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Pesticide Inhalation Exposure of Applicators and Bystanders Using Conventional and Innovative Cropping Systems in the Valencian Region, Spain

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Abstract: This paper provides scientific results from a European LIFE project carried out in the Valencian region of Spain during the 2017 to 2018 time frame. In 2018, more than 60,000 tons of pesticides were commercialized in Spain, with approximately 15% destined for Valencian crops. In order to improve the air quality in the agricultural areas of this region, an innovative cropping system based on irrigation was developed and compared to conventional treatments based on hand-spray and turbo application. After applying conventional treatments to five types of crops (citrus, persimmon, nectarine, watermelon, and other stone fruits), a total of 13 active substances were detected in the air. The same active substances were applied to crops using the novel irrigation system, and no pesticide was detected in the air. Moreover, applicator and bystander populations in the region were assessed for their risk of inhalation exposure to pesticides, and no risk was found when either of the techniques, the innovative and the conventional agricultural one, were applied.

Keywords: pesticide; inhalation; applicators; bystanders; human exposure; cropping systems

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Citation: Fuentes, E.; López, A.; Ibáñez, M.; Yusà, V.; Muñoz, A.; Vera, T.; Borrás, E.; Calvete-Sogo, H.; Coscollà, C. Pesticide Inhalation Exposure of Applicators and Bystanders Using Conventional and Innovative Cropping Systems in the Valencian Region, Spain. *Atmosphere* **2021**, *12*, 631. https://doi.org/10.3390/atmos12050631

Academic Editor: Maurice Millet

Received: 1 April 2021
Accepted: 11 May 2021
Published: 15 May 2021

1. Introduction

During the 2011 to 2018 time frame, approximately 360,000 tons of pesticides were sold in the European Union (EU) each year, and this value is expected to remain stable, according to data provided by Eurostat (2018) [1]. In this respect, Spain is the second-biggest consumer of pesticides in the EU. In fact, during 2018, it consumed a total of 61,344 tons, from which 38,067 were fungicides and bactericides, 16,593 were herbicides, and 6488 tons were insecticides.

It is widely known that intense agricultural activity is practiced in most Spanish territories, more specifically, the Valencian region having more than two million hectares (has) dedicated to crops. In Valencia, the agricultural sector generates significant economic benefits due to its high production and the large number of workers involved in all the farming tasks. Citrus fruit is, in this region, the most common crop, covering 170,000 has from the total cultivated surface, followed by non-citrus trees (extending over 154,000 has), and grain cereal crops, which are grown over 47,000 has [2].

In recent years, the control of crop pests and the diseases they cause in agricultural fields has become a major concern. This has been solved by applying pesticides (which only contain one active substance) and plant protection products (PPPs, which contain one or more active substances) in order to protect the crops, increase production efficiency, and reduce the losses caused by unwanted living organisms (insects, fungi, plants, etc.) [3].

Due to the widespread use of PPPs, people exposed to these products can suffer adverse health effects. PPPs exhibit high biological activity and can persist in the environment reaching the human body [4]. Although respiratory diseases and dermatological problems are the most common adverse effects reported [5], others such as reproductive disorders [6], DNA damage [7], or neurological diseases such as Parkinson's, Alzheimer's, and amyotrophic lateral sclerosis [8,9] have been described.

All of these health effects from pesticide exposure are even more relevant for a particular population group that has been classified, according to EFSA (European Food Safety Authority) [10], into four main groups: operators or applicators, workers, residents, and bystanders. The proposed definitions for residents and bystanders are related to the duration exposure, where a bystander is a person who has short-term exposure, while residents are subject to long-term exposure. On the other hand, an operator is defined as someone who mixes, loads, and applies the pesticides, being involved in all the application stages, while workers are defined as the people who are involved in collection tasks or others different than the application stages. All of these populations are highly exposed to pesticides through three main routes during their application in agricultural practices: inhalation (through breathing), dermal contact (via skin), and ingestion (through the mouth) [11]. For these two populations, operators (during the application) and bystanders (due to spray drift), dermal and inhalation exposure are the most important routes.

Pesticide products placed on the market are subject to the European Union Regulation (EC) No 1107/2009 [3] that ensures that these products have no harmful effects on human health, whereas legal residue limits in food and feed are covered by Regulation (EC) No 396/2005 [12]. In addition, EFSA published a "Guidance on Pesticides Exposure Assessment of Operators, Workers, Residents, and Bystanders" which describes a harmonized quantitative approach to the assessment of non-dietary pesticide exposure [10].

With a view to protecting operators´ health, personal protection equipment (such as glasses, masks, and coveralls) is employed to reduce, to a large extent, their exposure to pesticides [13]. Furthermore, several techniques have been developed to reduce the drift effect of pesticides during agricultural application, such as spinning nozzles that produce more uniformly sized droplets or air-assisted technology that improves leaf coverage and reduces the drift levels [14]. In this sense, a European project called Perfect Life "Pesticide Reduction using Friendly and Environmental Controlled Technologies" (Figure 1a) is currently demonstrating the reduction in environmental contamination of pesticides in the air using optimal volume rate adjustment tools (OVRA) and drift reduction tools (SDRT) [15].

(**a**) (**b**)

Figure 1. (**a**) Perfect Life Project and (**b**) Irrilife project.

In recent years, improved pesticide application equipment has been introduced to the market, which, despite its high prices, has led to lower levels of dermal and inhalation exposure (non-dietary exposure). For example, Mercier et al. developed sprayer equipment fitted with an anti-drift device [16], and Rincon et al. [6] reported that while workers were using knapsack sprayers on crops, they would stop for a few seconds in order to avoid dermal exposure. Moreover, currently, different fertigation and chemigation practices for small irrigation systems have been designed [17], but to date, there is no global system that can safely and efficiently inject pesticides into a large irrigation network.

In this respect, the aim of the LIFE_IRRILIFE project, "Environmentally efficient use of pesticides by localized irrigation systems" (Figure 1b), is to develop innovative technology for pesticide application in agriculture using extensive drip irrigation networks. Therefore, a prototype of this irrigation network was designed, installed, and put into operation during two agricultural seasons (2017 and 2018). By using this irrigation system, several health, environmental, social, and economic advantages are expected. The main benefits of implementing it in terms of the environment as compared to conventional systems are the increase in the frequency of treatments and their automation, which makes the use of ecological products easier since these require a higher frequency of application. On the other hand, social and health benefits are related to a significant decrease in air pollution due to a reduction in the exposure of applicators (in the field) and bystanders (via spray drift) to pesticides. Finally, economic benefits arise from the optimization of the amount of product applied, which clearly cuts the losses.

The objectives of this study are: (i) to evaluate whether airborne pesticide concentration is reduced when an alternative innovative crop irrigation system is applied during agricultural activities, (ii) to establish the drift effect of the studied pesticides, and (iii) to assess the risk to applicators and bystanders (infants, children, and adults) when both types of agricultural treatments (conventional and irrigation) are applied to Valencian crops.

2. Materials and Methods

2.1. Reagents and Chemicals

The following high purity standard pesticides were supplied by Dr. Ehrenstorfer (Augsburg, Germany) and Sigma Aldrich (Barcelona, Spain): imidacloprid (99% w/w, LC), oxamyl (sigma 98%, LC), difenoconazole (98.7% w/w, LC), acetamiprid (99% w/w, LC), azoxystrobin (99.5% w/w, LC), bupirimate (98%, sigma), fosetyl-Al (Dr. Ehrenstorfer, 96%, LC), oxyfluorfen (GC, 98 %, SIGMA), methyl-chlorpyrifos (98.5% w/w, GC), azadirachtin (95%, Sigma, LC), lambda-cyhalotrin (98% w/w, GC), and HCH gamma D6 (97.5% w/w).

To prepare the individual stock standard solutions, 10 mg of each pure analytical standard were weighed using a 5 decimal analytical balance (AX 205, Mettler Toledo, Barcelona, Spain) and then dissolved in 50 mL of acetone. They were stored in capped amber vials at -21 °C [18]. Mixed working solutions at 10 and 1 mg L^{-1} were prepared with acetone (GC) and H_2O:MeOH (70:30)(LC).

Methanol of HPLC-grade was supplied by Scharlau (Barcelona, Spain), and acetone, ethyl acetate, and water were of HPLC grade and were purchased from Merck (Darmstadt, Germany). Formic acid (98%) was provided by Panreac (Barcelona, Spain). Fluka (Steinheim, Switzerland) provided ammonium formate (solution Ultra, 100 mL, 10 M in water) and nonane (puriss p.a. standard for GC). N-hexane (99%, HPLC grade) was supplied by Scharlau (Sentmenat, Spain). Ethylene glycol was from Sigma-Aldrich (Barcelona, Spain).

XAD-2 (Sigma-Aldrich, Barcelona, Spain) and PUF (BSG Ingenieros, Valencia, Spain) were the two solid adsorbents used for sample collection. Amberlite XAD-2 polymeric adsorbent is a hydrophobic cross-linked polystyrene copolymer resin. This resin is widely employed to adsorb soluble organic compounds from aqueous streams and organic solvents, whereas PUF is a white polyurethane foam that turns yellow upon exposure to light. PUFs are suitable for trapping volatile compounds and are commonly used for sampling gaseous persistent organic pollutants such as polychlorinated biphenyls and organochlorine pesticides [19].

Also, for this purpose, two low-volume samplers from Digitel (Madrid) were used for the particulate and gaseous phases collection. For particulate phase collection, glass fiber filters of 47 mm of diameter supplied by Tecnylab (Valencia, Spain), were used. Additionally, for the gas phase collection, a PUF-XAD2-PUF sandwich was used as an adsorbent.

2.2. Field Trials

In 2014, the Valencia region, situated on the Eastern coast of Spain, reported more than 15% of total national pesticide usage. This research was conducted in L'Alcudia, where intensive farming is practiced on 642,843 has of cultivated land (28% of the total area) [20].

Field trials were carried out during the 2017 and 2018 growing seasons and a total of 18 cultivated plots were treated (9.5 has). They were divided into two groups: in one of them, crops were treated using the conventional method (3.8 has), while in the other group, the alternative method (5.7 has) was applied. Moreover, for each treatment (conventional or alternative), five types of crops were studied: citrus, persimmon, nectarine, watermelon, and other stone fruits.

On the one hand, the conventional pesticide application was based on the methods mostly used by growers in Valencia, i.e., hand-spray for watermelon crops and turbo for persimmon, nectarine, citrus, and other stone fruits crops treatment (Supplementary Tables S2 and S3). On the other hand, an innovative application system based on large drip irrigation networks was developed to optimize the amount of product applied with the purpose of reducing the exposure of operators and bystanders [21] (Supplementary Tables S4 and S5). This innovative system includes software that allows the injection of a predetermined type of pesticide at a specific point of the drip irrigation network (see Figure 2) and with a determined concentration. In this way, the distribution of pesticides in the different plots can be known. Additionally, a monitoring system, as well as an automatic injection system, were installed to control the distribution and amount of each pesticide injected.

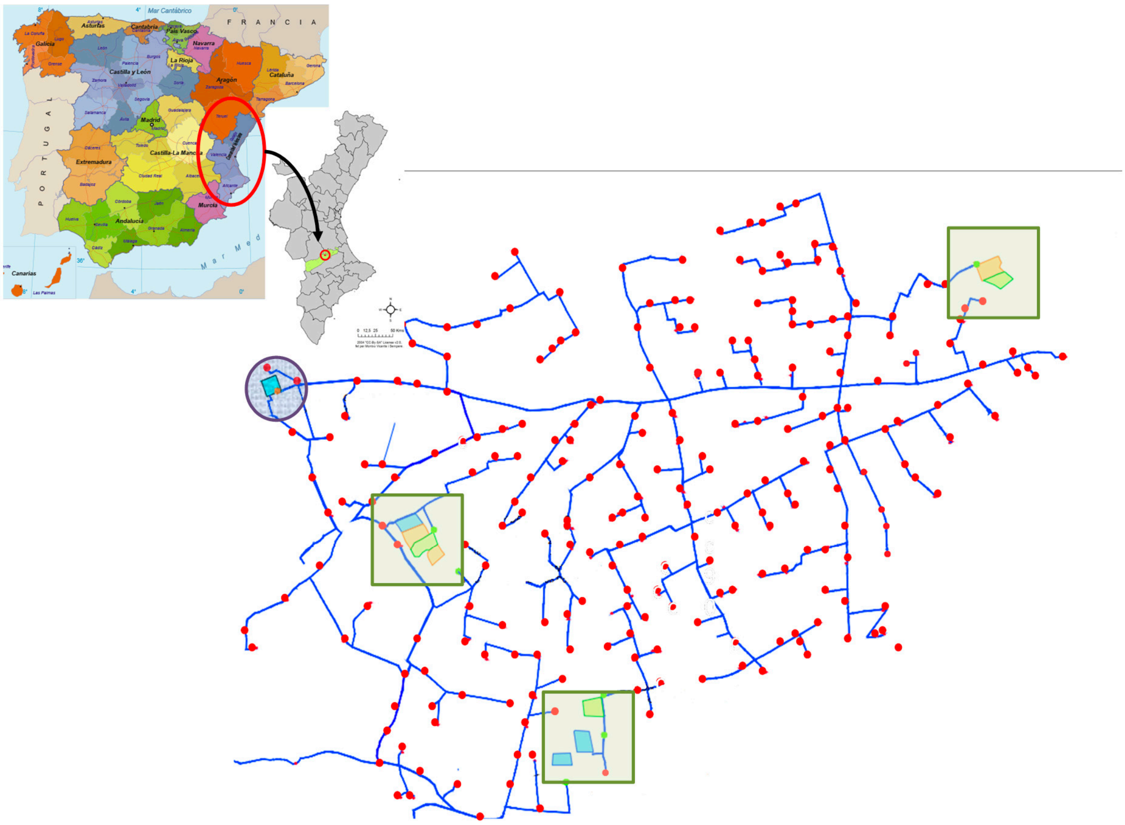

Figure 2. Main injection point (circled in purple) and secondary injection points (red) in the IRRILIFE drip irrigation network. The drip irrigation network's total surface area was >100 has. The surface of crops treated during the Irrilife project (green square) was >5.7 has. Location: L'Alcudia, Valencia, Spain.

2.3. Sample Collection

Two low-volume samplers were used for each application: one of them was located in the area where the pesticides were applied (crop sampler) to simulate the operator exposure, and the other one was placed in an adjacent area, at a distance of 100 m approximately, mimicked the bystander exposure and also measuring the drift effect (drift sampler). Each sampler worked at 2.3 m^3/h for 4 h from the start of the application, collecting a total volume of approximately 9200 L of air. During the pesticide application period from April to September 2017, a total of 11 samples were collected, and 59 samples were collected during different crop treatments from April to September 2018.

Two types of samples were taken from each sampler for both treatments (see Figure 3): (1) sample 1, which was called "gas phase" and was taken from the first PUF+XAD2+PUF sandwich; (2) sample 2, which was of the particulate matter retained on the filter.

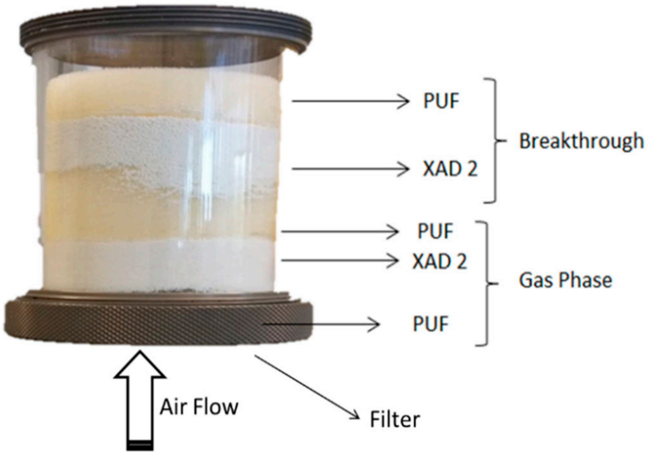

Figure 3. PUF+XAD2+PUF sandwich for the gas phase collection.

2.4. Sample Treatment

After the sample collection, the two types of samples (gas phase and particulate matter) were treated in the same way. First of all, samples were spiked with 250 µL of 200 $\mu g \cdot L^{-1}$ internal standard HCH gamma-D6 and then they were left at room temperature for 15 min to allow a homogeneous distribution of this compound in the sample. After 15 min, samples were chopped, and a generic extraction method, previously developed by our research group, was applied using microwave-assisted extraction (MAE) in 30 mL of ethyl acetate [22]. The extraction was carried out using a Mars system from CEM corporation (Mathews, NC, USA) equipped with Teflon® TFM 100 mL extraction vessels. The extraction conditions were the following: initially, a temperature ramp was applied, and 50 °C was reached in 5 min; this temperature was then kept for 20 min, using a power of 1200 W.

After cooling, the extracts were filtered and cleaned using 60 mL of ethyl acetate. Obtained solutions were evaporated in a Turbo Vap 500 (Zymark, Idstein, Germany) to less than 10 mL and transferred to 10 mL volumetric flasks in order to adjust them to this final volume. Next, two 5 mL aliquots were made from each sample and 100 µL of ethylene glycol (for LC analysis) and 20 µL of nonane (for GC analysis) were added to each aliquot. These substances will act as keepers reducing losses of the analytes during the next evaporation procedure. Finally, samples were evaporated to dryness in a Turbo Vap 50 (Zymark, Idstein, Germany) and re-dissolved in 1 mL of water:methanol (70:30) (for LC analysis) and in 500 µL of hexane (for GC analysis). Re-dissolved samples were filtered through a 0.22 µm GHP Acrodisc filter from Pall Life Science (Ann Arbor, USA), prior to the LC-HRMS and GC-MS/MS determination.

2.5. Analytical Determination

2.5.1. LC-HRMS

Liquid chromatographic separation was performed on an Accela liquid chromatography UHPLC system equipped with a Hypersil Gold aQ column (100 × 2.1 mm, 1.9 µm), both from ThermoFisher Scientific (Bremen, Germany). The flow rate was 300 $\mu L \cdot min^{-1}$, and the injection volume was 10 µL. Separations were carried out using a binary gradient. The mobile phases were H_2O with 0.1% formic acid and 4 mM ammonium formate (A) and methanol with 0.1% formic acid and 4 mM ammonium formate (B). The percentage of organic phase (B) was changed linearly as follows: 0 min, 0%; 1 min, 0%; 8 min, 100%; 12.0 min, 100%; 12.5 min, 0%; 16 min, 0%. The total run time was 16 min. The UHPLC system was coupled to a single-stage Orbitrap mass spectrometer (Exactive™, Thermo Fisher Scientific, Bremen, Germany). A heated electrospray ionization interface was used in positive mode, setting the following optimized parameters: spray voltage, 2.8 kV; sheath gas (N_2, >95%); skimmer voltage, 50 V; capillary voltage, 50 V; heater temperature, 205 °C; capillary temperature, 281 °C. High resolution mass spectrometry (HRMS) optimized parameters were published by Coscollà et al. (2014) [22]. Mass spectra were acquired in full scan (MS) mode fragmentation (resolution powder = 50,000 FWHM (full width half maximum) at m/z 400 mass range = 50 to 800 Da; scan time = 0.5 s (2 Hz)) or with MS2 fragmentation using the same parameter previously determined but adding a collision energy of 10 eV. Finally, data were acquired and processed using Thermo Scientific TraceFinder^{TM} software, version 3.2 (Thermo Scientific, Bremen, Germany).

2.5.2. GC-MS/MS

The analyses were performed on a Finnigan ITMS Polaris Q (Austin, TX, USA). A heated transfer line coupled the mass spectrometer to a Thermoquest Trace GC 2000 (Waltham, MA, USA) gas chromatograph equipped with a Combi Pal Autosampler from CTC Analytics AG (Zwingen, Switzerland). They were carried out using a 30 m × 0.25 mm i.d., 0.25-µm film thickness SGE-BPX5 capillary column (Trajan, Austin, TX, USA). The carrier gas was helium (constant flow, 1.2 mL/min). A PTV Silcosteel liner of 1 × 2.75 × 120 mm was installed in the split/split-less injector and the temperature was set at 250 °C. The high-pressure microseal septum was purchased from Supelco (Bellefonte, PA, USA). The GC temperature program was as follows: initial 90 °C, hold 5 min; rate 25 °C/min, to 180 °C; rate 5 °C min, to 280 °C, hold 3 min; rate 10 °C/min, to 300 °C, hold 3 min. Finally, the chromatographic column was heated at 310 °C for 3 min to avoid interferences caused by contaminants. The transfer line was set at 250 °C, and the electron impact ionization was selected to work with electron energy (EE) of 70 eV. The ionization source temperature was set at 250 °C. Additionally, XCalibur 1.2 software was used for data acquisition and processing. All the analytical methodology parameters had been optimized in previous research published by our research group [19].

2.6. Quality Control Protocol

To be able to determine the pollution background concentrations during the sampling, transport, and analytical processes, the quality assurance protocol included process blanks, field blanks, and reagent blanks filters. These blanks were treated in the same way as the samples. An analysis of the filters was performed immediately after sampling and after being spiked and stored for 3 months at −20 °C to check the potential losses during the storage period.

Breakthrough (XAD2-PUF) was included during the collection procedure (4 h, 2.3 m^3/h) as a sampling quality control to be analyzed. No compound was found in breakthrough, so it can be concluded the maximum volume of the collection sandwich (PUF-XAD2-PUF) was not exceeded. Furthermore, sampling sandwich and filters' retention capacity were previously assessed in the laboratory facilities [19].

In the same way, in order to ensure the quality of the results during the analytical process, filters were spiked with a pesticide mix at the following concentrations: 6.5, 26, and 131 ng/m^3 (HPLC-HRMS) and 10, 20, and 40 ng/cm^3 (GC-MS/MS). They were treated in the same way as the samples. These QCs were analyzed and checked in each analytical sequence.

2.7. Risk Assessment Calculation Methods

Depending on the physicochemical properties of pesticide substances, these will be present either in the gas phase or in the particulate phase. Harner and Bidleman (1998) [23] reported that substances with a vapor pressure higher than 10^{-2} Pa are to be found, in most cases, in the vapor phase, while the substances whose vapor pressure is lower than 10^{-5} Pa are to be found in the particulate phase.

In this case, pesticides such as imidacloprid, difenoconazole, acetamiprid, azoxystrobin, fosetyl-Al, azadirachtin, and lambda cyhalotrin have a vapor pressure lower than 10^{-5} Pa, for this reason, they are mostly found in the particulate phase. Oxamyl, bupirimate, oxyfluorfen, and methyl-chlopyrifos have a vapor pressure in between these two values and for this reason, they are distributed over the two phases (Supplementary Table S1). Therefore, the concentration used for risk assessment is the sum of the obtained concentrations in the two phases [24].

Human exposure was calculated for adults, children, and infants following this equation:

$$\text{DIE (ng/kg/day)} = \Sigma\ (\text{C} \times \text{IR}_{\text{inh}} \times \text{ED})/\text{BW} \tag{1}$$

where:

DIE: Daily inhalation exposure (ng/kg/day);
C: Total concentration (particle and gas phases), ng/m^3;
IR$_{\text{inh}}$: Inhalation rate per hour, m^3/h (adults 20 m^3/h, children 10 m^3/h, infants 8 m^3/h) [10,24];
ED: Exposure duration, h;
BW: Bodyweight, kg (adults 70 kg, children 15 kg, infants 10 kg) [10,25].

The population groups were classified into three main groups according to their age: infants (from 6 months to 1.5 years), children (from 1 to 6 years), and adults (people older than 12 years) [10,26].

A conservative exposure scenario was considered for the chronic exposure assessment using the maximum concentration obtained for each pesticide during the sampling period. A conservative ED of 24 h was taken into account.

Furthermore, exposure risk was assessed by using a hazard quotient (HQ) as a risk descriptor, which was calculated as follows:

$$\text{HQ} = \text{DIE}/\text{HBRVi} \tag{2}$$

where:

HBRVi: Health-based reference values.

HBRV was defined as the acceptable operator exposure level (AOEL), which was obtained for each pesticide by means of the EU Pesticides database [25] and applied in the assessment by comparing it with the calculated DIE.

The HQ level of concern was set to 1.0, where an HQ higher than 1 indicates that a potential risk may be present. However, individually assessing the risk calculated for each pesticide is not a very conservative procedure. For this reason, the cumulative exposure was estimated using a hazard index (HI) approach for pesticides that have a common mode of action (i.e., they are from the same pesticides family), applying the following formula:

$$\text{HI} = \text{HQ}_1\ (\text{pesticide 1}) + \text{HQ}_2\ (\text{pesticide 2}) + \text{HQ}_3\ (\text{pesticide 3}) \tag{3}$$

3. Results and Discussion

3.1. Airborne Pesticide Concentrations

Samples were collected in the fields sprayed with the conventional application system over three months (July, August, and September) in the 2017 season. In this period, four active substances were detected: imidacloprid, ethyl-chlorpyrifos, azadirachtin (insecticides), and metalaxyl (fungicide) (see Table 1). Imidacloprid was detected at the highest concentration in August, while metalaxyl was detected at the lowest concentration in September. In addition, this pesticide was not detected in the drift sampler located 100 m away from the application area. Overall, azadirachtin is the most frequently detected pesticide and the most commonly used active substance for citrus fruit treatments.

Table 1. Pesticide concentrations found in the 2017 season (ng/m^3) using the conventional treatment.

Crop	Product	Active Substance	Date	Conc. Crop	Conc. Drift
Citrus	Confindor	Imidacloprid	03/07/2017	262.25	123.51 *
Citrus	Confindor	Imidacloprid	23/08/2017	482.62 *	41.74
Nectarine		Ethyl-Chlorpyrifos	12/07/2017	116.72 *	91.24 *
Persimmon	Azatin	Azadirachtin	01/08/2017	219.54 *	27.44
Citrus	Azatin	Azadirachtin	02/08/2017	185.32	30.89
Citrus	Azatin	Azadirachtin	01/09/2017	122.46	30.61
Citrus	Azatin	Azadirachtin	25/09/2017	98.14	40.89 *
Citrus		Metalaxyl	04/09/2017	7.31 *	ND

* Maximum concentrations obtained for each pesticide in both samplers.

In total, 30 conventional treatments were applied in the 2018 season, where 11 active substances were detected. Of these, 55% were insecticides (imidacloprid, oxamyl, acetamiprid, methyl-clorpyrifos, azadirachtin, and cyhalotrin), 36% were fungicides (difenoconazole, azoxystrobin, bupirimate, and fosetyl-al), and 9% represented the herbicide applied (oxyflurofen) (see Table 2). The compound with the highest concentration in the samples collected was methyl-chlorpyrifos (July). In contrast, fosetyl-al was detected at the lowest concentration in the September application. In the same way that occurred in 2017, the most commonly found active substance is azadirachtin, followed, in this case, by imidacloprid.

Table 2. Pesticide concentrations found in the 2018 season (ng/m^3) using the conventional treatment.

Crop	Product	Active Substance	Date	Conc. Crop	Conc. Drift
Watermelon	Clorprid	Imidacloprid	17/04/2018	12.43	0.103
Citrus	Kopy	Imidacloprid	06/07/2018	221.35	98.77
Citrus	Kopy	Imidacloprid	18/07/2018	198.75	104.84 *
Citrus	Kopy	Imidacloprid	08/08/2018	471.34 *	29.84
Watermelon	Vydate	Oxamyl	30/04/2018	9.64 *	0.099 *
Stone Fruit	Score25	Difenoconazole	15/05/2018	77.43	0.99
Persimmon	Score25	Difenoconazole	11/06/2018	103.57 *	12.43 *
Stone Fruit	Gazel SP	Acetamiprid	18/05/2018	11.03	0.21
Citrus	Gazel SP	Acetamiprid	21/06/2018	77.44 *	6.45 *
Persimmon	Ortiva	Azoxystrobin	25/05/2018	112.44 *	77.43 *
Watermelon	Nimrod Quattro	Bupirimate	31/05/2018	9.34 *	0.083
Watermelon	Nimrod Quattro	Bupirimate	22/06/2018	8.77	0.187 *
Citrus	Aliette WG	Fosetyl-Al	12/06/2018	187.43 *	79.99 *
Citrus	Pombal	Fosetyl-Al	13/09/2018	7.31	0.83

Table 2. *Cont.*

Crop	Product	Active Substance	Date	Conc. Crop	Conc. Drift
Citrus	Inteike	Oxyfluorfen	09/07/2018	10.02 *	0.22 *
Stone Fruit	Sentosan	Methyl-chlorpyrifos	27/06/2018	167.40	92.33 *
Stone Fruit	Sentosan	Methyl-chlorpyrifos	16/07/2018	104.34	13.01
Stone Fruit	Sentosan	Methyl-chlorpyrifos	30/07/2018	478.58 *	29.57
Persimmon	Align	Azadirachtin	04/07/2018	98.44	1.02
Persimmon	Align	Azadirachtin	01/08/2018	47.23	0.52
Persimmon	Align	Azadirachtin	20/08/2018	101.23	9.66
Citrus	Align	Azadirachtin	21/08/2018	76.98	0.73
Citrus	Align	Azadirachtin	03/08/2018	41.23	0.44
Persimmon	Align	Azadirachtin	12/09/2018	55.79	0.34
Persimmon	Align	Azadirachtin	18/09/2018	27.63	9.872 *
Persimmon	Align	Azadirachtin	01/10/2018	28.90	6.58
Persimmon	Align	Azadirachtin	11/10/2018	131.57 *	8.34
Citrus	Karate Zeon	Azadirachtin	19/09/2018	122.72 *	7.97
Citrus	Karate Zeon	λ -Cyhalothrin	02/10/2018	95.81	10.57 *
Citrus	Karate Zeon	λ -Cyhalothrin	15/10/2018	50.67	6.51

* Maximum concentrations obtained for each pesticide in both samplers.

Yet when the innovative irrigation system was used for applying the pesticides, no pesticide was detected in the air (or their concentrations were lower than their LOQ). This system allows pesticides to be applied directly to the soil and, consequently, prevents these substances from traveling through the air. As expected, compound losses through the air were eliminated.

3.2. Comparison between the Crop Sampler and the Drift Sampler: Spray Drift

Concentrations obtained in the crop sampler and drift sampler (Tables 1 and 2) were compared to know the way in which pesticides behave in the air. The amount of substance that travels in the air is known as drift.

As shown in Tables 1 and 2, pesticide concentrations in the treated area are always higher than drift concentrations. Moreover, it can be observed that each pesticide produces a different drift effect. Imidacloprid and azadirachtin obtained the highest concentrations in the crop sampler for the 2017 season, and methyl chlorpyrifos and imidacloprid applications resulted in high concentrations during the 2018 season. However, the highest drift levels during 2017 were reported by chlorpyrifos (78%) and imidacloprid (47%). During the 2018 applications, if we compare the concentrations obtained from the crop samplers with those obtained from the drift samplers, the highest percentage of drift was observed for azoxystrobin (69%) and imidacloprid (53%). In contrast, lambda-cyhalothrin, azadiracthin, oxyfluorfen, and oxamyl presented low percentages of drift. In Supplementary Tables S6 and S7 it can be seen that, for the same substance, the reported drift values are different each sampling day. Hence, it can be concluded that the percentage of drift produced during the applications does not depend on the type of compound used but it can be influenced by other factors, such as meteorological conditions.

For this reason, wind direction, wind speed, and atmospheric conditions were studied. Meteorological and wind conditions were evaluated and registered during each application. Parameters such as wind speed, temperature, and humidity were recorded, and no relationship between humidity or temperature and drift was investigated. Nevertheless, a relationship was found between wind speed and drift. For instance, during the azoxystrobin application, the wind speed range was between 25 and 37 km/h, and after this treatment was applied, a 69% drift was reported. This trend could also be observed for the imidacloprid, fosetyl-al, and chlorpyrifos applications, which allows the conclusion that high wind speed rates lead to higher drift levels (see Supplementary Tables S6 and S7).

However, it was observed that a high wind speed does not always result in higher drift effects and this is because of the wind direction. For example, for lambda-cyhalotrin application during the 2018 season wind speed values between 20 and 40 km/h were reported and low drift was obtained (13%), the main reason for these results was that the drift sampler was located upwind.

Moreover, a reasonable relationship was found between the application technique and drift. Watermelon crops were treated with the hand-spray technique, and during the pesticide applications to these crops, their drift values were the lowest reported (0.5 to 2%).

3.3. Risk Assessment

Inhaled pesticide risk assessment was evaluated by collecting samples from two samplers that tried to mimic operator and bystander exposure. As expected, the concentrations obtained from the sampler located in the crop field were higher than the concentrations obtained in the adjacent area.

The daily inhalation exposure (DIE) values for adults, infants, and children were calculated with the concentrations obtained at the crop sampler and at the drift sampler. In this calculation, parameters such as height, inhalation rate, and body weight, which are determined by the age of the bystanders and operators, are relevant for risk assessment. Children and infants' risk assessment is of special importance since they are one of the population groups more susceptible to suffer respiratory and allergic diseases, such as asthma and rhinitis, caused by prolonged pesticide exposure [27,28].

For risk calculations, the worst case was assessed, using for DIE calculations the maximum concentration obtained for each pesticide in the conventional application. When the DIE values obtained are lower than the AOEL values (this is, $HQ < 1$) for the respective active substance, its risk exposure can be considered acceptable. In contrast, when DIE is higher than AOEL ($HQ > 1$), exposure levels of pesticides should be reduced through mitigation measures [29].

As can be seen in Tables 3 and 4, during conventional treatments, the obtained risk values of HQ for all pesticides are lower than one for both groups (applicators and bystanders) and in all populations (children, infants, and adults). Therefore, we can conclude that no health risk was found, including the worst case. However, considering that people who work or live near an agricultural area are usually only exposed to pesticides applied to one crop, this could lead to underestimating the total exposure [30]. For this reason, a cumulative risk assessment was performed by using a hazard index (HI). The cumulative assessment group (CAG) is based on a group of chemicals, with common modes of action, that act jointly, and, therefore, the risk must be assessed, taking into account all the compounds that integrate this group. The HI was calculated for the neonicotinoid group (i.e., imidacloprid and acetamiprid) as well as for the organophosphate group (fosetyl-al and methyl chlorpyrifos). During the 2018 conventional treatments, using the crop sampler, the HIs obtained for children, infants, and adults were 7.2×10^{-3}, 6×10^{-3}, and 2.6×10^{-3}, respectively, for the neonicotinoid group; and 3.8×10^{-2}, 3.2×10^{-2}, and 1.4×10^{-2}, respectively, for the organophosphate group. In the same season and using the same type of treatment and the drift sampler, the HIs for these groups were 1.3×10^{-3}, 6.2×10^{-3}, and 2.6×10^{-3}, respectively, for the neonicotinoid group; and 7.4×10^{-3}, 6.2×10^{-3}, and 2.6×10^{-3}, respectively, for the organophosphate group. In conclusion, the cumulative pesticide exposure in the 2018 season can be considered acceptable. However, during the 2017 season, all of the pesticides applied belonged to different families, and thus, no cumulative risk assessment could be conducted.

It is important to mention that when the alternative treatment was applied, both in 2017 and 2018, the concentrations of pesticides in the air were lower than the LOQ of the analytical method, and consequently, no risk was found when applying this technique in agricultural practice.

Table 3. DIE (ng/kg·bw/day) and HQ values for the three types of exposed population in crop and drift samples during the 2017 season.

Drift

Pesticide	Max. Conc. Drift (ng·m^{-3})	DIE (Infants)	DIE (Children)	DIE (Adults)	HQ (Infants)	HQ (Children)	HQ (Adults)
Imidacloprid	123.51	98.81	82.34	35.29	1.24×10^{-3}	1.03×10^{-3}	4.41×10^{-4}
Ethyl-Chlorpyrifos	91.24	72.99	60.83	26.07	7.30×10^{-3}	6.08×10^{-3}	2.61×10^{-3}
Azadirachtin	40.89	32.71	27.26	11.68	1.31×10^{-3}	1.09×10^{-3}	4.67×10^{-4}
Metalaxyl	Not Detected	0	0	0	0	0	0

Crop

Pesticide	Max. Conc. Crop (ng m^{-3})	DIE (Infants)	DIE (Children)	DIE (Adults)	HQ (Infants)	HQ (Children)	HQ (Adults)
Imidacloprid	482.62	386.09	321.75	137.89	4.83×10^{-3}	4.02×10^{-3}	1.72×10^{-4}
Ethyl-Chlorpyrifos	116.72	93.37	77.81	33.35	9.34×10^{-3}	7.78×10^{-3}	3.33×10^{-3}
Azadirachtin	219.54	175.6	146.36	62.73	7.03×10^{-3}	5.85×10^{-3}	2.51×10^{-3}
Metalaxyl	7.31	5.85	4.87	2.09	7.31×10^{-5}	6.09×10^{-5}	2.61×10^{-5}

Table 4. DIE (ng/kg·bw/day) and HQ values for the three types of exposed population in crop and drift samples during the 2018 season.

Drift

Pesticide	Max. Conc. Drift (ng·m^{-3})	DIE (Infants)	DIE (Children)	DIE (Adults)	HQ (Infants)	HQ (Children)	HQ (Adults)
Imidacloprid	104.84	83.87	69.90	29.96	1.05×10^{-3}	8.74×10^{-4}	3.74×10^{-4}
Oxamyl	0.099	0.08	0.07	0.03	7.90×10^{-5}	6.58×10^{-5}	2.82×10^{-5}
Difenoconazole	12.43	9.95	8.29	3.55	6.22×10^{-5}	5.18×10^{-5}	2.22×10^{-5}
Acetamiprid	6.45	5.16	4.30	1,84	2.07×10^{-4}	1.72×10^{-4}	7.38×10^{-5}
Azoxystrobin	77.43	61.95	51.62	22.12	3.10×10^{-4}	2.58×10^{-4}	1.11×10^{-4}
Bupirimate	0.19	0.15	0.12	0.05	3.00×10^{-6}	2.50×10^{-6}	1.07×10^{-6}
Fosetyl-Al	79.99	63.99	53.33	22.85	1.28×10^{-5}	1.07×10^{-5}	4.57×10^{-6}
Oxifluorofen	0.22	0.17	0.14	0.06	1.33×10^{-5}	1.11×10^{-5}	4.75×10^{-6}
Methylchlorpyrifos	92.33	73.87	61.56	26.38	7.39×10^{-3}	6.16×10^{-3}	2.64×10^{-3}
Azadirachtin	9.87	7.90	6.58	2.82	7.90×10^{-5}	6.58×10^{-5}	2.82×10^{-5}
λ -Cyhalothrin	10.57	8.46	7.05	3.02	1.34×10^{-2}	1.12×10^{-2}	4.79×10^{-3}

Crop

Pesticide	Max. Conc. Crop (ng·m^{-3})	DIE (Infants)	DIE (Children)	DIE (Adults)	HQ (Infants)	HQ (Children)	HQ (Adults)
Imidacloprid	471.34	377.07	314.23	134.67	4.71×10^{-3}	3.93×10^{-3}	1.68×10^{-3}
Oxamyl	9.64	7.71	6.43	2.76	7.71×10^{-3}	6.43×10^{-3}	2.76×10^{-3}
Difenoconazole	103.57	82.85	69.04	29.59	5.18×10^{-4}	4.32×10^{-4}	1.85×10^{-4}
Acetamiprid	77.44	61.95	51.62	22.12	2.48×10^{-3}	2.06×10^{-3}	8.85×10^{-4}
Azoxystrobin	112.44	89.95	74.96	32.12	4.50×10^{-4}	3.75×10^{-4}	1.61×10^{-4}

Table 4. *Cont.*

			Crop				
Pesticide	**Max. Conc. Drift ($ng \cdot m^{-3}$)**	**DIE (Infants)**	**DIE (Children)**	**DIE (Adults)**	**HQ (Infants)**	**HQ (Children)**	**HQ (Adults)**
Bupirimate	9.34	7.47	6.23	2.67	1.49×10^{-4}	1.25×10^{-4}	5.34×10^{-5}
Fosetyl-Al	187.43	149.94	124.95	53.55	3.00×10^{-5}	2.50×10^{-5}	1.07×10^{-5}
Oxyfluorfen	10.02	8.02	6.68	2.86	6.17×10^{-4}	5.14×10^{-4}	2.20×10^{-4}
Methylchlorpyrifos	478.58	382.86	319.05	136.74	3.83×10^{-2}	3.19×10^{-2}	1.37×10^{-2}
Azadirachtin	131.57	105.25	87.71	37.59	1.05×10^{-3}	8.77×10^{-4}	3.76×10^{-4}
λ -Cyhalothrin	122.72	98.18	81.82	35.06	1.56×10^{-1}	1.30×10^{-1}	5.57×10^{-2}

3.4. Comparison of the Innovative Treatment with the Conventional Treatment

In contrast to the conventional application, airborne pesticide concentrations at two samplers´ locations for the innovative irrigation system were "non-detected" for all the active substances applied. This means that all the pesticide applied reached the plant, but it did not flow into the air stream, and consequently, the risk of exposure by inhalation or dermal exposure was eliminated.

Additionally, using this new irrigation system, the amount of product applied can be optimized, and a smaller amount is needed since no losses have been observed during its application. This fact makes the crop treatment more affordable and also more environmentally friendly. The irrigation system enables the applications in the different areas to be automatized through a monitoring system in which the pesticide concentration and the application periodicity can be predetermined. In this way, field operator tasks are eliminated, and their exposure to pesticides is reduced. Nevertheless, some pesticides cannot be applied by means of this irrigation system because they are not soluble in water or due to one of their physicochemical properties.

4. Conclusions

After conventional agricultural treatments applied in the Valencian region during the 2017 and 2018 agricultural seasons, a total of seven insecticides, five fungicides, and one herbicide were detected in the air. Azadirachtin and imidacloprid were the pesticides most commonly used, and they were found at high concentrations. In contrast, for alternative applications based on drip irrigation systems, no active substances were found in the air.

A drift effect has been observed during conventional applications, of which 30 to 70% was reported for highly concentrated compounds. Furthermore, no relationship could be established between the active substance and the drift effect, but relationships were established between the drift effect and the wind speed and direction during the application: higher values of wind speed resulted in higher values of drift when the drift sampler was located downwind, but this did not occur when drift sampler was located upwind. Moreover, the mode of the application used was also shown to be a factor that influences drift. This allows for the conclusion that a lower drift effect can be achieved by using the hand spray application mode, and in consequence, a lower exposure.

Given that no pesticide concentrations were detected in the air when the innovative system was applied, no risk was found for applicators and bystanders. However, pesticide concentrations in the air were observed when conventional treatments were applied. In spite of this, no risk was observed when using the conventional treatment either, because the calculated HQs were lower than one for adults, infants, and children, and therefore, the exposure values were considered acceptable.

Thus, our findings confirm that the drip irrigation network developed within the IRRILIFE project successfully reaches its main objectives. First of all, reduction in air pollutants and human exposure has been achieved in that the concentrations found for all the compounds applied were lower than the LOQ. Secondly, the system's automation enables growers to apply treatments more frequently on their crops as required by regulations for the use of environmentally-friendly pesticides. Thirdly, the optimization of the amount of compound applied offers greater economic benefits to agricultural businesses.

Finally, economic, social, and environmental benefits make a drip irrigation system an interesting alternative to conventional crop treatment systems for the future. Nevertheless, other types of innovative application systems and tools, such as OVRA and SDRT, are currently under study with the aim of finding the best one.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/atmos12050631/s1, Table S1: Conventional treatments, 2017 season, Table S2: Conventional treatments, 2018 season, Table S3: Alternative treatments, 2017 season, Table S4: Alternative treatments, 2018 season, Table S5: Relationship between atmospheric parameters and drift effect. Conventional treatment, 2017 season., Table S6: Relationship between atmospheric parameters and drift effect. Conventional treatment, 2018 season, Figure S1: Temperature vs. drift effect, Figure S2: Wind rate vs. drift effect, and Figure S3: Humidity vs. drift effect.

Author Contributions: Conceptualization, A.M. and A.L.; investigation, T.V., E.B., H.C.-S., and V.Y.; writing—original draft preparation, E.F.; supervision, C.C. and M.I. All authors have read and agreed to the published version of the manuscript.

Funding: This work was developed in the framework of the projects PERFECT_LIFE (LIFE17 ENV/ES/000205) and LIFE_IRRILIFE (LIFE14 ENV/ES/000119) with the financial support of the LIFE program of the European Union.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work was developed in the framework of the projects PERFECT_LIFE (LIFE17 ENV/ES/000205) and LIFE_IRRILIFE (LIFE14 ENV/ES/000119) with the financial support of the LIFE program of the European Union. The authors want to thank all partners of the LIFE_IRRILIFE project, especially Lola Corvinos from JAP Energéticas Medioambientales, José Vila from Qualitas, and La Comunidad de Regantes de L'Alcudia.

Conflicts of Interest: The authors declare no conflict of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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