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Characterizing environmental contamination by plant protection products along the land-to-sea continuum:a focus on France and French overseas territories

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Abstract :

Environmental compartments are contaminated by a broad spectrum of plant protection products (PPPs) that are currently widely used in agriculture or, for some of them, whose use was banned many years ago. The aim of this study is to draw up an overview of the levels of contamination of soils, continental aquatic environments, seawaters and atmosphere by organic PPPs in France and the French overseas territories, based on data from the scientific publications and the grey literature. It is difficult to establish an exhaustive picture of the overall contamination of the environment because the various compartments monitored, the monitoring frequencies, the duration of the studies and the lists of substances are not the same. Of the 33 PPPs most often recorded at high concentration levels in at least one compartment, 5 are insecticides, 9 are fungicides, 15 are herbicides and 4 are transformation products. The PPP contamination of the environment shows generally a seasonal variation according to crop cycles. On a pluriannual scale, the contamination trends are linked to the level of use driven by the pest pressure, and especially to the ban of PPP. Overall, the quality of the data acquired has been improved thanks to new, more integrative sampling strategies and broad-spectrum analysis methods that make it possible to incorporate the search for emerging contaminants such as PPP transformation products. Taking into account additional information (such as the quantities applied, agricultural practices, meteorological conditions, the properties of PPPs and environmental conditions) combined with modelling tools will make it possible to better assess and understand the fate and transport of PPPs in the environment, inter-compartment transfers and to identify their potential impacts. Simultaneous monitoring of all environmental compartments as well as biota in selected and limited relevant areas would also help in this assessment.

Keywords : Pesticides, Phytopharmaceuticals, Pollution, Soil, Freshwater, Marine water, Air, French context

Introduction

Plant protection products (PPPs) are chemical or biological products that are directly introduced into the environment through various routes, due to both their agricultural and non-agricultural uses (Westlake and Gunther 1966). Back in 2008, growing awareness of the generalized environmental contamination resulting from these uses and the related ecotoxicological risks and effects (Aubertot et al. 2005) prompted the French Government to launch its first national action plan, called Ecophyto, which initially aimed – unsuccessfully – to reduce pesticide use (Guichard et al. 2017). This first French Ecophyto plan has since been revised twice, and it now explicitly aims not only to reduce the uses of PPPs but also their risks and impacts (French Republic 2018). This national plan strongly mobilizes the scientific community, both to develop new research and to provide expertise (Lamichhane et al. 2019).

In this context, 46 scientists were mobilized as experts for nearly two years to carry out a collective scientific assessment (CSA, Pesce et al. 2021) requested by the French Ministries responsible for the Environment, for Agriculture and for Research, to establish the state of the science on environmental contamination by PPPs along the land-to-sea continuum (without taking groundwater into account) in France and French overseas territories and the resulting impacts on biodiversity and ecosystem services. This CSA also aimed to highlight gaps and grey areas in the current science and propose directions for research to overcome these limitations (Donnars et al. 2021). Two reports were produced as CSA deliverables, one extremely detailed and exclusively in French, comprising more than 1400 pages (Mamy et al. 2022), and a more concise one, also available in English in the form of a book (Leenhardt et al. 2023). In order to make the main conclusions more accessible to the international scientific community, those were summarized in an article published in 2023 (Pesce et al. 2023) recently reported the main findings of this CSA work. CSAs also aim to highlight gaps and grey areas

in the current science and propose directions for research to overcome these limitations (INRA-DEPE 2018).

The present article is based on the above-mentioned CSA, which was extended by a targeted analysis of additional articles, some of which published subsequently to the report. It aims specifically to provide detailed overview of the knowledge on the contamination of terrestrial, inland, marine, and air ecosystems by organic PPPs in France and French overseas territories. By considering publications relating to comparable international contexts (in particular in the majority of European countries), it also aims to discuss grey areas, perspectives and opportunities for improving this knowledge.

Outlines of the survey and bibliographic methodology

The corpus of papers was collected by searching the bibliography spanning the period 2000–2021. The selected keywords used to build the search request combined: i) terms related to environmental contamination, ii) definitions of PPPs (e.g., pesticides, phytopharmaceuticals, phytosanitary products, plant protection products, and their various associated families, such as herbicides, insecticides, fungicides, acaricides, nematicides), iii) terms associated to characterization of the 4 environmental compartments considered (terrestrial or soil, atmospheric or air, continental or freshwater, and marine aquatic environments) and their related matrices (e.g., water, sediments, particles, rain, aerosols), and iv) the geographical areas (France and French overseas territories) (Margoum et al. 2024). These searches were then completed by specific search queries adapted to each of the 4 environmental compartments to remove off-topic documents (i.e., drinking waters, groundwaters or wastewaters).

The corpus thus obtained contained more than 11,310 references (all environmental compartments included) in the Web of Science (WoS) international bibliographic database. The majority of the corpus references continental terrestrial and aquatic environments and concerns

organic PPPs. The collected papers were then sorted by experts based on titles, keywords and abstracts. After this first round, only 1364 results were selected. Then, after reading through the full-text papers, we arrived at a final selection of 181 papers. Each expert then completed the corpus with relevant articles that were not listed in the WoS or that were published later (2021–2022), including also grey literature reports of environmental contamination by PPPs. Indeed, the scientific literature contains a number of environmental monitoring datasets, networks and observatories that have so far been underexploited in terms of contamination by PPPs. Furthermore, using only scientific articles to draw up an inventory of the issue would inevitably lead to an incomplete and fragmented overview of the situation in France, which is why each expert manually added the most relevant scientific and grey literature articles to our corpus. The repartition of the 561 references selected for analysis is represented in Figure 1 in terms of document type and of compartment considered.

Knowledge on environmental contamination by plant protection products in France

All environments contaminated by PPPs

Analysis of the scientific literature revealed that all the terrestrial, aquatic and atmospheric environmental compartments in France are contaminated by a wide range of PPPs and their transformation products (TPs), with extreme variability in the concentrations found. In addition, assessing environmental contamination is a complex issue, as the compounds searched were not the same in each compartment.

In this section, to further illustrate this near-ubiquitous environmental contamination by PPPs, we compared the levels of contamination by PPPs in the following 4 compartments: soil, freshwater, marine water, and air. The pesticide contamination data available in the literature

varies widely depending on (i) the objectives of the studies (i.e., spatial vs. temporal trends), (ii) the range of substances monitored and the number of samples collected, and (iii) the ongoing improvements in analytical equipment performances that have significantly enhanced sensitivity and thus enabled substantially lower limits of quantification (Masia et al. 2014). We therefore chose not to compare detection frequencies but to consider the maximum recorded levels of contamination by organic PPPs in order to compare contamination of the selected environments since the 2010s. In addition, not all the data is published in the scientific literature and much useful information is still available only in French-language reports, making it inaccessible to the international scientific community. The concentration data came from publications based on the bibliographic review (Leenhardt et al. 2022).

For that purpose, we considered 70 studies for soil, 82 for freshwater, 81 for marine water, and the Phytatmo database for atmospheric air (taking monitoring-campaign data since 2010).

For each compartment, we drew up a list of around 20 of the most frequently recorded PPPs, regardless of the monitoring or sampling strategies used (i.e., for water, we considered active and passive sampling). The PPPs were then ranked in each compartment in decreasing order of maximum concentration levels. Cross-referencing the 4 compartments led to a final list of 33 substances considered here as the most representative of the maximum levels of contamination in at least one compartment of the French environment.

Given the complexity of gathering data from all the compartments and the variability in the studies carried out (different time-scales, different spatial scales, different monitoring frequencies, different target compounds), we defined classes of concentration levels within each compartment (from “not recorded” in the literature, which does not always mean not present in the environment, up to higher concentration levels) without providing exact concentration values.

Table 1 shows the results obtained by cross-referencing the lists of 'top' compounds in each compartment, which resulted in 33 organic substances identified: 5 insecticides, 9 fungicides, 15 herbicides, and 4 transformation products. Among the 29 PPPs, 9 of them were already banned in 2010 (i.e., the start of the period reviewed here), 8 others have been banned between 2010 and 2023 and only 12 are still approved in France with no exemptions on their uses. Among the 29 selected compounds, only 4 (i.e., chlorpyrifos, glyphosate, chlorothalonil and metolachlor) are found to have the highest total annual pesticide load in Europe according to the recent study by Gensch et al. (2024). Furthermore, based on the European Union Water Framework Directive (WFD - 2000/60/EC, European Commission 2020), 6 of the compounds recorded in Table 1 (i.e., atrazine, chlorpyriphos ethyl, chlortoluron, diuron, isoproturon and simazine) are listed as European priority substances for which levels in waters are to be compared against Environmental Quality Standards – EQS- (European Commission 2015) in order to assess water quality status at the waterbodies scale (continental and marine waters). In French freshwaters, the concentration levels reported for all these PPPs exceed the thresholds except for chlorpyriphos, for which the EQS value is 30 $ng.L^{-1}$. For marine waters, these compounds were below marine EQS. Higher concentrations were reported on rare occasions before 2014, often during measurements in estuaries or semi-enclosed areas (e.g., lagoons and bays), or near the marine outlets of streams, canals (Bizarro et al. 2014).

In comparison to our selection, a recent review presented a list of PPPs with the highest concentration levels reported in surface waters in 146 studies worldwide (de Araujo et al. 2022). Ten PPPs listed in Table 1 were also reported in de Araujo et al. (2022) and most of the time correspond to the highest concentration ranges found in freshwater samples from different countries (atrazine, chlorpyrifos ethyl, diuron, imidacloprid, lindane, metolachlor, simazine, terbuthylazine, DEA, DIA). Schreiner et al. (2016) used routine monitoring data to compile a

list of the most frequently detected PPPs in freshwaters of several European countries and the USA. For France, all the PPPs detected with a relative occurrence higher than 20% are herbicides: diuron, isoproturon, MCPA (which is not listed in Table 1), atrazine, and simazine. In soils, chlordecone, an organochlorine insecticide used between 1972 and 1993 on banana crops in West Indies (Martinique and Guadeloupe), presents concentrations that can reach several tens of $mg.kg^{-1}$ (Martin-Laurent et al. 2014). Such concentration level is not encountered for other organic PPP, neither in France nor worldwide. The contamination of agricultural soils in France is generally comparable to other European ones, both in terms of concentrations and number of PPPs per sample (Silva et al. 2019), considering soils cultivated under conventional or organic management (Knuth et al. 2024). This general assertion has however to be tempered with many exceptions. For instance, higher contamination by AMPA is reported in Portugal (Silva et al. 2019; Knuth et al. 2024) or by atrazine and chloroacetanilides in Switzerland (Chiaia-Hernandez et al. 2020). On the contrary, French soils seem to be more contaminated with boscalid, imidacloprid, pendimethalin or diflufenican than other European ones.

The selected list of active substances based on the maximum recorded concentration levels was re-analysed in terms of the amounts of active substances sold and applied on crops and the physical-chemical properties of each substance (solubility, log Kow, log Koc, Henry's law constant, half-life, etc. – see Supplementary data) that modulate their transfer, fate and accumulation in the various environmental compartments. The concentration levels of a third of the compounds are in the 3 highest classes of concentration – apart from chlordecone - (Table 1) for at least 3 of the 4 environmental compartments; metolachlor, terbuthylazine and imidacloprid having even been quantified in all matrices which reflects the ubiquitous presence of these substances in the environment. On the contrary, other substances tend to be found in only one specific compartment, such as chlorothalonil, triallate and prosulfocarb that were only

reported in atmospheric air. It is important to remember, however, that our paper is based only on data from the scientific publications and not on French monitoring networks. For example, prosulfocarb has never been found in the water samples from the research papers covered in our present study, but this compound is regularly quantified in the surface waters of the WFD monitoring network with a quantification rate close to 20% in November (2007-2014) (Devault et al. 2022).

A clear decrease in contamination levels (Table 1) between agricultural soils, considered as the contamination source, on to freshwaters then marine waters is shown for some of the least soluble compounds (see Supplementary data). For example, boscalid, diflufenican, pendimethalin and chlordecone are 4 PPPs highly concentrated in French soils but much less present in the aqueous compartments. Higher lipophilic compounds such as lindane or chlorpyrifos ethyl show the opposite pattern, with higher ranges of peak concentrations found in the marine environment than in other compartments (Bizarro et al. 2014). More surprisingly, a high contamination level is also highlighted for the herbicide diuron, which is a less lipophilic substance that has a moderate half-life in water (9 days) and sediment (49 days). Note that diuron was banned from use as a PPP in 2008 but continued to be used as a biocide in France, notably as an antifouling paint for boats.

Numerous studies deal with PPP contamination in various biota, including arthropods, annelids, molluscs or even vertebrates such as birds, fishes and mammals. However, the results are often difficult to compare as 1) the sample considered may vary from the whole body to an internal organ (eg. liver), or result from a non-lethal sampling (eg blood, feather, hairs) or even externalities such as scats or rinsates, 2) the organisms may either be catched alive in the environment or found dead and then analysed if poisoning was suspected, and 3) the results are expressed as a PPP quantity per weight of fresh body (or organ), or dry body (or organ).

Among the PPP presented in Table 1, most of them were observed in terrestrial biota. The maximal concentrations in animals were generally in the same range as observed in soil (in the same or other studies), suggesting that bioconcentration factors could in general be in the 0.1 to 10 interval, eg. for the whole body fresh weight of invertebrates, in France (Chauzat et al. 2011; Wiest et al. 2011; Pelosi et al. 2021, 2022) as in other countries (Stahlschmidt and Brühl 2012; Botias et al. 2017; Slachta et al. 2020; Al-Alam et al. 2022). However, there are some exceptions, e.g.,spiroxamine was quantified in few soils (i.e., < 1 to 2 $\mu g.kg^{-1}$) but was found at 38 and 140 $\mu g.kg^{-1}$ in bumblebees and snails, respectively (Botias et al. 2017, Al-Alam et al. 2022). Some other exceptions exist also in vertebrates, such as the extremely high concentrations of imidacloprid, exceeding 10 $mg.kg^{-1}$, observed in liver or gizzard of granivorous birds ingesting treated seads (Millot et al. 2017).

Regarding marine water - as the final receptacle of the land-to-sea continuum -, while monitoring (French mussel watch) provides a detailed spatial analysis of contamination on the same taxa (filter-feeding bivalve molluscs), scientific literature data completes this analysis for several other taxa from different trophic levels. We found that 94% of organic PPPs detected in marine biota in mainland France are historically banned organochlorine POPs (OCs) (mainly insecticides DDT and its TPs, e.g., lindane, chloropyrifos, cyclodiene insecticides and the fungicide HCB). However, one study found fipronil in eels from the Vaccarès lagoon (140 µg/kg dw) (Ribeiro et al. 2005), while another found the metolachlor (the only herbicide from Table 1) in scallops from the Bay of Biscay and Brittany (max: 11.8 µg/kg dw) (Menet-Nedelec et al. 2018).

In addition, other biological matrices have also been used as bioindicators of PPP contamination in each environmental compartment, such as snails (Druart et al. 2011; Al-Alam et al. 2022) and earthworms (Rastetter and Gerhardt 2018) for soils, stream biofilms for coastal water (Bonnineau et al. 2021), and pine needles for air (Al-Alam et al. 2022).

Temporal trends in PPP contamination are shaped by various factors

The temporal evolution of PPP contamination can be evaluated on a crop-cycle scale or on a pluriannual scale. At crop-cycle scale, there is an observable seasonal pattern in the different compartments in relation to the periods of application of the PPPs combined with the time they take to reach the compartment, which depends on prevailing hydrometeorological conditions (rain, wind, temperature). Then, this dynamic is usually smoothed out for the compartments furthest from the sources, such as the marine environment. Regarding soil contamination, the half-life (DT50, as reviewed in Fantke et al. (2013)) can explain the time-course of concentrations in some cases (Cruz 2015 in vineyards) but not all cases (Roeben et al. 2020; Serra et al. 2020). Various factors can explain this observed differences: an effect of the different matrices (type and content of organic matter , litter), an effect of certain cropping practices, of microbial adaptation in response to repeated application of the same compound (Rouchaud et al. 2000), the formation of bound residues (Barriuso et al. 2008; Kastner et al. 2014), or interactions between compounds applied together (e.g., glyphosate and Bt; Accinelli et al. (2004)), and horizontal atmospheric or even hydrological transfers (Serra et al. 2020). Overall, the persistence in soil, and thus wildlife exposure, of both banned and currently used pesticides appears to be underestimated (Riedo et al. 2021; Fritsch et al. 2022). In surface waters, some studies presented monitoring of PPP contamination levels in small French agricultural watersheds over a crop year with different sampling strategies (grab, flow-dependent automatic or passive samplings) and frequencies (from one campaign per season to 121 samples collected on the same site during 10 months) (Bernard et al. 2019; Le Cor et al. 2021; Reoyo-Prats et al. 2017) .All studies highlighted strong seasonal variations in water concentrations, especially in regions exposed to intense meteorological events, such as the south of France (Reoyo-Prats et al. 2017). Spycher et al. (2018) and Belles et al. (2019) point out that

low-frequency monitoring does not reflect the true contamination in water, as three-quarters of the flows are only transported to rivers during 2 to 3 months of the year. A high-frequency water sampling strategy is also valuable for highlighting the presence of TPs (Le Cor et al. 2021). In Switzerland, La Cecilia et al (2021) have designed a very high frequency *in situ* measurement system. Time series of PPP and TP concentrations were measured every 20 minutes for 41 days using continuous sampling and on-site measurements with a high-resolution mass spectrometer. The obtained results showed that the Swiss national monitoring composite samples (3.5 days) underestimated concentration peaks, which can lead to confusion or misinterpretation when assessing contamination trends. Other research studies have focused mainly on the dynamics of transport after rain events, as these events are particularly conducive to the transfer of PPPs into the watercourses of small catchment areas (Rabiet et al. 2010; Taghavi et al. 2011; Doppler et al. 2014). Taghavi et al. (2011) estimated that 59% to 90% of active substances are transferred during summer flood events in small agricultural watersheds, with maximum concentrations found during flood rising for hydrophobic compounds (such as aclonifen) and during flood recession for more soluble compounds such as metolachlor. In addition, the transport of PPPs in the particulate phase is an important pathway that can contribute to pollution over longer periods than in water (Commelin et al. 2022). Suspended particles can accumulate and form sediments, which then constitute an integrating matrix for contamination, making them particularly appropriate for analysing the temporal evolution of watercourses contamination by hydrophobic persistent compounds (Gardes et al. 2021), provided that the sediment analysis is based on suitable techniques and methods (involving, in particular, standardization by organic carbon (OC) content for organic contaminants). However, it is still difficult to identify overall trends in sediment contamination according to season (Moschet et al. 2014). Some data from regional monitoring networks or single studies identified seasonal trends in coastal waters for more polar substances (herbicides/fungicides) in the Arcachon bay or Marennes-Oléron bay,

but to our knowledge these data analysis are not published in the academic literature. Conversely, Munaron et al. (2023) recently reported on seasonal trends in water contamination in two contrasted French Mediterranean lagoons, where mixtures of banned and approved pesticides and their TPs were detected in coastal waters using passive samplers that were renewed continuously for a full hydrological year. These mixtures (up to 37 herbicides and fungicides) were a threat for the three taxa studied (phytoplankton, crustaceans, and fish), and the risk level varied between lagoons, between taxa, and seasonally for the same taxa. This seasonal variation of the risk depends on agricultural uses of PPPs on the watersheds (vineyards vs. cereals and market gardening, each treatment being highly seasonal) and boating and fishing activities, which lead to an increase in antifouling biocide contamination in late spring-early summer waters (some of these substances are also PPPs). Up to now, such high-frequency monitoring has not been carried out in more open and/or deep marine environments in France, because of considerable logistical resources required and cost reasons. In such open waters, far from PPPs sources, integrative methods of sampling (passive samplers and biota) have been described as essential in both French (Breitwieser et al. 2020; Hedouin et al. 2011; Luna-Acosta et al. 2015; Zanuttini et al. 2019) and international literature (Jamal et al. 2024; Ojemaye et al. 2020) to sample contaminants . Regarding contamination of the atmosphere, the overall regional concentration is expected to be higher during the period when a given pesticide is applied over large areas, thus generating seasonal concentration patterns evolution (Coscollà and Yusà 2016). Recently, observations of atmospheric contamination over 50 sites in France (including French overseas territories) showed that levels of contamination generally matched to periods of PPP treatment, which thus reveals a signature of agricultural practices. Indeed, periods of higher contamination were identified in October–December and April–June in regions dominated by field crops, June–September in vineyard regions, lower but with a peak in June and August for orchard regions but more homogeneous in market-garden areas,

consistently with agricultural practices (LCSQA 2020). Note, however, that contamination occurs throughout the year, even outside the treatment period (Aasqa AirParif 2020), and that for some of the in-use pesticides detected, it is not always clear whether their concentration and frequency in the air are associated with local use and/or long-range transport from other sources as highlighted by (Coscollà and Yusà 2016) in their review. Krueger and Lindström (2019), observed that pesticides not used in Sweden contributed to atmospheric deposition in southern Sweden, suggesting significant transboundary atmospheric transport of pesticides. This is confirmed by the recent study of Mayer et al. (2024) who found currently used pesticides in the free troposphere as well as in Arctic sites, suggesting that atmospheric transport and persistence of pesticides have been underestimated.

At the pluriannual scale, the dynamics observed tend to be linked to the level of use of the compounds, which is influenced by the current year's pest pressure and the bans on certain PPPs. In continental surface water, despite methodological constraints and the resulting limitations for interpreting the results, the vast majority of studies converge towards a progressive decrease in PPP concentration levels, essentially linked to the decrease in herbicide concentrations (e.g., Statistical Data and Studies Department (SDES) (2020)).

However, Hossard et al. (2017) analysed the evolution of surface water contamination between 2007 and 2012 (i.e., following the adoption of the Ecophyto Plan in 2008) using two datasets based on monitoring in France, and they found no significant decrease in concentration levels despite a slight decrease in the use of PPPs on crops. The overall decreases of the PPPs concentrations observed in continental surface waters in mainland France have not been observed in surface waters of the French overseas territories (Mottes et al. 2017). In coastal waters, inter-annual trends are only available for DDT and lindane in shellfish based on data from the French "mussel watch" (ROCCH) since 1979, with samples taken every three months between 1979 and 2002, every six months for the period 2003-2016 and once a year in February

since then. Both DDT and lindane clearly decreased in mussels and oysters in the 1990s to the 2000s, and today their levels are relatively very low and stable. Yet, these levels remain quantifiable due to the high environmental persistence of these organic pollutants and the improvement in analytical techniques. In marine waters, despite bans on several organochlorine insecticides between the late 1970s (DDT) through the 1990s (aldrin, dieldrin, endrin, isodrin) and 2000s (lindane) and into the early 2010s (endosulfan), these compounds were always detected in striped dolphins in the western Mediterranean Sea between 1998 and 2016 (Dron et al. 2022). Although PPP contamination of dolphins has tended to decrease slowly overall, TP levels have been proportionately higher since 2010, probably reflecting the exposure of dolphins to greater remobilization of pollutants from contaminated soils and sediments, coming from rivers that carry PPPs from catchments to the open sea. In the atmosphere, the inter-annual contamination trends are variable, whether in terms of number of substances detected at various sites, frequency of detection per substance, or substance concentration levels.

We took the opportunity of this review on the environmental contamination to analyse the effect of bans on this contamination. . Illustrative examples include diuron, for which average levels in continental surface waters have decreased since 2007, first strongly just after the diuron ban but then levelling off at close to 40% of the initial concentrations 4 years later (Service de l'observation et des statistiques SOeS et al. 2015), and atrazine in marine waters (Nodler et al. 2013) or even fluzilazole in the atmosphere (Desert et al. 2018). In the Galion River (French overseas territories), chlordecone concentrations have also tended to decrease (Mottes et al. 2020). In the atmosphere, lindane has decreased in concentration but continued to be regularly detected. Villanneau et al. (2009) suggested that old lindane applied to intensively cultivated areas was volatilized, transported by prevailing winds and deposited on soil in a densely inhabited depression. Such behaviour has also been suspected in Poland (Ukalska-Jaruga et al. 2020). The former use of lindane as biocide has also to be considered. However, not all

compounds show post-ban decreases. Norflurazon, for example, was banned in 2003 but norflurazon concentrations in the water of a river in a wine-growing catchment area remained stable over the 2009–2012 period (Gouy et al. 2021). Similarly, regular monitoring of diuron in the surface water of a wine-growing catchment area between 2008 and 2013 showed only a slow decline in contamination (Pesce et al. 2016). Moreover, TPs may still be present in the environment a long time after the active substance has been banned, e.g., TPs of atrazine in marine waters or norflurazon in continental surface waters.

In conclusion, it remains difficult to get a clear picture of the evolution of environmental contamination by PPPs in France, particularly on a pluriannual scale, for several reasons, mainly the evolving methods of monitoring and analysis and the fact that the chemical form analysed may differ over time, and the need for fairly long continuous monitoring. Chow et al. (2020) argued that to properly assess contamination trends, it is first necessary to have at least 5 years of monitoring data that is homogeneous in terms of matrices sampled and substances screened, as well as analytical methods with equivalent performances over the entire monitoring period. In a recent paper, Chow et al. (2023a) even points out that, due to the influence of hydrological events, a sharp reduction in the use of PPPs or the implementation of mitigation measures is required to detect significant changes over ten years of monitoring data. Then, even when such data is available, interpreting the contamination trends remains a complex task due to fast-changing agricultural practices and the regulations governing PPP substances in France and neighboring countries, as well as possible exemptions from use and the lack of associated metadata.

Data collection is affected by various sources of variability

Several sources of variability have been identified that influence the availability or quality of data in the literature. First, this variability concerns the matrix studied and the sampling strategy

implemented. As an example, for soil or sediments sampling in research studies, different depths of cores and numbers of homogenized cores are considered to obtain a representative sample of the area studied, which varies from 1 to 10. Suszter and Ambrus (2017) recommend a minimum of 8 cores. Similarly, river-bottom sediments are sampled at variable depths, for example 2 cm in the study by Vulliet et al. (2014) but 10 cm in the study by Rooney et al. (2020), which can lead to variability in concentrations measured. For marine sediments, the level of organic carbon, the fraction of sediment sampled (between <63µm, the most frequently used, and <2mm), and the mode of sampling (sediment cores by diving, van veen, ekman, shiptex or reineck grabs from boats…), are also key parameters of variability in concentrations, essential for describing the adsorption of organic contaminants and enabling inter-comparison of samples and sites (Burgeot et al. 2017). For the water matrix, organic PPPs are generally analysed in the total fraction of the sample (dissolved and particulate phases) as part of regulatory monitoring campaigns (Campanale et al. 2021) or in certain studies that use spot measurements. However, most scientific studies consider the dissolved fraction instead, as the extraction methods currently used by laboratories are not all compatible with the analysis of samples containing suspended solids (SS) (Ademollo et al. 2012; Schmidt 2018). For example, House et al. (2000), cited by Warren et al. (2003), studied the partitioning of permethrin in river water and showed that the proportion of permethrin associated with SS varied from 3% to 87% depending on the samples taken. This distribution seems to be mainly linked to the composition of the SS. Comparing PPP levels in the water matrix can therefore be a tricky task, especially for the most hydrophobic substances, as the levels will depend on whether or not the particulate phase was taken into account in the analysis. In addition, the surface water sampling strategy (i.e., spot, composite or integrated sampling; manual sampling or using an automated time or volume proportional sampler) can also have a major influence on the results obtained, particularly in small rivers subject to wide variations in PPP concentrations (Bundschuh et al.

2014; Bernard et al. 2019), The same sources of variability are also observed in air samples, where monitoring only covers the gaseous and particulate atmospheric phase (without distinction between the two) and not the other matrices (rain, fog). Given this monitoring datasets, we therefore only have access to a part of actual atmospheric contamination. A few datasets have been published by research teams e.g., recently in France (Decuq et al. 2022). The assessment of gas/particle partitioning in the atmosphere is rare and is mainly the result of research work (Coscollà and Yusà 2016).

For all environmental samples, transport and storage conditions can also affect the quality of data acquired, but not all studies detail this information. However, it has long been proven that storage conditions have an effect even in soils: a 1976 study showed that 50% of metribuzin (triazine) was lost in a sandy loam soil after 282 days of storage at -37°C (Webster and Reimer 1976). Ziegler et al. (2019) reported the results of PPP stability tests in water samples involving 25 laboratories as part of a proficiency testing campaign. The stability of more than 100 PPPs was assessed in water samples stored for up to 9 days at 4°C. The majority of PPPs were stable under the test conditions, but a few (e.g., cymoxanil, fenoxycarb, procymidone, cypermethrin, flumioxazin, folpel) showed a rapid decrease in concentration.

The analytical process for the determination of PPPs in environmental matrices comprises several steps that are considered critical for ensuring the quality of concentration data. Schmidt (2018) illustrated the different sources of variability to address. Whatever the matrix, the analytical methods used are generally multiresidue analysis. However, these methods exclude certain commonly used PPPs, such as dithiocarbamates (mancozeb, maneb, etc.), glyphosate and AMPA, that require specific extraction and/or analysis methods (Chow et al. 2020).

The quality of quantification of trace PPPs in environmental samples is often affected by matrix effects linked to the presence of interferents in the matrix, so analytical laboratories need to

implement strategies to control and, if possible, correct these matrix effects. Raposo and Barceló (2021) reviews the different analytical strategies available to limit matrix effects when analysing organic contaminants such as PPPs in environmental samples, either by reducing the presence of interfering components, or by using appropriate calibration methods.

Opportunities to improve our current knowledge of environmental contamination status

Passive sampling for environmental matrices

Integrative passive samplers (PS) have undoubtedly been the most innovative tools developed to improve monitoring of chemical contamination by PPPs over the last 25 years. However, PS have limited use in soils. Solid-phase microextraction, Empore™ disks (sulfonate-functionalized styrene-divinylbenzene copolymer) and silicone membranes have been performance-tested for conazole fungicides in water-unsaturated soils and were found to give largely variable and illogical results (Sudoma et al. 2019). However, other studies find more promising results when deploying PS at higher humidity levels (in-laboratory), i.e., at 100% moisture content with the 'diffusive gradients in thin films' (DGTs) technique for 9 PPPs (Li et al. 2019) or atrazine and its degradation products (Lin et al. 2018), or at only 80% moisture content with DGTs containing a TiO2 layer for glyphosate (Wang et al. 2019). Other alternative methods, such as ELISA tests or biosensors, have been trialed but they appear to be under-sensitive for soil analysis compared to conventional PPP uses (Justino et al. 2017). Andreu and Pico (2012) noted some promising biosensors for PPP determinations in biota, but we found no reports of *in situ* use.

In aquatic environments, the use of PS has been widely developed over the past 3 decades for assessing dissolved organic and inorganic PPP contamination, either via holistic approaches to

approximate the ambient concentrations involved in chronic exposure of organisms, or via comparisons with 'historical' spot sampling. Passive samplers are small, low-cost tools that do not require a permanent power supply to operate while they are deployed in the aquatic environment (Assoumani et al. 2015; Chow et al. 2023b). The use of PS generally increases the rates of PPP detection in water, because these tools integrate the concentration variations, including flood peaks, during the *in situ* deployment period, and the lower quantification thresholds provided by the tools' *in situ* pre-concentration capability. The advantages of such a sampling strategy has been illustrated in both freshwater (Bernard et al. 2019) and coastal waters (Munaron et al. 2023) with the polar organic chemical integrative sampler (POCIS) system. Guibal et al. (2018) compared PPP analyses on POCIS and spot water samples (dissolved fraction only) realized in parallel in a small stream, and their results showed that the two approaches share complementarity. During high-transfer periods (floods), spot-measured concentrations were higher than POCIS-measured concentrations. During the base flow period, spot-measured concentrations were similar to POCIS-measured concentrations. When concentration levels are very low, PPPs are only detectable using integrative tools, which explains why these PS are particularly useful in the marine environment, where in-water PPP levels can be extremely diluted. Criquet et al. (2017) compared stream contamination data obtained with POCIS samplers and composite automated samplers in a peri-urban contamination context, and they found a good correlation (R^2=0.89) between the mean PPP concentrations of the two datasets. Nevertheless, differences were observed for certain compounds for which the calibration data (sampling rate) available in the literature does not appear to be suited to the hydro-biogeochemical conditions. PS were faced to the availability of suitable calibration data enabling suitable time-weighted average concentration of PPP *in situ* in water (Valenzuela et al. 2020). There has been a great deal of research focused on assessing the performance of *in situ* PS and their relevancy for environmental monitoring in

France, whether for prospective studies (Mathon et al. 2020; Munaron et al. 2012) or for research at different study scales (Bernard et al. 2019; Poulier et al. 2014). In theory, therefore, PS never take into account the proportion of PPPs adsorbed to total suspended sediments. Jonsson et al. (2019) developed *in situ* extraction tools to integrate the total fraction of the water sample. New tools are regularly emerging and evaluated to broaden the range of PPPs that can be sampled in aquatic environments (Berho et al. 2017; Fauvelle et al. 2014; Guibal et al. 2017; Martin et al. 2016; Taylor et al. 2020; Valenzuela et al. 2019). Finally, in an effort to obtain the most comprehensive information possible on the state of contamination of aquatic environments by PPPs and other organic contaminants, there have been various promising initiatives coupling passive integrative sampling with HRMS analysis, and various examples have been applied in France and worldwide (Guibal et al. 2015; Mazellier et al. 2018; Renaud et al. 2021; Taylor et al. 2021).

Passive samplers can also be used to assess air contamination, and various systems have been under development for several years. Coscollà and Yusà (2016) summarized the PS developed to explore air contamination by pesticides. In theory, these PS only trap the gas phase. Galon et al. (2021) noted differences between the XAD and polyurethane foam (PUF) sorbents in terms of ability to capture particles, although they necessarily require long exposure times, ranging from several weeks to several months. Trials have tested various systems based on PUF, XAD-2, solid-phase microextraction, and other techniques, and even new components (some of which have patent applications pending; Levy et al. (2020)), primarily for persistent organic micropollutants but also, recently, for currently-in-use pesticides. Raeppel et al. (2015) tested the Tenax adsorbent. However, there is still a challenge to be met: extrapolating from trapped quantities to environmental concentrations requires knowledge of the equilibration time, which depends on the samplers but also on the compounds screened. It is possible to estimate equilibration time based on the linear kinetics phase or on the equilibrium phase. The sampling

rate also needs to be established, as outlined by Galon et al. (2021) who presented the different principles of passive samplers. Schuster et al. (2021) reported a method for setting POPs sampling rates. Coscollà and Yusà (2016), citing Harner et al. (2006), claimed that passive samplers can over or underestimate the air concentrations by a factor of 2 to 3 compared with active samplings, and they concluded that even with possible improvements, these PS would likely remain less reliable than active sampling. But PS can easily be deployed to assess the overall level of air contamination by PPPs over a long and spatialized time-step. Their value therefore depends on the monitoring objective. Another option is to improve active samplers by engineering better field operability (power supply, for example) and by optimizing key parameters such as sampling rate, trapping efficiency, and analytical capacity.

Emerging analytical strategies

Since the 2010s, there has been a clear shift in the analytical strategies used to investigate and quantify a wider range of organic PPPs, including transformation products, in the different environmental matrices and at ever-lower levels of contamination (PPP concentrations in ambient air are generally around a few pg/m³ to several ng/m³, which is relatively low and classifies them as atmospheric 'trace gases'). Several reviews outline the benefits and opportunities of these new techniques, which a growing number of laboratories are now equipped to deploy for the preparation, extraction or preconcentration of PPPs in samples and their subsequent analysis (Deng et al. 2020; Gavage et al. 2021; Nasiri et al. 2020; Pico et al. 2020; Schmidt 2018). Based on the performance of chromatography coupled to HRMS, more and more studies are now presenting contamination data on very broad lists of substances (Altenburger et al. 2015; Moschet et al. 2014; Spycher et al. 2018). The main limitations to routine development are the high cost of the equipment and, above all, the technical skill and labor required to reprocess the huge quantity of data acquired.

Regarding the atmospheric compartment, coupling thermal desorption in-line with the analytical chain (GC/MS for example) avoids the use of solvents and allows to gain sensitivity. This method is suitable for non-thermolabile compounds, although it carries the disadvantage of destroying the sample during the analysis. It has recently been tested for multiresidue analysis in air and in rainwater (Decuq et al. 2022). One promising approach currently being tested is the Proton-transfer-reaction mass spectrometry (PTRMS) technique (Murschell et al. 2017; Vesin et al. 2013) that is designed to measure PPP concentrations at high frequency (and no longer over durations constrained by the minimum sampling time required for reliable quantification, which is often several hours) and over longer periods. However, the technique requires a calibration step, which may prove challenging, and its sensitivity depends on the type of PTRMS system, which may it limited for use on ambient air.

The investigation and quantification of polar pesticides, including most TPs, cannot generally be covered by reverse-phase liquid chromatography (RPLC). The review article by Knoll et al. (2020) presents techniques for sample preparation and analysis of highly polar and ionized compounds in water and biota. Among the fast-emerging techniques, hydrophilic interaction chromatography (HILIC), two-dimensional chromatography (RPLC-HILIC-LC-HRMS) or supercritical fluid chromatography (SFC) hold promise for meeting the challenges of analysing such compounds. Two recent reviews provide a synthesis of the latest analytical techniques for the separation of enantiomers of pesticides (Carrao et al. 2020; Deng et al. 2020). However, enantiomeric analyses are mainly performed for specific studies, and the different enantiomers are rarely distinguished in monitoring programs on aquatic environments within the Water Framework Directive (Amalric et al. 2013). Overall, most of the analytical methods currently used rarely if ever differentiate between diastereomers or enantiomers. However, these different forms of a pesticide can lead to different classes of persistence (e.g., pyrethroids; Li et al. (2009)) and/or bioaccumulation (e.g., second-generation anticoagulant rodenticides; Fourel et

al. (2017; 2018)) or even toxicity (e.g., triazole fungicides; Liu et al. (2021); Skulcova et al. (2020); Bielska et al. (2021)). Research efforts are ongoing, but remain largely undeveloped, especially in field situations; e.g., SFC-MS/MS couplings with high resolving capacity of chiral columns (Cutillas et al. 2020) in addition to LC-MS/MS (Galon et al. 2021)

It is now widely agreed that PPPs cannot be considered independently of each other, and that it is vital to systematically monitor the different compounds in each family of PPPs, including TPs and even emerging substances, in order to fully understand the chemical complexity of environmental contamination.

Many studies at national, French and international levels have investigated and demonstrated the multiple benefits of broad-spectrum analysis coupling liquid chromatography and high-resolution mass spectrometry. The main use-case for this analytical methodology is to screen for pesticide TPs (e.g., Climent et al. 2019; Reemtsma et al. 2013; Heffernan et al. 2017), at least qualitatively in the absence of analytical standards (Baran and Bristeau 2018), or for retrospective analysis of previously acquired and banked data (Gonzalez-Gaya et al. 2021). Laboratories equipped with this type of instrumentation may be able to screen for and identify new TPs. However, given the very large quantity of TPs potentially formed in the environment and the difficulty implementing such an approach for laboratories specializing in targeted analysis of organic contaminants, a growing number of papers are proposing prioritization strategies (Melin et al. 2020) and methodologies for identifying new TPs (Krier et al. 2021; Rocco et al. 2022; Zhang et al. 2021).

Advanced analytical technologies such as ion mobility and 2D chromatography associated with HRMS can more reliably identify contaminants in complex mixtures of environmental matrices (Celma et al. 2021; Knoll et al. 2020; Ochiai et al. 2011; Schmidt 2018).

Exploitation of all the existing and relevant data

In this paper, we focus mainly on data available in the scientific literature, with some exceptions for marine water and atmosphere compartments for which we also considered datasets provided by monitoring studies (French reporting only). Nonetheless, even when there is freely-available data from monitoring networks on environmental compartments, in particular in aquatic environments and air, the data still remains largely under-exploited in the scientific literature. As already pointed out in certain studies (e.g., by Ippolito et al. (2015), regarding the factors driving the contribution of runoff in the contamination of streams), this data could be used to more systematically compare overall contamination levels with complementary data, such as agricultural practices (treatment periods, equipment used), quantities used (BNBVD-S data in particular ; Martin et al. (2023)), physicochemical and environmental profile of the substances, meteorological conditions, distance from the treated area, or use ban dates, to analyse their effects. For water, we can cite the example of the meta-analysis carried out by Carles et al. (2019) for glyphosate, a few datasets used by Hossard et al. (2017) to assess the effect of the implementation of the Ecophyto plan on water quality, or the international study by Schreiner et al. (2016) comparing river contamination levels in 4 countries (France, Germany, the Netherlands and the USA) based on monitoring data. Models can also be used to analyse relationships between mitigation measures and reduction trends in pollution (Chow et al. 2023a). More generally, models developed to describe PPP dissipation in the different environmental compartments and at various spatial scales (Leenhardt et al., 2023) may help to: 1) better predict the dissipation of PPPs in the environment and thus the exposure of non-target ecosystems both spatially and temporally, 2) identify and gauge the contribution of the different sources of contamination, 3) better interpret observed contaminations, 4) define temporal sampling strategies by considering several environmental compartments and identify relevant compounds to be monitored, 5) spatially extrapolate pesticide contamination from monitoring programs (Fabre et al., 2023), or 6) predict potential contaminations from the cultures,

environment properties, sales and/or application rates (Pistocchi et al. 2009; Maggi et al. 2019; Tang et al. 2021).

In addition to per-compartment analysis, work is needed to acquire and interpret contamination data throughout the land-to-sea continuum at permanent sites/observatories in order to gain deeper insight into the temporal dynamics of PPP inputs, and fate and transfers within the environment.

Conclusion

This paper built on the scientific literature and available data to highlight and illustrate widespread contamination by agricultural organic PPPs of all French environmental compartments: agricultural soils, continental and marine surface waters, and atmospheric air. Among the substances most frequently reported at high concentration levels in at least one of these compartments over the 2010–2021 period, we listed 15 herbicides, 9 fungicides, 5 insecticides, and 4 transformation products. Some compounds are found in all compartments while others tend to be found in a specific environmental compartment. However, it is difficult to establish a representative picture of PPP contamination of the environment in France, as the list of compounds investigated was not the same in all studies, compartments and monitoring periods. The spatial variability of the concentrations depends on the distance to the treated area, on the properties of each individual PPP, and on the environmental compartment considered. There are temporal evolutions in contaminant concentrations that are observable at crop-cycle scale (in relation to treatment period) and at pluriannual scale (in relation to land-use change of the introduction of bans). Generally speaking, the literature shows that contamination of water by the PPPs which were selected in this study (Table 1) is tending to decrease in line with the gradual reduction in use imposed by regulations (limiting or banning use), but the

contamination pattern in other environments is harder to establish. To improve the quality of monitoring efforts, new strategies have been implemented to enable more integrative sampling or analyses that can detect and quantify a wider range of substances, including transformation products.

This paper also identified certain gaps that need to be addressed, such as the lack of data on transformation products or on certain regions (French overseas territories) that are not properly covered by monitoring campaigns (with the exception of the chlordecone insecticide). We also noted a lack of approaches addressing the soil–air–water continuum, which are nevertheless an important way forward to better understand the fate of PPPs in the environment and enable a more comprehensive assessment of their environmental impacts.

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Declaration

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Competing interests: Since 2022, Stéphane Pesce has held the position of Vice-Chairman of the evertéa Foundation, which is chaired since 2013 by Philippe Garrigues, Editor-in-Chief of the Environmental Science and Pollution Research journal. These functions of Vice-Chairman

and Chairman are performed on a voluntary basis with no compensation of any kind. He is co-author of this article as part of his role as scientific leader of the collective scientific assessment of the effects of plant protection products on biodiversity and ecosystem services along the land–sea continuum in France and French overseas territories on which this work is based.

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Table 1 Selection of PPPs based on the maximum concentration levels recorded in France in at least one environmental compartment across all the studies considered. The corresponding concentration ranges are given for each compartment.

			maximum concentration levels in environmental matrices			
substance	**family**	**year of ban (France)**	**soil**	**freshwater**	**marine water**	**air**
azoxystrobin	fungicide	-				
boscalid	fungicide	-				
chlorothalonil	fungicide	2020				
epoxiconazole	fungicide	2019				
fenpropidin	fungicide	-				
folpet	fungicide	-				
prochloraz	fungicide	2022				
spiroxamine	fungicide	-				
tebuconazole	fungicide	-				
acetochlor	herbicide	2013				
alachlor	herbicide	2008				
atrazine	herbicide	2003				
chlortoluron	herbicide	-				
diflufenican	herbicide	-				
diuron	herbicide	2008				
glyphosate	herbicide	-				
isoproturon	herbicide	2017				
metolachlor	herbicide	2004 (except for s-metolachlor)				
pendimethalin	herbicide	-				
prosulfocarb	herbicide	-				
simazine	herbicide	2003				
terbuthylazine	herbicide	2004 (with some exemptions)				
terbutryn	herbicide	2003				
triallate	herbicide	-				
AMPA	herbicide TP	(TP)				
atrazine deisopropyl (DIA)	herbicide TP	(TP)				
atrazine desethyl (DEA)	herbicide TP	(TP)				
DCPMU	herbicide TP	(TP)				
chlordecone	insecticide	1993				
chlorpyrifos ethyl	insecticide	2020				
chlorpyrifos methyl	insecticide	2022				
imidacloprid	insecticide	2018 (with some exemptions)				
lindane	insecticide	1998				

concentration ranges in all matrices				
	not recorded	not recorded	not recorded	not recorded
	C <1 $ng.g^{-1}$	C <1 $ng.L^{-1}$	C <1 $ng.L^{-1}$	C <0.1 $ng.m^{-3}$
	1 < C < 10 $ng.g^{-1}$	1 < C < 10 $ng.L^{-1}$	1 < C < 50 $ng.L^{-1}$	0.1 < C < 1 $ng.m^{-3}$
	10 < C < 100 $ng.g^{-1}$	10 < C < 100 $ng.L^{-1}$	50 < C < 200 $ng.L^{-1}$	1 < C < 10 $ng.m^{-3}$
	100 < C < 1000 $ng.g^{-1}$	100 < C < 1000 $ng.L^{-1}$	200 < C < 500 $ng.L^{-1}$	10 < C < 100 $ng.m^{-3}$
	1000 < C < 10000 $ng.g^{-1}$	C > 1000 $ng.L^{-1}$	C > 500 $ng.L^{-1}$	C > 100 $ng.m^{-3}$
	C> 10000 $ng.g^{-1}$			

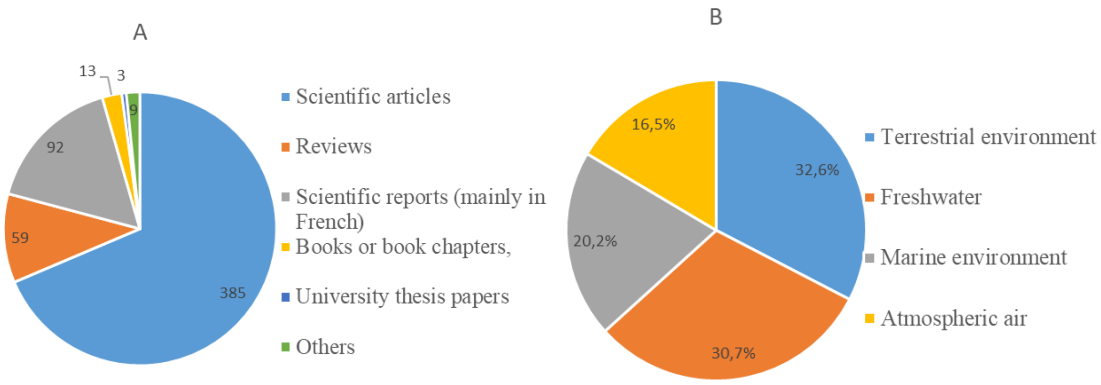

Figure 1 distribution of the 561 selected references of the corpus by (A) document type or (B) environmental compartments

SUPPLEMENTARY DATA

Characterizing environmental contamination by plant protection products along the land-to-sea continuum: a focus on France and French overseas territories.

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S1. Main physicochemical properties of the 33 selected PPPs (see Table 1)

PPP		physicochemical properrties (from PPDB, 2023 may)								
substance	**family**	**log P**	**Kd**	**Koc**	**water solubility - mg.L^{-1}**	**DT50 soil (typical) - day**	**DT50 water - day**	**DT50 (sediment) - day**	**H - Pa m^3 mol^{-1}**	**DT50 air -hr**
acetochlor	herbicide	4.14	3.21	156	282	14	40.5	19.7	2,1 X 10^{-03}	2.6
alachlor	herbicide	3.09	16.5	335	240	14	na	2	3,20 X 10^{-03}	2.8
AMPA	herbicide TP	-	-	-	-	-	-	-	-	-
atrazine	herbicide	2.7	3.2	100	35	75	na	80	1,50 X 10^{-04}	4.7
atrazine deisopropyl (DIA)	herbicide TP	1.51	-	110	-	45	-	-	-	-
atrazine desethyl (DEA)	herbicide TP	1.15	-	1310	-	-	-	-	-	-
azoxystrobin	fungicide	2.5	8.93	589	6.7	78	6.1	205	7,40 X 10^{-09}	
boscalid	fungicide	2.96	12.6	772	4.6	484.4	5	545	5,18 X 10^{-05}	142
chlordecone	insecticide	4.5	-	2500	3	450	stable	stable	2,53 X 10^{-03}	-
chlorothalonil	fungicide	2.94	42.99	2632	0.81	3.53	0.82	0.57	2.50 X 10^{-02}	-
chlorpyrifos ethyl	insecticide	4.7	126.6	5509	1.05	386	5	36.5	0.478	-
chlorpyrifos methyl	insecticide	4	44.9	4645	2.74	12	2.9	14	0,235	2.1
chlortoluron	herbicide	2.5	1.3	147	76	33.5	44.4	308.3	9,07 X 10^{-07}	-
DCPMU	herbicide TP	-	9.55	928	-	127	-	-	-	-
diflufenican	herbicide	4.2	134.3	5504	0.05	94.5	na	175	1,18 X 10^{-02}	79
diuron	herbicide	2.87	12.8	680	35.6	146.6	8.8	48	2,00 X 10^{-06}	12
epoxiconazole	fungicide	3.3	12.2	894	7.1	353.5	1000	103.6	1,649 X 10^{-05}	15
fenpropidin	fungicide	2.9	632	71790	530	90	1.8	34	3.39	-
folpet	fungicide	3.02	-	304	0.8	4.7	0.02	0.02	8,00 X 10^{-03}	61
glyphosate	herbicide	-6.28	209.4	1424	100000	16.1	9.9	20.8	2,10 X 10^{-08}	95
imidacloprid	insecticide	0.57	2.23	225	610	191	30	129	1,7 X 10^{-10}	85
isoproturon	herbicide	2.5	2.83	122	70.2	12	12	40	1,46 X 10^{-05}	4.7
lindane	insecticide	3.5	15.9	1270	8.52	980	21	394	1,483 X 10^{-06}	224
metolachlor	herbicide	3.4	0.67	120	530	90	88	365	2,40 X 10^{-03}	3.5
pendimethalin	herbicide	5.4	228	17491	0.33	182	4	16	1,27	12
prochloraz	fungicide	3.5	38	500	26.5	120	2	359	1,64 X 10^{-03}	4.9
prosulfocarb	herbicide	4.48	23.1	1693	13.2	11.9	0.94	214	0,0152	3.9
simazine	herbicide	2.3	15.88	130	5	60	46	33	5,60 X 10^{-05}	7.2
spiroxamine	fungicide	2.89	142.3	14567	405	25	0.8	66.2	3,80 X 10^{-03}	24
tebuconazole	fungicide	3.7	12.69	769	36	63	42.6	365	1,00 X 10^{-05}	62
terbuthylazine	herbicide	3.4	5.1	231	6.6	72	6	70	2,3 X 10^{-03}	13.5
terbutryn	herbicide	3.66	30.7	518	25	74	27	60	1,50 X 10^{-03}	12
triallate	herbicide	4.06	11.7	3034	4.1	82	104	57.4	0,89	3.8