

Article

Methodological Aspects for the Implementation of the Air Pesticide Control and Surveillance Network (PESTNet) of the Valencian Region (Spain)

Antonio López ¹, Pablo Ruiz ², Vicent Yusà ^{1,2,3} and Clara Coscollà ^{1,*}

¹ Foundation for the Promotion of Health and Biomedical Research in the Valencian Region, FISABIO-Public Health, 21, Avenida Catalunya, 46020 Valencia, Spain; lopez_antob@gva.es (A.L.); yusa_vic@gva.es (V.Y.)

² Public Health Laboratory of Valencia, 21, Avenida Catalunya, 46020 Valencia, Spain; pablorudo@gmail.com

³ Analytical Chemistry Department, University of Valencia, Edifici Jeroni Muñoz, 46100 Burjassot, Spain

* Correspondence: coscolla_cla@gva.es; Tel.: +34-961-926-333

Abstract: A large amount of pesticide, applied mainly during agricultural practice, is released into the atmosphere, decreasing air quality and potentially causing public health problems. The Valencian region, after Andalusia, is the Spanish region with the highest consumption of pesticides owing to its large areas of agricultural land and the existence of crops that require intensive use of pesticides. In this work, we describe the sampling and analytical tools developed in the last decade and their transference to the Regional Department for Environment, where the main objective of the research was the creation and implementation of an Air pesticide control and surveillance network (PESTNet) in the Valencian region in Spain. To be able to confirm that the established strategies were appropriate, a pilot scheme comprising three different sampling stations (two rural and one urban) was developed and implemented in 2020. The results showed that as many as 30 pesticides were detected in the three sampling stations, with the frequency detection ranging from 6% (beta-endosulfan, chlorpropham, endosulfan-sulfate, kresoxim-m, prochloraz) to 100% (azoxystrobin, chlorpyrifos-m, metalaxyl-M). On the other hand, the concentrations of the pesticides found oscillated between 14.4 (boscalid) and 4373.0 pg m⁻³ (chlorpyrifos-m). Moreover, a risk assessment was carried out, and no risks were observed for the studied population (infants, children, and adults) in the evaluated stations.

Keywords: pesticides; network; public health; ambient air; surveillance



Citation: López, A.; Ruiz, P.; Yusà, V.; Coscollà, C. Methodological Aspects for the Implementation of the Air Pesticide Control and Surveillance Network (PESTNet) of the Valencian Region (Spain). *Atmosphere* **2021**, *12*, 542. <https://doi.org/10.3390/atmos12050542>

Academic Editor: Maurice Millet

Received: 26 March 2021

Accepted: 21 April 2021

Published: 23 April 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The intensive use of pesticides, which includes herbicides, fungicides, acaricides, insecticides, and nematicides, is one of the main characteristics of European agriculture. Nowadays, around 500 active substances are authorized by the European Union for their application on different crops according to Regulation (EC) No. 1107/2009 [1]. During 2018, almost 400,000 tons of pesticide-active ingredients were sold in the EU-28, with the vast majority being used in the agricultural sector [2]. The countries with the highest consumption of pesticides are France, Spain, Italy, Germany, and Poland [2]. Within Spain, taking into account the data provided by each region, the agricultural regions with the highest pesticide use are Andalusia, the Valencian region, and Catalonia [3].

The Valencian region is one of the regions in Spain that uses the largest number of pesticides due to the fact that it is a region where agricultural activity is intense. Twenty-eight percent of its surface area is dedicated to agricultural production, where the main agricultural land uses are related to the cultivation of citrus fruits (24% of the agricultural land), fruit trees (around 20% of the agricultural land), olive groves (14%), vineyards (10%), cereals, mainly rice (6.3%), and vegetables (3.5%), covering around 650,000 hectares [4].

A well-known problem is that a fraction of the dose of pesticides applied can be deposited in adjacent areas (soil, water, plants) to the treated one, while another significant

fraction (up to 30–50% of the applied dose) is emitted into the atmosphere (spray drift). On the other hand, several days or weeks after the application, pesticides on the plants and soil can turn into vapor and volatilize into the air [5]. Moreover, there is a third mechanism by which pesticides can enter the atmosphere, which is due to the erosion caused by winds, which transports the soil particles loaded with pesticides elsewhere (soil tillage) [6]. As a result of all these processes, an important proportion of the pesticides applied in a given area is carried into the atmosphere [7]. Airborne pesticides are usually present in both gaseous and particulate phases. The phase distribution between the particulate and gaseous phase depends on the pesticide physicochemical properties (e.g., vapor pressure and water solubility), meteorological conditions (e.g., temperature and precipitation), the number of ambient particles, and their composition in the ambient air.

Pesticides are usually found in the atmosphere in concentrations ranging from 0.1 pg m^{-3} to 10 ng m^{-3} [8]. In the first decade of the 2000s, several studies provided data on the frequency of detection and concentrations of pesticides in the environment of several countries, mainly France, Canada, and the USA, in rural and urban ambient [9–12]. Nevertheless, authorized pesticides have been changed in the last years, and nowadays, some of the pesticides assessed by these studies are banned, and only a small percentage of them can be considered as pesticides commonly used in agricultural areas.

In Spain, our research group has published several studies related to the spatial and temporal distribution of pesticides currently used in the Valencian region, both in the particulate phase (PM10) [13,14] and gaseous phase [15,16]. A large number of authorized pesticides in the European Union, together with the formation of a range of different compounds (metabolites or transformation products), means that possibly a wide range of substances are present in the atmosphere, whose concentrations and temporal and spatial evolution must be known in order to carry out a continuous assessment of the potential risk in order to protect the population's health.

However, the monitoring of pesticides in the ambient air requires appropriate sampling and analysis methods. The sampling of the particulate phase is well characterized, given that quartz or glass fiber filters have been used in several countries in the last two decades [17]. On the other hand, to sample pesticides in the gaseous phase, several materials have been employed: PUF, XAD-2, XAD-4, Tenax-TA, or a mix of some of them [18–24]. In this respect, it is very important to choose an appropriate sorbent to be able to sample as many pesticides as possible and to report the gaseous phase concentrations accurately. In two previous studies of our research group [15,16], a PUF-XAD₂-PUF sandwich was chosen in order to sample pesticides in the gaseous phase.

Regarding the analysis, the increase over the last decade in the use of polar compounds, labile, and less volatile pesticides (such as carbamates, neonicotinoids, or triazines) has favored the use of liquid chromatography (LC) instead of gas chromatography (GC) [25]. Moreover, the use of analyzers such as high-resolution mass spectrometry (HRMS), e.g., TOF or Orbitrap, enables an unlimited number of species to be attained by means of accurate mass measurement (<5 ppm) combined with high-resolution power (25,000–50,000 FWHM) [26,27]. In the past decade, our group has published five analytical works for the analysis of pesticides in ambient air; two of them using LC-HRMS [28,29] (Thermo-Fisher, Bremen, Germany), two using LC-MS/MS (Thermo Fisher, Bremen, Germany) [30,31], and one using GC-MS/MS (Thermo Fisher, Bremen, Germany) [32].

Although the general population, including risk groups such as children, is exposed to pesticides mainly through diet [33], the inhalation of ambient air loaded with certain concentrations of pesticides commonly employed in agriculture can also be a significant route of exposure, especially for populations living in pesticide-intensive agricultural areas [34]. Nowadays, only a few studies related to the risk of pesticide inhalation for different population groups have been carried out [33–36]. Of these, our group has published two studies for Spain [34,35] and another one for France [36].

A still unsolved issue is hence the lack of standardization, which would enable a protocol to be developed for the sampling, analysis, and strategies in risk assessment since

it is necessary to protocol all these processes in order to compare results at a regional, national and international scale. As far as we know, inside the European Union, only French regions have their own pesticide control and surveillance networks [37]. Yet, in Spain, there is no region with a network for monitoring the presence of pesticides in the ambient air.

The implementation of such a network is therefore needed for the Valencian region (Spain), and the aim of this paper is to contribute to this objective through its description. The elaboration of this network derives from the developments achieved through our research group during the last decade concerning technologies and methodologies for sampling, analyzing, and assessing the risks of pesticides in the atmosphere of the region.

The main objectives of the implementation of an Air pesticide control and surveillance network (PESTNet) in the Valencian region are: (i) to establish a system of public health surveillance regarding the presence and impact of pesticides used in agriculture; (ii) to implement a system of indicators that will contribute to compliance with the European regulations regarding the sustainable use of pesticides; (iii) to improve air quality; and (iv) to contribute to the creation of European standards on the maximum concentrations of pesticides allowed in the ambient air.

2. Materials and Methods

2.1. Selection of Pesticides

An inventory of active substances, including those used in the Valencian region, was prepared. We considered the following criteria and reports to select and prioritize the substances to be monitored through the surveillance network:

- (i) Recommendations concerning the application of pesticides in crops of the Valencian region by the agricultural reports of the Regional Department of Agriculture of the Valencian Government [38];
- (ii) The frequency of pesticide residue detection in food according to the Valencian Public Health Regional Government reports [39];
- (iii) The most frequently used pesticide per crop in the region, as stated by the regional agri-food cooperatives [40];
- (iv) According to the Spanish Ministry of Agriculture, the most widely marketed plant protection products in Spain [41];
- (v) Previous studies of pesticide concentrations in the Valencian region [13,14,35].

2.2. Sampling Locations for the PESTNet Network

Suitable locations for the sampling of pesticides in the ambient air were selected according to the following criteria:

- (i) The sampling sites had to be in close vicinity of the major cultivation areas in the Valencian region (citrus, stone fruit trees, persimmon, vineyards, or rice);
- (ii) The number of pesticides applied in these areas;
- (iii) The areas had to have appropriate logistic conditions such as accessible surfaces to place the samplers and connection points to the power grid;
- (iv) An urban site had to be included in order to assess the medium atmospheric range transport from rural areas to urban areas.

2.3. Sampling Protocols

After taking into consideration different samplers and the sampling conditions, Digital DPA-16 was the one selected. To collect particulate phase, glass fiber filters (diameter of 47 mm) are employed, and to collect the gaseous phase, the sandwich PUF-XAD₂-PUF is used [15,16]. The sampler has a flow rate of 2.3 m³ h⁻¹ and samples a total air volume of approximately 386 m³ (one week of sampling). This can be considered an appropriate air volume to obtain adequate measurements and to be able to determine the concentrations of pesticides in both phases (particulate and gaseous) in the ambient air.

2.4. Sample Preparation

Samples (particulate and gaseous phases) have been prepared following the methodology described in several articles of our research group [15,16]. Briefly, a microwave extraction of the pesticides was carried out using a Mars System from CEM Corporation (Mathews, NC, USA) equipped with Teflon[®] TFM 100 mL extraction vessels. The corresponding filter or sorbent was extracted at 50 °C for 20 min, using a power of 1200 W and 30 mL of ethyl acetate. Then, the extracts were filtered and evaporated until 10 mL. Following these, a partition was carried out in two aliquots of 5 mL. Then, the extracts were evaporated and re-dissolved using hexane or a mix of H₂O: MeOH (70:30), depending on whether an analysis by gas chromatography (GC) or one by liquid chromatography (LC) was required.

2.5. Analysis

Pesticides were analyzed using either gas chromatography (GC) or liquid chromatography (LC), depending on their polarity and volatility.

2.5.1. GC-MS/MS

For volatile and apolar compounds, analyses were performed using a Finnigan Ion Trap mass spectrometer Polaris Q (Austin, TX, USA). We also used a 30 m × 0.25 mm i.d., 0.25 µm film thickness, SGE-BPX5 capillary column (Austin, TX, USA). We connected the mass spectrometer by means of a heated transfer line to a Thermoquest Trace GC 2000 (Waltham, MA, USA) gas chromatograph equipped with a Combi Pal Autosampler from CTC Analytics AG (Zwingen, Switzerland). The carrier gas was helium (constant flow, 1.2 mL min⁻¹). We installed a Silcosteel liner (1 × 2.75 × 120 mm) in the PTV split/splitless injector and set the temperature at 250 °C. The Microseal high-pressure septum was purchased from Supelco (Bellefonte, PA, USA). The transfer line was set at 250 °C. The electron impact ionization was selected by working with an electron energy of 70 eV, and the ionization source temperature was set at 250 °C. As to data acquisition, XCalibur 3.2 was employed.

To obtain a positive identification of the pesticides, which were assessed in accordance with the SANTE guidelines [42], the following rules were applied: (i) two or more SRM (selective reaction mode) transitions per compound were monitored, (ii) the GC relative retention time of the analyte in the sample had to be within 0.1 min of the retention time of the standard, (iii) the relative abundance of the SRM transition signals had to be within 30% of the ratio obtained for the standards, and iv) the signal/noise ratio (S/N) of the two diagnostic ions had to be >3.

2.5.2. LC-HRMS

For polar and less volatile compounds, the chromatographic separation was performed on an Accela liquid chromatography UHPLC system equipped with a Hypersil Gold aQ column (100 mm × 2.1 mm, 1.9 µm) both from ThermoFisher Scientific (Bremen, Germany). The flow rate used was 300 µL min⁻¹, and the injection volume, 10 µL. The separations were performed using a binary gradient. The mobile phase was a gradient of H₂O with 0.1% formic acid and 4 mM ammonium formate (A) and of methanol with 0.1% formic acid and 4 mM ammonium formate (B). The gradient conditions were as follows: 0–8 min, linear with 100% of A; 8–12 min, linear with 100% of B, and 12–16 min, linear with 100% of A. The total run time was 16 min. The UHPLC system was coupled to an Orbitrap ID-X Tribrid mass spectrometer (Thermo Fisher Scientific, Bremen, Germany).

Mass spectrometric analysis was performed on an Orbitrap ID-X Tribrid mass spectrometer (ThermoFisher Scientific, Bremen, Germany). The system was equipped with a heated electrospray ionization interface (HESI-II). The H-ESI parameters in positive polarity were the following: electrospray voltage of 2.8 kV; sheath gas of 25 arbitrary units (a.u.) (N₂, >95%) and auxiliary gas of 7 a.u. The ion transfer tube operated at 281 °C and the vaporizer temperature at 180 °C. The full scan was acquired using a mass resolving

power of 50,000 FWHM and a scan range = 70–485 Da. The MS² were acquired in the Orbitrap analyzer at a resolving power of 50,000 FWHM, with a precursor mass range of 70–485, using an HCD fragmentation (20%, 40%, and 90%). The external mass calibration of the spectrometer was performed using a Pierce Flexmix Calibration from ThermoFisher Scientific (Bremen, Germany). Data acquisition and processing were performed using Thermo Scientific TraceFinder TM software version 5.1.

In accordance with the EU guidelines [42], we used the following criteria to identify positive compounds: (a) the mass accuracy of the molecular ion (M+H⁺) had to be lower than 5 ppm; (b) the mass accuracy of the fragment ion had to be lower than 5 ppm; and (c) the isotopic pattern had to be similar to the theoretical isotopic pattern (the relative intensity of the A+1 and/or A+2 isotope peaks in the real sample shall correspond to the theoretical relative intensities). Moreover, (d) for confirmation, the retention time (RT) of the sample had to be similar to that of the reference standard (± 0.1 min).

2.6. Quality Assurance

After the sampling, samples were transported to our facilities and stored at -20 °C until they were analyzed. Process blanks were used and included during the transport in order to assess the transportation of field samples. Additionally, to be able to check potential losses during the storage period and assess recoveries during sample preparation, spiked blank samples were stored and analyzed as field samples.

2.7. Exposure and Risk Assessment

Risk assessment was carried out following the methodologies described by Yusà et al., 2014, and López et al., 2017 [34,35]. To sum up, chronic (>1 year) inhalation exposures were assessed for adults (>12 years), children (1–6 years), and infants (6 months–1.5 years) according to two different scenarios: (i) using the average concentration, and (b) using the maximum concentration.

To estimate the inhalation exposure to the atmospheric pesticides, the following equation was used [43,44]:

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

where DIE is the daily inhalation exposure; C is the total (particle + gas phases) concentration of each pesticide in the air (mg m^{-3}); IR_{inh} is the inhalation rate per hour ($\text{m}^3 \text{h}^{-1}$); ED is the exposure duration (24 h) to air and BW is the bodyweight of the subject (kg). IR_{inh} applied was $20 \text{ m}^3 \text{day}^{-1}$ for adults, $10 \text{ m}^3 \text{day}^{-1}$ for children, and $8 \text{ m}^3 \text{day}^{-1}$ for infants. BW was 70 kg for adults, 15 kg for children, and 10 kg for infants [45–47].

The risk assessment was based on hazard quotients (HQ). These were used as risk descriptors and were calculated as follows:

$$\text{HQ} = \text{DIE}_i/\text{HBRV}_i \quad (2)$$

where HBRV_i is the health-based reference value. The HBRVs were retrieved from databases of the European Union (EU) [1] and USEPA (the United States Environmental Protection Agency) [48–52]. The HBRV has been established as an acceptable operator exposure level (AOEL) and has been applied to assess and review pesticides and biocides within Europe.

The HQ level of concern was set to 1.0, thus an HQ > 1 indicated that a potential risk may be present.

The cumulative exposure was estimated using a hazard index (HI) approach for pesticides that have a common mode of action, applying the following formula:

$$\text{HI} = \text{HQ}_1 (\text{pesticide 1}) + \text{HQ}_2 (\text{pesticide 2}) + \text{HQ}_3 (\text{pesticide 3}) + \dots (\text{and so forth}) \quad (3)$$

These risks (HQ, HI) expressly apply to the populations in the vicinity of the air monitoring stations.

Moreover, for potential or possible carcinogen compounds, cancer risk has been calculated. The following equation has been used:

$$\text{Cancer risk} = \text{DIE (mg/kg – day)} \times \text{PF (mg/kg – day)}^{-1} \quad (4)$$

where PF is the potency factor. For possible or likely carcinogens, the potency factor ranges between >0.01 and 0.1 [53,54], so we have used 0.1 for all these pesticides.

2.8. Pilot Scheme

Throughout the year 2020, a pilot study was developed in the Valencian region. Three different sites were chosen for the sampling stations: two rural sites (Alzira and Burriana) and one urban site (Viveros-Valencia). The two rural stations are surrounded by citrus crops and the urban station is located in one of the largest parks in the city of Valencia called *Viveros* (70,000 m²). Six samples were collected in each station during the spring and summer seasons. The sampler employed was the selected one (Digitel DPA-16), which had a flow of 2.3 m³ h⁻¹ per week.

3. Results and Discussion

3.1. Selected Pesticides to Be Evaluated

In our first list, we included 192 pesticides to be evaluated. These pesticides were detected in some matrices (food, water, air) or were highly commercialized in the Valencian region or in Spain. Of these, currently, there are 117 authorized pesticides and 75 unauthorized ones (Table S1).

In a second step, we selected 78 out of 192 pesticides to be assessed in the pilot study taking into account the criteria described in Section 2.1 and also the likelihood of them being detected in the ambient air and quantified properly. Table 1 shows the pesticides selected for evaluation in the Valencia Region. This list is nonetheless a dynamic one since the authorization to use some of the pesticides is updated every year.

Table 1. Pesticides evaluated through the PESTNet network.

| Pesticide | Status | Pesticide Type | Substance Group | Analysis |
|------------------|--------|---|-----------------|----------|
| Acetamiprid | In | Insecticide | Neonicotinoid | LC |
| Aldrin | Out | Insecticide | Organochlorine | GC |
| Alpha-endosulfan | Out | Insecticide/Acaricide | Organochlorine | GC |
| Azoxystrobin | In | Fungicide | Strobilurin | LC |
| Benalaxyl-M | In | Fungicide | Phenylamide | LC |
| Bentazone | In | Herbicide | Benzothiazinone | LC |
| Beta-endosulfan | Out | Insecticide/Acaricide | Organochlorine | GC |
| Bifenthrin | Out | Insecticide/Acaricide | Pyrethroid | GC |
| Bitertanol | Out | Fungicide | Triazole | LC |
| Boscalid | In | Fungicide | Carboxamide | LC |
| Buprofezin | In | Insecticide/Acaricide | Unclassified | LC |
| Carbendazim | Out | Fungicide/Metabolite | Benzimidazole | LC |
| Carbofuran | Out | Insecticide/Nematicide/Acaricide/Metabolite | Carbamate | LC |
| Chlorpropham | Out | Herbicide/Plant Growth Regulator | Carbamate | GC |
| Chlorpyrifos-e | Out | Insecticide | Organophosphate | GC |
| Chlorpyrifos-m | Out | Insecticide/Acaricide | Organophosphate | GC |

Table 1. Cont.

| Pesticide | Status | Pesticide Type | Substance Group | Analysis |
|----------------------|--------|--|-------------------------|----------|
| Cyfluthrin | Out | Insecticide | Pyrethroid | GC |
| Cymoxanil | In | Fungicide | Cyanoacetamide oxime | LC |
| Cypermethrin | In | Insecticide/Veterinary substance | Pyrethroid | GC |
| Cyproconazole | In | Fungicide | Triazole | LC |
| Cyprodinil | In | Fungicide | Anilinopyrimidine | LC |
| Deltamethrin | In | Insecticide/Metabolite/Veterinary substance | Pyrethroid | GC |
| Diazinon | Out | Insecticide/Acaricide/Repellent/Veterinary substance | Organophosphate | GC |
| Dieldrin | Out | Insecticide/Metabolite | Chlorinated hydrocarbon | GC |
| Difenoconazole | In | Fungicide | Triazole | LC |
| Dimethoate | Out | Insecticide/Acaricide/Metabolite | Organophosphate | LC |
| Diphenylamine | Out | Plant growth regulator/Fungicide/Insecticide | Amine | GC |
| Diuron | Out | Herbicide | Phenylamide | LC |
| Endosulfan-sulfate | Out | Metabolite | Unclassified | GC |
| Ethoprophos | In | Insecticide/Nematicide | Organophosphate | GC |
| Fenbuconazole | In | Fungicide | Triazole | LC |
| Fenhexamid | In | Fungicide | Hydroxyanilide | LC |
| Fenitrothion | Out | Insecticide | Organophosphate | GC |
| Fipronil | Out | Insecticide/Veterinary substance | Phenylpyrazole | GC |
| Fluazifop | Out | Metabolite | Unclassified | LC |
| Fludioxonil | In | Fungicide | Phenylpyrrole | GC |
| Fluquinconazole | In | Fungicide | Triazole | LC |
| Fluroxypyr | In | Herbicide | Pyridine compound | LC |
| Flusilazole | Out | Fungicide | Triazole | LC |
| Folpet | In | Fungicide | Phthalimide | GC |
| Imazalil | In | Fungicide/Veterinary substance | Imidazole | LC |
| Imidacloprid | Out | Insecticide/Veterinary substance | Neonicotinoid | LC |
| Iprodione | Out | Fungicide | Dicarboxamide | GC |
| Iprovalicarb | In | Fungicide | Carbamate | LC |
| Kresoxim-m | In | Fungicide/Bactericide | Strobilurin | GC |
| Lambda-cyhalothrin | In | Insecticide | Pyrethroid | GC |
| Lindane | Out | Insecticide/Acaricide/Veterinary substance | Organochlorine | GC |
| Malathion | In | Insecticide/Acaricide/Veterinary substance | Organophosphate | GC |
| Metalaxyl-M | In | Fungicide | Phenylamide | LC |
| Methidathion | Out | Insecticide/Acaricide | Organophosphate | LC |
| Molinate | Out | Herbicide | Thiocarbamate | LC |
| Myclobutanil | In | Fungicide | Triazole | LC |
| Omethoate | Out | Insecticide/Acaricide/Metabolite | Organophosphate | LC |
| Oxyfluorfen | In | Herbicide | Diphenyl ether | LC |
| Penconazole | In | Fungicide | Triazole | GC |
| Penoxsulam | In | Herbicide | Triazopyrimidine | LC |
| Permethrin | Out | Insecticide, Veterinary substance | Pyrethroid | GC |
| Pirimicarb | In | Insecticide | Carbamate | LC |
| Pirimicarb-desmethyl | In | Fungicide | Imidazole | LC |

Table 1. Cont.

| Pesticide | Status | Pesticide Type | Substance Group | Analysis |
|-------------------------|--------|---|-------------------|----------|
| Prochloraz | In | Fungicide | Imidazole | LC |
| Propargite | Out | Acaricide | Sulphite ester | GC |
| Pyrimethanil | In | Fungicide | Anilinopyrimidine | LC |
| Pyriproxifen | In | Insecticide/Veterinary substance/ Insect growth regulator | Unclassified | LC |
| Pyroquilone | Out | Fungicide | Unclassified | LC |
| Quinoxifen | Out | Fungicide | Quinoline | GC |
| Spirotetramat | In | Insecticide | Tetramic acid | LC |
| Tebuconazole | In | Fungicide/Plant growth regulator | Triazole | LC |
| Tebufenpyrad | In | Acaricide | Pyrazolium | LC |
| Terbuthylazine | In | Herbicide/Microbiocide/Algicide | Triazine | LC |
| Terbuthylazine-desethyl | In | Metabolite | Unclassified | LC |
| Terbuthylzine-2-OH | In | Metabolite | Unclassified | LC |
| Thiabendazole | In | Fungicide/Veterinary substance | Benzimidazole | LC |
| Thiamethoxam | In | Insecticide | Neonicotinoid | LC |
| Thiophanate-methyl | Out | Fungicide | Benzimidazole | LC |
| Tolclofos-methyl | In | Fungicide | Chlorophenyl | GC |
| Triadimefon | Out | Fungicide, Metabolite | Triazole | GC |
| Trifluralin | Out | Herbicide | Dinitroaniline | GC |
| Vinclozolin | Out | Fungicide | Oxazole | GC |

3.2. Locations Selected in the PESTnet Network

To choose the most appropriate locations, we took into account the criteria described in Section 2.2. As a result, 10 locations in the Valencian region were selected. These locations are in the vicinity of six main crops grows in the Valencian region (citrus, rice, vineyards, stone fruits, persimmon, and dry-farming). There were two locations near to citrus crops (Alzira and Burriana, assessed in the pilot study), two locations near to vineyards (Villar del Arzobispo and Caudete de las Fuentes), two stations close to rice crops (Sollana and Silla), two stations close to stone fruits orchards (Callosa d'en Sarria and L'Alcudia), two stations next to persimmon crops (Silla and L'Alcudia) and one near to dry-farming crops (Sant Jordi). Moreover, one urban site is included (Viveros-Valencia city). Figure 1 shows the locations of the different stations within the Valencian region, and Table S2 shows the description of the sampling sites.

3.3. Results of the Pilot Scheme

Eighteen samples have been collected in three different stations (Alzira, Burriana, and Viveros) during 2020 (six samples for each station). The results showed that 30 pesticides were detected (see Table 2). These 30 pesticides included both authorized (17) and banned pesticides (13). The frequency of detection ranged from 6% (chlorpropham, kresoxim-methyl, beta-endosulfan, and endosulfan-sulfate) to 100% (azoxystrobin, metalaxyl-M, and chlorpyrifos-methyl). Concentrations detected in the assessed stations ranged from 14.35 (boscalid) to 4373.0 pg m^{-3} (chlorpyrifos-methyl). All the obtained results are shown in Table 2.

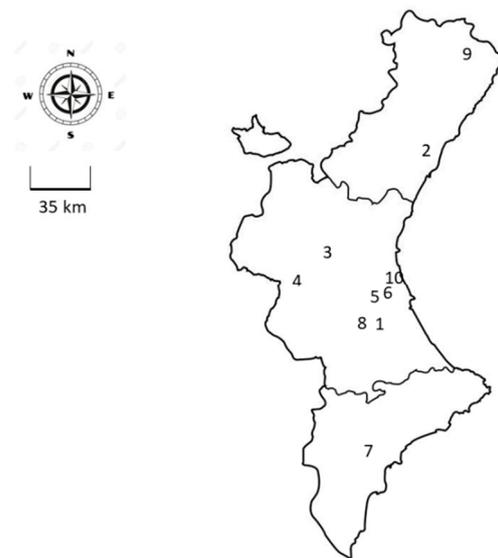


Figure 1. Locations selected in the Valencian region (Spain). 1: Alzira, 2: Burriana, 3: Villar del Arzobispo, 4: Caudete de las Fuentes, 5: Sollana, 6: Silla, 7: Callosa d'en Sarria, 8: L'Alcúdia, 9: Sant Jordi, 10: Viveros-Valencia city.

Table 2. Overall concentrations (P + G) detected in all sampling sites of the pilot scheme ($N = 18$).

| Pesticide | Frequency of Detection (%) ^a | Frequency of Quantification (%) ^b | Average (pg m^{-3}) ^c | Range (pg m^{-3}) | LOQ (pg m^{-3}) (P/G) |
|--------------------|---|--|---|------------------------------|----------------------------------|
| Acetamiprid | 83 | 6 | 18.52 | <LOQ-18.52 | 6.5/12.9 |
| Alpha-endosulfan | 11 | 11 | 74.35 | 61.98–86.72 | 10.0/16.1 |
| Azoxystrobin | 100 | 6 | 31.15 | <LOQ-31.15 | 6.5/12.9 |
| Beta-endosulfan | 6 | 6 | 91.33 | - | 10.0/16.1 |
| Boscalid | 56 | 6 | 14.35 | <LOQ-14.35 | 6.5/12.9 |
| Carbendazim | 67 | - | - | <LOQ | 6.5/12.9 |
| Chlorpropham | 6 | - | - | - | 6.6/129.3 |
| Chlorpyrifos-e | 39 | 33 | 726.58 | <LOQ-1553.58 | 6.5/129.3 |
| Chlorpyrifos-m | 100 | 100 | 1783.33 | 115.15–4372.96 | 6.5/16.1 |
| Cyproconazole | 67 | 33 | 20.88 | <LOQ-32.20 | 6.5/51.8 |
| Dimethoate | 89 | - | - | <LOQ | 6.5/12.9 |
| Diuron | 33 | - | - | <LOQ | 6.5/12.9 |
| Endosulfan-sulfate | 6 | 6 | 326.30 | 326.30 | 10.0/129.3 |
| Imidacloprid | 94 | - | - | <LOQ | 6.5/12.9 |
| Iprovalicarb | 61 | - | - | <LOQ | 6.5/12.9 |
| Kresoxim-m | 6 | 6 | 127.39 | 127.39 | 6.5/64.3 |
| Lambda-cyhalothrin | 22 | 22 | 186.42 | 80.60–492.26 | 6.5/16.1 |
| Metalaxyl-M | 100 | 28 | 27.48 | <LOQ-44.16 | 6.5/12.9 |
| Myclobutanil | 22 | - | - | <LOQ | 6.5/12.9 |
| Omethoate | 94 | 33 | 25.78 | <LOQ-37.37 | 2.6/12.9 |
| Permethrin | 28 | 28 | 147.11 | 52.75–324.00 | 6.5/16.1 |
| Prochloraz | 6 | - | - | - | 13.0/51.8 |
| Pyrimethanil | 72 | 6 | 106.47 | <LOQ-106.47 | 6.5/12.9 |
| Pyriproxifen | 61 | - | - | <LOQ | 6.5/12.9 |

Table 2. Cont.

| Pesticide | Frequency of Detection (%) ^a | Frequency of Quantification (%) ^b | Average (pg m ⁻³) ^c | Range (pg m ⁻³) | LOQ (pg m ⁻³) (P/G) |
|---------------------|---|--|--|-----------------------------|---------------------------------|
| Spirotetramat | 67 | 33 | 66.90 | <LOQ–232.35 | 6.5/12.9 |
| Tebuconazole | 67 | - | - | <LOQ | 6.5/12.9 |
| Terbuthylazine-2-OH | 11 | 11 | 19.79 | 19.52–20.06 | 6.5/12.9 |
| Thiabendazole | 28 | - | - | <LOQ | 75.0/12.9 |
| Trifluralin | 61 | 61 | 216.59 | 63.60–444.32 | 6.5/16.1 |
| Vinclozolin | 11 | 11 | 33.68 | 33.18–34.19 | 6.5/16.1 |

^a Frequency of detection was calculated based on samples with concentrations above the limit of detection (LOD). ^b Frequency of quantification was calculated based on samples with concentrations above the limit of quantification (LOQ). ^c The average was calculated from the arithmetic mean from samples with concentrations higher than the limit of quantification (LOQ).

On the other hand, if we divide the results according to the three different areas, 19 pesticides were detected in Viveros (urban station), 21 pesticides were detected in Burriana, and 24 pesticides were detected in Alzira. Table S3 shows the results for each station. Regarding the obtained results in the urban area (Viveros-Valencia city), some of the pesticides could have been detected due to the medium atmospheric transport from rural areas to urban areas.

Apart from monitoring the pesticide levels in the selected locations, the pilot scheme's objective was to assess the health risks of pesticide exposure for the population living in these areas. For all the pesticides detected, the risk was assessed for three different groups of population: adults, children, and infants. The detected concentrations do not imply a health risk because the hazard quotient was lower than one ($HQ < 1$) for all pesticides, and the hazard index for cumulative exposure was lower than one ($HI < 1$) for the organophosphate and pyrethroid groups. Figure 2 shows the maximum hazard quotient obtained in each station. Moreover, cancer risk was calculated for potential or possible carcinogenic pesticides, and the obtained cancer risk was lower than 1×10^{-6} (concern level) for all the evaluated pesticides. Tables S4–S8 show the results obtained in the risk assessment.

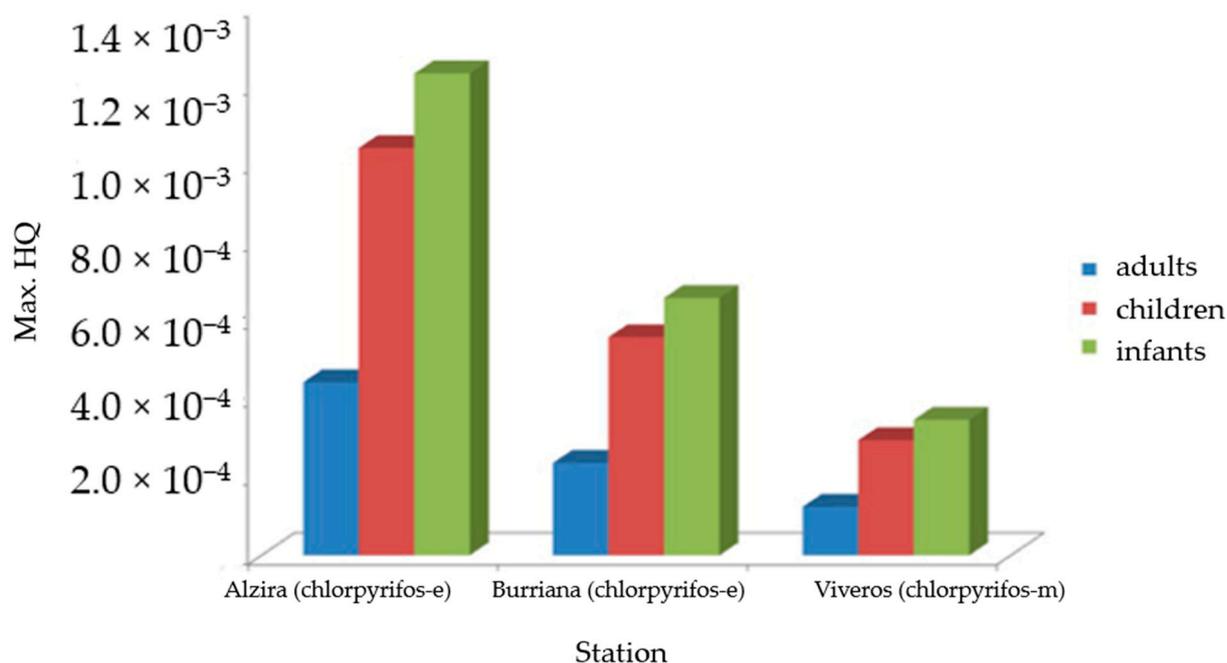


Figure 2. Maximum hazard quotient levels obtained in the different evaluated stations for adults, children, and infants in the Valencian region (Spain).

3.4. Impact of the Pesticide Control Network

The creation of an Air pesticide control and surveillance network (PESTNet) will impact fundamental aspects related to European policies, such as health, the population, and the economy. With regard to these policies, this monitoring network addresses the hazards arising from pesticide use, mainly in intensive agricultural areas. This is a European issue since the intensive use of these compounds has been reported in some European countries. Hence, this network aims to be a valuable tool for implementing a European Strategy to attain more sustainable use of pesticides and the European Commission policies to reduce the negative impact of pesticide use on people's health and the environment.

On the other hand, through the implementation of the pesticide network, risk indicators will be developed, which are very useful for measuring the strategy's success in the sustainable use of pesticides (Regulation 2009/128/EC).

In addition, the creation of the network can result in major benefits for public health. On the one hand, adverse effects related to the intensive use of pesticides will be reduced, such as chronic diseases (Parkinson's, Alzheimer's, and ALS), congenital disorders, or reproductive problems.

4. Conclusions

In this work, we have described the protocols used for sampling pesticide residues in the ambient air and subsequently analyzing them and which have been previously developed and validated by our group as well as successfully transferred to the Regional Department for Environment of the Valencian region in Spain.

Moreover, a strategy for assessing the risk of pesticide residues in the ambient air to the population's health has been provided. This strategy could be useful in establishing health indicators.

The sampling, analysis, and risk assessment tools have been satisfactorily validated in a pilot study for the Valencian region. The pilot study will be extended to the 10 sampling sites in the near future.

Implementing the PESTNet network is an innovative step, and it is also the first Spanish network that monitors this type of pollutants in outdoor air. The network will improve the air quality in the Valencian region and, consequently, its population's health. This work would like to contribute to implementing new pesticide networks in other EU regions. Furthermore, it could be interesting in the near future to have a harmonization about sampling, analysis, and risk assessment tools for pesticides in the ambient air.

Supplementary Materials: The following are available online at <https://www.mdpi.com/article/10.3390/atmos12050542/s1>, Table S1: Initial list of selected pesticide, Table S2: Spatial distribution of the detected pesticides in the evaluated stations, Table S3: Obtained hazard quotient using average concentrations and maximum concentrations for adults (>12 years), Table S4: Obtained hazard quotient using average concentrations and maximum concentrations for children (1–6 years), Table S5: Obtained hazard quotient using average concentrations and maximum concentrations for infants (6 months–1.5 years), Table S6: Cumulative exposure (using maximum concentrations), Table S7: Cancer risk of potential carcinogenic pesticides (using maximum concentrations), Table S8: Cancer risk of potential carcinogenic pesticides (using maximum concentrations)

Author Contributions: Conceptualization, V.Y. and C.C.; methodology, A.L.; software, A.L.; validation, A.L.; resources, A.L. and P.R.; writing—original draft preparation, A.L.; writing—review and editing, V.Y. and C.C.; supervision, V.Y. and C.C.; funding acquisition, V.Y. and C.C. All authors have read and agreed to the published version of the manuscript.

Funding: We would like to thank the FISABIO project "Diseño e Implantación de la Red de Vigilancia de los plaguicidas en la atmósfera de la Comunitat Valenciana" (UGP-18-295) and Conselleria d'Educació, Investigació, Cultura i Esports (APOTIP/2019/A/024) for its financial support.

Data Availability Statement: not applicable.

Acknowledgments: The authors wish to express their gratitude to BSG Ingenieros for their collaboration during this study.

Conflicts 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.

References

1. EU Pesticide Database. 2021. Available online: <http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN> (accessed on 8 January 2021).
2. Eurostat. Eurostat Statistical. 2018. Available online: <http://appsso.eurostat.ec.europa.eu/nui/show.do> (accessed on 8 January 2021).
3. AEPLA (Asociación Empresarial Para la Protección de las Plantas). 2015. Memoria AEPLA. 2015. Available online: http://www.aepla.es/tmp/images/publicaciones/P0017_Memoria_AEPLA_2015.pdf (accessed on 1 January 2021).
4. Portal Estadístico de la Generalitat Valenciana. 2021. Available online: <http://www.pegv.gva.es/va/temas/agriculturaganaderiaselviculturacazapescayacuicultura/agricultura/superficiesyproduccionesanualesdecultivo> (accessed on 8 January 2021).
5. Van Den Berg, F.; Kubiak, R.; Benjey, W.G.; Majewski, M.S.; Yates, S.J.; Reeves, G.L.; Smelt, J.H.; van der Linden, A.M.A. Emissions of pesticides into air. *Water, Air Soil Pollut.* **1999**, *115*, 195–218. [[CrossRef](#)]
6. Bedos, C.; Cellier, P.; Calvet, R.; Barriuso, E. Occurrence of pesticides in the atmosphere in France. *Agronomie* **2002**, *22*, 35–49. [[CrossRef](#)]
7. Bedos, C.; Bedos, C.; Cellier, P.; Calvet, R.; Barriuso, E.; Gabrielle, B. Mass transfer of pesticides into the atmosphere by volatilization from soils and plants: Overview. *Agronomie* **2002**, *22*, 21–33. [[CrossRef](#)]
8. Coscollà, C.; Yusà, V. Pesticides and agricultural air quality. In *The Quality of Air*; de la Guardia, M., Armenta, S., Eds.; Elsevier: Amsterdam, The Netherlands, 2016; pp. 423–490.
9. Yao, Y.; Tuduri, L.; Harner, T. Spatial and temporal distribution of pesticide air concentrations in Canadian agricultural regions. *Atmos. Environ.* **2006**, *40*, 4339–4351. [[CrossRef](#)]
10. Tuduri, L.; Harner, T.; Blanchard, P.; Li, Y.F.; Poissant, L.; Waite, D.T.; Murphy, C.; Belzer, W. A review of currently used pesticides (CUPs) in Canadian air and precipitation: Part 1: Lindane and endosulfans. *Atmos. Environ.* **2006**, *40*, 1563–1578. [[CrossRef](#)]
11. Scheyer, A.; Graeff, C.; Morville, S.; Mirabel, P.; Millet, M. Analysis of some organochlorine pesticides in an urban atmosphere (Strasbourg, east of France). *Chemosphere* **2005**, *58*, 1517–1524. [[CrossRef](#)] [[PubMed](#)]
12. Alegria, H.; Bidlemann, T.F.; Figueroa, M.S. Organochlorine pesticides in the ambient air of Chiapas, Mexico. *Environ. Pollut.* **2006**, *140*, 483–491. [[CrossRef](#)]
13. Hart, E.; Coscollà, C.; Pastor, A.; Yusà, V. GC–MS characterization of contemporary pesticides in PM10 of Valencia Region, Spain. *Atmos. Environ.* **2012**, *62*, 118–129. [[CrossRef](#)]
14. Coscollà, C.; Hart, E.; Pastor, A.; Yusà, V. LC-MS characterization of contemporary pesticides in PM10 of Valencia Region, Spain. *Atmos. Environ.* **2013**, *77*, 394–403. [[CrossRef](#)]
15. López, A.; Coscollà, C.; Yusà, V. Selection of sampling adsorbents and optimisation and validation of a GC-MS/MS method for airborne pesticides. *Int. J. Environ. Anal. Chem.* **2017**, *97*, 949–964. [[CrossRef](#)]
16. López, A.; Coscollà, C.; Yusà, V. Evaluation of sampling adsorbents and validation of a LC-HRMS method for determination of 28 airborne pesticides. *Talanta* **2018**, *189*, 211–219. [[CrossRef](#)] [[PubMed](#)]
17. Yusà, V.; Coscollà, C.; Mellouki, W.; Pastor, A.; de la Guardia, M. Sampling and analysis of pesticides in ambient air. *J. Chromatogr. A* **2009**, *1216*, 2972–2983. [[CrossRef](#)] [[PubMed](#)]
18. Baraud, L.; Tessier, D.; Aaron, J.J.; Quisefit, J.P.; Pinart, J. A multi-residue method for characterization and determination of atmospheric pesticides measured at two French urban and rural sampling sites. *Anal. Bional. Chem.* **2003**, *377*, 1148–1152. [[CrossRef](#)] [[PubMed](#)]
19. Raina, R.; Sun, L. Trace level determination of selected organophosphorus pesticides and their degradation products in environmental air samples by liquid chromatography-positive ion electrospray tandem mass spectrometry. *J. Environ. Sci. Health B* **2008**, *43*, 323–332. [[CrossRef](#)] [[PubMed](#)]
20. Morshed, M.M.; Omar, D.; Mohamad, R.; Wahed, S.; Rahman, M.A. Airborne paraquat measurement and its exposure to spray operators in treated field environment. *Int. J. Agric. Biol.* **2010**, *12*, 679–684.
21. Armstrong, J.L.; Dills, R.L.; Yu, J.; Yost, M.G.; Fenske, R.A. A sensitive LC-MS/MS method for measurement of organophosphorus pesticides and their oxygen analogs in air sampling matrices. *J. Environ. Sci. Health B* **2014**, *49*, 102–108. [[CrossRef](#)] [[PubMed](#)]
22. Hengel, M.; Lee, P. Community air monitoring for pesticides-part 2: Multiresidue determination of pesticides in air by gas chromatography, gas chromatography-mass spectrometry, and liquid chromatography-mass spectrometry. *Environ. Monit. Assess* **2014**, *186*, 1343–1353. [[CrossRef](#)]
23. Degrendele, C.; Okonski, K.; Melymuk, L.; Landlová, L.; Kukucka, P.; Audy, O.; Kohoutek, J.; Cupr, P.; Klánová, J. Pesticides in the atmosphere: A comparison of gas-particle partitioning and particle size distribution of legacy and current-use pesticides. *Atmos. Chem. Phys.* **2016**, *16*, 1531–1544. [[CrossRef](#)]
24. Raina, R.; Smith, E. Determination of Azole Fungicides in Atmospheric Samples Collected in the Canadian Prairies by LC/MS/MS. *J. AOAC* **2012**, *95*, 1350–1356. [[CrossRef](#)]

25. Coscollà, C.; León, N.; Pastor, A.; Yusà, V. Combined target and post-run target strategy for a comprehensive analysis of pesticides in ambient air using Liquid Chromatography—Orbitrap High Resolution Mass Spectrometry. *J. Chromatogr. A* **2014**, *1368*, 132–142. [[CrossRef](#)]
26. Gómez-Ramos, M.M.; Ferrer, C.; Malato, O.; Agüera, A.; Fernández-Alba, A.R. Liquid chromatography-high resolution mass spectrometry for pesticide residue analysis in fruit and vegetables: Screening and quantitative studies. *J. Chromatogr. A* **2013**, *1287*, 24–37. [[CrossRef](#)] [[PubMed](#)]
27. Polgár, L.; García-Reyes, J.F.; Fodor, P.; Gyepes, A.; Dernovics, D.; Abrankó, L.; Gilbert-López, B.; Molina-Díaz, A. Retrospective screening of relevant pesticide metabolites in food using liquid chromatography high resolution mass spectrometry and accurate-mass databases of parent molecules and diagnostic fragment ions. *J. Chromatogr. A* **2012**, *1249*, 83–91. [[CrossRef](#)]
28. López, A.; Coscollà, C.; Yusà, V.; Armenta, S.; de la Guardia, M.; Esteve-Turrillas, F.A. Comprehensive analysis of airborne pesticides using hard cap espresso extraction-liquid chromatography-high-resolution mass spectrometry. *J. Chromatogr. A* **2017**, *1506*, 27–36. [[CrossRef](#)] [[PubMed](#)]
29. López, A.; Yusà, V.; Millet, M.; Coscollà, C. Retrospective screening of pesticide metabolites in ambient air using liquid chromatography coupled to high-resolution mass spectrometry. *Talanta* **2016**, *150*, 27–36. [[CrossRef](#)] [[PubMed](#)]
30. Coscollà, C.; Yusà, V.; Martí, P.; Pastor, A. Analysis of currently used pesticides in fine airborne particulate matter (PM 2.5) by pressurized liquid extraction and liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A* **2008**, *1200*, 100–107. [[CrossRef](#)]
31. Coscollà, C.; Yusà, V.; Beser, M.I.; Pastor, A. Multi-residue analysis of 30 currently used pesticides in fine airborne particulate matter (PM 2.5) by microwave-assisted extraction and liquid chromatography-tandem mass spectrometry. *J. Chromatogr. A* **2009**, *1216*, 8817–8827. [[CrossRef](#)] [[PubMed](#)]
32. Coscollà, C.; Castillo, M.; Pastor, A.; Yusà, V. Determination of 40 currently used pesticides in airborne particulate matter (PM 10) by microwave-assisted extraction and gas chromatography coupled to triple quadrupole mass spectrometry. *Anal. Chim. Acta* **2011**, *693*, 72–81. [[CrossRef](#)]
33. Luo, Y.; Zhang, M. Multimedia transport and risk assessment of organophosphate pesticides and a case study in the northern San Joaquin Valley of California. *Chemosphere* **2009**, *75*, 969–978. [[CrossRef](#)] [[PubMed](#)]
34. Yusà, V.; Coscollà, C.; Millet, M. New screening approach for risk assessment of pesticides in ambient air. *Atmos. Environ.* **2014**, *96*, 322–330. [[CrossRef](#)]
35. López, A.; Yusà, V.; Muñoz, A.; Vera, T.; Borràs, E.; Ródenas, M.; Coscollà, C. Risk assessment of airborne pesticides in a Mediterranean region of Spain. *Sci. Total Environ.* **2017**, *574*, 724–734. [[CrossRef](#)]
36. Coscollà, C.; López, A.; Yahyaoui, A.; Colin, P.; Robin, C.; Poinsignon, Q.; Yusà, V. Human exposure and risk assessment to airborne pesticides in a rural French community. *Sci. Total Environ.* **2017**, *584–585*, 856–868. [[CrossRef](#)] [[PubMed](#)]
37. Fédération des Associations de Surveillance de la Qualité de l’Air de France. 2020. Available online: <http://www.atmo-france.org/fr/index.php?/20171128564/pesticides-dans-l-air-les-aasqa-se-mobilisent-pour-ameliorer-les-connaissances/id-menu-305.html> (accessed on 22 December 2020).
38. Conselleria d’Agricultura. Available online: <http://www.agroambient.gva.es/es/boletin-de-avisos> (accessed on 16 June 2019).
39. Conselleria de Sanitat Universal i Salut Pública, Directorate-General for Public Health. Plan de Control de la Cadena Alimentaria de la Comunitat Valenciana/Plan de Seguridad Alimentaria. 2018. Available online: http://www.sp.san.gva.es/DgspPortal/docs/PLAN_CO_CADENA_ALIMENTARIA2018.pdf (accessed on 18 June 2019).
40. Cooperatives Agroalimentaries de la Comunitat Valenciana. Available online: <http://www.cooperativesagroalimentariescv.com/> (accessed on 17 June 2019).
41. Ministerio de Agricultura. Available online: https://www.mapa.gob.es/images/es/informe_datos_utilizacion_eupf13_tcm30-122265.pdf (accessed on 7 January 2021).
42. European Commission, Directorate General Health and Consumer Protection, Brussels, Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. SANTE/12682/2019 (2019). Available online: https://www.eurlpesticides.eu/userfiles/file/EurlALL/AqcGuidance_SANTE_2019_12682.pdf (accessed on 21 December 2020).
43. USEPA. Exposure Factors Handbook. U.S. Environmental Protection Agency. EPA/600/P-95/002/F-a-c. 1997. Available online: <https://cfpub.epa.gov/ncea/risk/recordisplay.cfm?deid=12464> (accessed on 20 April 2021).
44. WHO (World Health Organization). Principle for the Assessment of Risks to Human Health from Exposure to Chemicals—Environmental Health Criteria 210. 1999. Available online: <https://apps.who.int/iris/handle/10665/42156> (accessed on 20 April 2021).
45. USEPA. 1989. Risk Assessment Guidance for Superfund (RAGS) (Part A). EPA/540/1-89/002. Available online: https://www.epa.gov/sites/production/files/2015-09/documents/rags_a.pdf (accessed on 20 April 2021).
46. USEPA. Region 9 Preliminary Remediation Goals. Memorandum from Standford Smucker, Ph.D.; Regional Toxicologist. 2004. Available online: <http://www.epa.gov/region09/waste/sfund/prg/index.html> (accessed on 22 July 2019).
47. USEPA. RAGS Volume I: Human Health Evaluation Manual. Supplemental Guidance “Standard Default Exposure Factors”. OSWER No. 9285.6-03. 1991. Available online: <https://nepis.epa.gov/Exe/ZyPDF.cgi/P100L3HP.PDF?Dockey=P100L3HP.PDF> (accessed on 20 April 2021).
48. EPA; IRIS. Environmental Protection Agency. United States. Integrated Risk Information System, IRIS. 2012. Available online: <http://cfpub.epa.gov/ncea/iris/index> (accessed on 22 July 2019).

49. USEPA. *Registration Eligibility Decision for Terbutylazine*; U.S. Environmental Protection Agency: Washington, DC, USA, 1995.
50. USEPA. *Tebuconazole—Pesticide Tolerance Petition 3/97*; U.S. Environmental Protection Agency: Washington, DC, USA, 1997.
51. USEPA. *EPA's Preliminary Risk Assessment on Diazinon*; U.S. Environmental Protection Agency: Washington, DC, USA, 2000.
52. USEPA. *Registration Eligibility Decision (RED) for Carbendazim*; U.S. Environmental Protection Agency: Washington, DC, USA, 2012.
53. Gunier, R.; Harnly, M.; Reynolds, P.; Hertz, A.; Von Behren, J. Agricultural pesticide use in California: Pesticide prioritization, use densities, and population distributions for a Childhood Cancer Study. *Environ. Health Perspect.* **2001**, *109*, 1071–1078. [[CrossRef](#)] [[PubMed](#)]
54. Lee, S.; McLaughlin, R.; Harnly, M.; Gunier, R.; Kreutzer, R. Community exposures to airborne agricultural pesticides in California: Ranking of inhalation risks. *Environ. Health Perspect.* **2002**, *110*, 1175–1184. [[CrossRef](#)] [[PubMed](#)]