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Worker Environment Research. VI: Rapid Estimation of Organophosphorus Pesticide Residues in Citrus Grove Soil

Charles A. Smith and Francis A. Gunther
Department of Entomology, University of California, Riverside, Calif. 92502

Organophosphorus (OP) insecticide residues in orchard soil dust have been suggested as one route of agricultural worker exposure to these residues (SPENCER et al. 1975, GUNTHER et al. 1977). The pesticide-bearing dust can become airborne through wind and/or worker activity and settle on workers' clothing and skin, where residues may then be absorbed into the workers' bodies; citrus pickers' lower extremities can become heavily coated with dust inside the trousers and well above the knees (GUNTHER et al. 1977). Alternatively, the dust may settle on foliage and be subsequently transferred to the workers during picking or thinning operations.

To measure dust residue concentrations SPENCER et al. (1975) analyzed extracts of soil-surface dust, collected by vacuuming through a 100-mesh screen, by gas chromatography. While the method is suitable for precise residue studies, the total time required from soil sampling to final results is quite long and requires large amounts of equipment, both in the field and in the laboratory. A rapid method using easily portable equipment was needed for analyzing OP residues in orchard soil to assess potential hazard to workers shortly prior to their entry into treated groves. The field method reported here is suitable for this purpose; it is based on the reaction of the residues with 4-(p-nitrobenzyl)pyridine (NBP), as in a previously described method for determination of foliar citrus residues (SMITH et al. 1976). NBP develops a color with both P=S and P=O compounds (GETZ and WATTS 1964), both of which can be important in a realistic assessment of worker hazard.

MATERIALS AND METHODS

Scraper. A small stainless steel scraper, constructed as shown in Figure 1, is used to sample the orchard soil under the dripline of the tree. The scraper removes the top 9 mm of soil in a strip 37 mm wide. To use, it is placed on the soil surface and pushed forward (toward the top in the figure) so that the sharpened lower edge of the 37 mm opening transfers the top 9 mm layer of soil into the trough behind it (the other end of the trough is closed). The metal extensions on either side of the trough prevent sampling of soil at depths greater than 9 mm.

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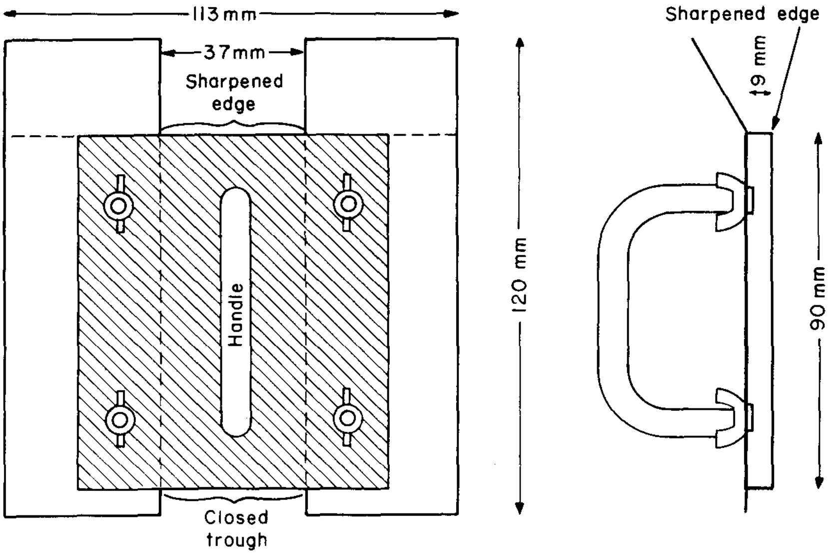

Fig. 1. Top and side views of soil scraper for sampling orchard soil surface under tree dripline. Shaded area is top plate.

Filter holder. Millipore XX30 012 40, 13 mm, stainless steel with Teflon® gasket.

Filter screen. A finely woven stainless steel screen of about 400 mesh is used in the filter. This gives a faster extractant flow rate than filter paper or membrane filters and can be quickly rinsed free of soil and reused.

Heater. A small portable heater is operated from a car or truck battery, thus freeing it from the need for AC line current. The unit is thermostatically regulated, and the temperature can be adjusted from 100° to 150°C. Details of the heater construction and an electrical schematic are given in Figure 2.

Measuring spoon. Capacity 0.10 cm^3 of sieved soil, constructed from 0.25-in. o.d. copper tubing as shown in Figure 3.

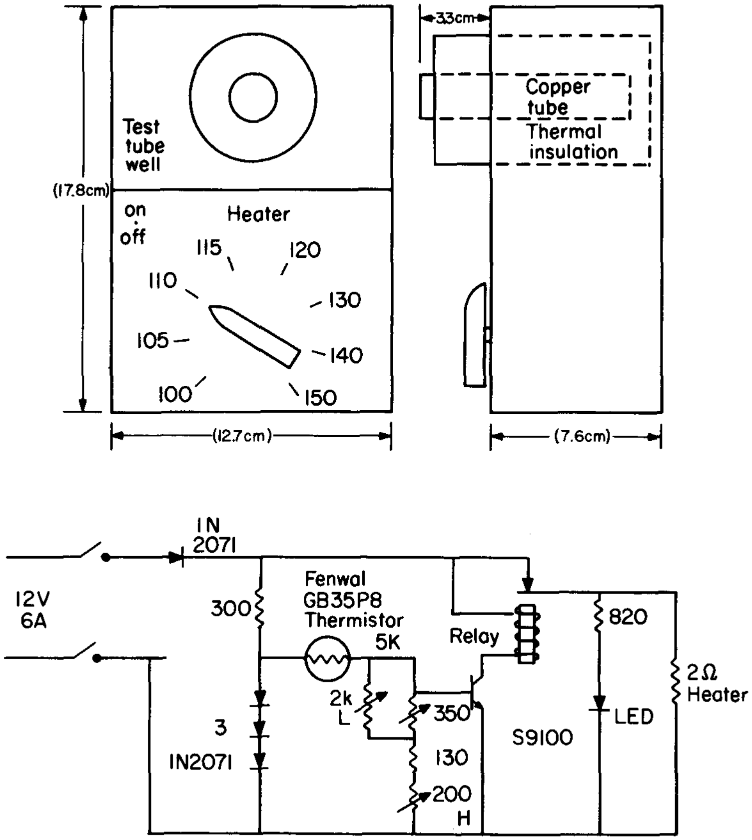

Fig. 2. Single test-tube heater for operation from 12 V DC source.

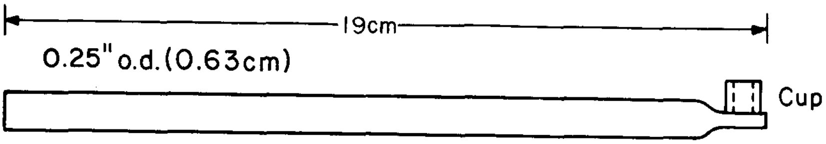

Fig. 3. Measuring spoon: Flatten cup end in vise, solder 0.25" (0.63 cm) length of 0.25"-diameter copper tubing on to flattened surface.

Extractant solution. Acetone-hexane, 1:9 v/v.

Base solution. Tetraethylenepentamine-toluene, 1:9 v/v. Solution is stable indefinitely if carbon dioxide and moisture are excluded.

Sieve. Standard 100-mesh testing sieve, 20 cm diameter.

Color comparison chart. Prepared from a series of 6 painted paper strips of graduated color intensity. The special rose-red paints were prepared by inspection from latex flat interior house paint. To make a set of color comparison standards, squares of each of the 6 colors, 12.5 mm on a side, were taped together to form a strip; this was then placed in a 15 x 125 mm test tube and stoppered. A set of color comparison standards will be furnished on request.

Prepared test tubes. Place 0.05 ml of a solution of 10% NBP in acetone, and 0.02 ml of a solution of 2% oxalic acid in acetone, in a 15 x 125-mm borosilicate test tube. Allow the acetone to evaporate, then cork the tube until needed. The prepared test tubes are stable for at least 3 months.

Procedure. Using the soil scraper, sample the top 9 mm of soil from the orchard floor under the tree dripline for a length of approximately 6 cm, and place the soil in the sieve. Collect the soil which passes through a 100-mesh screen when gently tilting it so the soil shifts to the side of the sieve; repeat tilting motion 9 times. Using the measuring spoon, place two spoonfuls (0.20 cm^3) of the sieved soil in the filter funnel, and add 3.0 ml of extractant mixture, allowing the filtrate to flow into a prepared test tube containing NBP and oxalic acid. Place the test tube in the battery-operated heater (130°C) for 15 min, then remove the tube and add 2.0 ml of base solution. Mix and compare the rose-red color produced to the visual color chart to estimate the total OP residue concentration. Results are expressed as μg of parathion/g of soil. The elapsed time from soil sampling to color measurement is *ca*. 20 min.

RESULTS AND DISCUSSION

The response of the method is shown in Figure 4 as calibration curves prepared using parathion and paraoxon standards. The absorbance values were obtained using a Beckman DB spectrophotometer with a wavelength setting of 530 nm and one-cm cells.

The precision of the method was studied for an actual soil sample taken from an orchard which had received a parathion treatment. For a series of five replicate determinations having a mean absorbance of 0.200, the standard deviation was 0.013.

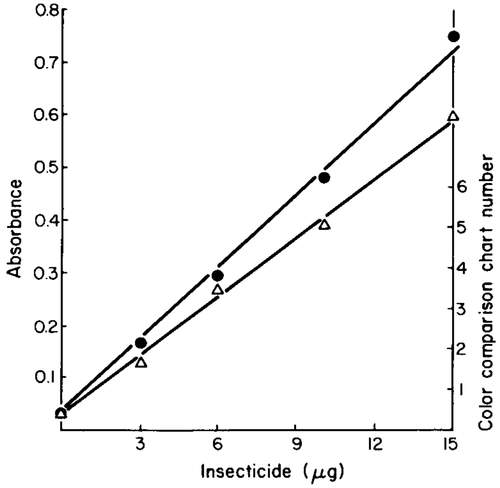

Fig. 4. Response of soil residue measurement method to parathion (●) and paraoxon (Δ); absorbance was measured at 530 nm.

The extraction efficiency of the rapid procedure described here was compared to a much longer residue extraction procedure for laboratory use. The results of the two methods are given in Table I. As would be expected, less residue is extracted by the rapid procedure than by the laboratory procedure. Assuming that the laboratory procedure extracts 100% of the unaltered residues, the rapid procedure extracts 56 ± 10%.

Parathion levels in orchard soil were followed using the rapid extraction procedure and NBP color development. Color intensity was measured spectrophotometrically, rather than with the color comparison chart. Residue concentrations after application of parathion as emulsifiable concentrate (EC) and as a wettable powder (WP) formulations were followed. In both cases the application was at the Citrus Research Center, Riverside, CA and was at the rate of 12.5 lb active ingredient/acre. Samples were taken at three locations under the tree dripline for each formulation and at each sampling time and analyzed separately. Results are shown in Figure 5.

The heating step actually consists of two parts. In the first, the temperature of the contents of the test tube remains nearly constant at about 70°C while the extracting solvents boil away and the reaction mixture is concentrated; this requires about 6 min, and no significant reaction occurs during this time. When all solvents have evaporated, the temperature rises rapidly to 130°C and the reaction of the OP residues with the NBP occurs.

Table 1

Comparison of rapid extraction procedure using NBP procedure for total OP residue with laboratory extraction procedure.

Sample no.	Rapid extraction (μg/g soil)	Laboratory extraction proced. μg/g of soil			Rapid extraction (% recovery)
		Parathion	Paraoxon	Combined	
1	75	157	10.5	168	45
2	100	168	13.5	181	55
3	85	102	9.0	111	77
4	165	231	10.5	241	68
5	50	126	4.5	130	38
6	165	261	4.5	265	62
7	68	85	12.0	97	70
8	58	120	17.2	137	42
9	138	196	33.8	230	60
10	70	124	21.0	145	48
11	69	110	16.5	126	55
12	82	148	19.5	167	49

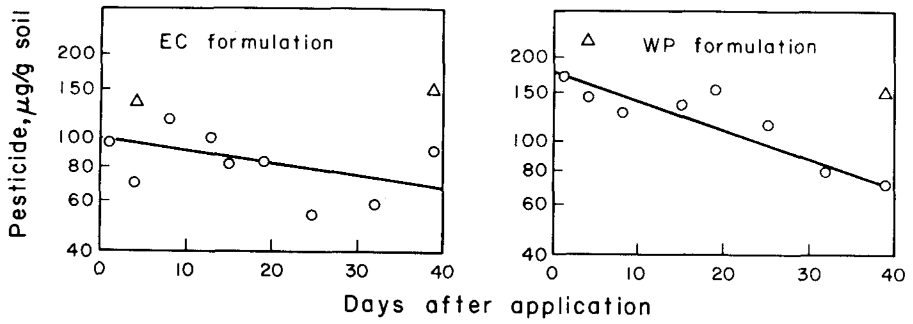

Fig. 5. Soil pesticide residues (parathion) measured by NBP method for EC (left) and WP (right). Data are uncorrected for extraction recoveries. Triangles are concentrations measured by liquid chromatography.

The choices of 130°C as the heating temperature and 15 min as the heating time gave the maximum color development with parathion. As alternative conditions, a temperature of 100°C, using a boiling water bath, and a heating time of 20 min give slightly less color development, but the conditions may be advantageous in some cases. Other temperatures and heating times may be required for maximum color development with other OP pesticides.

The use of a comparison chart to measure color intensity, as described here, is adequate for the intended field use; battery-operated spectrophotometers are available, however, which would increase the accuracy of the color measurement step of the procedure, which might be desirable in certain applications.

The average extraction efficiency of 56 ± 10%, which results in a minimum detectability of 20 μg of parathion or paraoxon/g of soil, is believed to be sufficient to indicate potentially hazardous residue concentrations in soil. The spread of the values for a series of soil samples (38 to 77%) probably demonstrates field sampling variability; this variation was not observed when replicate samples of soil were analyzed.

The method described here does not differentiate between the parent P=S compound and the oxon formed from it. The two compounds will differ in toxicity due to a number of factors such as ease of absorption through the skin (GUNTHER *et al*. 1977) and the rate at which the parent compound is converted to the oxon in the body. Thus, this method can give only an approximate indication of toxic hazard to workers. At present, no reliable value exists for the dividing line which separates hazardous from nonhazardous levels of soil OP insecticide residues, a case for public health professionals to resolve.

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