Worker Reentry Into Pesticide-Treated Crops. II. Procedures for the Determination of Pesticide Residues on the Soil Surface[1]

W. F. Spencer
Agricultural Research Service
U.S. Department of Agriculture
Riverside, Calif. 92521

Y. Iwata
Department of Entomology
University of California
Riverside, Calif. 92521

W. W. Kilgore
Dept. of Environmental Toxicology
University of California
Davis, Calif. 95616

J. B. Knaak
California Department of Food and Agriculture
Sacramento, Calif. 95814

Infrequent episodes of workers becoming ill from exposure to residues of parathion and other organophosphate insecticides even after long waiting periods following application have created considerable interest in establishing safe reentry times for workers to enter treated fields. Toxicities which occur many days after application of organophosphate insecticides under dry, hot conditions are due mainly to highly toxic alteration products of the parent compounds arising either from the foliage or soil surface and carried on dust particles to the worker's clothing or skin from which they are dermally absorbed (SPEAR et al., 1977). For example, in the case of parathion, paraoxon was found to be the principal toxic constituent of the weathered residues (SPEAR et al., 1974; 1977).

Considerable quantities of insecticides ultimately reach the soil surface either by direct application or by runoff from crops in excess water applied with the insecticide. Parathion dripping on dry soil from sprayed crops or sprayed directly on the soil surface can persist for long periods and be oxidized to the highly toxic paraoxon (SPENCER et al., 1975). They found residue concentrations were much higher on the loose dust particles than in the bulk soil. The importance of pesticide residues in mobile dust on the soil surface will depend on the concentration of pesticide on the dust as well as the amount of mobile dust. Some of the residue-containing dust can be blown onto foliage with which workers may later come in contact or workers reentering treated fields can be contaminated by direct contact with the soil surface or by stirring up dust as they move through the fields. Pesticides are much more persistent in

---

[1]Contribution of the Western Regional Research Project W-146, "Worker Safety Reentry Intervals for Pesticide-Treated Crops".

Bulletin of Environmental Contamination & Toxicology, Vol. 18, No. 6 © 1977 by Springer-Verlag New York, Inc.

dry soil than moist soil and soil dust residues may be particularly important in areas which do not receive irrigation water or rain on the soil surface between pesticide application and worker exposure.

The following is a suggested protocol for monitoring soil pesticide residues within the work environment in relation to worker reentry. Two types of samples are suggested, i.e., soil dust obtained by vacuuming the soil surface, and soil plugs obtained from the surface 1 cm of soil. The soil dust procedure is preferred and should be used in most cases, but either procedure can be used to monitor the work environment or evaluate the persistence of pesticides by periodic sampling following application.

SOIL DUST RESIDUES

Sampling--Equipment and Method. The dust sampling technique and apparatus are essentially that described by SPENCER et al. (1975). Samples of loose dust or easily dislodgable material on the soil surface are obtained by passing a stainless steel nozzle attached to a portable vacuum cleaner over a 100-mesh screen installed on the bottom of a wooden frame. The vacuum cleaner should be a relatively powerful handheld vacuum cleaner equipped with reusable felted-cloth bags and a modified collection nozzle. The nozzle is made from a 23-cm length of 3.1 cm O.D. stainless steel tubing. The nozzle tip is formed by flattening one end to an ovoid shape 1-cm high X 4.5-cm wide and cutting the tip to a 60° angle to improve contact with the screen as it is being held on the soil surface. One vacuum cleaner which has been found to be satisfactory is the Sear's Kenmore SPV,[2] powered with a 110-volt AC portable generator. The reusable cloth bags are relatively inexpensive, can be removed easily from the vacuum cleaner with the collected dust, and placed into glass jars for freezing and storage prior to analysis.

The screen stapled to the bottom of the wooden sampling frame is a composite 3-layer screen fabricated from three different types of material. The middle screen is 100-mesh brass strainer cloth commonly used in water-filtering systems which will pass particles finer than approximately 150 μm. The top screen is one-eighth inch (3.2 mm) hardware cloth to protect the 100-mesh screen from the abrasive action of the stainless steel nozzle; the lower screen is aluminum window screen placed below the brass strainer cloth to protect it from abrasive contact with the ground surface. The size of the frame can be variable but should be a minimum of 18- X 25-cm for ease of sampling and to provide an adequate sampling area. Dust samples are obtained by

---

[2]Mention of commercial products does not constitute an endorsement by the USDA over similar products.

firmly placing the screen over an unsampled soil surface and dragging the vacuum nozzle over the screen in five to six even passes within the frame. Loose dust or easily dislodgable material less than 150 μm is drawn through the composite screen over an effective area measured from the outside dimensions of the screen or an area of approximately 450 cm^2 per individual sampling site for an 18- X 25-cm screen.

The sampling pattern and number of individual sampling sites per composite sample will depend upon the crop, tillage practices, whether or not the crop is irrigated, the type of irrigation system, field variability, etc. Each composite sample should be made up of a minimum of 16 individual sampling sites and three replicates of composite samples are recommended. CARO and TAYLOR (1976) and TAYLOR et al. (1971) recently discussed the relationship between field variability and numbers of samples needed to ensure accurate evaluation of pesticide residues. With tree crops, such as citrus, composite samples should consist of 16 or more dust sampling sites obtained from 4 or more trees. Trees should be sampled near each of the cardinal points around the tree so that 4 samples will be obtained near the northwest, southwest, southeast, and northeast side of each designated tree. Samples should be obtained near the tree dripline since highest pesticide concentrations and most of the worker activity will occur at that location. Separate composite samples can also be obtained in the row middles or some other designated location with respect to the tree if workers are expected to come in contact with substantial amounts of dust in areas other than near the dripline. With grapes, row crops, etc., three composite dust samples should also be obtained. They should be taken from sites that receive substantial worker contact and which might be expected to contain the highest amounts of pesticide residues. If a significant proportion of the soil surface is not wetted by irrigation water or rain between pesticide application and sampling, dust samples should be obtained in the areas which remain dry. Avoid sampling in irrigation furrows, particularly if the wetted area represents only a relatively small proportion of the total ground surface.

With an 18- X 25-cm screen, each composite sample of 16 sites will represent the loose dust passing through a 100-mesh screen in an area of approximately 0.72 m^2. The cloth vacuum bag containing the dust sample should be removed from the vacuum cleaner and placed into a quart (0.95 L) Mason jar. Samples should be frozen immediately and kept frozen until processed in the laboratory unless they are to be extracted the same day as sampled.

Sample Preparation and Extraction. The dust sample is thawed and allowed to attain room temperature before opening the Mason jar.

The dust is carefully removed from the vacuum bag[3] and if the dust contains leaves or twigs it should be screened through a 50-mesh screen before placing into a pre-tared sample jar. Dust samples, taken from known sampling areas, should be weighed to enable calculation of pesticide residue concentrations on a unit area basis as well as on a weight basis. After the weight is recorded, the sample is mixed thoroughly, and subsamples are taken for extraction and for determination of water content if residue results are to be expressed on the basis of the oven dry weight of dust.

The extraction procedure is as follows: a 10-g subsample is weighed into a Soxhlet thimble containing a 1-cm layer of acid-washed coarse quartz sand. Approximately 3 g of sand is mixed with the dust in order to allow more complete extraction. The mixture in the thimble is then covered with a small piece of glass wool before placing into the Soxhlet. The extracting solvent should be one that readily extracts the pesticide and all alteration products of interest in worker reentry. For many organophosphate insecticides, a convenient extracting solvent is an azeotropic mixture of hexane and acetone (41/59). This extracting mixture at a volume of 250 ml has been found to be satisfactory for removing parathion, azinphosmethyl, phosalone, ethion, methidathion, and their respective oxons from soil dust. The sample should be extracted for a period of approximately four hours, assuming 15 minutes for a complete cycle of the Soxhlet or approximately 16 cycles during the 4-hour period. The thimble is then removed, rinsed into the Soxhlet, the dust sample is discarded, and the Soxhlet interior is rinsed into the reflux flask. The extract should be concentrated to an appropriate volume for convenient gas chromatographic analysis by use of a Kuderna-Danish concentrator or other suitable method.

The sample preparation and extraction procedure must be such that toxic alteration products are extracted and are stable in the extracts along with the parent compound. This may preclude the use of water in the extraction step to avoid partitioning of the more polar alteration products into the water phase or to prevent their hydrolysis in the water.

Residue Analysis. Most organophosphates and their toxic oxons can be readily determined in the concentrated extract without further clean-up. For analysis of parathion and paraoxon, for example, a Tracor 550 gas chromatograph equipped with a flame-photometric detector, selective to phosphorus, was used. The

---

[3]Before reuse, the cloth bag is soaked 20 minutes in dilute NaOH, rinsed, washed in detergent, rinsed in distilled water, and air dried.

gas chromatograph was equipped with a 1.8-m X 4-mm I.D. Pyrex glass column packed with 3% OV-1 Chromosorb W-HP (80/90 mesh). The operating parameters were: nitrogen carrier flow, 100 ml/min; burner flow rates, 75 ml hydrogen/min and 100 ml air/min; and inlet, column, and detector temperatures of 225°, 190°, and 205°C, respectively. Minimum detectable limits were 0.02 and 0.07 µg/g parathion and 0.07 and 0.25 µg/g paraoxon in soil and dust, respectively, well below the residue levels that may be hazardous to workers. Variations of the analytical procedure will depend on the pesticide and its alteration products. Any procedure for extraction, concentration, and analysis should be verified as being satisfactory before use in assessing residue levels in dust for reentry purposes.

Results for residues in soil dust should be reported in micrograms per gram of dust (µg/g or ppm) and as micrograms per cm^2 (µg/cm^2) of soil surface. Since the importance of soil dust residue levels will depend on the amount of dust as well as its residue concentration, amounts of dust per unit area should also be reported. In citrus groves, the weight of dust samples have varied between 2 and 6 mg/cm^2 from the tree dripline and between 2 and 20 mg/cm^2 from the row middle.

SOIL RESIDUES

An alternate method of assessing pesticide residues potentially hazardous to workers reentering treated crops is that of sampling and analyzing 1-cm deep soil plugs instead of loose dust from the soil surface. This procedure might be a suitable replacement for the soil dust method in areas where the soil remains moist or is moist during the worker reentry period or in cases where a cover crop precludes obtaining dust samples. However, making the procedure most useful requires the determination of the relationship between soil residue levels in such samples and the residue dose received by the workers.

Sampling--Equipment and Method. A sampling tool capable of obtaining a soil sample to a constant depth from a known area should be used. A soil sampling punch has been found to be satisfactory for removing a plug of surface soil 3 cm in diameter to a depth of 1 cm (SPENCER et al., 1975). For this purpose, a 3-cm diameter stainless steel tube, 1 m in length, was closed off with a stainless steel or aluminum plate at 1 cm from the sampling end to ensure sampling to only the 1-cm depth. The metal plate was placed 1 cm deep inside the sampling end and supported in place by contact with 0.64 cm bolts. The bolts were connected to perpendicular arms extending 10 cm on each side of the sampling tube. The arms also helped prevent the tube from penetrating the soil to depths greater than 1 cm. The soil plug is ejected from the sampling tube into a paper bag by

tapping lightly near the lower end of the tube with a rubber hammer or similar device. It may be difficult to obtain samples in loose or sandy soils with the soil punch and a scraper to obtain samples to the 1-cm depth may be substituted in these cases.

The sampling pattern and number of individual cores per composite sample will depend upon the crop grown, irrigation method, etc., in the same manner as the soil dust sample. Each composite sample should be made up of a minimum of 32 individual 3-cm soil cores or soil from approximately 226 cm^2 to a depth of 1 cm. With tree crops, such as citrus, composite samples should consist of 32 or more cores obtained from four or more trees sampled near each of the cardinal points around the tree. Samples should be obtained from a given location with respect to the tree, i.e., from near the tree dripline in most cases. Samples can also be obtained from the row middle or other location, but should be kept separate from tree dripline samples. With grapes, row crops, etc., soil samples should be obtained from sites that receive substantial worker contact and which might be expected to contain the highest amounts of pesticide residues. Avoid sampling in irrigation furrows, and, if a significant portion of the soil surface remains dry between pesticide application and sampling, soil plugs should be obtained in the areas which remain dry. The soil samples should be frozen as soon as possible and kept frozen until processed in the laboratory unless they will be extracted the same day as sampled.

Sample Preparation and Extraction. The entire soil sample taken from a known sampling area should be weighed to enable calculation of pesticide residue concentrations on a unit area as well as a weight basis. Soil samples are thawed and allowed to attain room temperature, weighed, then passed through a 2-mm sieve to break up any clods. Small sticks and other plant material are chopped into small pieces, and along with any gravel that does not go through the 2-mm sieve, are returned to the sample. The sample is mixed thoroughly and subsamples are taken for residue extraction and for determination of water content. For water content, 2 to 3 g of soil are dried in an oven at 105°C for four hours and all residue results are calculated on the basis of oven dry soil weights. Extracting a 50-g subsample of soil in a Soxhlet extractor with an azeotropic mixture of hexane and acetone for four hours has been found to be satisfactory for many organophosphate insecticides and their toxic oxons. Other extracting solvents and procedures could be used, depending upon the pesticide and soil, but all alternate procedures should be verified as being satisfactory before their use. Further preparation of the extract and the GC analysis are the same as described for the soil dust residues. Results for residues in soil should be expressed in µg/g of soil (ppm) and as µg/cm^2 of soil surface.

REFERENCES

CARO, J. H., and A. W. TAYLOR: Proc. Int. Conf. Environ. Sensing and Assessment. Inst. of Electrical and Electronics Engineers, Inc. (1967).

SPEAR, R. C., T. H. MILBY, J. T. LEFFINGWELL, and W. J. POPENDORF: Abstracts, 167th ACS Meeting, Los Angeles, Calif. (1974).

SPEAR, R. C., W. J. POPENDORF, J. T. LEFFINGWELL, T. H. MILBY, J. E. DAVIES, and W. F. SPENCER: J. Occup. Med. 19, 406 (1977).

SPENCER, W. F., M. M. CLIATH, K. R. DAVIS, R. C. SPEAR, and W. J. POPENDORF: Bull. Environ. Contam. Toxicol. 14, 265 (1975).

TAYLOR, A. W., H. P. FREEMAN, and W. M. EDWARDS: J. Agr. Food Chem. 19, 832 (1971).