Persistence of Methyl and Ethyl Parathion Following Spillage on Concrete Surfaces

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Since spills of liquid emulsifiable concentrate pesticides on concrete surfaces, such as loading docks and warehouse floors, are potential sources for contamination of foodstuff or other items set on such surfaces, it was of interest to study the decay of two typical highly toxic organophosphorus pesticides. Earlier work at this laboratory had indicated that there are difficulties in accomplishing adequate cleanup or decontamination of certain surfaces following spillage of concentrated liquid parathion (WOLFE et al. 1976). Cleanup of contaminated wood flooring was found to be almost impossible, with removal and replacement of flooring the best approach to safety. Decontamination tests on concrete surfaces gave less than satisfactory results. In view of the fact that, in many cases, it is almost impossible to remove and replace contaminated concrete, additional research was felt necessary to assess the contamination potential following spillage on such surfaces.

Methyl parathion (O,O-dimethyl O-p-nitrophenyl phosphorothioate) and ethyl parathion (O,O-diethyl O-p-nitrophenyl phosphorothioate) were applied to concrete and the potential contamination hazard at various periods of time following the simulated spillage was determined. The first experiment was to determine the persistence of methyl parathion spilled on concrete followed by no cleanup. Indoor and outdoor conditions were employed and the potential for contamination of foodstuff in contact with such spills was also determined. In the second experiment the persistence of both methyl and ethyl parathion were determined. These simulated spills were outdoors on concrete and were followed by a minimal decontamination effort similar to the haphazard cleanup procedure occasionally employed in actual spill situations.

MATERIALS AND METHODS

Concrete test blocks (20.3 x 20.3 x 7.6 cm) were especially made with surfaces finished to simulate the floor of a warehouse, a loading dock, or a worn highway (smooth-surfaced blocks) and to simulate the surface of a new highway (rough-surfaced blocks). The blocks were kiln dried and were allowed to cure for several weeks before being used.

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Outdoor and Indoor Persistence of Methyl Parathion

Sets of smooth blocks (six replicate blocks per set) were placed inside of a well-ventilated building, which would simulate warehouse floor conditions, and outside exposed to the elements, which would correspond to loading dock or highway conditions. Rainfall in our area of the Pacific Northwest averages approximately 25 cm per year with sunshine on over 275 days per year. Relatively high maximum temperatures are attained (over 32°C for an average of 14 days each summer) and the blocks were covered with snow for approximately 2 months.

Vinyl caulking material was applied in a narrow strip around the upper edge of each test block to provide an area on which the pesticide application would be confined without run-off. Methyl parathion (5 ml of 51% emulsifiable concentrate) was applied evenly over the surface of each block and was allowed to soak in for a period of 24 hours before the initial samples were taken. The applied methyl parathion was approximately 7 mg/cm^2.

Swab samples were taken periodically for one year. A metal template containing an open area of 96.5 cm^2 was placed over half of a block and the exposed surface was swabbed with 4 alcohol-soaked gauze pads using 25 strokes with both sides of each swab (50 strokes/swab). The swabs from each block were shaken for 20 minutes with 100 ml of ethanol, were well drained, and were re-extracted by shaking for 20 minutes with an additional 50 ml of ethanol.

After each of the swab testings, flour-filled muslin sacks, containing 60 g of flour, were placed in contact with the unswabbed half of the blocks and were held in place for 24 hours with a brick weighing approximately 2.1 kg. The contact surface area of each test sack was 30.6 cm^2. The flour sacks were used in order to obtain recoveries for a food item having maximum absorption. Similar sacks were also placed on the unswabbed half of the blocks, but inside of paper "boats" constructed from paper flour sack material, in order to determine the penetrability of that material. All flour sack samples were extracted with benzene in Soxhlet extractors.

Outdoor Persistence of Methyl and Ethyl Parathion

A second series of outside tests employed both rough and smooth-surfaced blocks to which methyl or ethyl parathion was applied. The application was followed by minimal cleanup, as described below, with 4 replicates used for each test.

Methyl parathion (12 ml of 51% emulsifiable concentrate) or ethyl parathion (12 ml of 45% emulsifiable concentrate) was applied to each block, prepared as described previously, and was allowed to stand for one hour. The vinyl dam was removed and the surface of the block was covered with dry soil, which was allowed to stand for 15 minutes to soak up excess pesticide. After removal of the pesticide-contaminated soil, the block surfaces were flushed with water while being scrubbed with a stiff brush for half a minute. The blocks were dried for 24 hours before the initial swab samples were obtained. These swab samples were taken in the same manner as described for the first experiment. Samples were taken periodically for 15 months.

Repeated Swabbing of a Single Block

A smooth-surfaced block soaked with parathion, and treated with minimal cleanup as described above, was allowed to weather outside for 5 months. Alcohol-soaked swabs (50 rubbing strokes per swab) were used to recover pesticide from the block surface starting at the 5-month period and intervals thereafter up to 40 days. Pairs of swabs were combined for extraction. The block was allowed to dry for at least 24 hours between swabbing intervals.

Analysis of Extracts

The extracts from swabs and flour sacks were analyzed on a Tracor MT-220 gas chromatograph equipped with a tritium electron capture detector. A 0.64 x 183 cm glass column packed with 10% DC-200 on 80/100 mesh Gas-Chrom Q was used. Inlet, column, transfer line, and detector temperatures were 215, 200, 230, and 210^{o}C, respectively.

RESULTS AND DISCUSSION

Outdoor and Indoor Persistence of Methyl Parathion

The results of the experiment to determine the persistence of methyl parathion spilled on smooth concrete surfaces are shown in Figure 1. It is apparent that the hazard due to methyl parathion is rapidly decreased, however, it is prolonged by protection of the concrete surface from direct sunlight and moisture.

The potential for contamination of foodstuff stored directly on a contaminated surface, as determined by our flour sack technique, is also indicated in Figure 1. Reduction of this toxic hazard parallels the decay of residues as determined by swab testing. The two assay procedures can be correlated as shown in Table 1. If the residue is above approximately 1 $\mu g/cm^2$ as determined by swab testing, then the flour sack technique would result in values in the region of 0.19 to 0.33 times the swab value. This allows one to roughly estimate the potential for contamination of foodstuff stored in contact with a contaminated surface by swab testing alone.

If one assumes that a 50 kg teenager; who is probably the maximum consumer of bread, cookies, or cake; eats baked goods

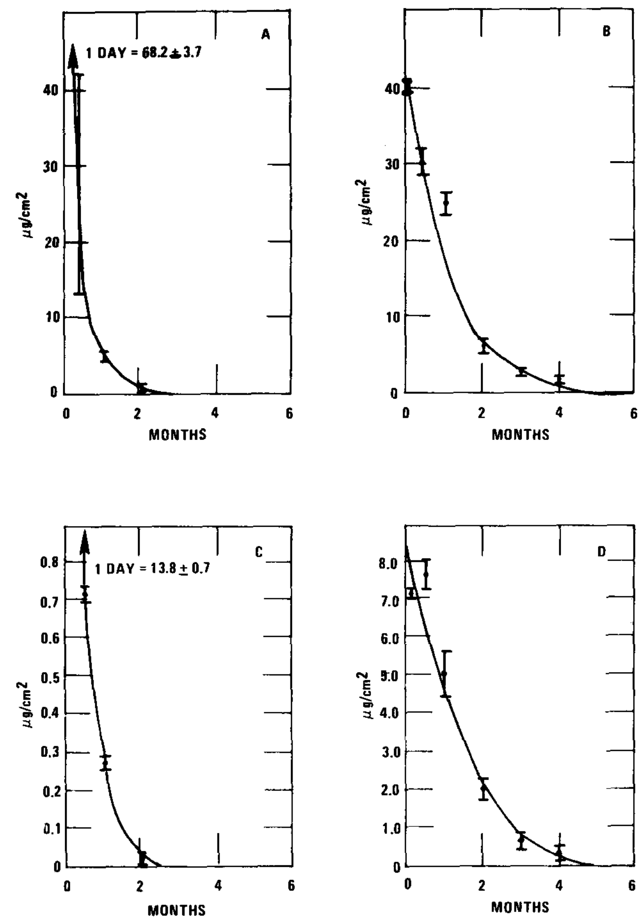

Figure I. Persistence of methyl parathion on smooth concrete surfaces. A = outdoors, swab tested; B = indoors, swab tested; C = outdoors, flour sack tested; D = indoors, flour sack tested. Experimental conditions are given under Methods. Bars indicate ± standard error for 6 replicates.

produced from flour contaminated at the levels we obtained, and assuming that no pesticide is lost during baking, then using a maximum acceptable daily intake of 0.001 mg/kg for methyl parathion (HAYES 1975), this maximum intake would be present in 7 g of the flour from the 1-day outside test. Even after 2 months our inside blocks resulted in contamination of the flour to a level that would provide our theoretical teenager with a maximum acceptable daily intake if he consumed 50 g.

Two opposing effects would alter the level of contamination in an actual storage of foodstuff over a spill. The level of

TABLE 1

Comparison of Methyl Parathion Persistence Data from Swab and Flour Sack Assays[a]

Location of Blocks	Sampling Period	Methyl Parathion Recovered ($\mu g/cm^2$)[b] Swab Value	Flour Sack Value	Swab Value Divided by Flour Sack Value
Indoors	1 day	39.0 ± 1.1	7.38 ± 0.26	5.31 ± 0.23
	1/2 mo.	30.9 ± 1.6	7.80 ± 0.42	4.02 ± 0.30
	1 mo.	24.8 ± 1.5	5.22 ± 0.58	5.20 ± 0.84
	2 mo.	6.12 ± 0.87	2.12 ± 0.31	3.00 ± 0.30
	3 mo.	2.63 ± 0.37	0.77 ± 0.18	4.31 ± 0.91
	4 mo.	1.84 ± 0.44	0.44 ± 0.15	5.03 ± 0.96
	5 mo.	0.15 ± 0.03	c	---
Outdoors	1 day	68.2 ± 3.7	13.8 ± 0.7	5.01 ± 0.34
	1/2 mo.	2.77 ± 1.45	0.72 ± 0.22	3.10 ± 0.97
	1 mo.	0.34 ± 0.06	0.28 ± 0.13	1.72 ± 0.36
	2 mo.	0.08 ± 0.02	c	---

[a]Experimental details are given under Methods.
[b]Mean ± standard error for 6 replicates.
[c]No detectable residue in part of the replicates.

pesticide would be expected to increase upon longer contact with the spill, however, the level would be decreased by the greater amount of flour contained in larger conventional sizes of sacks if the flour was mixed prior to use.

It was apparent from analysis of methyl parathion content of the flour sacks placed in paper "boats" that paper flour sack material affords considerably more protection against contamination than does muslin sacking. Only the 1-day outdoor samples contained detectable methyl parathion. These contained 0.48 ± 0.27 $\mu g/cm^2$. Flour sacks exposed at the same time but in direct contact with concrete contained 13.8 ± 0.7 $\mu g/cm^2$.

Outdoor Persistence of Methyl and Ethyl Parathion

The outdoor persistence of methyl and ethyl parathion on both smooth and rough concrete surfaces is shown in Figure 2. The decay of methyl parathion was similar to that obtained in the first experiment, while ethyl parathion exhibited a potential toxic hazard for a considerably longer period. The smooth blocks indicated a half-life of approximately 1/2 month for methyl parathion and 3-1/2 months for ethyl parathion. The apparent difference in residue levels between smooth and rough blocks was probably not due to a difference in persistence, but was a result of the difficulty encountered in swabbing the rough surfaces.

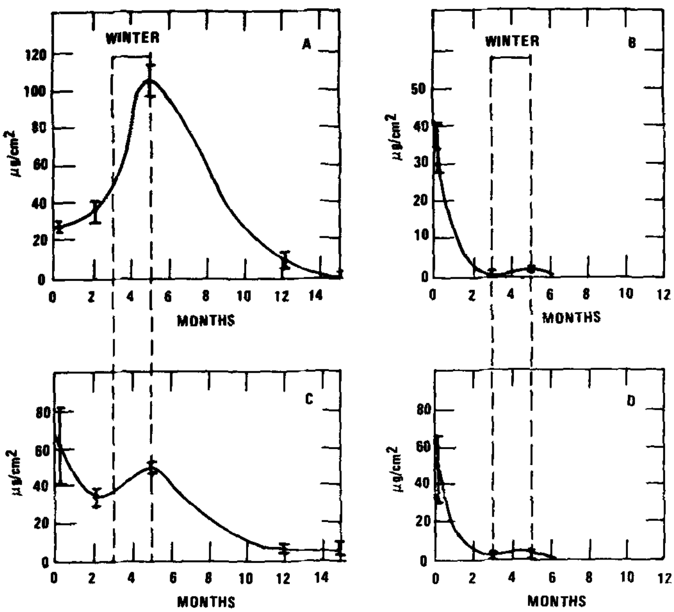

Figure 2. Persistence of methyl and ethyl parathion on concrete surfaces outdoors. A = ethyl parathion, rough surface; B = methyl parathion, rough surface; C = ethyl parathion, smooth surface; D = methyl parathion, smooth surface. Experimental conditions are given under Methods. Bars indicate ± standard error for 4 replicates.

Of special interest was the increase in available residues after the winter weathering, which occurred between the 3-month and 5-month samplings. This effect is particularly striking in the ethyl parathion samples, but is also indicated in the methyl parathion samples. This ability of cold damp winter weather to release entrapped pesticides has been noted as a general phenomenon in our studies. It also occurs in experimental plots used to investigate the persistence of pesticides that have been spilled on soil (EPA, FIELD STUDIES SECTION 1976).

The cold damp weather apparently enhances the migration of pesticides from the interior of the blocks, through the porous structures, to the surface. The ability of concrete to absorb pesticide deep into the interior and to transport it to the surface under suitable conditions is illustrated by the repeated swabbing of a single test block. Results shown in Table 2 indicate that pesticide deep within the block is transported to the surface at each swabbing, therefore, one must be very careful to reproduce conditions such as the number of swabs and the number of strokes per swab in order to obtain a valid comparison between sets of blocks.

TABLE 2

Recovery of Ethyl Parathion Residue by Repeated Swabbing of a Single Concrete Test Block Exposed to the Elements for 5 Months Prior to the First Swabbing[a]

Sampling Period	Recovery ($\mu g/cm^2$) By 2 Swabs	By all Swabs of a Sampling Period
5 mo.	41.2 31.8 29.6	103
5 mo. + 1 day	32.1 31.0 23.6	86.7
5 mo. + 2 days	39.8 21.7 45.3	107
5 mo. + 7 days	29.5 25.0 19.2	73.7
5 mo. + 8 days	20.2 17.2 21.2	58.6
5 mo. + 12 days	21.2 21.9	43.1
5 mo. + 19 days	23.4 33.5	56.9
5 mo. + 40 days	13.2 17.5	30.7

[a]Experimental details given in Methods.

The deep penetration of pesticides into the concrete was apparent when blocks that had been treated and then left to stand either outside or inside for one year were fractured. The yellow color of the *p*-nitrophenol formed during degradation of either methyl or ethyl parathion could clearly be seen to a depth of from 2.5 to 4.5 cm below the surface where the pesticides were applied.

This series of experiments indicate that although a toxic hazard exists, especially for potential contamination of foodstuff, when liquid concentrates of methyl or ethyl parathion are spilled outdoors on concrete surfaces, this hazard can be considered to have disappeared within 3 months for methyl parathion, but may persist for over 15 months for ethyl parathion. The hazard with more persistent organophosphorus pesticides, such as ethyl parathion, may be increased after outdoor exposure of concrete surfaces to cold damp weather. If the spill occurs inside, the toxic hazard for methyl parathion persists approximately twice as long as for an outside spill. It is assumed that the inside hazard for ethyl parathion would also be extended for a considerable time compared to the outside hazard. For more persistent pesticides, in lieu of the almost impossible task of removing the concrete surface to a considerable depth, a physical sealing of the surface may prove effective if suitable chemical decontamination cannot be accomplished. Additional research is being carried out to explore this possibility.

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