# Influence of Adjuvants on Pesticide Soil-Air Partition Coefficients: Laboratory Measurements and Predicted Effects on Volatilization

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## ABSTRACT

A solid-phase fugacity meter was used to measure the soil-air partition coefficient values of three semi-volatile pesticides (chlorpyrifos, pyrimethanil, and trifluralin) in the absence of additional adjuvants ($K_{\text{soil-air,AI}}$), as part of commercial formulations ($K_{\text{soil-air, formulation}}$), and as formulation mixtures with an additional spray adjuvant added ($K_{\text{soil-air,formulation+spray adjuvant}}$). Chlorpyrifos $K_{\text{soil-air,formulation}}$ values were also measured over 15-30 °C, allowing for the change in internal energy of the phase transfer reaction ($\Delta_{\text{soil-air}}U$) to be calculated and compared to the $\Delta_{\text{soil-air}}U$ for $K_{\text{soil-air,AI}}$ from the literature. Finally, measured $K_{\text{soil-air}}$ values were used as input parameters in a pesticide volatilization model to understand how their variability affects pesticide volatilization rates under different conditions. Initial experiments conducted at ~24 °C indicated that all pesticides volatilized more readily in the presence of adjuvants than in their absence and that the additional spray adjuvant had minimal impact. The $\Delta_{\text{soil-air}}U$ values were 328 and 90 kJ/mol for chlorpyrifos in the absence and presence of formulation adjuvants, respectively, suggesting that adjuvants may weaken or disrupt intermolecular attractions between pesticide molecules and soil. At temperatures below 24.5 °C, modelled chlorpyrifos volatilization rates were higher in the presence of adjuvants than their absence; however, the opposite occurred at temperatures above 24.5 °C.

## INTRODUCTION

Many commonly used pesticides (including insecticides, herbicides, and fungicides) undergo significant volatilization after application,[1-4] causing a reduction in their intended efficacy. Volatilized pesticides can also undergo atmospheric transport to downwind sites,[5-8] potentially creating unintended consequences for sensitive non-target organisms.[9-12] Volatilization rates depend on the strength of the intermolecular interactions between active ingredient (AIs) and the matrices they encounters in the agricultural field. The strength of interactions with soils and plants are best expressed by the AI's soil-air and plant-air partition coefficients ($K_{\text{soil-air}}$ and $K_{\text{plant-air}}$, respectively). $K_{\text{soil-air}}$ values can be estimated with a predictive equation, such as the one reported by Davie-Martin *et al.* that incorporates the AI's octanol-air partition coefficient ($K_{\text{octanol-air}}$) as well as temperature, relative humidity (RH), and the soil's fraction of organic matter.[13] Predictive equations for plant-specific $K_{\text{plant-air}}$ values have also been developed and a compilation can be found in Taylor *et al*.[14] The Pesticide Loss via Volatilization (PLoVo) model uses these partition coefficients to predict AI volatilization under different scenarios.[14]

While $K_{\text{soil-air}}$ and $K_{\text{plant-air}}$ values, and the predictive equations developed from them, provide quantitative information about AI interactions with soil and plants, these values do not take into account the effects that other chemicals applied with AIs may have on these interactions. This is an important consideration because pesticide AIs are generally applied to agricultural fields as components of formulations that contain a number of chemicals other than the AI and the main solvent; these additional chemicals are called adjuvants. Formulation adjuvants are premixed with AIs before sale whereas spray adjuvants (also called tank-mix adjuvants) are separate products that are added to the spray tank by the applicator.[15] Common adjuvants include surfactants, compatibility agents, antifoaming agents, and spray colorants (dyes) (Supporting Information (SI)

**Table S1**). Among other things, adjuvants may be used to improve mixing, application effectiveness, ease-of-use, or pesticide activity and they may be used to reduce spray drift, foaming, or buffer the pH.

Several studies have investigated the effects of adjuvants on pesticide volatilization rates from surfaces. Most such studies were conducted with pesticides applied to glass surfaces or filter paper; the results of five such studies are summarized in **Table S2**. In some cases, adjuvants led to reduced AI volatilization from these surfaces, but in other cases, the opposite occurred.[2, 16] Stevens and Bukovac reported a 3-6 times increase in atrazine volatilization from polytetrafluoroethylene (PTFE) disks in the presence of adjuvants but the same set of adjuvants caused a 45-70% decrease in DDT volatilization.[17] Houbraken *et al.* measured the effects of several adjuvant types on the volatilization of three AIs from glass surfaces and showed that the effects varied widely depending on the adjuvant-AI combination.[2, 18] To the best of our knowledge, only one previous study investigated the effects of adjuvants on pesticide volatilization from soil and in that case, atrazine volatilization was not significantly affected by the adjuvants in an emulsifiable concentrate.[19] An approach for measuring 'effective vapor pressures' of AIs in the presence of adjuvants has been developed and Houbraken *et al.* suggested that these values be used in chemical fate models in place of saturated vapor pressures.[2]

The advantage of conducting pesticide volatilization studies on glass or PTFE disks is that the adjuvant effects can be measured with minimal complicating factors; however, it is unlikely that such results fully predict pesticide behavior on soil or plant surfaces. Likewise, effective vapor pressures do not necessarily indicate how adjuvants effect the intermolecular interactions that bind AIs to soil or plant surfaces. This is particularly important considering previous work showing that multiphase partitioning better predicts AI volatilization than vapor pressure.[20] Additionally, there are no reports about temperature effects on pesticide volatilization in the presence of adjuvants; this is an important consideration in light of the significant effect that temperature has on volatilization rates. Thus, huge gaps in knowledge still exist in this research area.

The first objective of this study was to measure and compare the $K_{\text{soil-air}}$ values of three pesticides in the absence of adjuvants ($K_{\text{soil-air,AI}}$), in their common commercial formulations ($K_{\text{soil-air,formulation}}$ values), and in the commercial formulations containing an additional spray adjuvant ($K_{\text{soil-air,formulation+spray adjuvant}}$ values). These partition coefficients were measured for chlorpyrifos (an insecticide), pyrimethanil (a fungicide), and an herbicide (trifluralin). The second objective was to determine the effect of temperature on the $K_{\text{soil-air,formulation}}$ values of chlorpyrifos and use this information to better understand the mechanism underlying adjuvant effects. The third objective was to determine how pesticide volatilization, as predicted by the PLoVo model, varies when $K_{\text{soil-air}}$ values measured in the presence and absence of adjuvants were used as input parameters in the model. Partition coefficients were measured with a solid-phase fugacity meter and two designs were compared.

## MATERIALS & METHODS

### Chemicals.

Chlorpyrifos analytical standard was purchased from Fluka (Steinheim, Germany), pyrimethanil from Sigma Aldrich (St. Louis, MO), and trifluralin from Supelco (Bellefonte, PA). High-purity dichloromethane (>99.98%), ethyl acetate (>99.9%), *n*-hexane (>98%), and acetone (>99.98%) were obtained from Merck (Darmstadt, Germany). Isotopically labelled chlorpyrifos-$d_{10}$ was acquired from Cambridge Isotope Laboratories (Andover MA), pyrimethanil-$d_5$ from

Sigma-Aldrich (St Louis, MO), and trifluralin-$d_{14}$ from CDN Isotopes (Pointe-Claire, Quebec, Canada).

Commercial formulations and the spray adjuvant, all of which are currently registered for use in New Zealand, were purchased from a local farm store. The commercial formulations were Chlor-P-480EC (containing 48% of the insecticide AI, chlorpyrifos), Pyrus®SC (containing 38-41% of the fungicide, pyrimethanil) and Trifluralin 480 EC (containing 48% of the herbicide, trifluralin). The spray adjuvant was Synoil™, which contains >60% mineral oil, with the remainder of the composition being proprietary. The manufacturer of Synoil™ describes it as a proprietary blend of paraffinic and polyol fatty acid esters for use with herbicides, insecticides, and fungicides that enhances spreading, wetting, and sticking and acts as an anti-evaporant.[21] Additional details about each formulation, including available information about other mixture components, and the spray adjuvant are provided in **Table S3**.

## Soil Preparation.

Semi-arid soil was obtained from AgResearch at the Invermay Campus in Mosgiel, New Zealand. The organic carbon content ($f_{oc}$) of the soil was 2.81% and the sand, silt and clay contents of the soil were 21%, 60% and 19%, respectively. It had a particle density of 2.59 g $cm^{-3}$ and pH of 5.6 (**Table S4**). A detailed description of the soil characterization approach is given in **SI Section I**. The soil was sieved to <1-mm diameter particle size and dried by baking overnight at 110 °C so that the *initial* soil moisture content was equivalent for all experiments. This soil was then divided into two portions; one portion was used with Column Design experiments and was contaminated by adding a solution containing the three AIs in hexane and allowing the hexane to completely evaporate in a rotary evaporator using the previously described procedure.[13] The other portion of soil was stored in a sealed glass jar at -20 °C and used with the Flat Pan Design experiments.

### Measurement of $K_{\text{soil-air}}$ Values.

A solid-phase fugacity meter, based on the design originally described by Horstmann and McLachlan,[22] was used to measure pesticide $K_{\text{soil-air,AI}}$, $K_{\text{soil-air,formulation}}$, $K_{\text{soil-air,formulation+spray adjuvant}}$ values. All experiments were conducted in triplicate. Initially, two fugacity meter designs employing different types of soil compartments (the Column Design and the Flat Pan Design), were compared; details about the two designs are in the next section. In both systems, nitrogen (used as a proxy for air) from a compressed tank flowed through a humidity controller (Roscid Technologies, MA, USA), a soil container (column or pan), a sorbent trap, and finally through a gas flow meter (capable of measuring 0.0-0.5 L $\text{min}^{-1}$; Parkinson Cowan Industrial Products, England) for ~24 h at a flow rate of ~0.1 L $\text{min}^{-1}$ (**Figure S1 and Figure S2**). This flow rate was used because previous experiments conducted with the Column Design indicated that pesticide equilibrium between soil and air was established at this flow rate.[13] The RH of the nitrogen flowing through the system was maintained at 75% to ensure constant moisture content in the soil. While moisture has a significant effect on pesticide volatility, we did not vary it since the effects of RH on pesticide volatilization have been investigated in previous studies[23, 24]

The soil container and sorbent trap were housed in a temperature-controlled chamber. The sorbent trap was a 34-mL Accelerated Solvent Extractor (ASE) cell body containing 12 g XAD-2 sorbent (Restek, Australia) and 30-mm glass fiber filters (GFFs) (Restek, Australia) at each end. When experiments were completed, AI concentrations were measured in the XAD-2 sorbent and soil samples. Gas-phase pesticide concentrations were determined by dividing the pesticide mass in the XAD-2 sorbent by the total volume of nitrogen that had passed through the fugacity meter. Additional details about the experimental procedure and validation are provided in **SI Section II**.

## Comparison of Fugacity Meter Designs

The Column Design (**Figure S2 (a)**) employed a glass column containing pesticide-contaminated soil whereas the Flat Pan Design (**Figure S2 (b & c)**) employed a glass pan containing soil onto which an aqueous pesticide solution was applied. We compared $K_{\text{soil-air,AI}}$ values measured with these designs because the Column Design was used in previously described experiments;[13] however, the Flat Pan Design better represents a field scenario in which pesticides are applied to a soil surface over which air flows. We hypothesized that the designs would produce different $K_{\text{soil-air}}$ values, with those from the Flat Pan Design being more relevant for predicting pesticide volatilization from agricultural soils.

Details about the Column Design set-up are provided elsewhere.[13] Briefly, the glass column contained 200-500 g of dry pesticide-contaminated soil through which nitrogen flowed. At the end of the experiment, the XAD-2 sorbent trap was removed and the contaminated soil was moved from the glass column to a glass jar where it was mixed thoroughly before removing three aliquots for analysis (1.1 g each).

When using the Glass Pan Design, 250-400 g of dry soil (~1 cm depth) was placed in a glass pan (34-cm length × 24-cm width × 5-cm depth) at the start of each experiment. For these experiments, 0.5 mL of a solution containing 10 g $L^{-1}$ of all three AIs in distilled water (prepared from solid analytical standards) was applied uniformly across the soil surface with a microsyringe, resulting in 5 mg of each AI being applied to the soil (~50 droplets of ~0.1 mL each). This resulted in an AI application rate in the baking tray of 63 mg $m^{-2}$ or 630 g $ha^{-1}$, which is similar to those recommended by the manufacturers for field applications (**Table S5**). A flat glass lid was then sealed onto the pan with a thin strip of silicone; the lid contained inlet and outlet ports for nitrogen flow. After pesticide application, the pan was immediately placed in the temperature-controlled chamber and nitrogen flow was established. At the end of the experiment, the XAD-2 sorbent trap was removed and three soil samples were collected from random locations in the pan by placing a copper ring (19.6-cm diameter × 3-cm height) on the soil surface and removing the soil (~10 g) within the ring's area. The soil from the three locations was mixed thoroughly in a glass jar and three aliquots (1.1 g each) were removed for analysis.

In sum, several differences between Column Design and Flat Pan Design existed. First, nitrogen flowed *through* the contaminated soil in the Column Design but flowed primarily *over* the soil surface in the Flat Pan Design. Second, the Column Design used soil contaminated with pesticides several weeks earlier to allow for an 'aged sorption' effect and thus stronger pesticide-soil binding, a topic discussed in several previous publications.[25, 26] In contrast, time for an ageing effect was not incorporated into the Flat Pan Design experiments. Third, the soil used in the Column Design was contaminated with pesticides by applying a pesticide solution in hexane to the soil and fully evaporating the hexane. In contrast, pesticides applied to soil in the Flat Pan Design were applied as aqueous solutions. With regards to this last point, however, the volume of water (~0.5 mL) applied to the soil in the pan (~250-400 g) was small relative to the amount of soil and we suspect that it sorbed into soil without significantly affecting pesticide AI behavior.

## Quantifying the Effect of Adjuvants and Temperature on Soil-Air Partitioning

All experiments designed to assess the effects of adjuvants and temperature on soil-air partitioning was conducted in triplicate. For the measurement of $K_{\text{soil-air,formulation}}$ values, separate solutions were prepared from each of the three purchased formulations. Formulations were diluted in distilled water such that the AI concentrations (10 g $L^{-1}$) were identical to those used for the experiments conducted to determine $K_{\text{soil-air,AI}}$ values. As with the $K_{\text{soil-air,AI}}$ experiments, 0.5 mL of the solution was applied to the baking pan, resulting in 5 mg of AI applied to the pan. For the measurement of $K_{\text{soil-air,formulation+spray adjuvant}}$ values, spray adjuvant was included in the diluted formulation solutions such that its concentration was 10 μL of Synoil$^{\text{TM}}$ per mL of solution. This resulted in a Synoil$^{\text{TM}}$ application rate in the baking tray of 0.063 mL $m^{-2}$ or 630 mL $ha^{-1}$, which is similar to that recommended by the manufacturer for field applications. Each formulation and formulation/adjuvant combination was tested in separate experiments. Otherwise, these experiments were conducted in an identical manner to those described above for the determination of $K_{\text{soil-air,AI}}$ with the Flat Pan Design.

The effect of temperature on the soil-air partitioning of chlorpyrifos in the presence of formulation adjuvants was determined by measuring chlorpyrifos $K_{\text{soil-air,formulation}}$ values at four temperatures (~15, ~20, ~24, and ~30 °C). **Table S6** summarizes all experiments conducted with the Flat Pan Design. When comparing $K_{\text{soil-air,formulation}}$ values obtained with this study to $K_{\text{soil-air,AI}}$ values reported previously, partition coefficients from both studies were normalized to 1% $f_{\text{oc}}$ by dividing $K_{\text{soil-air}}$ values by the $f_{\text{oc}}$ of the soils used and multiplying by 0.01.

## Pesticide Extraction, Quantification, and Quality Control

Pesticide extraction and quantification methods are described in detail in **SI Section III**. Quality control procedures are described in **SI Section IV**.

### Statistical Analysis

Welch t-tests (assuming unequal variance, α of 0.05) were conducted with Microsoft Excel 2010 to compare the means of pesticide $K_{\text{soil-air,AI}}$ values obtained with the Column Design and Flat Pan Design and to compare the means of $K_{\text{soil-air,AI}}$, $K_{\text{soil-air,formulation,}}$ $K_{\text{soil-air,formulation+spray adjuvant}}$ for each AI.

### Predicting the Effects of Adjuvants on Pesticide Volatilization Rates

We used the PLoVo model[14] to predict the cumulative percent volatilization during the 24 h after application ($\text{CPV}_{24\text{h}}$) of each AI from a model agricultural field containing no plants by using our measured $K_{\text{soil-air,AI}}$ , $K_{\text{soil-air,formulation}}$, and $K_{\text{soil-air,formulation+spray adjuvant}}$ as input parameters (**Table S9**). All of the measured soil-air partition coefficients used in the modeling were obtained from the Flat Pan Design experiments. We also compared $\text{CPV}_{24\text{h}}$ values for chlorpyrifos along a temperature trend by using our measured $K_{\text{soil-air,formulation}}$ values at various temperatures and $K_{\text{soil-air,AI}}$ values obtained from the literature for the same temperature range. The pesticide properties used in the model are in **Table S10** and other key input parameters are in **Table S11**. Although trifluralin is often mixed into the soil during its application, the predicted $\text{CPV}_{24\text{h}}$ values reported here represent a situation in which it is applied to the soil surface.

## RESULTS AND DISCUSSION

### Influence of Chamber Design on Soil-air Partitioning.

Mean log $K_{\text{soil-air,AI}}$ values obtained for chlorpyrifos, pyrimethanil, and trifluralin using the two fugacity meter designs were compared using experiments conducted at ~24 °C and ~75% RH (**Table S12 and Figure S8**). The mean log $K_{\text{soil-air,AI}}$ values obtained with the Column Design for chlorpyrifos, pyrimethanil, and trifluralin were 8.3, 7.9, and 7.4, respectively, while those obtained with the Flat Pan Design were 8.1, 8.9, and 7.1, respectively. Thus, the mean values obtained with the two designs were not significantly different for chlorpyrifos ($p$ = 0.6) or trifluralin ($p$ = 0.1) but the value for pyrimethanil was around one log unit higher and significantly different ($p$ = 0.003) when using the Flat Pan Design compared to the Column Design (**Table S13**).

Results from a number of studies suggest a strong correlation between $K_{\text{octanol-air}}$ and $K_{\text{soil-air}}$.[13, 27] The EPIsuite-predicted log $K_{\text{octanol-air}}$ values for chlorpyrifos, pyrimethanil, and trifluralin at 25 °C are 8.9, 8.7, and 7.7, respectively (**Table S10**).[28] Thus, the values obtained with the Column Design are better correlated with log $K_{\text{octanol-air}}$ than those obtained with the Flat Pan Design. This could suggest an error in our measured $K_{\text{soil-air,AI}}$ of pyrimethanil with the Flat Pan Design even though reproducibility was exceptionally good (**Figure S8**). However, it is also possible that the estimated $K_{\text{octanol-air}}$ value for pyrimethanil is inaccurate. Since there are no previous reports of $K_{\text{soil-air,AI}}$ values for pyrimethanil, it is difficult to confirm this.

Regarding our hypothesis concerning fugacity meter design, we expected the Flat Pan Design to produce partition coefficients representing pesticide interactions with the soil surface layer and therefore to be more representative of actual field conditions than the Column Design. However, since the design impacted the results for one pesticide but not the other two, the potential effect of fugacity meter design was not conclusive. It is also worth noting that the $K_{\text{soil-air,AI}}$ value for pyrimethanil was *higher* when using the Flat Pan Design; this suggests that the proposed 'aged sorption' effect for soils used with Column Design experiments was not significant. In other words, there was no evidence that incorporating the pesticide into soil and allowing a 'rest period' of a few weeks led to tighter pesticide-soil interactions because that would have resulted in significantly *lower* $K_{\text{soil-air,AI}}$ values with the Flat Pan Design. Although Wong *et al.* reported an aged sorption effect for organochlorine pesticides and polychlorinated biphenyls and suggested that spiked chemicals become increasingly tightly bound to the soil over time,[29] Cousins *et al.* reported no aging effect on the soil-air partitioning of polychlorinated biphenyls.[25] Similarly, Sharer *et al.* reported no difference in sorption in one day and 30-day aged atrazine in soil.[26]

### Effect of Adjuvants on Soil-Air Partition Coefficients.

The $K_{\text{soil-air,formulation}}$ values for chlorpyrifos, pyrimethanil, and trifluralin were approximately an order of magnitude lower and significantly different than their corresponding $K_{\text{soil-air,AI}}$ values ($p$ = 0.07, 0.0001, 0.006, respectively) when measured at ~24 °C and ~75% RH (**Figure 1, Table S14**). These results suggest that these active ingredients were more volatile when applied in the selected formulations (**Table S1**) than when applied in an aqueous solution not containing adjuvants under these conditions. On the other hand, the addition of the spray adjuvant, Synoil,™ to the tested formulations, had minimal additional effect on partitioning (**Figure 1**).

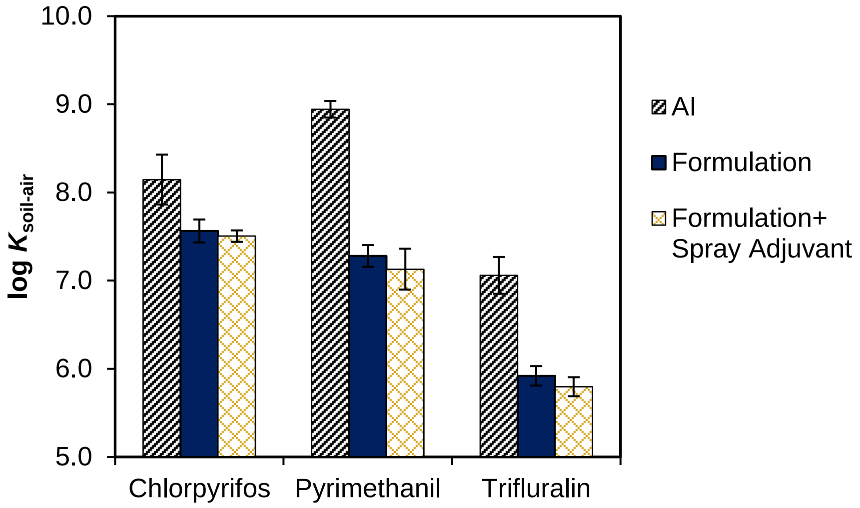

**Figure 1. Measured log $K_{\text{soil-air}}$ values of active ingredients applied in aqueous solution, in a commercial formulation, and in a commercial formulation with Synoil™ added as a spray adjuvant. Experiments were conducted at ~24 °C and ~75% RH. Error bars represent one standard deviation (*n*=3).**

Intermolecular interactions (including van der Waals forces and hydrogen bonding) exist between pesticide active ingredients, adjuvants, and the soil matrix.[30, 31] Thus, at this point, we hypothesized that the active ingredients we tested underwent more volatilization when applied as a formulation because the adjuvants disrupted or weakened the intermolecular interactions between the active ingredient and the soil molecules (**Figure 2**). For example, because of its lone

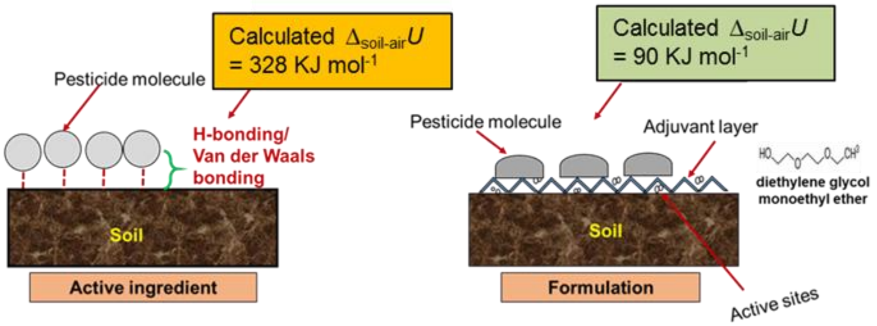

**Figure 2. Simplified depiction of proposed mechanism for disruption of pesticide-soil intermolecular attractive bonds by adjuvants, explaining our observation that $K_{\text{soil-air}}$ values and $\Delta_{\text{soil-air}}U$ values were lower in the presence of formulation adjuvants.**

electron pairs, the diethylene glycol present in the chlorpyrifos formulation would likely outcompete chlorpyrifos for soil binding sites, leading to increased chlorpyrifos volatilization.

The formulations we employed were emulsifiable concentrates in the cases of chlorpyrifos and trifluralin and a suspension concentrate in the case of pyrimethanil (**Table S3**). While the complete chemical compositions of the formulations we used in this study are not publicly available, emulsifiable concentrates often include solvents and co-solvents (**Table S1**).[32] Houbraken *et al.* reported that the volatility of fenpropimorph and pyrimethanil from glass slides was strongly affected by solvent type.[2] For example, they found that pesticide volatility was not affected by the presence of a relatively *high volatility solvent* (dichloromethane) in formulations, but that the volatilization of pyrimethanil and fenpropimorph from glass slides was reduced by 79% and 53%, respectively, in the presence of a relatively *low volatility solvent* (Solvesso™ 200ND). Their explanation was that highly volatile solvents evaporate from surfaces before they can affect pesticide AI behavior whereas lower volatility solvents remain on surfaces and trap the

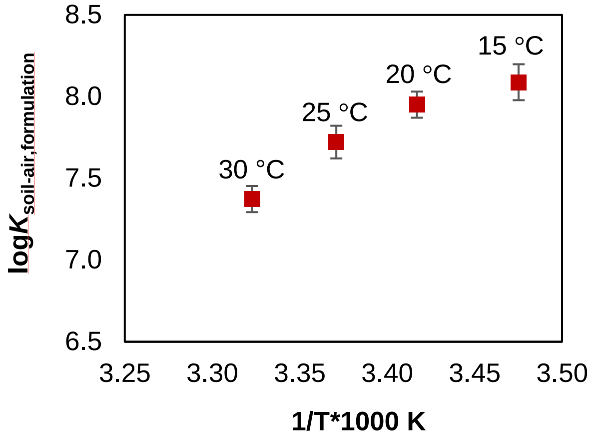

**Figure 3.** **Effect of temperature on log $K_{\text{soil-air,formulation}}$ values of chlorpyrifos at RH of 75%. Error bars represent one standard deviation ($n$=3).**

AI in a protective matrix. However, the relevance of results obtained with glass slides in relation to pesticide partitioning *to soil* is not currently known.

### Influence of Temperature on Soil-air Partitioning with and without Formulation Adjuvants.

Chlorpyrifos $K_{\text{soil-air,formulation}}$ values decreased by approximately half an order of magnitude with each 10 °C increase in temperature (**Figure 3**). While it is not surprising that temperature affected $K_{\text{soil-air,formulation}}$ values,[27, 33, 34] Davie-Martin *et al.* reported a much larger temperature effect on chlorpyrifos for the same temperature range using pure AI bound to soil in a fugacity meter with the Column Design (**Figure 4**).[13] In that study, $K_{\text{soil-air,AI}}$ values decreased by approximately one order of magnitude with each 10 °C increase in temperature. The internal energy for the phase transfer of the AI from the soil phase to the gas phase ($\Delta_{\text{soil-air}}U$) was calculated for chlorpyrifos in the presence and absence of formulation adjuvants using Eq. 1 and the slopes shown in **Figure 4**.

$$\Delta_{\text{soil-air}}U = 2.303 \cdot A \cdot R \qquad \text{(Eq 1)}$$

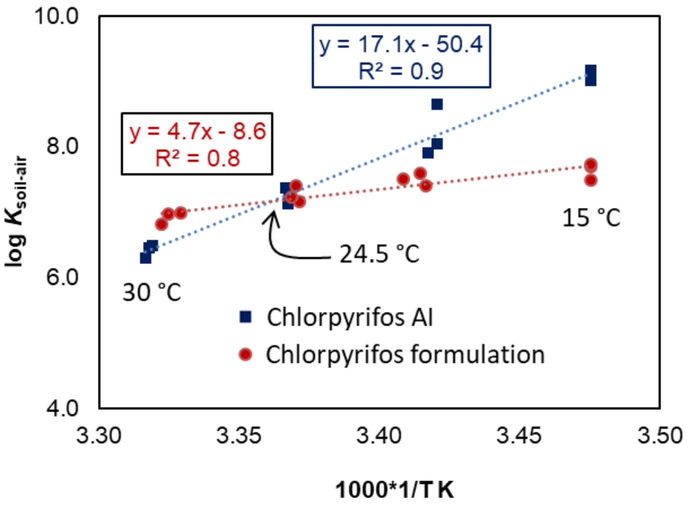

**Figure 4. Comparison of temperature effects on $K_{\text{soil-air}}$ values for chlorpyrifos when applied in the absence (data from Davie-Martin *et al.*[1] and presence of formulation adjuvants (data from this study).**

where $A$ is the slope, $R$ is the ideal gas constant (0.008314 kJ mol$^{-1}$ K) and 2.303 is the multiplication factor to convert from the natural logarithm to the common logarithm. The $\Delta_{\text{soil-air}}U_{\text{AI}}$ and a $\Delta_{\text{soil-air}}U_{\text{formulation}}$ values were 328 kJ mol$^{-1}$ and 90 kJ mol$^{-1}$, respectively (**Figure 2**), indicating that ~3.5 times less energy was required for the phase transfer when the formulation adjuvants were present, supporting our hypothesis about formulation adjuvants disrupting or

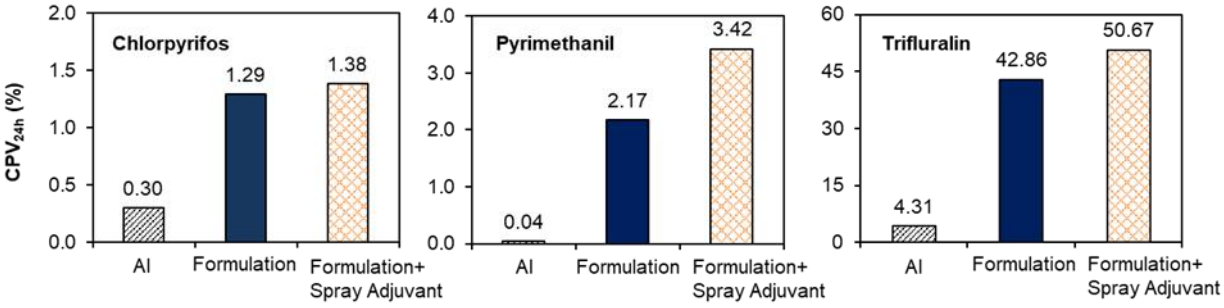

**Figure 5. Comparison of predicted pesticide volatilization rates, obtained with the PLoVo model and expressed as CPV$_{24h}$, when applied in the absence of adjuvants, in the formulation, and in the formulation with an additional spray adjuvant. $K_{\text{soil-air}}$ input values used in the PLoVo were measured in the laboratory at ~25 °C and 75% relative humidity.**

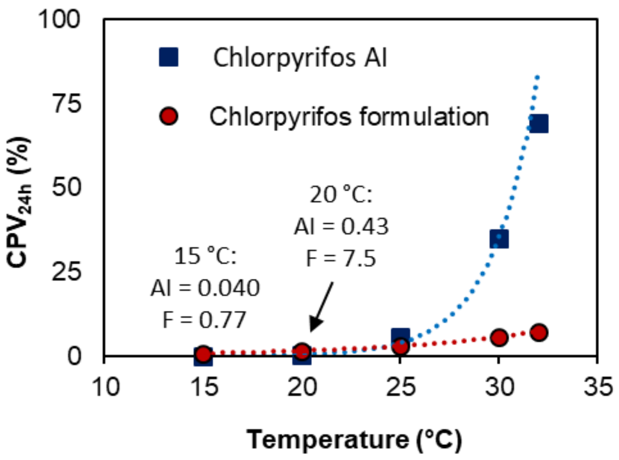

**Figure 6. Comparison of predicted $CPV_{24h}$ values, obtained with the PLoVo model, for chlorpyrifos applied in the absence of adjuvants (AI) and in the formulation (F), at various temperatures.**

weakening the intermolecular attraction bonds between pesticides and soil. Future research should focus on measuring $\Delta_{\text{soil-air}}U$ from additional soil types and with other RHs; however, Meijer *et al.* showed that $\Delta_{\text{soil-air}}U$ values of organochlorines did not vary significantly when using three soils (Hawaii, soybean, and muck soil) with different soil organic carbon contents.[27]

Another interesting feature of **Figure 4** is that the two lines intersected at 24.5 °C. This means that the formulation adjuvants had a relatively small effect on chlorpyrifos interactions with soil at around this temperature; but that chlorpyrifos interactions with soil were *weaker* in the presence of formulation adjuvants at lower temperatures and *stronger* in the presence of formulation adjuvants at higher temperatures. While this data suggests that the effects of adjuvants on pesticide interactions with soil may be much more complicated and difficult to predict that suspected, **Figure 4** led us to hypothesize that the proposed mechanism shown in **Figure 2** was relevant at relatively low temperatures but that at relatively high temperatures, the interactions in the more complicated chlorpyrifos-adjuvant-soil system were more robust and not as effected by temperature.

Due to the substantial amount of time required for each fugacity meter experiment, we did not evaluate the effects of temperature on the partitioning behaviors of trifluralin and pyrimethanil in the presence and absence of adjuvants. Considering the important implications associated with the temperature affects we observed for chlorpyrifos, more work in this area is certainly warranted.

**Effect of Formulation on Predicted Volatilization Losses.**

**Figure 5** compares the predicted pesticide $CPV_{24h}$ values from the model non-planted agricultural field when using the $K_{\text{soil-air,AI}}$, $K_{\text{soil-air,formulation}}$, and $K_{\text{soil-air,formulation+spray adjuvant}}$ values we measured at ~24 °C and 75% RH as input parameters in the PLoVo model. For chlorpyrifos, the $CPV_{24h}$ was around four times higher in the presence of formulation adjuvants than without. For trifluralin and pyrimethanil, the $CPV_{24h}$ values were around ten times higher in the presence of formulation adjuvants than without. For all three pesticides, the addition of the spray adjuvant to the formulation had a minimal effect on $CPV_{24h}$ values.

**Figure 6** shows the predicted $CPV_{24h}$ values for chlorpyrifos from the model non-planted agricultural field when using the $K_{\text{soil-air,formulation}}$ values that we report herein and the $K_{\text{soil-air,AI}}$ values reported previously[1] as input parameters in the PLoVo model. As expected from the trends in $K_{\text{soil-air,AI}}$ and $K_{\text{soil-air,formulation}}$ shown in **Figure 4**, $CPV_{24h}$ were *higher* for chlorpyrifos in the absence of formulation adjuvants *at the relatively low temperatures* but significantly *lower* for chlorpyrifos in the presence of adjuvants at the relatively high temperatures. Due to the exponential relationship between temperature and volatilization, $CPV_{24h}$ values were approximately twice as high for chlorpyrifos in the absence of formulation adjuvants at ~24 °C but ~10 times higher at ~32 °C. This temperature effect could be responsible for some previously observed inconsistencies in the effects of adjuvants on pesticide volatilization in the literature.

The average volatilization losses of chlorpyrifos, pyrimethanil and trifluralin after applications in various lab and field studies, as reported here and in the literature, are compiled in **Tables S15-17**. Despite a variety of soil types and experimental conditions being used, it is clear that pesticide volatilization from glass surfaces was substantially higher than from soil for all three pesticides. This is not surprising considering the potential for much stronger and more complex interactions between pesticides and soil relative to pesticides and glass surfaces.

## RECOMMENDATIONS

The results from this study provide information about the effects of adjuvants on the soil-air partitioning for three specific pesticides, formulations, and adjuvants. However, more research is needed to gain a broader understanding of these effects, for example, with other pesticides, adjuvants, soil types, relative humidities, and on plant surfaces. Improved access to detailed chemical composition data in pesticide formulations would facilitate better understanding of chemical interactions and more systematic investigations into adjuvant effects.

## SUPPORTING INFORMATION

Additional details about pesticide formulations, previous studies, methods and materials, quality control, and results.

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## TABLE of CONTENTS ART