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Selection and ranking method for currently used pesticides (CUPs) monitoring in ambient air

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Abstract Chronic exposure to pesticides can induce adverse human health effects. Even though ingestion is considered as the main exposure pathway, it is now suggested that inhalation might also be important not only in rural but also in urban locations. Therefore, assessment of currently used pesticides (CUPs) concentrations in ambient air is important for better understanding of human exposure through inhalation and potential health effects. Analytical methods do not allow assessing ambient air concentration of all the CUPs registered. Designing a cost-effective and a fitted-for-purpose monitoring strategy at the local/regional scale must therefore rely on a methodology allowing targeting CUPs by a ranking approach accounting for the most relevant selection criteria. In this study, after a first selection, a ranking method is used to identify most relevant CUPs for ambient air assessment in Wallonia, Belgium. This method took into account not only toxicological endpoints but also national and regional data on sales and uses along with other uses criteria. Moreover, probability to detect CUPs in ambient air was investigated using international, national, and regional studies and physicochemical properties. The ranking method used three main criteria (i.e., chronic toxicity, sales and uses, and presence in ambient air), which are divided in 17 sub-criteria, to provide the most accurate identification of CUPs that might be measured in ambient air and that might impact human health. After final selection based on analytical methods, 43 CUPs were further submitted to analytical method development.

Keywords Currently used pesticides · Ambient air monitoring · Prioritization · Ranking · Toxicity · EXPOPESTEN

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Abbreviations

AASQA	French Accredited Associations for Air Quality Monitoring
ADI	Acceptable daily intake
AMPA	Aminomethylphosphonic acid
CRAAQ	Quebec Reference Center for Agriculture and Agri-Food
CUPs	Currently used pesticides
ETU	Ethylene thiourea
IARC	International Agency for Research on Cancer
PPDB	Pesticides Properties Database
US-EPA	US Environmental Protection Agency
WHO	World Health Organization

Introduction

Due to their massive use for intensive food production and preservation in both developed and developing countries, pesticides are among the most widely used anthropogenic

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chemicals thus contributing to a global contamination of the environment (Baraud et al. 2003; Yusà et al. 2009; Espallardo et al. 2012). Chronic exposure to pesticides can induce adverse human health effects such as cancer, endocrine disruption, and developmental and reproductive toxicity (Kamel and Hoppin 2004; Mnif et al. 2011; Mostafalou and Abdollahi 2013; NTP 2014). Humans are exposed to pesticides through three main pathways, namely dermal exposure, ingestion, and inhalation. Even though ingestion is considered as the main pathway for chronic exposure to pesticides (Sheldon 2010), there are growing evidences for a significant contribution of inhalation exposure in rural as well as in urban locations (Baraud et al. 2003; Scheyer et al. 2007; Schummer et al. 2010). Indeed, pesticides are emitted in ambient air through spray drift and volatilization from plants and soil with an estimated loss of up to 90% of the applied dose either during or after application (Bedos et al. 2002; Espallardo et al. 2012; Sarigiannis et al. 2013). Even though currently used pesticides (CUPs) metabolize and degrade more efficiently than historical ones (e.g., organochlorine compounds), several studies in North America and Europe reported ambient air concentrations in rural and urban areas as well as in remote sites located far from any pesticide uses (LeNoir et al. 1999; Baraud et al. 2003; Yao et al. 2006; Scheyer et al. 2007; Aulagnier et al. 2008; Gouin et al. 2008; Coscollà et al. 2010; Kurt-Karakus et al. 2011; Mai et al. 2013). While CUPs levels in ambient air are usually in the ng/m^3 range, some are measured at concentrations over 100 ng/m^3 in agricultural regions (Baraud et al. 2003; Garron et al. 2012; Hart et al. 2012; Coscollà et al. 2013) hence potentially affecting health of exposed populations.

Therefore, the measurement of CUPs concentrations in ambient air is required for a better understanding of non-dietary human exposure and to assess potential health effects related to inhalation. The major drawback to cope with ambient air pesticides assessment is the diversity of active substances used. Indeed, more than 400 active substances were registered in European Union in 2014 (EU 2014), but analytical methods do not allow assessing all the registered molecules in ambient air (Segawa et al. 2014). Moreover, all CUPs are not susceptible to be found in ambient air either due to low volatilization or to fast metabolization. The selection of most relevant CUPs for ambient air concentration monitoring appears then a crucial point before sampling and analysis.

Designing a cost-effective and a fitted-for-purpose monitoring strategy at the local/regional scale must therefore rely on a methodology allowing targeting CUPs by a ranking approach accounting for the most relevant selection criteria. Environmental loads are related to the amount used, to the frequency of application, and to the physicochemical properties of the CUPs (Gunier et al. 2001; Juraske et al. 2007; Egeghy et al. 2011). Thus, identifying and prioritizing pesticides of concern need to emphasize (i) pesticide uses, (ii) toxicity related to chronic exposure, and (iii) exposure potential in order to more accurately assess health risks related to pesticides (Sugeng et al. 2013). Different screening and ranking methods were developed in Europe, the USA, and Canada to identify and quantify the degree of concern for pesticide toxicity to human health and ecosystems related to exposure (Reus et al. 2002; Juraske et al. 2007; Egeghy et al. 2011; Mitchell et al. 2013; Segawa et al. 2014). These modeling approaches were developed in response to the need for rapid and efficient risk characterization with respect to the thousands of chemicals used throughout industry and agriculture. The prioritized lists of chemicals established using models helped identifying chemicals of highest concern regarding toxicity and uses so to ensure better protection for human and ecosystem health (Egeghy et al. 2011; Mitchell et al. 2013). Moreover, these modeling approaches are usually developed on a nationwide scale (Egeghy et al. 2011; Mitchell et al. 2013) but can sometimes be applied to smaller scales thus responding to local needs for management or health outcomes related to local exposures (Gunier et al. 2001; Sugeng et al. 2013; Segawa et al. 2014).

These lists are developed and used in a regulatory purpose (Egeghy et al. 2011; Mitchell et al. 2013), but environmental concentrations and biomarker levels of identified chemicals, which are required to assess ecosystem and human exposure, are not further measured. Recently, a study focused on the use of a prioritization method to select pesticides to be analyzed in ambient air for a yearlong air monitoring study in California (Segawa et al. 2014). This study used four criteria (i.e., statewide reported uses, volatility, priority in risk assessment, and availability of analytical methods) to assign points to the top 100 pesticides used in agriculture in California allowing selecting 13 pesticides monitored in ambient air. In addition, some lower scoring pesticides were monitored because they were easy to include in the multi-residue analysis used to achieve a total of 24 CUPs (Segawa et al. 2014).

Belgium is among the five largest pesticide consumers in Europe when considering the amount used per agricultural acreage (PWRP 2013) with more than 300 plant protection products registered for professional and non-professional uses in 2014. The EXPOPESTEN study aims at assessing exposure of Walloon population to CUPs through ambient air measurement and biomonitoring. For this study, we developed a selection and a ranking method to identify CUPs that will be monitored in ambient air in Wallonia, Belgium, during a yearlong study. In this study, CUPs are selected using three main criteria (i.e., chronic toxicity, sales in Belgium and uses in Wallonia, probability of presence in ambient air). These three main criteria are divided in a total of 17 sub-criteria. Points are attributed to each sub-criterion to establish a prioritized list to select relevant CUPs that will be analyzed in ambient air in Wallonia over a yearlong. This selection method considered all registered CUPs to finally select the most relevant for final ambient air analysis.

Materials and methods

In Belgium, over 300 plant protection products were registered for both professional and non-professional uses in 2014. Prior to the ranking of CUPs for ambient air analysis, the list of CUPs is reduced by selecting the most relevant candidates based on their sales and uses and on their chronic toxicity. Points are then attributed to CUPs for each of the 17 sub-criteria using information from selected databases. The total of the points attributed to each CUP allowed ranking candidates. CUPs are finally selected based on the possibility to develop analytical method for ambient air monitoring.

Currently used pesticides selection

Some microorganisms (e.g., *Bacillus subtilis*, *Streptomyces*…), molecules derived from plants and animals (e.g., fatty acids, rapeseed oils…), and insect pheromones (e.g., codlemon, *n*-tetradecyl acetate…) are listed among the registered plant protection products for their uses as fungicides or insecticides. Microorganisms and molecules derived from animals and plants naturally occur in the environment and are thus out of the scope of this study and discarded from the candidate list.

Selection based on sales and uses

To further reduce the list of candidates for the ranking method, some CUPs are removed based on their uses. Indeed, CUPs defined as "other plant protection products" in the Annex III of the Commission Regulation (EU) No. 656/2011 of 7 July 2011 Implementing Regulation (EC) No. 1185/2009 of the European Parliament and of the Council concerning statistics on pesticides (OJEU 2011) are used as adjuvants and surfactants in combination with other CUPs defined as active substances. These other plant protection products are out of the scope of our study and were also removed from the list submitted to the selection method.

After reduction, the number of CUPs retained (i.e., 231) is still difficult to manage for the ranking. Therefore, Belgian sales for the year 2010 to 2013 are used to further reduce the number of CUPs considered for the ranking using 17 sub-criteria. These data are compiled in the frame of Eurostat requirements for pesticides sales statistics in Europe and were obtained from the Belgian Federal Public Service. The CUPs representing 95% of the total quantities sold between 2010 and 2013 to both professional and non-professional users in Belgium are retained in the candidate list.

Selection based on chronic toxicity

As the objective of pesticide management is to ensure protection of the environment as well as human health (OJEU 2009; Egeghy et al. 2011), chronic toxicological data are considered for the 231 CUPs. Analysis of toxicological data will help identify CUPs sold in lower quantities, which were not selected in the list of CUPs representing the 95% highest quantities sold in Belgium, but with potentially high human toxicity. Chronic toxicity criteria used are carcinogenicity, neurotoxicity, endocrine disruption, developmental and reproductive toxicity, and mutagenicity and genotoxicity (Table 1). As lack of data in databases is a critical endpoint when assessing pesticide toxicity (Sugeng et al. 2013), at least two databases are consulted for each toxicological endpoint. The first, Pesticides Properties DataBase (PPDB) developed by the Agriculture & Environment Research Unit of the University of Hertfordshire, is a comprehensive compilation of pesticide chemical identity, physicochemical properties, and data on human and environmental health (Lewis et al. 2016). The second, SAgE pesticides database developed by the Quebec Reference Center for Agriculture and Agri-Food (CRAAQ) in Canada, is also dedicated to pesticides and compiles physicochemical properties along with toxicological and ecotoxicological data (Samuel et al. 2012). These two databases, specific to pesticides and peer reviewed by working groups of specialists, are used for all toxicological criteria considered (Table 1). Moreover, two additional data sources not specific to pesticides are investigated to assess carcinogenicity. The first is the International Agency for Research on Cancer (IARC) list of carcinogens. The IARC is the specialized cancer agency of the World Health Organization (WHO) and regularly publishes monographs in which environmental factors that increase the risk of human cancer are identified and ranked based on the strengths of association between exposure and carcinogenicity (IARC 2006; Cogliano et al. 2011). The second source used is the list of chemicals evaluated for carcinogenic potential that is annually released by the Office of Pesticide Programs of the US Environmental Protection Agency (US-EPA 2014).

The CUPs with suspected or proven toxicity for at least three toxicological endpoints reported in at least one of the databases are retained for the ranking method.

Currently used pesticides ranking

CUPs retained from both sales and uses selection and chronic toxicity selection are then submitted to the ranking method. In this method, three main criteria are defined: chronic toxicity, sales and uses, and presence in ambient air. These criteria are divided in a total of 17 sub-criteria. Points are attributed for all the 17 sub-criteria to each candidate CUP based on data available. Points are then summed to rank CUPs for the final selection based on the possibility to develop analytical method for ambient air monitoring. The sub-criteria and points allocated are described in Table 1.

Table 1 Points assigned to the different criteria used to prioritize chemicals for ambient air monitoring in Walloon Region, Belgium, in ranking method 1

Criteria	Points				
1 Chronic toxicity—maximum 14 points					
1.A—acceptable daily intake (mg/kg bw/day)	0—not applicable	1—ADI ≥ 0.1	2—0.03 > ADI ≥ 0.1	3—0.01 > ADI ≥ 0.03	4—ADI < 0.01
1.B—carcinogenicity	0—not likely	2—suspected or proved			
1.C—neurotoxicity	0—not likely	2—suspected or proved			
1.D—endocrine disruption	0—not likely	2—suspected or proved			
1.E—reproductive and developmental toxicity	0—not likely	2—suspected or proved			
1.F—mutagenicity and genotoxicity	0—not likely	2—suspected or proved			
2 Sales and uses—maximum 21 points					
2.A—quantity sold in Belgium between 2010 and 2013	0—not sold	1—0 to 10,385 kg	2—10,386 to 66,778 kg	3—66,779 to 122,722 kg	4—over 122,723 kg
2.B—quantity used in Wallonia between 2010 and 2013	0—not used	1—0 to 867 kg	2—868 to 8443 kg	3—8444 to 31,049 kg	4—over 31,050 kg
2.C—areas treated in Wallonia between 2010 and 2013	0—not used	1—0 to 4059 ha	2—4060 to 38,277 ha	3—38,278 to 118,924 ha	4—over 118,925 ha
2.D—number of commercial formulations	0—not sold	1—1 to 5	2—6 to 10	3—10 to 20	4—over 20
2.E—number of crops treated	0—not used	1—1 to 2	2—3 to 4	3—over 5	
2.F—non-professional uses	0—no	1—yes			
2.G—biocide uses	0—no	1—yes			
3 Presence in ambient air—maximum 13 points					
3.A—volatility	1—low volatility	2—medium volatility	3—high volatility		
3.B—maximum concentrations measured in ambient air	0—no data	1—< 0.5 ng/m^3	2—0.5 to 1 ng/m^3	3—1 to 10 ng/m^3	4—over 10 ng/m^3
3.C—number of studies	0—no data	1—1 to 5	2—6 to 10	3—over 10	
3.D—last year of detection in a French study	0—no data	1—2000 to 2005	2—2006 to 2010	3—after 2010	

Criterion 1: chronic toxicity criterion

The chronic toxicity criterion is divided into six sub-criteria (Table 1). Five of them were previously used for the reduction of the candidate list (i.e., carcinogenicity, neurotoxicity, endocrine disruption, developmental and reproductive toxicity, and mutagenicity and genotoxicity). Points are allocated to CUPs based on information available in each database consulted for chronic toxicity (i.e., PPDB, SAgE, IARC, US-EPA). Then, only the highest score is retained for the final ranking as it is a more conservative assumption (Sugeng et al. 2013). One more toxicity sub-criterion (i.e., acceptable daily intake (ADI)) is considered in the ranking method. ADI is defined by the European Food Safety Authority (EFSA) as an estimate of the amount of the CUP that can be consumed (i.e., ingestion exposure through food and beverages) over a lifetime without presenting an appreciable risk to human health. ADI is evaluated using results of long-term studies in animals and observations on human. Though, this sub-criterion is useful to evaluate the toxicity of CUPs related to the dose of exposure. ADI data calculated by the EFSA are compiled from the PPDB database.

Criterion 2: sales and uses

In addition to quantity sold in Belgium between 2010 and 2013, the sales and uses criterion is divided into six additional sub-criteria (Table 1). Amount used and areas treated by farmers in Wallonia are data worth considering for the evaluation of emissions at the regional scale. These data were obtained from the Direction de l'Analyse Économique Agricole of the Walloon Public Service for the year 2012. The number of crops on which the CUP can be applied is also considered. Indeed, different crops undergo different pressures at different periods, therefore conditioning the pesticides uses. Broad-spectrum CUPs can be used on several different crops or against several different pests. Therefore, such CUPs can be used not only in larger amount but also during longer periods compared to more specific CUPs. Emissions of pesticides in atmosphere are higher from permanent crops, such as orchards, than emissions from non-permanent crops (e.g., cereal, maize, potato...) conditioning spatial and temporal concentrations in ambient air (Sarigiannis et al. 2013). The number of commercial products containing the CUP is also considered in the ranking method. Finally, non-professional uses and biocidal uses (both professional and non-professional), in commercial products, might also contribute to increase the amount of CUPs released in the atmosphere. Therefore, these data are also considered in the sales and uses criterion. The sales and uses data (i.e., professional and non-professional uses, type of crops treated, amount sold, and the number of commercial product containing the CUP) were obtained from the Federal Public Service of Health, Food Chain Safety and Environment website in autumn 2014 (http://fytoweb.be).

Criterion 3: presence in ambient air

The third criterion used in this ranking method is the potential presence in ambient air. This criterion is divided into four sub-criteria (Table 1). The first is volatility and is assessed based on two relevant physicochemical properties of CUPs, namely vapor pressure and Henry's law constant. Henry's law constant measures the volatilization tendency of a pesticide from dilute solution, whereas vapor pressure is a measurement of volatilization of the pure compound in its condensed state. Volatility is defined as "low" for CUPs with a vapor pressure $< 1.10^{-4}$ Pa and a Henry's law constant $< 1.10^{-5}$ Pa m^3/mol, as "high" for CUPs with a vapor pressure $> 1.10^{-4}$ Pa and a Henry's law constant $> 1.10^{-5}$ Pa m^3/mol, and as "medium" for other CUPs (Bedos et al. 2002; Espallardo et al. 2012; Lichiheb et al. 2015). Data used for the three other sub-criteria (i.e., maximum concentration measured in ambient air, number of studies that measured CUP concentrations in ambient air, and last year of detection) are compiled from scientific literature reporting CUPs' ambient air concentrations. In addition to peer-reviewed literature, reports from different French Accredited Associations for Air Quality Monitoring (AASQA) are also thoroughly investigated. Indeed, these regional associations monitor ambient air concentrations of several CUPs not only in rural but also in urban locations sometimes for more than a decade. France is a neighboring country with similar agricultural practices. Therefore, the last year of detection of CUPs in a French study is considered as particularly relevant information in the ranking method.

Robustness of the ranking method

To assess the robustness of the ranking method, points allocated to sub-criteria are modified to increase or reduce the weight of each criterion in the final score. Based on the points attributed as shown in Table 1, the most important criterion is sales and uses and accounts for a maximum of 44% of the total score, whereas presence in ambient air and chronic toxicity criteria are of similar weight (27 and 29%, respectively). Two alternative ranking methods are used. In the second ranking method, chronic toxicity is the most important criterion with 41% of the total points, followed by sales and uses criterion that accounts for 36% and presence in ambient air criterion represents 22%. Using the third ranking method, points attributed to presence in ambient air, sales and uses, and chronic toxicity accounted for 43, 34, and 23%, respectively. The top 60 CUPs identified with each of the three ranking methods are further investigated for the possibility of analysis using a multi-residue analytical method. CUPs finally selected will be submitted to the analytical method development and validation.

Results and discussion

Currently used pesticides selection

In Belgium, 303 plant protection products were registered for both professional and non-professional uses in 2014. This high number of chemicals prevents the ease of use of a ranking method that attributes points to several criteria. Therefore, before ranking CUPs that will be monitored in ambient air, we first used a selection method that helped reducing the number of candidates from 303 to 108 (Fig. 1). The first reduction of the candidate list consisted in the removal of 72 plant protection (i.e., microorganisms, molecules derived from plants and animals, insect pheromones, and other plant protection products) that are out of the scope of the project. The number of candidate CUPs is further reduced using data on sales and uses as well as chronic toxicological information available in databases (Fig. 1).

Selection based on sales and uses

Between 2010 and 2013, cumulative amounts of 79 CUPs represented 95% of the total amount of CUPs sold to professional and non-professional users in Belgium that is 18,757 t (supplementary material, Table S1). Two CUPs, the fungicide mancozeb and the herbicide glyphosate, contributed to almost 30% of this amount. Asulam is discarded from the candidate list as it was banned for use in Belgium by the end of 2012.

Selection based on chronic toxicity

The databases consulted for toxicological data (i.e., carcinogenicity, neurotoxicity, endocrine disruption, developmental and reproductive toxicity, and mutagenicity and genotoxicity) allow identifying 53 CUPs potentially toxic for human health

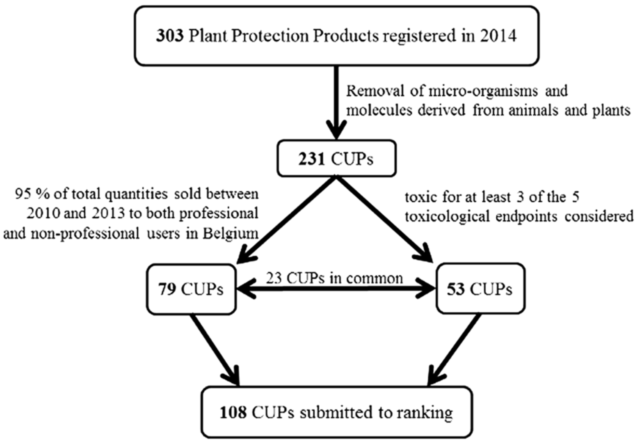

Fig. 1 Selection method used to reduce the number of CUPs considered for the final ranking method

for at least three toxicological endpoints (supplementary material, Table S2).

One hundred and ten CUPs are identified as possible, probable, or known carcinogens in at least one of the four databases consulted (Table 2). The data not only from human and experimental animal studies but also from mechanistic and other relevant data available are evaluated by working groups that define the strengths of evidence between exposure and carcinogenicity (IARC 2006; Cogliano et al. 2011). The classification of carcinogens based on the strengths of evidence highlighted that 54 CUPs are defined as "possibly carcinogenic to humans" in at least one of the four databases, whereas 28 CUPs are defined as "probably carcinogenic to humans" and 28 others are defined as "known carcinogens" (Table 2). Interestingly, 23 CUPs of the 95% most sold in Belgium between 2010 and 2013 are listed as probable (12) or known carcinogens (11). Moreover, the cumulative amount sold for these 23 CUPs represents almost half (i.e., 48.2%) the total quantity sold during this period in Belgium (known carcinogens represent alone 14.3%). This highlights that even though CUPs are suspected or recognized as human carcinogens, some were still sold in large quantities between 2010 and 2013. This is particularly emphasized by mancozeb, which is listed as probably carcinogenic to humans in at least one of the four databases consulted and was the most sold CUPs between 2010 and 2013 (supplementary material, Tables S1 and S2).

Table 2 Number of CUPs classified for their toxicological endpoints in at least one of the database consulted (total of 231 CUPs considered)

Carcinogenicity	
Known	28
Probable	28
Possible	54
Not likely	121
Neurotoxicity	
Suspected or proved	74
Not likely	157
Endocrine disruption	
Suspected or proved	49
Not likely	182
Reproductive and developmental toxicity	
Suspected or proved	162
Not likely	69
Mutagenicity and genotoxicity	
Suspected or proved	15
Not likely	216

The strengths of evidence for other toxicological endpoints are weaker as data are less available for these endpoints and are therefore not considered (Sugeng et al. 2013). Thus, for the four other toxicological endpoints (i.e., neurotoxicity, endocrine disruption, developmental and reproductive toxicity, and mutagenicity and genotoxicity), CUPs are either classified as suspected/proved toxicants or as non-toxic. These criteria are assessed using the two databases dedicated to pesticides (i.e., PPDB and SAgE). Approximately one third of CUPs, (i.e., 74 CUPs) are identified for potential neurotoxic effects (Table 2) among which 32 contribute to the 95% most sold in Belgium between 2010 and 2013. Similarly to carcinogens, cumulative amount of CUPs with suspected or proved neurotoxicity also represents 48.2% of the total quantities sold in Belgium between 2010 and 2013. Epidemiological studies that investigated neurotoxicity of pesticides on human mainly focused on neurobehavioral and neurodevelopmental impacts of prenatal and perinatal exposure of children and on neurologic effects of adult occupationally exposed to pesticides (Koureas et al. 2012). These studies mainly focused on organophosphate, carbamate, and pyrethroid pesticides. Still, some carbamate pesticides in our list (e.g., metam sodium, metam potassium, prosulfocarb, and phenmedipham) and a pyrethroid (tau-fluvalinate) are not identified as neurotoxic. The cumulated amount sold of the other 28 organophosphate, carbamate, and pyrethroid pesticides identified as neurotic represents 27.2% of the total quantities sold in Belgium between 2010 and 2013. Sales of mancozeb, a carbamate fungicide, represent alone 16.9% of the Belgian sales during this period (supplementary material, Table S1).

Endocrine disruptors can affect human health through interactions with hormone synthesis, hormone storage and/or release, hormone transport or clearance, and hormone receptor binding or post-receptor activation (Damstra et al. 2002). These interactions with the endocrine system can lead to alterations of the reproduction (e.g., reduced semen quality, adverse pregnancy outcomes) and of the development (e.g., delayed puberty, development of secondary sex characteristics) in humans (Kortenkamp et al. 2011; Bergman et al. 2013). Only 49 out of the 231 CUPs are identified as potential endocrine disruptors. The cumulated amount of these potential endocrine-disrupting CUPs represents 35.6% of the total amount sold in Belgium between 2010 and 2013. Twenty

CUPs of the 95% most sold in Belgium between 2010 and 2013 are identified as potential endocrine disruptors. Testing methods available for the assessment of endocrine properties mainly focus on in vitro interaction with receptors (Bergman et al. 2013). However, assessment of endocrine disruption is difficult as these effects present non-linear dose-response relationship. Moreover, endocrine-disrupting impacts on health depend on the period of exposure during the organisms' life cycle (Kortenkamp et al. 2011; Bergman et al. 2013). With the development of new tests and the increasing literature on endocrine-disrupting effects of pesticides in vitro as well as in vivo, the number of CUPs identified with endocrine-disrupting properties will probably increase. Several specific lists identifying endocrine-disrupting pesticides are developed by governments and intergovernmental organizations. Therefore, using these lists might help better identify potential endocrine-disrupting CUPs.

For developmental and reproductive toxicity, 162 CUPs are listed in at least one of the two databases consulted as suspected or proved toxicants. This appears to be a particularly high number. Indeed, in a hazard-ranking method used in Yuma County, Arizona, USA, only 7 out of the 74 pesticides considered were associated with reproductive and developmental toxicity (Sugeng et al. 2013). The high proportion of CUPs ranked for this toxicological endpoint in our study is influenced by the PPDB database in which 156 CUPs are classified as probable (97) or known (59) reproductive and/or developmental toxicants. In contrast, SAgE database only identified 12 CUPs with possible reproductive effects on animals and 39 CUPS with possible (22) or confirmed (17) developmental effects on animals. This observation suggests that it might be useful to also consider peer-reviewed literature to improve the hazard assessment for CUPs (Sugeng et al. 2013). In our selection, we also consider mutagenicity and genotoxicity as additional health effect. To our knowledge, it is the first study that includes this toxicological endpoint for the classification of CUPs. However, data for these endpoints are scarce, and only 15 CUPs are identified for their genotoxicity and/or mutagenicity among which only glutaraldehyde is not identified for any of the other toxicological endpoints. Nevertheless, these 15 CUPs accounted for 24.8% of the total quantities sold in Belgium between 2010 and 2013.

In this study, only 30 CUPs are never identified for any of the five toxicological endpoints analyzed, and their cumulated amounts sold between 2010 and 2013 only represent 6.2% of the total quantities of CUPs sold during this period in Belgium. In contrast, 23 out of the 53 CUPs potentially toxic for at least three toxicological endpoints are among the 95% most sold CUPs in Belgium between 2010 and 2013 (Fig. 1). These 23 CUPs accounted for 37.3% of the total quantities sold during this period. It should be noted that 6 CUPs are identified in at least one of the databases consulted as toxic for each of the five toxicological endpoints (supplementary material, Table S2). Quantities of these 6 CUPs sold between 2010 and 2013 in Belgium accounted for 21.4% of total sales (supplementary material, Table S1).

Sugeng et al. (2013) observed that approximately 80% of the total pesticide amount used in Yuma County, Arizona, USA, between 2006 and 2011 was associated with chronic toxicity (i.e., cancer, endocrine disruption, and/or reproductive/developmental toxicity). Therefore, monitoring concentrations of CUPs suspected or known for their toxicity in humans and sold in large quantities appears important to evaluate population exposure and the subsequent potential health effects. The use of quantities sold in Belgium between 2010 and 2013 and of data on the five toxicological endpoints helped to reduce the number of CUPs candidates for ambient air monitoring in Wallonia from 231 to 108 (Fig. 1). These CUPs are then further submitted to the ranking method using the sub-criteria of the three main criteria (i.e., chronic toxicity, sales and uses, and presence in ambient air) (Table 1).

Currently used pesticide ranking

Points are attributed for all the 17 sub-criteria to each of the 108 CUPs based on data available in pesticides databases, international studies and reports on ambient air monitoring, along with data from national and regional sales and uses as presented in the Table 1. Two additional methods are used for the attribution of points in order to assess robustness of the ranking and avoid potential bias due to overestimation of one criterion over the two others. The first method (Table 1) attributes more points to the sales and uses criterion, whereas in the second and third methods, the most important criteria are chronic toxicity and presence in ambient air, respectively. The 60 CUPs with the highest total score after ranking using each of the three methods are identified as candidates for analytical method development (supplementary material, Table S3). Sixty-six CUPs are identified in at least one top 60 of the three ranking methods. Interestingly, only 14 CUPs are not identified in the top 60 of all the ranking methods (supplementary material, Table S3). This highlights that even if adjustments are used to mitigate the importance of the three main criteria in the ranking, the most interesting CUPs to assess in ambient air could be consistently identified. The first method of points attribution (Table 1) is used to further discuss results.

All CUPs have a total score of 23 or higher on a maximum of 48 points attributed using the ranking method 1 (Table 3). The highest score is attributed to chlorothalonil with 38 points. Indeed, chlorothalonil was used in large quantities in Wallonia on wheat, beet, and potato crops and was measured in ambient air in several studies in Europe and North America (White et al. 2006; Yao et al. 2006; Gouin et al. 2008; Schummer et al. 2010; Coscollà et al. 2011; Garron et al. 2012). Among these studies, the highest chlorothalonil concentration

Table 3 Total scores attributed to the 66 CUPs for the three main criteria using ranking method 1

Currently used pesticides	CAS number	Chemical family	Score for chronic toxicity	Score for sales and uses	Score for presence in ambient air	Total of points
Chlorothalonil	1897-45-6	Chloronitrile	7	19	12	38
Cymoxanil	57966-95-7	Cyanoacetamide oxime	9	16	12	37
Fluazinam	79622-59-6	Phenylpyridinamine	11	15	11	37
MCPA	94-74-6	Aryloxyalkanoic acid	10	20	7	37
2,4-D	94-75-7	Aryloxyalkanoic acid	10	16	10	36
Epoxiconazole	133855-98-8	Triazole	8	17	11	36
Mecoprop-P	16484-77-8	Aryloxyalkanoic acid	7	17	12	36
Pendimethalin	40487-42-1	Dinitroaniline	7	16	13	36
Tebuconazole	107534-96-3	Triazole	8	18	10	36
Dimethenamid-P	163515-14-8	Chloroacetamide	7	17	11	35
Linuron	330-55-2	Urea	10	16	9	35
Prochloraz	67747-09-5	Imidazole	11	16	8	35
Propiconazole	60207-90-1	Triazole	10	16	9	35
Terbuthylazine	5915-41-3	Triazine	8	16	11	35
Cypermethrin	52315-07-8	Pyrethroid	10	14	10	34
Fenpropimorph	67564-91-4	Morpholine	6	15	13	34
Mancozeb	2234562	Carbamate	12	19	3	34
Chlorpyrifos	2921-88-2	Organophosphate	10	10	13	33
Dimethoate	60-51-5	Organophosphate	14	10	9	33
Deltamethrin	52918-63-5	Pyrethroid	9	12	11	32
Diflufenican	83164-33-4	Carboxamide	3	18	11	32
Ethofumesate	26225-79-6	Benzofuran	4	17	11	32
Prosulfocarb	52888-80-9	Thiocarbamate	4	16	12	32
S-metolachlor	87392-12-9	Chloroacetamide	5	14	13	32
Triallate	2303-17-5	Thiocarbamate	9	11	12	32
Flufenacet	142459-58-3	Oxyacetamide	10	19	2	31
Aclonifen	74070-46-5	Diphenyl ether	6	13	11	30
Difenoconazole	119446-68-3	Triazole	7	16	7	30
Iprodione	36734-19-7	Dicarboximide	10	11	9	30
Isoproturon	34123-59-6	Urea	5	17	8	30
Oxadiazon	19666-30-9	Oxidiazole	8	9	13	30
Boscalid	188425-85-6	Carboxamide	6	16	7	29
Dichlorprop-P	15165-67-0	Aryloxyalkanoic acid	8	12	9	29
Flusilazole	85509-19-9	Triazole	10	8	11	29
Glyphosate	1071-83-6	Phosphonoglycine	1	20	8	29
Metaldehyde	9002-91-9	Cyclo-octane	11	15	3	29
Spiroxamine	118134-30-8	Morpholine	3	13	13	29
Thiram	137-26-8	Carbamate	13	14	2	29
Alpha-cypermethrin	67375-30-8	Pyrethroid	9	10	9	28
Chlorpropham	101-21-3	Carbamate	8	13	7	28
Tetraconazole	112281-77-3	Triazole	10	8	10	28
Captan	133-06-2	Phthalimide	3	12	12	27
Dimethomorph	110488-70-5	Morpholine	4	12	11	27
Fenoxycarb	72490-01-8	Carbamate	10	6	11	27
Fenpropidin	67306-00-7	Unclassified	5	10	12	27
Metribuzin	21087-64-9	Triazinone	7	13	7	27
Phenmedipham	13684-63-4	Carbamate	4	17	6	27
Pirimicarb	23103-98-2	Carbamate	6	10	11	27

Table 3 (continued)

Currently used pesticides	CAS number	Chemical family	Score for chronic toxicity	Score for sales and uses	Score for presence in ambient air	Total of points
Prothioconazole	178928-70-6	Triazolinthione	7	18	2	27
Trifloxystrobine	141517-21-7	Strobilurin	3	15	9	27
Azoxystrobin	131860-33-8	Strobilurin	3	15	8	26
Cyprodinil	121552-61-2	Anilinopyrimidine	4	9	13	26
Dicamba	1918-00-9	Benzoic acid	7	12	7	26
Metazachlor	67129-08-2	Chloroacetamide	4	11	11	26
Clopyralid	1702-17-6	Pyridine compound	3	16	6	25
Metamitron	41394-05-2	Triazinone	6	17	2	25
Pyrimethanil	53112-28-0	Anilinopyrimidine	7	7	11	25
Thiophanate-methyl	23564-05-8	Benzimidazole	12	11	2	25
Amitrole	61-82-5	Triazole	14	9	1	24
Beta-cyfluthrin	68359-37-5	Pyrethroid	10	7	7	24
Bromoxynil	1689-84-5	Hydroxybenzonitrile	9	6	9	24
Carbendazim	10605-21-7	Benzimidazole	11	8	5	24
Chlorotoluron	15545-48-9	Urea	6	12	6	24
Fluroxypyr	69377-81-7	Pyridine compound	5	18	1	24
2,4-DB	94-82-6	Aryloxyalkanoic acid	9	10	4	23
Metiram	9006-42-2	Carbamate	12	9	2	23

measured was 108 ng/m^3 in Center Region, France (Coscollà et al. 2010). This broad-spectrum fungicide was also detected in urban sampling sites as well as in forested areas located far from any agricultural uses suggesting long-range transport (White et al. 2006; Yao et al. 2006; Gouin et al. 2008; Garron et al. 2012; Wofford et al. 2014). Potential carcinogenicity of chlorothalonil is listed in the four databases consulted. Moreover, PPDB database identified this fungicide as known to cause reproduction and development effects. Chlorothalonil also received the third highest score in a ranking method developed by the California Department of Pesticide Regulation to select CUPs further analyzed in ambient air in California (Segawa et al. 2014).

A total score of 37 is attributed to cymoxanil, fluazinam, and MCPA. These CUPs are classified as suspected or proved toxicants for at least three endpoints (supplementary material, Table S2) and were all used in large quantities on large areas in Wallonia between 2010 and 2013. The fungicide cymoxanil was monitored in France and Spain (Sauret et al. 2008; Coscollà et al. 2013) but was only detected at concentrations above its quantification limit in France at a maximum of 40 ng/m^3 in Britany (AirBreizh 2007). The fungicide fluazinam was also measured in some French studies, however, at a maximum concentration of 2.2 ng/m^3 (Coscollà et al. 2010). The herbicide MCPA was only measured in Canada at a maximum concentration of 5.83 ng/m^3 in an agricultural region (Aulagnier et al. 2008; Yao et al. 2008). None of these CUPs were ranked in the Californian ranking method (Segawa et al. 2014). However, it was not specified if these pesticides were among the top 100 used in California.

Mancozeb is the CUP with the highest cumulative amount sold in Belgium and with the highest quantity used in Wallonia between 2010 and 2013. Furthermore, this carbamate fungicide is also suspected or proved toxicant for all toxicological endpoints (supplementary material, Table S2). However, mancozeb has only the fifth highest score (i.e., 34 points) of the 108 CUPs classified (Table 3). Indeed, to our knowledge, mancozeb was only investigated once in ambient air monitoring studies with concentrations always under detection limit of the analytical method (Baker et al. 1996). This lack of data on mancozeb concentrations is probably due to its degradation to ethylene thiourea (ETU) in the environment (Kurttio et al. 1990). ETU analysis requires specific methods and was never investigated along with other CUPs in ambient air. Moreover, other ethylene bisdiothiocarbamate fungicides such as maneb or zineb also degrade to ETU (Lentza-Rizos 1990), which implies that ETU measured in the environment can hardly be linked to the emissions of a particular CUP.

Glyphosate is the most sold and used herbicide worldwide and is the second most sold CUP in Belgium between 2010 and 2013 after mancozeb (supplementary material, Table S1). Yet, its total score in our selection method is only the 10th highest (Table 3). Indeed, this broad-spectrum herbicide is not reported as suspected or known human toxicant for any of the five toxicological endpoints in the databases. However, it should be noted that since the consultation of the databases, IARC classified

Table 4 CUPs selected for the development of sampling and analysis methods for ambient air monitoring in Wallonia, Belgium, during a year

Currently used pesticides	Chemical family	CUP class	Currently used pesticides	Chemical family	CUP class
2,4-D	Alkylchlorophenoxy	Herbicides	Fluazinam	Phenylpyridinamine	Fungicides
2,4-DB	Alkylchlorophenoxy	Herbicides	Iprodione	Dicarboximide	Fungicides
Aclonifen	Diphenyl ether	Herbicides	Linuron	Urea	Herbicides
Alpha-cypermethrin	Pyrethroid	Insecticides	MCPA	Aryloxyalkanoic acid	Herbicides
Boscalid	Carboxamide	Fungicides	Mecoprop-P	Aryloxyalkanoic acid	Herbicides
Captan	Phthalimide	Fungicides	Metazachlor	Chloroacetamide	Herbicides
Chlorothalonil	Chloronitrile	Fungicides	Metribuzin	Triazinone	Herbicides
Chlorpyrifos	Organophosphate	Insecticides	Oxadiazon	Oxidiazole	Herbicides
Clopyralid	Pyridine compound	Herbicides	Pendimethalin	Dinitroaniline	Herbicides
Cymoxanil	Cyanoacetamide oxime	Fungicides	Pirimicarb	Carbamate	Insecticides
Cypermethrin	Pyrethroid	Insecticides	Propiconazole	Triazole	Fungicides
Cyprodinil	Anilinopyrimidine	Fungicides	Prosulfocarb	Thiocarbamate	Herbicides
Deltamethrin	Pyrethroid	Insecticides	Pyrimethanil	Anilinopyrimidine	Fungicides
Difenoconazole	Triazole	Fungicides	S-metolachlor	Chloroacetamide	Herbicides
Diflufenican	Carboxamide	Herbicides	Spiroxamine	Morpholine	Fungicides
Dimethenamid-P	Chloroacetamide	Herbicides	Tebuconazole	Triazole	Fungicides
Dimethoate	Organophosphate	Insecticides	Terbuthylazine	Triazine	Herbicides
Epoxiconazole	Triazole	Fungicides	Tetraconazole	Triazole	Fungicides
Ethofumesate	Benzofuran	Herbicides	Thiram	Carbamate	Fungicides
Fenoxycarb	Carbamate	Insecticides	Triallate	Thiocarbamate	Herbicides
Fenpropidin	Morpholine	Fungicides	Trifloxystrobine	Strobilurin	Fungicides
Fenpropimorph	Morpholine	Fungicides			

glyphosate as probably carcinogenic to humans (group 2A) (IARC 2015). Though, this modification has only little effect on its ranking. This change in classification highlights the need to constantly review knowledge on health effects associated to pesticide exposure, especially for endocrine disruption and reproductive and developmental toxicity outcomes (Sugeng et al. 2013). Glyphosate can be measured in ambient air along with its degradation product aminomethylphosphonic acid (AMPA) (Feng-chih et al. 2011; Majewski et al. 2014). Glyphosate and AMPA were detected in over 60% of air samples taken in Mississippi, Iowa, and Indiana, USA, throughout the growing season in 2007 and 2008 with a maximum concentration of 9.1 ng/m^3 (Feng-chih et al. 2011; Majewski et al. 2014). Yet, glyphosate and AMPA analysis in ambient air requires an analytical method that is specific to these molecules and might not be included in a multi-residues method (Feng-chih et al. 2011; Majewski et al. 2014).

These observations highlight the need to evaluate each of the 66 CUPs to assess the possibility to develop multi-residues method that includes the highest number of different CUPs. Review of analytical method allowed a final selection of 43 CUPs that will be submitted to the further development of the sampling and analysis methods for ambient air assessment in Wallonia, Belgium. These 43 CUPs are listed in Table 4.

Conclusions and perspectives

In this study, we used a selection method followed by a ranking method that helped identify a manageable number of CUPs for a yearlong study on ambient air concentrations in Wallonia, Belgium. The selection method reduced the number of plant protection products considered in the ranking method from 303 to 108. The criteria used for this selection were the origins (i.e., microorganisms, molecules derived from plants and animals, and insect pheromones), data on sales and uses, and chronic toxicological information.

The ranking method used 3 main criteria divided in a total of 17 sub-criteria. This method took into account not only toxicological endpoints but also national and regional data on sales and uses along with other uses criteria such as the number of commercial products containing the CUP or the number of crops that might be treated with the pesticide. Moreover, as the aim is to assess ambient air concentrations in Wallonia, probability to detect CUPs in ambient air was investigated using international, national, and regional studies as well as physicochemical properties. All these criteria were used in the ranking method to provide the most accurate identification of CUPs that might be measured in ambient air and that might potentially impact human health.

Using three different methods of points attribution to criteria highlighted the robustness of the ranking method to identify the most interesting CUPs to assess in ambient air in Wallonia. These selection and ranking methods helped reduce the number of CUPs that will be analyzed in ambient air in Wallonia during 1 year from over 300 to 43. Results of the monitoring study will provide better insight on spatial and temporal variations and help identify most preoccupant CUPs for human health in Wallonia. In the frame of the European Union Directive 2009/128/EC, which establishes a framework to achieve sustainable use of pesticides by reducing the risks and impacts of pesticides use on human health and the environment (OJEU 2009), it will be interesting to set up a second survey in a few years. Comparison of results of the present study with a future study will allow assessing effectiveness of regulations taken by the Walloon government.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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