

# Development of Determination Method for Carbofuran and Oxydemeton-methyl in Ambient Air

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A gas chromatographic method was developed for the determination of carbofuran and oxydemeton-methyl (ODM) as well as ODM's potential transformation product, deoxydemeton-methyl (DODM), in ambient air. The chemicals were trapped using XAD-4 resin and recovered with an organic solvent. The extraction efficiencies of carbofuran, ODM, and DODM from a XAD-4 resin with ethyl acetate were near 100%. A trapping efficiency study for ODM and DODM demonstrated that both compounds were relatively nonvolatile at  $35 \pm 5$  °C. Using the method developed, air sampling was conducted at agricultural sites in California where carbofuran, ODM, and DODM have been applied. The highest amount of carbofuran found in the ambient air samples was 2.1 mg (ca. 97 pg/L of air). However, none of the samples collected from ambient air had a sufficient amount of ODM or DODM for the limit of quantitation (0.05 mg).

**Keywords:** Air sampling; carbofuran; gas chromatography; oxydemeton-methyl; resin trapping

## INTRODUCTION

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methyl carbamate), which is most commonly sold under the trade name Furidan, is widely used as an insecticide, nematicide, and acaricide. For example, approximately 316 183 pounds was applied in the state of California in 1992 (*Farm Chemicals Handbook*, 1995). The major use of carbofuran was on alfalfa for the control of weevils. Approximately one-fourth of the total was applied to rice for the control of water weevils.

There are only a few papers on carbofuran residue analysis. Rao et al. (1990) detected carbofuran in grape berries at levels of 0.07 and 0.08 mg/kg in the application of 4 and 6 kg of active ingredient (ai)/ha, respectively, using a colorimetric method.

Oxydemeton-methyl, *S*-[2-(ethylsulfinyl)ethyl] *O,O*-dimethyl phosphorothioate (ODM), which is most commonly sold under the trade name of Metasystox R, is a systemic contact insecticide with approximately 120 000 pounds applied in the state of California during 1993 (*Farm Chemicals Handbook*, 1995; CDPR, 1993). Approximately 50% of the total was applied to broccoli, and 20% was applied to cauliflower during the year. It was assumed that ODM would be detected in air samples near application sites due to its relatively low vapor pressure (3.80 kPa), but would not be found long distances from application sites. Dioxymeton-methyl, *S*-[2-(ethylsulfonyl)ethyl] *O,O*-dimethyl phosphorothioate (DODM), is a potential transformation product of ODM in air samples.

Numerous sample collection methods for pesticides in air have been developed. The most commonly used method involves the use of trapping media such as polyurethane foam, ethylene glycol impingers, charcoal, glass fiber filters, and resins. Of the resins that have been used, the XAD series have proved to be the most efficient for air sampling for pesticides, with diverse ranges of physicochemical properties and sampling duration. XAD-2, -4, and -7 have been preferred for use

in air sampling. Of these resins, the styrene–divinylbenzene copolymer XAD-4 (20/50 mesh) macroreticular resin is most commonly used for pesticides because of its high surface area, bulk price, and ability to remain stable for long periods of sampling.

Chromatographic methods have been most commonly used to determine the presence of ODM. For example, ODM in formulated products was analyzed by HPLC using reversed phase (Slahck, 1990). Mukherjee and Gopal (1993) developed a simplified method for estimating extractable residues of ODM as its sulfone from a crop matrix. ODM was oxidized with *m*-chloroperbenzoic acid to yield the oxydemeton methyl sulfone and then determined by gas chromatography. The average percent recovery for the procedure was 90–95%, and the detection limit was 0.05 mg/mL.

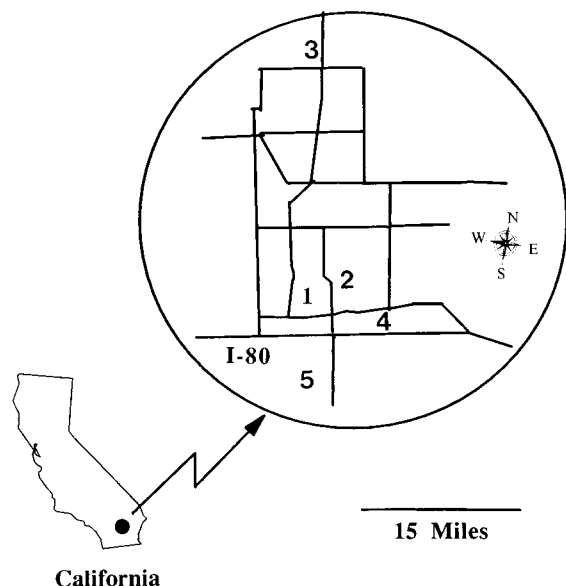
Because of the extensive and long-term use of pesticides in agriculture, public concerns have arisen over possible contamination of food, water, and air. In addition, the adverse effects on human health have begun to receive much attention. Therefore, careful monitoring of the presence of these chemicals in ambient air is one avenue to avoid possible exposure. In the present study, easy, rapid, sensitive, and effective analytical methods to detect the presence of carbofuran, ODM, and DODM were developed, and subsequently these methods were applied to determine the chemicals' concentrations in samples collected from ambient air.

## EXPERIMENTAL PROCEDURES

**Chemicals.** Carbofuran (99%), ODM (95%), and DODM (99%) standards were purchased from Chem Service (West Chester, PA). Neat standards were kept at  $-20$  °C until used. One hundred milliliters each of ethyl acetate stock solutions (1 mg/mL) were prepared and kept at 4 °C until used. Fresh analytical standards were prepared as needed. Further standard solutions for spiking and analysis were prepared from the stock solutions using pesticide-grade acetone.

**Recovery Test on Carbofuran from XAD-4 Resin.** A standard ethyl acetate solution of carbofuran (1, 10, and 100 mg) was added to 30 mL of XAD-4 resin in a 125 mL Erlenmeyer flask. The solvent was allowed to evaporate at room temperature. After evaporation of the solvent, 80 mL of ethyl acetate was added to the resin. The flask was sealed

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**Figure 1.** Air sampling sites for carbofuran: 1, El Centro (background); 2, Imperial; 3, Calipatria (1 and 2); 4, Holtville; 5, Heber.

and then placed on a rotating platform shaker for 30 min. The extract was either analyzed directly or condensed to the appropriate volume by evaporation and then analyzed by gas chromatography. Each experiment was replicated two times.

**Freezer Stability Test on Carbofuran.** A standard ethyl acetate solution of carbofuran (1, 10, and 100 mg) was added to 30 mL of XAD-4 resin in a wide-mouth screw-top glass jar (8.5 cm high  $\times$  5 cm o.d.). The glass jars were capped and placed in a freezer at  $-20^{\circ}\text{C}$  for 12 days. Ethyl acetate (80 mL) was added to each jar and extracted on a rotating platform for a minimum of 30 min. The extracts were either analyzed directly or evaporated to the appropriate volume and then analyzed by gas chromatography. The experiment was done in triplicate.

**Air Sampling for Carbofuran.** The sampling apparatus consisted of a motorized pump and tubing connected to 12 cm  $\times$  4 cm (i.d.) Teflon cartridges (Savillex Corp, Minnetonka, MN) filled with 30 mL of XAD-4 resin as previously described (Hall et al., 1997). The cartridges were placed in five air sampling sites near the town of El Centro in southern California (Figure 1). The selection of sites and time of year was based on the use of carbofuran on alfalfa for the control of weevils. The sites included four ambient air sampling sites and one urban site (background). Each sampler had an average flow rate of 15 L/min, and the sampling duration was 24 h.

The sample collections were performed three days a week from February 15 to February 24, 1995, and four days a week from February 28 to March 10, 1995. Immediately after collection, all samples were stored in an ice chest packed with dry ice and transferred to the analytical laboratory, where the samples were kept in a freezer at  $-20^{\circ}\text{C}$  until analysis.

**Recovery Test on ODM and DODM from XAD-4 Resin.** In separate experiments, 5 mL of a standard ODM (5 mg) or DODM (5 mg) solution was added to 30 mL of XAD-4 resin and the solvent was allowed to evaporate. Pesticide-grade ethyl acetate (75 mL) was added to the resin sample jars, and the jars were swirled for 1 h using a rotary platform shaker. After the resin was filtered, one-fourth of the ethyl acetate (18 mL) extract was quantitatively transferred to a 50 or 100 mL round-bottom flask and concentrated to dryness using a rotary evaporator at  $40^{\circ}\text{C}$ . Acetone (2 to 4 mL) was added to the sample to remove any residual ethyl acetate and subsequently evaporated to dryness. After the sample volume was adjusted with acetone, the pesticide was analyzed by gas chromatography. One-fourth of the ethyl acetate extract (18 mL) was oxidized with potassium permanganate. The oxidized samples were analyzed as DODM using gas chromatography. Each experiment was replicated three times.

**Oxidation Test on ODM.** One-fourth of the ethyl acetate extract (18 mL) was evaporated to dryness, and 2 mL of acetone was added to each flask with swirling. Samples were oxidized to DODM by adding 5 mL of a 20% aqueous magnesium sulfate solution, followed by 20 mL of a 0.5 N aqueous potassium permanganate solution. The samples were swirled for 30 min. The oxidized samples were transferred to 125 mL separatory funnels and partitioned three times with pesticide grade chloroform. The chloroform solution was passed through anhydrous sodium sulfate to remove water, and the filtrate was collected in 100 mL round-bottom flasks. The sodium sulfate was rinsed with an additional 5 mL of chloroform. The samples were taken to dryness and then rinsed with acetone. After the acetone solutions were taken to dryness again, the samples were brought up to 2 mL in volume with acetone, and subsequently DODM was analyzed by gas chromatography. Each experiment was replicated three times.

**Storage Stability Test on ODM and DODM.** An XAD-4 resin (30 mL) was fortified with 50 mg of either ODM or DODM. After the 44 samples containing ODM (12) and DODM (12) were stored at  $-20^{\circ}\text{C}$  for 29 days, ODM and DODM were analyzed according to the procedures described above.

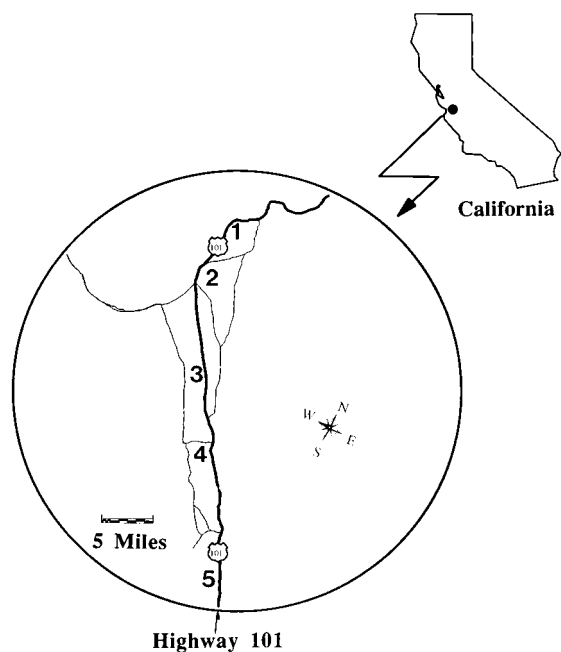
**Study on Trapping Efficiencies for Carbofuran, ODM, and DODM.** To validate the method for carbofuran, ODM, and DODM determination, air samplers fortified with 100 mg of carbofuran, 50 mg of ODM, or 50 mg of DODM were run at  $32^{\circ}\text{C}$  for a 12 h period on the roof of a four-story building in Davis, CA, in July 1995 according to the method previously reported (Hall et al., 1997). The primary and backup traps packed with 30 mL of XAD-4 resin were interfaced in series. Glass wool spiked with 100 mg carbofuran, 50 mg of ODM, or 50 mg of DODM was placed on top of the primary trap. The solvent was allowed to evaporate before the air pumps were started. After a 12 h period of trapping at a flow rate of 25–35 L/min, the resin and glass wool were extracted with ethyl acetate and the extract was prepared for gas chromatographic analysis of carbofuran, ODM, and DODM as described above. A blank sample (unfortified) was prepared for each experiment. The trapping efficiency of volatilized carbofuran, ODM, and DODM on XAD-4 resin was calculated using the following equation:

$$\text{trapping efficiency} = \frac{\text{amt trapped on resin}}{\text{amt spiked} - \text{amt recovered from glass wool}} \times 100$$

**Ambient Site Study for ODM and DODM.** ODM and DODM in ambient air were trapped using the method described for carbofuran. Five ambient air sampling sites were established in Monterey County, on the central coast of California, by the California Air Resources Board (Figure 2). Sites consisted of four ambient air sampling sites and an urban background site. The selection of sites and time of year were based on the use of ODM.

Sampling started on August 14, 1995, and concluded on September 8, 1995. Each week, with the exception of the last week, had four 24 h sampling periods. The final week had three days due to the Labor Day holiday. Immediately after collection, all samples were stored in ice chests packed with dry ice and transported directly to the laboratory for analysis at the end of each week.

**Application Site Study for ODM and DODM.** An application site for ODM was selected for monitoring the week after the completion of the ambient air site study. The location of the site was northwest of the city of Salinas in Monterey County, California. ODM was applied to  $\sim 14$  acres at a rate of 0.25 qt of ai/acre. The chemical was applied via ground application on September 12, 1995. The application took approximately 1 h to complete. The samples were collected at the time intervals shown in Figure 3. Each period had four sampling sites placed around the field at the northwest, southwest, southeast, and east compass points. There were a total of seven periods of sampling for various durations in addition to a background or control sample prior to pesticide



**Figure 2.** Air sampling sites for ODM and DODM: 1, Prunedale; 2, Salinas; 3, Chualar; 4, Gonzales; 5, Greenfield.

Application							
Period	1	2	3	4	5	6	7
Duration	1 h	2 h	4 h	12 h	12 h	24 h	24 h
Date	9/12/95			9/13		9/14	9/15

**Figure 3.** Sampling periods of ODM and DODM.

application. Samples were transported to the laboratory for analysis as described above.

**Quantitative Analysis of Carbofuran, ODM, and DODM.** Two gas chromatographic systems were used for this study. A Perkin-Elmer Autosystem model gas chromatograph equipped with a nitrogen/phosphorus detector (NPD), a 15 m  $\times$  0.53 mm i.d. DB-5 Megabore capillary column (J&W Scientific, Folsom, CA), and an autosampler was used to quantitate carbofuran. The oven temperature was programmed from 170 to 220  $^{\circ}$ C at 10  $^{\circ}$ C/min. The carrier gas flow rate was 5 mL/min. The injector and detector temperatures were 225 and 280  $^{\circ}$ C, respectively.

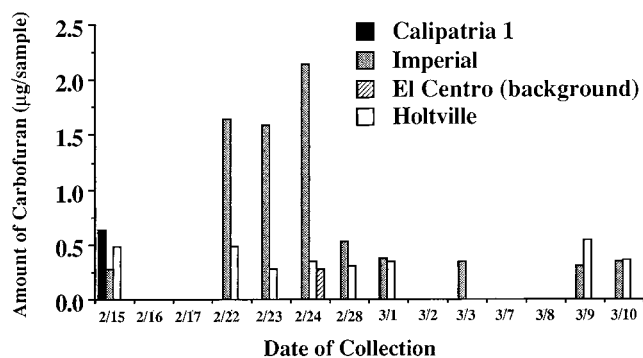
A Hewlett-Packard 5890A gas chromatograph equipped with a NPD, a 30 m  $\times$  0.53 mm i.d. XTI-5 Megabore column (Restek, Inc., Bellefonte, PA), and an autosampler was used to quantitate ODM and DODM. The isothermal oven temperature was 200  $^{\circ}$ C. Carrier gas flow rate was 20 mL/min. The injector and detector temperatures were 250 and 280  $^{\circ}$ C, respectively.

The NPD bead voltage was adjusted to provide minimum detection of a 3 mL injection of a 62.5 pg/mL standard for carbofuran and a 31.5 pg/mL standard for ODM or DODM. Peak quantitation was accomplished via a TurboChrom data station (Perkin-Elmer, Norwalk, CT) into an IBM PC, where the peaks were integrated and the results entered into an EXCEL (Microsoft, Bothell, WA) spreadsheet program.

**Qualitative Analysis of Carbofuran, ODM, and DODM.** Confirmation of carbofuran, ODM, and DODM identification in a sample was conducted using gas chromatographic retention time data and mass spectra obtained by a Hewlett-Packard 5871 mass selective detector.

## RESULTS AND DISCUSSION

**Carbofuran.** The recovery of carbofuran with solvent extraction from the resin spiked at 1 mg was 99.2%,



**Figure 4.** Results of carbofuran analysis. Refer to Figure 1 for the sampling sites.

10 mg spike recovery was 98.7%, and 100 mg spike recovery was 107.9%. The values are averages of two replicates. The results indicate that carbofuran is extracted with ethyl acetate satisfactorily from XAD-4 resin. The recovery percents of carbofuran from the freezer stability tests were  $107.0 \pm 3.7\%$  from samples spiked at 1 mg,  $110.1 \pm 0.4\%$  from samples spiked at 10 mg, and  $91.7 \pm 0.6\%$  from samples spiked at 100 mg. The values are mean  $\pm$  standard deviation ( $n = 3$ ). The result indicates no degradation of the compound over the 12-day interval and complete extraction from the resin in all cases. Also, a shape of carbofuran GC peak exhibited no occurrence of degradation in a GC injector. The recovery of carbofuran from the trapping efficiency test was  $96.7 \pm 0.9\%$ . The value is mean  $\pm$  standard deviation ( $n = 3$ ).

Figure 4 shows the analytical results of the samples for carbofuran from the collection sites. The values were not corrected for the recovery efficiencies. The highest amount of carbofuran found was 2.1 mg ( $\sim 97$  pg/L of air) at the Imperial site on February 24, 1995. The Imperial site also had the most positive hits, with 9 of 12 samples having amounts of carbofuran above the limit of detection ( $< 0.25$  mg/sample). The site at Holtville had 8 positive samples of a total of 14 samples. The highest amount found in the samples at the Holtville site was 0.54 mg ( $\sim 24$  pg/L of air) on March 9, 1995.

Only two samples at the Calipatria 1 site (0.64 mg on February 15, 1995) and the El Centro site (0.28 mg on February 24, 1995) had a positive above the limit of detection. Samples from the sites Calipatria 2 and Heber did not contain carbofuran above the limit of detection. The highest residue was detected for the sample from the Imperial site. Trace amounts of residue were also detected from the urban background at El Centro. The distance between these two sites is  $\sim 10$  miles, suggesting that carbofuran was transported by air in the vapor phase and/or in the particle phase. This is comparable to other pesticides such as molinate (Seiber et al., 1989). It has long been established that pesticides in air can be transported over long distances (Kurtz, 1990).

**ODM and DODM.** Recovery efficiencies of nonoxidized DODM, oxidized ODM, and oxidized DODM from XAD-4 resin with ethyl acetate were  $108 \pm 3.6\%$ ,  $102 \pm 11.6\%$ , and  $112 \pm 8.3\%$ , respectively. The values are mean  $\pm$  standard deviation ( $n = 3$ ). Recovery of the pesticide and its transformed product was quite satisfactory.

The results of storage stability tests for ODM and DODM were  $93 \pm 3.9\%$  and  $102 \pm 2.5\%$ , respectively. The values are mean  $\pm$  standard deviation ( $n = 4$ ). The

stability tests indicated that ODM and DODM are sufficiently stable under the conditions used over 29 days.

The trapping efficiency test on ODM and DODM resulted in <50% recoveries. The results are not satisfactory, but Seiber et al. (1989) encountered similar problems with methylparathion using the above procedures when methylparathion was monitored after commercial application during a rice crop season. The results were similar to those found for both ODM and DODM. It should be noted that there is a large degree of experimental error when a small amount of material volatilizes from the glass wool.

There were no detectable residues of ODM or DODM above the limit of quantitation (0.25 mg/sample) in the air samples collected at any of the ambient air sites shown in Figure 2.

There were also no detectable residues of ODM or DODM above the limit of quantitation in the air samples collected at Salinas, CA, after ODM application. There were only a few samples that had responses above the limit of detection (0.05 mg/sample). ODM had the maximum trace residue during the application sampling period (period 1, Figure 3) at the southwest site. The next highest residue occurred during period 5 at the southeast site. In all, 14 of the 41 samples had ODM residues at or above the limit of detection. There were no residues of DODM for the initial 24 h sampling period. The highest residue found for DODM occurred during the second 24-h period (period 7) at the southeast site. There were only four samples that gave residues above the detection limit for DODM. Samples that have values less than the limit of quantitation but greater than the limit of detection are only estimates of residues. The results suggest that oxidation of ODM to DODM does not occur within 48 h after the application.

Since only trace amounts of carbofuran, ODM, and DODM were recovered at application sites, these chemicals are not significantly present in ambient air even shortly after the application. The method used in the present study shows that resin trapping is simple and

efficient and can be applied satisfactorily for monitoring carbofuran, ODM, and DODM in ambient air.

#### ACKNOWLEDGMENT

We gratefully acknowledge the technical assistance of Don Fitzell.

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Received for review April 28, 1997. Accepted August 25, 1997.<sup>⊗</sup> This research was funded, in part, by the California Air Resources Board, the U.S. EPA (R819658) Center for Ecological Health Research at UC Davis, and the USDA IR-4.

JF970343P

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 15, 1997.