

# Air Levels of Volatile Organic Compounds following Indoor Application of an Emulsifiable Concentrate Insecticide

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Insecticidal formulations contain volatile inert ingredients that may be responsible for many of the general health complaints associated with indoor applications. Recent indoor air modeling results suggested that the levels of these volatile organic compounds (VOCs) could be high enough to cause health complaints among certain individuals. To confirm these findings, we performed broadcast and perimeter insecticide applications in four identical, unoccupied student apartments at Rutgers University. Passive dosimeters were used to obtain time-weighted average VOC measurements during the 24 h following each application. Levels were consistently higher in the apartments treated with broadcast applications, reflecting the greater amount of material applied by this method. Peak broadcast levels ( $21 \text{ mg/m}^3$ ) were similar to peak levels generated by the model and were in the range expected to result in health complaints. Peak perimeter levels were approximately two-thirds as high as peak broadcast levels. Both broadcast and perimeter applications peaked around 10–14 h following application, which is considerably later than the model prediction (2–4 h). These results suggest that the potential for exposure may be greater than originally predicted and that ventilation and reentry recommendations may need to be prolonged well past the 3–6 h implied by the model results.

## Background

Organic solvents may comprise a large percentage of the inert ingredients found in insecticidal formulations registered for indoor use. These solvents are usually many

times more volatile than the active insecticides themselves. Exposure to volatile organic compounds (VOCs) can result in general health complaints, such as headache, irritated eyes, and chest tightness, that are similar to many of the health complaints associated with mild insecticide intoxication (1).

Recently, we performed a series of computer simulations to estimate the VOC air levels associated with indoor insecticide applications. These simulations were run using the Indoor Air Quality (IAQ) model developed by the U.S. EPA, which is based upon indoor measurements taken at a seven-room test house. The hypothetical applications that we modeled included perimeter-room and broadcast (whole-floor) treatments, using both emulsifiable concentrate and aerosol insecticide formulations (1).

The simulations suggested that the VOC levels were relatively substantial and that they could be high enough to cause symptoms in at least some of the exposed persons. However, there was no way to quantify how closely the model approximated reality, since simplifying and worst-case assumptions were employed that may have somewhat distorted the true pattern of VOC exposure associated with these applications. Therefore, in an attempt to validate the results reported from the model, we measured VOC time-weighted average (TWA) air levels following actual indoor applications of an emulsifiable concentrate (EC) chlorpyrifos formulation. This paper presents the air-monitoring results and compares them to the levels predicted by the model. The impact that these results may have on ventilation and reentry recommendations is also discussed.

## Methods

During August 1995, indoor insecticide applications were made to four vacant apartments located on the middle two floors of a four-level student apartment complex at Rutgers University. There were two apartments on each floor, and each contained approximately  $90 \text{ m}^2$  living area,  $200 \text{ m}^3$  volume, and 100 m perimeter distance. These apartments were identical and consisted of a living room and attached dining area, kitchen, bathroom, storage area, and two bedrooms. Windows were located only in the bedrooms and the living room, with the latter room being on the opposite end of the apartment from the bedrooms.

The apartments were also identically furnished. Each contained a number of potential VOC sinks, including a sofa, two living room chairs, four beds, and window curtains. The living room and both bedrooms were carpeted, with linoleum covering all other floor surfaces. The ceiling and all walls were poured concrete that had been painted.

The heating, ventilation, and air conditioning unit (HVAC) was located in the storage area. The HVAC was maximized for cooling with vents located at the entrance to the living room, bath, kitchen, and bedrooms. The HVAC in each apartment was self-contained and did not communicate with other apartments. All four thermostats were set for  $68^\circ\text{F}$  throughout the study. All windows were kept closed throughout the study, and entry in and out of the apartments was minimized.

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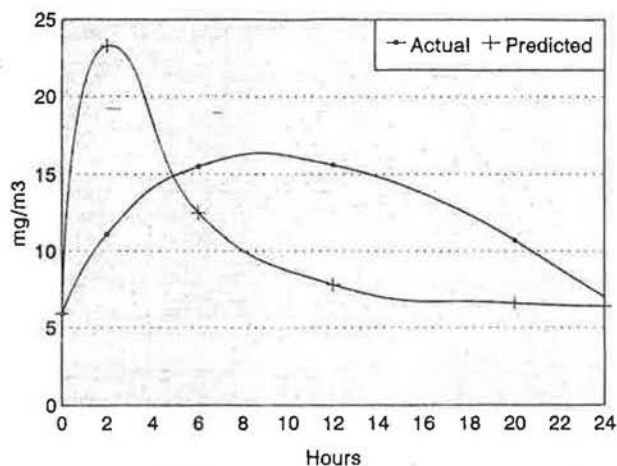


FIGURE 3. TWA VOC levels from perimeter chlorpyrifos applications compared to predicted levels. The actual results are averages for the four apartment/room combinations. Predicted results have been scaled to the average baseline VOC level.

mg/m<sup>3</sup> for perimeter) to the predicted levels at each time period. All TWA results were plotted at the midpoint of their respective time periods.

The broadcast applications resulted in peak levels that were the same as predicted (approximately 21 mg/m<sup>3</sup>), although actual and predicted results were not exactly comparable, as the current application was made at only 63% of the label rate assumed under the simulations. Also, the model predictions were based on the release of 1.25 more VOCs (20 g) than calculated under the label rate (16 g) in order to capture both broadcast and perimeter estimates (1). Therefore, the model is estimated to have predicted only about 80% of the actual peak broadcast levels ( $0.63 \times 1.25$ ). The peak perimeter levels were only about two-thirds of that predicted, reflecting the smaller amount of material applied.

Both perimeter and broadcast peak levels occurred at approximately 10–14 h, much later than predicted by the model (2–4 h). The observed levels rose and degraded gradually, while the model predicted a sharp rise and degradation. This difference resulted in higher estimates of average levels over 24 h (17.8 mg/m<sup>3</sup> for broadcast, 13.2 mg/m<sup>3</sup> for perimeter) than predicted (8.9 mg/m<sup>3</sup> for broadcast, 10.8 mg/m<sup>3</sup> for perimeter).

## Discussion

The most important finding of this research is that measured VOC levels were comparable to those predicted by the model, at least for the broadcast application. In fact, peak levels were even higher than originally predicted, since the model both ignored existing background concentrations and slightly underestimated exposure. Actual peak levels would also be higher than levels measured by the dosimeters, since these passive monitors gauged only average exposure over time (not maximum exposure at any point in time). Furthermore, these elevated VOC levels would appear to last longer than originally predicted, prolonging exposure.

Overall these results confirm the findings of our original simulations, which suggested that levels were high enough to be associated with symptoms, at least among certain individuals (1). Certainly, the concentrations demonstrated by this current research are consistent with problematic

levels cited in the literature. Hudnell et al. had demonstrated that eye and throat irritation, headache, and nausea were significantly elevated among subjects exposed to 25 mg/m<sup>3</sup> of a VOC mixture (3). Similarly, Koren et al. found evidence of nasal irritation at this same exposure level (4). Results from earlier research using the same 22 chemical VOC mixture showed increased mucous membrane irritation at levels as low as 5 mg/m<sup>3</sup> (5, 6).

Generally, the model was good at predicting peak VOC levels following indoor application. The predicted broadcast results underestimated the peak levels by only about 20%, which is a relatively small error considering the many simplifying assumptions employed. The poorer prediction of peak results following perimeter application reflects the fact that one-third less material was applied by this treatment scenario (4.5 g) as compared to broadcast (7 g). This difference is the result of an improper estimation of the original input parameters and should not be viewed as a failure of the model. Furthermore, although less material was used for our perimeter treatment (compared to the broadcast treatment), there are certainly situations where the two treatments could release similar amounts of VOCs. For example, a more thorough perimeter treatment, including interior cupboards, water pipes, and the wall/ceiling interface (as may be done in some applications for roaches), may generate levels of VOCs that are similar to—or even greater than—the broadcast level.

The model does not perform as well predicting levels over time. The slower release and degradation of the VOCs suggests that the presence of water, emulsifiers, and other agents in the finished formulation may be retarding release of the volatile component. Furthermore, the applied material is probably binding to the treated surfaces (especially carpets), resulting in slower release. These surfaces as well as others may also be acting as more effective secondary sources than previously estimated, slowing elimination of the VOCs. Additionally, the baseline ventilation rate may be less in the student apartments than the rate assumed for the model (0.5 air changes/h).

The observed results suggest the need for changes to the model. Discussions with the developer of the model suggests that a single-stage, gas-phase-limited, mass-transfer model may better predict the results obtained (7).

The current results were generated only under closed conditions, since ventilation at the student apartments would be difficult to quantitate. However, these results imply that ventilation should be extended well past the 3–6 h suggested by the model. In fact, 12–24 h of enhanced ventilation may be needed to both significantly impact average/peak VOC levels and to lower levels below a symptoms threshold. It would seem prudent to delay rehabilitation until this ventilation had been performed.

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# Role of Reduction in the Photocatalytic Degradation of TNT

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The reduction of TNT by electrochemical and photoelectrochemical techniques has been investigated to obtain insight into the role of reductive transformations in a photocatalytic degradation process. TNT was observed to be labile to reductive transformation by a platinum electrode at electrochemical potentials commensurate with the flat band potential of TiO<sub>2</sub>, and aminodinitrotoluene species were detected as early reduction products. Oxygen did not influence the rate of reductive TNT transformation, but byproducts were more stable in aerated than deaerated conditions. Photocatalytic reduction of TNT was analyzed using CdS as a chromophore coupled to TiO<sub>2</sub> and visible light excitation so that direct photolysis of TNT was precluded. Under deaerated conditions, reduction of TNT occurred through both direct and sensitized mechanisms, predominantly forming aminodinitrotoluene compounds as relatively stable byproducts. Photocatalytic transformation and mineralization of TNT was also examined with particulate films of TiO<sub>2</sub> immobilized on optically transparent electrodes. Varying levels of positive bias were applied to the photocatalyst in order to decrease the availability of photoexcited electrons. The rate of TNT degradation was found to decrease with increasing positive bias, indicating that conduction band electrons facilitate overall compound degradation. Results from studies with TiO<sub>2</sub> thin films support the proposal that photocatalytic TNT destruction proceeds through oxidative pathways, where molecular oxygen accelerates byproduct degradation, and reductive pathways in which byproduct degradation is retarded by oxygen.

## Introduction

Residues of explosives are a widespread environmental contaminant and have been identified in soil and groundwater samples at hundreds of current and former U.S. Department of Defense sites (1). Extensive research has

been conducted in search of effective remediation strategies for munitions-contaminated water and soil (2), and many of these investigations have focused on 2,4,6-trinitrotoluene (TNT) due to its prevalence at contaminated sites (3), its continued wide use as a secondary explosive (4), and its recalcitrance to complete degradation by traditional bioremediation techniques (5, 6). A number of research groups have lately examined the use of irradiated semiconductor particulate systems for the treatment of TNT-contaminated water (7-11).

In a recent paper (8), we presented data on the photocatalytic degradation of dissolved TNT using aqueous TiO<sub>2</sub> (P25) slurries. This study observed that when a 220  $\mu$ M solution of TNT was exposed to the TiO<sub>2</sub> photocatalyst in the presence of oxygen and near UV radiation ( $\lambda > 340$  nm) more than 90% of the TNT was oxidized to CO<sub>2</sub>. Additionally, approximately 35% of the TNT nitrogen was recovered as ammonium ion, a reduced nitrogen species, while 55% was oxidized to nitrate ion.

The formation of a substantial amount of ammonia during the photocatalytic mineralization of TNT is of interest because it suggests that the degradation pathway involved significant reductive transformations. Mahdavi *et al.* (12) observed that nitroaromatic compounds were reduced to the corresponding amine (e.g., nitrobenzene reduced to aniline) in high yield through interfacial electron transfer by excited TiO<sub>2</sub> in solutions of deaerated ethanol. Our earlier findings (8) as well as work by Low *et al.* (13) and Pelizzetti *et al.* (14) indicate that this reaction can occur readily in aerated aqueous systems as well.

Photocatalytic reactions transpire when an electron is promoted from the filled valence band to the empty conduction band of a semiconductor by excitation with ultra-bandgap radiation. The electron hole pair so formed then reacts either by recombination or through participation in interfacial redox reactions with reduction occurring by the photoexcited electron and oxidation taking place at the site of the positive hole. In aqueous solution, a preponderance of evidence, as summarized by Turchi and Ollis (15), indicates that oxidative degradation of aromatic compounds occurs primarily via either bound or free hydroxyl radicals formed through the oxidation of adsorbed H<sub>2</sub>O, hydroxide, or surface titanol groups by photogenerated holes trapped at the semiconductor surface (16). Direct oxidation by trapped holes has also been reported (17). The predominant initial reductive step in aerated systems is a transfer of the photoexcited electron to adsorbed molecular oxygen to create a superoxide radical anion that may then form other activated oxygen species such as HO<sub>2</sub><sup>•</sup> and H<sub>2</sub>O<sub>2</sub> (18-20). The superoxide radical has been proposed to enhance the oxidation of certain organic compounds (21). Preliminary results have indicated that nitroaromatic compounds effectively compete with O<sub>2</sub> to

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The insecticide employed was the same indoor chlorpyrifos preparation used previously to model EC applications (1). This preparation consisted of a 40-mL concentrate (containing 59% inert ingredients) that produced a 0.5% chlorpyrifos solution when added to 1 gal of water. This finished formulation was applied by a licensed applicator using a 1-gal, stainless steel pump sprayer with an adjustable tip. Broadcast insecticide treatments were made to the entire floor surface area of two of the apartments, and perimeter applications were made to the entire perimeter distance of the other two. The treatments were randomly assigned within floors so that one broadcast and one perimeter application was performed on each floor. The perimeter treatment was confined to the visible floor/wall interface, ignoring the wall/ceiling interface and the cracks and crevices in interior cupboards. The sprayer tip was adjusted so as to provide a fan spray for the broadcast treatment and a stream spray for the perimeter.

The two perimeter applications were performed first, followed by the two broadcast applications. A fresh gallon of finished formulation was mixed for each pair of applications. The amount applied to each room was estimated by measuring the amount remaining after each pair of applications and dividing by two.

Applications were begun immediately after the background sampling was completed and lasted approximately 15 min each. Approximately 765 mL of finished formulation was used for each perimeter application, and approximately 1245 mL was used for each broadcast treatment. These amounts represent approximately 4.5 and 7 g of inert material, respectively. The amount applied during the broadcast applications represented approximately 63% of the label rate. The label rate is the maximum allowable rate of application, which should not be exceeded in practice.

Passive dosimeters (3M Model 3510 organic vapor monitors) were used to estimate levels of total VOCs. These were placed in each apartment at identical locations in both the living room and the kitchen at a height of approximately 125–150 cm. The living room was chosen because it was the largest room and was most similar to the main room modeled in the simulations. The kitchen was chosen because it represented a long (12 ft), narrow (approximately 5 ft), windowless cul-de-sac, which might be expected to accumulate vapors.

Time-weighted average measurements were taken over the following time periods: -4 to 0 (background), 0–4, 4–8, 8–16, and 16–24 h after application. Post-application sampling was begun immediately following each application. Temperature and relative humidity were recorded for one room on each floor at the beginning of each sampling interval. At the end of each interval, monitors were collected, sealed, and returned to 3M for analysis within 24 h. Due to resource constraints, field blanks were not submitted.

The 3M laboratory performed a solvent extraction (using 1.5 mL of carbon disulfide or other suitable solvent) and gas chromatographic analysis as outlined in NIOSH Physical and Chemical Analytical Method 127. All results were reported in mg/m<sup>3</sup> of total hydrocarbons as *n*-hexane. A complete description of the laboratory methods, quality assurance, concentration calculations, etc. are available from 3M (2).

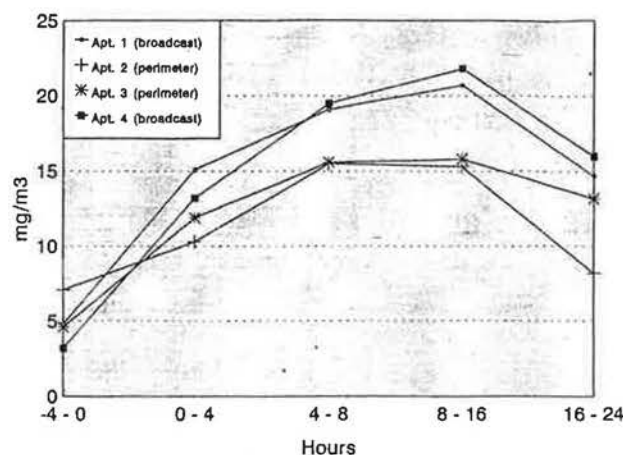


FIGURE 1. TWA VOC levels following broadcast and perimeter chlorpyrifos applications. Results are averages for the kitchen and living room for each apartment.

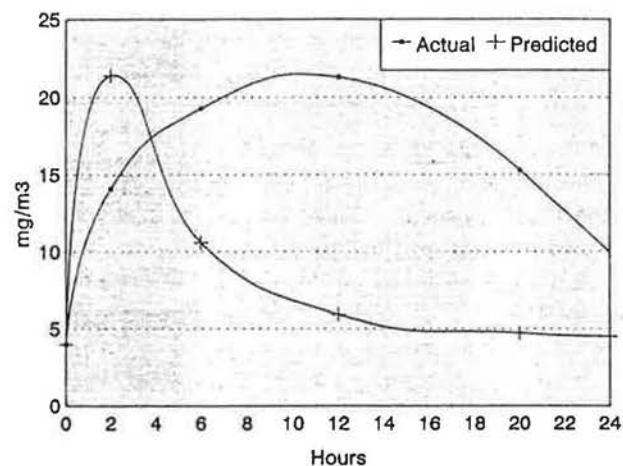


FIGURE 2. TWA VOC levels from broadcast chlorpyrifos applications compared to predicted levels. The actual results are averages for the four apartment/room combinations. Predicted results have been scaled to the average baseline VOC level.

## Results

The AC in each apartment operated most of the time during the 28-h sampling period, assuring fairly constant air movement. Temperature and relative humidity were recorded for each room and remained fairly consistent, in the range of approximately 71–73 °F and 63–69%, respectively.

The results of a general linear model (using SAS), which included the variable of treatment, room, and time demonstrated that only type of treatment ( $F = 22.19, p = 0.0001$ ) and time following treatment ( $F = 57.68, p = 0.0001$ ) were significant predictors of VOC level. Therefore, the kitchen and living room results were averaged within each apartment. The mean time-weighted average results for each perimeter application were similar and were consistently lower than the broadcast results. The broadcast results were also quite similar to each other (Figure 1).

The room and apartment results were averaged for each treatment (broadcast or perimeter) and compared to level predicted by the previous simulations (Figures 2 and 3). The hourly predictions were converted to 4 or 8 h TW levels, as appropriate. These predictions were also adjusted to the background level by adding the mean background level for each treatment (4 mg/m<sup>3</sup> for broadcast and 5.

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