SUPPORTING INFORMATION

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

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----Introduction----

Table S1. Common pesticide formulation types and classes of adjuvants they contain (adapted from Katagi, T. 2008 and Copping, L. *et al.* 2000).[1, 2]

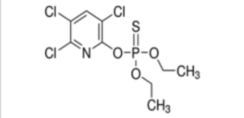
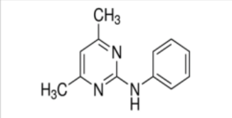
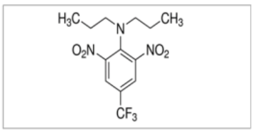
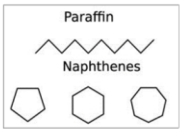
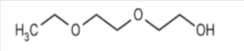
Formulation Type	AI %	Adjuvants and Other Ingredients (%)
Granules	1-40	Surfactant (0-5), stabilizer (1-2), polymer or resin (0–10), binder (0–5), carrier (to 100)
Wettable powder	10-80	Surfactant (1-2), dispersing agent (2–5), antifoaming agent (0.1–1), inert filler/carrier (to 100)
Soluble concentrate	20-70	Surfactant (5-15), antifreeze agent (5–10), water-miscible solvent (to 100)
Emulsifiable concentrate	20-70	Surfactant (5-10), solvent/co-solvent (to 100)
Suspension concentrate	20-70	Surfactant (2-5), propylene glycol antifreeze (5–10), anti-settling agent (0.2–2), water (to 100)
Water-dispersible granules	50-90	Surfactant (1-3), dispersing agent (3–15), disintegrating agent (0–15), soluble or insoluble filler (to 100)
Oil-in-water emulsion	5-30	Surfactant (< 5%), stabilizer, thickener

Table S2. Summary of previously published studies about effects of adjuvants on pesticide volatilization from inert surfaces and soil.

Experiment Type	Active Ingredient (AI)	Commercial Formulation	Additional Adjuvants	Matrix	Amount volatilized (%)			Time (hour)	Citation
					Pure AI	Commercial Formulation	AI/Formulation with Adjuvant		
Laboratory	Chlorpyrifos	Lorsban™ 4E: 480 g L^{-1} Chlorpyrifos	**Added to commercial formulation**: alkyl polyethylene ether solution (Adsee 815) and oil	Glass surface	–	21	7.1	1	[3]
Wind tunnel	Fenpropimorph	Corbel®: 750 g L^{-1} fenpropimorph (emulsifiable concentrate)	**Added to commercial formulation**: Methylated seed oil (Actirob B)	Glass surface	90.3	87.1	53.1	48	[4]
	Pyrimethanil	Scala®: 400 g L^{-1} pyrimethanil (suspension concentrate)			70.1	39.3	22.3		
Wind tunnel	Fenpropimorph	Corbel™, 750 g L^{-1} fenpropimorph (emulsifiable concentrate)	**Added to fenpropimorph and pyrimethanil commercial formulation**: (A) alcohol ethoxylate EO3 (B) alcohol ethoxylate EO11 (C) alcohol ethoxylate EO20 (D) methylated seed oil (E) pinolene-based film-forming emulsion	Glass surface	66.2	73.5	(A)74.5 (B) 55.3 (C) 65.4 (D) 32.9 (E) 48.4	48	[5]
	Tebuconazole	Horizon™, 250 g tebuconazole L^{-1} (emulsifiable concentrate)			22.3	19.4	–		
	Pyrimethanil	Scala®: 400 g L^{-1} pyrimethanil (suspension concentrate)			59.2	43.7	A) 48.3 (B) 45.1 (C) 46.5 (D) 38.7 (E) 44.4		
Laboratory	Purified alachlor	Lasso 4EC: 479 g L^{-1} alachlor (emulsifiable concentrate)	–	Glass bottle containing soil	0.4 (average)	0.5 (average)	–	24	[6]
Laboratory	2D-glucose	–	**Added to AI**: (A) 4-(171,3,3-tetramethylbutyl)phenol (OP) (B) T X-45 (OP+ poly(ethoxy)ethanol derivatives (5 EO)) (C) T X-114 (OP+ 7.5 EO) (D) T X-100 (OP+ 9.5 EO) (E) T X-102 (OP+ 12.5 EO) (F) T X-165 (OP+ 16 EO) (G) T X-305 (OP+ 30 EO) (H) T X-405 (OP+ 40 EO)	PTFE disc	0	-	0	24	[7]
	Atrazine	–			2.0	-	(A)12 (B) 6.1 (C) - (D) 6.3 (E) – (F) 6.9 (G) – (H) 7.7		
	0 , p ‘ – DDT	–			25.0	-	A)14 (B) 8.3 (C) - (D) 13 (E) – (F) 9.9 (G) – (H) 8.6		

----Materials and Methods----

Table S3. Properties of the formulations and spray adjuvants used in this study.

Formulation/ Surfactant Name	CHLOR-P-480EC	PYRUS®SC	TRIFLURALIN 480 EC	Synoil™
Purpose	Insecticide	Fungicide	Herbicide	Adjuvant
Active Ingredient	Chlorpyrifos	Pyrimethanil	Trifluralin	Mineral oil
Structure (active ingredient)				
Active Ingredient Content % (w/v)	48%	38-41%	48%	>60%
Other Components & CAS No. (other ingredient content % (w/v))	1. Diethylene glycol monoethyl ether & 111-90-0 (30-60%) 2. Other ingredients, surfactants, etc. (not available)	No information available	1. Liquid hydrocarbon (CAS No.: proprietary) (46%) 2. Non-hazardous ingredients (CAS No.: proprietary)	Other ingredients, surfactants, etc. (remainder)
Structure (other components)				

Section I: Soil characterization approach

Soil organic carbon fraction (%f_{oc}) analysis was performed in the Campbell Microanalytical Laboratory, Department of Chemistry, University of Otago using a Flash Smart Elemental Analyzer (Thermo Scientific, MA) and a method based on the complete and instantaneous oxidation of the soil sample by "flash combustion." The particle size distribution was determined using a method described by Day.[8] The soil particle density was determined by the technique described in a Globe® document,[9] and soil pH was measured using a pH meter in a mixed solution of soil and distilled water in a ratio of 1:2.5.

Table S4. Selected physico-chemical properties of the semi-arid soil used in this study.

f_{oc}	2.81%
Sand, 0.05-2.00 mm	21%
Silt, 0.002-0.5 mm	60%
Clay, <0.002 mm	19%
Particle density	2.59 g cm^{-3}
pH	5.6

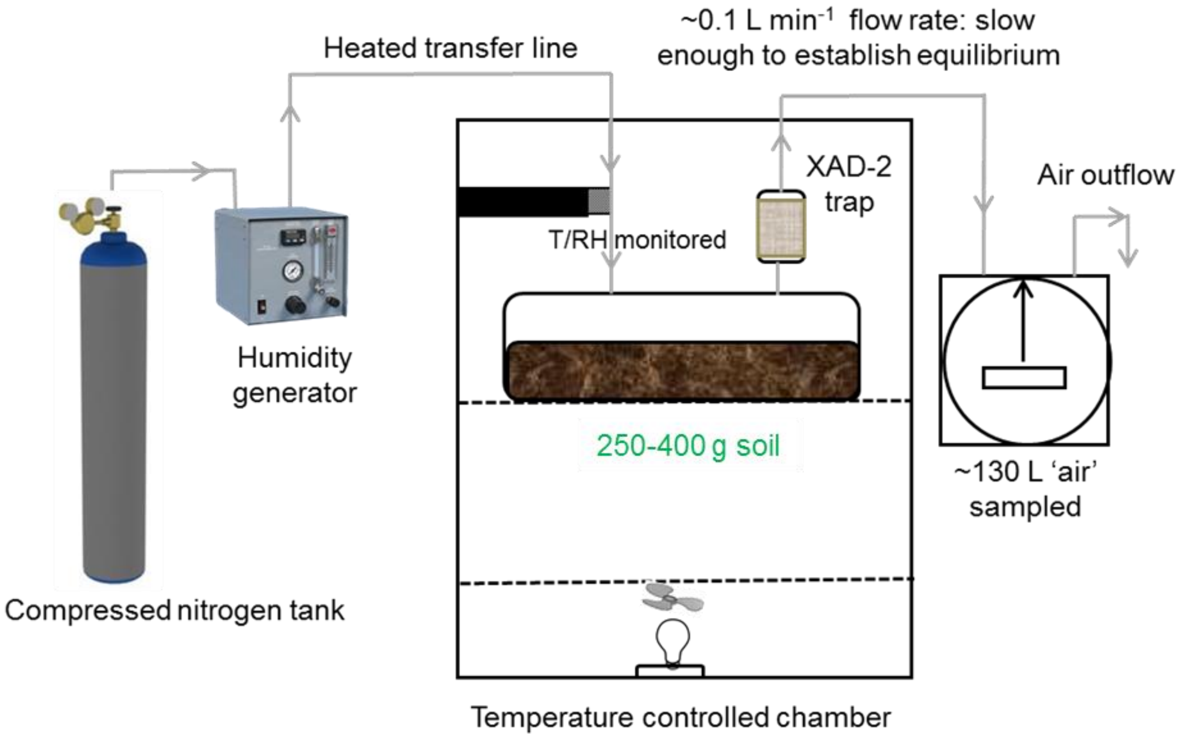


Figure S1. Schematic diagram of the solid-phase fugacity meter with Flat Pan Design.

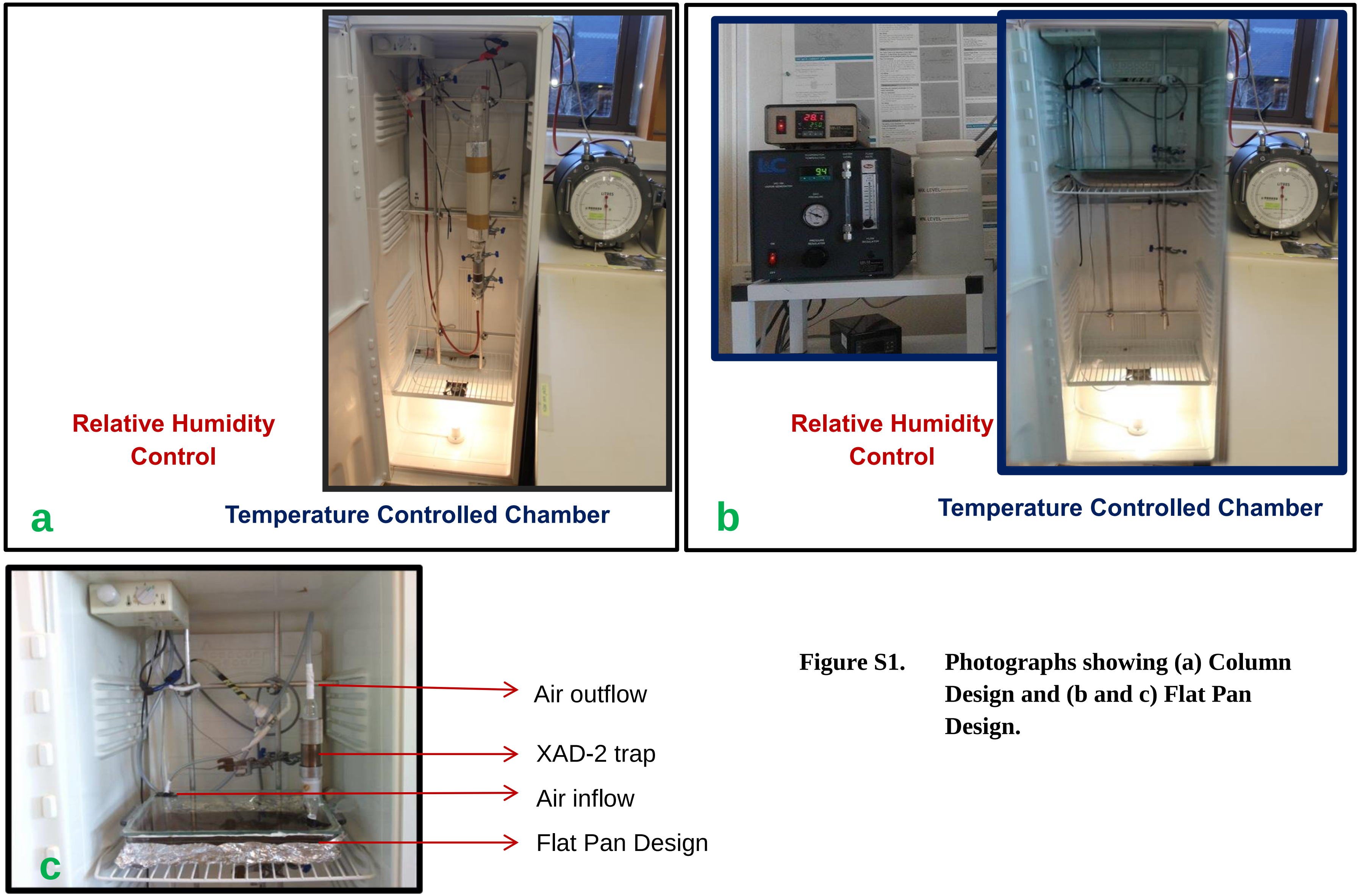


Figure S1. **Photographs showing (a) Column Design and (b and c) Flat Pan Design.**

Section II: Experimental procedure and validation

Temperature Control

All components of the solid-phase fugacity meter apparatus were placed in a purpose-built temperature-controlled chamber. The temperature control system included a thermostat controller (STC-1000, Brewshop Limited, New Zealand), a 75-Watt light bulb and a small fan; together these served to heat, cool, and distribute the warm or cold air in the temperature-controlled chamber (**Figure S2**). The thermostat controller was set to control the heating or cooling cycles when the temperature deviated by ±0.5 °C from the set-point. With increasing set-point temperature, an increasing deviation from the set-point was observed (**Figure S3**). However, the achieved temperature was very stable; it did not vary by more than ±0.5 °C during the course of any experiment.

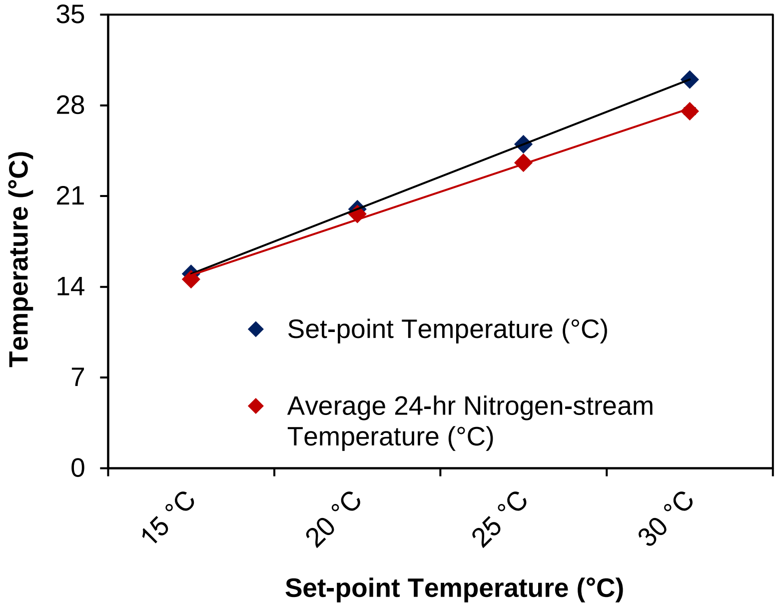


Figure S3. **Mean measured nitrogen stream temperature (°C) compared to the set-point temperature. Triplicate Flat Pan Design experiments were conducted at four temperatures (15 °C, 20 °C, 25 °C, and 30 °C) and each experiment ran for 24 hours. Error bars, although barely visible, indicate the ±1 standard deviation of the measurements made over 24 h (*n*=3).**

Relative Humidity (RH) and Flow Rate Control

The relative humidity generator was used to supply nitrogen at a given RH to the temperature-controlled chamber. A dry nitrogen supply line from a compressed nitrogen tank was connected to the rear panel port of the humidity generator (**Figure S1**). Input gas flow from the compressed nitrogen tank was controlled with a regulator and fine tuning of the flow was achieved with a pressure regulator mounted on the front panel of the humidity generator. The flow rate was manually adjusted at the start of each experiment. The nitrogen entered the temperature-controlled evaporator of the humidity generator and was saturated with water. The humidified nitrogen stream was then directed towards the temperature-controlled environmental chamber through a port on the rear panel of the humidity generator.

The RH of the nitrogen stream in the temperature-controlled chamber was monitored using an Omega RH511 data logger (Stamford, CT) and the Glass Column or Flat Pan was placed into the chamber only when the RH reached the set-point humidity, which was usually achieved within ~30 minutes from the humidity generator start time. For computer-controlled operation, temperature control of the humidity generator evaporator was achieved through an RS-232 port using Metravib Software (Ver. 3.6.12 w/Rotronic Probe & Valve). The deviation between the set-point and achieved RH was always less than 1.5% (**Figure S4**).

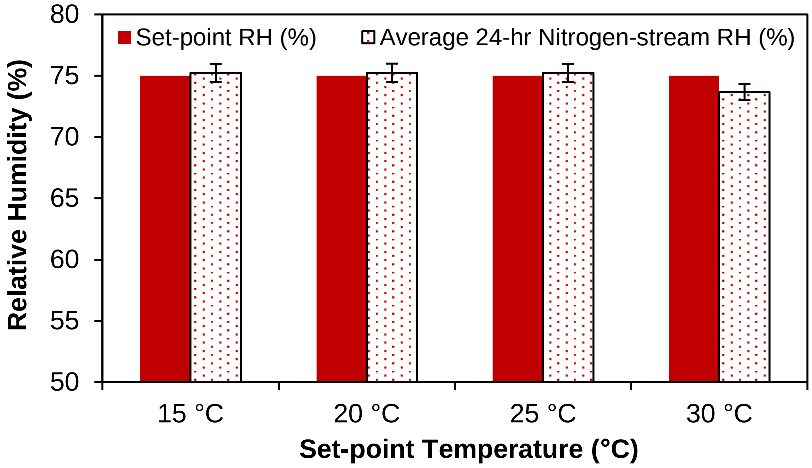


Figure S4. **Mean measured nitrogen stream RH values compared with the set-point RH. Triplicate Flat Pan Design experiments were conducted at four different temperatures (15 °C, 20 °C, 25 °C, and 35 °C) and the RH was set to 75% in all cases. Error bars indicate the ±1 standard deviation of the measurements made over 24 h (*n*=3).**

The flow rate set-point was 0.1 L/min, which was previously found to be low enough to achieve equilibrium for pesticide partitioning between soil and air.[10] A gas/flow meter (0.0-0.5 L/min, Parkinson Cowan Industrial Products, England) was placed beside the temperature-controlled chamber and the nitrogen outflow was manually recorded 3-4 times over the course of the experiment to monitor the stability and uniformity of the nitrogen flow (**Figure S5**). The actual flow rate varied from 0.03-0.14 L/min (Table S12); however, since the pesticide concentration in air was calculated from the total volume, which we measured with the gas/flow meter, the flow rate did not have to be exact. Lower than set-point flow rates were also not problematic since they would not disrupt equilibrium.

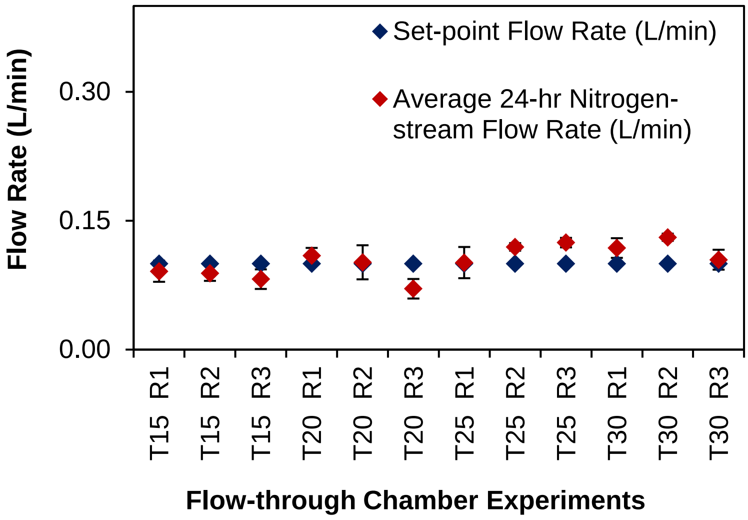


Figure S5. **Nitrogen flow rates compared to set-point flow rates. Triplicate Flat Pan Design experiments were conducted at four different temperatures (15 °C, 20 °C, 25 °C, and 35 °C) and the flow-rate set-point was kept at 0.1 L/min in all cases. Error bars, which are barely visible in some cases, indicate the ±1 standard deviation of the measurements made over 24 h (*n*=3). In the figure labels, T is temperature (°C), R is replicate and 1, 2, 3 denotes the triplicate experiment number.**

Preparation of the Experimental Equipment

All experimental equipment (i.e., Flat Pan, Glass Column, adapter, tubing, etc.) were washed in warm soapy water then rinsed thoroughly with tap water and distilled water prior to use. All glassware and metal ware then baked at 400 °C for 4 h. Any equipment that could not be baked was instead solvent rinsed or sonicated (5 min per solvent) with acetone, ethyl acetate, and *n*-hexane and left in the fume hood for 20 minutes prior to use to allow the residual solvents to evaporate. XAD-2 was pre-cleaned using an Accelerated Solvent Extractor 300 System (Dionex, Sunnyvale, CA). The SDVB resin (untreated), which is equivalent to XAD-2 resin, was purchased from Restek (Australia). To clean the XAD-2 resin, three separate extractions were performed using acetone, dichloromethane and ethyl acetate. All extractions were conducted with the following conditions: 5-min heat time, 5-min static time, 1 static cycle, 100% flush volume, 240-s purge time, 1500 psi, and 75 °C. The XAD-2 was left in the fume hood for at least 4 h to allow solvent residues to evaporate and was then stored in pre-baked glass jars until use. All Florisil, diatomaceous earth, and acid-washed sand were pre-cleaned by baking at 400 °C for 4 h prior to use.

Table S5. **Commercial formulations used in this study, with manufacturer-recommended application rates.**

Pesticide/adjuvant name	AI Concentration ($g\ L^{-1}$)	Formulation application rate ($L\ ha^{-1}$)	AI application rate ($mg\ m^{-2}$)	Water application rate ($L\ ha^{-1}$)
CHLOR-P-480EC	480	1.7	81.6	100
PYRUS®SC	400	2.0	80.0	1000
TRIFLURALIN 480EC	480	1.7	81.6	450
Synoil™ (spray adjuvant)	-	0.5	-	-

Table S6. **Pesticide and temperature combinations used for triplicate $K_{soil\text{-}air}$ measurements.**

	Chlorpyrifos		
Set-Point Temperature (°C)	AI	**Formulation**	**Formulation + Spray Adjuvant**
15		X	
20		X	
25	X	X	X
30		X	

	Pyrimethanil & Trifluralin		
Set-Point Temperature (°C)	AI	**Formulation**	**Formulation + Spray Adjuvant**
15			
20			
25	X	X	X
30			

Section III: Extraction and Quantification of Pesticides.

Soil and XAD-2 samples were extracted using an ASE-300 (Dionex, CA, USA). Soil samples were packed in 34-mL stainless steel extraction cells as follows (from bottom to top, *i.e.* opposite to the solvent flow direction): a 30-mm GFF, 12 g Florisil, 2 g aluminum oxide, a mixture of 1 g diatomaceous earth and 1.1 g soil, acid-washed sand to fill the void volume, and an additional 30-mm GFF (**Figure S6**). Since sorbent traps for XAD-2 were made from ASE cell bodies, no transfer of XAD-2 was needed following experiments. Prior to extraction, packed ASE cells were spiked with surrogates, which were used to account for potential losses of target analytes during sample workup, using a microsyringe inserted through the GFF. For chlorpyrifos and trifluralin quantification, soil samples were spiked with 15 µL of a solution containing 36 ng μL^{-1} chlorpyrifos-d_{10} and trifluralin-d_{14} in ethyl acetate and XAD-2 samples were spiked with 15 µL of a solution containing 12 ng μL^{-1} of each surrogate. For pyrimethanil quantification, soil and XAD-2 samples were spiked with 5 and 15 µL of a 40 ng μL^{-1} solution of pyrimethanil-d_5 in ethyl acetate, respectively.

Pesticides were extracted from soil using ethyl acetate as the solvent and the following conditions: 5-min heat time, 6-min static time, 3 static cycles, 50% flush volume, 60 s purge time, 1500 psi and 80 °C. Extracts were concentrated to 350 µL under a constant stream of nitrogen using a Zymark Turbovap II. Each cell containing XAD-2 was extracted twice, first with dichloromethane and then with ethyl acetate, using the following conditions: 5-min heat time, 10-min static time, 1 static cycle, 50% flush volume, 240-s purge time, 1500 psi, and 75 °C temperature. Extracts were combined, solvent exchanged to ethyl acetate, and concentrated to 350 µL.

Analytes were quantified with an Agilent 6890N gas chromatograph coupled to an Agilent 5957B mass selective detector (Santa Clara, CA) using selected ion monitoring. Chemical ionization mode, with methane as the reagent gas, was used for chlorpyrifos and trifluralin whereas electron ionization mode was used for pyrimethanil detection. An 11-point calibration curve was prepared from the peak area ratios of target analytes to corresponding surrogates. GC-MS retention times, and the quantitation and confirmation ions used for each analyte, are provided in **Table S7**.

Section IV: Quality Control.

Recovery experiments for each AI were conducted with both soil and XAD-2 by packing extraction cells (as described in Section III) and then spiking a solution containing a known concentration of target analytes into the cell through the top GFF with a microsyringe. The mean recoveries for all AIs spiked into soil and XAD-2 were 78% and 80%, respectively (**Figure S7**).

Fugacity meter blanks were measured before and after each triplicate experiment using the same method as for real experiments except that the baked glass column/pan contained no soil. Although all three pesticides were detected in the blank experiments, the concentrations were typically orders of magnitude lower than the concentrations measured during real experiments (**Table S8**). Nonetheless, blank subtractions for each matrix were performed prior to the calculation of $K_{\text{soil-air}}$. Breakthrough analysis was conducted by placing a second XAD-2 trap downstream of the main trap; <1% breakthrough of chlorpyrifos occurred when 15 g of XAD-2 was used in the main trap at 30 °C temperature and 75% RH.

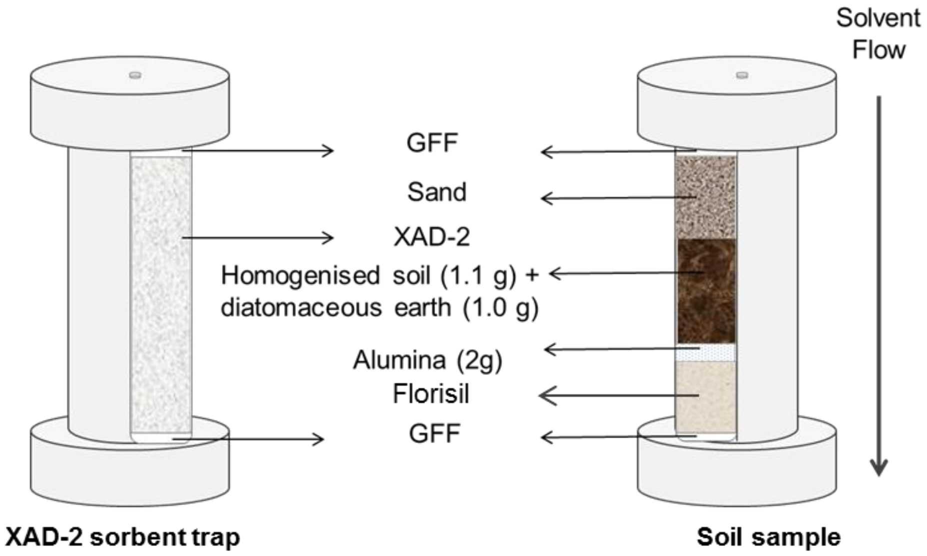


Figure S6. **Packing of the ASE extraction cells for XAD-2 sorbent trap and soil sample.**

Table S7. **GC-MS retention times (RTs), ionization mode, quantitation ions, and confirmation ions.**

Compound	Ionization Mode	RT (min)	Quantitation Ion Q1	Confirmation Ions Q2	Q3
Chlorpyrifos-d$_{10}$	**Chemical Ionization**	**30.34**	**214**	**212**	**322**
Chlorpyrifos	Chemical Ionization	30.73	313	315	214
Pyrimethanil-d$_5$	**Electron Ionization**	**22.90**	**202**	**204**	**203**
Pyrimethanil	Electron Ionization	23.12	198	199	
Trifluralin-d$_{14}$	**Chemical Ionization**	**18.28**	**349**	**350**	**348**
Trifluralin	Chemical Ionization	18.53	335	336	305

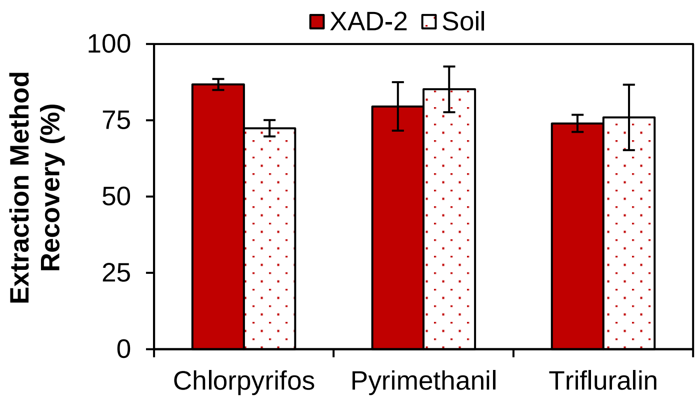


Figure S7. **Mean recoveries of spiked analytes in XAD-2 and soil. Error bars represent ± 1 standard deviation (*n* = 3).**

Table S8. **Background chlorpyrifos, pyrimethanil and trifluralin concentrations in fugacity meter blank (FMB) and lab blanks.**

Exp. Name	**Analyte**	**FMB Conc. (pg μL^{-1})**	**Lab Blank Conc. (pg μL^{-1})**
Glass-column Blank	Chlorpyrifos	1.1	3.7
Glass-column Blank	Trifluralin	Below Cal Curve	Below Cal Curve
Glass-column Blank	Pyrimethanil	Below Cal Curve	Below Cal Curve
FTC Blank	Chlorpyrifos	10.8	4.8
FTC Blank	Trifluralin	Below Cal Curve	Below Cal Curve
FTC Blank	Pyrimethanil	Below Cal Curve	Below Cal Curve
FTC Chp F Blank	Chlorpyrifos	18.3	4.8
FTC Chp F+A Blank	Chlorpyrifos	49.7	4.8
FTC Pyr F Blank	Pyrimethanil	Below Cal Curve	Below Cal Curve
FTC Pyr F+A Blank	Pyrimethanil	2.4	Below Cal Curve
FTC TRF F Blank	Trifluralin	52.3	Below Cal Curve
FTC TRF F+A Blank	Trifluralin	13.9	Below Cal Curve
FTC Temp 15 Blank	Chlorpyrifos	32.5	36.3
FTC Temp 20 Blank	Chlorpyrifos	51.9	36.3
FTC Temp 30 Blank	Chlorpyrifos	120.2	36.3

Table S9. List of default input values used in PLoVo model.

Abbreviation	Definition	Units	Default Value[11]
A_{field}	Area of the standard agricultural field	m^2	10 000
$d_{air\text{-}boundary\ (soil)}$	Depth of soil-air boundary layer	m	0.001
$D_{air\ (T)}$	Air diffusion constant at atmospheric temperature	$m^2\ h^{-1}$	0.018308027
f_{OC}	Fraction of organic carbon in soil	$(g\ g^{-1})$	0.028
h	Atmospheric height of the standard agricultural field	m	5
h_{soil}	Depth of soil surface layer	m	0.001
$m_{i,\ applied}$	Total mass of pesticide, *i*, applied	g	1000
$m_{i,\ soil}$	Mass of pesticide, *i*, applied on the soil phase	g	1000
ρ_{soil}	Soil solid density	$kg\ L^{-1}$	2.59
ρ_{water}	Water density	$kg\ L^{-1}$	1.0
R	Ideal gas constant	$kJ\ mol^{-1}\ K^{-1}$	0.008314
$V_{air\ (turbulent)}$	Volume of turbulent air	L	$1x10^{10}$
$V_{air\text{-}boundary\ (soil)}$	Volume of air in soil boundary layer	L	10000
V_{soil}	Volume of soil	L	10000
$V_{water\ (soil)}$	Volume of water in soil	L	1390
WS	Wind speed	$m\ s^{-1}$	8.89

Table S10. Pesticide chemical-physical properties used as input data in PLoVo model.

Pesticide	**Log K_{OW}**	**Log K_{AW}**	**Log K_{OA}**	**Vapor Pressure**
	at 298.15 K	at 298.15 K	at 298.15 K	Pa, at 298.15 K
Chlorpyrifos	4.96	-3.922	8.882	0.00398
Pyrimethanil	2.84	-5.835	8.675	0.0112
Trifluralin	5.34	-2.376	7.716	0.0105

Table S11. Other input data used in PLoVo modelling for CPV_{24h} prediction.

Pesticide	**%RH**	**Temperature (K)**	**Log $K_{soil-air}$**
Chlorpyrifos (AI)	73.8	297.1	8.2
Chlorpyrifos (Formulation)	73.8	297.1	7.6
Chlorpyrifos (Formulation+Adjuvant)	75.9	296.9	7.5
Pyrimethanil (AI)	73.8	297.1	9.0
Pyrimethanil (Formulation)	75.3	296.9	7.3
Pyrimethanil (Formulation+Adjuvant)	74.3	296.9	7.1
Trifluralin (AI)	73.8	297.1	7.1
Trifluralin (Formulation)	73.5	296.9	5.9
Trifluralin (Formulation+Adjuvant)	73.9	296.9	5.8

----Results & Discussion----

Table S12. Measured pesticide log $K_{soil\text{-}air}$ values and the conditions for each measurement. Values of ln $K_{soil\text{-}air}$ as well as log $K_{soil\text{-}air}$ normalized to an organic carbon content of 1% are included for reference and comparison.

Name	Soil Chamber Type	Pesticide Combination	Actual Temperature (°C)			Actual Relative Humidity			Flow Rate (ave.)	f_{OC} (%)	Soil p_{soil} (kg L^{-1})	log $K_{soil\text{-}air}$	ln $K_{soil\text{-}air}$	log $K_{soil\text{-}air}$ (f_{oc} normalized to 1%)
			Ave.	SD	%RSD	Ave.	SD	%RSD						
Chlorpyrifos	Glass-column	Technical-grade	23.6	0.4	1.5	74.5	1.2	1.6	0.07	2.8	2.6	8.1	1.0	7.7
Chlorpyrifos	Glass-column	Technical-grade	23.5	0.3	1.3	74.7	1.3	1.8	0.07	2.8	2.6	8.5	1.0	8.1
Chlorpyrifos	Glass-column	Technical-grade	23.6	0.3	1.1	74.3	1.0	1.3	0.07	2.8	2.6	8.2	1.0	7.8
Chlorpyrifos	Flat Pan	Technical-grade	23.9	0.2	0.9	73.7	0.9	1.3	0.13	2.8	2.6	8.4	1.0	7.9
Chlorpyrifos	Flat Pan	Technical-grade	24.0	0.2	0.7	73.4	2.6	3.5	0.14	2.8	2.6	8.3	1.0	7.8
Chlorpyrifos	Flat Pan	Technical-grade	23.9	0.2	0.7	74.3	2.3	3.1	0.12	2.8	2.6	7.8	1.0	7.3
Chlorpyrifos	Flat Pan	Formulation	23.9	0.2	0.9	73.7	0.9	1.3	0.13	2.8	2.6	7.7	1.0	7.3
Chlorpyrifos	Flat Pan	Formulation	24.0	0.2	0.7	73.4	2.6	3.5	0.14	2.8	2.6	7.4	1.0	7.0
Chlorpyrifos	Flat Pan	Formulation	23.9	0.2	0.7	74.3	2.3	3.1	0.12	2.8	2.6	7.5	1.0	7.1
Chlorpyrifos	Flat Pan	Formulation + Adjuvant	23.3	0.4	1.7	76.2	1.6	2.0	0.13	2.8	2.6	7.4	1.0	7.0
Chlorpyrifos	Flat Pan	Formulation + Adjuvant	23.4	0.4	1.7	76.7	1.6	2.1	0.11	2.8	2.6	7.6	1.0	7.1
Chlorpyrifos	Flat Pan	Formulation + Adjuvant	23.7	0.4	1.9	74.8	1.4	1.8	0.13	2.8	2.6	7.4	1.0	7.0
Chlorpyrifos	Flat Pan	Formulation	14.6	0.1	1.0	74.4	1.4	1.9	0.09	2.8	2.6	8.1	1.0	7.7
Chlorpyrifos	Flat Pan	Formulation	14.6	0.1	1.0	75.8	1.4	1.8	0.09	2.8	2.6	7.9	1.0	7.5
Chlorpyrifos	Flat Pan	Formulation	14.6	0.1	1.0	75.5	1.4	1.8	0.08	2.8	2.6	8.2	1.0	7.7
Chlorpyrifos	Flat Pan	Formulation	19.7	0.2	1.1	75.8	1.6	2.2	0.11	2.8	2.6	8.0	1.0	7.6
Chlorpyrifos	Flat Pan	Formulation	19.5	0.2	1.1	75.5	1.3	1.8	0.10	2.8	2.6	7.8	1.0	7.4
Chlorpyrifos	Flat Pan	Formulation	19.6	0.3	1.5	74.4	1.3	1.8	0.07	2.8	2.6	8.0	1.0	7.5
Chlorpyrifos	Flat Pan	Formulation	27.2	0.5	1.9	72.9	3.0	4.1	0.12	2.8	2.6	7.4	1.0	7.0
Chlorpyrifos	Flat Pan	Formulation	27.8	0.6	2.2	74.1	2.0	2.7	0.13	2.8	2.6	7.3	1.0	6.8
Chlorpyrifos	Flat Pan	Formulation	27.6	0.8	2.9	74.1	1.7	2.3	0.10	2.8	2.6	7.4	1.0	7.0

Name	Soil Chamber Type	Pesticide Combination	Actual Temperature (° C)			Actual Relative Humidity			Flow Rate (ave.)	f_{OC} (%)	Soil p_{soil} (kg L^{-1})	log $K_{soil-air}$	In $K_{soil-air}$	log $K_{soil-air}$ (f_{oc} normalized to 1%)
			Ave.	**SD**	**%RSD**	**Ave.**	**SD**	**%RSD**						
Pyrimethanil	Glass-column	Technical-grade	23.6	0.4	1.5	74.5	1.2	1.6	0.07	2.8	2.6	7.9	1.0	7.4
Pyrimethanil	Glass-column	Technical-grade	23.5	0.3	1.3	74.7	1.3	1.8	0.07	2.8	2.6	7.9	1.0	7.4
Pyrimethanil	Glass-column	Technical-grade	23.6	0.3	1.1	74.3	1.0	1.3	0.07	2.8	2.6	8.0	1.0	7.6
Pyrimethanil	Flat Pan	Technical-grade	23.9	0.2	0.9	73.7	0.9	1.3	0.13	2.8	2.6	8.9	1.0	8.5
Pyrimethanil	Flat Pan	Technical-grade	24.0	0.2	0.7	73.4	2.6	3.5	0.14	2.8	2.6	9.1	1.0	8.6
Pyrimethanil	Flat Pan	Technical-grade	23.9	0.2	0.7	74.3	2.3	3.1	0.12	2.8	2.6	8.9	1.0	8.4
Pyrimethanil	Flat Pan	Formulation	23.4	0.4	1.6	75.6	0.9	1.2	0.08	2.8	2.6	7.3	1.0	6.8
Pyrimethanil	Flat Pan	Formulation	23.5	0.4	1.8	75.6	1.3	1.8	0.10	2.8	2.6	7.4	1.0	7.0
Pyrimethanil	Flat Pan	Formulation	23.9	0.4	1.5	74.7	1.4	1.8	0.03	2.8	2.6	7.1	1.0	6.7
Pyrimethanil	Flat Pan	Formulation + Adjuvant	24.0	0.3	1.3	72.7	1.5	2.0	0.10	2.8	2.6	7.4	1.0	6.9
Pyrimethanil	Flat Pan	Formulation + Adjuvant	24.0	0.4	1.5	74.1	1.3	1.8	0.10	2.8	2.6	7.2	1.0	6.7
Pyrimethanil	Flat Pan	Formulation + Adjuvant	23.3	0.5	2.3	76.1	1.7	2.3	0.07	2.8	2.6	6.8	1.0	6.4
Trifluralin	Glass-column	Technical-grade	23.6	0.4	1.5	74.5	1.2	1.6	0.07	2.8	2.6	7.4	1.0	6.9
Trifluralin	Glass-column	Technical-grade	23.5	0.3	1.3	74.7	1.3	1.8	0.07	2.8	2.6	7.5	1.0	7.1
Trifluralin	Glass-column	Technical-grade	23.6	0.3	1.1	74.3	1.0	1.3	0.07	2.8	2.6	7.4	1.0	7.0
Trifluralin	Flat Pan	Technical-grade	23.9	0.2	0.9	73.7	0.9	1.3	0.13	2.8	2.6	7.3	1.0	6.9
Trifluralin	Flat Pan	Technical-grade	24.0	0.2	0.7	73.4	2.6	3.5	0.14	2.8	2.6	7.0	1.0	6.6
Trifluralin	Flat Pan	Technical-grade	23.9	0.2	0.7	74.3	2.3	3.1	0.12	2.8	2.6	6.8	1.0	6.4
Trifluralin	Flat Pan	Formulation	23.8	0.2	0.8	73.5	0.8	1.0	0.11	2.8	2.6	6.0	1.0	5.6

Name	Soil Chamber Type	Pesticide Combination	Actual Temperature (° C)			Actual Relative Humidity			Flow Rate (ave.)	f_{OC} (%)	Soil p_{soil} (kg L^{-1})	log $K_{soil-air}$	In $K_{soil-air}$	log $K_{soil-air}$ (f_{oc} normalized to 1%)
			Ave.	**SD**	**%RSD**	**Ave.**	**SD**	**%RSD**						
Trifluralin		Formulation	23.6	0.2	1.0	73.2	1.0	1.4	0.06	2.8	2.6	5.8	1.0	5.3
Trifluralin	Flat Pan	Formulation	23.9	0.3	1.3	73.7	2.8	3.8	0.09	2.8	2.6	5.9	1.0	5.5
Trifluralin	Flat Pan	Formulation + Adjuvant	24.0	0.3	1.2	73.7	0.7	1.0	0.07	2.8	2.6	5.8	1.0	5.3
Trifluralin	Flat Pan	Formulation + Adjuvant	23.8	0.3	1.2	73.6	0.7	1.0	0.09	2.8	2.6	5.9	1.0	5.5
Trifluralin	Flat Pan	Formulation + Adjuvant	23.7	0.3	1.3	74.4	1.2	1.7	0.06	2.8	2.6	5.7	1.0	5.2

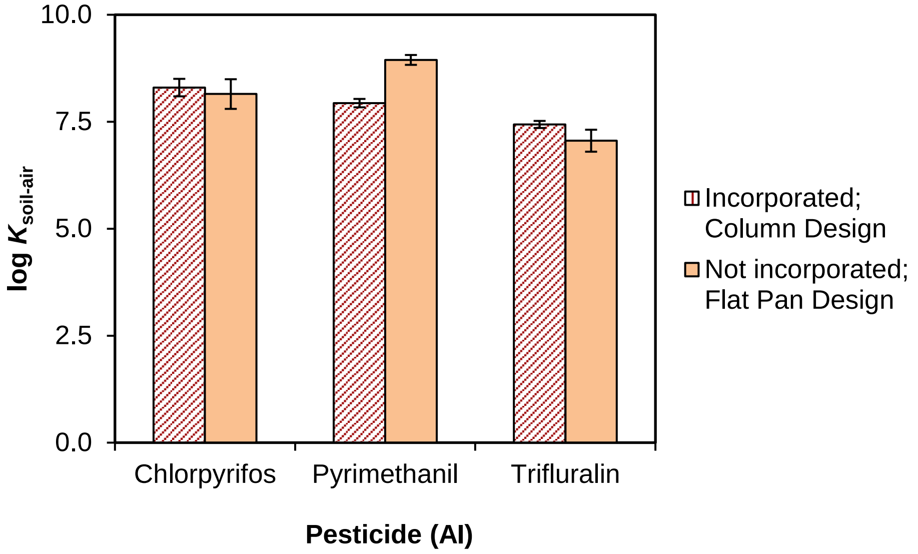


Figure S8. **Comparison of $K_{soil-air}$ values obtained with Column Design and Flat Pan Design experiments at 25 °C and 75% RH. Error bars represent standard deviation ± 1 (*n*=3).**

Table S13. **Statistical test results when comparing Column Design and Flat Pan Design.**

	Mean (Column Design)	Mean (Flat Pan Design)	df (*n*-1)	*t*-stat	*p* (two-tail)	(α,*p*)
Chlorpyrifos	8.3	8.1	5	0.7	0.6	0.05<0.6
Pyrimethanil	7.9	8.9	5	-11.5	0.0003	0.05>0.0003
Trifluralin	7.4	7.1	5	2.4	0.1	0.05<0.1

Table S14. **Statistical test results when comparing $K_{soil-air}$ values.**

	Mean ($K_{soil-air,AI}$)	Mean ($K_{soil-air,formulation}$)	df (*n*-1)	*t*-stat	*p* (two-tail)	(α,*p*)
Chlorpyrifos	8.1	7.6	5	2.6	0.07	0.05<0.07
Pyrimethanil	8.9	7.3	5	15.1	0.0001	0.05>0.0003
Trifluralin	7.1	5.9	5	6.8	0.006	0.05>0.006

Table S15. Chlorpyrifos volatilization rates reported in literature and comparison with results from this study.

Pesticide Chemical Name	Type of Experiment	Temperature (°C)	% RH	Soil Type	Wind Speed (m s^{-1})	% of Mass Volatilized	Time in hours	Literature Cited
Chlorpyrifos (EC formulation)	Lab Study	27	65	Muck Soil	-	>1%	48	[12]
Chlorpyrifos (EC formulation)	Lab Study	27	65	Sandy Soil	-	4%	48	[12]
Chlorpyrifos (Granular formulation)	Lab Study	27	65	Muck Soil	-	2%	48	[12]
Chlorpyrifos (Granular formulation)	Lab Study	27	65	Sandy Soil	-	6%	48	[12]
Chlorpyrifos (EC formulation)	Lab Study	25	75	Silt Loam		1.2%	24	**This Study**
Chlorpyrifos (A.I.)	Lab Study	25	75	Silt Loam		0.3%	24	**This Study**
Chlorpyrifos (A.I.)	Field Study (Wind Tunnel)	21	-	NA	0.1	82.2% (from glass surface)	48	[4]
Chlorpyrifos (A.I. & anionic surfactant)	Field Study (Wind Tunnel)	21	-	NA	0.1	35.2% (from glass surface)	48	[4]
Chlorpyrifos (EC formulation)	Field Study	19.5	-	NA	3	65% (from leaf surface)	8	[13]

Table S16. Pyrimethanil volatilization rates reported in literature and comparison with this study results.

Pesticide Chemical Name	Type of Experiment	Temperature (°C)	% RH	Soil Type	Wind Speed (m s^{-1})	% of Mass Volatilized	Time in hours	Literature Cited
Pyrimethanil (A.I.)	Field Study (Wind Tunnel)	21	-	NA	0.1	70.1% (from glass surface)	48	[4]
Pyrimethanil (A.I. & anionic surfactant)	Field Study (Wind Tunnel)	21	-	NA	0.1	57.5% (from glass surface)	48	[4]
Pyrimethanil (SC formulation)	Lab Study	25	75	Silt Loam (OM-2.81%)		2.5%	24	This Study
Pyrimethanil (A.I.)	Lab Study	25	75	Silt Loam (OM-2.81%)		<1%	24	This Study

Table S17. Trifluralin volatilization rates reported in literature and comparison with this study results.

Pesticide Chemical Name	Type of Experiment	Temperature (°C)	% RH	Soil Type	Wind Speed (m s^{-1})	% of Mass Volatilized	Time in hours	Literature Cited
Trifluralin (formulation)	Field Study	19 (Surface soil)	-	Silt Loam (OM-1.2%)	5	71%	50	[14]
Trifluralin (formulation)	Field Study	-	-	Sandy Loam (OM- 0.6%)	-	25%	50	[14]
Trifluralin (EC formulation)	Field Study (wind tunnel)	20	40-60	Silty Sand (OM-1.5%)	1	64%	24	[15]
Trifluralin (aqueous emulsion formulation)	Field Study (wind tunnel)	21	40-80	-	1	59%	26	[16]
Trifluralin (formulation)	Field Study	25	-	-	-	36%	12	[17]
Trifluralin (aqueous emulsion formulation)	Field Study	0-20	60-100	Sandy Loam (OM-2.36%)	0-3	8.5%	24	[18]
Trifluralin (EC formulation)	Field Study	25	-	(OM- 1.09%)	-	6%	24	[19]
Trifluralin (EC formulation)	Lab Study	25	75	Silt Loam (OM-2.81%)	-	40%	24	This Study
Trifluralin (A.I.)	Lab Study	25	75	Silt Loam (OM-2.81%)	-	3%	24	This Study

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