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Spatio-temporal variation of outdoor and indoor pesticide air concentrations in homes near agricultural fields

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HIGHLIGHTS

- Outdoor air concentrations were a factor 5 to 10 higher during the spraying period as compared to the off-season period.
- Exposure to pesticides via air occurs throughout the entire year, with concentrations higher closer to the fields (<250 m).
- Concentrations in the indoor and outdoor air were moderately correlated for almost all pesticides.
- Main determinants of outdoor air concentrations were wind direction, evaporation and agricultural area surrounding a home.

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ABSTRACT

Background: Previous research has shown that many current-use pesticides can be detected in air around application areas. Environmental exposure to pesticides may cause adverse health effects, necessitating accurate assessment of outdoor and indoor air concentrations for people living close to spraying sites. We evaluated outdoor and indoor air concentrations of different pesticides, as well as factors influencing spatial and temporal variations.

Methods: We collected outdoor air samples at 58 homes located within 250 m of bulb fields and 15 control homes located further than 500 m from any agricultural field. Outdoor air sampling following a pesticide spray event was performed 24-h a day for 7 consecutive days. Two full day samples were collected at the same locations during a non-use period. In homes located within 50 m from agricultural fields (N = 18), indoor air was also sampled for the first 24 h after field spraying. Samples were analysed for a total of 46 pesticides and degradation products. From these, 11 were actively used on nearby fields, 3 were used in bulb disinfection and 6 were degradation products.

Results: Compared to non-use periods, pesticides concentrations were 5–10 times higher in outdoor air during application periods. Similar concentration differences were observed between exposed homes and controls both during pesticide use and non-use period. For 14 pesticides, there were moderate correlations (spearman > 0.4–0.7) between outdoor and indoor air concentrations. Wind direction, evapotranspiration and agricultural area surrounding a home were the most important determinants of air concentration of the applied pesticides.

Conclusions: This study provides strong evidence suggesting that environmental exposure to pesticides via air is not limited to the day of application and may occur year-round. The concentrations appeared higher during the use period. Factors influencing the local fate of pesticides in air may differ significantly between compounds.

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1. Introduction

Currently there are almost 500 active ingredients (pesticides) approved for use in the European Union (EU) (EC, 2020). These pesticides differ greatly in environmental persistence, toxicity and other physico-chemical properties. Questions are posed regarding the health effects of acute and long-term exposures of residents to these current-use pesticides (CUPs) (Rull et al., 2009; Galea et al., 2011; Park et al., 2020; Dereumeaux et al., 2020).

CUPs enter the atmosphere via spray drift (Zivan et al., 2016), volatilization from plants and soil (Bedos et al., 2002) or surface water (Liu et al., 2018), and erosion of agricultural soils (Yang et al., 2016). Pesticide degradation occurs, mainly via soil microorganisms (Parte et al., 2017), sunlight (Borrás et al., 2017) and atmospheric oxidants (Socorro et al., 2017). These compounds are redistributed (Tiryaki and Temur, 2010) into different environmental compartments (i.e. air, water, and soil) via wind dispersion, as well as via wet (Cindoruk and Ozturk, 2016) and dry deposition (Sauret et al., 2009). Some pesticides and degradation products may remain in the environment long after application. Environmental persistence is one of the main factors leading to public concern regarding pesticide use, exposure (Saillenfait and Malard, 2020) and possible health risks (Coscollà et al., 2017; Upadhayay et al., 2020).

One of the main environmental compartments where pesticides are present is air (e.g. López et al., 2017; Córdoba Gamboa et al., 2020). Large spatial and temporal differences in CUPs concentrations in the atmosphere have been reported (Désert et al., 2018; Villiot et al., 2018). Distance to the site of pesticide application is an important factor for the exposure level of residents (Brouwer et al., 2017; Teysseire et al., 2020). Several studies have reported possible links between non-occupational exposure via air and respiratory and allergic symptoms such as rhinitis (Mamane et al., 2015; Raherison et al., 2019). Therefore, to assess possible health effects of CUPs it is imperative to understand exposure distributions and drivers of the outdoor and indoor CUPs concentrations.

The specific aims of the study where: i) to investigate differences in air concentrations between different CUPs and to look at seasonal differences covering the *use* and *non-use* period; ii) to study the effect of distance from application site per CUP, by following specific spray applications and measuring the applied pesticides in outdoor and indoor air of surrounding homes; and iii) for the applied CUPs, to evaluate predicting factors (e.g. meteorological conditions and agricultural area surrounding a home) via statistical models.

2. Materials and methods

2.1. Study design

The observational study was carried out from May 2016 to December 2017. Outdoor air samples were taken during periods of *use* and *non-use* for 73 homes. 58 homes were located within 250 m from bulb fields, labelled Location Homes (Loc Homes); 15 were located further than 500 m from any agricultural field, labelled Control homes (Controls).

We tried to include Loc Homes situated at different distances from the bulbs fields in order to have a good representation of three different distance categories: homes located within 50 m, between 50 and 150 m and within 150 m and 250 m from the fields.

In the *use* period, measurements of CUPs in air outside homes were carried out 24-h a day for seven consecutive days. Sampling began when a selected field was sprayed. In the *non-use* period (i.e. period where the selected CUPs were not used), measurements were carried out 24-h a day on two consecutive days. Finally, for Loc Homes situated within 50 m (N = 18) from the selected fields, one 24-h indoor air sample was collected on the day spraying took place (i.e. the first day).

2.2. Pesticides & fields

A total of 46 CUPs and degradation products with a large range of physicochemical properties (see Supplementary material 2, Figueiredo et al., 2021) were selected for analysis (11 herbicides, 12 insecticides and 23 fungicides). The selection was based on CUPs frequently used in bulb fields (N = 37), CUPs used in bulb disinfection (N = 3), and degradation products of CUPs in the former groups (N = 6). A list of all analysed CUPs and degradation products can be found in Supplementary material A.

Eligible fields needed to have: flower bulbs present at the time of the study, farmers willing to participate, and at least one planned application of the selected CUP. A total of fourteen eligible fields were available and we randomly selected nine for the study (selected fields). Detailed information on the spraying applications in these fields, including CUPs used in the tank mixtures and quantities applied in each field have been previously described (Table 2, Figueiredo et al., 2021).

2.3. Loc Homes & controls

Homes close to fields were selected to study spatial variation of atmospheric concentrations in relation to local spraying applications. Homes further away were selected as controls to assess rural background concentrations.

We initialized a recruitment process which consisted of contacting the farmers of eligible bulb fields to participate in the study and then, in case of acceptance, contacting residents living close to those fields. All residential addresses within 250 m of the perimeter of the field (i.e. potential Loc Homes) were selected using the Dutch Register of Addresses and Buildings (BAG).

Potential Controls were selected using the BAG to identify residential addresses located more than 500 m from any agricultural fields, situated within 20 km from a selected field and located in a not strongly urbanized area (i.e. <1500 addresses/km2). This choice falls upon the fact that we wanted to capture the rural background concentrations. Homes located in fully urbanized areas (e.g. city) were not selected as these would not capture more local background effects (Coscollà et al., 2013; Balmer et al., 2019).

In total, 80 Loc Homes and 16 Controls were included in the study. Not all Loc Homes participated in the collection during both periods. Three homes missed a collection during the *use* period (i.e. seven-day measurements) due to holidays and four homes ended their participation while the study was ongoing.

Due to budget constraints not all samples were analysed. The selection of homes for which samples were analysed was done in a "semi-random" fashion per experiment. To have a good spatial distribution we randomly selected homes from predefined distance categories. In addition, homes both up and down-wind at time of the application were selected in all cases. All samples collected from Control homes were analysed.

In total, we analysed 369 and 134 outdoor air samples in Loc Homes during *use*, and *non-use* period, respectively. We also analysed 89 and 26 outdoor air samples in Controls during *use* and *non-use* period, respectively.

2.4. Sampling outdoor and indoor air

Air sampling system was constructed by TNO (OBO, 2019). In this system, air is sampled through a standard PM10 inlet (sampling the fraction of particles with an aerodynamic diameter smaller than 10 μm), drawn through a glass fibre filter, and a tube containing XAD-2 absorbent (Amberlite XAD-2). The filter/XAD-2 combination absorbs both gaseous and particle bound pesticides.

Sampling was started by remotely initiating air pumps using a GSM connection. This was done at the time the farmer notified the study team that the plan was to carry out the application on the selected field.

Sampling rate was controlled at 60–70 dm^3/min. Sampling started with the first inlet and filter set. After a 24 h period it automatically switched to use the second inlet and filter set, and so on. The same procedure was used for indoor sampling, with the only differences being that a pump with a lower capacity (drawing air at 25 dm^3/min) was used.

Outdoor air was collected, either in the front or back garden of the home. The indoor air was collected inside the home on the ground floor.

2.5. Chemical analyses

We transferred 30 g of XAD-2 resin and the 102 mm glass fibre filter from the sampling filter holder into a metal extracting cell. A mix of Deuterium labelled pesticides was added to the samples to act as an internal standard.

The samples were extracted using low temperature Accelerated Solvent Extraction (ASE) and concentrated to a fixed volume of 1000 μl. With each batch of samples, a reagent blank and a quality control sample were included. The quality control consists of 5 ng/pesticides mixture added to 10 g blank XAD-2. The pesticide concentration in the concentrated extracts was determined using liquid chromatograph coupled to a Mass spectrometer (LC-MS/MS). A detailed explanation can be found in OBO 2019. The LOD (lower limit of detection in ng/m3) was determined based on the average sample volume of air used. The lower limit of quantification (LOQ) was estimated as 10 times the standard deviation of the lowest concentration measured. The LOD was derived as three times this standard deviation. Limits of detection (LODs) varied between 0.003 and 0.03 ng/m^3. The LOD specific to each pesticide can be found in Supplementary material A.

To test the method and ensure no breakthrough of pesticides, two containers with XAD-2 were mounted one after the other. The first containing 8 g of XAD-2 and the second containing 4 g of XAD-2. Pesticide recovery on the XAD in both containers and the percentage of pesticide in the second holder indicates the degree of breakthrough. The results of the breakthrough measurements may be found in Supplemental material F.

2.6. Results below the limit of detection

Levels above the LOD but below the LOQ may be more accurate than imputed values (Succop et al., 2004), therefore we used the LOD as cut-off for detection. Imputation of levels below the LOD was performed using methods proposed by Lubin et al. (2004). The imputation consists of imputing the values below LOD based on the maximum likelihood estimation while accounting for both correlation and distribution of all pesticide data. Imputation was only done when the pesticide (or by-product) was detected (>LOD) in at least 40% of the measured samples.

2.7. Statistical analysis

During our measuring period, 7 CUPs were applied in the selected fields and 4 on fields within 250 m of location homes. Therefore, our focus was on this group of 11 CUPs. A full list of the 46 targeted pesticides and their detection frequency in both outdoor and indoor air samples can be found in Supplementary Material A and B, respectively. A list of relevant physico-chemical properties of the 11 focused pesticides can be found in Supplementary Material C.

Results of samples were grouped as *use* and *non-use* period separately for each CUP. This grouping was done using the information supplied by the farmers, who provided a list of the CUPs they used in each month.

Different statistical tests were used to analyse the data. All analyses were performed using *R, version 3.5* (R Core Team, 2017). The data was log10 transformed to meet the requirements of inferential statistics. Student's *t*-Test was used to determine whether CUPs concentrations differed significantly between *use* and *non-use* periods and between Loc Homes and Controls.

In some of the Loc Homes (N = 7) one or more residents were farmers (i.e. worked in agricultural sector). Therefore, samples from these homes (Farm Homes) were excluded from the general analysis. It is known that these farmers have a higher pesticide exposure (Curl et al., 2002) compared to other residents. This is not solely related to applications in the direct surroundings but also involves other factors such as the take-home (or para-occupational) pathway (Hyland et al., 2017). This refers to bringing home pesticides via clothing, shoes and other means (Deziel et al., 2017; Pardo et al., 2020). The detection frequency of all CUPs in both outdoor and indoor air samples in farm homes is shown in the supplementary material (A and B, respectively).

Concentration of CUPs in outdoor air applied in the selected fields were plotted as a function of distance. Here, we grouped distance by our a-priori defined distance categories (<50 m; 50–150 m; 150–250 m; >250 m; controls). This grouping was based on previous research done on drift effect on air concentrations downwind at different distances from agricultural crops (e.g. Table 5, Siebers et al., 2003). A trend line was added to the graphs using *loess* regression based on polynomial function.

Temporal variation of air concentrations is studied for CUPs sprayed in the selected fields during the *use* period. Plots were created for each applied CUP and respective location where the selected fields are located. A detailed list of the sprayed tank mixtures per location can be found in Figueiredo et al. (2021). Spearman's rank correlation coefficient was used to study the relationship between indoor and outdoor air concentrations. All 46 pesticides were included in this analysis if there were at least 10 pairs of detectable outdoor and indoor concentrations.

Mixed-effect models were built, using the *nlme* R package (Pinheiro et al., 2021), for each CUP to evaluate predicting factors of outdoor air concentrations. This analysis was only done with data collected in the *use* period and for pesticides that were applied during the measurement period (N = 11). Controls were excluded since level in these homes were considered mainly representative of background concentrations. We used mixed-effect models for variable selection rather than a fixed-effects structure to account for possible correlations in our outcome data due to the repeated measurements taken over time (7 consecutive days). Here, an autocorrelation structure (AR1) was added to the model making the correlations (r) decay over time with the assumption that concentrations measured shortly after the application are more strongly correlated (i.e. r(day1,day2) = r(day2,day3), but r (day1,day2) > r(day1,day7)).

For independent variables, daily average evapotranspiration, humidity, cloud cover, wind speed and wind direction were retrieved from the Royal Netherlands Meteorological Institute (KNMI). Evapotranspiration is calculated based on temperature and solar radiation. Hence, temperature was not included as an independent variable to avoid multicollinearity, given that it is highly correlated (Pearson's correlation coefficient [95%CI] = 0.92 [0.91, 0.93]) with evapotranspiration. Meteorological information is collected continuously and its available from De Kooy and Schiphol meteorological stations, both located near (<20 km) the selected fields. In addition, distance to closest agricultural field and total area of agricultural fields within 500 m from a home (Buffer) were taken from ArcGIS (ArcMap Version 10.4) based on the Netherlands 2017 crops registration ("Basis registratie Percelen 2017") (Esri Nederland) and on the Netherlands registration of addresses and buildings ("Basis registraties adressen en gebouwen") (Overheid).

A stepwise algorithm was run backward and forward for variable selection. Each model was built using a 5-fold cross validation, meaning that the dataset was split into 5 groups (with the condition that data from homes cannot be split). Four groups were used to build the model and the remaining group to test model fit. This step was repeated until all groups were used as test dataset. To see which variables were repeatedly selected (probability of inclusion > 95%), the 5-fold cross validation was executed 20 times resulting in 100 iterations.

From the collected information on the spraying techniques used, most fields within 250 m from the included homes reported very similar

application settings. These settings are: height of the boom sprayer, distance between nozzles, speed of the boom sprayer and spraying pressure used (see Supplementary material D). Sprayed quantities were also quite similar between different applications (see Table 2, Figueiredo et al., 2021). Hence, difference in application technique was not included in data interpretation.

Finally, household use of pesticides was also not taken into account in the interpretation of results. No home owner reported use of any of the included pesticides. See supplementary material D for a full list of reported used products and/or active ingredients.

3. Results and discussion

3.1. Concentrations in outdoor air

Fig. 1 shows the concentrations in the *use* and *non-use* period for both Loc Homes and Controls. Panel A displays the 7 CUPs that were applied in the selected fields. Panel B displays the 4 CUPs that were applied during the measurement period in other fields located within 250 m from Loc Homes. The highest 24-hr air concentrations were found for CUPs that were routinely applied and sprayed in higher dosages (CBS, 2020), such as chlorpropham and pendimethalin. These were found in concentrations up to 2754 ng/m3 and 123 ng/m3, respectively.

3.1.1. Use vs non-use period

Overall, concentrations were significantly higher (generally factor 5 to 10) in the *use* period than in the *non-use* period. For Loc Homes, concentrations were significantly higher in the *use* period for all CUPs except prochloraz. These results are not surprising, given that active spraying occurs during the *use* period and weather conditions are more favourable for pesticides to volatilise to air (warmer weather and less rainfall). For Controls, the same result was observed, with the exception of prochloraz and pendimethalin. For both these CUPs, concentrations in the *use* period were very similar to those in the *non-use* period. For pendimethalin, we hypothesize that this is a consequence of i) low persistence as a gas in the atmosphere but high persistence in soil (see Supplementary material C) and ii) the potential to be carried significantly through the air (Vighi et al., 2016). This combination of factors indicates that, although pendimethalin can reach Loc Homes and Controls in the gas-phase, it will be rapidly degraded. Therefore, the effect of spraying applications and volatilization during *use* period is less important than the contribution of pendimethalin bound to small particles (i.e. particle-phase) that are carried with the wind. This also would explain the similar concentrations in the *non-use* period.

The reasoning for no difference in prochloraz concentrations between Controls in *use* and *non-use* period is similar to pendimethalin. Prochloraz also shows low atmospheric persistence (<2 h, see Supplementary material C) and high persistence in soils (several months, EFSA, 2011).

Finally, CUPs in Fig. 1 with higher vapour pressures, namely chlorpropham, pendimethalin, dimethenamid-P and s-metolachlor (Lewis et al., 2016), show higher differences in concentrations between *use* and *non-use* period for Loc Homes. This observation is an indication that more volatile compounds will be found in higher concentrations in the *use* period. Whilst for pesticides that have lower vapour pressure and persist longer in agricultural soils, such as boscalid and flonicamid, differences in concentrations between both periods are less pronounced.

3.1.2. Loc Homes vs controls

Concentrations were, overall, significantly higher (generally factor 5 to 10) at Loc Homes compared to Controls. In the *use* period, concentrations were significantly higher in Loc Homes versus Controls for nearly all CUPs, with the exception of flonicamid and boscalid. For boscalid, the combination of persistence in soil (dt50 > 1 year) and atmospheric persistence (dt50 < half-day) leads to a continuous release (when weather conditions allow) to the atmosphere (Karlsson et al., 2016). These leads to an even distribution of this compound in a larger area. However, for flonicamid, the story is inversed but the outcome is the same. A low persistence in soil (days, Liu et al., 2014) is accompanied by a higher persistence in the atmosphere, which gives enough time for gas-phase flonicamid to travel over long distances during the *use* period.

For the *non-use* period, concentrations were significantly higher around Loc Homes for 8 out of the 11 sprayed CUPs. Similar to the *use* period, no difference was observed for flonicamid concentrations. In addition, no differences were observed for dimethenamid-P and tebuconazole. Both these CUPs are non-persistent in soil (Kočárek et al., 2018; Matadha et al., 2020) and rapidly degrade in the atmosphere. Therefore, given that it is a period where no sprayings occur, both dimethenamid-P and tebuconazole concentrations in Loc Homes and Controls are likely reflecting just background concentrations.

In sum, the differences shown in air concentrations over the use and non-use period and between location and control homes are largely explained by a combination of three factors. These are: persistence in the soil, medium to long-range transport of pesticides (influenced by atmospheric persistence) and release into the atmosphere via volatilization. The latter is mainly governed by some dominant physicochemical factors, such as vapour pressure (see Houbraken et al., 2015 for detailed explanation on volatilization) and by meteorological conditions.

3.2. Concentrations – distance from spraying field to home

A decrease in concentrations with distance from the main field is observed for all pesticides (Fig. 2). This finding is in line with conclusions drawn in other studies, where concentrations in ambient outdoor air were higher closer to the applying fields than further away (Garron et al., 2009; Coronado et al., 2011; Fang et al., 2017). Moreover, concentrations in controls are predominately governed by long-range (i.e. regional) transport of CUPs (Guida et al., 2018).

Above the x-axis are the number of samples per category. Summary statistics in boxplots (min, max, 1st and 3rd quartile and median). Black dotted line indicates the detection limit (LOD). Each dot above the black dotted line is a measured value and below is an imputed value. The blue line represents the trend (via Loess smoothing) without accounting for Controls, while the black line includes the controls as an additional group.

3.3. Temporal variability of outdoor air concentrations during use period

No consistent temporal pattern in outdoor air concentrations during the *use* period (day 1–7) was observed (Fig. 3). This is likely due to shifting wind directions and the fact that these homes are located in areas where there is an abundancy of agricultural fields in addition to the selected field. So, our measurements do not only capture the contribution of the selected field to air concentrations but also pesticide drift and volatilization from other crops that might be sprayed during that week. Also, in many of the sampling days, homes where not downwind from most of the agricultural fields, which indicates that measured concentrations are likely background. This explains the small variability in concentrations seen for some of the CUPs, such as fluopyram and tebuconazole (A-UP1), flonicamid (E-UP2) and prochloraz (D-UP2).

There are however singularities that are worth pointing out. We see that the temporal patterns are similar for CUPs present in the same tank mixture and applied in the same selected fields (pendimethalin and chlorpropham in C-UP1 and D-UP1; flonicamid and tebuconazole in E-UP2). We also see a clear influence of wind direction in some of the temporal trends, especially when most homes are located downwind of the agricultural fields. This is the case on day 3 of C-UP2 and day 5–7 of G-UP1 (displayed in Fig. 3). Here, we see an increase in air concentrations of tebuconazole (C-UP2) and metamitron (G-UP1), when the wind blows from east (day 3) and blows from south, respectively. These

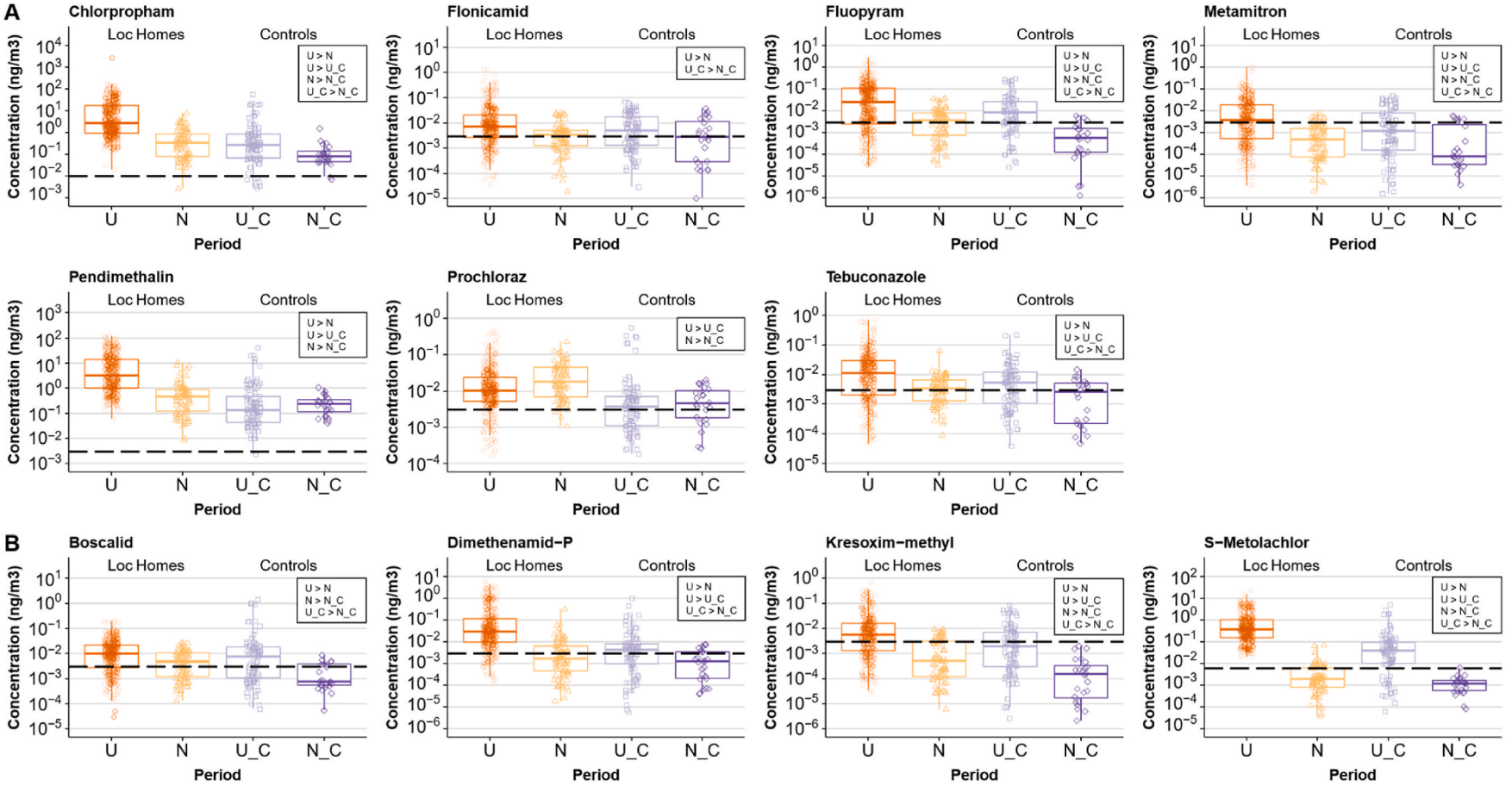

Fig. 1. Concentration in outdoor air of applied CUPs, grouped per location and period. Use (U) and Non-Use period (N) for locations and U_C and N_C for Controls. Panel (A) refers to CUPs applied in the main fields and panel (B) to CUPs used in other fields in the vicinity (<250 m). Summary statistics in boxplots (min, max, 1st and 3rd quartile and median). Black dotted line indicates the detection limit. Each dot above the black dotted line is a measured value and below that line is an imputed value. The average concentrations which are significantly higher (alpha = 0.05) than others are shown in the right top box of each graph.

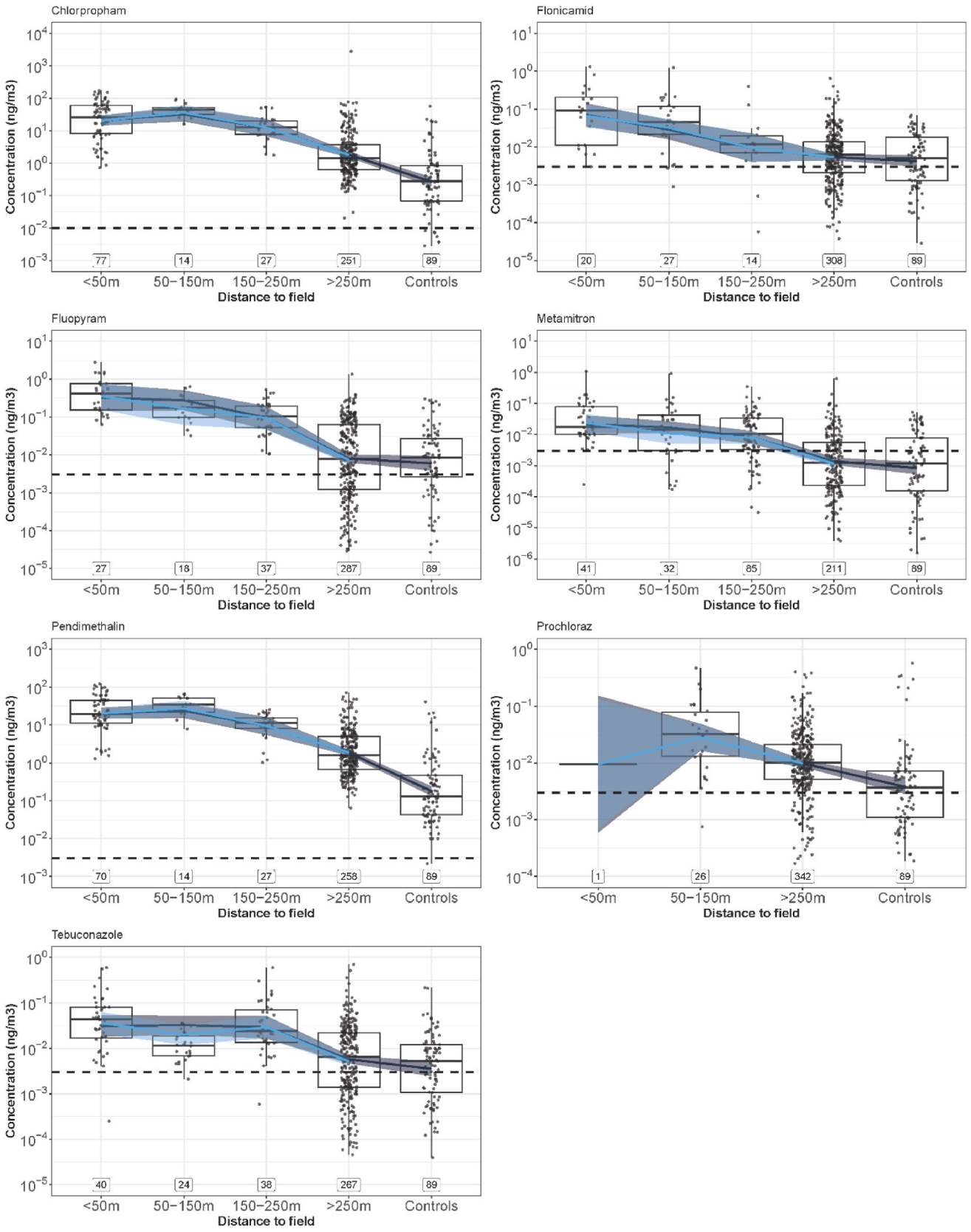

Fig. 2. Concentration of CUPs vs distance from home to applying field. Grouped by categories: <50 m – less than 50 m from applying field; 50–150 m – within 50–150 m from applying field; 150–250 m – within 150–250 m from applying field; >250 m – more than 250 m from applying field but still in the vicinity; Controls – more than 500 m from any field.

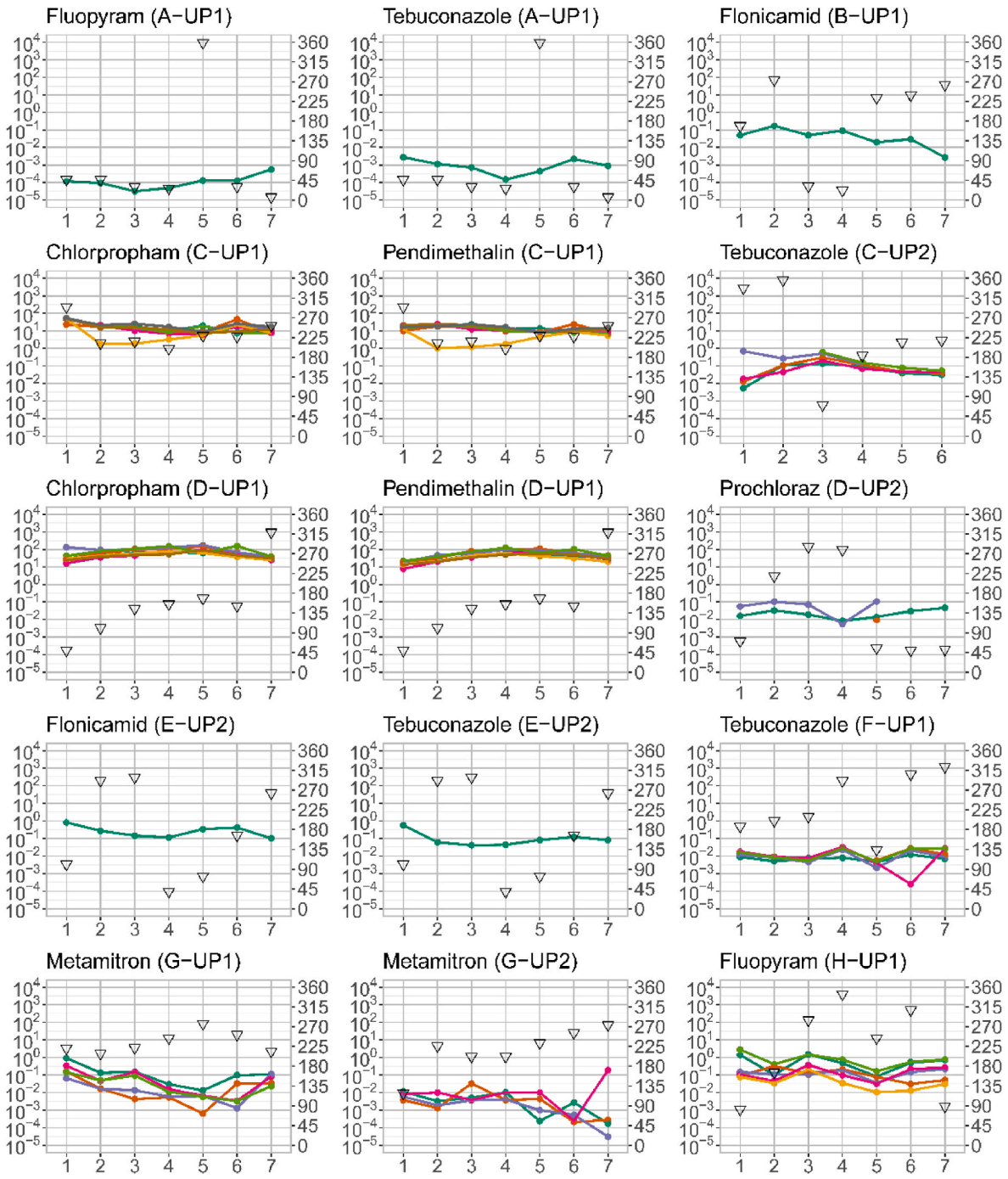

Fig. 3. Daily atmospheric concentrations at Loc Homes for CUPs applied in selected fields and wind direction during use period. Each plot represents a measured pesticide in a specific location (see Table 2, Figueiredo et al., 2021). For each plot: Lines represent the different homes where measurements were taken. Dots are measured cumulative 24-h air concentrations and inverted triangles are daily averaged wind direction. The x axis is days 1–7; primary y axis (left) is the concentration in outdoor air (ng/m^3), secondary y axis (right) is the wind direction (blowing from).

results show that concentration increases when the wind is coming from the source in the direction of the home, even when there was no active spraying at the source.

Our measurements also highlight important relating to temporal variation of CUPs concentrations in air. Increases in 3–4 orders of magnitude in concentrations can happen from one day to the other (e.g. Metamitron day 6–7 in G-UP2). We hypothesize that, given the sudden shift in concentrations, this is related to spray drift and not volatilization, and is likely to only occur if a home is downwind from an ongoing spraying application.

In summary, the temporal variability of CUPs concentrations near houses located in areas with intensive bulb growing is determined by two processes: 1) low background concentrations related to medium and long range transport of CUPs used in areas further away and 2) high concentrations related to use in the vicinity of a house located downwind. Air concentrations may vary several orders of magnitude.

3.4. Concentrations in indoor air

Fig. 4 shows the concentrations in indoor air of Loc Homes for both

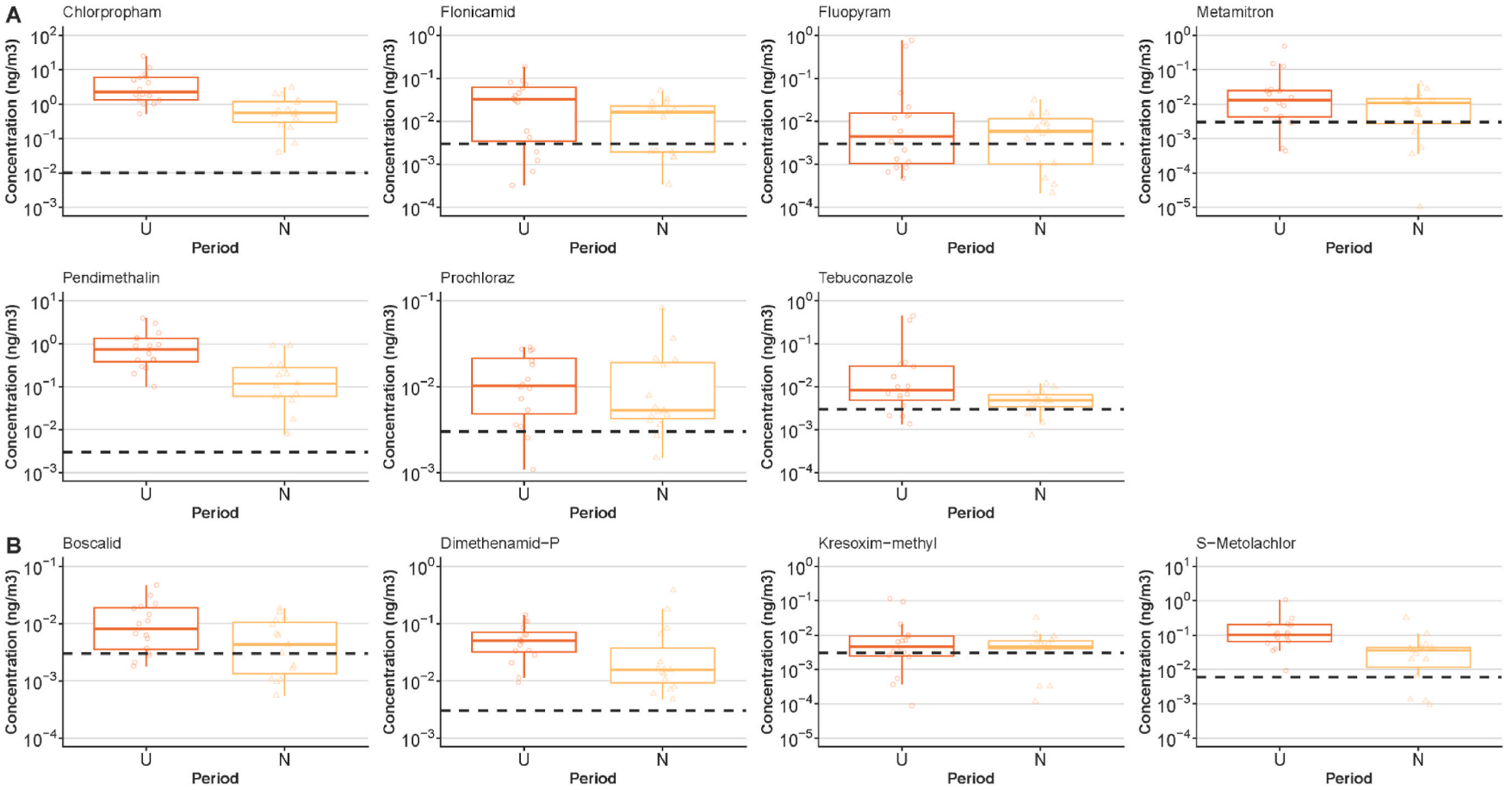

Fig. 4. Indoor air concentrations of applied CUPs, grouped per period. Use (U) and Non-Use period (N). Panel (A) refers to pesticides applied in the selected fields and panel (B) to pesticides used in other fields in the vicinity. Summary statistics in boxplots (min, max, 1st and 3rd quartile and median). Black dotted line indicates the detection limit. Each concentration above the level of the black dotted line is a measured value and below is an imputed value.

the *use* and *non-use* period. The observed indoor concentrations show patterns similar to the observed outdoor air concentrations. The highest measured 24-hr air concentrations were 25 ng/m3 and 4 ng/m3, from chlorpropham and pendimethalin, respectively.

For most pesticides, concentrations were significantly higher in the *use* period than they were in the *non-use* period, with the exception for flonicamid, prochloraz and kresoxim-methyl. For prochloraz we did not observe a difference in outdoor air concentrations between the *use* and *non-use* period. However, for flonicamid and kresoxim-methyl we did observe a difference in outdoor air concentrations between the *use* and *non-use* period, which is not reflected here in the indoor air concentrations. This is likely due to the fact that during the sampling day homes were not downwind of applications. Therefore measured concentrations in the *use* period are likely reflecting background concentrations.

We hypothesize that resuspended particle bound pesticides may contribute to the observed indoor air concentrations during the *non-use*. These are transported through air to the homes, settled inside the homes and persist more easily in the indoor environment (see comparison of pesticides in indoor and outdoor dust from Hung et al. (2018). Higher persistence in the indoor environment can be caused by limited ventilation, lower photodegradation (particularly in darker zones), and trapping surfaces (e.g. carpets).

3.5. Comparison between outdoor and indoor air concentrations

Table 1 shows the CUPs ordered by vapour pressure and the respective spearman correlation between paired outdoor and indoor samples (concentrations in Supplementary material C). The median day 1 indoor/outdoor ratio was 1.16, showing that overall, the concentrations were very similar between both environments on day 1. The minimum and maximum I/O ratios, 0.33 and 3.85, are found for Pendimethalin and Carbendazim, respectively.

The correlation between indoor and outdoor air concentrations was moderate for most pesticides (>0.4 for 76%). As discussed by Bennet & Furtaw, there is a large set of parameters such as type of flooring, dust loading and many more that are involved in the occurrence of pesticides in the indoor environment (Bennet and Furtaw, 2004). These parameters can affect individual pesticide concentrations in different ways making it a complex system (see Fig. 1, Liang et al., 2018). Important unknowns are the influence of indoor sources (e.g. resuspension) and sinks (e.g. accumulation in different indoor surfaces) on indoor pesticide concentrations (Weschler and Nazaroff, 2008; Chandra Yadav et al., 2020). These affect the ratio of outdoor-indoor concentrations. In addition, it should be realized that we are only looking at a small time window (1 day), so concentrations indoors can be quite different from those outdoors because equilibrium might not have been reached (Kulmala et al., 1999). Even with this complexity we observed that correlations seem to be higher for more volatile compounds, such as chlorpropham and s-metolachlor. We hypothesize that this is because gas-phase pesticides are less affected by indoor sources and sinks than those that are mainly bound to particles and usually present in settled dust (Wei et al., 2019). These indoor sources and sinks may cause quasi random fluctuations in indoor concentrations thereby preventing relationships between indoor and outdoor concentrations from being found.

Table 1
Spearman correlation: Outdoor and Indoor air concentrations.

CUPs[b]	ρ[a]	95% CI	p-value
Chlorpropham	0.60	[0.26, 0.81]	0.002
S-Metolachlor	0.68	[0.39, 0.85]	<0.001
Fluopyram-benzamide	0.41	[0.01, 0.70]	0.051
Pendimethalin	0.51	[0.13, 0.76]	0.012
Dimethenamid-P	0.65	[0.33, 0.83]	0.001
Toclofos-methyl	0.45	[0.06, 0.72]	0.028
Prochloraz	0.54	[0.18, 0.78]	0.007
Carbendazim	0.51	[0.14, 0.76]	0.011
Linuron	0.45	[0.06, 0.72]	0.028
Kresoxim-methyl	0.57	[0.22, 0.79]	0.004
Tebuconazole	0.42	[0.02, 0.70]	0.044
Fluopyram	0.49	[0.11, 0.75]	0.016
Flonicamid	0.33	[-0.09, 0.65]	0.118
Metamitron	0.36	[-0.05, 0.67]	0.081
Boscalid	0.43	[0.03, 0.71]	0.038
Prothioconazole-desthio	0.40	[-0.01, 0.69]	0.056
Pyraclostrobin	0.31	[-0.11, 0.63]	0.140

[a] Spearman correlation coefficient/
[b] Pesticides ordered by decreasing vapour pressure. Vapour pressure reported in Supplementary material A.

3.6. Variable selection for mixed effect models describing outdoor air concentrations

Results from the variable selection of the mixed-effect models are presented in Table 2. Wind direction was the variable selected most consistently (>95% of the iterations for 7 CUPs) as an important determinant of air concentrations amongst almost all CUPs. It stands to reason since wind direction determines dispersion. We also see that for some CUPs (Pendimethalin, Prochloraz, Tebuconazole and Metamitron) this variable was selected less often. This means that other parameters that determine concentration are important. In this group we find CUPs that are either frequently applied in the Netherlands (e.g. Pendimethalin) or CUPs with a high persistence in the environment, such as prochloraz and metamitron (Mamy et al., 2005). Both these characteristics can attenuate the variability of concentrations at a local scale (Chiaia--Hernandez et al., 2017; Désert et al., 2018). This brings out variables, such as the total area of agricultural fields within 500 m from a home (Buffer) and evapotranspiration (EV), as more important predictors for these CUPs.

An interesting finding is that EV was mainly selected for CUPs with lower vapour pressure. This is counterintuitive, since it was expected that this variable would be frequently selected for more volatile CUPs. There are two reasons that might explain this finding. Firstly, EV is calculated based on temperature and global radiation. Therefore, it might be acting as a proxy for sunlight photodegradation, which is one of the "most destructive pathways for pesticides" (cited from Katagi, 2004). However, this is unlikely given the short time scale of transport of sprayed pesticides from the fields to the homes. Secondly, we can see that Buffer was selected over EV for the more volatile compounds. It seems that, for this group, buffer acts as a proxy for emission to the atmosphere. Therefore, it is plausible that the area of agricultural crops around homes explains more than local EV for the one-week period.

Relative humidity was also selected in all models as an important explanatory variable for air concentrations of the three more volatile compounds (chlorpropham, pendimethalin and prochloraz). This finding can be partially explained as humidity goes hand in hand with temperature, which largely affects pesticide evaporation. But, it also might be an indicator of pesticide atmospheric degradation. For example, pendimethalin is degraded in the atmosphere by ozone (Mattei et al., 2019) and we know that, in sites with large leaf area index, there is a stronger ozone-humidity correlation (Kavassalis and Murphy, 2017).

Finally, Buffer was frequently selected as an important predictor for the more volatile compounds. Also, it seems that for some pesticides (metolachlor-S, dimethenamid-P and kresoxym-methyl), Buffer was selected over distance to closest field in almost all iterations. All three pesticides were not applied in the selected field but are reported as being applied in other fields in the vicinity (Panel B, Fig. 1).

3.7. Strengths & limitations

In our study we incorporated several pesticides with different physico-chemical properties. The collection of samples at different distances and at different periods provided a good indication of both temporal and spatial CUPs air concentration distribution. The inclusion

Table 2
Results of individual mixed effect models describing air concentrations. Percentage of the model runs in which the parameter is dominant.

CUPs[a]	Distance (m)[b]	Wind direction (degrees)	Wind speed (m/s)	Evapotranspiration (mm)	Buffer	Humidity (%)	Cloud cover
Chlorpropham	40	*100*	94	0	89	*100*	29
Metolachlor-S	1	*100*	35	63	*99*	46	17
Pendimethalin	63	12	7	39	*97*	*100*	*100*
Dimethenamid-P	3	*100*	88	90	*100*	29	0
Prochloraz	93	47	1	18	*100*	*100*	55
Kresoxym-methyl	4	*96*	*100*	*100*	*100*	4	5
Fluopyram	5	*100*	*100*	*100*	64	14	1
Tebuconazole	8	63	73	*100*	12	0	0
Flonicamid	6	*100*	47	24	85	1	*99*
Boscalid	82	*98*	1	*100*	*97*	9	23
Metamitron	8	21	93	*100*	52	38	26

[a] Vapour pressure reported in Table S1. Italic – Selected in more than 95% of the model runs.
[b] Distance to closest field (meters); Buffer – Area (radius 500 m) of agricultural crops surrounding a home (m2).

of both sprayed and non-sprayed CUPs is quite unique. This allowed us to see differences between these two and better understand their occurrence in the environment. Moreover, the incorporation of indoor air samples besides the outdoor air samples gave us new insights in the concentration equilibrium between both environments.

The large number of analysed samples allowed us to build a robust variable selection process in the empirical modelling. Also, by measuring for consecutive days we were able to account for the temporal variability.

Knowing the exact time of spraying for selected fields proved to be very important, allowing us to start sampling shortly before application and capture both drift and volatilization for an extended period (7 days). However, this might introduce some bias. Some farmers may change spraying practice when they are aware of our measurement target and strategies.

As a limitation, our targeted pesticide group did not comprise all CUPs and mixtures. Therefore, some of the drawn conclusions may not apply to pesticides outside of this selection. Also, samples were taken around fields where downward spraying occurred, therefore it remains to be seen if our results can be extrapolated to other crops and application technique (e.g. upward spraying).

Finally, when comparing concentrations between the different periods and locations we could only do an assessment based on available data. Some information that might be relevant to understand release of the different CUPs into the atmosphere, such as soil moisture and canopy height, was not available. This inherently leads to a more limited interpretation of our results.

4. Conclusions

We detected several pesticides and degradation products in air around both homes located close to (<250 m) and further away (>500 m) from spraying fields, during and outside spraying periods. Outdoor air concentrations were generally 5 to 10 times higher for homes close to fields (<250 m) than control homes (>500 m) for almost all CUPs. Outdoor and indoor air concentrations during the spraying of CUPs were also a factor of 5–10 higher than those outside the spraying periods.

Differences in outdoor air concentrations between location and control homes were also seen outside the spraying periods. This suggests evaporation of earlier used pesticides in or outside the study area. Frequently applied CUPs or CUPs with low persistence in the environment (soil or air) showed the largest contrast in average concentrations for the above comparisons.

We saw a decrease in outdoor air concentrations with distance from the field of application. This indicates that spatial variability in air concentrations around homes located at least 250 m of spraying fields is mostly driven by local spraying applications. Temporal variability in air concentrations during the spraying period seems to be mainly driven by local spraying applications and wind direction.

Concentrations in the indoor and outdoor air were moderately correlated for almost all CUPs and the observed correlations seemed to be higher for more volatile CUPs. Given that people spend most of their time in the indoor environment, it stands to reason that the next step in research should be to study the impact of different indoor sources and sinks on pesticide concentrations in indoor air and the temporal variance of indoor air concentrations during longer periods of time. A key source of pesticides inside houses, as suggested in literature, could be indoor dust.

Lastly, the area of agricultural crops surrounding the receptor (at least 250 m) seems to act as proxy for pesticide use in past years and persistence (i.e. past applications). This parameter should be taken into account, or at least not be neglected, in future modelling developments, given that it might explain part of the variability in pesticide atmospheric concentrations.

CRediT authorship contribution statement

Daniel M. Figueiredo: Conceptualization, Methodology, Validation, Formal analysis, Supervision, Data curation, Writing – original draft, Writing – review & editing, Formal analysis, Investigation. **Jan Duyzer:** Conceptualization, Methodology, Resources, Supervision, Writing – review & editing. **Anke Huss:** Conceptualization, Methodology, Writing – review & editing. **Esmeralda J.M. Krop:** Conceptualization, Methodology, Data curation, Visualization, Writing – review & editing, Project administration. **M.G. Gerritsen-Ebben:** Conceptualization, Methodology, Resources, Writing – review & editing. **Yvonne Gooijer:** Investigation, Writing – review & editing. **Roel C.H. Vermeulen:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration.

Declaration of competing interest

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2021.118612.

References

AG, Overheid.nl. https://data.overheid.nl/dataset/basisregistratie-adressen-en-gebouwen–bag-, accessed on 17 July 2020.

Balmer, J.E., Morris, A.D., Hung, H., Jantunen, L., Vorkamp, K., Rigét, F., Evans, M., Houde, M., Muir, D.C.G., 2019. Levels and trends of current-use pesticides (CUPs) in the arctic: an updated review, 2010–2018 Emerg. Contam. ISSN: 2405-6650 5, 70–88. https://doi.org/10.1016/j.emcon.2019.02.002, 2019.

Bedos, C., Cellier, P., Calvet, R., Barriuso, E., 2002. Occurrence of pesticides in the atmosphere in France. Agronomie 22, 35–49. https://doi.org/10.1051/agro:2001004.

Bennett, D.H., Furtaw, E.J., 2004. Fugacity-based indoor residential pesticide fate model. Environ. Sci. Technol. 38, 2142–2152.

Borrás, E., Ródenas, M., Vera, T., Gómez, T., Muñoz, A., 2017. Atmospheric degradation of the organothiophosphate insecticide – Pirimiphos-methyl. Sci. Total Environ. 579, 1–9. https://doi.org/10.1016/j.scitotenv.2016.11.009.

Brouwer, M., Huss, A., van der Mark, M., Nijssen, P.C.G., Mulleners, W.M., Sas, A.M.G., Vermeulen, R.C.H., 2017. Environmental exposure to pesticides and the risk of Parkinson's disease in The Netherlands. Environ. Int. 107 (January), 100–110. https://doi.org/10.1016/j.envint.2017.07.001.

CBS, 2020. Statistics Netherlands. Use plant protection products in agriculture; active substance, application. https://opendata.cbs.nl/#/CBS/nl/dataset/84010NED/table?defaultview. (Accessed 2 June 2020).

Chandra Yadav, I., Devi, N.L., Li, J., Zhang, G., 2020. Polychlorinated biphenyls and organochlorines pesticides in indoor dust: an exploration of sources and health exposure risk in a rural area (Kopawa) of Nepal. Ecotoxicol. Environ. Saf. 195, 110376. https://doi.org/10.1016/j.ecoenv.2020.110376.

Chiaia-Hernandez, A.C., Keller, A., Wächter, D., Steinlin, C., Camenzuli, L., Hollender, J., Krauss, M., 2017. Long-term persistence of pesticides and TPs in archived agricultural soil samples and comparison with pesticide application. Environ. Sci. Technol. 51 (18), 10642–10651. https://doi.org/10.1021/acs.est.7b02529.

Cindoruk, S.S., Ozturk, E., 2016. Atmospheric deposition of organochlorine pesticides by precipitation in a coastal area. Environ. Sci. Pollut. Control Ser. 23 (24), 24504–24513. https://doi.org/10.1007/s11356-016-6697-y.

Córdoba Gamboa, L., Solano Diaz, K., Ruepert, C., van Wendel de Joode, B., 2020. Passive monitoring techniques to evaluate environmental pesticide exposure: results from the Infant's Environmental Health study (ISA). Environ. Res. 184 (September 2019), 109243. https://doi.org/10.1016/j.envres.2020.109243.

Coronado, G.D., Holte, S., Vigoren, E., Griffith, W.C., Barr, D.B., Faustman, E., 2011. Organophosphate pesticide exposure and residential proximity to nearby fields: evidence for the drift pathway. J. Occup. Environ. Med. 53, 884–891. https://doi.org/10.1097/JOM.0b013e318222f03a.

Coscollà, C., Hart, E., Pastor, A., Yusà, V., 2013. LC-MS characterization of contemporary pesticides in PM10 of Valencia Region, Spain. Atmos. Environ. 77, 394–403. https://doi.org/10.1016/j.atmosenv.2013.05.022.

Coscollà, C., López, A., Yahyaoui, A., Colin, P., Robin, C., Poinsignon, Q., Yusà, V., 2017. Human exposure and risk assessment to airborne pesticides in a rural French community. Sci. Total Environ. 584–585, 856–868. https://doi.org/10.1016/j.scitotenv.2017.01.132.

Curl, C.L., Fenske, R.A., Kissel, J.C., Shirai, J.H., Moate, T.F., Griffith, W., Thompson, B., 2002. Evaluation of take-home organophosphorus pesticide exposure among agricultural workers and their children. Environ. Health Perspect. 110 (12), 787–792. https://doi.org/10.1289/ehp.021100787.

Dereumeaux, C., Fillol, C., Quenel, P., Denys, S., 2020. Pesticide exposures for residents living close to agricultural lands: a review. Environ. Int. 134 (May 2019), 105210. https://doi.org/10.1016/j.envint.2019.105210.

Désert, M., Ravier, S., Gille, G., Quinapallo, A., Armengaud, A., et al., 2018. Spatial and Temporal Distribution of Current-Use Pesticides in Ambient Air of Provence-Alpes-Côted'Azur Region and Corsica, France, vol. 192. Atmospheric Environment, Elsevier, pp. 241–256. https://doi.org/10.1016/j.atmosenv.2018.08.054, 2018.

Deziel, N.C., Beane Freeman, L.E., Graubard, B.I., Jones, R.R., Hoppin, J.A., Thomas, K., Friesen, M.C., 2017. Relative contributions of agricultural drift, para-occupational, and residential use exposure pathways to house dust pesticide concentrations: meta-regression of published data. Environ. Health Perspect. 125 (3), 296–305. https://doi.org/10.1289/EHP426.

EC, 2020 (Last access March) 2020. http://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/public/?event=activesubstance.selection&language=EN.

EFSA. European Food Safety Authority, 2011. Conclusion on the peer review of the pesticide risk assessment of the active substance prochloraz, 2323 EFSA J. 9 (7), 120. https://doi.org/10.2903/j.efsa.2011.2323. Available online: www.efsa.europa.eu/efsajournal.html.

Fang, Y., Nie, Z., Die, Q., Tian, Y., Liu, F., He, J., Huang, Q., 2017. Organochlorine pesticides in soil, air, and vegetation at and around a contaminated site in southwestern China: concentration, transmission, and risk evaluation. Chemosphere 178, 340–349. https://doi.org/10.1016/j.chemosphere.2017.02.151.

Figueiredo, D.M., Krop, E.J., Duyzer, J., Gerritsen-Ebben, R.M., Gooijer, Y.M., Holterman, H.J., Huss, A., Jacobs, C.M., Kivits, C.M., Kruijne, R., Mol, H.J., Oerlemans, A., Sauer, P.J., Scheepers, P.T., van de Zande, J.C., van den Berg, E., Wenneker, M., Vermeulen, R.C., 2021. Research on exposure of residents to pesticides in The Netherlands: study Protocol. JMIR Res. Protoc. 10 (4), e27883 https://doi.org/10.2196/27883, 2021.

Galea, K.S., Maccalman, L., Jones, K., Cocker, J., Teedon, P., Cherrie, J.W., Tongeren, M. Van, 2015. Comparison of residents pesticide exposure with predictions obtained using the UK regulatory exposure assessment approach. Regul. Toxicol. Pharmacol. 73 (2), 634–643. https://doi.org/10.1016/j.yrtph.2015.09.012.

Garron, C.A., Davis, K.C., Ernst, W.R., 2009. Near-field air concentrations of pesticides in potato agriculture in Prince Edward Island. Pest Manag. Sci. 65 (6), 688–696. https://doi.org/10.1002/ps.1746.

Guida, Y. de S., Meire, R.O., Torres, J.P.M., Malm, O., 2018. Air contamination by legacy and current-use pesticides in Brazilian mountains: an overview of national regulations by monitoring pollutant presence in pristine areas. Environ. Pollut. 242, 19–30. https://doi.org/10.1016/j.envpol.2018.06.061.

Houbraken, M., van den Berg, F., Butler Ellis, C.M., Dekeyser, D., Nuyttens, D., De Schampheleire, M., Spanoghe, P., 2016. Volatilisation of pesticides under field conditions: inverse modelling and pesticide fate models. Pest Manag. Sci. 72 (7), 1309–1321. https://doi.org/10.1002/ps.4149.

Hung, C.C., Huang, F.J., Yang, Y.Q., Hsieh, C.J., Tseng, C.C., Yiin, L.M., 2018. Pesticides in indoor and outdoor residential dust: a pilot study in a rural county of Taiwan. Environ. Sci. Pollut. Control Ser. 25 (23), 23349–23356. https://doi.org/10.1007/s11356-018-2413-4.

Hyland, C., Laribi, O., 2017. Review of take-home pesticide exposure pathway in children living in agricultural areas. Environ. Res. 156 (March), 559–570. https://doi.org/10.1016/j.envres.2017.04.017.

Karlsson, A.S., Weihermüller, L., Tappe, W., Mukherjee, S., Spielvogel, S., 2016. Field scale boscalid residues and dissipation half-life estimation in a sandy soil. Chemosphere 145, 163–173. https://doi.org/10.1016/j.chemosphere.2015.11.026.

Katagi, T., 2004. Photodegradation of pesticides on plant and soil surfaces. In: Ware, G. W. (Ed.), Reviews of Environmental Contamination and Toxicology. Continuation of Residue Reviews, vol. 182. Springer, New York, NY. https://doi-org.proxy.library.uu.nl/10.1007/978-1-4419-9098-3_1.

Kavassalis, S.C., Murphy, J.G., 2017. Understanding ozone-meteorology correlations: a role for dry deposition. Geophys. Res. Lett. 44 (6), 2922–2931. https://doi.org/10.1002/2016GL071791.

Kočárek, M., Kodešová, R., Sharipov, U., Jursík, M., 2018. Effect of adjuvant on pendimethalin and dimethenamid-P behaviour in soil, 2018 J. Hazard Mater. 354, 266–274. https://doi.org/10.1016/j.jhazmat.2018.04.073. ISSN 0304-3894.

Kulmala, M., Asmi, A., Pirjola, L., 1999. Indoor air aerosol model: the effect of outdoor air, filtration and ventilation on indoor concentrations. Atmos. Environ. 33 (14), 2133–2144. https://doi.org/10.1016/S1352-2310(99)00070-9.

Lewis, K.A., Tzilivakis, J., Warner, D., Green, A., 2016. An international database for pesticide risk assessments and management. Hum. Ecol. Risk Assess. 22 (4), 1050–1064. https://doi.org/10.1080/10807039.2015.1133242.

Liang, Y., Bi, C., Wang, X., Xu, Y., 2019. A general mechanistic model for predicting the fate and transport of phthalates in indoor environments. Indoor Air 29 (1), 55–69. https://doi.org/10.1111/ina.12514.

Liu, X., Zhu, Y., Dong, F., Xu, J., Zheng, Y., 2014. Dissipation and residue of flonicamid in cucumber, apple and soil under field conditions. Int. J. Environ. Anal. Chem. 94 (7), 652–660. https://doi.org/10.1080/03067319.2013.871714.

Liu, L., Tang, J., Zhong, G., Zhen, X., Pan, X., Tian, C., 2018. Spatial distribution and seasonal variation of four current-use pesticides (CUPs) in air and surface water of the Bohai Sea, China. Sci. Total Environ. 621, 516–523. https://doi.org/10.1016/j.scitotenv.2017.11.282.

López, A., Yusà, V., Muñoz, A., Vera, T., Borràs, E., Ródenas, M., Coscollà, C., 2017. Risk assessment of airborne pesticides in a Mediterranean region of Spain. Sci. Total Environ. 574, 724–734. https://doi.org/10.1016/j.scitotenv.2016.08.149.

Lubin, J.H., Colt, J.S., Camann, D., et al., 2004. Epidemiologic evaluation of measurement data in the presence of detection limits. Environ. Health Perspect. 112 (17), 1691–1696. https://doi.org/10.1289/ehp.7199, 2004.

Mamane, A., Raherison, C., Tessier, J.F., Baldi, I., Bouvier, G., 2015. Environmental exposure to pesticides and respiratory health. Eur. Respir. Rev. 24, 462–473. https://doi.org/10.1183/16000617.00006114.

Mamy, L., Barriuso, E., Gabrielle, B., 2005. Environmental fate of herbicides trifluralin, metazachlor, metamitron and sulcotrione compared with that of glyphosate, a substitute broad spectrum herbicide for different glyphosate-resistant crops. Pest Manag. Sci. 61, 905–916. https://doi-org.proxy.library.uu.nl/10.1002/ps.1108.

Mattei, C., Dupont, J., Wortham, H., Quivet, E., 2019. Influence of pesticide concentration on their heterogeneous atmospheric degradation by ozone. Chemosphere 228, 75–82. https://doi.org/10.1016/j.chemosphere.2019.04.082.

Matadha, N.Y., Mohapatra, S., Siddamallaiah, L., Udupi, V.R., Gadigeppa, S., Raja, D.P., Donagar, S.P., Hebbar, S.S.(, 2020. Persistence and dissipation of fluopyram and tebuconazole on bell pepper and soil under different environmental conditions. Int. J. Environ. Anal. Chem. https://doi.org/10.1080/03067319.2019.1704745.

OBO, 2019. Research on exposure of residents to pesticides in The Netherlands: OBO flower bulbs. Onderzoek Bestrijdingsmiddelen en Omwonenden.

Pardo, L.A., Beane Freeman, L.E., Lerro, C.C., et al., 2020. Pesticide exposure and risk of aggressive prostate cancer among private pesticide applicators. Environ. Health 19, 30. https://doi.org/10.1186/s12940-020-00583-0.

Park, S., Choi, J.R., Kim, S.K., Lee, S., Lee, K., Kim, J.Y., Oh, S.S., Koh, S.B., 2020. Increased risk of atherosclerosis associated with pesticide exposure in rural areas in Korea. PLoS One 15 (5), 1–11. https://doi.org/10.1371/journal.pone.0232531.

Pinheiro, J., Bates, D., DebRoy, S., Sarkar, D., R Core Team, 2021. Nlme: Linear and Nonlinear Mixed Effects Models. R Package Version 3.1, p. 152. https://CRAN.R-project.org/package=nlme.

R Core Team, 2017. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. URL. https://www.R-project.org/.

Raherison, C., Baldi, I., Pouquet, M., Berteaud, E., Moesch, C., Bouvier, G., Canal-Raffin, M., 2019. Children: a pilot study. Environ. Res. 169 (November 2018), 189–195. https://doi.org/10.1016/j.envres.2018.11.002.

Rull, R.P., Gunier, R., Von Behren, J., Hertz, A., Crouse, V., Buffler, P.A., et al., 2009. Residential proximity to agricultural pesticide applications and childhood acute lymphoblastic leukemia. Environ. Res. 109, 891–899. https://doi.org/10.1016/j.envres.2009.07.014.

Saillenfait, A.M., Malard, S., 2020. Human risk associated with long-term exposure to pyrethroid insecticides. In: Eljarrat, E. (Ed.), Pyrethroid Insecticides, The Handbook of Environmental Chemistry, vol. 92. Springer, Cham. http://doi-org-443.webvpn.fjmu.edu.cn/10.1007/698_2019_427.

Sauret, N., Wortham, H., Strekowski, R., Herckès, P., Nieto, L.I., 2009. Comparison of annual dry and wet deposition fluxes of selected pesticides in Strasbourg, France. Environ. Pollut. 157 (1), 303–312. https://doi.org/10.1016/j.envpol.2008.06.034.

Siebers, J., Binner, R., Wittich, K.P., 2003. Investigation on downwind short-range transport of pesticides after application in agricultural crops. Chemosphere 51 (5), 397–407. https://doi.org/10.1016/S0045-6535(02)00820-2.

Socorro, J., Lakey, P.S.J., Han, L., Berkemeier, T., Lammel, G., Zetzsch, C., Pöschl, U., Shiraiwa, M., 2017. Heterogeneous OH oxidation, shielding effects, and implications for the atmospheric fate of terbuthylazine and other pesticides. Environ. Sci. Technol. 51 (23), 13749–13754. https://doi.org/10.1021/acs.est.7b04307.

Succop, P.A., Clark, S., Chen, M., Galke, W., 2004. Imputation of data values that are less than a detection limit. J. Occup. Environ. Hyg. 1, 436–441. https://doi.org/10.1080/15459620490462797, 2004.

Teysseire, R., Manangama, G., Baldi, I., Carles, C., Brochard, P., Bedos, C., Delva, F., 2020. Assessment of residential exposures to agricultural pesticides: a scoping review. PLoS One 15 (4), 1–19. https://doi.org/10.1371/journal.pone.0232258.

Tiryaki, O., Temur, C., 2010. The fate of pesticide in the environment. J. Biol. Environ. Sci. 4 (10), 29–38.

Upadhayay, J., Rana, M., Juyal, V., Bisht, S.S., Joshi, R., 2020. Impact of pesticide exposure and associated health effects. Pestic. Crop Prod. 69–88. https://doi.org/10.1002/9781119432241.ch5.

Vighi, M., Matthies, M., Solomon, K.R., 2017. Critical assessment of pendimethalin in terms of persistence, bioaccumulation, toxicity, and potential for long-range transport. J. Toxicol. Environ. Health, Part B 20 (1), 1–21. https://doi.org/10.1080/10937404.2016.1222320.

Villiot, A., Chrétien, E., Drab-Sommesous, E., Rivière, E., Chakir, A., Roth, E., 2018. Temporal and seasonal variation of atmospheric concentrations of currently used pesticides in Champagne in the centre of Reims from 2012 to 2015. Atmos. Environ. 174 (November 2017), 82–91. https://doi.org/10.1016/j.atmosenv.2017.11.046.

Wei, W., Ramalho, O., Mandin, C., 2019. A long-term dynamic model for predicting the concentration of semi volatile organic compounds in indoor environments: application to phthalates. Build. Environ. 148 (October 2018), 11–19. https://doi.org/10.1016/j.buildenv.2018.10.044.

Weschler, C.J., Nazaroff, W.W., 2010. SVOC partitioning between the gas phase and settled dust indoors. Atmos. Environ. 44 (30), 3609–3620. https://doi.org/10.1016/j.atmosenv.2010.06.029.

Yang, X., Van Der Zee, S.E.A.T.M., Gai, L., Wesseling, J.G., Ritsema, C.J., Geissen, V., 2016. Integration of transport concepts for risk assessment of pesticide erosion. Sci. Total Environ. 551–552, 563–570. https://doi.org/10.1016/j.scitotenv.2016.02.058.

Zivan, O., Segal-Rosenheimer, M., Dubowski, Y., 2016. Airborne organophosphate pesticides drift in Mediterranean climate: the importance of secondary drift. Atmos. Environ. 127, 155e162. https://doi.org/10.1016/j.atmosenv.2015.12.003.