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Assessment of pesticide volatilization potentials to atmosphere from their molecular properties using the TyPol tool

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ABSTRACT

Following treatment, amounts of pesticides can reach the atmosphere because of spray drift, volatilization from soil or plants, and/or wind erosion. Monitoring and risk assessment of air contamination by pesticides is a recent issue and more insights on pesticide transfer to atmosphere are needed. Thus, the objective of this work was to better understand and assess pesticide emission potentials to air through volatilization. The TyPol tool was used to explore the relationships between the global, soil and plant volatilization potentials of 178 pesticides, and their molecular properties. The outputs of TyPol were then compared to atmospheric pesticide concentrations monitored in various French regions. TyPol was able to discriminate pesticides that were observed in air from those that were not. Clustering considering parameters driving the emission potential from soil (sorption characteristics) or plant (lipophilic properties), in addition to vapor pressure, allowed better discrimination of the pesticides than clustering considering all parameters for the global emission potential. Pesticides with high volatilization potential have high total energy, and low molecular weight, molecular connectivity indices and polarizability. TyPol helped better understand the volatilization potentials of pesticides. It can be used as a first step to assess the risk of air contamination by pesticides.

Keywords:
Air contamination
Soil
Plant
Measures
Risk
Molecular descriptors

1. Introduction

Air contamination by pesticides is known for several years, with observed concentrations ranging from pg m^{-3} to ng m^{-3} that could reach µg m^{-3} in treated fields (ANSES, 2017; Atmo Grand Est, 2018; Bedos et al., 2002b; Chataing, 2016; Désert et al., 2018; Guiral et al., 2016; Lig'Air, 2018; Villiot et al., 2018). In France, measurements started in 2000 years (ANSES, 2017; Hulin et al., 2020) when the Approved Air Quality Monitoring Associations

(AASQAs) began to collect data on pesticide concentrations in ambient air from different locations in the country (Atmo Grand Est, 2018; Chataing, 2016; Lig'Air, 2018). Indeed, the presence of pesticides in the atmosphere damages air quality, and may affect human and environmental health (ANSES, 2017; ANSES, 2020; Houbraken et al., 2015; Hulin et al., 2020).

The level of atmospheric contamination by pesticides depends on several processes, from source to sink ones (Degrendele et al., 2016). Following field treatment, amounts of pesticides can reach the atmosphere as a result of drift during application, volatilization from soil or plants, and wind erosion (Bedos et al., 2002a; Bedos et al., 2002c; Bedos et al., 2010; van den Berg et al., 1999; Cessna et al., 2006; Guiral et al., 2016). Volatilization is one of the major pathways of mass transfer to atmosphere (from 2 to 90% of pesticide initial dose), and results from evaporation from a liquid phase, sublimation from a solid phase, evaporation from an aqueous solution or desorption from the soil matrix (Bedos et al., 2002a; Bedos et al., 2002c). Pesticide volatilization depends on the physico-chemical properties of the compounds such as vapor pressure or water solubility, on the environmental conditions, and on the agricultural practices (Bedos et al., 2002b; van den Berg et al., 1999). Pesticides can also reach the atmosphere through the droplets emitted from the nozzles which can either evaporate before reaching the soil or the plant surface, or be transported downwind of the treated field during the application. Moreover, due to the wind erosion process, soil particles with pesticide molecules fixed on them can be removed from the soil surface (Bedos et al., 2002b). Once in the atmosphere, the pesticide is dispersed by atmospheric turbulence, and the distance of transport from sources will depend on its physical state (gas or aerosols), on its persistence in the atmosphere, and on the meteorological conditions (Bedos et al., 2002a; Bedos et al., 2002b; Guiral et al., 2016). Subsequent atmospheric deposition (through dry or wet pathways, aerosols) may lead to further soil and water contamination.

The prediction of air contamination by pesticides is based on various approaches describing these processes. These approaches range from simple empirical relationships (e.g. Raupach et al., 2001; van Wesenbeeck et al., 2008) to mechanistic models such as AGDRIFT which is designed to address the assessment of offsite drift of pesticides from agricultural applications (Bird et al., 1997), IDEFICS which computes downwind spray drift from conventional boom sprayers (Holterman et al., 1997), PEARL which simulates volatilization based on a resistance description (van den Berg et al., 2003), or Volt'Air Pesticides and SURFATM-Pesticides which are designed to assess volatilization flux following pesticide application on soil or crop, respectively (Bedos et al., 2009; Garcia et al., 2014; Guiral et al., 2016; Lichiheb et al., 2014; Lichiheb et al., 2016). Between simple relationships and mechanistic models, screening methods, such as those of Jury et al. (1983) and of Hulin et al. (2020), allow classification of the pesticide emission potentials.

For many years, some approaches have been developed to assess the fate of organic compounds in the environment from their molecular properties based on the assumption that the structure of a molecule contains the features responsible for its physical, chemical and biological properties (Mamy et al., 2015; Walker et al., 2003). Thus, several QSAR (quantitative structure-activity relationships) were established to allow assessment of the vapor pressure, the Henry constant or the octanol-air partition coefficient of various organic compounds (Mamy et al., 2015). However, to the best of our knowledge, no method based on molecular properties is available to assess pesticide volatilization potential into the air. The TyPol tool (Servien et al., 2014) was built to classify organic compounds and their transformation products according to their fate and effects, and their molecular properties (e.g. Benoit et al., 2017; Storck et al., 2016). It appeared to be relevant to analyse the pesticide volatilization potential which is determined by such properties.

Therefore, the objectives of this work were to identify key molecular properties driving the transfer of pesticides to the atmosphere through volatilization using the TyPol tool, and to provide elements to better understand the atmospheric contamination by pesticides. The performance of TyPol was assessed by comparing outputs to measurements of pesticides in the air of various French regions.

2. Materials and methods

2.1. TyPol

The TyPol (Typology of Pollutants) tool was developed to classify organic compounds, and their transformation products, according to both their behaviour in the environment and their ecotoxicological effects, and their molecular properties (Servien et al., 2014). TyPol can also be used to assess the fate and effects of an organic compound from its molecular properties by similarity with compounds having comparable properties, and for which environmental and ecotoxicological parameters are known (e.g. Benoit et al., 2017; Storck et al., 2016).

To cover the main processes involved in the fate of organic compounds in the environment, each compound is characterized by six environmental parameters: water solubility (Sw) and octanol-water partition coefficient (log Kow, referred as Kow in the text) for dissolution; vapor pressure (P_{vap}) and Henry constant (K_H) for volatilization; adsorption coefficient normalized to soil carbon organic content (Koc) for adsorption; and half-life (DT50) for degradation in the soil (Servien et al., 2014). Each organic compound is also characterized by 40 molecular descriptors such as molecular weight (MW), number of atoms (n_{at}), dipole moment (μ), polarizability (α) or total energy (E_{tot}) (Servien et al., 2014). The calculation of molecular descriptors is performed using an *in sillico* approach, while the environmental parameters are extracted from several available databases (e.g. PPDB, 2020) and literature.

In TyPol, the PLS (Partial Least Squares) model is carried out to find the multidimensional directions in the X observable variables (molecular descriptors) space that explains the maximum multidimensional variance direction in the Y predicted variables (environmental parameters) space. The optimal number of PLS components to perform clustering is selected according to Wold rules (Wold, 1978). In addition, TyPol uses the NIPALS (Non-linear Iterative PArtial Least Squares) algorithm, which allows performing PLS without removing the individuals with missing values and without estimating these missing values (Tenenhaus, 1998). After PLS analysis, a hierarchical clustering algorithm is used on the X and Y PLS axes to categorize the molecules by assignment of similar compounds into one cluster. At this step, the final number of clusters is chosen by comparison of the heights of the dendrogram using a barplot, a statistical map resuming Ward clustering. Minimization of intra-variability and maximization of inter-variability are the parameters retained to choose the most appropriate number of clusters (Servien et al., 2014).

The information system is based on a management system for relational database MySQL DBMS-R (version 5.1), an Apache web server (version 2.2), and the statistical R software. More details concerning TyPol can be found in Servien et al. (2014).

2.2. Monitoring of pesticides in the air

2.2.1. Experimental sites

Five experimental sites managed by several AASQAs and located in four French regions (Bretagne, Centre-Val de Loire, Grand Est (Alsace and Lorraine), Nouvelle-Aquitaine) were selected because they cover a wide diversity of agricultural practices and climates (Table 1). For each site, the agricultural practices were considered in 1 to 1.5 km radius around the air samplers (from 63 to 100% of the agricultural surfaces were surveyed depending on the areas). In particular, the compounds locally used and the corresponding applied amounts were crucial information for this work. Daily climatic data (temperature, precipitation, wind speed and orientation…) were obtained from Meteo France (2017 for Alsace, Lorraine and Val de Loire) and from Climatik (2016 for Bretagne, 2017 for Nouvelle Aquitaine) meteorological stations located close to the experimental sites (Fig. S1). According to the date of pesticide application, data such as wind speed were used to assume the potential contribution of volatilization and/or drift on the individual pesticide concentration measured in the air.

The Alsace site is surrounded by arable crops, mainly maize but also winter wheat and sugar beet. The study period (13 March to 17 July 2017) was warm and dry (Table 1). The second arable crops site was located in Lorraine. The main crops were winter wheat, oilseed rape, barley and maize. From 20 March to 20 July 2017, the temperatures were in agreement with the normal seasonal levels but the amount of precipitation was low (Table 1). The Bretagne site was selected because it is located among mixed crop-livestock systems, with 38% of pastures and 57% of arable crops such as maize and winter wheat. The precipitations were lower than usual but the temperatures were consistent with the average ones (Table 1). The orchard (mainly apple trees) and arable crops (mostly winter wheat and winter barley) site was located in Centre-Val de Loire. From 20 March to 3 July 2017, the amount of precipitation was low and the climate was warm (Table 1). Finally, the last experimental site was located in Nouvelle Aquitaine close to vineyards. Apart from vines, some arable crops were cultivated (winter wheat, maize), and a significant percent of surface was also dedicated to pasture and fallow. Contrary to the four previous sites, the measurements were carried out in 2016. The climate was warmer than usual and there was more precipitation, especially in autumn (Table 1).

2.2.2. Measurements and analyses of pesticides

In all experimental sites, monitoring of pesticide concentrations in the air was achieved with a Partisol^{TM} 2000 Ambient Particulate Sampler (ThermoFischer Scientific). The cartridge of the sampler was equipped with quartz filter to trap aerosols, and with polyurethane foam to trap gaseous pesticides. The flow rate was 1 m^3 per hour. The cartridges were replaced every week during the experiments according to AFNOR XP X43-058 standard (2007), then they were analysed by two COFRAC (French Committee of Accreditation) accredited laboratories: Micropolluants Technologies SA laboratory (Saint-Julien-lès-Metz) for Alsace and Lorraine sites, and IANESCO-chimie laboratory (Poitiers) for Bretagne, Centre-Val de Loire and Nouvelle Aquitaine sites. In any cases, analyses were done according to AFNOR XP X43-059 standard (2007). The number of analysed molecules were 86 for Alsace, 74 for Lorraine, 63 for Centre-Val de Loire, 60 for Nouvelle Aquitaine, and 58 for Bretagne. The measured concentrations will refer to both aerosols and gaseous pesticides because the monitored amounts were too low compared to the limits of quantification (from 0.048 to 1.19 ng m^{-3} depending on the pesticide) to allow separate analyses.

2.3. Analysis of the pesticide emission potentials with TyPol

2.3.1. Pesticides selection

The pesticides to consider in the TyPol analyses were chosen according to the following criteria: (1) they are priority substances to monitor in the air, as defined by Hulin et al. (2020) according to their potential presence in the air and hazard potential for metropolitan France, (2) they were observed in the air of the selected French regions by AASQA (Atmo Grand Est, 2018; Chataing, 2016; Lig'Air, 2018), (3) they were applied around the experimental sites (Table S1). A total of 178 pesticides (74 herbicides, 57 fungicides, 38 insecticides, 7 plant growth regulators, 1 molluscicide, 1 safener) was therefore taken into account in this work (Table S2).

2.3.2. TyPol analyses

TyPol was used to explore the relationships between the emission potentials of pesticides and their molecular properties, and to assess the risk of pesticides emission to air through a clustering approach. As TyPol only considers volatilization (neither drift nor wind erosion), this work assumes that a compound that is found in the air but that is not identified as by TyPol is probably transferred to air by drift or by wind erosion.

Following application on soil, the dominant factors that affect pesticide volatilization are pesticide physico-chemical properties (P_{vap}, Sw), persistence (DT50) and adsorption in soil (Koc), soil properties such as organic matter content, climatic data, and agricultural practices (Bedos et al., 2002a; Bedos et al., 2017; van den Berg et al., 1999; Houbraken et al., 2015). The emission by volatilization from plant, as for it, mainly depends on P_{vap}, Kow and Sw, in addition to environmental conditions such as atmospheric stability, wind speed, temperature and humidity (Bedos et al., 2010; van den Berg et al., 1999; Lichiheb et al., 2016). Consequently, to study the emission potential from soil, TyPol analyses were performed considering P_{vap}, Sw, Koc and DT50 as parameters; whereas we considered P_{vap}, Sw and Kow to assess the emission potential from plant. Finally, for global emission potential, the five parameters, i.e. P_{vap}, Sw, Kow, Koc and DT50, were included in the analyses. The values of Koc and DT50 retained in the analyses corresponded to the mean values which were referenced in PPDB (2018) and which are recommended at the European regulatory level for risk assessment for pesticide approval and for the placing of plant protection products on the market (FOCUS, 2000) (Table S2). The Henry constant K_H was not taken into account because it was redundant with P_{vap} and Sw. In any case, the 40 molecular descriptors implemented in TyPol (Servien et al., 2014) were considered.

3. Results and discussion

3.1. Pesticides measured in the air

Among the pesticides identified as used locally (for one cropping season), a total of 26 different compounds, mainly fungicides which are applied on plant foliage, were measured in the air of the five sites (Table 2; Fig. S2). These pesticides are frequently detected in France and various countries (e.g. Bedos et al., 2010; Bedos et al., 2017; Degrendele et al., 2016; Désert et al., 2018; Follak et al., 2005; Houbraken et al., 2016; Liaud et al., 2016; Locke et al., 1996; Villiot et al., 2018; Whang et al., 1993), except dimethenamid-P and fenbuconazole for which no data could be found. The pesticides that were observed in the highest number of sites (four over five) were chlorothalonil (fungicide), dimethenamid-P and pendimethalin (two herbicides), while the highest concentrations were found for chlorpyrifos-methyl (insecticide; it has to be underlined that chlorpyrifos-methyl was recently banned in Europe in December 2019; EU - Pesticides database, 2020) followed by dimethenamid-P, pendimethalin, folpet (fungicide), S-metolachlor (herbicide) and chlorothalonil (Table 2; Fig. S2). Among these 26 pesticides, 13 are “high priority” substances (boscalid, chlorothalonil, chlorpyrifos-methyl, diflufenican, fenpropidin, folpet, pendimethalin, propyzamide, prosulfocarb, S-metolachlor, spiroxamine, tebuconazole, tri-allate), four are “priority” substances (cyprodinil, clomazone, dimethenamid-P, trifloxystrobin) and nine are not classified (bromoxynil octanoate, dimethomorph, ethofumesate, fenbuconazole, fenpropimorph, kresoxim-methyl, propiconazole, quinoxyfen, tetraconazole) according to ANSES criteria for pesticides monitoring in air (ANSES, 2017; Hulin et al., 2020). Pendimethalin, chlorothalonil, cyprodinil, S-metolachlor and spiroxamine were detected in each site where they were applied contrary to trifloxystrobin and boscalid, and tebuconazole, that were detected in one site out of four, and one site out of five, respectively (Table S1; Fig. S2). Most of these 26 pesticides have high P_{vap} and/or were applied in high amounts, which are the main factors explaining the presence of pesticides in air (Tables S1 and S2) (Bedos et al., 2002a; Bedos et al., 2002b; van den Berg et al., 1999; Degrendele et al., 2016; Houbraken et al., 2015). In addition, most of the observed pesticides could have been applied on foliage, except two herbicides which were only applied on soil (diflufenican and propyzamide) (Table 2): higher volatilization rates have been found from plant surfaces than from soil (Bedos et al., 2010). Finally, some seasonal variations of pesticide concentrations in air were also observed, due to agricultural activity but also to climatic conditions, in agreement with the findings of Degrendele et al. (2016): for example, S-metolachlor was mainly observed from April to July (Fig. S2 a-c), and fenpropimorph in July (Fig. S2 a).

In the two sites located in arable crops area (Alsace and Lorraine), the observed pesticides were mainly herbicides (Table 2; Fig. S2). In the Alsace site, S-metolachlor, which was only used in maize, was the most frequently detected pesticide, followed by pendimethalin, dimethenamid-P, ethofumesate, fenpropimorph, chlorothalonil and clomazone which were applied in various crops (Tables 1 and 2; Atmo Grand Est, 2018). Among the 27 applied and analysed pesticides, 20 were not detected (Table S1). Most of them have P_{vap} lower than 0.1 or 0.01 mPa, which are the trigger values as defined by FOCUS (2008) to determine whether a substance has the potential to reach the air following volatilisation from soil and plant, respectively, except prochloraz and dicamba (Table S2). The applied doses of both pesticides are not known but they can be assumed to be low for prochloraz, contrary to dicamba (Table S1) (E-Phy, 2020). In the Lorraine site, pendimethalin had the highest rate of detection (66.7%) (Table 2; Fig. S2; Atmo Grand Est, 2018). This herbicide was used in several crops such as winter wheat, sunflower, maize, oilseed rape and peas, and it has high P_{vap} (3.34 mPa) (Table 2). The other detected pesticides were mostly pesticides of winter wheat which was the main crop in the area around the sampler (Tables 1 and 2). Twelve pesticides over 17 that were applied were not detected (Table S1): they have very low P_{vap} (< 0.01 mPa) or were applied in low amounts (< 0.1 kg for cypermethrin and dicamba) what might explain they were not transferred to air (Table S2). However, contrary to the Bretagne site where propiconazole was found in the air (see below), it was not in Lorraine site (Tables 2 and S1). This might be due to local meteorological conditions (Table 1).

In arable crops and orchard area (Centre-Val de Loire), pendimethalin was the most observed pesticide in the air (60% of detection), due to its application in apple trees and peas (Table 2; Fig. S2; Lig'Air, 2018). Then the observed pesticides were tri-allate and spiroxamine, used in barley crop; S-metolachlor used in maize; cyprodinil used in apple trees; and chlorothalonil used in winter wheat (Table 2). Twenty-five applied pesticides (over 31 which were analysed) were not observed in the air (Table S1). The majority of them have P_{vap} lower than 0.1 or 0.01 mPa, except chlorpyrifos, dimethenamid-P and pyrimethanil (Table S1). Dimethenamid-P and chlorpyrifos were applied in October what can explain they were not detected during the monitoring period starting in March (Table 1). Pyrimethanil was not detected probably because of the wind orientation (data not shown).

In the Bretagne site, surrounded by mixed crop-livestock systems, the most observed pesticides were tri-allate, used in spinach crops, and pendimethalin, used in maize (Table 2; Fig. S2), followed by (> 15%) chlorothalonil, S-metolachlor, prosulfocarb, and dimethenamid-

P which are pesticides of maize and cereals crops (Table 2; Fig. S2). Seven pesticides were applied but not detected (over 18 analysed) (Table S1). Their low P_{vap} (< 0.1 or < 0.01 mPa) (FOCUS, 2008), combined to their modes of application (soil or plant foliage), might explain why they were not found in the air (Table S2) (Degrendele et al., 2016).

Finally, in the Nouvelle Aquitaine site, mainly covered by vineyards and arable crops, the most detected pesticide was folpet which is used in vine and cereals, followed by propyzamide, quinoxyfen and kresoxim-methyl also used in vine and/or cereals (Table 2; Fig. S2; Chataing, 2017). Only two pesticides that were applied and analysed (over 16) were not detected (it has to be underlined that the survey was not complete): beta-cyfluthrin and difenoconazole (Table S1). This is consistent with their very low P_{vap} ($5.6\ 10^{-5}$ and $3.3\ 10^{-5}$ mPa, respectively) (Table S2).

A joint analysis of the temporality of pesticide concentrations in the atmosphere (Fig. S2) with the application periods as recorded in the five sites and local meteorological conditions (Fig. S1) was carried out to identify if the transfer routes that caused air contamination were droplet drift during application and/or post-application volatilization. This question was difficult to answer because both processes can be involved, and not all surveys on pesticide use were complete (see 2.2.1), so contamination by an unidentified application could have occurred. However, it remained possible to suspect one route rather than another, for example when a compound was found only during the spreading period, which suggests drift, or when a compound was found after its spreading period with decreasing concentrations over time, suggesting a volatilization phenomenon. This analysis evidenced that, except clomazone in Alsace, and pendimethalin and fenpropidin in Lorraine, whose detection might be due to drift because they were measured in the air shortly after their application (however volatilization cannot completely be excluded), most of the observed pesticides were probably volatilized because the meteorological conditions (low wind speed) and the dates of measurement could not explain the transfer to air by drift. Consequently, for the 26 pesticides that were detected in air, volatilization was identified as the main route of transfer, making the use of TyPol highly relevant. Therefore, we assumed that the monitoring results obtained in the five sites could be compared to TyPol clustering analyses on the pesticide emission potentials to air through volatilization, and that TyPol can help better understanding of pesticide emission potentials to air by volatilization.

3.2. Assessment of pesticide emission potentials to the air by volatilization with TyPol

3.2.1. Global emission potential

To identify the properties driving the global emission potential of pesticides to air by volatilization, the 178 pesticides were classified considering their P_{vap}, Sw, Kow, Koc and DT50, and the 40 molecular descriptors (see 2.3.2). The number of PLS components were chosen equal to 4 according to Wold rules (Wold, 1978). The PLS model was found acceptable ($R^2_X = 0.61$, $R^2_Y = 0.22$, $Q^2_Y = 0.21$) however the low value of R^2_Y indicates that the regression did not describe all parameters. The main characteristics of the first component explained 20.2% of the variance of molecular descriptors and 12.6% of parameters, while the second component explained 41.1% of the variance of molecular descriptors and 9.0% of that of parameters (Fig. 1b). More variance was explained by the second component because PLS (contrary to principal component analysis) aims at optimizing covariance between X and Y and not only the variance of X.

The number of clusters was chosen by plotting the heights of the dendrogram nodes and looking for a break in the corresponding barplots (Fig. S3a) (Servien et al., 2014). To minimize intra-variability and maximize inter-variability, the best choice was to classify the 178 pesticides into six clusters (Fig. 1a; Table S3; Fig. S3a). The clusters 1 to 6 contained 35, 47, 14, 56, 18 and 8 compounds, respectively (Table S3). The results of the PLS analysis also showed that, for the first component, there were positive loadings with DT50 and numbers of chlorine (n_{Cl}) and halogen (n_{Hal}) atoms, number of circuits ($n_{Circuits}$), and some molecular connectivity indices (MCI). For the second component, there were positive loadings of P_{vap} and Sw with E_{tot}, together with negative loadings with constitutional (especially MW and molecular surface area MSA), topological (MCI) and quantum-chemical (α) descriptors (Fig. 1b). On the contrary, Kow and Koc were found negatively correlated with E_{tot} and positively correlated with MW, MSA, MCI and α (Fig. 1b). Increase in the persistence of organic compounds with MCI and n_{Cl} was already observed; as well as increase in P_{vap} with E_{tot} and decreasing α; and increase in Kow and Koc with MW and MCI (Mamy et al., 2015).

The 26 pesticides that were detected in the air were distributed in three clusters: clusters 1, 2 and 4 (Table S3). Cluster 1 groups compounds having low median P_{vap} (8.13 10^{-4} mPa), Sw (0.25 mg L^{-1}) and DT50 (26 d) values, high Koc (15800 L kg^{-1}) and Kow (4.78), together with the highest energy of the highest unoccupied molecular orbital (E_{HOMO}) and α, high MSA and μ, medium MW and MCI, and low E_{tot} (Fig. S4; Table S3). Pesticides of cluster 2 are mainly herbicides, they have medium P_{vap} (0.121 mPa), Sw (240 mg L^{-1}) and DT50 (16 d); and moderate Kow (2.5) and Koc (224 L kg^{-1}) linked to low MW, MSA, MCI and α, and high E_{HOMO} and E_{tot} (Fig. S4; Table S3). Cluster 4 contains compounds (mainly fungicides) having the highest number of carbon atoms (n_C) but medium values of the remaining molecular descriptors (Fig. S4; Table S3). The compounds have high DT50 compared to the pesticides of the other clusters (50.1 d) but medium P_{vap} (5.88 10^{-3} mPa), Sw (6.30 mg L^{-1}), Kow (3.45) and Koc (930 L kg^{-1}) (Fig. S4; Table S3). Pesticides of clusters 1, 2 and 4 belong to a wide diversity of chemical families. Nevertheless, cluster 1 gathers all pyrethrins and dinitroanilines, and some strobilurins; cluster 2 contains all chloroacetamides and many carbamates and triazoles; and cluster 4 some benzamides, strobilurins and triazoles (Table S3). Excluding pendimethalin, cluster 1 is composed of measured pesticides having low P_{vap} (< 0.024 mPa) that were quantified at concentrations < 0.55 ng m^{-3} which are among the lowest measured ones (Table 2). Cluster 2 gathers nine observed pesticides over 26 which tend to have the highest P_{vap} (from 0.021 to 27 mPa), and, on average, the highest measured concentrations (from 0.1 to 14.7 ng m^{-3}) (Tables 2 and S2). Half of the observed pesticides in air are in cluster 4 (Table S3). They have an intermediate behaviour: the range of their P_{vap} is wide (from 3.4 10^{-4} to 12 mPa) but are generally lower than 0.1 mPa (Table S2), and the measured concentrations are lower than 6.21 ng m^{-3} except for chlorpyrifos-methyl (33.8 ng m^{-3}) (Table 2). The clusters 1, 2 and 4 include 25 pesticides that were applied but not detected (Table S3). Looking at these 25 pesticides, most of them have low P_{vap} (i.e. < 0.1 or < 0.01 mPa (FOCUS, 2008)) (Fig. S4, Tables S2 and S3) except chlorpyrifos, prochloraz and pyrimethanil (Tables S1 and S2; Bedos et al., 2002b). However, as indicated in section 3.1, prochloraz was probably applied in low amount, while chlorpyrifos and pyrimethanil might be observed in air. Their clustering in this group is therefore consistent. Clusters 1 and 4 mostly gathered measured pesticides that are applied on foliage while cluster 2 gathered measured pesticides independently of their modes of application (soil, shoot or foliage) (Table 2).

Cluster 3 mainly groups herbicides, and especially all sulfonylureas. The compounds of this cluster have the highest MW, MSA, MCI and μ, high number of atoms and α, and the lowest E_{HOMO}, and E_{tot} (Table S3). They also have the lowest median values of P_{vap} (3.32 10^{-5} mPa) and Koc (34.1 L kg^{-1}), low DT50 (12.25 d) and Kow (-0.59), and high Sw (2819 mg L^{-1}) (Table S3). Cluster 3 contained five pesticides that were applied but not detected which is consistent with low P_{vap} values. This suggests that pesticides having similar molecular descriptors than those of this cluster will present a low potential of volatilization (Fig. 1a and S4; Table S3).

Cluster 5 gathers the compounds having the highest Sw (25087 mg L^{-1}), high P_{vap} (0.497 mPa), low Koc (55.3 L kg^{-1}), and the lowest DT50 (6.5 d) and Kow (-0.82), related to the lowest MW, MSA, MCI, number of various atoms and α, and to the highest E_{tot} (Table S3). Among the 18 pesticides of this cluster, there are three organophosphates, one organochlorine and some acids. This cluster contains two applied but not detected pesticides, dicamba and flonicamid (Table S3). They were not found in the air probably because of low amounts applied (dicamba: 0.1 kg during the cropping season) or low P_{vap} (flonicamid: 9.4 10^{-4} mPa; FOCUS, 2008) (Tables S1 and S3).

Finally, cluster 6 is composed of eight withdrawn organochlorine insecticides, having the highest median P_{vap} (2.41 mPa) and persistence in soil (DT50 = 672.5 d), high Kow (3.60) and Koc (10954 L kg^{-1}), and low Sw (0.075 mg L^{-1}) (Tables S2 and S3). These pesticides were not applied in the five experimental sites because they are not approved for many years (EU - Pesticides database, 2020). However, they are all considered as high priority or priority substances according to Hulin et al. (2020) as they may be transferred to the atmosphere from the locations where they were previously applied because of their high persistence in soil. Indeed, lindane is still frequently observed in the air (Chataing, 2017; Désert et al., 2018; Lig'Air, 2018; Villiot et al., 2018).

This first analysis with TyPol showed that the tool gives an acceptable classification of the global emission potential of pesticides as it was able to discriminate pesticides that were observed in the air (clusters 1, 2 and 4) from those that were not (clusters 3, 5), while cluster 6 contains withdrawn pesticides with high volatilization potential. Thus, pesticides having similar molecular properties as those of clusters 1, 2 and 4 may lead to a risk of air contamination through volatilization while those with molecular properties similar to those of clusters 3 and 5 may not. In any case, P_{vap}, and consequently the risk of pesticide transfer to air, increased with E_{tot} and n_{Cl}, and with low MW, MSA, MCI, μ and α. Indeed, several authors showed that the polarizability α was a fundamental descriptor to explain the P_{vap} range of organic compounds, and that MW, n_{Cl}, MCI, E_{tot} and μ were also good descriptors of P_{vap} (Basak et al., 1997; Liang and Gallagher, 1998; Mamy et al., 2015; Wang et al., 2008; Wania and Dugani, 2003; Yang et al., 2003). TyPol also showed that the observed pesticides have first high P_{vap}, then were those that were applied in the greatest amounts among all studied pesticides (Bedos et al., 2002a; van den Berg et al., 1999; Houbraken et al., 2015). However, no clear relationship was found between volatilization and Sw, Kow, Koc and DT50 (Table S3).

To better understand the emission potentials of pesticides, and the role of Sw, Kow, Koc and DT50 in pesticides volatilization, further analyses were done to study emission potentials from soil and from plant.

3.2.2. Emission potential from soil

To analyse the pesticides volatilization potential from soil, the parameters driving their fate in soils, Sw, Koc and DT50, were considered in addition to P_{vap} (Bedos et al., 2002a; Bedos et al., 2017; van den Berg et al., 1999; Houbraken et al., 2015). The number of PLS components was 3 (Wold, 1978). The PLS model was found as acceptable as for global emission potential analysis ($R^2_X = 0.61$, $R^2_Y = 0.22$, $Q^2_Y = 0.19$). The main characteristics of the first component explain 20.2% of the variance of molecular descriptors and 12.7% of parameters, while the second component explain 41.1% of the variance of molecular descriptors and 8.8% of that of parameters.

The 178 pesticides were classified in eight clusters of 49, 22, 43, 15, 25, 20, 2 and 2 compounds, and their distribution was different from the previous one (Fig. 2a, Tables S2, S3 and S4; Fig. S3b). The circle of correlations was similar to the one obtained after the analysis of the global emission potential, showing the same trends: positive correlations between DT50,

n_{Cl}, n_{Hal} and $n_{Circuits}$, and between P_{vap}, Sw and E_{tot}; negative correlations between P_{vap}, and Koc, number of various types of bonds, MCI, and α (Fig. 1b and 2b). As observed before, P_{vap}, and consequently the volatilization of pesticides after emission from soil, increases with n_{Cl}, and E_{tot}, and when Koc, MW, MSA, MCI, n_{at}, and α decrease (Table S4).

The distribution of the 26 observed pesticides changed compared to the analysis of the global emission potential (see 3.2.1) as they were found in five different clusters (Table S4): seven in cluster 1, six in cluster 2, six in cluster 3, five in cluster 5 and two in cluster 6. The soil applied pesticides were gathered in clusters 2, 3, 5 and 6, not in cluster 1.

The pesticides (mainly fungicides) of cluster 1 have low median P_{vap} values ($2.0\ 10^{-3}$ mPa, which is lower than the trigger of 0.1 mPa for soil volatilization (FOCUS, 2008)), low DT50 (24.4 d), and moderate Sw (5.20 mg L^{-1}) and Koc (894 L kg^{-1}) compared to the other clusters (Fig. S5; Table S4). They are also characterized by high number of various atoms, and moderate to low values of the remaining molecular descriptors (Table S4). The pesticides belong to a wide diversity of chemicals families but include several triazoles (Table S4). Except folpet, cluster 1 contains pesticides that were measured at concentrations among the lowest ones (< 0.85 ng m^{-3}) (Table 2), which is consistent with the low P_{vap} of these compounds (Table S2). All the measured pesticides of this cluster were applied on crop foliage (Table 2), however their volatilization may also be driven by their fate in the soil they may reach following foliar wash-off (Bedos et al., 2002a; Bedos et al., 2010). Consequently, the high concentration of folpet in the air compared to the measured pesticides of the same cluster can be due to its low Koc (304 L kg^{-1}) (Table S2) (McCall et al., 1980) as pesticide volatilization from soil increases when sorption decreases (Alavarez-Benedi et al., 1999). This cluster also contains nine pesticides that were applied but not detected. They all have P_{vap} < 0.1 mPa (FOCUS, 2008) (Tables S2 and S4).

Cluster 2 is composed of 22 pesticides (mainly herbicides) having high P_{vap} (0.15 mPa) and Sw (20.49 mg L^{-1}), moderate Koc (593 L kg^{-1}) and DT50 (43.5 d), low number of atoms, MW, MSA and MCI, but the highest values of E_{tot} (Table S4). It contains six measured pesticides having concentrations among the highest measured ones (from 0.23 to 33.8 ng m^{-3}) (Tables S2 and S4). The high P_{vap} of chlorpyrifos-methyl (3.0 mPa) and its application on foliage might explain why it was measured at 33.8 ng m^{-3} despite high Koc (4645 L kg^{-1}) (Mc Call et al., 1980). The concentrations of chlorothalonil and prosulfocarb (Koc > 1600 L kg^{-1}), ranging from 1.43 to 6.21 ng m^{-3}, were among the highest ones of cluster 2 (Tables 2 and S2). Chlorothalonil (P_{vap} = 0.076 mPa) is foliage applied and the amounts were significant during the cropping season (> 17 kg) (Table 2), while prosulfocarb can be soil or foliage applied and has high P_{vap} (> 0.79 mPa) (Table S2). The lowest measured pesticide concentrations of this cluster were found for the three pesticides that can be soil applied, cyprodinil, propyzamide, tri-allate (Tables 2 and S4), which is in agreement with their high sorption coefficients (Koc > 800 L kg^{-1}) (Table S2) (Alavarez-Benedi et al., 1999; McCall et al., 1980). Cluster 2 also contains pyrimethanil that was applied but not detected (Tables S1 and S4).

Cluster 3 groups pesticides (mainly herbicides) with high P_{vap} (0.026 mPa) and Sw (483 mg L^{-1}), but low Koc (122 L kg^{-1}) and DT50 (21.6 d) (Table S4). The compounds of this cluster have moderate to low values of molecular descriptors (MCI, MW, MSA, n_C, α) but the highest values of μ (Table S4). It contains several sulfonylureas, and some organochlorines and organophosphates (Table S4). Cluster 3 tends to gather pesticides for which the measured concentrations were among the lowest measured ones (from 0.1 to 2.02 ng m^{-3}), except for S-metolachlor (11 ng m^{-3}) (Table 2). S-metolachlor can be soil applied, but its Koc is low (226.1 L kg^{-1}, Table S2) (Mc Call et al., 1980) so adsorption did not prevent volatilization (Alavarez-Benedi et al., 1999). In addition, the applied amounts of S-metolachlor reached 55 kg during the cropping season (Table S1). This cluster also contains ten pesticides that were applied but not detected in the air. Excluding prochloraz, they have $P_{vap} < 0.1$ mPa (FOCUS, 2008). However, as indicated above, the amounts of prochloraz were probably low (E-Phy, 2020).

Cluster 5 gathers 25 pesticides (mainly fungicides) belonging to various chemical families (Table S4). They have high Koc (7061 L kg^{-1}) and DT50 (117 d) but moderate P_{vap} ($1.60\ 10^{-2}$ mPa) and Sw (0.93 mg L^{-1}). As compounds of cluster 3, they have moderate to low values of molecular descriptors (MCI, MW, MSA, n_{at}, n_C, α) but high E_{tot} values (Table S4). Cluster 5 contains five measured pesticides: for boscalid, bromoxynil octanoate, diflufenican and quinoxyfen, concentrations ranged from 0.14 to 0.28 ng m^{-3}, while for pendimethalin they ranged from 1.07 to 15.5 ng m^{-3} (Table 2). Boscalid, bromoxynil octanoate and quinoxyfen, which are applied on foliage, have low P_{vap} (<0.1 mPa), and the applied amounts were lower than 2.6 kg (Table S1). Diflufenican is soil applied but the amount was low (0.04 kg, Table S1) and it is strongly sorbed to soil (Koc = 5500 L kg^{-1}) (McCall, 1980). On the contrary, pendimethalin has a high vapor pressure (3.34 mPa) and the used amounts reached 27.1 kg during the cropping season (Table S1). This pesticide has a high Koc (17900 L kg^{-1}) which should have prevented its transfer to air (Alavarez-Benedi et al., 1999) but it might have been applied post-emergence rather than pre-emergence (Table 2) (E-Phy, 2020). Cluster 5 also includes five applied but not detected pesticides: except chlorpyrifos (1.43 mPa), they have P_{vap} < 0.1 mPa (Table A2; FOCUS, 2008).

Cluster 6 contains 20 pesticides of various chemical families. The compounds of this cluster have the highest P_{vap} (0.61 mPa) and Sw (20914 mg L^{-1}), the lowest Koc (52.6 L kg^{-1}) and DT50 (8.73 d), combined with the lowest values of most of the molecular descriptors (in particular α), but high E_{tot} (Table S4). Cluster 6 only contains two measured pesticides: clomazone (0.15 ng m^{-3}) and dimethenamid-P (from 0.15 to 14.7 ng m^{-3}) (Tables 2 and S4). Clomazone has high P_{vap} (27 mPa) but was applied in low amount during the cropping season (0.36 kg) while dimethenamid-P combined high P_{vap} (2.51 mPa) and significant quantities (47 kg) (Tables S1 and S2). Both can be soil applied but, as their Koc are low (< 300 L kg^{-1}) (McCall et al., 1980), sorption did not decrease volatilization. Cluster 6 also contains two pesticides that were applied but not detected: dicamba and flonicamid. As explained in section 3.2.1, dicamba was applied in very low amounts (0.1 kg) and flonicamid has a low P_{vap} (9.4 10^{-4} mPa) (Table S1).

Cluster 4 is composed of the pesticides (mainly pyrethroids) having the lowest P_{vap} (1.24 10^{-5} mPa), low Sw (0.02 mg L^{-1}) and DT50 (13 d), and the highest Koc (124 000 L kg^{-1}) (Tables 2 and S4), together with high values of most of the molecular descriptors but low values of E_{tot} (Table S4). The cluster contains five pesticides that were applied but not detected (Table S1): they have low P_{vap} (< 0.0068 mPa) and high Koc (> 1780 L kg^{-1}) (Table S2) (FOCUS, 2008; McCall et al., 1980). Consequently, the pesticides of cluster 4 have a low potential of volatilization from soil.

Finally, clusters 7 and 8 are only composed of two pesticides. Cluster 7 contains the biggest molecules of the dataset, abamectin and mirex, which have the highest MW, MSA, MCI and α, together with low Sw (0.01 mg L^{-1}), high DT50 (164.34 d) and Koc (5715 L kg^{-1}), and moderate P_{vap} (1.67 10^{-2} mPa) (Table S4). Cluster 8 contains two withdrawn organochlorine pesticides, endrin and toxaphene, that are very persistent in soil (DT50 > 2700 d), have low Sw (< 0.24 mg L^{-1}), median Kow (< 3.51), but have very contrasted P_{vap} (2 10^{-7} mPa for endrin and 11.7 mPa for toxaphene) and Koc (10000 and 1 L kg^{-1}, respectively) (Tables S2 and S4). As indicated in 3.2.1, these pesticides are considered as high priority substances according to Hulin et al. (2020) and are susceptible to be transferred into the air (see 3.2.1).

In summary, TyPol classification based on potential emission from soil allowed a better understanding of the role of pesticide adsorption in their volatilization. Combined to the P_{vap}, to the applied amounts and to the values of some molecular descriptors (MCI, MW, MSA, E_{tot}), the Koc helped explain the clustering of the measured pesticides and to discriminate pesticides that might be found in the air due to volatilization from soil (clusters 1, 2, 3, 5, 6) from the others (clusters 4, 7, 8). It has to be underlined that no clear relationship was found between the persistence of compounds in the soil and their detection in the air.

3.2.3. Emission potential from plant

Finally, we studied the pesticides emission potential by volatilization from plant considering Sw, Kow and P_{vap} (Bedos et al., 2010; van den Berg et al., 1999; Lichiheb et al., 2016). The number of PLS components was 3 (Wold, 1978). The performance of the PLS model was as follows: $R^2_X = 0.57$, $R^2_Y = 0.35$, $Q^2_Y = 0.30$. There is an improvement of the description of parameters (R^2_Y value) compared to the two previous analyses but a slight decrease in the description of molecular descriptors (R^2_X). The main characteristics of the first component explain 48.7% of the variance of molecular descriptors and 22.2% of parameters, while the second component explain 8.1% of the variance of molecular descriptors and 12.9% of that of parameters. The 178 pesticides were clustered in nine groups of 16, 32, 11, 29, 7, 41, 15, 26 and 1 compound(s) (Fig. 3a, Table S5; Fig. S3c). The distribution was also different from those of the two previous analyses (Tables S3, S4 and S5). The 26 measured pesticides were in five clusters (clusters 1, 2, 4, 6 and 8), but differently as for soil emission potential clustering, while the 32 pesticides which were applied but never detected were distributed in all clusters (except cluster 9 which is only constituted by abamectin) (Table S5). As previously observed, P_{vap} and Sw tend to increase with E_{tot}, and with low MW, MSA, MCI, n_{at} and α, while Kow increases with n_{Cl}, n_{Hal}, $n_{Circuits}$ and MCI (Fig. 3b and S6, Table S5).

Clusters 1 and 8 are composed of pesticides that were measured at the lowest concentrations in the air (< 0.60 ng m^{-3}): one herbicide (diflufenican) in cluster 1, and six fungicides (boscalid, dimethomorph, fenbuconazole, propiconazole, tebuconazole, tetraconazole) in cluster 8 (Table S5). TyPol differentiated soil and foliage applied pesticides as diflufenican, which is the sole observed pesticide of cluster 1, was soil applied, while the six measured pesticides of cluster 8 were applied on plant foliage (Table 2). The low observed concentrations of the seven pesticides are consistent with low median P_{vap} (< 0.0027 mPa) and Sw (< 30.1 mg L^{-1}) values, but high Kow (> 3.00) (Fig. S6; Tables 2 and S5). Indeed, for foliar applied pesticides, volatilization rate tends to decrease when Kow increases because high Kow (characteristic of lipophilic compounds) favours leaf penetration so decrease pesticide volatilization (Bedos et al., 2010; Lichiheb et al., 2016). Both clusters also have medium number of atoms, MW, MSA, MCI, moderate to high α, and low E_{tot} (Table S5). Cluster 1 contains many strobilurins and organochlorines, while cluster 8 mainly contains fungicides (17 over 26 pesticides) and, among them, almost all triazoles (except difenoconazole which is in cluster 1, and amitrole which is in cluster 7) (Table S5). Both groups, constituted of pesticides with high Kow, have a low potential of transfer to air from plant. This is reinforced by the presence of seven applied but not detected pesticides in these clusters (Tables S1 and S5).

On the contrary, clusters 2 and 4 gather pesticides having the highest median P_{vap} values (> 0.12 mPa), what can explain they contain the observed pesticides which were measured at the highest concentrations, but contrasted values of Sw and Kow (Tables 2 and S5). They also have the lowest α, low number of atoms, MW, MSA, MCI and high E_{tot} as previously observed for compounds with high P_{vap} (see 3.2.1 and 3.2.2) (Table S5). The eight measured pesticides, which were distributed in cluster 2, are five herbicides (ethofumesate, propyzamide, prosulfocarb, S-metolachlor and tri-allate), two fungicides (chlorothalonil and cyprodinil), and one insecticide (chlorpyrifos-methyl). Chlorpyrifos-methyl is the pesticide that was measured at the highest concentration, followed by S-metolachlor, chlorothalonil and prosulfocarb which were detected at concentrations higher than 1 ng m^{-3} (Table 2). These pesticides are mainly applied on plant foliage, their P_{vap} are higher than 0.01 mPa which is the trigger for volatilization from plant (FOCUS, 2008) (Tables 2 and S2), and/or they were used in significant amounts (4.5 to 55 kg) (Table 2). The four measured pesticides of cluster 4 (clomazone, dimethenamid-P, fenpropidin and spiroxamine) were found in concentrations ranging from 0.15 to 14.7 ng m^{-3} (Table 2) which is consistent with high P_{vap} (> 3.5 mPa), low Kow (< 2.89) and/or significant used amounts (Tables S1 and S2). The two clusters also contain ten pesticides that were not detected: most of them have P_{vap} < 0.01 mPa except metazachlor, pyrimethanil and thiram. These results indicate that pesticides with similar properties as those of clusters 2 and 4 may have a high emission potential to air from plant.

Pesticides of cluster 6 have moderate P_{vap} (0.016 mPa), low Sw (0.68 mg L^{-1}) and high Kow (4.37), together with low number of atoms, MW, MSA and MCI but high E_{tot} (Table S5). The seven observed pesticides (five fungicides: fenpropimorph, folpet, kresoxim-methyl, quinoyfen and trifloxystrobin, and two herbicides: bromoxynil octoanoate and pendimethalin) belonging to this group are mainly applied on plant foliage, except pendimethanil that could also be soil applied (Table 2). They were found in concentrations ranging from 0.2 to 0.85 ng m^{-3}, excluding folpet and pendimethalin which were found at maximum concentrations of 11.8 ng m^{-3} and 15.5 ng m^{-3}, respectively (Tables 2 and S1). Despite high Kow (> 3), both pesticides have P_{vap} > 0.01 mPa (0.021 and 3.34 mPa, respectively) what may explain their presence in the air (Table S2). On the contrary, the measured concentration of fenpropimorph was among the lowest one (0.85 ng m^{-3}) though it has a high P_{vap} (3.9 mPa). However, this fungicide has high Kow (4.5) and, as indicated above, high Kow favours leaf penetration so decrease pesticides availability for volatilization (Table S2) (Bedos et al., 2010; Lichiheb et al., 2016).

Finally, clusters 3, 5, 7 and 9 do not gather any of the pesticides that were measured in the air of the five sites. Cluster 3 groups only herbicides (and all sulfonylureas) (Table S5). They have the lowest P_{vap} ($1.1\ 10^{-5}$ mPa), low Kow (-0.70) but high Sw (3200 mg L^{-1}) (Fig. S6; Table S5). Compounds of this group have very low volatilization potential to air from plant as confirmed by four applied but not detected pesticides (Table S1). In addition, they are generally applied at very low doses (Table 2) (E-Phy, 2020). Cluster 5 contains only insecticides which are all pyrethroids. They have the lowest Sw (0.0012 mg L^{-1}), low P_{vap} (2 10^{-4} mPa), and the highest Kow (6.0). As cluster 3, this cluster does not contain pesticides susceptible of transfer to air following plant treatment, as shown by beta-cyfluthrin and lambda-cyhalothrin that were applied during the cropping seasons but that were not detected (Table S1). Cluster 7 gathers 15 pesticides (mainly herbicides and plant growth regulators) having the highest Sw (100 000 mg L^{-1}), the lowest Kow (-1.88) and high P_{vap} (0.031 mPa) (Table S5). Among the 15 pesticides, there are two applied but not detected ones: dicamba (low applied amount: 0.1 kg) and flonicamid (low P_{vap}: 9.4 10^{-4}) (Table S2). Finally, cluster 9 only contains abamectin which is one of the high priority substances to be monitored in the air according to Hulin et al. (2020). However as analytical developments are needed (ANSES, 2017; Hulin et al., 2020), it was not measured during the study period.

This analysis allowed discrimination of pesticides according to their volatilization potential from plant (pesticides that were found in the air and those that were not), considering simultaneously molecular properties, P_{vap} and Sw but also Kow which is a key parameter driving pesticide leaf penetration so its availability for volatilization (Lichiheb et al., 2016). The volatilization of pesticides from crops will also depend on wash-off by rainfall and on turbulence above and inside the foliar coverage (Bedos et al., 2002a; Bedos et al., 2010).

4. Conclusion

The presence of pesticides in the atmosphere may impact human and environmental health. Due to the high number of pesticides, agricultural practices and pedoclimatic contexts, comprehensive measurements of pesticide concentrations in the air would be time consuming and cost prohibitive. The TyPol tool was therefore used to better understand and assess pesticide global, soil and plant emission potentials to air through volatilization, from measurements of pesticide concentrations in the air of five French sites.

In any case, TyPol was able to discriminate pesticides that were observed in various air concentration levels from those that were not observed, so to classify pesticides according to high or low potential of emission to air through volatilization. Pesticides with high potential of transfer to air have high total energy and number of chlorine atoms, together with low molecular weight, molecular surface area, molecular connectivity indices, polarizability and dipole moment. This is consistent with the findings of several authors who showed that increase in molecular weight, number of chlorine atoms, polarizability and dipole moment, and decrease in total energy, favour intermolecular dispersive interactions which are known to reduce volatilization (Yang et al., 2003; Zeng et al., 2007; Zeng et al., 2013; Mamy et al., 2015).

It has to be underlined that TyPol categorizes different volatilization potentials and does not consider the amounts of pesticides that are applied which is one of the key factor driving their concentrations in the air. However, we accounted for this information, when it was available, to discuss the presence or absence of the monitored pesticides in the different clusters obtained with TyPol. In addition, pesticides are applied to soil or plants as commercial formulations, whereas vapor pressure, water solubility and adsorption coefficient are characteristics of the active ingredient. But little is known about the differences between the physico-chemical properties of the active substance within the applied formulation and those of the pure active substance (Bedos et al., 2002a; Houbraken et al., 2016). Nevertheless, TyPol proved to be an efficient tool for a first step in the risk assessment of air contamination by pesticides to preserve air quality.

CRediT authorship contribution statement

Laure Mamy: Conceptualization; Formal analysis; Funding acquisition; Investigation; Methodology; Supervision; Writing - original draft; Writing - review & editing. **Kevin Bonnot:** Formal analysis; Investigation; Writing - review & editing. **Pierre Benoit:** Conceptualization; Formal analysis; Funding acquisition; Methodology; Supervision; Writing - review & editing. **Christian Bockstaller:** Conceptualization; Formal analysis; Funding acquisition; Methodology; Supervision; Writing - review & editing. **Eric Latrille:** Conceptualization; Methodology; Supervision; Writing - review & editing. **Virginie Rossard:** Conceptualization; Methodology; Supervision; Writing - review & editing. **Rémi Servien:** Conceptualization; Methodology; Supervision; Writing - review & editing. **Dominique Patureau:** Conceptualization; Methodology; Supervision; Writing - review & editing. **Laëtitia Prevost:** Project administration; Funding acquisition; Writing - review & editing. **Frédéric Pierlot:** Formal analysis; Writing - review & editing. **Carole Bedos:** Conceptualization; Formal analysis; Funding acquisition; Methodology; Supervision; Writing - review & editing.

Declaration of Competing Interest

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

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Appendix A. Supporting information

Supplementary data associated to this article can be found in the online at...

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Tables

Table 1

Experimental sites and corresponding main agricultural practices and climates (data from Meteo France for Alsace, Lorraine and Val de Loire, and from Climatik for Bretagne and Nouvelle Aquitaine), dates and duration of experiments.

Site	Agricultural practices (% of surface)	Climate			Dates of sampling
		Daily mean temperature (°C)	Precipitation (mm)	Wind speed (m s^{-1})	
Alsace	Arable crops: Maize (70%) Winter wheat (12%) Sugar beet (8%) Soybean (5%)	From 4.6 to 26.7	199	Mean < 4.7 Maximum: 12	13 March to 17 July 2017
Bretagne	Mixed crop-livestock: Pasture (38%) Maize (28%) Winter wheat (18%) Winter barley (7%) Oilseed rape (4%)	From 5.1 to 25.4	134	Mean < 4.9 Maximum: 14	22 March to 21 June 2017
Centre-Val de Loire	Arable crops and orchards: Winter wheat (24%) Winter barley (18%) Apple trees (17%) Oilseed rape (8%) Sunflower (7%) Pasture (6%)	From 5.8 to 28.0	120	Mean < 8.4 Maximum: 22	20 March to 3 July 2017
Lorraine	Arable crops: Winter wheat (35%) Oilseed rape (19%)	From 2.7 to 27.4	163	Mean < 4.6 Maximum: 9.9	20 March to 20 July 2017

	Barley (14%) Maize (8%) Sunflower (3%) Peas (3%) Pasture (16%)				
Nouvelle-Aquitaine	Vineyard and arable crops: Vine (36%) Winter wheat (10%) Maize (9%) Winter barley (4.5%) Sunflower (2.7%) Pasture and fallow (9.9%)	From -1.9 to 27.6	655	Mean < 7.9 Maximum: 24	1st January to 31 December 2016

Table 2

Pesticides which were observed in the air of the five French experimental sites, among the pesticides identified as used locally, with their use and mode of application, % of detection and maximum measured concentrations, and total amount of pesticides applied in the area surrounding the sampler and treated crops. H: Herbicide, F: Fungicide, I: Insecticide.

Site	Detected pesticide (use; application)	% of detection	Maximum observed concentration (ng m^{-3})	Treated crops	Amount applied during study period (kg)
Alsace	Chlorothalonil (F; foliage)	5.9	1.62	Winter wheat, winter barley	21.0
	Clomazone (H; soil, shoot)	5.9	0.15	Maize, soybean, sugarbeet	0.8
	Dimethenamid-P (H; soil, foliage)	35.3	3.75	Maize, sugarbeet	47.0
	Ethofumesate (H; soil, foliage)	17.6	0.30	Sugarbeet	21.5
	Fenpropimorph (F; foliage)	11.8	0.85	Sugarbeet	28.0
	Pendimethalin (H; soil, foliage)	47.0	4.18	Maize, winter wheat, soybean	17.0
	S-metolachlor (H; soil, shoot)	82.3	11.0	Maize	55.0
Bretagne	Bromoxynil octanoate (H; foliage)	7.1	0.14	Maize	2.6
	Chlorothalonil (F; foliage)	78.6	6.21	Maize, winter barley	21.1
	Clomazone (H; soil, shoot)	7.1	0.15	Winter wheat, soybean, spinach, faba bean	0.36
	Cyprodinil (F; foliage)	14.3	0.84	Winter wheat, winter barley	0.6
	Diflufenican (H; soil)	7.1	0.03	Winter wheat, winter barley	0.004
	Dimethenamid-P (H; soil, foliage)	35.7	14.7	Maize	47.1
	Pendimethalin (H; soil, foliage)	100.0	15.5	Maize	27.1
	Propiconazole (F, foliage)	7.1	0.31	Winter wheat, winter barley	1.6
	Prosulfocarb (H; soil, foliage)	50.0	2.10	Winter wheat, winter barley	0.8
	S-metolachlor (H; soil, shoot)	64.3	1.06	Maize	6.2
	Tri-allate (H; soil, foliage)	100.0	0.73	Spinach	3.5
Centre-Val de Loire	Chlorothalonil (F; foliage)	6.7	1.43	Winter wheat	17.16
	Cyprodinil (F; foliage)	6.7	0.37	Apple tree	0.147
	Pendimethalin (H; soil, foliage)	60.0	2.72	Apple tree, peas	14.2
	S-metolachlor (H; soil, shoot)	13.3	0.21	Maize	15.4

	Spiroxamine (F; foliage)	13.3	0.33	Barley, vine	3.5
	Tri-allate (H; soil, foliage)	26.7	0.40	Barley	76.7
Lorraine	Chlorothalonil (F; foliage)	50.0	3.55	Winter wheat	17.5
	Cyprodinil (F; foliage)	25.0	0.23	Winter wheat, winter barley	3.5
	Dimethenamid-P (H; soil, foliage)	8.3	0.15	Maize, oilseed rape	32.5
	Fenpropidin (F; foliage)	41.7	2.02	Winter wheat, winter barley	8.5
	Pendimethalin (H; soil, foliage)	66.7	1.07	Winter wheat, sunflower, maize, oilseed rape, peas	22
Nouvelle Aquitaine	Boscalid (F; foliage)	3.6	0.28	Vine, winter wheat, barley, oilseed rape, sunflower	2.1
	Chlorpyrifos-methyl (I; foliage)	28.6	33.8	Vine	4.5
	Dimethenamid-P (H; soil, foliage)	3.6	0.17	Oilseed rape, maize, sunflower	0.9
	Dimethomorph (F; foliage)	14.3	0.60	Vine, winter wheat, maize, winter barley, sunflower	6.5
	Fenbuconazole (F; foliage)	3.6	0.18	Vine	0.065
	Folpet (F; foliage)	57.1	11.8	Vine, winter wheat, winter barley	123.5
	Kresoxim-methyl (F; foliage)	35.7	0.33	Vine	3.7
	Propyzamide (H; soil)	46.4	0.33	Vine, oilseed rape	0.47
	Quinoxyfen (F; foliage)	39.3	0.20	Winter wheat, winter barley	1.8
	Spiroxamine (F; foliage)	32.1	0.88	Vine, winter wheat, winter barley	10.5
	Tebuconazole (F; foliage)	25.0	0.34	Vine, winter wheat, maize, winter barley, sunflower	19
	Tetraconazole (F; foliage)	3.6	0.10	Vine, winter wheat, winter barley	0.052
	Trifloxystrobin (F; foliage)	17.8	0.55	Vine, winter wheat, maize, winter barley, sunflower	2.1

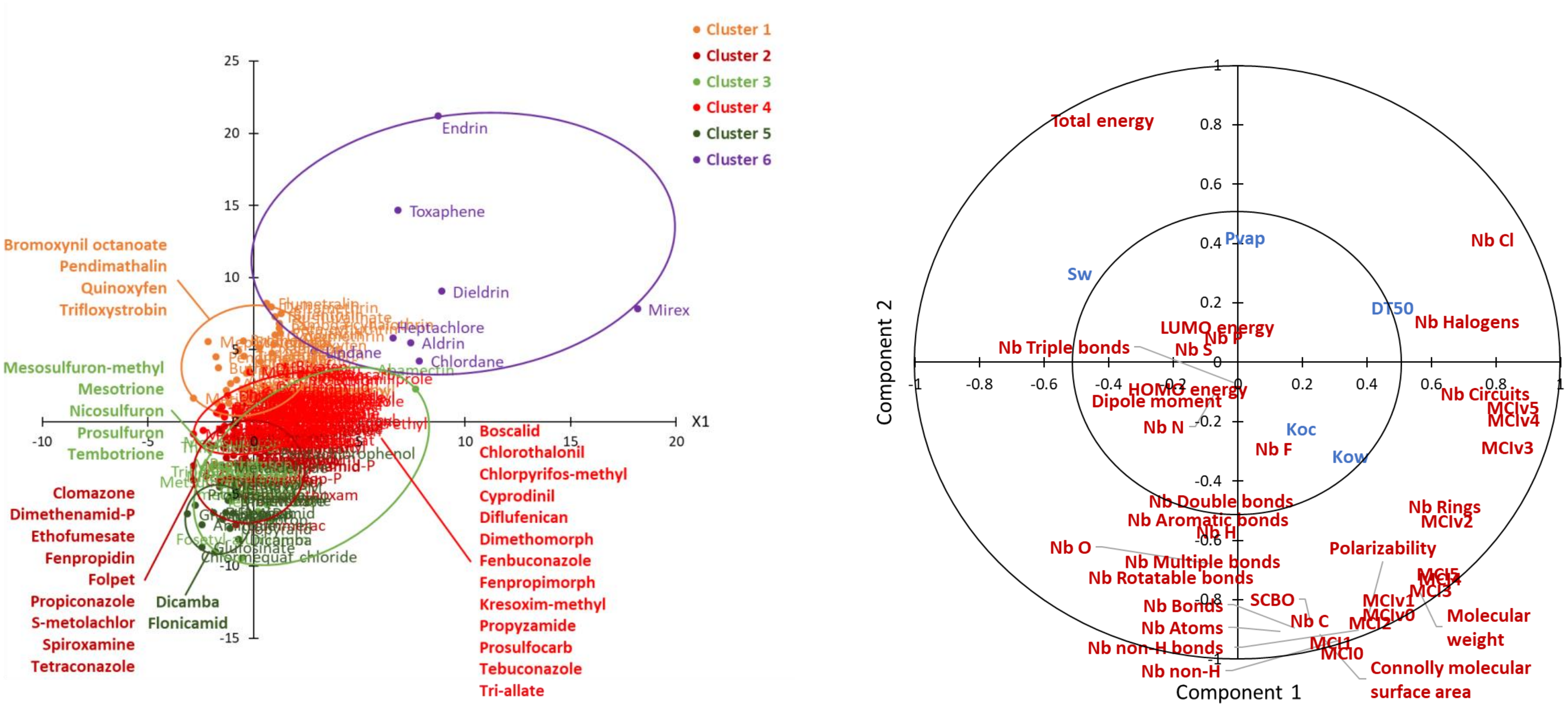
Figures legends

Fig. 1. (a) Graphical representation of the clusters obtained in the X1 and Y1 axes of the PLS with the 40 molecular descriptors (MCIi: Molecular connectivity index of order i (i = 0 to 5); MCIvi: Valence molecular connectivity index of order i (i = 0 to 5); Nb: Number; Nb X: Number of X atoms; SCBO: Sum of conventional bond order) and five parameters (vapor pressure P_{vap}, water solubility Sw, octanol-water distribution coefficient log Kow, adsorption coefficient of pesticide in soil Koc, and degradation half-life of pesticide in soil DT50) on the 178 pesticides: clustering for the study of global potential emission to air. Clusters in dark red, red and orange contain pesticides which were measured in the air (among others) while dark green and green clusters contain pesticides that were not measured and present a low risk of air contamination. The distribution of the 178 pesticides in the various clusters is indicated in Table S3. (b) Circles of correlations of the parameters (in blue) and molecular descriptors (in red) variables on the two main components of the PLS.

Fig. 2. (a) Graphical representation of the clusters obtained in the X1 and Y1 axes of the PLS with the 40 molecular descriptors (MCIi: Molecular connectivity index of order i (i = 0 to 5); MCIvi: Valence molecular connectivity index of order i (i = 0 to 5); Nb: Number; Nb X: Number of X atoms; SCBO: Sum of conventional bond order) and four parameters (vapor pressure P_{vap}, water solubility Sw, adsorption coefficient of pesticide in soil Koc, and degradation half-life of pesticide in soil DT50) on the 178 pesticides: clustering for the study of global potential emission to air. Clusters in dark red, red and orange contain pesticides which were measured in the air (among others) while dark green cluster contain pesticides that were not measured and present a low risk of air contamination. The distribution of the 178 pesticides

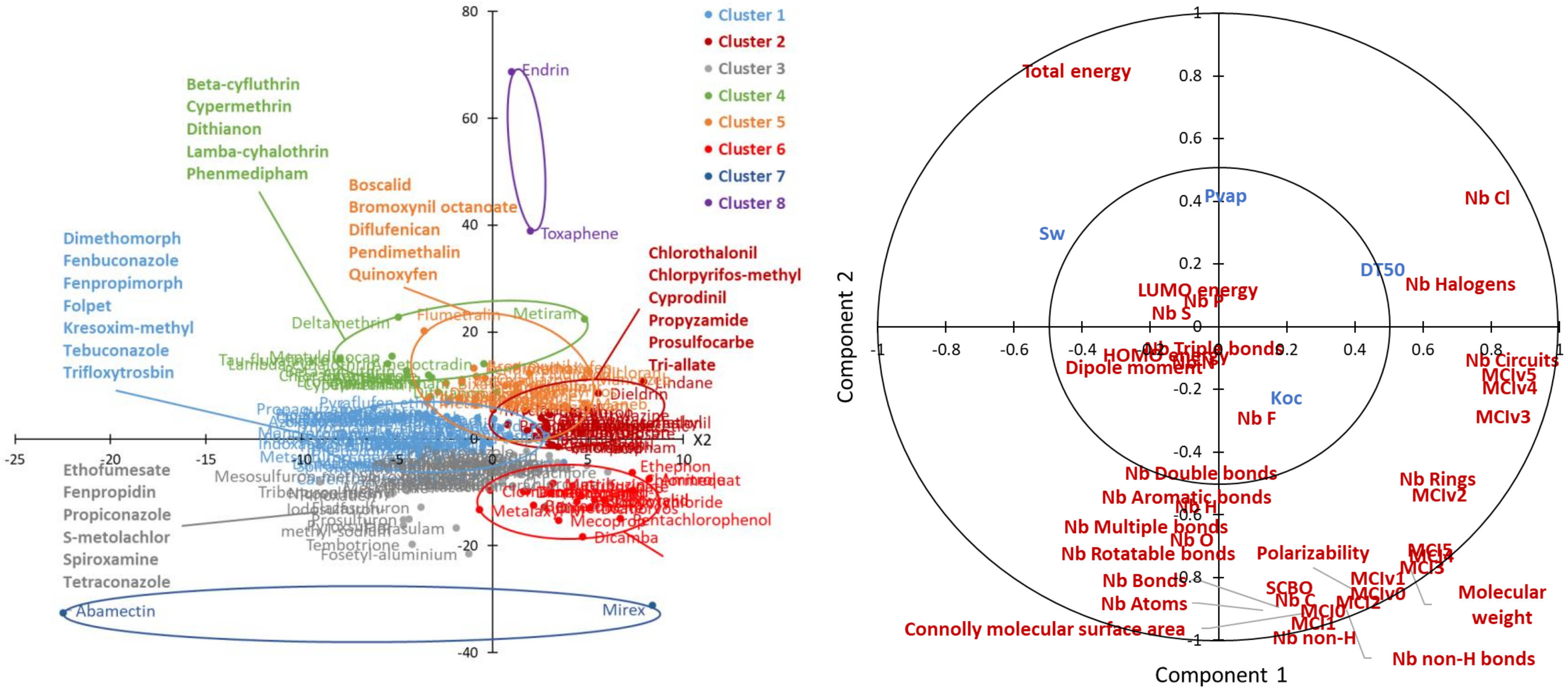
in the various clusters is indicated in Table S4. (b) Circles of correlations of the parameters (in blue) and molecular descriptors (in red) variables on the two main components of the PLS.

Fig. 3. (a) Graphical representation of the clusters obtained in the X1 and Y1 axes of the PLS with the 40 molecular descriptors (MCIi: Molecular connectivity index of order i (i = 0 to 5); MCIvi: Valence molecular connectivity index of order i (i = 0 to 5); Nb: Number; Nb X: Number of X atoms; SCBO: Sum of conventional bond order) and three parameters (vapor pressure P_{vap}, water solubility Sw, octanol-water distribution coefficient log Kow) on the 178 pesticides: clustering for the study of global potential emission to air. Clusters in dark red, red and orange contain pesticides which were measured in the air (among others) while dark green and green clusters contain pesticides that were not measured and present a low risk of air contamination. The distribution of the 178 pesticides in the various clusters is indicated in Table S5. (b) Circles of correlations of the parameters (in blue) and molecular descriptors (in red) variables on the two main components of the PLS.



(a) (b)

Fig. 1. (a) Graphical representation of the clusters obtained in the X1 and Y1 axes of the PLS with the 40 molecular descriptors (MCIi: Molecular connectivity index of order i (i = 0 to 5); MCIvi: Valence molecular connectivity index of order i (i = 0 to 5); Nb: Number; Nb X: Number of X atoms; SCBO: Sum of conventional bond order) and five parameters (vapor pressure P_{vap}, water solubility Sw, octanol-water distribution coefficient log Kow, adsorption coefficient of pesticide in soil Koc, and degradation half-life of pesticide in soil DT50) on the 178 pesticides: clustering for the study of global potential emission to air. Clusters in dark red, red and orange contain pesticides which were measured in the air (among others) while dark green and green clusters contain pesticides that were not measured and present a low risk of air contamination. The distribution of the 178 pesticides in the various clusters is indicated in Table S3. (b) Circles of correlations of the parameters (in blue) and molecular descriptors (in red) variables on the two main components of the PLS.



(a) (b)

Fig. 2. (a) Graphical representation of the clusters obtained in the X1 and Y1 axes of the PLS with the 40 molecular descriptors (MCIi: Molecular connectivity index of order i (i = 0 to 5); MCIvi: Valence molecular connectivity index of order i (i = 0 to 5); Nb: Number; Nb X: Number of X atoms; SCBO: Sum of conventional bond order) and four parameters (vapor pressure P_{vap}, water solubility Sw, adsorption coefficient of pesticide in soil Koc, and degradation half-life of pesticide in soil DT50) on the 178 pesticides: clustering for the study of global potential emission to air. Clusters in dark red, red and orange contain pesticides which were measured in the air (among others) while green cluster contain pesticides that were not measured and present a low risk of air contamination. The distribution of the 178 pesticides in the various clusters is indicated in Table S4. (b) Circles of correlations of the parameters (in blue) and molecular descriptors (in red) variables on the two main components of the PLS.

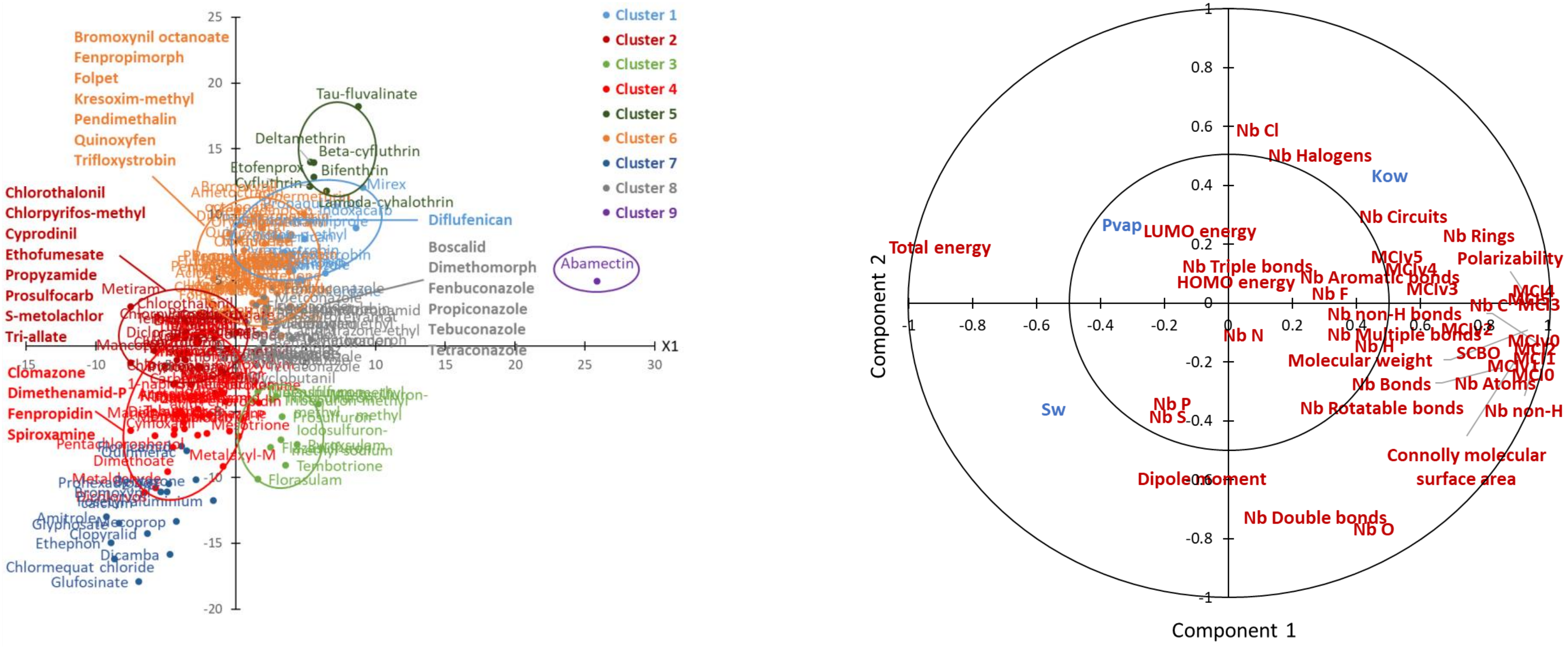


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Fig. 3. (a) Graphical representation of the clusters obtained in the X1 and Y1 axes of the PLS with the 40 molecular descriptors (MCIi: Molecular connectivity index of order i (i = 0 to 5); MCIvi: Valence molecular connectivity index of order i (i = 0 to 5); Nb: Number; Nb X: Number of X atoms; SCBO: Sum of conventional bond order) and three parameters (vapor pressure P_{vap}, water solubility Sw, octanol-water distribution coefficient log Kow) on the 178 pesticides: clustering for the study of global potential emission to air. Clusters in dark red, red and orange contain pesticides which were measured in the air (among others) while dark green and green clusters contain pesticides that were not measured and present a low risk of air contamination. The distribution of the 178 pesticides in the various clusters is indicated in Table S5. (b) Circles of correlations of the parameters (in blue) and molecular descriptors (in red) variables on the two main components of the PLS.