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Irene Navarro, Adrián de la Torre, Paloma Sanz, Isabelle Baldi, Paula Harkes, Esperanza Huerta-Lwanga, Trine Nørgaard, Matjaž Glavan, Igor Pasković, Marija Polić Pasković, Nelson Abrantes, Isabel Campos, Francisco Alcon, Josefina Contreras, Abdallah Alaoui, Jakub Hofman, Anne Vested, Mathilde Bureau, Virginia Aparicio, Daniele Mandrioli, Daria Sgargi, Hans Mol, Violette Geissen, Vera Silva, María Ángeles Martínez

PII: S0048-9697(23)06424-0

DOI: https://doi.org/10.1016/j.scitotenv.2023.167797

Reference: STOTEN 167797

To appear in: *Science of the Total Environment*

Received date: 28 July 2023

Revised date: 22 September 2023

Accepted date: 11 October 2023

Please cite this article as: I. Navarro, A. de la Torre, P. Sanz, et al., Occurrence of pesticide residues in indoor dust of farmworker households across Europe and Argentina, *Science of the Total Environment* (2023), https://doi.org/10.1016/j.scitotenv.2023.167797

Title

Occurrence of pesticide residues in indoor dust of farmworker households across Europe and Argentina

Authors

Irene Navarro[a*], Adrián de la Torre[a], Paloma Sanz[a], Isabelle Baldi[b], Paula Harkes[c], Esperanza Huerta-Lwanga[c], Trine Nørgaard[d], Matjaž Glavan[e], Igor Pasković[f], Marija Polić Pasković[f], Nelson Abrantes[g], Isabel Campos[h], Francisco Alcon[i], Josefina Contreras[j], Abdallah Alaoui[k], Jakub Hofman[l], Anne Vested[m], Mathilde Bureau[b], Virginia Aparicio[n], Daniele Mandrioli[o], Daria Sgargi[o], Hans Mol[p], Violette Geissen[c], Vera Silva[c], María Ángeles Martínez[a].

[a-] Unit of POPs and Emerging Pollutants in Environment, Department of Environment, CIEMAT, Madrid, Spain.
[b-] University of Bordeaux, INSERM, BPH, U1219, Bordeaux, France
[c] Soil Physics and Land Management Group, Wageningen University & Research, Wageningen, Netherlands.
[d-] Department of Agroecology, Aarhus University, Denmark.
[e] Agronomy Department, Biotechnical Faculty, University of Ljubljana, Ljubljana, Slovenia.
[f] Department of Agriculture and Nutrition, Institute of Agriculture and Tourism, Porec, Croatia.
[g-] Department of Biology and CESAM, University of Aveiro, Aveiro, Portugal.
[h-] Department of Environment and Planning and CESAM, University of Aveiro, Aveiro, Portugal.
[i-] Department of Business Economics, Universidad Politécnica de Cartagena, Spain.
[j-] Department Agricultural Engineering. Universidad Politécnica de Cartagena, Spain.
[k-] Institute of Geography, University of Bern, Bern, Switzerland.
[l-] RECETOX, Faculty of Science, Masaryk University, Brno, the Czech Republic
[m-] Department of Public Health - Unit for Environment, Occupation, and Health, Danish Ramazzini Centre, Aarhus University, Denmark.
[n-] EEA INTA Balcarce, Buenos Aires, Argentina.
[o-] Cesare Maltoni Cancer Research Center, Ramazzini Institute, Bologna, Italy.
[p-] Wageningen Food Safety Research - part of Wageningen University & Research, Wageningen, Netherlands.

[*]Corresponding author: Irene Navarro

Address: Av Complutense nº 40, Madrid (28040), Spain.

e-mail: i.navarro@ciemat.es

Telephone: +34 913 466 019

Abstract

Pesticides are widely used as plant protection products (PPPs) in farming systems to preserve crops against pests, weeds, and fungal diseases. Indoor dust can act as a chemical repository revealing occurrence of pesticides in the indoor environment at the time of sampling and the (recent) past. This in turn provides information on the exposure of humans to pesticides in their homes. In the present study, part of the Horizon 2020 funded SPRINT project, the presence of 198 pesticide residues was assessed in 128 indoor dust samples from both conventional and organic farmworker households across Europe, and in Argentina. Mixtures of pesticide residues were found in all dust samples (25-121, min-max; 75, median). Concentrations varied in a wide range (<0.01 ng/g-206 µg/g), with glyphosate and its degradation product AMPA, permethrin, cypermethrin and piperonyl butoxide found in highest levels. Regarding the type of pesticides, insecticides showed significantly higher levels than herbicides and fungicides. Indoor dust samples related to organic farms showed a significantly lower number of residues, total and individual concentrations than those related to conventional farms. Some pesticides found in indoor dust were no longer approved ones (29%), with acute/chronic hazards to human health (32%) and with environmental toxicity (21%).

Highlights *(3-5 bullets; maximum 85 characters, including spaces, per bullet point)*

- Multiple pesticide residues were detected in all European and Argentine indoor dust.
- Indoor dust samples from organic farms showed lower number and levels of pesticides.
- Insecticides were found in levels significantly higher than herbicides and fungicides.
- Glyphosate, AMPA and several pyrethroids were most common.
- 42% of pesticides quantified are recognized as highly hazardous.

Keywords:

Plant protection products, herbicides, insecticides, fungicides, indoor dust, organic/conventional farming system

1. Introduction

Plant protection products (PPPs), also referred to as “pesticides” are used to: (a) protect plants or plant products against harmful organisms, (b) influence the life processes of plants, or (c) destroy undesired plants or parts of plants. These chemicals are designed to be inherently toxic, eliminating unwanted insects, plants, fungi and other living organisms and many peer-reviewed scientific studies have linked the exposure of pesticides to adverse effects also to non-target organisms (Palma et al., 2015; Richardson and Kimura, 2016; U.S. EPA, 2017a; Casado et al., 2019; Silva et al., 2019; Fritsch et al., 2022). For this reason, PPPs that at first fulfilled approval criteria for authorization of use (Regulation (EC) Nº 1107/2009; EC, 2009) in some cases end up being prohibited, which highlights the need for their systematic monitoring and re-evaluation. Fueled by the demand for food, livestock feed, fibers and biofuels, together with the intensification of agricultural production, global pesticide use has expanded by about 30% in the past two decades (from 2.0 to 2.7 million tonnes in 2000 and 2020, respectively; FAOSTAT, 2023). In the same period, mean pesticide use per hectare of cropland also increased from 1.5 to 1.8 kg/ha (FAOSTAT, 2023). Pesticide use has remained relatively stable in the European Union (EU), fluctuating ± 6 % around the 350,000 tonnes per year, during the 2011 and 2020 period, with fungicides and herbicides being the pesticide groups with the highest annual sales (Eurostat, 2023).

The International Labour Organization recently identified pesticides as one of the top 10 priorities of concern globally among the exposure to hazardous chemicals at work and resulting health impacts (ILO, 2021). Once applied in the fields, pesticides can move to other environmental compartments, and people living in agricultural areas may experience higher exposure to pesticides (residents and bystanders) than people living in non-rural areas (Khan and Damalas, 2015; Carvalho, 2017; Hung et al., 2018; Boedeker et al., 2020; Dereumeaux et al., 2020). Occupational exposure affects both farmworkers and their families, comprising a relevant target population in many health risk assessments (Tamaro et al., 2018; Bennet et al., 2019; Teysseire et al., 2020; Mu et al., 2022). Many studies have evidenced that the indoor environment can be a relevant source of exposure to pollutants (de la Torre et al., 2019; Andersen et al., 2020; Salthammer, 2020), and considering the time spent by people indoors, the chance of exposure to certain chemicals has been reported to increase by 1000-fold compared to outdoor exposures (Hwang et al., 2008). The transfer of pesticides from household surfaces to foods has been evidenced (Rohrer et al., 2003; ILO, 2021), but also the ingestion of indoor dust (30-60 mg/day dust ingestion rate for adults and children, respectively, U.S. EPA, 2017b) is a potential route of exposure. In some cases, intake of chemicals through dust can be equal to or more significant than exposure through food consumption (Hwang et al., 2008; Anh et al., 2019). Indoor dust is a heterogeneous mixture of organic and inorganic materials composed of animal fibers, pollen, particulate matter deposited from aerosols, and soil particles translocated by foot traffic (Arbuckle et al., 2005; Curwin et al., 2007a; Thompson et al., 2014), being a representative chemical repository to assess the exposure potential to environmental pollutants in the indoor environment. Even currently used non-persistent pesticides can remain stable indoors for extended periods of time compared to outdoor environments due to the lack of sunlight, moisture, biotic and abiotic degradation or other dissipation processes and there is growing evidence of pesticide accumulation in indoor dust from imported soil particles or direct indoor applications. Studies dealing with currently used pesticides in indoor dust are scarce and mainly restricted to a small geographic area or only a few compounds (Glorennec et al., 2017; Béranger et al., 2019; Figueiredo, et al., 2022).

The aim of the present study was to obtain a comprehensive insight in occurrence of 198 pesticide residues (156 active substances and 42 metabolites) and mixtures thereof in households of conventional and organic farmers in 10 European countries and Argentina. Occurrence in households of people not occupationally involved in PPP use was also investigated.

2. Material and Methods

2.1. Sample collection

A total of 128 indoor dust samples were collected during the 2021 growing season in households from conventional or non-organic (n=65) and organic (n=63) farms. These samples originated from Spain (case study site 1, CSS1, n=9), Portugal (CSS2, n=5), France (CSS3, n=13), Switzerland (CSS4, n=12), Italy (CSS5, n=7), Croatia (CSS6, n=16), Slovenia (CSS7, n=12), Czech Republic (CSS8, n=14), the Netherlands (CSS9, n=16), Denmark (CSS10, n=11) and Argentina (CSS11, n=13) of the main European crops, or of a crop notably imported and used in Europe (Table S1, Figure 1). Organic farming is an agricultural method that aims to produce food using natural substances and processes with a limited environmental impact. It encourages responsible use of energy and natural resources, maintenance of biodiversity and preservation of regional ecological balances (EC, 2023a). The conventional or non-organic term, including integrated pest management (IPM) approach, has been used to those farms that have not met the standards for organic certification. Furthermore, 40 indoor dust samples were also collected in neighbours and consumers (control) households without direct occupational exposure from CSS3 (n=15) and CSS10 (n=25). The farmers, neighbours and consumers were asked to collect the dust from their house during a month, around the middle of the growing season, via vacuum cleaning (Alaoui et al., 2021, Silva et al. 2021). Then, vacuum cleaner bags were covered with aluminum film and introduced in polyethylene sealable bags and sent refrigerated (-20ºC) to CIEMAT labs. Once arrived at the laboratory, dust samples were sieved through a stainless steel sieve (500 µm), homogenized and stored at -20 °C until analysis. Participants were asked to complete a questionnaire that included details related to the home environment, working conditions, and pesticide use by farmers and neighbors/consumers. Main results are summarized in supplementary material (SM; Table S2).

2.2. Chemical analysis

A total of 198 pesticides (156 active substances and 42 metabolites) including 71 fungicides, 63 herbicides, 63 insecticides and 1 synergist, were analysed in the present study. The selection of the analytes was based on known usage in the CSS, known occurrence in environmental and food matrices, and a pre-screen of dust and soil samples using non-target full scan LC-HRMS and GC-HRMS analysis (Silva et al., 2021). Three different methodologies were optimized and validated for pesticide determination. Briefly, for multi-residue analysis of pesticides, the indoor dust (1 g) spiked with surrogate labeled standards was extracted with a mixture of water and acidified acetonitrile, followed by a salt-induced phase separation (QuEChERS approach, details see SM). The acetonitrile extract was divided into two aliquots for the GC and HPLC analyses. An additional purification step with $MgSO_4$, C18 and PSA was required for the GC aliquot. HPLC analyses were performed on UHPLC-MS/MS (ExionLC Shimadzu-SCIEX Triple Quad 3500) and GC analyses were conducted in a GC-MS/MS (Varian CP-3800 GC-320 MS-TQ). Glyphosate and aminomethylphosphonic acid (AMPA) were extracted based on Mendez et al. (2017) methodology. In short, 0.1 g dust sample spiked with $^{13}C_2$,^{15}N- glyphosate and ^{13}C,^{15}N-AMPA labeled standards was extracted with $KH_2PO_4/Na_2B_4O_7$ (0.1 M, pH=9). The derivatization was conducted overnight (≈15 h) with FMOC (1 mg/mL) in darkness at room temperature. Instrumental determinations were performed on UHPLC-MS/MS (ExionLC Shimadzu-SCIEX Triple Quad 3500). Organochlorinated pesticides were extracted by sonication and centrifugation from 0.1 g indoor dust spiked with ^{13}C labeled surrogate standards (ES-5344-50X from Cambridge Isotope Laboratories Inc.) using hexane:acetone (3:1) mixture and subsequently purified by 1 g florisil column eluted with hexane. Instrumental analyses were carried out by HRGC-HRMS (Agilent 6890 HRGC-MicroMass Autospec Ultima HRMS) (de la Torre et al., 2020a). See details related to the three different methodologies at supplementary material.

2.3. Quality assurance and statistical evaluation

The three analytical methodologies were validated according to the SANTE/2020/12830 (SANTE, 2021a) and SANTE/11312/2021 (SANTE, 2021b) performance criteria, see SM for complete validation results. The mean recoveries obtained during initial and on-going validations were within the range 70 - 120%, with an associated repeatability RSDr ≤ 20%, for all analytes within the scope of the method (Table S3). The limits of quantification (LOQs), defined as the lowest level that has been validated with acceptable accuracy by applying the complete analytical method and identification, recovery, precision and repeatability criteria for each analyte (SANTE, 2021a,b), ranged between 0.75 (fenvalerate) and 114 ng/g (pyrimethanil metabolite). In most cases (n=139), LOQs of 1 ng/g were achieved. For 41 pesticides the LOQ was 10 ng/g, in the remaining cases higher, (Table S3). The limits of detection (LODs), defined as the lowest level at which the analyte can be detected and also identified, were calculated as the concentration at which signal to noise ratio for qualifier transition is at least 3 in matrix spiked at LOQ level, and ranged between 0.01 and 38 ng/g (Table S3). Procedural blanks were conducted with each batch and extracted under the same conditions as samples. In addition, instrumental blanks were run before each sample injection to check the possibility of cross-contamination from the analysis system.

Statistical analyses were performed with the software SPSS 14.0 and Statgraphics Centurion XVII.I for Windows. Mann-Whitney U or Kruskal-Wallis Tests were performed to evaluate differences between groups (CSS, type of farm, compounds, etc.). Relationships between compound concentrations were assessed by Spearman Rho correlations. Statements regarding differences in this study are based on a significance level of $p < 0.05$, although significance level of $p < 0.01$ was also mentioned in the text when it was reached. Descriptive statistics (mean, median, min-max range and other calculations) were conducted on positive samples (> LOD). Principal Component Analysis (PCA) was also used to display possible relationships between the content of pesticides in indoor dust and their distribution (type of field system and CSS). In this test, only the first 25 pesticides with the highest median concentration and detection frequency (Df, samples % > LOD) > 30% were considered. Furthermore, to include all samples in this PCA, those with concentrations below LOD were replaced by the LOD divided by the square root of two (Fraser et al., 2013, de la Torre et al., 2020b).

3. Results and Discussion

3.1 Number of pesticides in indoor dust from farmworker households

Pesticide residues were detected in all the 128 analysed dust samples of farmworker households (116 approved, 47 non-approved and 1 synergist, Table S4). The number of residues detected (> LOD) in each sample (pesticides/sample) ranged between 25 and 121 (75 median; Table S5) and was similar in all CSS, except in Denmark (CSS10) which showed the lowest ($p < 0.05$) pesticides/sample values (55, median). This result could reflect the outcome of Danish policies implemented years ago, such as the tax on pesticides linked to their toxicity on human health, environment, and groundwater instead of their nominal value, which resulted in a noteworthy decrease in pesticide use in Denmark (MEFD, 2017; Tostado and Bollmohr, 2022). Dust samples collected in households from conventional farms (80 pesticides/sample; median) presented a higher ($p < 0.01$) number of pesticides than those derived from organic farms (65, median) (Figure 1, Table S5). This tendency could be sensed within most CSS: Spain (CSS1; 85 versus 81, median number of pesticides/sample in conventional – organic, Table S5), Portugal (CSS2; 74 versus 51), France (CSS3; 86 versus 80), Switzerland (CSS4; 116 versus 76), Croatia (CSS6; 65 versus 55), Slovenia (CSS7; 73 versus 57), Czech Republic (CSS8; 85 versus 64), the Netherlands (CSS9; 102 versus 80), Denmark (CSS10; 59 versus 55) and Argentina (CSS11; 73 versus 69) (Table S5), but only presented statistically significant for CSS4, CSS7 and CSS8. A similar finding was described in a previous study conducted with CSS from Spain, Portugal and the Netherlands, in which agricultural topsoils from organic fields presented fewer residues per sample than conventional ones (Geissen et al., 2021).

3.2. Type of pesticides in indoor dust from farmworker households

The presence of 198 pesticides was evaluated in 128 dust samples and only one of the tested chemicals, chlorpyrifos-methyl-desmethyl, was not identified in any of the samples. Detection frequencies did not reveal significant differences ($p > 0.05$) among pesticide types (Dfs of 40, 51 and 52% for herbicides, insecticides and fungicides, respectively; Figure S1, Tables S6 and S7) and most of the pesticides (82%) showed Df > 10%, reflecting a wide distribution of pesticides among CSS. However, among all the compounds analysed, 34 of them (17%) stand out with detection frequencies above 75%. The insecticides fipronil, fipronil sulfone, imidacloprid, fungicides fludioxonil, hexachlorobenzene, azoxystrobin, carbendazim, tebuconazole, and a synergist component of pesticide formulation, piperonyl butoxide, presented the highest Df values (> 99%). Piperonyl butoxide was also found to be highly common in, rural house dust from France (Béranger et al., 2019). Tebuconazole was also reported by Béranger et al. (2019) as the most prevalent agricultural pesticide in dust from French households. A high detection frequency was also observed for imidacloprid and carbendazim in dust samples from rural areas in China (> 99% and > 84%, respectively; Wang et al., 2019) and from farm homes in the Netherlands (> 63% and > 88%, respectively; Figueiredo et al., 2022). It results of special interest that in the dust samples collected at homes of conventional farmers up to 38 compounds showed Dfs > 75% (azoxystrobin, fludioxonil, hexachlorobenzene, imidacloprid, tebuconazole, > 99%) while 32 did in dust samples from homes of organic farmers (carbendazim, chlorpyrifos-methyl TCPy, fipronil, fipronil sulfone, fludioxonil, hexachlorobenzene, imidacloprid, piperonyl butoxide, > 99%) (Table S7). Some compounds, such as azoxystrobin and tebuconazole were applied as PPP in several of the sampled conventional farms (Table S8). Nevertheless, fludioxonil was not applied and hexachlorobenzene and imidacloprid were not approved as PPP (Table S4), suggesting a historical use and/or different source of these pesticides. The low LOD for hexachlorobenzene (0.01 ng/g) explains its high detection frequency compared to other compounds (Tables S3 and S7). The physicochemical properties of hexachlorobenzene, such as long field half live DT_{50} (soil degradation rate of 2000 days, Table S4), could explain its persistence in dust households, but it is essential to take into consideration rather low concentrations detected of this compound (0.3 ng/g, median, Table S7). Furthermore, the use of some pesticides as biocides and anti-flea/tick/mosquito pet treatments could contribute as an additional source of these compounds in indoor dust (Deziel et al., 2015; Salis et al., 2017; Hung et al., 2018). Imidacloprid and carbendazim were also detected with higher frequency in household dust from residential areas in Italy (Salis et al., 2017), pointing out their possible use as biocides. In our study, 69% of the participants had pets (Table S2) and recognized the use of pet grooming products (10%), external anti-flea treatments (29%) or other pet products (9%). Besides, data gathered in the questionnaires revealed that 40% of the farmers have used pesticides inside the house and 29% have also utilized insect repellents and anti-parasite products for human use (Table S2).

Detection frequencies also varied between CSS (Table S6). Atrazine, clothianidin, cyproconazole and pirimiphos-methyl were more frequently (Df > 92%) observed at CSS11 (Argentina) than in the European locations. Differences found are surely related to the fact that during household dust sampling the use of some of them was allowed in Argentina (Geronimo et al., 2014), but not in the European Union (EC, 2023b). In some CSS there are some compounds that stand out from the rest: CSS1 (oxyfluorfen, pyriproxyfen, spirotetramat-enol and spirotetramat-keto-hydroxy, with Df > 89%), CSS2 (AMPA, folpet PHI, kresoxim-methyl and penconazole, with Df > 80%), CSS3 (cyflufenamide, cyprodinil, fenbuconazole,, quinoxyfen and tau-fluvalinate, with Df > 85%), CSS8 (chlorotoluron, with Df = 93%) and CSS9 (ethofumesate, methabenzthiazuron, metobromuron and pencycuron, Df > 88%). In theory, the high presence of pesticides in dust samples obtained in the same CSS could reflect its recent application in the CSS (see coloured cells in Table S8), although some of them were also detected in organic farms where they were not applied (Table S9). Pesticides could persist in the indoor environment for long periods (Rudel et al., 2003; Nakagawa et al., 2019) reflecting the intensiveness of the agricultural practices related to close fields from the preceding seasons. However, some pesticides, such as tau-fluvalinate in CSS1 or lambda-cyhalothrin in CSS5 were not found in the dust samples despite of their recognised use in the fields. Their relative quick soil degradation (DT_{50} < 42 days, Table S4) and the low mean application rates (< 0.1 kg/ha) in those CSS would reduce their possible transport into homes. These results evidenced that the presence of pesticides in the dust may be influenced by other factors like pesticide physicochemical properties or specific environmental transport and degradation conditions at each CSS that should not be ruled out.

3.3. Concentrations of pesticides in indoor dust from farmworker households

Descriptive statistics (Df in %, mean ± S.D., median, min, max in ng/g) of pesticide concentrations obtained in household indoor dust samples are detailed in Table S7. Total pesticide content (sum of 198 pesticides) showed very high variability (8.62 µg/g, median) with a maximum value of 283 µg/g. Significant differences ($p < 0.01$) were found between conventional (13.4 µg/g, median) and organic (4.38 µg/g, median) field systems. The CSS with the highest median pesticide content was Argentina (25.2 µg/g), followed by Croatia (17.0 µg/g), Italy (13.4 µg/g), France (13.1 µg/g), Portugal (12.7 µg/g) and Spain (12.2 µg/g). Total agricultural use of pesticides (tonnes) and consumption per area of cropland (kg/ha) in the countries evaluated are listed in Table S10. According to the Food and Agriculture Organization of the United Nations (FAOSTAT, 2022, 2023), Argentina is currently the fourth largest consumer of pesticides worldwide, only surpassed by US, Brazil and China. In Europe, Italy, Spain and France are the EU countries with the highest pesticide annual sales, which is not surprising since they are also the main agricultural producers in the EU (Eurostat, 2023). Regarding the type of pesticides, there was a statistically significantly higher median concentration of insecticides (2.49 μg/g) in indoor dust than herbicides (1.18 μg/g) and fungicides (0.58 μg/g). Additionally, important differences were obtained between conventional and organic farming systems (Figures 2 and 3). Dust samples related to the formers presented the following tendency ($p < 0.01$) herbicide (3.67 μg/g, median) ≈ insecticide (3.53 μg/g) > fungicide (1.61 μg/g), while in samples related to latter was insecticide (1.83 μg/g) > herbicide (0.32 μg/g) ≈ fungicide (0.32 μg/g). The higher predominance of the insecticides could be the result of the combination of agricultural and domestic use, such as pet grooming products (10%), external anti flea treatments (29%), biocides into homes (31%) or insect repellents or anti-parasite products (29%) (Table S2).

A detail of the first 25 pesticides with higher median concentration and Df > 30% in each type of field system is shown in Figure 3, highlighting again the predominance of the dust samples related to the conventional fields. Significant differences ($p < 0.05$) in concentration values were observed between compounds (see Table S11). Glyphosate was the pesticide with the highest median concentration (1.39 μg/g; Table S7) followed by permethrin (0.62 μg/g), cypermethrin (0.40 μg/g), AMPA (0.33 μg/g), tetramethrin (0.32 μg/g) and piperonyl butoxide (0.16 μg/g). The three chemicals with the highest median levels in each case study site are detailed in Table 1. Glyphosate dominated in all CSS, although it was not applied in some of them (Tables S6 and S8). The content of glyphosate and AMPA was similar to the values observed in indoor dust from French rural dwellings (1.68 μg/g and 0.46 μg/g, median, for glyphosate and AMPA, respectively; Saurat et al., 2023) and indoor dust from farmhouses in the US (0.92 μg/g - 1.10 μg/g for glyphosate; Curwin et al., 2007b). Similar concentrations of pyretroids were reported in indoor dust from farmworker homes (0.42 μg/g for permethrin and 0.19 μg/g for cypermethrin, Trunnelle et al., 2013) or rural areas (0.55 μg/g and 0.18 μg/g, respectively, Blanchard et al., 2014; 0.37 μg/g for cypermethrin, Hung et al., 2018). The lack of sunlight and moisture limits the hydrolysis, photodegradation, and microbial degradation inside the house and the pyrethroids applied indoors could persist longer (Leng et al., 2005). It is worth to mention that lower pyrethroid levels quantified in the French samples agree with concentrations described for house dust from urban and rural areas in the same country (0.77 μg/g and 0.14 μg/g, permethrin and cypermethrin, respectively, Glorennec et al., 2017). Piperonyl butoxide values were also in concordance with levels obtained in indoor dust from residential areas (0.43 μg/g, Rudel et al., 2003). Different compounds were also quantified in a wide range, comparable to previous studies (Table S15). The first 20 pesticides with higher contribution (%) and Df > 30% in each CSS are shown in Figure S2. In general, permethrin (12 - 39%, min-max), glyphosate (17 - 34%), cypermethrin (6 - 35%) and piperonyl butoxide (3 - 25%) were the compounds with the highest contribution to the total pesticide content. The different habits of the farmers, such as the use of biocides into home, pet treatments, repellent products, pesticides in the garden and the ventilation conditions or indoor use of shoes (Table S2), could contribute notably to the levels detected. On the other hand, the lowest median concentration was led by bixafen desmethyl (0.22 ng/g, median; Table S7), with Df > 10%, followed by pirimiphos-methyl-desmethyl (0.25 ng/g), clomazone and hexachlorobenzene (0.32 ng/g).

Table S12 presents the correlation matrix for the 92 pesticides with detection rates > 30 %. Good correlations were observed between pesticides and their metabolites and degradation products (r_s: 0.41* - 0.92**, min - max, $p < 0.01$, Spearman's rank correlation Test), such as, glyphosate and AMPA, chlorpyrifos and TCPy, fipronil and fipronil sulfone or imidacloprid and imidacloprid-desnitro. Some pesticides from the same chemical family also correlated, especially benzamides ($r_s > 0.45$**), strobilurins ($r_s = 0.45$**), acid herbicides ($r_s > 0.40$**), neonicotinoids ($r_s > 0.26$**), organochlorines ($r_s > 0.32$*, $p < 0.05$), pyrethroids ($r_s = 0.26$*), carbamates ($r_s > 0.29$*) and azoles ($r_s > 0.19$*). It should be noted that some analytes revealed positive correlations with several pesticides (> 40), such as azoxystrobin (50), difenoconazole, fluopyram, metalaxyl-M (48), chlorpyrifos-methyl TCPy (47), tebuconazole (43) and prothioconazole (42), suggesting their presence in the same commercial formulations, similar applications, environmental behaviour and/or degradation rates. Some compounds tended to be correlated with other chemicals negatively, such as 2,4-D, flonicamid or the tolylfluanid metabolite DMST or propiconazole.

Principal Component Analysis was performed to explore relationships between pesticide content in indoor dust and their distribution (type of farming system and CSS), considering only the first 25 pesticides with higher median concentration and Df > 30% (Figures 4, S3 and Table S13). Models depicted in three principal components (PC) 42% of the variance. The first component (PC1) was mainly influenced by the herbicides glyphosate and AMPA, and to a lesser extent the fungicides azoxystrobin and pyraclostrobin, explaining 19% of the variance. The second component (PC2) accounted for 13% of the total variance and included the insecticides cypermethrin, chlorpyrifos and permethrin. The third component (PC3) was determined by three fungicides (metrafenone, zoxamid and boscalid) and explained 10% of the variance. As shown in the score plots (Figures 4b and S3a) indoor dust samples related to organic fields were distributed in the negative side of PC1, indicating lower concentrations of glyphosate ($p<0.01$), AMPA, azoxystrobin ($p<0.01$) and pyraclostrobin ($p<0.01$) in this type of field. On the other hand, conventional and organic fields were distributed in both sides of PC2 and PC3 (Figure S3c) reflecting that cypermethrin, chlorpyrifos, permethrin, metrafenone, zoxamid and boscalid dust concentrations were not influenced by the type of farming system. The score plot distribution of CSS9 (The Netherlands) and CSS11 (Argentina) samples (shown in Figures 4a and S3b) revealed higher pollutant concentrations with influence in the first component compared to CSS7 (Slovenia) and CSS10 (Denmark) (see also Table S8). Similarly, the score plot in Figure 4a and c (right) for CSS6 (Croatia) and CSS11 reflected higher levels for cypermethrin, chlorpyrifos and permethrin, than samples from CSS9 and CSS10. As shown in the score plots (Figures 4c and S3b) indoor dust samples related to CSS10 and CSS11 were distributed in the negative side of PC3, indicating lower concentrations of metrafenone, zoxamid and boscalid compared to CSS3 (France) and CSS5 (Italy). It is important to remark that the score plot distribution showed lower and higher concentrations from CSS10 and CSS11 samples, respectively, for the three components compared to the other sites.

3.4. Pesticides in indoor dust from households of people not occupationally involved in PPP use

Residues of pesticides were also found in all samples (n=40) analysed from neighbours and consumer (control) households (Table S14). The number of pesticides per sample (pesticides/sample) ranged between 36 and 80 (57 median), slightly lower in samples from CSS10 (Denmark, 55 median) than CSS3 (France, 63 median), and significantly ($p < 0.01$) lower than that determined in indoor dust from farmer households (75 median). 167 out of 198 pesticide residues were identified and 60% showed DF > 10%, with a total pesticide content (4.84 µg/g, 0.41-25.0 µg/g, median, min-max) significantly lower ($p < 0.05$) than that found in dust from farmers households. Regarding the type of pesticides, the same pattern ($p < 0.01$) was observed, insecticides (1.09 µg/g, median) > herbicides (0.48 µg/g) > fungicides (0.31 µg/g) with values very similar to samples related to organic farms. Glyphosate was the most predominant compound (0.66 µg/g median) followed by permethrin (0.52 µg/g), AMPA (0.36 µg/g), piperonyl butoxide (0.09 µg/g) and cypermethrin (0.08 µg/g). Although levels detected in households without direct occupational exposure were lower than those observed in agricultural areas, these findings evidences the significant domestic use of these chemicals, as can be also corroborated in Table S2

Many pesticides and mixtures thereof have been found in indoor dust, including no longer approved ones (29%-26% for samples from farmers - neighbours/consumers; Regulation 1107/2009; EC, 2009, 2023; Table S4) and 42%-34% referred to as highly hazardous pesticides included in the PAN International List of Highly Hazardous Pesticides (HHPs) (PAN, 2021): 32%-26% with acute or chronic hazards to human health and 21%-17% with environmental toxicity (PAN, 2021; WHO, 2019; ILO, 2021). Humans may be exposed to these pesticides through dust inhalation or ingestion, but the relative contribution to the overall exposure is unknown and further research is needed on this.

4. Conclusions

An extensive investigation into the presence of 198 pesticide residues in indoor dust from farmworker households across Europe and Argentina was performed. The comparison between dust samples related to two farming systems (conventional and organic) established significant differences related to number of residues, total pesticide content and individual pesticide concentrations. This finding suggests that improvements in pesticide management and application, such integrated pest management, use and promotion of ecological alternatives and organic farming made to support the Farm to Fork Strategy, could diminish the human and environmental exposure to these compounds. Nevertheless, the occurrence of pesticide residues in households without occupational exposure highlights their wide domestic use and should be of concern. The results obtained provide valuable information on the exposure of humans to pesticides in their homes and reveals the necessity to regulate their marketing, use and disposal throughout their life-cycle, and reduce their application to protect the health and ecosystems. Further research based on health risk assessment related to indoor environments is essential to evaluate the effect of complex pesticide mixtures.

Credit authorship contribution statement

Irene Navarro: Sample analysis, Data curation, Investigation, Formal analysis, Methodology, Validation, Writing - original draft, Writing – review & editing. **Adrián de la Torre**: Sample analysis, Investigation, Methodology, Validation, Writing - review & editing. **Paloma Sanz**: Sample analysis, Investigation, Methodology, Validation, Writing - review & editing. **Isabelle Baldi**: sample collection, Writing – review & editing. **Paula Harkes**: sample collection, Writing – review & editing. **Esperanza Huerta-Lwanga**: sample collection, Writing – review & editing. **Trine Nørgaard**: sample collection, Writing – review & editing. **Matjaž Glavan**: sample collection, Writing – review & editing. **Igor Pasković**: sample collection, Writing – review & editing. **Marija Polić Pasković**: sample collection, Writing – review & editing. **Nelson Abrantes**: sample collection, Writing – review & editing. **Isabel Campos**: sample collection, Writing – review & editing. **Francisco Alcon**: sample collection, Writing – review & editing. **Josefina Contreras**: sample collection, Writing – review & editing. **Abdallah Alaoui**: sample collection, field work coordination, Writing – review & editing. **Jakub Hofman**: sample collection, Writing – review & editing. **Anne Vested**: sample collection, Writing – review & editing. **Mathilde Bureau**: sample collection, Writing – review & editing. **Virginia Aparicio**: sample collection, Writing – review & editing. **Daniele Mandrioli**: sample collection, Writing – review & editing. **Daria Sgargi**: sample collection, Writing – review & editing. **Hans Mol**: Investigation, Writing – review & editing. **Violette Geissen**: Conceptualization, Funding acquisition, Project administration, Writing – review & editing. **Vera Silva**: Sample collection, Conceptualization, Funding acquisition, Project administration, Writing – review & editing. **María Ángeles Martínez**: Conceptualization, Investigation, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Acknowledgements

The SPRINT project (on Sustainable Plant Protection Transition, https://sprint-h2020.eu/), leading to this publication has received funding from the European Union’s Horizon 2020 Programme for research & innovation under grant agreement nº 862568. Jakub Hofman thanks the RECETOX Research Infrastructure (LM2023069) and the CETOCOEN EXCELLENCE project (CZ.02.1.01/0.0/0.0/17_043/0009632) financed by MEYS for supportive background. This work was supported from the European Union’s Horizon 2020 research and innovation program under grant agreement No 857560. This publication reflects the author’s view. The European Commission is not responsible for any use that may be made of the information it contains. The authors would like to thank all Case Study Sites participants for their support to this publication and SPRINT activities.

Appendix A. Supplementary material

Supplementary material to this article can be found online at

Conflict of interest

The authors declare that there is no conflict of interest.

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Figure 1. Location of the different case study sites (CSS) and number of pesticides found per dust household sample (%) distributed to conventional and organic farm systems.

Figure 2. Concentration (Log [1+X]; ng/g) of fungicides, herbicides and insecticides in household dust related to conventional and organic fields. Upper edge of the box, line within the box and lower edge of the box, represents the 75th, 50th, and 25th percentiles. Vertical lines extend from the minimum to the maximum value, excluding outliers (circles) values.

Figure 3. Concentration (Log [1+X]; ng/g) of some pesticides in household dust related to conventional and organic fields. Only the first 25 pesticides with higher median concentration and Df > 30% are shown. Upper edge of the box, line within the box and lower edge of the box, represents the 75th, 50th, and 25th percentiles. Vertical lines extend from the minimum to the maximum value, excluding outliers (circles) and extreme (asterisks) values.

Figure 4. Diagrams of dispersion related to the three components resulting from a principal components analysis (PCA) derived from the content of pesticides in indoor dust and pesticide distribution (type of farming system and CSS). a) PC1 and PC2, b) PC1 and PC3, and c) PC2 and PC3. Loading plots (left) contribution of each variable to each component; FU: fungicide, HB: Herbicide, IN: insecticide, S: synergist. Score plots (right), markers set by CSS (a and c) and farming system type (b), of all samples on each component.

Table 1. Descriptive statistics (mean, (median), min-max, µg/g, Df (%) of positives) obtained for the first three pesticides detected in each case study site. Only pesticides with higher median concentration and Df > 10% are shown.

Figure 1

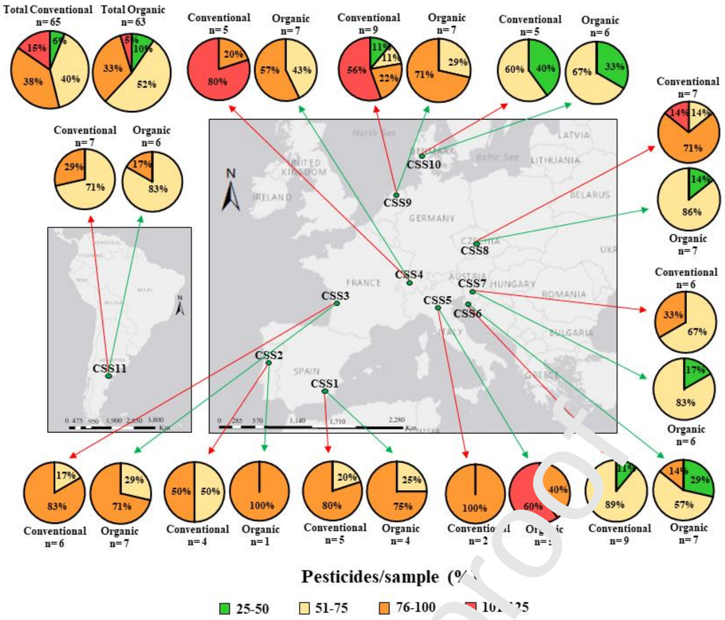

Total Conventional n= 65
15%
6%
38%
40%
Total Organic n= 63
5%
10%
33%
52%
Conventional n= 5
20%
80%
Organic n= 7
57%
43%
Conventional n= 9
11%
11%
56%
22%
Organic n= 7
29%
71%
Conventional n= 5
60%
40%
Organic n= 6
67%
33%
Conventional n= 7
14%
14%
71%
14%
86%
Organic n= 7
Conventional n= 7
29%
71%
Organic n= 6
17%
83%
CSS10
CSS9
CSS8
CSS4
CSS7
CSS3
CSS5
CSS6
CSS2
CSS1
CSS11
North Sea
Baltic Sea
UNITED KINGDOM
IRELAND
DENMARK
LATVIA
LITHUANIA
BELARUS
GERMANY
CZECHIA
UKR
FRANCE
AUSTRIA
HUNGARY
ROMANIA
ITALY
BULGARIA
GREECE
SPAIN
N
0 285 570 1,140 1,710 2,280 Km
0 475 950 1,900 2,850 3,800 Km
Conventional n= 6
33%
67%
17%
83%
Organic n= 6
17%
83%
Conventional n= 6
29%
71%
Organic n= 7
50%
50%
Conventional n= 4
100%
Organic n= 1
20%
80%
Conventional n= 5
25%
75%
Organic n= 4
100%
Conventional n= 2
40%
60%
Organic
11%
89%
Conventional n= 9
14%
29%
57%
Organic n= 7
Pesticides/sample (%)
🟩 25-50
▨ 51-75
🟧 76-100
🟥 101-125

Figure 2

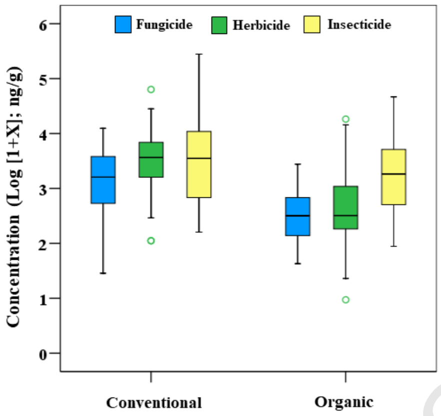

Fungicide
Herbicide
Insecticide
Concentration (Log [1+X]; ng/g)
0
1
2
3
4
5
6
Conventional
Organic

Figure 3

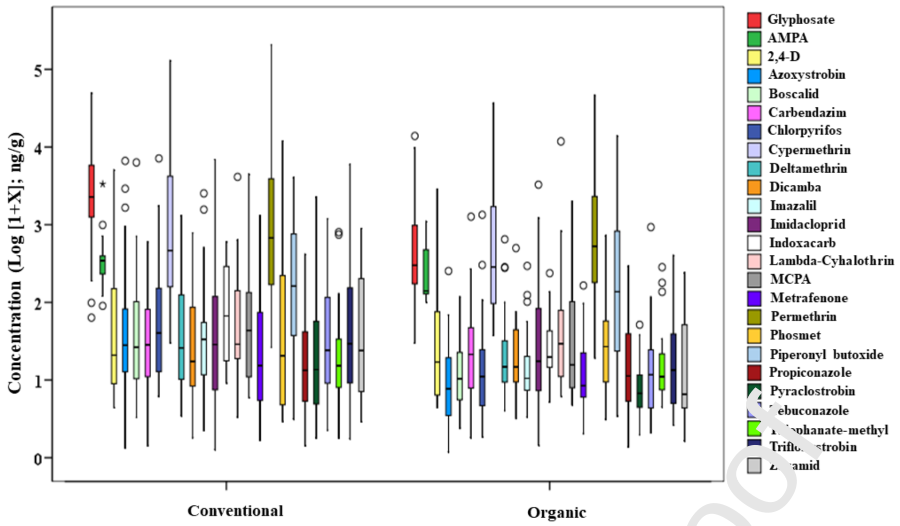

Concentration (Log [1+X]; ng/g)
0
1
2
3
4
5
Conventional
Organic
Glyphosate
AMPA
2,4-D
Azoxystrobin
Boscalid
Carbendazim
Chlorpyrifos
Cypermethrin
Deltamethrin
Dicamba
Imazalil
Imidacloprid
Indoxacarb
Lambda-Cyhalothrin
MCPA
Metrafenone
Permethrin
Phosmet
Piperonyl butoxide
Propiconazole
Pyraclostrobin
ebuconazole
phanate-methyl
Trifl strobin
amid

Figure 4

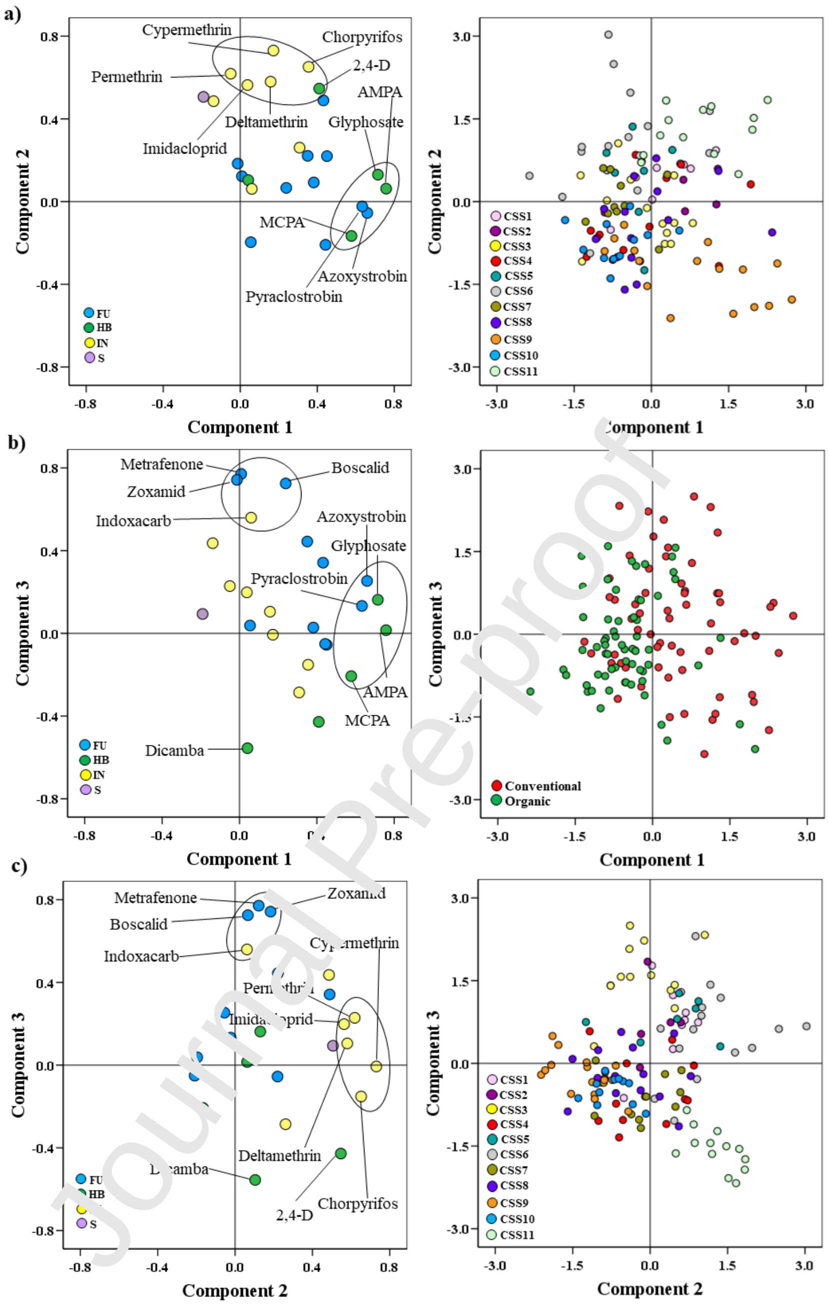

a)
Cypermethrin
Chorpyrifos
2,4-D
Permethrin
AMPA
Deltamethrin
Glyphosate
Imidacloprid
MCPA
Azoxystrobin
Pyraclostrobin
FU
HB
IN
S
Component 1
Component 2
CSS1
CSS2
CSS3
CSS4
CSS5
CSS6
CSS7
CSS8
CSS9
CSS10
CSS11
-0.8
-0.4
0.0
0.4
0.8
-3.0
-1.5
1.5
3.0
b)
Metrafenone
Boscalid
Zoxamid
Indoxacarb
Azoxystrobin
Glyphosate
Pyraclostrobin
AMPA
MCPA
Dicamba
Component 3
Conventional
Organic
c)
Zoxamid
Cypermethrin
Permethrin
Imidacloprid
Deltamethrin
Dicamba
2,4-D
Chorpyrifos

Table 1

	Mean (µg/g)	Median (µg/g)	Min-Max (µg/g)	Df (%)
CSS1				
Permethrin	10.9	(2.41)	<0.01 - 72.8	100%
Glyphosate	1.96	(1.68)	<0.02 - 4.92	89%
Piperonyl butoxide	0.77	(0.64)	<0.01 - 1.66	100%
CSS2				
Glyphosate	4.58	(5.38)	<0.02 - 7.85	100%
Pyrethrin I	2.55	(2.55)	<0.01 - 5.09	40%
Permethrin	2.54	(0.69)	<0.01 - 8.61	80%
CSS3				
Glyphosate	5.80	(1.25)	<0.02 - 24.8	85%
Permethrin	5.31	(1.07)	<0.01 - 46.1	100%
Ametoctradin	1.22	(0.52)	<0.01 - 7.63	100%
CSS4				
Glyphosate	2.11	(0.91)	<0.02 - 10.3	58%
Spinosyn A	0.49	(0.27)	<0.01 - 1.52	58%
Cypermethrin	0.22	(0.22)	<0.01 - 0.34	17%
CSS5				
Permethrin	3.10	(1.98)	<0.01 - 9.28	100%
Cypermethrin	5.86	(0.77)	<0.01 - 26.4	71%
Glyphosate	1.36	(0.56)	<0.02 - 3.05	71%
CSS6				
Permethrin	19.0	(4.35)	<0.01 - 206	100%
Glyphosate	4.94	(1.28)	<0.02 - 27.4	88%
Piperonyl butoxide	1.96	(1.00)	<0.01 - 13.9	100%
CSS7				
Glyphosate	0.88	(0.76)	<0.02 - 1.91	58%
Permethrin	0.81	(0.32)	<0.01 - 4.94	100%
Cypermethrin	0.44	(0.19)	<0.01 - 1.39	42%
CSS8				
Glyphosate	3.00	(1.25)	<0.02 - 17.3	86%
Pyraclostrobin	1.13	(1.13)	<0.01 - 2.26	14%
Cypermethrin	0.72	(0.66)	<0.01 - 1.49	36%
CSS9				
Glyphosate	4.57	(2.51)	<0.02 - 15.4	94%
Permethrin	1.16	(0.26)	<0.01 - 10.1	94%
AMPA	0.34	(0.25)	<0.04 - 0.71	50%
CSS10				
Piperonyl butoxide	0.81	(0.69)	<0.01 - 2.25	100%
Glyphosate	1.44	(0.45)	<0.02 - 6.01	91%
Permethrin	0.67	(0.35)	<0.01 - 3.24	91%

CSS11				
Cypermethrin	11.1	(5.33)	<0.01 - 36.6	100%
Glyphosate	9.56	(2.58)	<0.02 - 49.5	85%
Permethrin	2.34	(1.28)	<0.01 - 7.87	100%
Total				
Glyphosate	4.03	(1.39)	<0.02 - 49.5	82%
Permethrin	5.22	(0.62)	<0.01 - 206	95%
Cypermethrin	6.06	(0.40)	<0.01 - 129	48%

Credit authorship contribution statement

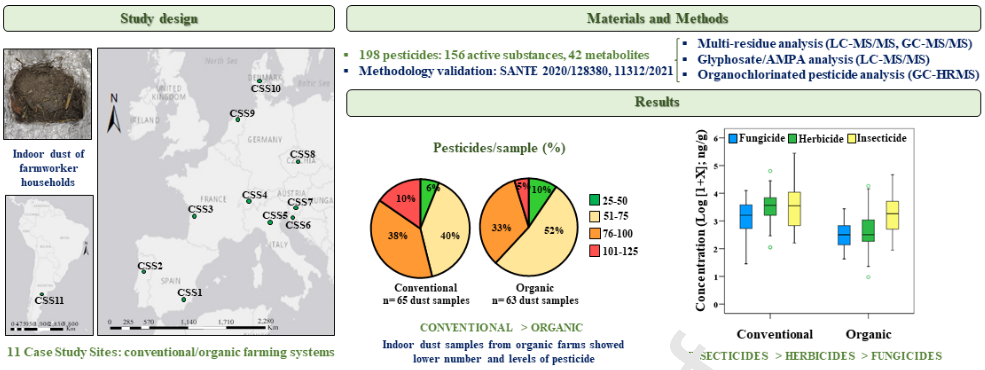
Irene Navarro: Sample analysis, Data curation, Investigation, Formal analysis, Methodology, Validation, Writing - original draft, Writing – review & editing. **Adrián de la Torre**: Sample analysis, Investigation, Methodology, Validation, Writing - review & editing. **Paloma Sanz**: Sample analysis, Investigation, Methodology, Validation, Writing - review & editing. **Isabelle Baldi**: sample collection, Writing – review & editing. **Paula Harkes**: sample collection, Writing – review & editing. **Esperanza Huerta-Lwanga**: sample collection, Writing – review & editing. **Trine Nørgaard**: sample collection, Writing – review & editing. **Matjaž Glavan**: sample collection, Writing – review & editing. **Igor Pasković**: sample collection, Writing – review & editing. **Marija Polić Pasković**: sample collection, Writing – review & editing. **Nelson Abrantes**: sample collection, Writing – review & editing. **Isabel Campos**: sample collection, Writing – review & editing. **Francisco Alcon**: sample collection, Writing – review & editing. **Josefina Contreras**: sample collection, Writing – review & editing. **Abdallah Alaoui**: sample collection, field work coordination, Writing – review & editing. **Jakub Hofman**: sample collection, Writing – review & editing. **Anne Vested**: sample collection, Writing – review & editing. **Mathilde Bureau**: sample collection, Writing – review & editing. **Virginia Aparicio**: sample collection, Writing – review & editing. **Daniele Mandrioli**: sample collection, Writing – review & editing. **Daria Sgargi**: sample collection, Writing – review & editing. **Hans Mol**: Investigation, Writing – review & editing. **Violette Geissen**: Conceptualization, Funding acquisition, Project administration, Writing – review & editing. **Vera Silva**: Sample collection, Conceptualization, Funding acquisition, Project administration, Writing – review & editing. **María Ángeles Martínez**: Conceptualization, Investigation, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Declaration of interests

☒The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Graphical abstract



Study design

Indoor dust of farmworker households

11 Case Study Sites: conventional/organic farming systems

Materials and Methods

- 198 pesticides: 156 active substances, 42 metabolites
- Methodology validation: SANTE 2020/128380, 11312/2021
- Multi-residue analysis (LC-MS/MS, GC-MS/MS)
- Glyphosate/AMPA analysis (LC-MS/MS)
- Organochlorinated pesticide analysis (GC-HRMS)

Results

CONVENTIONAL > ORGANIC

Indoor dust samples from organic farms showed lower number and levels of pesticide

INSECTICIDES > HERBICIDES > FUNGICIDES