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Ambient air concentrations of plant protection products: Data collection for the combined air concentration database and associated risk assessment

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ABSTRACT

CropLife Europe collected literature values from monitoring studies measuring air concentrations of Plant Protection Products (PPPs) that may be inhaled by humans located in rural areas but not immediately adjacent to PPP applications. The resulting "Combined Air Concentration Database" (CACD) was used to determine whether air concentrations of PPPs reported by the French "Agency for Food, Environmental and Occupational Health & Safety" (ANSES) are consistent with those measured by others to increase confidence in values of exposure to humans. The results were put into risk assessment context. Results show that 25–90% of samples do not contain measurable PPP concentrations. Measured respirable fractions were below EU default air concentrations used for risk assessment for resident exposure by the European Food Safety Authority. All measured exposures in the CACD were also below established toxicological endpoints, even when considering the highest maximum average reported concentrations and very conservative inhalation rates. The highest recorded air concentration was for prosulfocarb (0.696 μg/m^3 measured over 48 h) which is below the EFSA default limit of 1 μg/m^3 for low volatility substances. In conclusion, based on the CACD, measured air concentrations of PPPs are significantly lower than EFSA default limits and relevant toxicological reference values.

1. Introduction

Plant Protection Products (PPPs) are released into the environment as a result of their application to crops. They can enter the atmosphere during or after application via three different emission sources (Coscollà et al., 2013): 1) spray drift during an application, 2) volatilisation occurring post-application via emissions from the soil and plants, which can take place days or weeks after an application and 3) wind erosion of soil particles containing adsorbed PPPs into the troposphere occurring for several days or weeks after an application. From these primary emission sources, PPPs can enter the atmosphere as a gas or as an aerosol. The gas to particle distribution and the particle transformation rate are two processes that can explain the particle size distribution of PPPs in the atmosphere (Coscollà et al., 2013). Humans may potentially be exposed on a daily basis to a wide range of airborne contaminants from a wide range of sources, both outdoors and inside homes and work locations. When considering human exposure to an airborne contaminant, it is important to assess its prevalence and, therefore, the likelihood of exposure, as well as any associated risk from the exposure.

Exposure to bystanders and residents is evaluated for every PPP formulation on the market, taking into account several routes of exposure (dermal, oral and inhalation), spray drift, drift deposit, and re-entry into the treated crop. The estimation of inhalation exposure to PPP vapour uses very conservative values, as demonstrated by Felkers et al. (2022a and b). Therefore, we have evaluated measured concentrations of residues of pesticides that are conveyed via the air and to which the general population can be exposed. To this end, air concentration monitoring data from publications, as well as monitoring studies conducted by agencies and institutions, were compiled, and compared to relevant toxicological values. The project is called the "Pesticides in Air Project" and was set up by CropLife Europe (CLE, formerly the European

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Abbreviations:

(AEC)	Acceptable Exposure Concentration
(AOEL)	Acceptable Operator Exposure Limit
(CACD)	Combined Air Concentration Database
(DNEL)	Derived No Effect Level
(EFSA)	European Food Safety Authority
(ANSES)	French “Agency for Food, Environmental and Occupational Health & Safety”
(LOD)	Limit of Detection
(LOQ)	Limit of Quantification
(PPPs)	Plant Protection Products
(PUF)	Polyurethane Foam
(ISSeP)	Scientific Institute of Public Services
(SERI)	Systemic exposure of residents via the inhalation route

Crop Protection Association) because air concentrations of pesticides are increasingly measured and reported by agencies and institutions, thus providing a rich source of information and quality data. The outcome of the Pesticides in Air Project was the “Combined Air Concentration Database” (CACD). This contains air concentrations of PPPs obtained from a report published by the French “Agency for Food, Environmental and Occupational Health & Safety” ANSES (2020), literature data, as well as the PROPULPPP project (Ruthy et al., 2019) in which air concentrations of PPPs in Belgium were measured. The CACD also contains data from regulatory documents reporting PPP concentrations in air at the regional and/or national scale, as well as additional data from industry.

The ANSES report represented the first harmonized inventory of air concentrations of pesticide active substances outside of situations in close proximity to applications or under the direct influence of a single crop. The ANSES study followed a single sampling strategy and analytical protocol, allowing a direct comparison of all the data within France. Therefore, this current CLE project aimed to determine whether air concentrations of PPPs measured by other researchers were similar or significantly different to those reported by ANSES. We also used the CACD to compare measured air concentrations in monitoring studies with near-field default values defined by the European Food Safety Authority (EFSA) and, for several PPPs, with the relevant toxicity value of the active substance. Risk assessments are presented for 10 PPPs with the highest number of reported vapour concentrations (chlorothalonil, chlorpyrifos, diflufenican, dimethachlor, dimethoate, lambda-cyhalothrin, MCPA, pendimethalin, prosulfocarb and trifluralin (Coscollà et al., 2017; López et al., 2017). The overall aim of this evaluation was show that PPP residues are present in the air at very low concentrations and are thus of no health concern to the population.

2. Methods

2.1. Open literature search method

The open literature search was carried out via the Web of Science (Clarivate Analytics https://access.webofknowledge.com/) and PubMed (https://pubmed.ncbi.nim.nih.gov/). Both databases were searched over the period 2010 to 2020 using a search string: (pesticide OR “plant protection product”) AND (emission* OR occurrence OR drift OR concentration OR measure* OR monitor* OR “air quality”) AND (indoor* OR “in-door”” OR outdoor OR atmosphere* OR air). This retrieved 4617 papers following the removal of duplicates. Although the search was for worldwide reports, the papers selected covered mainly Europe. Relevant papers (based on the search strings used during the literature search) were identified in an initial screen based on abstract content, i.e., mention of pesticides or specific chemicals and air concentrations and other acceptance criteria. This step reduced the number of papers to 144 potential candidate papers. The number of potential candidate papers was further reduced to 41 by considering the relevance and reliability (Klimisch et al., 1997) and which could be thoroughly reviewed and interpreted. For example, the following categories were made based on phrases:

- Reliability 1: Guideline study (e.g., OECD); method validated; comparable to a guideline study; test procedure according to national standards.
- Reliability 2: Acceptable, method validated; well-documented publication/study report which meets basic scientific principles; basic data given comparable to guidelines/standards; comparable to guideline study with acceptable restrictions.
- Reliability 3: Method not validated; documentation insufficient for assessment; does not meet important criteria of current standard methods; relevant methodological deficiencies; unsuitable test system.
- Reliability 4: Only a short abstract is available; only secondary literature available (review, tables, books etc.).
- Reliability 5: Regulatory document.
- Reliability 6: Not relevant to the specific project aims and objectives.

All but 3 of the 41 candidate papers were category 2 papers according to Klimisch et al. (1997) (reliable with restrictions). The remaining 3 papers were category 3 (not reliable). The papers considered to be the most relevant to the current study were fully reviewed, and data were extracted into the CACD database (Supplementary Table 1, which also contains the references). Of note, data for the 10 PPPs used for the risk assessment calculations in Table 2 were all taken from two publications, Coscollà et al. (2017) and (López et al., 2017) (both are from the same research group).

2.2. Methods used to generate regulatory/regional/national data

2.2.1. ANSES project methods

The ANSES report (ANSES, 2020) summarized results from a year-long sampling strategy (June 2018 to June 2019) where 1800 samples were collected from 50 rural, urban and semi-urban sampling sites distributed throughout France and its territories. Seventy-five PPP active substances (including 1 metabolite) were monitored following a harmonized methodology. The sampling was designed to capture semi-volatile substances. Volatility of the active substances was defined according to EFSA guidance (EFSA, 2014). In addition, 8 sites were specifically set up to measure 3 polar substances (glyphosate, AMPA and glufosinate). The frequency of sampling varied according to the agricultural profile and application periods but remained homogeneous across all 50 sites. The samplers were positioned at least 200 m from an agricultural plot, so the results were not influenced directly by the application (the objective was not to look at concentration of pesticides at vicinity of treated fields but rather to measure them at a minimal distance). Weekly samples (7 days/168 h) were collected using low volume samplers (pump flow rate of 1 m^3/h) with a sampling head of particle size cut-off 10 μm (PM_{10}) apart from for glyphosate, glufosinate and AMPA (polar substances) which were collected using high volume (pump flow rate of 30 m^3/h) samplers equipped with a cut off sampling head particle size 10 μm (PM_{10}) over a period of 48 h. The PM_{10} particle size cut-off was used to assess the fraction of inhaled particles. Samples were taken at a height of at least 1.5 m from the ground to represent the height of the breathing zone for adults. Filters and PUF (Polyurethane Foam) collecting media were used to capture the particulate and gas phases, respectively. A single laboratory conducted all the analysis. Each active substance had a single Limit of Detection (LOD) and Limit of Quantification (LOQ). Particulate (PM_{10}, representing the inhalable fraction) and gaseous phases were collected but a common extraction method was used to determine the concentration on both types of sampling media (filters and PUF plugs). The detection and quantification frequencies were calculated from the total number of analyses obtained from all the sites throughout the year. These calculations, therefore, do not consider the variability of sampling over the year. The annual average concentration was calculated from the monthly concentrations, which themselves were calculated from individual concentration data and weighted according to the duration of sampling for each month. This approach eliminates the variability of the sampling throughout the year (ANSES, 2020).

2.2.2. PROPULPPP project methods

The PROPULPPP project (Ruthy et al., 2019) was designed to assess the exposure of the Walloon population in Belgium to PPPs and to recommend protective measures intended to limit exposure. It was conducted in 2018 and was coordinated by the Scientific Institute of Public Services (ISSeP) in partnership with the Walloon Agricultural Research Center (CRA-W) and the Gembloux Agro-Bio Tech Plant Pharmacy Laboratory (ULiege). The PROPULPPP study measured pesticide air concentrations (via drift, volatilisation, aerosols, and particles) at or near sites of pesticide application durations over 2, 12, 24 and 48 h after the application. This point can be considered as a worst-case situation when compared to collection design of ANSES campaign. Measurements were also taken at sites determined as "at risk" (near schools or nurseries). The PROPULPPP study used 3 main types of sampling devices. These were horizontal passive samplers (collecting deposits from drift) located on the ground (which are not relevant as they are not near the breathable level) or on supports raised above the vegetation; vertical passive samplers that collected solid and liquid aerosols, and also vapours; and active air samplers that collected particulate matter/fine aerosols and vapours. Values from the latter air samplers are relevant for comparisons with results from the ANSES report and open literature. The vertical and horizontal samplers used cellulose filters as the trapping media and XAD cartridges and quartz filters were used for the active air samplers and for collecting vapours. The vertical passive collectors deployed in the study collected vapour, droplets and aerosols.

2.3. Industry methods

The CLE database also included data derived from field studies conducted by CLE, which measured air concentrations (vapour fraction and fine particulates) immediately after applications of two PPPs using airblast sprayers (HSE, 2021). These studies are important because they give precise information of the sampling period in relation to a known application event. The data collected from these studies represent a worst-case scenario in terms of measured air concentrations due to the study design. A total of 16 resident exposure studies were conducted between 2015 and 2017 in central and southern Europe by CLE with the aim of investigating dermal and inhalation exposure to residents during and after applications in orchard crops (pome fruit and vineyards) (HSE, 2021). The concentration of vapours in the air surrounding the application sites was measured continuously for up to 168 h post-application using sorbent tubes attached to SKC pumps. Air pumps to collect vapour were placed 10 m away from the treated crops on all sides of the treated area and at two heights, 0.7 m and 1.5 m, to reflect child and adult breathing zones, respectively. Pumps were exchanged and new air tubes used approximately every 8 h.

2.4. Risk assessments

2.4.1. Risk assessments conducted by ANSES

The risk assessments in the ANSES report were designed to allow prioritization and ranking of risk rather than be robust quantitative assessments. The first approach calculated a ratio, expressed as a percentage, between the daily exposure via ambient air and the relevant toxicological reference value (e.g., Acceptable Operator Exposure Limit (AOEL)). This is in accordance with the risk assessment approach outlined in the EFSA guidance whereby the exposure to residents/bystander (i.e., the general population) is compared to the acute AOEL or (A)AOEL. In the ANSES report, in the absence of an AOEL different Toxicological Reference Values were considered, e.g., Chronic Acceptable Exposure Level and Acceptable Daily Intake; however, AOELs were available for all substances included in the evaluations described in the Figures and Tables. Ratios were calculated for individual substances and for mixtures by the summing of the relevant ratios (ANSES, 2020). The second approach considered Quantification Frequencies of the substances detected, which aimed to compare the rating of intrinsic hazard of a substance with its quantification frequency based on chronic toxicity. Acute toxicity criteria specific to the respiratory tract were taken into account to put results into perspective (ANSES, 2020).

2.4.2. Risk assessments for inhalation exposure

Currently, the systemic exposure of residents via the inhalation route (SERI) is adjusted for body weight according to the European Food Safety Authority (EFSA) Guidance Document (2022) according to the following equation:

SERI (mg/kg bw per day) = (VC x IR x IA)/BW.

Where VC = vapour concentration (mg/m^3); IR = inhalation rate (m^3/day); IA = inhalation absorption (%); BW = body weight (kg). Exposure for children is with respect to acute (i.e., those that could occur in a single day), and longer term (the level of exposure an individual in the population can experience repeatedly each day over a season) (as defined by the EFSA guidance (EFSA et al., 2022), and adult exposure is only calculated for longer term. For these, inhalation rates according to EFSA et al. (2022) are 8.0 m^3/day (0.80 m^3/day/kg bw) for longer term exposures and 2.28 m^3/h (0.228 m^3/h kg/bw) for acute exposures to children (<1 year); and for adults, inhalation rates for longer term exposures are 16.0 m^3/day (0.27 m^3/day kg/bw). Child and adult body weights are 10 and 60 kg, respectively. For all active substances considered here, the inhalation absorption is assumed to be 100%, as a Tier 1 default approach recommended by EFSA (EFSA et al., 2022).

The risk assessment was based on the daily exposure via ambient air as a percentage of the relevant toxicological reference value (e.g., AOEL). AOELs were taken from the ANSES report (ANSES, 2020). This enabled consistency between our results and those of the ANSES report, as well as being compliant with the EFSA guidelines.

3. Results

3.1. Information and data from studies included in the "combined air concentration database" (CACD)

The "Combined Air Concentration Database" (CACD) is an Excel chart (see Supplementary Table 1) contains information from the open literature, regulatory data from the ANSES and PROPULPPP project reports and CLE field study data. It contains data from the following:

1. Literature data: A review of abstracts in the open literature, followed by screening according to relevance and reliability, resulted in the identification of information for 211 active substances, excluding metabolites and other degradation products.
2. The ANSES report contains 1800 air samples collected using the same methodology across all sites/locations. In total 75 active substances were identified (including 1 pesticide metabolite).
3. The PROPULPPP project analysed 19 active substances from 7 spray events during a single growing season with specific weather conditions.
4. CLE field exposure data for bystander/resident exposure.

The CACD contains over 2000 lines of information for over 350 chemicals. Chemicals include currently used pesticides, historic pesticides, bisphenols, fragrances, musks, polyaromatic hydrocarbons, PCBs, phthalates, polybrominated biphenyl ethers and volatile organic chemicals. Information was also collected regarding the outdoor and indoor air concentrations of PPPs in vapour, droplets and aerosols according to distance from the crop and time after spraying.

3.2. ANSES results and comparison with other data in the CACD

A total of 112,000 data points were obtained from the ANSES sampling campaign, with approximately 1400 results for mostly semi-volatile substances and 400 from polar substances.

Notably, 90.2% of the collected samples contained non-detectable concentrations of pesticides; 4% of samples had concentrations between the LOQ and LOD (non-quantifiable) and 5.8% contained quantifiable concentrations. The percentage of samples that were quantifiable is comparable with those reported by Felkers et al. (2022b), who reported 4.7% of a total of 961 individual measurements were quantifiable (with 66% below the LOD and 29% between the LOD and LOQ).

In addition to the recorded annual concentrations measured at the national level, maximum measured air concentrations were also reported by ANSES. Twenty out of the 75 substances (27%) had a maximum concentration of between 1 and 10 ng/m^3 and 5 (7%) had maximum average concentrations between 10 and 100 ng/m^3. These higher concentrations were occasionally observed at a local scale. The detection frequency of the 75 active substances measured in the ANSES project was zero for 5 substances (carbetamide, chlordecone, dieldrin, oryzalin and tebuthiuron, for which the LODs were 0.045–0.089 ng/m^3) and ranged from 0.07% to 96.51% for the remaining 70 substances (Fig. 1A). There was a general trend with respect to detection frequency, such that the higher the vapour pressure the greater number of substances with a higher detection rate. A comparison of the vapour pressure with the reported concentration (Fig. 1B) indicated that concentration in the air was not related to the volatility and that the air concentration was no higher for substances considered to be moderately volatile (>5 mPa (EFSA et al., 2022)) compared to substances with a low volatility (i.e., <5 mPa, as defined by EFSA (EFSA et al., 2022).

Out of 75 substances measured by ANSES, there were 32 active substances for which data were available in the CACD. Table 1 lists the annual average air concentrations, P95 and P99 values from the ANSES report, together with the range of air concentrations from the CACD for the same active substances. The highest measured air concentration (P99 value) reported in the ANSES study was 49.49 ng/m^3, detected for prosulfocarb. The range of maximum average concentrations for this sub-set of 32 substances from the CACD ranged from 0.0002 to 695.6 ng/m^3, again with the highest measured air concentration reported for prosulfocarb (695.6 ng/m^3, which was from the PROPULPPP project). The highest reported mean for prosulfocarb in the CACD ranged from 0.008 to 91.93 ng/m^3. Peaks in measured air concentrations have been observed but also troughs, which are reflected in the reported "low values" for the 32 active substances: 29 (91%) had reported "low values" that were non-detectable concentrations; 2 (6%) had low concentrations between the LOQ and LOD (non-quantifiable) and only 1 (3%) low value was quantifiable (fluopyram, 0.019 ng/m^3). Eleven of the 32 substances (34%) had a maximum average concentration between 1 and 10 ng/m^3 and 12 (38%) had maximum average concentrations between 10 and 100 ng/m^3. For the same 32 PPPs, the ANSES project reported 5 substances (16%) had a maximum average concentration between 10 ng/m^3 and 2 (6%) had maximum average concentrations between 10 and 100 ng/m^3.

3.3. Risk assessments using ANSES and CACD data

For the risk assessment, the measured concentration in ng/m^3, inhalation exposure was calculated on the basis of the m^3 inhaled per day with a 10 kg (child) or 60 kg (adult) bodyweight and this was compared to the relevant toxicity value (AOEL) of the active substance measured. The exposures were based on the highest reported air concentrations (vapour and particulate), conservative daily breathing rates and 100% inhalation absorption. For the ANSES data, measured exposures to PPPs for which the maximum average concentrations were greater than the LOD represented less than 1% of the associated AOEL (Fig. 2A), indicating a high level of safety for adults and children. Measured exposures to PPPs for which the maximum average concentrations were measured in multiple reports in the CACD were also compared with the associated AOEL.

For practical reasons, the top 10 individual active substances with the highest reported vapour concentrations (by the ANSES project and/or in the CACD) were used to compare with the associated AOEL (Table 2, 5 of which were also assessed in the ANSES report (Fig. 2B)). The measured exposure values from the ANSES report and from the CACD are all below the relevant AOELs. For currently approved PPPs, the predicted child exposures (worst case scenario), were between 0.06% and 22% of the associated AOEL (Table 2). For the non-approved active substances, chlorpyrifos, dimethoate, trifluralin and chlorothalonil, predicted exposures ranged between 0.4% and 33% of the relevant AOELs. For lambda-cyhalothrin, which showed the highest predicted exposure for currently approved active substances, the CACD contained 15 records of which 11 reported measured air concentrations were below the reported LOD. The highest recorded air concentration of 172.61 ng/m^3 was for lambda-cyhalothrin from an urban site and was reported by Lévy et al. (2018). The reported minimum detectable air concentration was 11.25 ng/m^3 and the mean 91.93 ng/m^3 over 4 years. Based on the mean reported air concentration the predicted inhalation exposure of lambda-cyhalothrin is 12% of the AOEL. The lowest reported detectable air concentration represents 1.4% of the AOEL.

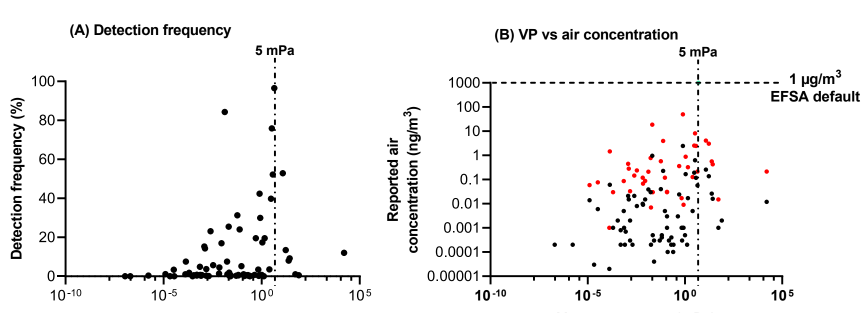

Fig. 1. A comparison of vapour pressure and (a) detection frequency and (B) measured air concentrations of 75 active substances measured in the ANSES project. In (B), the red symbols denote the P99 values and the black symbols denote reported average air concentrations over the year (calculated as described in Section 2.2.1).

Table 1
Comparison of ANSES and CACD reported air concentrations. ND = not detected; NR = not reported.

Active substance	Reported air concentrations – ANSES (ng/m^3)			Range of air concentrations in the CACD (ng/m^3)		
	Reported annual average air concentration	Raw data reported P95	Raw data reported P99	Low	Maximum	Highest reported mean
2,4-D	0.015	0.015	0.088	ND	4.52	4.52
2,4-DB	0.0007	0	0	ND	0.56	0.56
Clomazone	0.016	0.076	0.425	ND	0.68	0.33
Cypermethrin	0.01	0	0.119	ND	0.237	NR
Cyprodinil	0.024	0.096	0.36	ND	68.29	68.29
Deltamethrin	0.014	0	0.059	ND	79.01	40.3
Difenoconazole	0.006	0	0.076	ND	8.478	0.35
Diflufenican	0.021	0.044	0.146	ND	267.57	53.73
Etofenprox	0.0002	0	0	ND	0.0002	NR
Fenpropidin	0.136	0.28	3.028	ND	7.21	7.01
Fluazinam	0.03	0.075	0.78	ND	2.64	1.08
Flumetralin	0.0003	0	0	ND	0.0004	NR
Fluopyram	0.021	0.078	0.45	0.019	0.056	NR
Folpet	0.955	3.564	18.73	ND	82.22	13.96
Glyphosate	0.039	0.088	0.209	ND	1.04	NR
Lambda-cyhalothrin	0.001	0	0.03	ND	172.61	91.93
Lenacil	0.0002	0	0	ND	0.0002	NR
Metamitron	0.001	0	0	ND	16.18	6.79
Metazachlor	0.005	0.036	0.12	ND	3.13	0.93
S-Metolachlor	0.118	0.561	2.442	<LOQ	63.93	19.13
Metribuzin	0.003	0	0.03	ND	0.032	NR
Oxyfluorfen	0.00004	0	0	ND	71.02	71.02
Pendimethalin	0.63	3.31	8.169	ND	117.33	35.07
Phosmet	0.0005	0	0	ND	1.33	0.56
Pirimicarb	0.003	0	0	ND	1.516	NR
Propyzamide	0.04	0.182	0.57	ND	3.207	0.21
Prosulfocarb	2.447	13.8	49.492	ND	695.6	1.45
Pyrimethanil	0.168	0.102	0.884	ND	11.011	0.008
Spiroxamine	0.061	0.075	1.458	ND	55.4	44.94
Tebuconazole	0.015	0.079	0.283	ND	7	1.74
Tri-allate	0.257	1.452	4.079	<LOD	0.274	1.15
Trifloxystrobin	0.008	0.059	0.237	ND	4.58	2.62

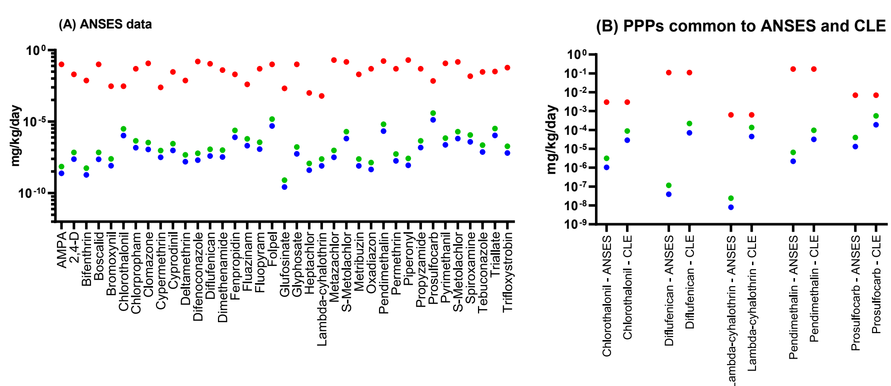

Fig. 2. Comparison of the longer-term exposure to children (green symbols) and adults (blue symbols) of PPPs with recorded air concentrations > LOQ from (A) the ANSES report and (B) the top 10 PPPs with the most reported valuesfrom the CACD with the associated AOEL (red symbols). Longer-term child and adult exposures were calculated using the EFSA calculation described in the methods.

4. Discussion

We investigated the occurrence of PPPs in the air that may be available and respirable by humans located in rural areas but not immediately adjacent to a PPP application. To this end, a literature review was conducted to identify relevant papers describing monitoring studies published in the open literature and by national regulatory agencies. As a result, all relevant data were collected in a Combined Air Concentration Database (CACD) and used to investigate whether air concentrations of PPPs reported by ANSES and those measured by others are consistent.

4.1. Comparison of ANSES and open literature data

The ANSES project aimed to specifically monitor commonly used PPPs with potential health concerns associated with their use. The outcome of the study represented a robust dataset with which to compare data from other sources. To allow meaningful comparison between datasets, the methodology used to collect the data should be as similar as possible and ideally be identical. However, data from the open literature often showed high variability and different variables/factors have been proposed to explain the observed variation, e.g., climatic conditions (e.g., temperature, rainfall and humidity), temporal variation (seasonality) and physical/chemical properties of the active substance.

The reported mean and maximum average air concentrations

Table 2
Simple risk assessments for the top ten individual active substances with the most reported values with the highest reported vapour concentrations for children and adults by comparing air exposure with the associated AOEL. The values for vapour pressure at 20 °C are from the University of Hertfordshire database (https://sitem.herts.ac.uk/aeru/ppdb/en/).

Substance	Vapour pressure (mPa)	Volatility classification	Child/ adult	AOEL (mg/ kg/day)	Maximum reported average concentration (μg/m^3)	Longer-term exposure (mg/day kg/bw)	% Of AOEL
Pendimethalin	3.34	Low	Child	0.17	0.117	0.000096	0.06
			Adult			0.000032	0.02
Dimethachlor	0.64	Low	Child	0.1	0.271	0.000216	0.2
			Adult			0.000072	0.07
Diflufenican	4.25×10^{-3}	Low	Child	0.11	0.268	0.00022	0.2
			Adult			0.00007	0.07
MCPA	0.4	Low	Child	0.04	0.155	0.000128	0.3
			Adult			0.000047	0.1
Prosulfocarb	0.79	Low	Child	0.007	0.696	0.00056	8
			Adult			0.00019	3
Lambda cyhalothrin	0.0002	Low	Child	0.00063	0.172	0.000136	22
			Adult			0.000045	7
Trifluralin (not approved)	9.5	Moderate	Child	0.026	0.141	0.00011	0.4
			Adult			0.000037	0.1
Chlorothalonil (not approved)	0.076	Low	Child	0.003	0.108	0.000088	2.9
			Adult			0.000029	0.98
Dimethoate (not approved)	0.247	Low	Child	0.001	0.200	0.00016	16
			Adult			0.000053	5
Chlorpyrifos (not approved)	1.43	Low	Child	0.001	0.408	0.00033	33
			Adult			0.00011	11

reported for 32 active substances were generally much lower in the ANSES project than those from other sources captured in the CACD. In studies in the ANSES project, the samplers were positioned at a minimal distance of at least 200 m from an agricultural plot (i.e., under defined conditions); however, information on the distance between the measured samples and the source are not always available or possible to derive from the literature reports; therefore, a direct comparison of the distances cannot be made to account for the differences in air concentrations. Differences in values may be due to differences in the intensity of the farming activities covered in the ANSES report and those from literature values in the CACD. The two main European sampling areas used in the open literature were the Valencia region in Spain and the Alsace region of France. The focusing of work on specific areas could produce data that is biased due to the specific conditions found at the sampling sites/regions. For example, the studies reported by Liaud et al. (2016) were conducted in and around Strasbourg. Strasbourg is the main city of Alsace, a region of intensive farming in the north-east of France. Focusing on areas of intensive farming does provide important information on air concentrations of PPPs but the data may not be relevant to other areas where the agricultural systems are less intensive, or have different environmental conditions (temperature, humidity, which may impact volatilisation).

There was no single explanation for the observed variability in terms of one or two key variables, rather, as observed by Felkers et al. (2022b), it seems a combination of factors impacts the presence of PPPs in the air. Schummer et al. (2010b) reported that most of the observed variability was due to time, temperature or atmospheric pressure. Generally, higher air concentrations are observed during the main application windows. This is supported by the EXOPESTEN project which highlighted differences between the seasons with low concentrations in the winter, very high concentrations in the spring and moderate levels in the summer (Ruthy et al., 2019). Coscollà et al. (2010) also reported an observed seasonal trend and that the predominate PPPs detected were related to the main crops of the sampling region and the authors concluded this showed that the main sources of PPPs in the air were from local sources. The work by ANSES, 2020 revealed inter-annual variability in air concentrations of the measured PPPs and concluded this was due to local weather conditions and pest pressure. By contrast, Carratalá et al. (2017) reported that herbicide concentrations were highest in winter than in other seasons at a Mediterranean coastal lagoon location. Perhaps surprisingly, the ANSES report indicated no clear difference between urban, suburban and rural locations in terms of measured air concentrations of PPPs (ANSES, 2020), although Coscollà et al. (2010) reported minor differences in the profiles of PPPs between urban and rural areas. Désert et al. (2018) reported that the observed spatial distribution showed that PPPs were detected in both rural and urban sites suggesting atmospheric transport from agricultural areas to cities. This may be the case, but PPPs are also used in urban places, so their presence doesn't necessarily mean they have been transported there. The botanical garden in Strasbourg was used for several studies (Lévy et al., 2018; Schummer et al., 2010a, 2010b), but in none of the papers is it clear if PPP applications were done in the garden to maintain the vegetation.

The sampling method appears to affect the magnitude of measured air concentrations. The air can be split into three different phases: gaseous/vapour, liquid/aerosol and particulate. Different sampling devices are specific to the collection of specific phases, with some being able to collect all three phases, whilst others collect only one of the phases. The sampling may also only be selective for a certain particle size, e.g., the ANSES study only measured particles smaller than 10 μm (PM_{10}). Differences in methods was demonstrated from two studies in Strasbourg, one used high volume air samplers (Schummer et al., 2010a, 2010b) and the other resin-based passive samplers (Lévy et al., 2018). The passive-based system consistently reported higher measured air concentrations although there could have been temporal variations at play as well. Another important factor that needs consideration is the phase/fraction that is collected by the sampling device. Vapour and particulate material <10 μm in diameter (PM_{10}) are the main focus of this paper as they represent the fractions that are relevant for true inhalation exposure and are respirable into the deep lung. Liaud et al. (2016) collected total suspended particulate matter and gas phase samples and reported the gas-particle distribution was 60% in the gas phase and 40% in particulate phase. The reported distribution is of interest as the gas phase is less likely to reach the soil or other trapping material quickly and is therefore, potentially available for transport away from the application site. This could explain why measurable concentrations of PPPs are observed away from agricultural areas.

The sensitivity of the analytical methods needs to be considered when interpreting data as it may be that an analytical setup is simply not sensitive enough to detect the required levels of a chemical, or conversely, an instrument is so sensitive it is reporting apparent concentrations that are so low as to be of no concern, or at least needs further context. An analytical method that is not sensitive enough is potentially problematic during data interpretation because it can lead to apparent concentrations of a substance being detected that are simply an artefact of analytical insensitivity (i.e., if there is a value below the LOQ, it could be reported as the LOQ value, but it could actually be much lower, as discussed by Felkers et al. (2022a)).

Despite difference in the values recorded in the ANSES report and other values from the open literature captured in the CACD, none of the highest recorded values from any source exceeded 1 μg/m^3. The two sets of data both reflected a high percentage (~90%) of collected samples with non-detectable concentrations of PPPs and both identified prosulfocarb as having the highest concentration in the air samples collected (49.49 ng/m^3 and 695.6 ng/m^3 in the ANSES report and open literature, respectively). The high level of non-detectable air concentrations was also reported by Felkers et al. (2022b).

4.2. Risk assessments using CACD values

Inhalation exposure assessments were conducted based on reported air concentrations of selected pesticide active substances. Due to the size and amount of data extracted from the candidate papers, the focus of the in-depth review and interpretation was refined to ten active substances (Table 2) which were selected by those having the greatest number of individual data points in the database (see Supplementary Table 1 for a summary of the number of reports per substance). Based on current field data collected in the EU, which are considered to be representative of the envisaged EFSA exposure scenario for considering inhalation of vapours, the highest recorded air concentration reported was 0.696 μg/m^3 which was measured for prosulfocarb. The vapour pressure of prosulfocarb is 0.79×10^{-3} Pa at 20 °C and is classed as having low volatility.

Following current European approaches (EFSA et al., 2022) to assess non-dietary exposure and risk of the general population to concentrations of PPPs in the air when present as vapours, two default air concentrations have been established. For active substances with low volatility (having a vapour pressure of $<5 \times 10^{-3}$ Pa), the surrogate default average concentration in air for the 24 h after application is 1 μg/m^3 (EFSA et al., 2022). For moderately volatile active substances (having a vapour pressure between 5×10^{-3} Pa and 10^{-2} Pa), the default average concentration in air for the 24 h after an application is 15 μg/m^3. Within the current EFSA Model, the relevant default air concentration is used to calculate resident and bystander exposure to vapours using conservative inhalation rates (see Section 2.4.2). The calculated systemic exposure, expressed in mg/kg bw/day, is then compared to the relevant toxicological endpoint (the AOEL). For currently approved active substances, the predicted child exposures (worst-case scenario) were between 0.06% and 22% of the associated AOEL. For the non-approved active substances, chlorpyrifos, dimethoate, trifluralin and chlorothalonil, predicted exposures ranged between 0.4% and 33% of the relevant AOELs. Therefore, based on the data obtained in the current analysis, an air concentration of 1 μg/m^3 – and not 15 μg/m^3 - represents the worst-case scenario for all vapour pressure classes of approved active substances. The EFSA default of 15 μg/m^3 for volatile active substances is based on a study done on chlorpyrifos, for which there were 30 records within the database. The highest recorded air concentration (based on vapours and/or PM_{10}) was 0.408 μg/m^3 (Désert et al., 2018) and was measured in ambient air. Therefore, it seems that the 15 μg/m^3 default air concentration currently used by EFSA is unrealistic, and both default values deserve further investigation and consideration. Additionally, the grouping of active substances according to the vapour pressures as well as justification of the current EFSA default air concentrations for use in non-dietary risk assessments as applied by EFSA (EFSA, 2014; EFSA et al., 2022), was reviewed by Felkers et al., 2022a, 2022b, concluding that the currently applied assumptions might not be appropriate.

5. Conclusions

In conclusion, based on the data collected in the CACD, measured air concentrations of PPPs in monitoring studies are significantly lower than EFSA default limits and relevant toxicological reference values. Inhalation exposure assessments were conducted based on reported air concentrations of selected pesticide active substances. Based on the results of the evaluated studies, we observed that in the air monitoring campaigns for PPPs described here, a significant proportion (between 25 and 90%) of samples do not contain measurable air concentrations. Where air concentrations of active substances were quantifiable, the measured respirable fractions were below EU regulatory limits and EU default air vapour concentrations. Predicted inhalation exposures were also all below established toxicological endpoints, even when considering the highest maximum reported average concentrations and very conservative inhalation rates. The highest recorded air concentration in the current dataset was 0.696 μg/m^3 for a low-volatile substance, prosulfocarb. Based on the current database, an air concentration EFSA default value of 1 μg/m^3 represents the worst-case scenario for all vapour pressure classes of approved active substances.

In conclusion, based on the data collected, measured air concentrations of PPPs in monitoring studies are significantly lower than EFSA default limits based on near-field exposure and relevant toxicological reference values.

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Anne-Kim Vinck: Writing – review & editing, Visualization, Project administration, Data curation. **Edgars Felkers:** Writing – review & editing, Visualization, Formal analysis, Data curation, Conceptualization. **Michel Urtizberea:** Writing – review & editing, Visualization, Data curation, Conceptualization. **Nicola J. Hewitt:** Writing – original draft, Visualization, Data curation. **Kathrin Bürling:** Writing – review & editing, Visualization, Formal analysis, Data curation, Conceptualization. **Alistair Morriss:** Writing – review & editing, Investigation, Formal analysis, Data curation.

Declaration of competing interest

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

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests. Anne-Kim Vinck, Edgars Felkers, Michel Urtizberea, Kathrin Bürling and Alistair Morriss are employees of companies that conduct and evaluate risk assessments for regulatory purposes in the context of authorization and marketing of their companies' products. They contribute as scientific experts to the industry association CropLife Europe for evaluation and development of the state-of-the-art methodology. Nicola Hewitt is a scientific consultant.

Data availability

All data are available in Supplementary Table 1

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Appendix A. Supplementary data

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