Persistence and Uptake of Phorate in Mineral and Organic Soils

Sunny Y. Szeto,* Patricia M. Price, John R. Mackenzie, and Robert S. Vernon

Agriculture Canada Research Station, 6660 N.W. Marine Drive,
Vancouver, British Columbia, Canada V6T 1X2

When Thimet 15G (15% phorate) at 3.2 g of AI/10 m of row was applied as an in-furrow band to potatoes at planting in silt loam and muck, the initial concentrations of phorate were higher in the muck (22.9–24.5 ppm) than in the silt loam (19.5–20.6 ppm). Total phorate, including its oxidative metabolites, persisted in both soils with and without potatoes: 39.7–55.5% of the applied phorate remained after 64 days. The disappearance of total phorate followed first-order kinetics, and the calculated rate constants were comparable (0.009–0.014 day^{-1}). Phorate was translocated into potato leaves much more readily from silt loam than from muck. There were 10.9 and 2.39 ppm, respectively, in leaves of 37- and 65-day-old plants from silt loam. Only 2.13 and 0.03 ppm, respectively, were found in leaves of 36- and 64-day-old plants from muck. Marketable potatoes grown in muck and also in clay treated similarly at 3.2 g of AI/10 m of row contained less residues than those grown in silt loam. There were 0.12 ppm in potatoes harvested 112 days after planting in clay and muck and 0.22 ppm in potatoes harvested 178 days after planting in silt loam.

Phorate [*O*,*O*-diethyl *S*-(ethylthio)methyl phosphorodithioate] is currently registered in Canada for aphid control in potatoes. In spite of its high water solubility it appeared to be only slightly mobile in soil when the mobilities of 11 insecticides in silty clay loam and sandy loam were evaluated by Harris (1969). Their mobilities were, in the order of chlorinated hydrocarbon, insecticides < phorate and disulfoton < diazinon and thionazin. The relatively low mobility in soil makes phorate an attractive candidate as an alternative to aldicarb. However, the current label excludes the use of phorate in muck soils, probably because it has low activity and exceedingly high persistence in muck.

Aldicarb [2-methyl-2-(methylthio)propionaldehyde *O*-(methylcarbamoyl)oxime] has been used extensively for control in potatoes of tuber flea beetle, *Epitrix tuberis* Gent., green peach aphid, *Myzus Persicae* Sulz., and potato aphid, *Macrosiphum euphorbiae* (Thomas), especially in the growing of virus-free seed potatoes. In British Columbia, a furrow treatment of Temik 10G (10% aldicarb) at 2.2 kg of AI/ha is recommended for this purpose. But repeated use of aldicarb in areas with sandy soils on Long Island, NY, and in The Netherlands has resulted in contamination of shallow wells with aldicarb including its oxidative metabolites (Enfield et al., 1981; Smelt et al., 1983). Residues of aldicarb have also been detected in groundwater from wells in potato growing areas of Prince Edward Island (Ernst and Matheson, 1988; Lapcevic and Bobba, 1988). To reduce its use, other systemic insecticides may be used as alternatives.

To understand better the efficacy and persistence of phorate as an alternative, we evaluated it from 1986 to 1988 for control of aphids and tuber flea beetles on potatoes grown in silt loam and muck. This paper reports findings from the 1987 field trials on the persistence and uptake of phorate in those soils and from the 1987 and 1988 field trials on its total residues in potato. The results on efficacy were reported elsewhere.

MATERIALS AND METHODS

Field Trials. Field trials were run in 1987 to determine the residues in potato tubers and the persistence and uptake of phorate in a silt loam soil (Abbotsford soil series, classification Orthic Humo-Ferric Podzol, pH 5.76; 5.1% organic matter content, 39.6% sand, 54.1% silt, 6.3% clay) at the Research Substation, Agriculture Canada, Abbotsford, B.C., and in a muck soil (pH 5.00; 58.0% organic matter content, 18.0% sand, 54.1% silt, 27.9% clay) near Cloverdale in Surrey, B.C. All treatment rows were 3.0 m long and 2 m apart, and potatoes were planted at 30-cm spacings, 15-cm depth, on May 20 at Abbotsford and on May 21 at Cloverdale. Field trials were similarly conducted again in 1988 to determine only the residues in potato tubers. One more soil was selected at Delta, B.C., a clay soil (pH 5.9) consisting of 3.4% organic matter content, 4.2% sand, 76.5% silt, and 19.3% clay.

With use of a hand-held shaker, Thimet 15G (15% phorate) was applied alongside the seed pieces at 3.2 g of AI/10 m of row at planting to V-shaped furrows, 20 cm wide at the top and 10 cm wide at the bottom. Concurrently, a second set of soil treatments with phorate was run in a similar manner but without potatoes in the treated furrows. Therefore, the main study consisted of four treatments, namely, silt loam with and without potatoes and muck with and without potatoes. Each treatment was replicated four times in a randomized block design.

Total phorate in the treated soil, including all toxic oxidative metabolites, were determined at various intervals after application. Twenty cores of soil (2.5-cm diameter × 20-cm depth) were taken randomly from within the phorate-treated band in each replicate to form a composite sample. The four replicates of each treatment were analyzed separately for total phorate. There were thus four readings per treatment per sampling date for statistical analysis (Szeto et al., 1986), and the data in the results (Figure 1) were the means of those readings.

After the emergence of potato foilage, the uptake of phorate in the leaves was investigated by determining the residues at various intervals. There were 10 plants in each replicate. One trifoliate leaf cut about 8 cm from the base of the petiole was picked from each plant near the top of the main haulm on each sampling date to form the composite sample for each replicate. The four replicates of each treatment were analyzed separately, and the results shown (Figure 2) were the means of those readings.

Total phorate residues in potato tubers were determined at harvest. Only the potato samples from Abbotsford were analyzed in 1987, but potato samples taken from all three locations were analyzed in 1988. At harvest, 12 potato tubers were randomly collected from each replicate to form a composite sample for residue determination. There were four composites per each treatment, and they were analyzed separately.

Determination of Residues. Concentrations of phorate including its toxic oxidative metabolites were determined by the method of Szeto and Brown (1982) with minor modifica-

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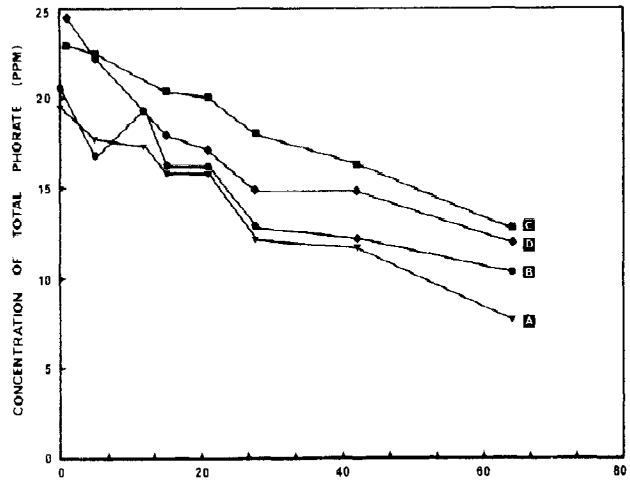

Figure 1. Concentrations of total phorate in unplanted silt loam soil (A), silt loam soil planted with potatoes (B), unplanted muck soil (C), and muck soil planted with potatoes (D) after in-furrow band treatment at 3.2 g of AI/10 m of row.

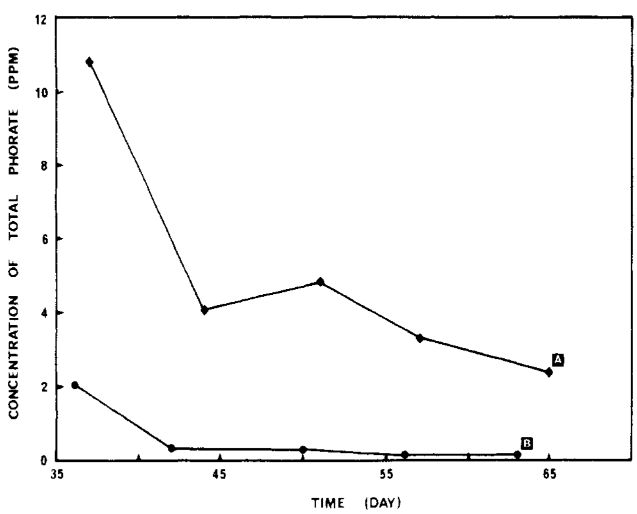

Figure 2. Concentrations of total phorate in leaves of potato plants grown in silt loam soil (A) and muck soil (B) after in-furrow band treatment at 3.2 g of AI/10 m of row.

tion. After elution from the Nuchar C-Whatman CF-11 cellulose column, phorate and its metabolites were oxidized to phorate sulfone and phorate oxon sulfone for GC determination. The sum of the two sulfones was reported as total residues. A DB-1 megabore column (15 m × 0.53 mm (i.d.); J&W Scientific, Inc.) was used. The column was programed as follows: initial temperature, 150 °C for 0.5 min; program rate, 5 °C/min to 215 °C and hold for 6 min. Under these conditions the absolute retention times were 11.04 min for phorate oxon sulfone and 11.76 min for phorate sulfone. The modified method was evaluated with samples of soil and potato leaf and tuber, fortified with phorate at 0.1 and 10 ppm. The recoveries of total residues ranged from 90.3 to 98.5%.

RESULTS AND DISCUSSION

Persistence of Phorate. The mean concentrations of total phorate, including all toxic oxidative metabolites in soils from the four replicates of each treatment, are given in Figure 1. Phorate sulfone accounted for about 90% or more of the total, and the oxon sulfone accounted for the rest. Since phorate and its sulfoxide and phorate oxon and its sulfoxide were both oxidized in situ to their corresponding sulfones for determination, it was apparent that 90% or more of the residues was either phorate or its sulfoxide and sulfone and the rest was either phorate oxon or its sulfoxide and sulfone. Our results are in general agreement with the laboratory studies of Getzin and Shanks (1970) and Chapman et al. (1982). However, phorate oxon sulfoxide and phorate oxon sulfone were not detected by the TLC method used by Getzin and Shanks (1970). Other findings from field studies with granular phorate applied as a broadcast were varied. Phorate oxon and its sulfoxide and sulfone were not detected by Suett (1971) in any soil sample after application of phorate at 2.0 kg of AI/ha, whereas large amounts of phorate oxon sulfone and minute amounts of phorate oxon and its sulfoxide were detected in treated soil by Menzer et al. (1970). In our study phorate oxon sulfone, which may have derived from either phorate oxon or its sulfoxide and sulfone, accounted for only 10% or less of the total residues. Soil type could not account for this difference because similar patterns of oxidation were observed not just in our study with silt loam and muck but also with the loamy sand and silt loam studied by Menzer et al. (1970). However, the biochemical components of the different soils may have been responsible for such differences in the oxidation of phorate. In the study of Chapman et al. (1982) the transformation of phorate sulfoxide to phorate sulfone in sterilized soil occurred concurrently with microbial contamination, and they suggested that microorganisms were required for oxidation of phorate sulfoxide.

On the basis of the application rate of 3.2 g of AI/10 m of row, the bulk density, and moisture content of the soil, samples taken from the treated band (10 cm wide at the bottom) to a depth of 20 cm would have an initial concentration of 20.5 ppm (dry weight) in silt loam at Abbotsford and 24.7 ppm (dry weight) in muck at Cloverdale. The actual concentrations were in close agreement with the theoretical values: 20.6 ppm in silt loam planted with potatoes, 19.5 ppm in unplanted silt loam on treatment day; 24.5 ppm in muck planted with potatoes, 22.9 ppm in unplanted muck 1 day after treatment (Figure 1).

The persistence of phorate and its oxidative metabolites appeared to be higher in muck than in silt loam. A much higher percentage of the applied phorate remained after 64 days in unplanted muck (55.5%) than in unplanted silt loam (39.7%) (Figure 1). Our findings were in general agreement with the published data (Suett, 1971; Chapman et al., 1982).

The plant canopy appeared to have an effect on the persistence of phorate. A higher percentage of the applied phorate remained after 64 days in silt loam planted with potatoes than in unplanted silt loam (Figure 1), possibly because shading by the plant canopy reduced the loss of residues from soil through volatilization (Harris and Lichtenstein, 1961; Lichtenstein et al., 1962). In comparison, shading on muck soil with its high organic content and tightly bound residues would have less effect on residue loss: after 64 days, 48.6% of the phorate remained in the planted muck and 55.5% in the unplanted muck.

To understand better the effects of soil type and plant canopy on the disappearance of total phorate, residue concentrations were transformed to natural logarithms for regression analysis. Linearity of the relationship between ln (concentration, y) and time (x) was tested by adding x^2 to the regression. There were no statistically significant deviations from linearity ($p > 0.05$) in all four treatments. Therefore, a first-order process was assumed. The calculated rate constants and half-lives are given in Table I.

Regression analysis of ln (concentration) on time blocked

Table I

soil	treatment	rate const, day^{-1}	half-life, days
silt loam	unplanted	0.014	49.2
silt loam	planted	0.011	65.0
muck	unplanted	0.009	74.6
muck	planted	0.011	64.0

by treatment (Gilbert, 1973) indicated that there were significant differences between the intercepts ($p < 0.05$) but not between the slopes ($p > 0.05$) of the four treatments. This suggests that the initial concentrations were different but the rates of disappearance were comparable. However, how the intercepts differed from each other was not analyzed by statistics. With and without potatoes, the initial concentrations were higher in muck than in silt loam (Figure 1). Muck soil has a lower bulk density than silt loam, and therefore, at the same application rate the initial concentrations would be higher in muck than in silt loam. For the same reasons, in muck the higher percentages of total phorate remaining after 64 days were attributed to the higher initial concentrations rather than the rates of disappearance, which were comparable among all four treatments (Figure 1).

Unlike our findings, most of the published data show that the transformation of phorate in natural soils did not obey first-order kinetics (Chapman et al., 1982). A possible explanation for this discrepancy is that the transformation of phorate to its oxidative metabolites does not follow first-order kinetics whereas the disappearance of total phorate does. In the absence of well-behaved, first-order rate constants, Chapman et al. (1982) transformed data published by themselves and others and assumed first-order kinetics. When compared with the transformed data of Chapman et al. (1982), our rate constant for the disappearance of total phorate in silt loam (0.011–0.014 day^{-1}) was similar to that reported by Suett (1971, 1975) in sandy loam (0.012–0.013 day^{-1}) but slower than the rate constant for the disappearance in sand reported by Chapman and Harris (1980) (0.027 day^{-1}). Our rate constant for the disappearance in muck (0.009–0.011 day^{-1}) was comparable with that reported for muck by Chapman and Harris (1980) (0.014 day^{-1}) but faster than the rate constant in peaty loam reported by Suett (1971) (0.006 day^{-1}). Such differences in the rate constants may be attributed both to the differences in soil types and to methods of application. Nevertheless, our results clearly confirm that phorate persists in soil.

Uptake of Phorate. Translocation of phorate into potato plants occurred in both soils (Figure 2). The composition of total phorate in leaves was similar to that in the treated soil. Phorate sulfone resulting from in situ oxidation accounted for more than 90% of the total phorate and phorate oxon sulfone for the rest. The concentrations were much higher in plants grown in treated silt loam than in those grown in treated muck (Figure 2).

The ratio of total phorate between the leaves and treated silt loam (Figures 1 and 2) was highest (0.85) in 37-day-old plants and lowest (0.23) in 65-day-old plants. The availability of phorate in the soil did not appear to be a limiting factor in the uptake as 10.3 ppm of total phorate remained in the soil 64 days after treatment (Figure 1). Growth dilution was the major factor contributing to the decrease in the ratio of uptake by the maturing plants. The ratio of total phorate between the leaves and treated muck (0.003) was almost 2 orders of magnitude lower than that observed in silt loam (0.23). Phorate and its oxidative metabolites were probably tightly bound to the muck soil because of its very high organic content, thus greatly reducing their uptake by the plants. The effects of organic content on the sorption and inactivation of chlorinated hydrocarbon insecticides have been well documented (Lichtenstein, 1959; Harris and Sans, 1967; Oloffs et al., 1971). The results of our study confirm the importance of soil type to the degree of translocation of total phorate into plants.

Insecticides are inactivated in organic soils probably because of adsorption, but the mechanism of inactivation is not clear. Harris (1964) demonstrated that in moist soils inactivation was proportional to the organic content of the soil. The strong adsorption of phorate as evidenced in its low uptake (Figure 2) suggests that it was inactivated in muck soil. In fact, efficacy studies conducted concurrently in the muck soil at Cloverdale clearly showed that phorate was ineffective at the rate of 3.2 g of AI/10 m of row against tuber flea beetle, green peach aphid, and potato aphid (Vernon and Mackenzie, 1988; Mackenzie and Vernon, 1988a,b). This is probably the reason why the current label for phorate in Canada excludes its use in muck soil for pest control.

Table II

residue, ppm	range, ppm	days after planting
0.51	0.22–0.70	68
0.13	0.08–0.28	83

Table III

residue, ppm	range, ppm	soil
0.02	0.01–0.03	muck
0.06	0.01–0.14	clay

Residues in Tubers. In the 1987 field trials, residues of total phorate were determined only for potatoes grown in silt loam at Abbotsford. The mean concentrations ($n = 4$) were high with a short preharvest interval as shown in Table II. The application rate of 3.2 g of AI/10 m of row for the 1987 field trials was about 50% higher than the label rate of 2.1 g of AI/10 m for light soils, such as the Abbotsford silt loam. Therefore, it was not surprising that the total residues were above the tolerance of 0.1 ppm.

The effects of soil type on the adsorption of residues by crops were again evidenced in 1988. Marketable potatoes were harvested 112 days after planting in Cloverdale and Delta. Both soils contained high percentages of clay, viz. 27.9% in muck at Cloverdale and 19.3% in clay at Delta. At the label rate of 3.2 g of AI/10 m of row for heavy soils, the total residues averaged 0.12 ppm (0.05–0.18 ppm, $n = 4$) and 0.12 ppm (0.06–0.15 ppm, $n = 4$), respectively, in potatoes from Cloverdale muck and Delta clay. The residues were slightly above the tolerance of 0.1 ppm for potatoes. At the label rate of 2.1 g of AI/10 m of row for light soils, the total residues (mean and $n = 4$) were as shown in Table III. The residues were below the tolerance.

Potatoes were harvested 178 days after planting in Abbotsford. At the label rate the total residues of 0.04 ppm (0.02–0.09 ppm, $n = 4$) were well below the tolerance. However, when phorate was applied as recommended for heavy soils, the total residues of 0.22 ppm (0.1–0.3 ppm, $n = 4$) were above the tolerance.

Our results confirmed that phorate was ineffective in muck soil against aphids and tuber flea beetles and that if the application rate in light soils exceeds the label rate, residues above the tolerance for potatoes are possible. It is important that growers adhere strictly to label rates.

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