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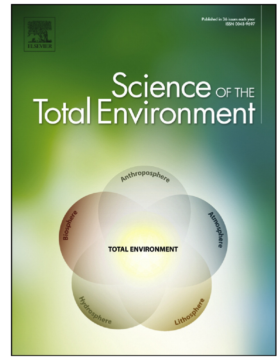

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Monitoring of pesticides in ambient air: prioritization of substances

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Abstract: Despite the richness of data collected on pesticide concentrations in ambient air in France, knowledge on this topic remains partial and heterogeneous in the absence of specific regulations. The population exposure remains thus difficult to estimate; therefore it was necessary to define modalities for implementing national monitoring of pesticides in ambient air in metropolitan France and in the overseas territories. The objective of this work was to identify which active substances (a.s.) have to be monitored in priority. As part of a collective expertise, a group of multidisciplinary experts has developed a method to rank active substances authorized as plant protection products, biocides and antiparasitic agents, which were available on the French market in 2015. A 3-steps approach has been developed. The first step consisted of a theoretical approach based on a hierarchy of substances according to four criteria: (a) national uses, (b) emission potential to the air, (c) persistence in the air, and (d) chronic toxicity. The three first criteria give information on their potential to be present in the atmosphere, and the fourth criterion allows to consider their potential of hazard. The second step was an observational approach based on existing database on pesticide air measurements in France. In the third step, both approaches were combined using decision trees to select priority pesticides. Among the 1,316 a.s. first identified from the EU Pesticides database, 90 were selected, among which 43 required metrological and/or analytical development. The experts recommended confirming the relevance of performing a longer term monitoring of these a. s. after a one-year exploratory campaign. The proposed method is reproduceable, transparent, easy to update (e.g. in the light of a change in product authorization), and can be adapted to other agricultural and geographical conditions, and objectives (e.g. monitoring of the ecotoxicological effects of pesticides).

1. Introduction

Pesticides are products used for the prevention, control or elimination of organisms considered as undesirable, such as plants, animals, insects, fungi or bacteria. This definition covers a wide range of uses: plant protection products (PPPs), biocidal products, and antiparasitic agents. Pesticides are available in different formulations, containing one or more active substances and formulants, and can be obtained in solid, liquid or gaseous form. PPPs are intended to protect plants against harmful organisms and their effects. In 2015, out of all the active substances approved in Europe, nearly 350 were authorized for used in France in commercial products (EU Pesticides database, 2015). The same year, a total of around 68 thousands of tons of active substances were sold in France (Agreste, 2019), which places France between the first and third places in Europe in terms of tonnage sold depending on the type of pesticides (fungicides, herbicides or insecticides) . However, with 54% of the metropolitan surface occupied for agricultural use Agreste Memento, 2015), France becomes the 10th largest PPP user in Europe (2016 data) in terms of PPP tonnage per hectare. Biocidal products are used to destroy, repel or render harmless harmful organisms, to prevent their effects or control their action by chemical or biological means (disinfectants, protective products, pest control products, etc.). In 2015, nearly 265 active substances were authorised (or in the process of being authorised) in France (EChA, 2015). Finally, veterinary or human antiparasitic agents with curative or preventive properties against human or animal diseases, and any substance or composition that may be used or administered to humans or animals for the purpose of making a medical diagnosis or restoring, correcting or modifying their physiological functions by exercising pharmacological, immunological or metabolic action, are also considered to be pesticides. In 2015, about 50 active substances were used in France. Like biocidal products, no concise information describing the quantities of active substances used in antiparasitic agents is available either. In addition to these authorised substances, some prohibited ones are likely to be present in the environment because of their high persistence (see for example Cabidoche et al., 2009; Orton et al., 2013).

The impact of pesticides on health is the subject of much debate. Several epidemiological studies have shown relationships between some of these substances and chronic diseases (Inserm, 2013). However, exposure to pesticides remains difficult to estimate, whether for farmers, residents or the general population, due to the number of substances and different pathways of exposure. Although food exposure is now increasingly well known, the contribution of other exposure pathways, particularly through the air, remains insufficiently documented. In France, knowledge of pesticide contamination levels in the air has been addressed for more than 15 years through local and ad hoc initiatives, in particular by the Approved Air Quality Monitoring Associations (AASQAs) and research teams (Coscollà et al., 2017; Villiot et al., 2018; Désert et al., 2018, and references therein as early as the mid-1990s, such as Chevreuil et al. (1996) or Millet et al. (1997)). However, in the absence of specific regulations on the monitoring of pesticides in ambient air and without a shared methodology and a list of active substances sought, this knowledge remains partial and heterogeneous. The assessment of airborne exposure to pesticide residues and associated risks for the general population is therefore currently complex to implement.

In this context, monitoring pesticides in the ambient air nationwide may help in such an assessment as resulting data can be used to analyse the contribution of this compartment to the population's total exposure to pesticides. Although analytical methods are becoming more and more efficient, with lower limits of quantification and an increasing number of compounds that can be analysed per sample, it is not possible to search for all the compounds potentially present in the air. It is therefore necessary to draw up lists of compounds to be sought as a matter of priority according to criteria to be defined. Such an initiative has been proposed in the USA (California) (Segawa et al., 2014) and in Belgium (Giusti et al., 2018). Both countries have developed a ranking method to identify pesticides to be measured in the air during monitoring campaigns. Their methods are based on selected criteria focused on local use, toxicity or potential presence in the air. Recently, the French ministries asked the National Agency for Food, Environment and Occupational Health & Safety (ANSES) and the French National Reference Laboratory for Air Quality Monitoring (LCSQA) to define the outlines for national monitoring of pesticides in ambient air. The data will feed into the phytopharmacovigilance scheme which is designed to monitor exposure to active substances available on the market in pesticides and their adverse effects in general populations and bystanders, assessing the level of contamination in the environment, their impacts on living organisms and ecosystems, and the emergence of resistance. Therefore, the objective of this work was to develop an approach to define the list of priority active substances to monitor in France. For the purposes of this study, "pesticides" means all active substances authorised or having been authorised for PPPs, including those that may currently have other uses, such as biocides and human and/or veterinary antiparasitic agents.

2. Material and Methods

2.1 Identification of substances of interest

In order to identify the compounds to be considered, an initial list was established from the EU Pesticides database of the European Commission's Directorate-General for Health and Food Safety (EU Pesticides database, 2015). Substances likely to be found in the air were taken into account in the subsequent selection process if they belonged to the EU pesticides database and met at least one of the following criterion: (1) the authorised active substances are currently sold in France as PPP and/or as biocidal and antiparasitic products for veterinary and human use; (2) the prohibited active substances were either sold in France for less than 3 years previously or are persistent in the environment according to EC regulation 1107/2009 (2009), i.e. if their half-life (DT50) in soil > 120 days; and (3) the active substances were found during previous measurement campaigns by Approved Air Quality Monitoring Associations (AASQAs). The same substance can be present in more than one of these categories. These three criteria were checked according to several French, European and international databases (Table S1).

2.2 Approach for pesticide selection

The selection of pesticides was based on a three-phase approach (Figure 1). The first phase consisted of a theoretical approach based on drawing up a hierarchy of substances according to various criteria. The second one consisted of an observational (or empirical) approach based on the results of previous measurement campaigns. Finally, in the third phase, the theoretical and observational selections were compared via decision trees aiming at dividing up substances into three groups: "priority", "non-priority", and "non-classified" when it was not possible to rank priority due to the lack of data.

The determination of selection criteria and the prioritisation method had to be operational, robust, traceable, transparent, scalable, and as homogeneous as possible between the different types of compounds. In addition, as this list was intended to be used for national monitoring, it had to be easy to update following a change in product authorisation.

2.2.1 The theoretical approach

The *theoretical* approach was based on the Sph'Air screening tool (Gouzy et al, 2005; L'Hermite and Gouzy, 2008) previously developed for the prioritisation of pesticides to be sought in ambient air. Briefly, the Sph'Air tool prioritises substances used as PPPs according to their occurrence in the air compartment and their hazard potential, using the ELECTRE-III multi-criteria aggregation method (Roger and Bruen, 1998; Roy, 1985). This method consists in discriminating substances by comparing them criterion by criterion.

2.2.1.1 Potential of pesticide occurrence in the air

To assess the potential occurrence of the active substances in the air, a conceptual scheme for the transfer of pesticides to the air was established considering the main processes involved in their occurrence in the atmosphere: their distribution between the soil, crop, and air at the time of application; volatilisation from the soil and the plant; and its degradation in the air, taking into account the gas/particle partition of the compound. Based on this scheme, three criteria were identified to estimate the potential of a compound to be present in the air: (1) the quantities of substances used in France from 2012 to 2015, only considering products used in agriculture (BNV-d, 2016); (2) their potential for emission into the air (during and after application), which is estimated given the initial distribution estimated by experts (depending on crops, type of sprayers used and period of application) and following predicted volatilisation rates as estimated by models (soil component) or empirical equations (plant component) (see details in Supplementary materials); (3) their persistence in the atmosphere, or their time of residence in the atmospheric compartment, which is estimated considering indirect photodegradation with OH radicals (using AOPWin, the Atmospheric Oxidation Program for Microsoft Windows; AOPWIN model v.1.92a) and a specific degradation rate for the adsorbed fraction on atmospheric particles (partition between gaseous and particles is based on the Junge-Pankow relation) (Meyland and Howard 1993).

For biocidal products and antiparasitic agents, a simplified version of Sph'Air was proposed based on the criteria that can be provided for these substances (see details in Table 1).

Finally, as no specific data were available for active substances authorised in a non-agricultural area, the working group conducted interviews with specialised public or private bodies in order to collect relevant information on these substances.

In order to cover as much as possible of France, this approach was applied and adapted for French overseas territories — Guadeloupe, Martinique, French Guiana, and Reunion Island — when usage data were available. The adaptations were necessary due to a lack of knowledge on the applicability of the models used for emission and dispersion under the specific pedoclimatic context of these territories (Table 1).

2.2.1.2 Hazard potential

The hazard score is based on the method used to calculate the toxicological risk index (TRI), which is included in the calculation of the PIReQ-Health developed in Quebec (Samuel et al., 2012). Even if this hazard score can be declined for acute and chronic hazards, only the chronic component was selected here to assess the general population's exposure. The following chronic effects were considered: specific toxicity to certain target organs following repeated exposure; carcinogenic effects; genotoxicity; endocrine disruption; reprotoxic and developmental effects, including neurodevelopment; neurodegenerative effects (Parkinson's, Alzheimer's, amyotrophic lateral sclerosis, cognitive disorders). Hazard points are applied according to the type of effects and to the classification of the substance by different agencies such as IARC (International Agency for Research on Cancer) (Table 2, see Supplementary material for details). If an active substance had several classifications for the same effect (e.g. IARC classification and CLP - Classification labelling and packaging - for carcinogenicity), only the highest score among the available classifications was used. For each active substances, a hazard score for each of the substances was then calculated by adding all the scores obtained for each selected chronic effect.

2.2.1.2 Ranking method

The criteria to be considered depend on the purpose of the ranking. For contamination assessment purposes, only criteria related to potential occurrence in the atmosphere were considered (i.e. persistence, quantity, sources for the atmosphere). The same weighting coefficients were allocated to each of the criteria (Table 3). For health risk assessment purposes, the potential presence (persistence, quantity, and sources) and potential hazard were both considered. The weighting coefficients were allocated to these four criteria so that each potential had the same weight (Table 3).

As the Sph'Air tool classifies substances in relation to each other, it only allows relative comparisons. Deciding on priority substances, therefore implies setting a threshold. Virtual substances, for which the criteria values were predefined and known, were created to access an estimate of the variations. Thus, twelve virtual substances corresponding to the zero, 10^{th}, 20^{th}, 30^{th}, 40^{th}, 50^{th}, 60^{th}, 70^{th}, 80^{th}, 90^{th}, 95^{th}, and 100^{th} percentiles were added to the studied active substances and used to set the threshold. At the end of this theoretical approach, the substances were divided into three categories. Provisional category 1 listed the relevant substances to be considered according to the results of the theoretical approach. At this stage of the ranking, these substances were said to be provisional, as they would then be confronted with the observational approach before being included in or excluded from the list of priority substances for the monitoring of pesticides in ambient air. Category 2 grouped substances for which there were insufficient data and which could not be included in the prioritisation process. Category 3 listed substances considered as non-priority according to the results of the theoretical approach.

2.2.2 The observational approach

The observational approach was based on measurement data collected by the AASQAs and followed the approach proposed by the NORMAN network (Dulio et al. 2013).

2.2.2.1 Description of the NORMAN approach and data used

The NORMAN network was developed to identify emerging substances to be monitored in water, based on available occurrence data. The categorisation of substances is based on the research rate, the quantification rate, and the comparison of observed concentrations and/or analytical limits with a threshold value. This method was adapted here in as follows: (1) the categorisation of the substances according to the results observed by the AASQAs during their measurement campaigns on ambient air allowed us to identify relevant substances for the purpose of "contamination monitoring" and to compare the results of the theoretical approach with measurement data; (2) the identification of relevant substances to be considered from a toxicological point of view on the basis of the measured concentrations made it possible to identify relevant substances for the health risk assessment purpose. By implementing this approach, we were also able to identify substances for which additional data are needed.

The observational approach was applied on data collected from 2011 to 2015 by at least one of the AASQAs on their background sites and available in their PHYTATMO database (see Supplementary materials). Around 120,000 analyses were therefore considered, which covered 210 compounds.

2.2.2.2 Categorisation of the substances based on their frequency of detection

In order to categorise substances based on their frequency of detection, two ratios were calculated for each substance measured at least once: (1) the quantification rate per search, corresponding to the number of times the substance has been quantified over the number of times it has been sought, and (2) the quantification rate per site, corresponding to the number of sites where the substance has been quantified at least once out of the number of sites where it has been sought. This approach has the advantage of taking into account the spatial and temporal variability that may exist among AASQA data, as the substances were not sought on all sites and during the same periods.

The substances were divided up into four classes depending on the distribution of these two ratios: (A) substances that were poorly or not researched and poorly or not quantified; (B) substances frequently sought but not frequently quantified; (C) substances frequently sought and frequently quantified; (D) substances that were rarely sought but that were frequently quantified, known as emerging substances. The percentiles of the distribution were calculated for each of these two ratios based on all available data. The 30^{th} percentile of the distribution was chosen as the limit to qualify a poorly quantified substance, and the 70^{th} percentile as the limit to qualify a substance as frequently quantified. When the classification was different according to the criterion considered (by site or by research), the most discriminating category was chosen (A vs. B ; C or D vs. B).

2.2.2.3 Categorisation of substances from a toxicological point of view

The NORMAN network approach is based on the comparison of measured concentrations against a toxicity threshold value known as the "predicted no-effect concentration (PNEC) in the case of prioritising emerging substances in water). However, for the atmospheric compartment, there is no threshold value. We therefore, suggested relying on the approach used for exposure assessment of residents and bystanders as required in the PPP authorisation procedure defined by EFSA (2014). The EFSA method relies on a model to estimate the exposure of these populations following pesticide application to different types of crops. EFSA then recommends comparing the exposure to the most appropriate toxicological reference value. Among the toxicological values available for a large number of pesticides, we decided to use the AOEL (acceptable operator exposure level), which was proposed in 2010 by EFSA as a reference value to be considered in the risk assessment for residents and bystanders (EFSA, 2010). This value refers to the maximum amount of active substance to which operators can be exposed on a daily basis without any harmful effect on their health. This is an internal reference value covering all exposure pathways.

To compare this value with the AASQA measurement data, the exposure was estimated according to the following equation:

$$E = C \times RR \times AR$$

where E is the exposure (ng. d^{-1}.kg bw^{-1}), C is the observed concentration (ng.m^{-3}), RR is the respiratory rate (m^3.d^{-1}.kg bw^{-1}), and AR is the absorption rate (dimensionless). Concerning the concentration value, the 95th percentile of the maximum concentrations of each of the sites was selected as suggested in the NORMAN network approach (NORMAN Association, 2013). It has the advantage of being protective while not taking into account extreme situations. Concerning the respiratory and absorption rates, the specific exposure factors for children and adults as defined by EFSA (EFSA 2014) were selected. The calculated exposure was then compared with the AOEL.

It should be noted that the objective of this approach was not to actually assess risk but to screen substances to identify those of highest priority taking into account their toxicity for health risk assessment purposes. Indeed, some uncertainties in the approach can be identified: 1) the choice of AOEL, which does not take into account any inhalation toxicity data. This toxicological reference value (TRV) is, however, one of the few available for a large proportion of the substances considered in our study; 2) the use of an internal TRV when the exposure used was only estimated for the inhaled route, and 3) the use of AASQA data that are not representative of all situations. As a result of these uncertainties, we decided to prioritise substances for which the estimated exposures were higher than the AOEL using a safety factor of 1000 (referred to as AOEL*). The highest estimate ("worst-case scenario") was used for comparison with the AOEL*.

2.2.2.4 Identification of substances for which additional data are needed

This approach allowed us to identify substances for which additional data were needed: substances lacking health data, and substances which need improved analytical methods. Among the substances frequently sought but not frequently quantified (category B), the relevance of the analytical limit used was studied. For these substances, the NORMAN network proposes comparing the analytical limits (minimum and maximum) to the PNEC (to distinguish substances for which monitoring is not considered a priority from substances for which analytical development is necessary and therefore about which it is not possible to conclude). Here, we compared exposure estimated from the analytical limits with the AOEL*, based on the same formula as before.

At the end of this second approach, the substances were divided into three categories like for the theoretical approach. Provisional category 1 lists the relevant substances to be considered according to the results of the observational approach: for the purpose of health risk assessment, substances identified as relevant from a toxicological point of view (see section 2.2.2.3) were considered as priorities; for the purpose of contamination assessment only, substances frequently quantified (categories C and D, see section 2.2.2.2) were considered as provisionally high-priority. These substances were then confronted with the theoretical approach before being included in or excluded from the list of priority substances for the monitoring of pesticides in ambient air. Category 2 lists substances for which data are missing and which could not be included in the prioritisation process. Category 3 lists what are considered non-priority substances in the light of the results of the theoretical and observational approaches.

2.2.3 Selection of priority and non-priority substances

The different lists obtained through *theoretical* and *observational* approaches were compared to identify priority and non-priority compounds to be monitored in the air.

2.2.3.1 Priority substances

The substances considered as a priority for national monitoring were (Table 4): authorised substances identified as relevant (rank > P70) according to the *theoretical* approach and often found in the air according to AASQA data (C or D classification); substances considered as a priority from a toxicological point of view according to the *observational* approach (exposure estimated from AASQA data close to AOEL*); substances often found in the air (C or D classification) according to authorised uses (or persistence for banned substances) and tonnages. However, in some cases, the comparison of the results highlighted the need for additional measurement data to decide whether or not a substance should be included in the list of priority substances: (1) when a substance had recently been banned, the ranking from AASQA data based on measurements taken before 2015 could be obsolete; and (2) when a substance was considered relevant according to the *theoretical* approach but had been measured only rarely or not at all by the AASQAs (A classification), or when it had been often sought and rarely found (B classification) but that the AASQA data were not considered sufficiently representative from a spatio-temporal point of view to draw conclusions. In this case, we recommend measuring these substances during a one-year national exploratory campaign. At the end of this campaign and depending on the results, these substances will be added to or excluded from the core list for national monitoring. Information on the analytical and/or metrological feasibility of each identified substance was also provided in consultation with the French central laboratory for monitoring air quality (LCSQA)

2.2.3.2 Non-priority substances

Non-priority substances were substances with specific and irrelevant use to the problem of ambient air, and substances often sought by the AASQAs but rarely or never found.

2.2.3.3 Non-classified substances

Finally, a list of non-classified substances was defined for substances with missing health and physico-chemical data or missing criteria necessary for the prioritisation processes. This list of substances was submitted to relevant expert committees in order to identify substances that they think should be included in the list of priority substances. Depending on their uses and tonnages, the experts added certain non-hierarchical substances to the list of relevant substances (see Table S11).

3. Results

A total of 1,316 substances were first identified from the EU Pesticides database (2015). From this list, 420 substances were then considered of interest because they are likely to be found in the air (Figure 1). Among them, 90 substances were finally selected for the whole of France (Table 4), 43 of which required metrological and/or analytical developments. For 74 substances, the selection method could not be applied, mainly due to a lack of data on physico-chemical characteristics, uses and/or the chronic hazard score.

Details on substances selected by steps are available in the Supplementary materials (Table S11).

For metropolitan France, the 76 priority pesticides include 20 fungicides, nine insecticides (cypermethrin and zeta-cypermethrin are also veterinary drugs), 25 herbicides, six biocides without current authorisation in France as a PPP (permethrin is both a human and veterinary antiparasitic and is the only human drug on the list; fipronil is a veterinary drug), 15 persistent compounds (including seven POPs) and one growth regulator (Table 4, Figure 2).

In the overseas territories, the distribution between the various pesticides used among PPPs is as follows (Table 4, Figure 2): for Guadeloupe, nine fungicides, six insecticides, ten herbicides, and one rodenticide; for Martinique, seven fungicides, seven insecticides, and nine herbicides; for French Guiana, seven fungicides, seven insecticides, three herbicides, and one rodenticide; and for Reunion Island, ten fungicides, eight insecticides, ten herbicides, and one nematicide.

There is a fairly homogeneous distribution of priority pesticides among PPP uses (herbicides, fungicides, insecticides) for all territories (Figure 2). However, there were fewer herbicides in French Guiana than in the other territories because of the majority use of glyphosate (more than half of PPP uses).

4. Discussion

The approach developed in this work allowed us to shortlist, from a list of more than 1,300 compounds, 90 relevant active substances to monitor in priority in ambient air (by territory – metropolitan France and overseas territories). This approach also had the advantage of being adaptable according to the objectives pursued (e.g. health risk assessment or air contamination) and to the available data. All the defined criteria can be updated following the acquisition of new knowledge or the availability of operational tools describing a given process. Compared to the approaches previously proposed in the literature, for which emission is based on vapour pressure alone (Segawa et al., 2014) or on vapour pressure and Henry's law constant (Giusti et al., 2018), a higher number of factors driving pesticide emission were taken into account in our study. Indeed, our approach distinguishes emission during application from post-application emission, and, after application, distinguishes application on bare soil from application on plants. Regarding other criteria, uses and toxicity were considered in all methods, as were the availability of analytical methods. The comparison of our priority list to the Belgian list, farming practices in Belgium being potentially closer than US practices to French practices, showed that of the 44 substances identified by Giusti et al. (2018), 32 were also selected in this study.

The results from the theoretical and observational approaches led us to propose an exploratory campaign to identify substances for which the priority characteristics should be confirmed before being measured in a longer-term monitoring programme. Nevertheless, some limits of our approach have to be underlined. The selection of compounds of interest was based on the active substance found in the commercial products, without consideration of co-formulants or adjuvants that might change the emission of pesticides into air but for which little knowledge is available (Lichiheb et al., 2015). Similarly, transformation products were not taken into account due to a lack of knowledge. This highlights the need for research documenting the presence of these compounds in the air compartment. In the different phases of the atmosphere (gaseous and particulate), the degradation of pesticides can lead to various transformation products but the current literature is limited to the study of a limited number of substances (El Masri et al., 2014; Al Rashidi et al., 2013). In addition, the identified transformation products do not always have associated toxicological information or analytical standards for their quantification. It is therefore difficult to gain a comprehensive understanding of the fate of these products. An inventory of known airborne transformation products with a view to their potential subsequent integration into the monitoring programme is needed, knowing that a transformation product may be more toxic than the parent substance (Socorro et al. 2016).

Regarding the theoretical approach, limits are related to the limits of the approaches selected to assess the criteria in the Sph'Air tool. The models used to estimate pesticide emission by volatilisation are not very suitable for active substances in the chemical form of salts and acids, or for substances applied by fumigation. Similarly, the interactions of active substances with vegetation are currently neglected due to a lack of both operational tools for their description on a wide range of substances, and information on the formulation's effect on these interactions. Thus, regarding systemic fungicides whose formulation may enhance penetration (Lichiheb et al., 2015), the Sph'Air "Source" criterion for volatilisation emissions from the canopy may be overestimated, leading to a potential over-classification of these substances during Sph'Air prioritisation. The analysis carried out on the existence of such an effect for systemic fungicides in the core list showed that a number of them were also observed by AASQAs (C classification) and that others were highly toxic. Thus, this potential bias had no significant impact on the ranking, as these compounds were also identified either by their toxicity or during the observational phase. In addition, the "Source" and "Residence time" criteria do not include the possible effect of the seasonality of PPP treatments, or of local conditions (e.g. overseas territories). Finally, the estimation of atmospheric persistence is based on 1) a distribution between both phases calculated with the Junge-Pankow relation, though other approaches could also be tested such as that of Lohman and Lammel in 2004 and 2) degradation in the particulate phase based, as an initial approach, on the gas phase degradation (given a percentage of this degradation), which may not be suitable for all compounds. In addition, regarding some prioritisation choices, it has to be noted that tests could be carried out on weighting coefficients in order to assess their potential impact on the final list of pesticides. In the same vein, the available approaches could be compared and tests carried out to ascertain the impact on prioritisation of the choice of models used to calculate the criteria applied. Apart from Sph'Air limits, the simplified approach used to prioritise other compounds than active substances authorized in PPPs in metropolitan France (*e.g.* biocides), which was based on a reduced number of criteria (due to lack of information), can lead to less robust ranking. In order to enhance the reliability of the prioritisation, it is essential to complete the missing criteria, which requires improving our current state of knowledge on process determinism.

From the point of view of data, prioritisation could only be conducted when datasets were available. However, the consultation of the various databases showed that some physico-chemical, toxicity or tonnage data were missing and that there were some inconsistencies between databases both for physico-chemical data and uses. In addition, as the physico-chemical data provided may not always be reliable, the calculation methods based on these data are therefore subject to some uncertainty. Moreover, there is no centralisation of ongoing pesticide use waivers, which makes the analysis of the information itself complex. Finally, the BNV-d database gives the sales in terms of tonnage rather than uses, so we assumed that the sold substances were used locally in the year of their purchase. It is not possible to take into account either potential storage phenomena or potentially undeclared imports. Therefore, data on these different elements are needed to update the Sph'Air tool.

5. Conclusion

An original approach was developed to identify and select pesticides to be monitored in ambient air. This approach allowed us to define a list of 90 priority substances for both metropolitan France and overseas territories. Based on this list, a nationwide measurement campaign will be implemented over a full year to assess the average exposure of the general population to pesticides in the air. The objectives of this first national campaign are to improve knowledge of pesticides present in ambient air and to better understand the exposure of the general population. It will also allow us to optimise the choice of sites, sampling strategy, and analysis procedures for the implementation of a sustainable national monitoring programme focusing on pesticides in ambient air.

The proposed method can be adapted to other agricultural and geographical situations by using corresponding pesticide properties and sales data. By considering, in the theoretical approach, the acute danger score, the acute exposure of people living near agricultural areas could be evaluated. Finally, an ecotoxicity score could be developed to monitor the impacts of pesticides on ecosystems.

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References

Agreste Chiffres et Données Agriculture - n° 2019-3 - juin 2019.

Al Rashidi, M. J., Chakir, A., Roth, E., 2013. Heterogeneous Ozonolysis of Folpet and Dimethomorph: A Kinetic and Mechanistic Study. J Phys Chem A, 117: 2908-2915

Cabidoche, Y. M., Achard, R., Cattan, P., Clermont-Dauphin, C., Massat, T., Sansoulet, J., 2009. Long-term pollution by chlordecone of tropical volcanic soils in the French West Indies: A simple leaching model accounts for current residue. Environmental Pollution 157, 1697-1705.

Chevreuil, M., Garmouma, M., Teil, M.-J., Chesterikoff, A., 1996. Occurrence of organochlorines (PCBs, pesticides) and herbicides (Triazines, phenylureas) in the atmosphere and in the fallout from urban and rural stations of the Paris area. Science of the Total Environment 182, 25–37.

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. Science of the Total Environment 584–585, 856–868. https://doi.org/10.1016/j.scitotenv.2017.01.132.

Désert, M., Ravier, S., Gille, G., Quinapallo, A., Armengaud, A., Pochet, G., Savelli, J.-L., Wortham, H., Quivet, E., 2018. Spatial and temporal distribution of current-use pesticides in ambient air of Provence-Alpes-Côte-d'Azur Region and Corsica, France. Atmospheric Environment 192, 241–256. https://doi.org/10.1016/j.atmosenv.2018.08.054.

EFSA. 2010. Scientific Opinion of the Panel on Plant Protection Products and their Residues (PPR) on Preparation of a Guidance Document on Pesticide Exposure Assessment for Workers, Operators, Bystanders and Residents. In EFSA Journal 2010. Parma: EFSA.

EFSA. 2014. Guidance on the assessment of exposure of operators, workers, residents and bystanders in risk assessment for plant protection products. In EFSA Journal 2014. Parma: EFSA

El Masri, A., Al Rashidi, M., Laversin, H., Chakir, A., Roth, E., 2014. A mechanistic and kinetic study of the heterogeneous degradation of chlorpyrifos and chlorpyrifos oxon under the influence of atmospheric oxidants: ozone and OH-radicals. RSC Adv., 4 : 24786-24795

Giusti, A., Pirard, C., Charlier, C., Petit, J. C. J., Crevecoeur, S., Remy, S.. 2018. Selection and ranking method for currently used pesticides (CUPs) monitoring in ambient air. Air Qual Atmos Health, 11: 385. https://doi.org/10.1007/s11869-017-0516-6

Gouzy, A., and Farret, R.. 2005. Détermination des pesticides à surveiller dans le compartiment aérien: approche par hiérarchisation. Synthèse du comité de pilotage Verneuil-en-Halatte: INERIS.

Inserm. 2013. Pesticides : Effets sur la santé. Rapport. Paris : Inserm, 2013, XII-1001 p. - (Expertise collective). - http://hdl.handle.net/10608/4820

L'Hermite, N., and Gouzy, A., 2008. Utilisation de l'outil Sph'Air pour déterminer les substances phytosanitaires à surveiller dans le compartiment aérien, Rapport INERIS n° DRC-08-94291-16614A, 63 p.

Lichiheb, N., Bedos, C., Personne, E., Benoit, P., Bergheaud, V., Fanucci, O., Bouhlel, J., Barriuso, E., 2015. Measuring Leaf Penetration and Volatilization of Chlorothalonil and Epoxiconazole Applied on Wheat Leaves in a Laboratory-Scale Experiment. Journal of Environment Quality 11: 1782–1790.

Lohmann, R., Lammel, G., 2004. Adsorptive and Absorptive Contributions to the Gas-Particle Partitioning of Polycyclic Aromatic Hydrocarbons: State of Knowledge and Recommended Parametrization for Modeling. Environ. Sci. Technol. 38, 3793–3803. https://doi.org/10.1021/es035337q

Meylan, W.M. and Howard, P.H., 1993. Computer estimation of the atmospheric gas-phase reaction rate of organic compounds with hydroxyl radicals and ozone. Chemosphere, 26: 2293-2299

Millet, M., Wortham, H. Sanusi, A. and Mirabel, Ph., 1997. Atmospheric contamination by pesticides: Determination in the liquid, gaseous and particulate phases. Environ. Sci. and Poll. Res., 4 (3) : 172-180.

NORMAN Association. 2013. Network of reference laboratories and related organisations for monitoring and bio-monitoring of emerging environmental substances. Working Group on Prioritisation of Emerging Substances. NORMAN Prioritisation framework for emerging substances. edited by Valeria Dulio & Peter C. von der Ohe. Verneuil-en-Halatte: NORMAN Association.

Orton, T.G., Saby, N.P.A., Arrouays, D., Jolivet, C.C., Villanneau, E.J., Marchant, B.P., Caria, G., Barriuso, E., Bispo, A., Briand, O., 2013. Spatial distribution of lindane concentration in topsoil across France. Science of the Total Environment 443: 338-350.

Regulation EC No 1107/2009, 2009. Regulation of the European parliament and of the council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC. Off. J. Eur. Union L309.

Roger, M., and Bruen M.. 1998. "Choosing realistic values of indifference, preference and veto thresholds for use with environmental criteria within ELECTRE." European Journal of Operational Research 107:542-551.

Roy B., Méthodologie multicritère d'aide à la décision, Ecomonica, Paris, 1985.

Samuel, O., Dion, S., St-Laurent, L., April, M. H., 2012. Quebec Pesticides Risk Indicators – QPRI – Health and Environment. Québec: Ministère de l'Agriculture, des Pêcheries et de l'Alimentation/ministère du Développement durable, de l'Environnement et des Parcs/Institut national de santé publique du Québec

Segawa, R., Levine, J., Neal, R., Brattesani, M., 2014. Community air monitoring for pesticides. part 1: selecting pesticides and a community. Environmental Monitoring and Assessment 186, 1327–1341. https://doi.org/10.1007/s10661-013-3507-6.

Socorro, J., Marque, S.R.A., Temime-Roussel, B., Ravier, S., Gligorovski, S., Wortham, H., Quivet, E., 2016. Products and mechanisms of the heterogeneous reactions of ozone with commonly used pyrethroids in the atmosphere. Sci. Total Environ., 573: 1287-1293

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. Atmospheric Environment 174, 82–91. https://doi.org/10.1016/j.atmosenv.2017.11.046

Table 1: Prioritization approach for pesticides selection based on their potential of occurrence in the air

List	Criteria used for the theoretical approach			
	Quantity used	*Potential of emission (=source)*		*Potential of persistence*
		During application	*After application (plant and soil)*	
Active substances authorized and sold in metropolitan France as PPP for agricultural uses	From BNV-d database on the period from 2012 to 2015	Use of the Sph'Air tool	Used of the Sph'Air tool	Use of the Sph'Air tool
Active substances authorized and sold in French overseas territories as PPP for agricultural uses	From BNV-d database on the period from 2012 to 2015	Not considered due to lack of knowledge	Use of the Sph'Air tool but with uncertainties due to the lack of knowledge of the impact of pedoclimatic conditions on the results of the models used in Sph'AIR	Use of the Sph'Air tool but with uncertainties due to the lack of knowledge of the impact of pedoclimatic conditions on the results of the models used in Sph'Air
Active substances authorized in biocidal products	Not considered due to lack of knowledge	Not considered due to lack of knowledge	Adaptation of the Sph'Air tool: only vapor pressure was considered without calculation via the sub-model used in Sph'Air for PPPs, due to the lack of knowledge on the type of materials used;	Use of the Sph'Air tool
Active substances authorized in anti-parasitic products for veterinary and human use	Not considered due to lack of knowledge	Not considered due to lack of knowledge	Adaptation of the Sph'Air tool: only vapor pressure was considered without calculation via the sub-model used in Sph'Air for PPPs, due to the lack of knowledge on the type of materials	Used of the Sph'Air tool
Forbidden Active substances but persistent	Not relevant	Not relevant	Identification of persistent a.s. (DT50 soil > 120 days) and ranking as a function of vapor pressure	Identification of persistent a.s. (DT50 soil > 120 days) and ranking as a function of vapor pressure
Active substances authorized in a non-agricultural area	Auditions			

Table 2: Hazard scores calculated attributed according to chronic effects

Effect	Hazard points applied according to effect types*					
	16	**8**	**4**	**2**	**1**	**0**
Carcinogenicity for humans	Carcinogenic	Probably carcinogenic	Possibly carcinogenic		No or insufficient data	unlikely carcinogenic
Mutagenicity for humans		Known as mutagenic	Probably mutagenic	Possibly mutagenic	Unclassified substances	
Endocrine disruptive effects (ED)		Evident ED	Probable ED	Suspected ED	No or insufficient data	Unlikely to be ED
Reprotoxicity for humans	Known as reprotoxic	Probablyreprotoxic	Possibly reprotoxic		Inadequate data or unclassified substances	
Specific target organ toxicity for humans – Repeated exposure		Causes damage to organes	May cause damage to organes		Unclassified substances	
Neurodegenerative effects for humans	Neurodegenerative effects	Probably neurodegenerative effects	Possiblyneurodegenerative effects		Inadequate data	

ED = Endocrine disruptors

* Hazard score based on the toxicological risk index (TRI) developed in Quebec (Samuel et al., 2012). Points are applied according to the type of effects and to the classification of the substance by different agencies such as IARC (International Agency for Research on Cancer) (Table 2, see supplementary material for details).

Table 3: Weighting coefficients in the criteria aggregation within the Sph'Air tool

Objective of contamination assessment			
Criterion	Sub-criterion	Weighting coefficient Mainland France	Weighting coefficient Overseas territories
Quantity		1	1
Potential of emission (=source)	$Source_{air}$	0.33	
	$Source_{soil}$	0.33	0.5
	$Source_{plant}$	0.33	0.5
Persistence in the air		1	1
Objective of Health risk assessment			
Hazard		3	3
Quantity		1	1
Potential of emission (=source)	$Source_{air}$	0.33	
	$Source_{soil}$	0.33	0.5
	$Source_{plant}$	0.33	0.5
Persistence in the air		1	1

Table 4: Lists of priority substances to be monitored in the air for metropolitan France and French overseas territories (Guadeloupe, Martinique, Guyana, Reunion)

substances		Metropolitan territory	Overseas territories				Objecti substanc
Name	N_CAS		Guadeloupe	Martinique	Guyana	Reunion	
2,4-D	94-75-7	X	X	X	X	X	Health I
2,4-DB	94-82-6	X					Health
Abamectin (aka avermectin)	71751-41-2	X	X	X	X	X	Health
Acetochlor	34256-82-1	X					Health
Aldrin	309-00-2	X	X	X	X	X	Health
Amitrole (aminotriazole)	61-82-5	X					Health
Bifenthrin	82657-04-3	X	X	X	X	X	Health
Boscalid (formerly nicobifen)	188425-85-6	X					Contami
Bromadiolone	28772-56-7		X				Health
Bromoxynil	1689-99-2	X					Contami
Butralin	33629-47-9	X	X	X	X	X	Contami
Camphechlor (Toxaphene)	8001-35-2	X	X	X	X	X	Health
Carbetamide	16118-49-3	X					Health
Chlordane	57-74-9	X	X	X	X	X	Health
Chlordecone	143-50-0		X	X			Health
Chlormequat	999-81-5	X					Contami
Chlorothalonil	1897-45-6	X	X	X	X	X	Health
Chlorpropham	101-21-3	X					Contami
Chlorpyrifos	2921-88-2	X	X	X	X	X	Health
Chlorpyrifos-methyl	5598-13-0	X					Health
Clomazone	81777-89-1	X					Contami
Cymoxanil	57966-95-7	X					Health
Cypermethrin	52315-07-8	X	X	X	X	X	Health
Cyproconazole	94361-06-5					X	Health
Cyprodinil	121552-61-2	X					Contami
Deltamethrin	52918-63-5		X	X	X	X	Health
Dicamba	1918-00-9	X	X				Contami
Dicloran	99-30-9	X	X	X	X	X	Contami
Dicofol	115-32-2					X	Health
Dieldrin	60-57-1	X	X	X	X	X	Health
Difenoconazole	119446-68-3	X	X	X	X	X	Health
Diflufenican (DFF)	83164-33-4	X					Contami
Dimethenamid-P	163515-14-8	X					Contami
Dimethoate	60-51-5	X		X		X	Health
Diuron	330-54-1					X	Health
Endrin	72-20-8	X	X	X	X	X	Health
Epoxiconazole	133855-98-8	X			X		Health
Ethion (aka diethion)	563-12-2	X	X	X	X	X	Contami
Ethoprophos	13194-48-4					X	Health
Etofenprox	80844-07-1	X					Health
Fenarimol	60168-88-9	X	X	X	X	X	Health
Fenpropidin	67306-00-7	X	X				Contami
Fipronil	120068-37-3	X	X	X	X	X	Health
Fluazinam	79622-59-6	X					Health
Flumetralin	62924-70-3	X	X	X	X	X	Contami
Fluopyram	658066-35-4	X					Health

Folpet	133-07-3	X					Contami
Glufosinate	77182-82-2	X	X	X		X	Health
Glyphosate (incl trimesium aka sulfosate)	1071-83-6	X	X	X	X	X	Health
Heptachlor	76-44-8	X	X	X	X	X	Health
Iprodione	36734-19-7		X	X	X	X	Health
lambda-Cyhalothrin	91465-08-6		X	X	X	X	Health
Lenacil	2164-08-1	X					Contami
Lindane	58-89-9	X	X	X	X	X	Health
Linuron	330-55-2		X	X		X	Health
Mancozeb	8018-01-7	X	X	X	X	X	Health
Maneb	12427-38-2	X		X	X	X	Health
Metamitron	41394-05-2	X					Contami
Metazachlor	67129-08-2	X					Contami
Metiram	9006-42-2	X				X	Health
Metribuzin	21087-64-9	X	X	X		X	Health
Myclobutanil	88671-89-0		X	X		X	Health
Oryzalin	19044-88-3		X	X			Health
Oxadiazon	19666-30-9	X				X	Health
Oxyfluorfen	42874-03-3		X				Health
Pendimethalin	40487-42-1	X	X	X	X	X	Contami
Pentachlorophenol	87-86-5	X	X	X	X	X	Health
Perchlordecone (mirex)	2385-85-5	X	X	X	X	X	Health
Permethrin	52645-53-1	X	X	X	X	X	Health
Phosmet	732-11-6	X				X	Health
Picloram	26952-20-5		X	X		X	Health
Piperonyl butoxide	51-03-6	X	X	X	X	X	Contami
Pirimicarb	23103-98-2	X	X	X	X	X	Health
Prochloraz	67747-09-5	X					Contami
Propyzamide	23950-58-5	X					Health
Prosulfocarb	52888-80-9	X					Health
Pyrimethanil	53112-28-0	X					Health
Quinmerac	90717-03-6	X					Contami
S-Metolachlor	87392-12-9	X	X	X	X	X	Contami
Spiroxamine	118134-30-8	X					Health
Tebuconazole	107534-96-3	X	X			X	Health
Tebuthiuron	34014-18-1	X	X	X	X	X	Contami
Tembotrione	335104-84-2	X					Health
Terbutryn	886-50-0	X	X	X	X	X	Health
Thiram	137-26-8	X	X			X	Health
Tolylfluanid	731-27-1	X	X	X	X	X	Health
Triadimenol	55219-65-3	X					Health
Tri-allate	2303-17-5	X					Contami
Trifloxystrobin	141517-21-7	X		X			Contami
zeta-Cypermethrin	52315-07-8	X	X	X	X	X	Health

Figures

Figure 1: Summary of the approach developed to select priority pesticides to be monitored in the air

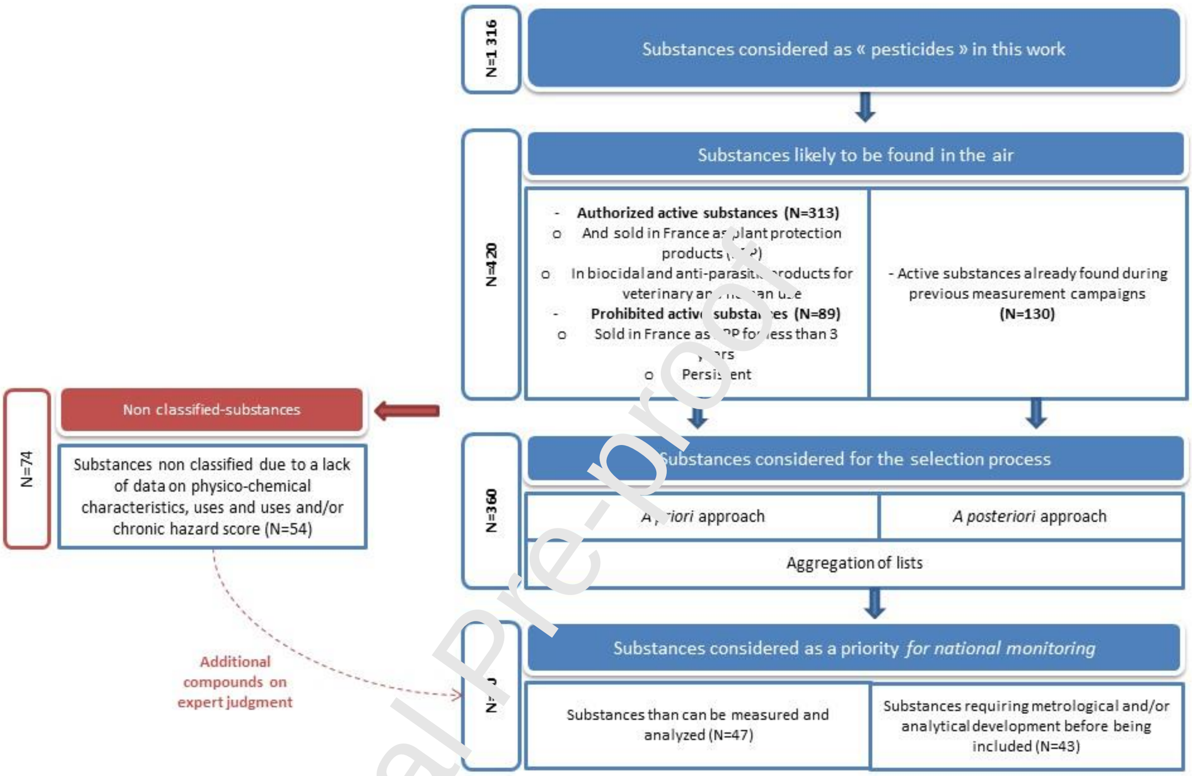
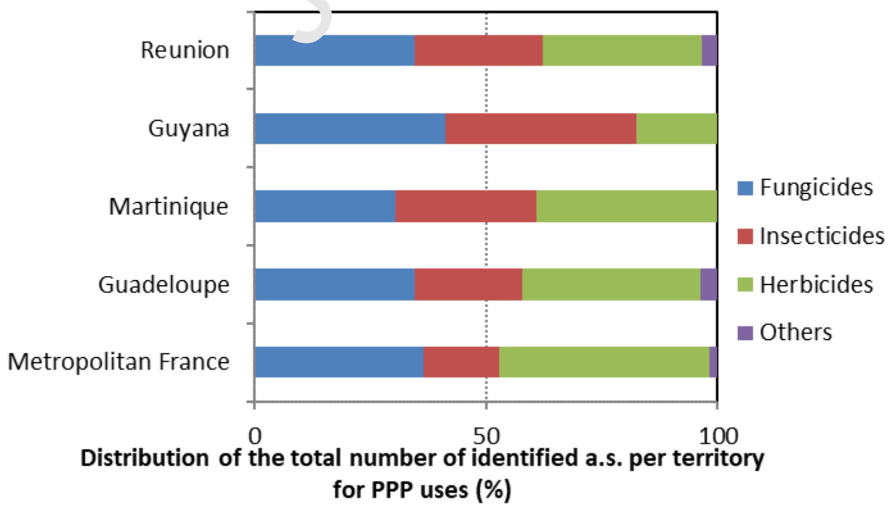


Figure 2: Distribution of the priority pesticides according to their use for metropolitan France and French overseas territories for the PPP uses



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Declaration of interests

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

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

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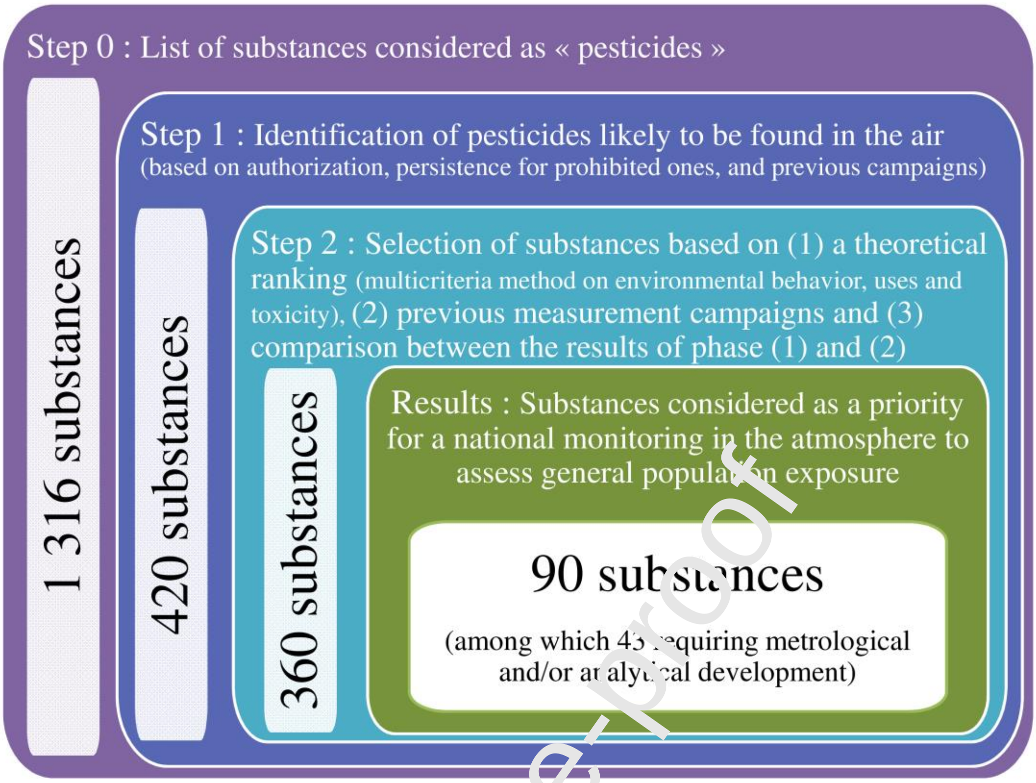

Graphical abstract

Highlights :

- Substance selection combining theoretical ranking and measurements
- Multicriteria approach based on environmental behavior, uses and toxicity
- A selection of 90 priority pesticides among a list of more than 1000 substances
- An adaptable approach to other objectives (*e.g.* ecotoxicological effects)