

# Development and Validation of an Analytical Method for Naled and Dichlorvos in Air

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A new gas chromatographic method for analysis of the thio organophosphate pesticide naled and its transformation product dichlorvos (DDVP) was developed and validated. Naled and DDVP in air were trapped on XAD-4 resin. The pesticides were recovered from the resin with ethyl acetate. Ethyl acetate extract was analyzed for naled and DDVP by using a gas chromatograph equipped with a DB-5 Megabore capillary column and a nitrogen-phosphorus detector. The limits of quantitation for naled and DDVP were 0.05 and 0.10  $\mu\text{g}/\text{sample}$ , respectively. Naled and DDVP trapped on the resin were stable over 21 days at  $-20\text{ }^\circ\text{C}$ . Trapping efficiencies of naled and DDVP in the air samples were  $74.5 \pm 3.5\%$  and  $49.7 \pm 3.3\%$ , respectively. The newly developed method showed excellent results for the air samples collected at the application sites. Maximum observed concentrations of naled and DDVP at the application sites were 6.30 and 0.99  $\mu\text{g}/\text{m}^3$ , respectively.

**Keywords:** Air sample; naled; dichlorvos; gas chromatography

## INTRODUCTION

Naled, *O,O*-dimethyl *O*-(1,2-dibromo-2,2-dichloroethyl)phosphate, is an insecticide that is widely used on commodities such as citrus and grapes. For example, approximately 164 904 lb of it was applied in California in 1992 (CDFA, 1992).

Dichlorvos (DDVP) is a potential air transformation product of naled. Synthetic DDVP has been used both as a contact insecticide and as a fumigant. Approximately 5000 lb was used in California in 1992. In prior years, DDVP was used in household products and in flea collars for pets. The results of toxicology and carcinogenesis studies of DDVP in rats and mice showed unequivocal evidence of carcinogenicity (NTP, 1989). DDVP induced forestomach tumors in mice when it was administered in corn oil for 103 weeks (Chan et al., 1991).

Because of the relatively high vapor pressures of naled (266 kPa) and DDVP (1600 kPa), both have the potential to be detected in air samples both near and far from application sites. Therefore, it is worthwhile to develop a method to determine these insecticides in air to investigate their impact on human health. In the present study, an analytical method for trace naled and DDVP in air samples was developed and the method was validated using the air samples collected from application sites.

## EXPERIMENTAL PROCEDURES

**Insecticides.** Analytical standards of naled (93.7%) and DDVP (99.8%) were obtained from AMVAC Chemical Corp. (Los Angeles, CA). Neat standards were kept at  $-20\text{ }^\circ\text{C}$  until used. Stock solutions (100 mL each) for analysis were prepared by dissolving naled and DDVP in ethyl acetate (1.0 mg/mL) and kept at  $4\text{ }^\circ\text{C}$  until used. *Caution:* Both insecticides

are suspected carcinogens and should be handled with care. Dilute spiking and analytical standards were prepared from these stock solutions. Initial gas chromatographic (GC) analysis of the diluted standards indicated that the analytical standard of naled contained approximately 6.8% DDVP at the time the naled standard was received from AMVAC.

**Trapping Medium.** XAD-4 (Rohm and Haas, through Supelco, Bellefonte, PA), a macroporous resin, was employed as the trapping medium for naled and its transformation product, DDVP. XAD-4 resin was prepared prior to use as described in Seiber et al. (1989).

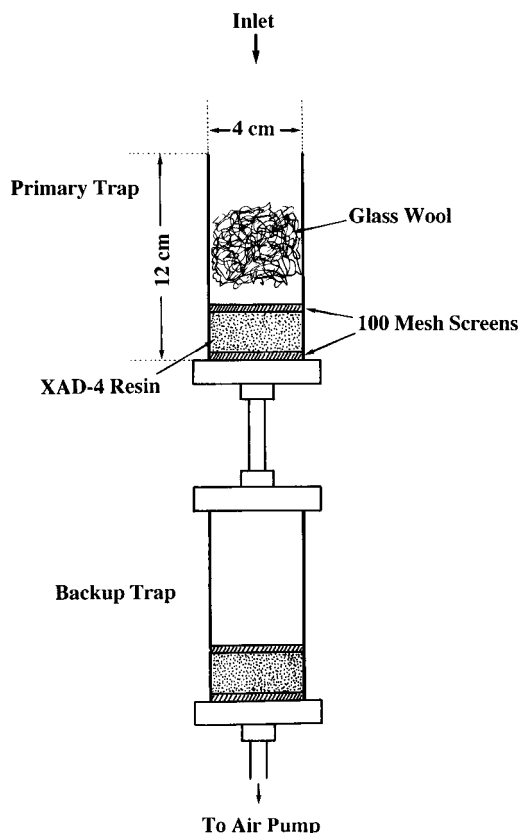
**Storage Stability Tests on Naled and DDVP.** Naled (2  $\mu\text{g}$ ) or DDVP (2  $\mu\text{g}$ ) was added to 30 mL of resin in a jar with a Teflon-lined lid either directly (dry set) or as a 50 mL ethyl acetate solution (wet set). The sample jars were stored at  $-20\text{ }^\circ\text{C}$  for 21 days. The compounds in the sample jars were analyzed according to the method described above. The experiment had four replicates.

**Recovery Efficiency Tests on Extraction of Naled and DDVP from XAD-4 Resin.** A standard solution (0.1 mL each) of naled or DDVP was added to 30 mL each of XAD-4 resin, and the solvent was allowed to evaporate at room temperature. After evaporation of the solvent, 50 mL of ethyl acetate (ca. 1.5 bed volumes) was added to the resin sample jars and the jars were swirled for 1 h using a rotary platform shaker. The extract (0.5 mL) was quantitatively transferred to an appropriate volumetric flask and the parent compound was analyzed by gas chromatography. The experiment was done in triplicate.

**Recovery Efficiency Tests on Distillation of Ethyl Acetate Solutions of Naled and DDVP.** Naled or DDVP (2 and 50  $\mu\text{g}$  each) in 50 mL of ethyl acetate was placed in a 300 mL round-bottom flask. The solvent was carefully evaporated to dryness at  $30\text{ }^\circ\text{C}$  using a rotary evaporator. The residue in a flask was redissolved with ethyl acetate and quantitatively transferred to an appropriate volumetric flask; the parent compound was then analyzed by gas chromatography. The experiment was done in triplicate.

**Trapping Efficiency Tests on Naled and DDVP in Air.** The collection cup prepared for trapping naled and DDVP in air is shown in Figure 1. A 100 mesh stainless steel screen was tightly fitted to the inside bottom of each cup to keep the resin intact. The cups were connected in tandem via a Teflon tube with the top cup the primary trap and the bottom the

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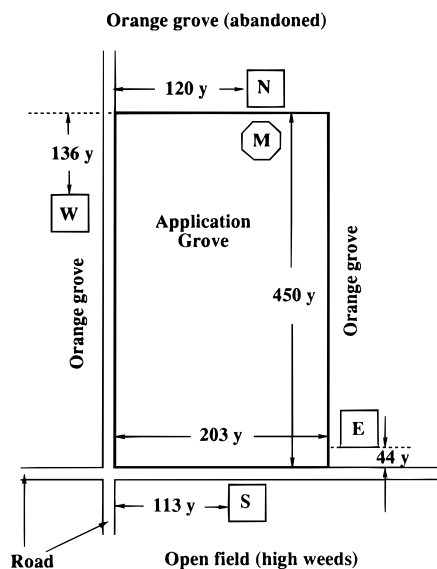
**Figure 1.** Schematic of air sampling cups.

backup. Tygon tubing (1 cm i.d.  $\times$  1 mm wall  $\times$  1.25 cm o.d.) was connected to a Staplex high-volume air pump which was fitted with a five-port manifold that allowed the air flow range through the samplers to be 50–100 L/min.

Each cartridge was filled with 30 mL of XAD-4 resin, and a top Teflon retainer was added to form a sandwich and keep the resin from "vortexing" and thus causing a buildup of resin on the sides and a thin bed in the center ("dishing" effect) when the cap was added. The backup trap was then attached to the primary trap. The backup trap also contained a 30 mL resin sandwich. Acetone-washed glass wool was placed above the resin sandwich in the primary cup and fortified with 100  $\mu$ g of naled or DDVP, and then the air pump was turned on. Flow rates were measured at the beginning and end of each sampling period. The experiments consisted of one control (primary and backup traps) and three replicated glass-wool-fortified sets of traps. Trapping experiments were run under laboratory conditions of 20 °C and approximately 35% humidity.

The compounds trapped in the resin and remaining in the glass wool were recovered according to the same method described above and analyzed by gas chromatography.

**Quantitative Analysis of Naled and DDVP.** A Perkin-Elmer Autosystem model gas chromatograph equipped with a nitrogen-phosphorus detector (NPD), a 30 m  $\times$  0.53 mm (i.d.)  $\times$  0.5  $\mu$ m (*d<sub>f</sub>*) bonded phase DB-5 Megabore capillary column (J&W Scientific, Folsom, CA), and an autosampler was used to quantitate naled and DDVP in the recovery efficiency experiment. The oven temperature was programmed from 100 to 200 °C at 20 °C/min. The GC retention times of naled and DDVP were 5.15 and 5.42 min, respectively. The injector and detector temperatures were 250 and 280 °C, respectively. The helium carrier gas flow rate was 11 mL/min. The voltage for the NPD bead was adjusted to provide a minimum detectable of a 2  $\mu$ L injection of a 5 pg/ $\mu$ L standard. Data reduction was accomplished via a TurboChrom data station (Perkin-Elmer, Norwalk, CT), and the results were entered into an EXCEL (Microsoft) spreadsheet program. Analysis of samples was quantified by using a five-point external linear regression standard curve for both naled and DDVP. Each sample was



**Figure 2.** Naled and DDVP application monitoring sites. N, E, S, and W are sampling sites, and M is the meteorology station.

injected twice, and a standard was interspersed between samples during each analysis (set). The average of both analyses was reported.

A Hewlett-Packard (HP) 5890A gas chromatograph equipped with an NPD, a 30 m  $\times$  0.53 mm (i.d.)  $\times$  0.5  $\mu$ m (*d<sub>f</sub>*) XTI-5 Megabore capillary column (Restek Corp., Bellefonte, PA) and an HP 7673 autosampler was used to quantitate naled and DDVP from the samples from application sites. The helium carrier gas flow rate was 20 mL/min. The injector and detector temperatures were 250 and 280 °C, respectively. The oven temperature was programmed from 100 to 220 °C at 20 °C/min and held for 0.5 min. The GC retention times of naled and DDVP were 2.72 and 2.87 min, respectively. The NPD bead voltage was adjusted to provide a minimum detectable of a 3  $\mu$ L injection of a 5 pg/ $\mu$ L standard (at least 3 times above the noise level of the detector). Peak quantitation was accomplished via a TurboChrom data station (Perkin-Elmer) into an IBM PC, where the peaks were integrated and the results were entered into an EXCEL (Microsoft) spreadsheet program.

**Air Sampling over the Application Sites.** Air sampling was conducted immediately after the insecticide application in Tulare County, California (an orange grove of about 20 acres) during the week of June 5, 1995, using the trap developed for this study (Figure 1). Naled was applied at a rate of 1 pint/acre using an air-blast sprayer. Carzol SP (an insecticide) was applied with naled at a rate of 1.5 lb/acre; a fertilizer, 10–12–0, was applied simultaneously at a rate of 0.2 gal/acre.

Five samplers—one at north (N), two at east (E), one at south (S), and one at west (W)—were placed as shown in Figure 2. Each sampler was set up at about 1.5 m above ground. The collection intervals were June 5, 7:00 p.m., to June 6, 6:00 a.m. (background); June 6, 6:30 a.m. to 11:30 a.m. (1); June 6, 11:30 a.m. to 1:30 p.m. (2); June 6, 1:30 p.m. to 4:30 p.m. (3); June 6, 4:30 p.m. to 7:30 p.m. (4); June 6, 7:30 p.m., to June 7, 7:00 a.m. (5); June 7, 7:00 a.m., to June 8, 7:00 a.m. (6); and June 8, 7:00 a.m., to June 9, 7:00 a.m. (7). Background samples were collected prior to insecticide application. The trapping air flow rates were measured at the beginning and at the end of each sampling period, and the average of two flow rates (14.8 L/min) was used to determine total volume of samplings.

## RESULTS AND DISCUSSION

There are only a few publications on applicable methodology for analysis of either naled or DDVP in air samples. Nakamura et al. (1993) reported simultaneous

determination of naled and DDVP in agricultural products, such as apples and pumpkins, using gas chromatography. Leidy et al. (1987) analyzed DDVP in air by gas chromatography after DDVP was trapped in an impinger containing 2-methyl-2,4-pentenediol.

The limits of quantitation for naled and DDVP were 0.05 and 0.10  $\mu\text{g}/\text{sample}$ , respectively, in the present study. The minimum detectable amount was 5  $\text{pg}/\mu\text{L}$ .

The results of storage stability tests on the "dry set" and the "wet set" of naled are  $103 \pm 8.1\%$  and  $116 \pm 3.2\%$ , respectively. The results of those of DDVP are  $110 \pm 6.0\%$  and  $108 \pm 6.7\%$ , respectively. The values are the mean  $\pm$  standard deviation of four replicate experiments. On the basis of our prior experience, optimal recoveries of naled in/on other crop matrices could only be achieved by extracting samples into an organic solvent within 24 h after sampling. Therefore, we decided to do a "wet experiment" in tandem with the dry set because the "dry experiment" may have been less than quantitative. The results indicate that there are no significant differences between the wet and dry sets for the 21-day storage period. Essentially 100% recovery efficiency was achieved from the extraction tests.

The results of the recovery efficiency tests from distillation of the ethyl acetate solutions containing 2 and 50  $\mu\text{g}$  of naled are  $97 \pm 3.1\%$  and  $94 \pm 1.9\%$ , respectively. The results of those of DDVP are  $105 \pm 5.7\%$  and  $101 \pm 0.3\%$ , respectively. The values are the mean  $\pm$  standard deviation of three replicate experiments. In spite of their high vapor pressure, naled and DDVP can be quantitatively evaporated to dryness using a rotary evaporator.

The results of trapping efficiency tests on naled and DDVP in the air samples were  $74.5 \pm 3.5\%$  and  $49.7 \pm 3.3\%$ , respectively. The values are the mean  $\pm$  standard deviation of three replicate experiments.

The trapping efficiency was calculated using the equation

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

where the amount that actually evaporated was the original amount fortified on the glass wool minus the amount found on the glass wool after the experiment was completed.

Naled was quantitatively trapped at ambient conditions with flow rates of 50 L/min for 24 h. The trapping efficiency of naled was approximately 75%. Virtually no naled or DDVP was recovered from the backup traps, suggesting that almost all of the compounds were trapped in the primary traps. Approximately 50% of DDVP was found on the primary trap with only one backup trap containing a detectable amount of DDVP. When 100  $\mu\text{g}$  of DDVP was added directly to 30 mL of resin in a trap and then air was pulled through it for approximately 24 h, over 95% of the DDVP was recovered, indicating that there was no loss due to breakdown or breakthrough.

The validation of a newly developed analytical method for naled and DDVP in the air samples was conducted using the samples collected over the application sites. A trap shown in Figure 1 was used without glass wool. Figures 3–6 show the results of naled and DDVP analysis in the air samples collected over the application sites. Maximum air concentrations of naled ( $6.30 \mu\text{g}/\text{m}^3$ ) were obtained during collection period 1 at the north

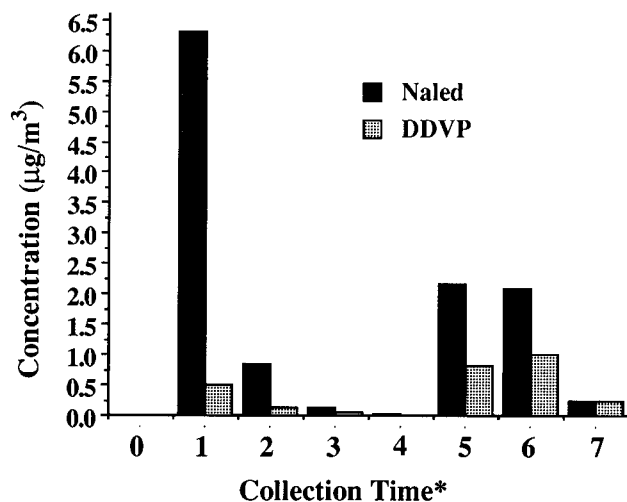


Figure 3. Naled and DDVP residues in air collected at site N. \*Refer to Experimental Procedures.

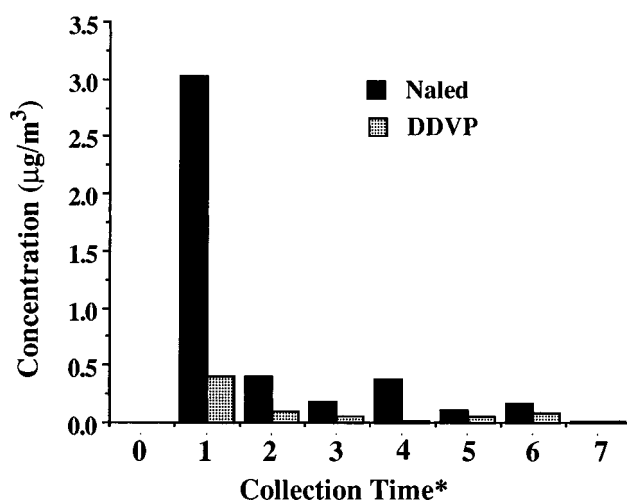


Figure 4. Naled and DDVP residues in air collected at site E. Values are averages of the results from two samples. \*Refer to Experimental Procedures.

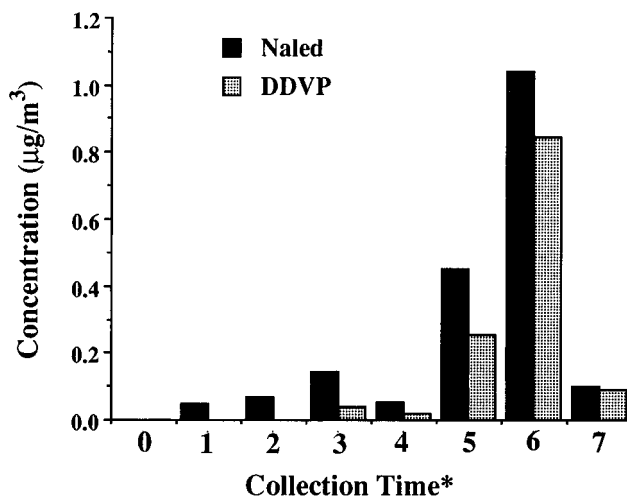
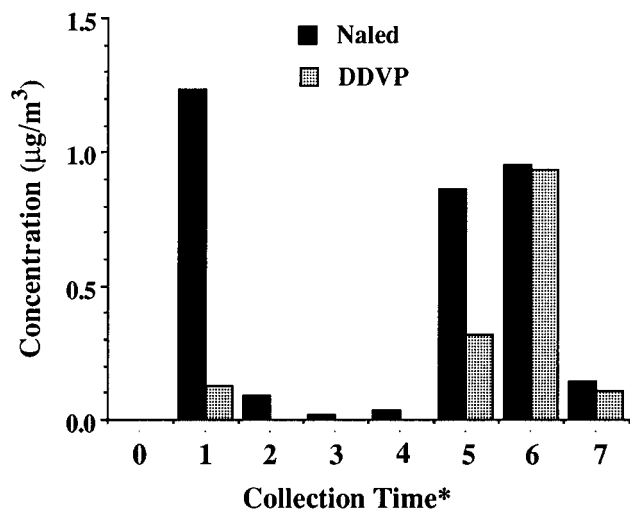


Figure 5. Naled and DDVP residues in air collected at site S. \*Refer to Experimental Procedures.

site (Figure 3). The maximum air concentration of DDVP ( $0.99 \mu\text{g}/\text{m}^3$ ) was obtained during collection period 6 at the north site (Figure 3). The most naled was recovered during collection period 1 at all sampling sites except south. The most DDVP was recovered during collection period 6 at all sampling sites except



**Figure 6.** Naled and DDVP residues in air collected at site W. \*Refer to Experimental Procedures.

east. Recoveries and collection periods of naled and DDVP did not show any clear relationships. DDVP, which is a transformation product of naled, was recovered more during the later collection periods, suggesting that naled transformed into DDVP over the passage of time. Because thio organophosphates were reportedly converted to their corresponding oxons (Yamamoto and Fukami, 1979), naled (amount) was fortified directly on resin and air was pulled through the resin for 24 h. However, no conversion of naled to DDVP was observed. Therefore, the presence of DDVP in the samples may be due to conversion of naled caused by soil pH, soil

moisture, photolysis, and/or microbial action. Also, the oxons were not observed through the experiments.

This newly developed method of analysis is useful for monitoring pesticide residues in the air.

#### LITERATURE CITED

- CDFA (California Department of Food and Agriculture). *1992 Pesticide Use Report*; Sacramento, CA, 1992; p 2.
- Chan, P. C.; Huff, J.; Haseman, J. K.; Alison, R.; Prejean, J. D. Carcinogenesis studies of dichlorvos in Fisher rats and B6C3F1 mice. *Jpn. J. Cancer Res.* **1991**, *82*, 157–164.
- Leidy, R. B.; Sheets, T. J.; Wright, C. G. DDVP residues in air following application to a tobacco-storage warehouse. *Environ. Monit. Assess.* **1987**, *9*, 263–268.
- Nakamura, Y.; Sekiguchi, Y.; Tsumura, Y.; Tonogai, Y.; Ito, Y. Simultaneous determination of naled and its reduced product dichlorvos by gas chromatography. *J. Food Hyg. Soc. Jpn.* **1993**, *34*, 426–433.
- NTP (National Toxicology Program). *Toxicology and Carcinogenesis Studies of Dichlorvos in F344/N Rats and B6C3F1 Mice*; U.S. Department of HHS, PHS, NIH NTP Technical Report 334; U.S. GPO: Washington, DC, 1989.
- Seiber, J. N.; McChesney, M. M.; Woodrow, J. E. Airborne residues resulting from use of methyl parathion, molinate and thipencarb on rice in the Sacramento Valley, California. *Environ. Toxicol. Chem.* **1989**, *8*, 577–588.

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