrothion (EC) on maize was measured using adults of *Tribolium castaneum* and *Sitophilus oryzae*. Activity declined as grain moisture increased from 10 to 24% m.c. by about x 15 times, the greatest change occurring at moisture contents above about 14% m.c.. This occurred regardless of whether the grain was treated with fenitrothion when moist or was moistened after treatment, and it was not reversed by drying the treated grain. Differences in activity between moisture contents could not be explained by the chemical residues. However, the proportion of the residue on the outside of the grain kernels did decline at high moistures. Therefore, the suggested mechanism is a reduction in the availability of fenitrothion for pick-up by insects.

Against *T. castaneum*, the activities of emulsifiable concentrate, wettable powder and dust formulations of fenitrothion were reduced in the same proportion by increasing grain moisture in the range 10-18% m.c.. Among five organophosphorus compounds tested against *T. castaneum*, fenitrothion was the most adversely affected by moisture content (14 and 18%) and chlorpyrifos-methyl the least, and all were more affected than the pyrethroid deltamethrin. Against *Rhizopertha dominica*, the activity of methacrifos and carbaryl was much reduced at the higher moisture content, while that of five pyrethroids was slightly reduced. Curves relating activity to moisture content (10-28%) were measured for chlorpyrifos-methyl against *T. castaneum*, carbaryl against *R. dominica* and deltamethrin against both species. Moisture had a considerable effect on activity of chlorpyrifos-methyl only above an equivalent equilibrium relative humidity of 70 to 80%. No such threshold was measured for carbaryl. The effect of moisture on the activity of deltamethrin was significant but relatively small.

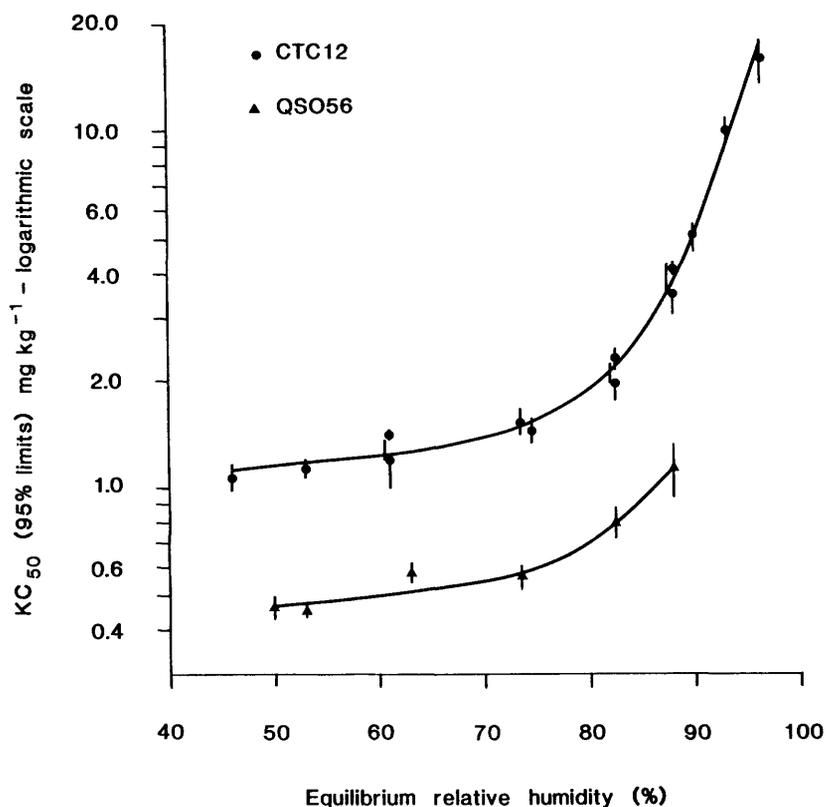
## Introduction

At high grain moisture contents, the persistence of biological activity of certain grain protectants such as malathion and fenitrothion may be reduced (Strong and Sbur, 1960; King et al., 1962; Tyler and Green, 1969; Champ et al., 1969). Insecticide deposits on grain break down more rapidly at higher moisture contents (Desmarchelier, 1978), but this might not be the whole explanation for reduced persistence: moisture might also affect the activity of the residue that remains. If so, would such an effect be reversed by drying the treated grain, or would choice of a different protectant formulation or compound be advantageous? The present paper summarises work recently completed

concerning the effect of grain moisture content on the biological activity of protectants on maize in the laboratory. First, the effect of moisture was studied in detail for fenitrothion (emulsifiable concentrate), an organophosphorus protectant widely used in Australia. Then effects of moisture were compared between different fenitrothion formulations and single formulations of ten other protectants, including other organophosphorus compounds, synthetic pyrethroids, and carbaryl.

#### Effect of Moisture on Biological Activity of Fenitrothion (EC)

Fenitrothion was applied to maize of different moisture contents from 10 to 24% m.c., at a range of application rates (Samson et al., in press). Treated grain was stored in glass jars for 1 day and then test insects were exposed to the grain for 3 days at 25°C. Response was assessed as knockdown and analysed by the Probit method.



**Fig. 1.** Effect of the equilibrium relative humidity of maize on the biological activity of fenitrothion against *T. castaneum* (CTC12) and *S. oryzae* (QSO56) (3 day exposure of adults to treated grain at 25°C, 1 day after treatment).

Figure 1 gives  $KC_{50}$  values when treated grain was bioassayed with either *Tribolium castaneum* (Herbst) (strain CTC12) or *Sitophilus oryzae* (L.) (strain QS056). Moisture contents were converted to equilibrium relative humidities (Pixton, 1982) as this gave a simpler curve form. Biological activity decreased with increasing grain moisture, particularly above 70% e.r.h.. A similar effect was observed using both test species. The effect was considerable: against *T. castaneum*, fenitrothion was about x 15 times more potent at 45% e.r.h. (= 10% m.c.) as at 96.5% e.r.h. (= 24% m.c.).

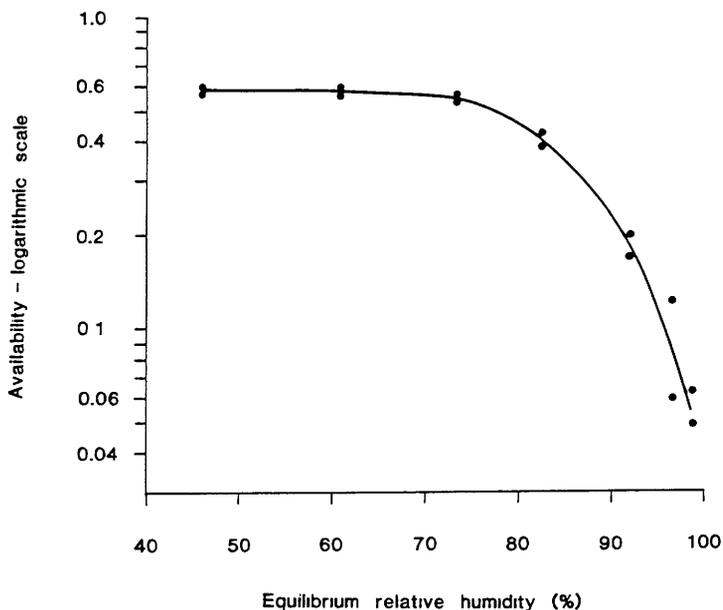
It was possible that grain moisture acted on the test insects directly, influencing their responsiveness to the insecticide. We designed an experiment to see whether moisture content at the time of bioassay was an important consideration; in other words, what would happen if grain was treated with insecticide at one moisture content but conditioned to a new moisture content before test insects were added? The procedure was that maize was first conditioned to either low or high relative humidity (45% and 85% r.h., respectively). Fenitrothion treatments were applied. Treated grain was then conditioned in shallow trays at either the same or the alternative humidity for 10 days before bioassay. This gave four moisture treatments as outlined in Table 1. Residues had low potency if fenitrothion was applied to initially moist grain or if grain was moistened after treatment. Drying of grain that was treated when moist did not restore potency, indicating that moisture did not primarily affect the test insects. We concluded that moisture must have affected the fenitrothion residues.

**Table 1.** Effect of equilibrium relative humidity of maize during dosing and bioassay on the biological activity of fenitrothion residues against *T. castaneum* (3 day exposure of adults to treated grain at 25°C, 14 days after treatment)

e r h. during dosing	e r.h. during bioassay	Relative potency (95% limits)
Low	Low	1.00
High	High	0.080 (0.065-0.099)
Low	High	0.122 (0.099-0.152)
High	Low	0.120 (0.097-0.148)

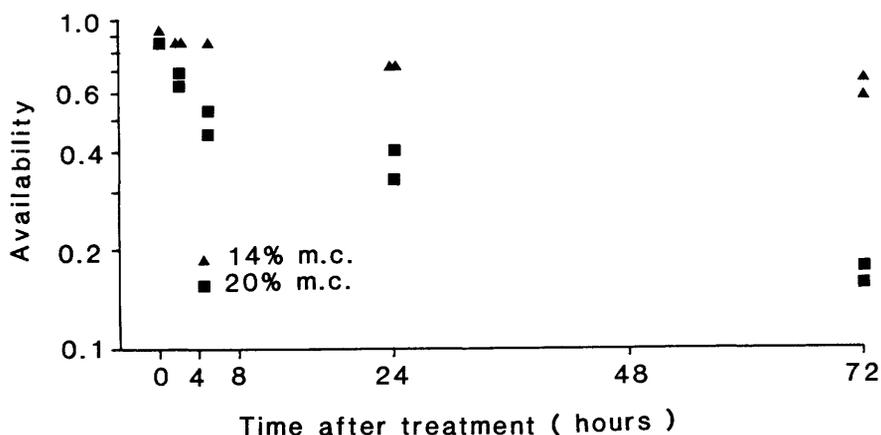
Therefore, fenitrothion residues on maize of different moisture contents were looked at in more detail. We were interested in two things: first, the total residue; and second, the residue that was biologically active, that is, available to be picked up by insects. We equated the biologically active residue with the insecticide present on the outside of the grain kernels. This external residue was extracted by washing treated whole grain in methanol for 1 minute, and the remaining insecticide was then extracted in methanol for 36 hours. Residues were measured by gas-liquid chromatography.

Residues were measured 4 days after fenitrothion application, which equalled the time of completion of the standard biological assay. When fenitrothion was applied at  $10 \text{ mg kg}^{-1}$  to maize in the moisture range 10 to 28% m.c., there was little difference in the total residue 4 days later (highest and lowest values were 8.1 and  $6.0 \text{ mg kg}^{-1}$  at 10 and 24% m.c., respectively). Therefore, chemical breakdown did not cause the observed effects of moisture on biological activity. However, there was a large difference in availability, that is the proportion of the residue on the outside of the kernels, as shown in Figure 2. Availability decreased greatly above an equilibrium relative humidity of about 70% r.h. This curve is qualitatively a mirror image of the curve presented earlier in Figure 1, the reduction in availability corresponding to the reduction in biological activity.



**Fig. 2.** Effect of the equilibrium relative humidity of maize on the availability of fenitrothion ( $10 \text{ mg kg}^{-1}$ ) 4 days after treatment (availability = proportion of the total recovered residue that was extracted by soaking grain in methanol for 1 minute).

The rate of change in availability was also measured, at times from 5 minutes to 72 hours after fenitrothion application, at two moisture contents only. As shown in Figure 3, availability was reduced at the higher moisture in comparison with the lower moisture (20% as against 14% m.c.) almost immediately after application. Availability at 20% m.c. continued to decline relative to that at 14% m.c. for the duration of the experiment.



**Fig. 3.** Availability of fenitrothion ( $10 \text{ mg kg}^{-1}$ ) on maize at 14 and 20% m.c. during 72 hours storage after treatment.

To sum up the work on biological activity of fenitrothion (EC), high grain moisture affected the behaviour of residues such that they were less available for pick-up from the surface of the maize kernels. The effect was rapid and not reversible. The mechanism was not established, but perhaps at higher moisture contents a greater proportion of the applied insecticide deposit penetrated the kernels and so became unavailable to insects moving through the grain mass (Rowlands, 1971; Samson, 1986). A moisture content of 14% m.c., corresponding to about 70% e.r.h. at  $25^{\circ}\text{C}$ , seemed critical for availability, and may explain published accounts of a critical level of moisture for effectiveness of organophosphorus residues on grain (Strong and Sbur, 1960).

There are two practical conclusions. First, treatment of maize with fenitrothion at high moisture contents may be ineffective. Second, if fenitrothion is to be used, any drying of maize for storage should be done before the insecticide is applied, not after.

#### Comparative Effect of Moisture on Biological Activity of Different Formulations and Compounds

Further work was done to determine effective protectant treatments for high moisture maize. Different formulations of fenitrothion were compared at three moisture contents as outlined in Table 2. The biological activity of a water dispersed powder and a dust was reduced in the same proportion at higher moisture content as that of an emulsifiable concentrate. This suggests that fenitrothion readily

separated from the carrier and insecticide-grain interactions proceeded regardless of initial formulation.

**Table II.** Effect of maize moisture content on the biological activity of three formulations of fenitrothion against *T. castaneum* (3 day exposure of adults to treated grain at 25°C, 1 day after treatment).

M.C. %	Relative potency compared to lowest moisture content (95% limits)		
	EC	WDP	Dust
10	1.00	1.00	1.00
14	0.55 (.49-.61)	0.61 (.54-.68)	0.62 (.55-.69)
18	0.28 (.25-.32)	0.27 (.24-.31)	0.24 (.22-.27)

Relative potency at two moisture contents, 14 and 18% m.c., was compared between eleven protectant compounds. Among five organophosphorus compounds tested against *T. castaneum* - fenitrothion, chlorpyrifos-methyl, pirimiphos-methyl, etrimfos, and methacryfos (all EC) - fenitrothion was the most adversely affected by higher moisture and chlorpyrifos-methyl the least. All were more affected than the pyrethroid deltamethrin (suspension concentrate). The activity of five pyrethroids tested for specific control of *Rhyzopertha dominica* (F.) (strain QRD63) - deltamethrin, fenvalerate, d - phenothrin, permethrin, and bioresmethrin - was only slightly reduced at the higher moisture, and there was no evidence that any compound was better or worse than the others. All were less affected than the carbamate carbaryl (water-dispersed colloid) which is presently in widespread use in Australia for control of *R. dominica*.

The relationship between biological activity and moisture content in the range 10 or 11% to 28% m.c. was investigated for one compound from each chemical group. Activity of chlorpyrifos-methyl against *T. castaneum* was affected by moisture content in a similar way to that of fenitrothion, with a sharp decrease above a critical moisture level of 70 to 80% e.r.h.. The loss of activity was less than measured for fenitrothion, activity at 28% m.c. being about one tenth that at 10% m.c.. Moisture had a slight effect on activity of deltamethrin against both *T. castaneum* and *R. dominica*: activity at 28% m.c. was about one third the value at 11% m.c. Activity of carbaryl against *R. dominica* was reduced to about one tenth at 28% compared to 11% m.c., but in contrast to the organophosphorus compounds there was no evidence of a critical moisture level. An increase in moisture content reduced the activity of carbaryl even when the grain was quite dry.

Several factors influence choice of the best protectant to use under high moisture conditions. Depending on the leeway allowed by

maximum residue limits, it may be more economic to increase the application rate of a protectant that is sensitive to moisture, rather than switch to an alternative compound that may be more expensive. However, the results do indicate that when moisture content is high, use of particular compounds such as the pyrethroids should become increasingly attractive.

#### Acknowledgement

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