



Occurrence, dispersal, and associated environmental risk assessment of pesticides and their transformation products in small water bodies of Northeastern France

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Abstract

The widespread use of pesticides, specifically plant protection products (PPPs), has led to their transformation products (TPs) being increasingly detected in various environmental compartments, notably surface waters. This study integrates field-detected TPs into an environmental risk assessment of lentic small water bodies (LSWBs). For this purpose, measured environmental concentrations (MECs) of PPPs and TPs in 12 LSBWs, influenced by tributaries under varying agricultural pressures, were collected. Ecotoxicological data from multiple sources were compiled to calculate risk quotients (RQs) and identify potentially harmful PPPs and TPs. Among 86 molecules investigated, 17 PPPs and 30 TPs were detected, representing nearly half of those initially targeted. Ponds exhibited diverse PPP and TP compositions and levels with 12 substances posing high pesticide risk, primarily atrazine-2-hydroxy, MCPA, and metolachlor. Various pond conditions indicated moderate to high risk to aquatic organisms at corresponding MECs. Despite diverse agricultural pressures, only one site was deemed low-risk, highlighting widespread contamination risk due to co-occurring molecules. Given the prevalence of TPs in water bodies, urgent efforts are needed to gather ecotoxicological data on these contaminants to enhance environmental risk assessments. This study provides novel insights into pesticide risks in a less-studied yet common European landscape, focusing on TPs.

Keywords Ponds · Evaluation of hazards · Agrochemicals · Metabolites · Ecotoxicology · Risk assessment

Abbreviations

ERA	Environmental risk assessment
EU	European Union
GS	Grab sampling
LSWB	Lentic small water bodies
MEC	Measured environmental concentration
PNEC	Predicted no-effect concentration
POCIS	Polar organic chemical integrative sampler

PS	Passive sampling
PPP	Plant protection product
RQ	Risk quotient
TP	Transformation product
WFD	Water frame directive

Introduction

In order to maintain crop yields, the current European agricultural system relies on the use of large quantities of pesticides, with sales volumes remaining around 350,000 mt per year (Eurostat; https://doi.org/10.2908/AEI_FM_SALPE_ST09). Under the general heading of pesticides, plant protection products (PPPs) continue to face much debate and questioning around human and environmental health (Mahmood et al. 2016; Kim et al. 2017; Tudi et al. 2021). Despite being initially beneficial to the development of food-producing agriculture and associated with remarkable agricultural yield and production, PPPs are now the subject of controversy (Aktar et al. 2009; Kudsk and Mathiassen 2020; Rumschlag

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et al. 2020). This is particularly true regarding the maintenance of non-degraded and functional ecosystems, which are associated with health benefits.

Globally, the widespread use of PPPs results in their release and detection in varying quantities and proportions across the main environmental compartments: air, soil, and water (Rathore and Nollet 2012; Sharma et al. 2019). In the aquatic compartment, agrochemicals emitted into the environment, either in an undirected or more selective manner, have become a major concern for water quality and the survival of aquatic wildlife. In the meantime, multiple impacts of PPPs on living organisms fauna (Berny 2007; Mamy et al. 2023), flora (Mohr et al. 2007; Wijewardene et al. 2021), and humans (i.e., consumers (Kim et al. 2017)) have been well established for numerous contaminants. Their use has repercussions on the state of biodiversity (McLaughlin and Mineau 1995; Beketov et al. 2013; Pesce et al. 2023), affecting many non-target species and driving a decline in some of them (Van Dijk et al. 2013; Dudley et al. 2017; Brühl and Zaller 2019).

Environmental contaminants often include residual forms of PPPs, known as pesticide degradation or transformation products (TPs), which can arise from both abiotic and biotic degradation processes. Certain authors have warned of the risks posed by TPs, which could add to the toxicity of the precursor PPPs (Somasundaram and Coats, 1991; Barceló, 1993). Additionally, research has predominantly focused on the confirmed or potential effects of TPs from organochlorine or triazine pesticides. The diversity of pesticides used in agriculture has naturally resulted in a multitude of TPs, as each PPP may degrade into several distinct TPs. Despite recent regulatory efforts to restrict certain PPPs, advancements in analytical techniques have enabled the reliable detection of various TPs in environmental matrices (Martínez Vidal et al. 2009; Dufour et al. 2021; Huang et al. 2023), revealing a wide variety of TPs in the environment (Le Cor et al. 2021; Ulrich et al. 2022). By undergoing multiple transformation processes, PPPs degrade into more polar substances, resulting in increased mobility and persistence in the environment, as observed with TPs from atrazine (Belfroid et al. 1998; Fenner et al. 2013). This enhanced polarity complicates analytical detection, as evidenced by TPs such as desphenyl-chloridazon (derived from chloridazon), which can remain prevalent in the environment (Reemtsma et al., 2013). This has led to the widespread detection of these substances in water bodies across many regions worldwide (Hernández et al. 2008; Ulrich et al. 2021; Anagnostopoulou et al. 2022).

The assessment and comparison of the toxicity of TPs in regard to their precursor PPPs are usually conducted on a case-by-case basis, as toxicity appears to be molecule-dependent. In fact, TPs from pesticides can exhibit higher (Belfroid et al. 1998; Sinclair and Boxall 2009; Ji et al.

2020), equivalent, or reduced toxicity (Sinclair and Boxall 2003; Mahler et al. 2021) when compared to their parent molecules. It is crucial to incorporate these PPP-generated products into environmental risk assessments (ERAs). However, these molecules are largely neglected or have no consortium related to them in present-day ERAs (Escher and Fenner 2011; Hensen et al. 2020). Some authors have underlined that this integration is essential for a more accurate estimation of overall pesticide exposure (Mahler et al. 2021) and the associated risk. This positioning seems all the more important considering that TPs may be more abundant in the environment compared to PPPs. This principle of integrating TPs is increasingly being applied by evaluation agencies worldwide, underscoring the need to complete research in this area (European Chemicals Agency (ECHA) and European Food Safety Authority (EFSA et al. 2023).

Among the aquatic ecosystems exposed to pesticides, lentic systems (e.g., ponds and lakes), serve as receptacles for numerous tributaries, which themselves may drain agricultural watersheds where pesticide use is significant. While these water bodies are ecosystems capable of harboring a wide amount of biodiversity (e.g., avifauna, ichthyofauna, amphibians, and vegetation), this fauna and flora will be exposed to multiple contaminants. In order to preserve this biodiversity and assess the potential toxicological pressure on it, it is particularly important to quantify the exposure levels of these systems to contaminants of agricultural origin. Gathering quantitative data on pesticide pollution in lentic systems, while assessing the state of continental water bodies, remains challenging. These systems are disproportionately affected by pesticide contamination, receiving considerably higher inputs compared to larger water bodies (Lorenz et al. 2017).

The EU Water Framework Directive (WFD) aims to safeguard all water bodies by requiring their maintenance, restoration, and achievement of a “good condition” in terms of chemical, physico-chemical, and ecological quality by 2027 (Directive 2000/60/EC). However, the EU’s water and nature-related policies often neglects small lentic aquatic environments, such as ponds, due to their relatively small size (< 50 ha). Consequently, lentic small water bodies (LSWBs) such as ponds are not included within the monitoring networks established by the WFD. This exclusion persists despite the fact that these diminutive water bodies constitute a significant component of many landscapes, both in terms of physical size and visual impact. In fact, in several EU countries (e.g., France, Czech Republic, and Germany), LSBWs, long neglected, constitute the majority of water surface areas (Terasmaa et al. 2019). Furthermore, ponds play a critical role in connecting freshwater habitats, serving as ecological stepping stones that facilitate species movement across different landscapes (Cuenca-Cambronero et al. 2023).

To better understand the pressures impacting small lentic systems, particularly concerning pesticide risks, it is essential to monitor PPPs and TPs that may enter these water bodies. Monitoring should emphasize their persistence across various matrices, including water, sediments, and biota (Slaby et al. 2022). Ponds serve as valuable study sites for TPs because specific processes, such as sorption and sedimentation, along with transformation patterns like microbiological degradation, significantly influence the presence of these compounds within this lentic ecosystem (Ulrich et al. 2018). Furthermore, the monitoring of pesticides in these systems, in the same way as for other surface water (de Souza et al. 2020), as well as monitoring these pesticides' impacts on non-target organisms, requires ongoing scientific research.

These observations underscore the urgent need to better anticipate future pesticide-related risks (Schäfer 2019). Achieving this requires empirical data to effectively assess the dangers posed by PPPs and TPs. In the scope of the aforementioned WFD, certain pesticides have been classified as requiring increased monitoring due to their hazard potential. The case of TPs is more complex; EU legislation mandates consideration of a TP only if it forms in significant concentrations (above 10% of the parent compound; Guidance Document on Aquatic Ecotoxicology in the context of the Directive 91/414/EEC, GD SANCO 221/200). If there is suspicion of significant similarity in ecotoxic activity with the parent compound, a TP could be considered ecotoxicologically relevant, whatever the degree of transformation (in %) (Sect. 10.2.2; EFSA Panel on Plant Protection Products and their Residues (PPR), 2013). This would require its inclusion in ecological risk assessments (ERAs).

In order to assess the risks posed by contaminants, several studies (Bouzas-Monroy et al. 2022; Casillas et al. 2022; Peris et al. 2022; Khezami et al. 2024) have followed the EU recommendations and risk assessment methodology for aquatic organisms elaborated in the EU-specific guidance on Plant Protection Products and their Residues (EFSA, 2013). This methodology involves deriving a risk quotient (RQ) by comparing measured environmental concentrations (MEC) with predicted no-effect concentrations ($PNEC$). In fact, it is assumed that to obtain a realistic idea of the risk posed by these substances, it is essential to compare the realistic level of exposure to these substances (exposition) and their intra-shell toxicity (hazard). The first step involves defining contaminant concentrations (PPPs and TPs) that may be found in the aquatic environment (Postigo and Barceló, 2015; Rousis et al. 2017; Herrero-Hernández et al. 2020; Le Cor et al. 2021; Huang et al. 2023). Next, it is necessary to gather knowledge and data regarding the ecotoxicity of the quantified molecules.

For a risk assessment to be relevant, it is essential that the (eco)toxicity data for PPPs and TPs are accurate and

verified. Within the EU, the Klimisch method (Klimisch et al. 1997) is a well-established approach method for evaluating ecotoxicological data, demonstrating its effectiveness across various environments and types of contaminants (Burns and Davies 2021; Sun et al. 2022). More recently, a new methodology was proposed by Moermond et al. (2016): the Criteria for Reporting and Evaluating ecotoxicity Data (CRED) methodology. The CRED method involves the use of reliable and relevant information when collecting data for risk assessment (Moermond et al. 2017). Both methods are based on a scoring system, whereby the rating of a datum enables it to be discarded or used when carrying out a risk assessment (Kase et al. 2016). However, transparency in data quality assessments for derived $PNEC$ values is often lacking in the scientific literature (Lahr et al. 2023). Risk assessments of PPPs in the European Commission No 1107/2009 framework have shortcomings with regard to the issue of TPs. Therefore, within the scope of EU legislation, it is essential to generate ecotoxicological data to determine whether a particular TP should be considered or not as a potentially harmful molecule.

In this context, the aim of this study is threefold: (1) to characterize the contamination status of 12 lentic aquatic ecosystems (i.e., ponds) supplied by streams covering a wide range of agricultural pressures in their watershed (i.e., from nearly entirely forested to nearly entirely agricultural), and the content of PPPs and TPs; (2) to search for, verify, and gather ecotoxicity data for the substances found in these environments (assigning them a score); and (3) to carry out a complete and relevant ERA for the aquatic fauna associated with these ecosystems. This study provides exclusive data within a land–water environment by incorporating poorly-studied molecules, while conducting a critical risk assessment.

Materials and methods

Study site

All sites involved in this study were fishponds located on headwater streams in northeastern France. A longstanding collaboration with fish farmers and farmers who operate the ponds and surrounding fields, developed within the framework of previous research (Gaillard et al. 2016a, b; Slaby et al. 2022), has provided in-depth knowledge of these ecosystems, particularly regarding the composition of their watersheds and the agricultural and fish farming activities carried out in the ponds and their watersheds in the region. The watersheds and the 12 studied ponds are distributed as described in Fig. 1 (GPS coordinates of ponds and the composition of their respective catchments are given in Table S1. A and B of the Supplementary Material (SM)).

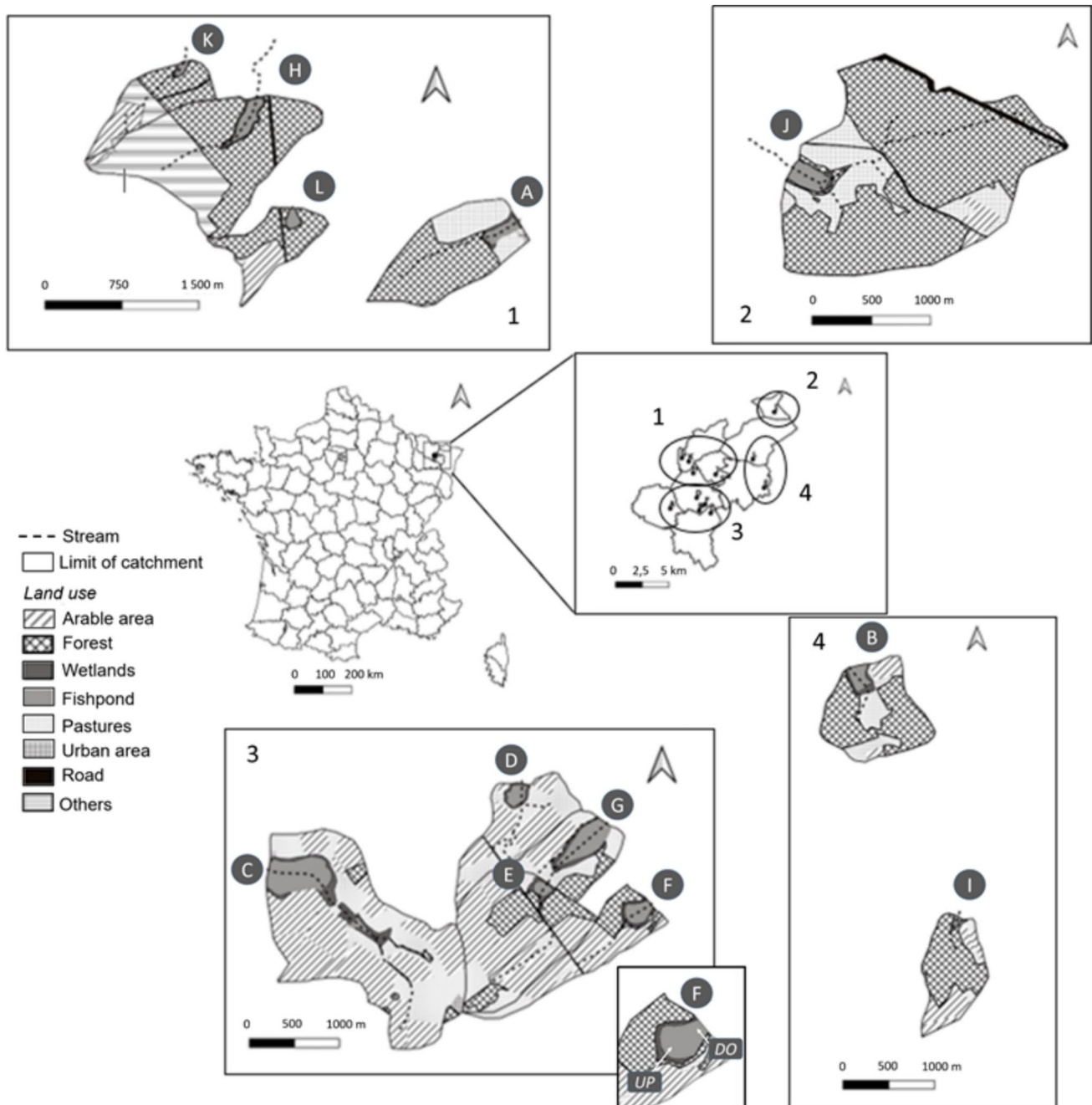


Fig. 1 Map of the overall study area with the 12 ponds studied. The ponds are denoted by letters A to L (map generated via QGIS v.3.18, Zürich). The inset map of pond F includes indications of upstream (UP) and downstream (DO) areas

The determination of the surface areas and tracing of the watersheds and their associated composition were performed using QGIS software (v.3.18.3 with GRASS 7.8.5, data and background map from DataGrandEst, data from BD TOPO@IGN for streams). The ponds, reliant on the position of their watersheds, lie along an agricultural gradient representative of a wide range of agricultural practices (conventional, sustainable, organic, or zero-pesticide) commonly applied in

the study area. In accordance with environmental requirements, all studied ponds adjacent to agricultural plots are surrounded by a grass buffer strip at least 5-m wide (serving as a non-treatment zone). The ponds receive water through inflows from their tributaries, as well as from water runoff, drainage, and precipitation. All ponds are located within the same geographical region, sharing similar geological characteristics and aquaculture practices, which results in

broadly comparable environmental conditions and management approaches. However, this quasi uniformity does not guarantee comparable contamination levels, which is the primary focus of this study.

Chemical analysis: preparation and measurement of PPP environmental concentrations

Chemicals, standards, and reagents

Individual solutions of analytical standards and internal standards of the studied pesticides (all were of high purity (> 96%), with most > 99% according to the method described by Dufour et al. (2021) were prepared in ACN (100 mg/L), stored at $-18\text{ }^{\circ}\text{C}$ and mixed before analysis to obtain a concentration of $5\text{ }\mu\text{g/L}$. The classification by chemical class of all of these compounds (Table S2. A) and physico-chemical properties only of those detected in the field (Table S2. B) are reported in the SM.

Water grab sampling (GS) and extract preparation

Water samples from the ponds were collected at both upstream (UP) and downstream (DO) locations, providing two representative sampling points per pond, at both the initial (T_0) and final (T_F) time points of the experiment. The study spanned 26 days during the spring season (mid-May to mid-June), resulting in a total of four concentration data points for each pond. Samples were stored in 250 mL amber screw-neck glass bottles, transported in refrigerated containers, and subsequently kept at $-18\text{ }^{\circ}\text{C}$ until chemical analysis. The sampling period was selected based on historical data on pesticide inputs and peak concentrations following runoff, as reported by Le Cor et al. (2021), to capture transient concentration peaks that are critical for environmental risk assessment (ERA). Unlike composite sampling, which may dilute these short-lived spikes, grab sampling provides a precise snapshot of pesticide levels at the time of collection. This contrasts with the passive sampling (PS) approach using polar organic chemicals integrative sampler (POCIS, see 2.2.3), which is designed to integrate contaminant levels over time. The analytical method used for sample analysis followed the protocol outlined in Le Cor et al. (2021).

PS and extract preparation

The integrative passive sampling system named POCIS was employed to provide a complementary, qualitative assessment of the contamination state of ponds in a time-integrated manner. As applied in this study, the passive sampling (PS) does not provide quantitative concentration data but instead qualitatively indicates the presence or absence of target molecules over a 26-day immersion period. This

tool complements the conventional water sampling (i.e., grab sampling) described above by enabling the detection of molecules with different profiles, and is among the sampling methods currently used in the WFD to assess the chemical status of water bodies (Jones et al. 2015). This methodology has been extensively studied and implemented at the French national level, particularly through the work of Mathon et al. (2020), who assessed the applicability of passive integrative samplers to the regulatory monitoring of aquatic environments. Passive samplers were purchased and prepared from AFFINISEP (Le Houlme, France) and were constituted thus: 0.23 g of Oasis HLB sorbent phase between two semi-permeable membranes ($0.2\text{ }\mu\text{m}$) sealed by stainless steel rings. This phase was first spiked with DIA-d5, a Performance Reference Compound (PRC), for which the dissipation during the exposure was utilized to monitor sampling efficiency and adjust theoretical accumulation parameters. Triplicate POCIS, enclosed within deployment canisters, were immersed in each pond for 26 days, from T_0 to T_F , with deployment and retrieval carried out simultaneously across all sites. They were gently exposed 30 cm below the surface in a stainless-steel cage attached to a metal rod embedded in the sediment that was connected by a rope to a fixed position 3 m from the deepest point of the pond. At the end of the experiment, POCIS were rinsed thoroughly with demineralized water, softly dried with a paper towel, wrapped in an aluminum sheet, and stored at $-20\text{ }^{\circ}\text{C}$ until the extraction phase. Later, the accumulative phase was collected in a solid phase extraction cartridge with demineralized water and dried under vacuum for several hours (drying efficiency was mass controlled). Consecutive elutions were carried out with 3 mL of methanol, 3 mL of a methanol-dichloromethane mix (1:1 volume), and 3 mL of dichloromethane at 15 mL/min. A volume of 500 μL of the eluate was aliquoted and mixed with 20 μL of a 100 $\mu\text{g/mL}$ solution of internal standards, and then evaporated under gentle nitrogen flow. Dried residues were dissolved in 500 μL ACN. The final extract was diluted 10 times in acidified ultrapure water (formic acid 0.1%) for proper injection in HPLC–ESI–MS/MS.

Accumulative phases artificially spiked with standards were extracted in each sample series in order to control extraction efficiency and to assess the quantification yields. A clean accumulative phase was also extracted and was considered as a protocol blank in order to control the potential contamination during the experiment. Field blanks (not exposed to pond water) were extracted as described previously to characterize field contamination. All control and field blanks were submitted to the same extraction protocol and remained negative (below the limit of quantification of the analytical method).

Pesticide and TP analysis

The list of PPPs and associated TPs investigated in this study was established upon analysis of the treatments applied to the different watersheds since the 2000s as well as the historic contaminants now banned from use that can still be detected in the environment today. This listing also reports molecules that the EU WFD provides for close monitoring of water quality (such as alachlor, atrazine, chlorpyrifos, isoproturon, and terbutryn) and that are retrievable among the 45 priority substances listed in Annex X of Directive 2000/60/EC. Finally, we integrated “relevant” metabolites according to EU Directive 2020/2184 (which repealed Directive 1998/83/EC), incorporated into French national law, to better address the chemical contamination of French waters. The contaminants were analyzed with HPLC–ESI–MS/MS methods, as described in Le Cor et al. (2021) and Slaby et al. (2022). The list of analytes (analyzed based on internal standards) arranged by chemical class is presented in Table S2.A, and includes a total of 86 substances, with 19 herbicides and 37 of their TPs, 2 fungicides, 10 insecticides and 17 of their TPs, and 1 common TP of the benzamide family. Regardless of the samples or the technique used, the analysis of parent compounds (i.e., PPPs) was systematically included for all TPs. Exceptions included some phytopharmaceuticals for which the analysis of TPs is limited due to the lack of knowledge about them, the difficulty of accessing their analytical standards, or lack of suitable techniques having been developed. PPPs were analyzed together with their main metabolite (except for nine PPPs: boscalid, chlorotoluron, dimethoate, MCPA, omethoate, prosulfocarb, tebuconazole, terbutryn, and thiamethoxam, which required dedicated analytical procedures).

In brief, HPLC–LC20AD (Shimadzu, Marne-la-Vallée, France) coupled with a QTRAP® 5500 system (Sciex, Villebon-sur-Yvette, France) was employed in both positive and negative ionization modes. Quantification was performed using internal standards to ensure accuracy and reliability in detecting and quantifying the analytes (for details, see Table S3.B., C.). These standards account for potential variability in the analytical process and enhance the precision of the measurements. The process was approved according to the French standard NF T90–210 (AFNOR 2018), which aligns with the SANTE guidelines by incorporating European regulatory requirements (EC, 2020). Potential contamination during the analytical procedure was checked by using blank samples comprising internal standard solution in LC–MS quality water in each analytical series. Every ten samples, and at the end of each series, control solution (internal standard solution + analytes in ACN + LC–MS-quality water with 0.1% formic acid) was also used for quality control. Dilution was performed when the concentration exceeded (~ 10%) the highest calibration points in order to reach the calibration

rate. Recoveries were assessed by spiking one natural sample per injection series (shown in Table S3. A). If the recovery was not included between 80 and 120%, the quantified concentration was adjusted. The corresponding limits of detection (LODs) and quantification (LOQs) are provided in Table S3. A, according to the two sampling techniques deployed. LOQ was defined as the smallest tested concentration with an inter-day precision lower than 30% and LOD was obtained by dividing LOQ by 2 (Gaillard et al. 2016a; Le Cor et al. 2021; Slaby et al. 2022). Interpretation of the data was performed with MultiQuant software (v.3.0.1, Sciex, Villebon-sur-Yvette, France). All pesticide concentrations measured in the monitored ponds through grab sampling (GS) constitute the exposure dataset for this study.

Collection and selection of ecotoxic data

In addition to determining exposure (i.e., retrieved environmental concentrations of PPPs and TPs), ecotoxicological data were collected for the quantified molecules to elucidate the potential associated hazard. The approach used involved conducting an extended review of the substances quantified (PPP + TP) supported by the collection of data from various sources. These data were used to derive PNEC for the substances detected in the ponds. The PNEC estimation was calculated by applying the EU methodology and allows for determining the concentration below which an “unacceptable” effect will not occur (European Commission, Directorate General for Health and Food Safety, 2017). PNEC calculation is based on data generated in the laboratory. These data are of the following type: effect-concentration retrieved post-pesticide exposure in the three major trophic levels of a system (such as might be the case with a pond), namely primary producers (algae), primary consumers (invertebrates), and secondary consumers (fish). As far as possible, data are obtained from standard species for algae (*Desmodesmus subspicatus* and *Raphidocelis subcapitata*), invertebrates (*Daphnia magna* and *Ceriodaphnia dubia*), and fish (*Cyprinus carpio*, *Danio rerio*, *Gasterosteus aculeatus*, *Oncorhynchus mykiss*, *Oryzias latipes*, and *Pimephales promelas*).

In short, multiple data sources were used to collect the data: (i) Databases such as (a) AGRITOX (Base de données AGRITOX — data.gouv.fr), (b) ECHA (registration dossiers), (c) ECOTOX (United States Environmental Protection Agency (US EPA), <https://cfpub.epa.gov/ecotox/search.cfm>, Olker et al. 2022), (d) INERIS PSC (chemical substances portal, <https://substances.ineris.fr/fr/>), (e) OECD eChemPortal (<https://www.echemportal.org/echemportal/substance-search>), (f) PPDB (<https://sitem.herts.ac.uk/aeru/ppdb/>, Lewis et al. 2016), and (g) NORMAN Ecotoxicology Database (<https://www.norman-network.com/nds/ecotox/>). Despite the relevance of the consulted databases, some

substances still remained insufficiently studied in terms of ecotoxicology; this was particularly true for TPs. Therefore, other data sources were employed: (ii) EU risk assessment documents from EFSA concerning pesticides, (iii) notification of an active substance under Commission Regulation (EU) 844/2012 (https://eur-lex.europa.eu/eli/reg_impl/2012/844/oj), and (iv) marketing authorizations for PPP-containing active substances of interest from the French Agency for Food, Environmental and Occupational Health & Safety (ANSES), the competent authority for issuing marketing authorizations for PPPs in France since 2015. Finally, data were also extracted from (v) recent peer-reviewed studies that may not have been included in databases (for which updates can be time-consuming) at the time of this work. To ensure coherence, the ecotoxicological data were selected using the decision flowchart depicted in Fig. S1 of the SM, which provides a comprehensive explanation of the selection process. At the end of the process, to clarify the origin and traceability of the data, we created a table summarizing these ecotoxicological data for each of the three major trophic levels mentioned earlier. If obtaining the most recent data required it, the bibliographic reference for the original values was specified.

Before deriving the *PNEC* from the experimental ecotoxicological data, the final key data were assessed following the abovementioned CRED methodology. This methodology involves a scoring system to assess the reliability and relevance of the data, ensuring that only high-quality studies are used in the risk assessment process for robust and transparent results. Reliability focuses on the quality of the study design, including effective concentrations, replication, and the use of control groups. Studies are rated from 1 (well-executed and well-documented) to 4 (significant flaws or insufficient detail). Relevance assesses the study's applicability to the risk assessment, considering factors such as appropriate species, endpoints, and both acute and chronic data, with a similar rating system from 1 (highly relevant) to 4 (limited relevance). Only studies with high reliability and relevance were included in the final assessment. For more details on the scoring criteria, readers can refer to Moermond et al. (2016).

Assessment of the environmental risk to ascertain the ecotoxicological impact

The risk associated with certain pesticides in the aquatic compartment, specifically in surface water, was assessed by calculating a risk quotient (*RQ*), an approach widely used by various authors and recommended by the European Commission. Prior to this, the predicted no-effect concentration (*PNEC*) was derived using a deterministic approach, which employed extrapolation factors, commonly known as safety factors or assessment factors (*AF*).

These factors were defined according to the richness of the toxicity data set available and applied to the smallest effect data reported in multiple data sources (*Technical guidance for deriving environmental quality standards (EQS)*; European Commission 2017). Henceforth, *PNEC* values were calculated from the lowest median effect concentrations or median lethal concentrations (EC_{50} and LC_{50} , acute data) or the lowest no observed effect concentration (*NOEC*, chronic data) found previously for PPPs or TPs (cf. 2.3), and the appropriate *AF* (*AF* applied are listed in Table S4, e.g., a safety factor of 1000 was applied if short-term EC_{50} was used, versus a factor of 10 for a long-term *NOEC*), shown in Eq. (1):

$$PNEC = \frac{\text{Lowest } NOEC, EC_{50}, LC_{50 \text{ species}}}{\text{Assessment factor } (AF)} \quad (1)$$

This factor attempts to compensate for the many uncertainties inherent in the extrapolation from laboratory-generated effect data to effects in natural systems such as ponds (Chapman et al. 1998). Indeed, the concept of *AF* has been implemented to account for variability in sensitivity both within and between species and across different media of exposition.

Then, the *RQ*s for individual compounds were denoted as RQ_i and calculated from the measured concentrations (*MECs*) of the single substance (PPP or TP) in the water samples from each pond, and their predicted no-effect concentration (*PNEC*), using the following Eq. (2):

$$RQ_i = \frac{MEC}{PNEC} \quad (2)$$

In order to provide a comprehensive perspective that considers different scenarios, both RQ_{mean} and RQ_{max} were determined. RQ_{mean} was based on the mean environmental concentrations (*MeanECs*), calculated from the average of measurements taken at two sampling points (UP and DO) at T_0 and T_F ($n = 4$). In contrast, RQ_{max} was based on the maximum environmental concentrations (*Max-ECs*) measured for each substance in each pond during the study period. This allowed for the consideration of two scenarios: the worst-case and the basic/mean scenario. Then, a commonly used risk-ranking criterion was applied according to the values of *RQ* (the risk posed by a substance was determined), in which $RQ < 0.01$ represents no risk to the environment considered, $0.01 < RQ < 0.1$ indicates low/minimal risk, $0.1 < RQ < 1$ indicates moderate/medium risk, and $RQ > 1$ indicates high risk (Hernando et al. 2006). The ERA was initially conducted on a global scale, incorporating all ponds and considering the quantified maximum values within the pond gradient.

Afterward, to complement the latter analyses, an *RQ* for the mixture specific to each pond was calculated as the

sum of all RQ_i at the pond considered (all PPPs or TPs, which is denoted as i), following Eq. (3):

$$RQ_{\text{mix}} = \sum_{i=1}^{n(\text{PPP})} RQ_i \quad (3)$$

This approach conveys the increased risk that could be caused by the simultaneous presence of contaminants in the ponds and is based on an additive model, specifically on the assumption of a Concentration Addition (CA) model (Backhaus et al. 2000; Backhaus and Faust 2012; Cedergreen 2014). This additive model enables the assessment of potential ecotoxicological risks arising from the co-occurrence of various pesticides in a specific location. However, it has some limitations, as it does not account for unpredictable synergistic or antagonistic effects. According to this approach, $RQ_{\text{mix}} < 1$ indicates no or low risk; RQ values between 1 and 10 indicate moderate risk; and $RQ > 10$ indicates high environmental risk. When $RQ_{\text{mix}} > 1$, then either one of the constituents of the mixture has exceeded its *PNEC* (it is therefore likely to have an effect on at least one species), or none of the constituents have exceeded its *PNEC*, but it is instead the effect of the mixture (according to the concept of addition of concentrations) that is likely to affect the most fragile species in the ecosystem.

Moreover, to accurately determine the relative contribution in toxicity of each substance among the mixture, we tested an alternative approach to the “toxic units” concept (dating from Sprague and Ramsay 1965) proposed by Dietrich et al. 2022. This approach allows for elucidating how a substance can contribute to the mixture’s toxicity by comparing its RQ_i to the RQ_{mix} : This is the proportional risk quotient (*PRQ*), shown in Eq. (4):

$$PRQ_i = \frac{RQ_i}{RQ_{\text{mix}}} \quad (4)$$

This calculation allows for pinpointing a risk driver wherein a single substance significantly contributes to the overall risk within the mixture, meaning that the highest RQ_i associated with one active substance accounts for the majority of the RQ for the entire mixture.

Statistical analysis

All statistical analyses were performed with R software v.2023.12.0. For grab samples, it is advisable to exercise caution when the compound is detected at a concentration below the limit of quantification (*LOQ*) (Hecht et al. 2018) to prevent averaging based on a significant number of unquantified values. To avoid doing so and facilitate statistical analysis, concentrations below *LOD* were set to 0 (estimated as null), and those between *LOD* and *LOQ* were set to *LOQ*/2 when needed (Gaillard et al. 2016a; Le Cor et al. 2021; Slaby et al.

2022). This data transformation mitigated the impact of zero values while still incorporating low levels in the calculation of the average. The potential connections among pesticide occurrences throughout all the sites were assessed by conducting pairwise correlations through the Spearman’s rank test, setting a significance level of 0.01. Principal component analysis (PCA) was employed to extract valuable insights from the data, allowing for the examination of multivariate correlations among the concentrations of various pesticides. A Kruskal–Wallis test followed by a Dunn post hoc test was conducted to assess the differences in contamination levels among multiple sites (based on rank sums).

Results and discussion

Occurrence and levels of PPPs and TPs detected

First, the comparison of detection is conducted, achievable by both passive sampling (PS) and grab sampling (GS) of pond waters. This comparison offers a qualitative assessment of the molecules detected by each method over the study period. Next, the focus is shifted to quantification, which can only be carried out rigorously and accurately by GS, as it is the only method allowing for the determination of actual concentrations of PPPs and TPs in the ponds. Indeed, POCIS is a useful screening tool for pesticides, but quantitative results require more defined water-flow conditions (Berho et al. 2013). Finally, a comprehensive view of both the presence and concentration of PPPs and TPs across the study sites is provided.

Qualitative approach: capacity and efficiency of contaminant detection by grab (GS) and passive sampling (PS)

The aim here is to compare the substances detected by PS which provide an integrative assessment over a 26-day period, with those identified through GS conducted at the beginning (T_0) and end (T_F) of the same period. The objective is to assess the relative efficiency of both methodologies and explore potential differences in the profiles of PPPs and TPs detected by each approach. Out of the 32 PPPs and 54 TPs analyzed in the water, 17 PPPs and 30 TPs were detected at least once in the ponds, accounting for 53% of the PPPs and 56% of the TPs studied, or more than one contaminant out of two in each category. In terms of sampling methods, the efficiency was well-balanced between GS and PS, each detecting 38 molecules—with 29 being common—of a total of 47 molecules (see Fig. S2 and Table S5. A, B for details of distribution). Among these 29 molecules detected in common by GS and PS, 10 were PPPs and 19 were TPs (Table S5. A). The chloroacetanilide and triazine

class, affiliated with herbicides, were the most represented among the contaminants found in the various water bodies. Respectively, there were 14 and 9 representatives of these families among the total of 38 molecules detected by both GS and PS. As regards the range of analytically identified contaminants, it is noteworthy that 54.7% of the 86 molecules initially targeted were detected.

The use of PS allowed the detection of 6 PPPs and 3 TPs that had not been detected by GS (atrazine, desethyl-atrazine (DEA), chloridazon, fipronil, fipronil sulfide, isoproturon, isoproturon-monodemethyl, metazachlor, and terbutometon). Conversely, the GS led to the detection of 1 PPP (prosulfo-carb) and 8 TPs (TCP = chlorpyrifos TP; deethylhydroxy-atrazine (DEA-OH) + deisopropyl-hydroxy-atrazine (DIA-OH) + desethyl-desisopropyl atrazine (DEDIA) = atrazine TPs; acetochlor-OXA; dimethenamid-OXA; metolachlor-NOA + CGA-357704 = metolachlor TPs) that had not been detected by PS. Using the PS method alone resulted in missing, on average, 18% of the molecules detected when combining both methods (PS + GS).

Although both PS and GS methods had the capacity to detect 38 out of the 86 molecules analyzed within all the water and POCIS samples studied (12 combined ponds), implementing POCIS in the ponds led to the detection of more contaminants than did the GS method. It was in pond H (the least-contaminated pond, with a total of 10 contaminants detected by PS + GS) that the difference was most pronounced between GS and PS, with 4 and 9 contaminants detected, respectively. In the two most-contaminated ponds, this difference was smaller: In pond C, 26 contaminants were detected by PS versus 20 by GS, while in pond D, both methods detected the same number of contaminants ($n=24$). On average, across the 12 ponds studied, using GS alone resulted in missing 39% of the molecules detected by PS + GS. Moreover, an average of 23 contaminants (ranging from 10 to 32) were detected in the ponds by PS + GS. GS detected an average of 15 (ranging from 4 to 24), while PS detected an average of 19 (ranging from 9 to 26) (Table S5. A).

In light of this study, it was observed that both PS and GS methods were capable of detecting a wide range of contaminants overall (38 PPPs or TPs whose presence was identified by both methods). However, during specific assessments aimed at evaluating the contamination of a single site, PS detected more molecules. This higher capacity of PS to detect contaminants in water bodies could result either from its ability to detect contaminants present at concentrations undetectable by GS, or from the use of PS preventing the overlooking of certain contaminants whose concentrations in the water column are more variable and were not present in sufficiently high concentrations during GS.

Thus, PS serves as a valuable complement to GS in assessing the contamination status of LSWBs. It reveals the

presence of contaminants that may not be detected by GS, either individually or in mixtures, which are likely to contribute to the toxic pressure exerted on organisms inhabiting ponds. However, while this method provides information on the number of contaminants present in the environment that potentially demonstrate toxicity, it is limited in its ability to assess contaminant concentrations in the water, as utilized in this study. Indeed, while quantitative measurement through passive sampling is possible, it requires the prior determination of specific sampling rates (R_s) for various contaminants to be feasible (Illatou et al. 2022; Tarábek et al. 2023). However, data on R_s for transformation products are scarce, limiting the applicability of this approach in the present study.

Quantitative approach: concentrations assessed with grab sampling

Grab sampling uses instantaneous information on the contamination status of a water sample to tally target molecules. The method used here allowed for the detection of 9 exclusive molecules in the water samples: 3,5,6-Trichloro-2-pyridinol (TCP), acetochlor-OXA, DEA-OH, DIA-OH, DEDIA, dimethenamid-OXA, s-metolachlor CGA-357704, prosulfocarb, and terbutometon. The data provided by the GS were not only qualitative but also quantitative, providing a dual level of information. The quantification yielded contamination levels in ng/L for the 30 contaminants analyzed by HPLC–ESI–MS/MS. The pesticide concentration data, when detected and quantified, are presented in Table 1. These results indicate that 34.9% of the targeted molecules were successfully quantified in the selected samples.

Within the top 10 most quantified molecules (%FQ), 9 were TPs. The only notable PPP in this list was metolachlor. This observation held true for the top 10 molecules with the highest maximum and mean concentrations. Furthermore, the pesticide retrieved at the highest concentration was MCPA, a PPP from a currently authorized acidic pesticide family, which reached 879.4 ng/L. Nevertheless, it remained very poorly quantified (4.17%), and this value corresponded to an isolated data point related to a specific site: the pond D. MCPA is known to frequently appear in the water matrix (Morton et al. 2020) due to its hydrophilicity and high solubility, with a log P of -0.81 (see Table S2. B for details on the physico-chemical properties of the quantified pesticides).

Such concentrations in pond D could thus have resulted from drained fields by recent transfer, but also from remobilization from the anoxic sediments of the pond, given the absence of MCPA degradation processes under anoxic conditions (Santé Canada 2006).

The most prominent molecules, both in terms of mean concentrations and quantification frequency, were from the chloroacetanilide class. The widespread use of these herbicides could explain their ubiquity, which raises concerns

Table 1 Mean, maximum, and minimum environmental concentrations in ng/L of the PPPs and TP quantified ($n=30$) by grab sampling (GS) of pond water (mean from upstream (UP) and downstream (DO), at initial (T_0) and final (T_F) time), along with their frequency of quantification (%FQ). Quantifications were performed on 4 measurements (T_0 , T_F , UP, DO) across the 12 ponds ($n=48$)

Chemical class	Molecule name	Concentration (ng/L)			Number of quantification	Frequency of quantification (%)	Corresponding LOQ	
		Min	Max	Mean \pm SEM				
<i>Anilide herbicides</i>	Flufenacet✓	9.12	22.79	1.35 \pm 0.65	4	8.33	5.0	
	Flufenacet ESA ¹ ✓	14.35	695.30	122.41 \pm 29.42	28	58.33	5.0	
	Flufenacet OXA ¹ ✓	13.89	337.00	50.04 \pm 13.06	23	47.92	10.0	
<i>Anilide fungicides</i>	Boscalid✓	5.23	9.32	1.75 \pm 0.49	9	18.75	5.0	
<i>Conazoles</i>	Tebuconazole✓	13.50	20.72	1.56 \pm 0.71	4	8.33	5.0	
<i>Chloroacetanilides</i>	Dimethachlor ESA ¹ ✓	5.15	21.19	5.67 \pm 0.92	25	52.08	5.0	
	Dimethenamid✗	11.04	47.97	4.20 \pm 1.74	6	12.50	10.0	
	Dimethenamid ESA ¹ ✗	7.07	38.64	11.13 \pm 1.69	28	58.33	5.0	
	Dimethenamid OXA ¹ ✗	21.22	41.04	9.03 \pm 1.78	12	25.00	20.0	
	Metazachlor ESA ¹ ✓	22.26	157.46	51.48 \pm 6.84	34	70.83	20.0	
	Metazachlor OXA ¹ ✓	26.57	215.88	63.23 \pm 8.33	36	75.00	20.0	
	Metolachlor✗	6.05	57.05	9.83 \pm 1.83	21	43.75	5.0	
	CGA 357704 ¹ ✗	18.85	19.65	3.30 \pm 0.79	2	4.17	20.0	
	Metolachlor ESA ¹ ✗	5.55	153.61	35.27 \pm 6.79	30	62.50	5.0	
	Metolachlor OXA ¹ ✗	25.24	63.91	18.08 \pm 3.06	20	41.67	20.0	
	S-metolachlor NOA ¹ ✗	50.01	102.53	21.55 \pm 4.57	9	18.75	50.0	
	<i>Organophosphorus</i>	TCP ¹ ✗	23.36	23.36	0.49 \pm 0.49	1	2.08	20.0
	<i>Phenoxy</i>	MCPA✓	11.27	879.40	18.56 \pm 18.32	2	4.17	10.0
<i>Pyridazinone</i>	Me-DPC ¹ ✗	20.36	38.12	2.01 \pm 1.17	3	6.25	10.0	
<i>Pyridylmethylamine</i>	Imidacloprid✗	14.53	18.60	1.11 \pm 0.58	3	6.25	10.0	
<i>Thiocarbamates</i>	Prosulfocarb✓	5.37	12.20	0.53 \pm 0.32	3	6.25	5.0	
<i>Triazines</i>	Atrazine-2-hydroxy ¹ ✗	10.93	156.91	31.60 \pm 5.15	36	75	10.0	
	DEA-OH ¹ ✗	10.28	18.53	1.37 \pm 0.59	4	8.33	10.0	
	DIA ¹ ✗	11.59	11.59	0.24 \pm 0.24	1	2.08	10.0	
	DIA-OH ¹ ✗	24.02	113.04	38.57 \pm 4.25	37	77.08	20.0	
	Terbutylazine✓	22.61	48.35	3.76 \pm 1.56	4	8.33	5.0	
	Terbutylazine desethyl ¹ ✓	4.51	84.50	8.07 \pm 3.07	14	29.17	5.0	
	Terbutylazine-2-hydroxy ¹ ✓	45.29	61.76	4.72 \pm 2.19	4	8.33	5.0	
<i>Ureas</i>	Chlorotoluron✓	14.65	23.70	1.60 \pm 0.70	4	8.33	5.0	

All data calculated considering values $< LOD$ as zero and values $LOD < x < LOQ$ as $LOQ/2$. The %FQ of molecules is calculated if $LOD < x < LOQ$

ESA, ethane sulfonic acid; OXA, oxalinic acid; TCP: trichloropyridinol; DEA-OH: deethylhydroxyatrazine, DIA: deisopropylatrazine; DIA-OH: deisopropyl-hydroxy-atrazine; MCPA: (4-chloro-2-methylphenoxy) acetic acid; Me-DPC, methyl-desphenyl-chloridazon; S-metolachlor NOA, N-(2-Ethyl-6-methylphenyl)-N-(2-sulfoacetyl)-L-alanine

¹Transformation products (TPs); ✓ authorized; ✗ banned; SEM standard error of the mean. Classification according to ECHA chemical class labeling, with alphabetical order within each class. Italicized terms indicate the chemical classes of pesticides. Number of quantifications only for strictly $> LOQ$

not only about their environmental persistence (Mohanty and Jena 2019) but also about the potential ecotoxic risks associated with their occurrence. These herbicides are the ones predominantly sold (BNV-D Grand Est 2021, in kg) and used on the scale of the studied region—Grand Est, France. This region ranks first in cereal and oilseed

production, as well as in the amount of area dedicated to cereals, spring barley, and rapeseed. The pesticides applied to these main crops grown include molecules such as metolachlor, metazachlor, and dimethenamid. Additionally, pre-emergence herbicides, such as flufenacet, and those typically used for overall crop weeding,

like prosulfocarb, are also noteworthy. Concerning TPs of these herbicides, the oxalinic and ethanesulfonic acids derived from flufenacet, metazachlor, and metolachlor ranged from 50 to 700 ng/L.

For comparison, the environmental quality standard set by the EU for pesticides is 100 ng/L per individual substance, commonly referred to as the “quality limit.” Thus, water containing parent compounds or their derived TPs at concentrations exceeding 100 ng/L is considered “non-compliant” according to this standard. The default threshold of 100 ng/L for individual pesticides has not been demonstrated to provide adequate protection for human health and groundwater ecosystems. This threshold can often exceed the established limits for many herbicides and fungicides listed as priority substances in Annex I of Directive 2008/105/EC. For this very reason, the European Parliament recently implemented a threshold limit of 500 ng/L for the combined total of active substances in pesticides, encompassing their respective transformation and reaction products, within a proposal (Report EP—A9-0238/2023).

Of the two fungicides assessed in this study, boscalid was quantified (35%) more frequently compared to tebuconazole (12.5%). The former is a well-known succinate dehydrogenase inhibitor (SDHI) fungicide from the carboxamide family. This broad-spectrum fungicide works by blocking the ubiquinone-binding sites in mitochondrial complex II, thus inhibiting fungal respiration and affecting the Krebs cycle (Avenot and Michailides 2007). Furthermore, it is known to affect processes related to antioxidant and detoxification systems in various aquatic organisms (Qian et al. 2018, 2021; Aksakal 2020; Wang et al. 2020), which could foreshadow an ecotoxicological impact.

The most-quantified molecule overall was atrazine-2-hydroxy, present in 11 out of 12 of the studied ponds. Similarly, a report from the United States Environmental Protection Agency (US EPA) (Ging 2002) states that it ranks among the most frequently detected molecules in lakes in the USA. It is important to mention that atrazine is still authorized for use in the USA, in contrast to France, where it has been banned for 20 years (March 2004). This context likely partly explains why this atrazine metabolite is quantified by the US EPA at much higher average concentrations (410 ng/L) than those observed at our study sites (31 ng/L). In French streams, which are strongly connected to ponds through the hydrographic network and constitute direct sources of pesticides, this atrazine TP was detected in over 86% of water samples (Le Cor et al. 2021) at an average concentration of 21 ng/L, similar to those measured in our ponds. These authors demonstrated that for this pesticide metabolite banned for over 20 years, concentrations in the downstream creek were very close to those measured in the upstream one. Even as these authors highlighted the extensive remediation induced by the pond for numerous contaminants,

they noted that the retention of atrazine-2-hydroxy was the lowest (<20%). This can be explained by the widespread distribution of this atrazine TP across terrestrial and aquatic environments two decades after this herbicide was banned. Consequently, the source of this TP is no longer the agricultural plot but rather various matrices that may have accumulated it, particularly soils and sediments, including the pond itself (Slaby et al. 2022). Concentrations of similar magnitude (72 ng/L) were observed in small streams by Sposito et al. (2018). These authors highlighted that this contaminant was notably correlated with changes in the expression of the brain aromatase gene *cyp19a1b* of *Danio rerio*, a widely recognized indicator of exposure to estrogens, placing fish that might populate these fishponds among the first species impacted.

This ubiquitous contamination by a pesticide widely used in the past and banned over 20 years ago in Europe highlights the repercussions of large-scale anthropogenic practices over space and time. For instance, Slaby et al. (2023) observed in their study conducted on two ponds (corresponding to ponds D and H in the present study) that despite farmers in the watershed of pond H having practiced organic agriculture for 14 years, their pond was not free from contaminants—particularly not from this atrazine metabolite. The present work, aiming to characterize contamination pressure and potential risks for biocenoses across a wider range of ponds, also underscores the importance of recognizing and reporting historical contaminations. Riedo et al. (2021) similarly demonstrated that pesticide residues persist in soils even after 20 years of organic farming, continuing to affect microbial communities. This highlights the enduring impact of past contaminations on ecosystems, even after the cessation of pesticide use.

While atrazine is among the pesticides now banned in France, the present work also highlights the ubiquitous contamination of the studied ecosystems by molecules that are still currently used at the EU scale. For instance, metolachlor was the only molecule detected in all the examined ponds. The “S” form of this herbicide recently underwent a non-renewal of its authorization at both national and EU levels. This was undertaken in light of recommendations from the European Food Safety Authority (EFSA) due to concerns about its potential as an endocrine disruptor. The implementing regulation officially prohibiting S-metolachlor was published in January 2024 (Authority (EFSA et al. 2023a, b; “Implementing regulation—EU—2024/20—EN—EUR-Lex,” 2024). This ban highlights ongoing concerns regarding contamination by metolachlor and its TPs, as both forms produce the same TPs. While these TPs are not as widespread as the parent molecule (Table S5), they are typically found at concentrations much higher than that of metolachlor itself (Table 1). These findings are consistent with recent studies that have identified pesticide residues in nearly all

water samples collected from agricultural areas (Lorenz et al. 2017; Slaby et al. 2022; Ulrich et al. 2022).

The pairwise correlation matrix of concentrations (Fig. 2) helps identify the molecules most likely to be found concomitantly in the ponds, thereby forming possible predominant mixtures of contaminants of interest. Only highly significant correlations (p -value > 0.01) are represented in Fig. 2 (the corresponding cross-correlation table is available in Table

S6 and details are visualized in the network plot in Fig. S3. B.). The triazines seemed to co-occur, indicating commonalities in the way they degrade and persist in the environment (Navarro et al. 2004). The pattern by family was also observable for the TPs of metolachlor, which were, however, dissociated from their parent molecule. This observation nuances the notion that TPs are systematically found in the same locations as their parent compounds. Within this set,

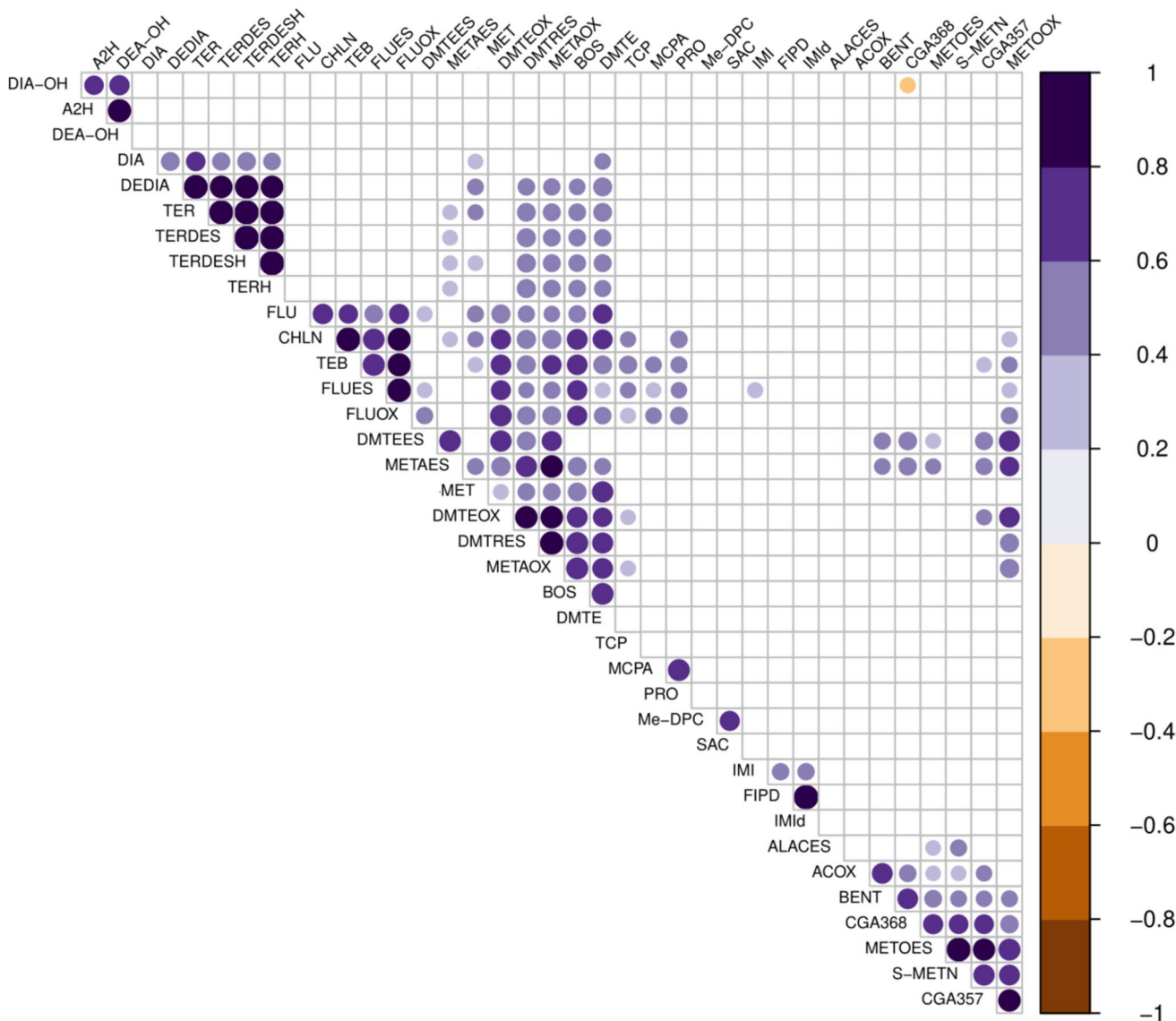


Fig. 2 Pairwise correlations between pesticide concentrations quantified across all ponds (Spearman's Rank test; $\alpha=0.01$). PPPs — BENT, bentazon; BOS, boscalid; CHLN, chlorotoluron; DMTE, dimethenamid; FLU, flufenacet; IMI, imidacloprid; MCPA, 2-methyl-4-chlorophenoxyacetic acid; PRO, prosulfocarb; MET, metolachlor; TEB, tebuconazole; TER, terbuthylazine. TPs — ACOX, acetochlor OXA; ALACES, alachlor-acetochlor ESA; A2H, atrazine-2-hydroxy; CGA357, CGA 357704; CGA368, CGA 368208; DEA-OH, atrazine-desethyl-2-hydroxy; DEDIA, desethyl-deisopropylatrazine; DIA, deisopropylatrazine; DIA-OH, deisopropyl-hydroxy-atrazine;

DMTRES, dimethachlor ESA; DMTEES, dimethenamid ESA; DMTEOX, dimethenamid OXA; FIPD, fipronil desulfanyl; FLUES, flufenacet ESA; FLUOX, flufenacet OXA; IMId, desnitro-imidacloprid; Me-DPC, methyldephenylchloridazon; METAES, metazachlor ESA; METAOX, metazachlor OXA; METOES, metolachlor ESA; METOOX, metolachlor OXA; SAC, saccharin; S-METN, S-metolachlor NOA; TCP, 3,5,6-Trichloro-2-pyridinol; TERDESH, terbuthylazine desethyl; TERDES, terbuthylazine desethyl; TERH, terbuthylazine-2-hydroxy

TPs derived from different molecules were also detected and strongly correlated, as seen, for example, with metazachlor-ESA and dimethenamid-ESA, both ethane sulfonic acid derivatives.

The presence of multiple contaminants should be considered with interest, both for the simultaneous presence of pesticides with similar modes of action, which may exacerbate toxic effects, and for the presence of pesticides with different modes of action, suggesting that the effect may be, in addition to being cumulative, similar or reduced. Indeed, predicting the cumulative effects of such cocktails composed of parent molecules as well as TPs, for which there are numerous gaps in knowledge regarding their toxicity, proves to be particularly complex.

Consequently, PCA was employed to statistically examine the general pattern of pesticide contamination (additional information in SM, Fig. S4). A maximum of 52.4% of the data variance could be explained using four principal components. Overall, each component revealed a widespread contamination scheme, with contributions from several different pesticides, including TPs from different classes, in each case. The major insight revealed by this analysis was the dichotomy between chloroacetanilide and triazines, each contributing to a different dimension, and doing so quite prominently. These observations, at the trend level, do not seem to indicate strictly differential uses between these two herbicide families but rather a behavior in the environment suggesting different persistence or release characteristics.

Pesticide distribution within the ponds

The total number of PPPs and TPs detected in each pond, by PS and/or GS, allows for classifying these ponds from the most contaminated to the least contaminated as

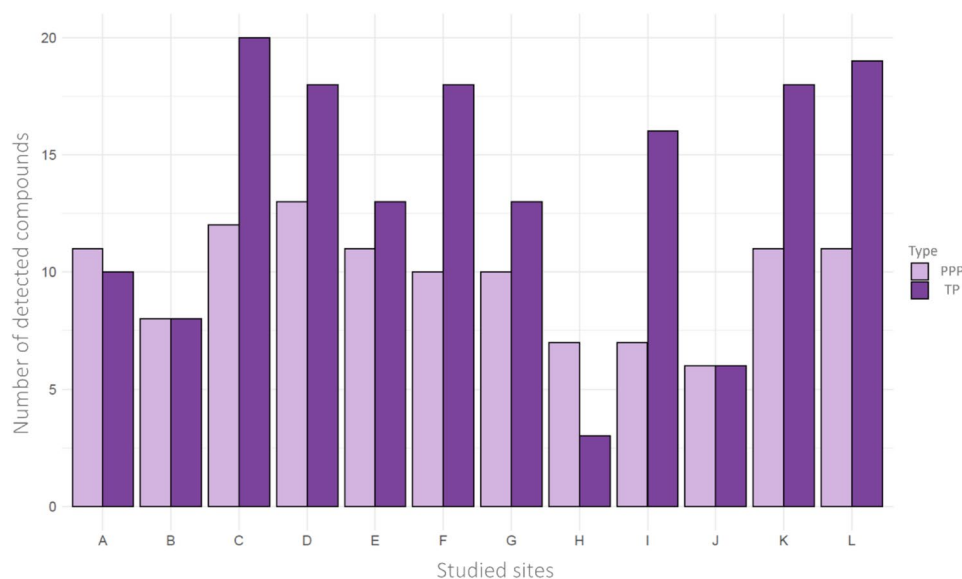
follows: pond C ($n=32$), D ($n=31$), L ($n=30$), K ($n=29$), F ($n=28$), E ($n=24$), I ($n=23$), G ($n=23$), A ($n=21$), B ($n=16$), J ($n=12$), and H ($n=10$). The number of PPPs and TPs detected within the 12 ponds allowed for the observation of different contamination profiles (Fig. 3).

Only pond H (whose watershed is almost exclusively forested; Table S1. B) presented a contamination profile dominated by PPPs (7 PPPs + 3 TPs). The contamination profiles of ponds B and J (whose watersheds are largely non-agricultural) were balanced between PPPs and TPs (6 PPPs + 6 TPs in pond J; 8 PPPs + 8 TPs in pond B). Similarly, the profile of pond A (whose watershed is covered by 23% arable land but is operated under organic farming) showed a contamination profile (PPP/TP ratio) with 11 PPPs + 10 TPs detected.

In the other 8 ponds, where arable lands cover 19 to 55% of the watershed surface (Table S1. B), the number of detected contaminants was higher (from 23 to 32), with a majority being TPs (Fig. 3). The predominance of TPs in the studied water bodies underscores the need to develop analytical methods for their detection in the environment and to systematize the search for these degradation products, for which environmental occurrence data are very scarce.

This lack of data leads to a deficit in knowledge regarding the fate of these contaminants in the environment and within various biotic or abiotic matrices (Slaby et al. 2022), even though they are consistently detected in large numbers when searched for. Moreover, it is challenging to compare the contamination profiles of our sites to other aquatic environments and/or to validate hypotheses that could justify these profiles. For example, the predominance of TPs in the majority of ponds can be explained by the degradation of a single PPP into multiple TPs within a relatively short period, given that PPPs with low DT_{50} are favored by EU legislation. For the four ponds with different contamination profiles

Fig. 3 Pesticide occurrence across the twelve sites: comparison of detected compounds, namely parent compound (plant protection product, PPP) or transformation product (TP)



(majority of TPs or balanced PPP/TP ratio), such profiles could have resulted from the fact that these ponds and their watersheds are not intentionally exposed to pesticides (as they are not operated under conventional agriculture), and the main contamination pathway might be aerial, resulting from direct transfer of PPPs during spraying onto neighboring watersheds (Bish et al. 2021).

The multitude of TPs originating from the same parent compound (such as terbuthylazine or metolachlor), combined with the diversity of parent molecules, raises questions about their potential individual or combined toxicity. To delve further in the process of characterizing the contamination status of the sites, the analysis of contamination levels revealed significant variation depending on the different sites (Fig. 4).

These concentrations are not weighted by the toxicity of the molecules (which will be the subject of the final part

of this manuscript), but they once again lead to the identification of ponds A, B, H, and J as the least contaminated, with median contamination values ranging between 5 and 14 ng/L (0.7 and 1.15 ng/L on the logarithmic scale), while reaching 17 to 37 ng/L (up to 1.57 on the logarithmic scale) in the other 8 ponds. These ponds had accumulated high concentrations, exacerbated by a higher number of contaminants, thus potentially intensifying cocktail effects. The lack of ecotoxicological data regarding these multiple contaminants, which predominantly comprised TPs, is particularly concerning in the context of these water bodies, as they may harbor diverse fauna and flora.

These analyses revealed that pond L, due to its high median concentration of pesticides, differed distinctly from ponds B, E, H, and J (Fig. 4). Pond D, which ranked second in terms of pesticide concentration, had a significantly different profile than J, the least-contaminated pond in the

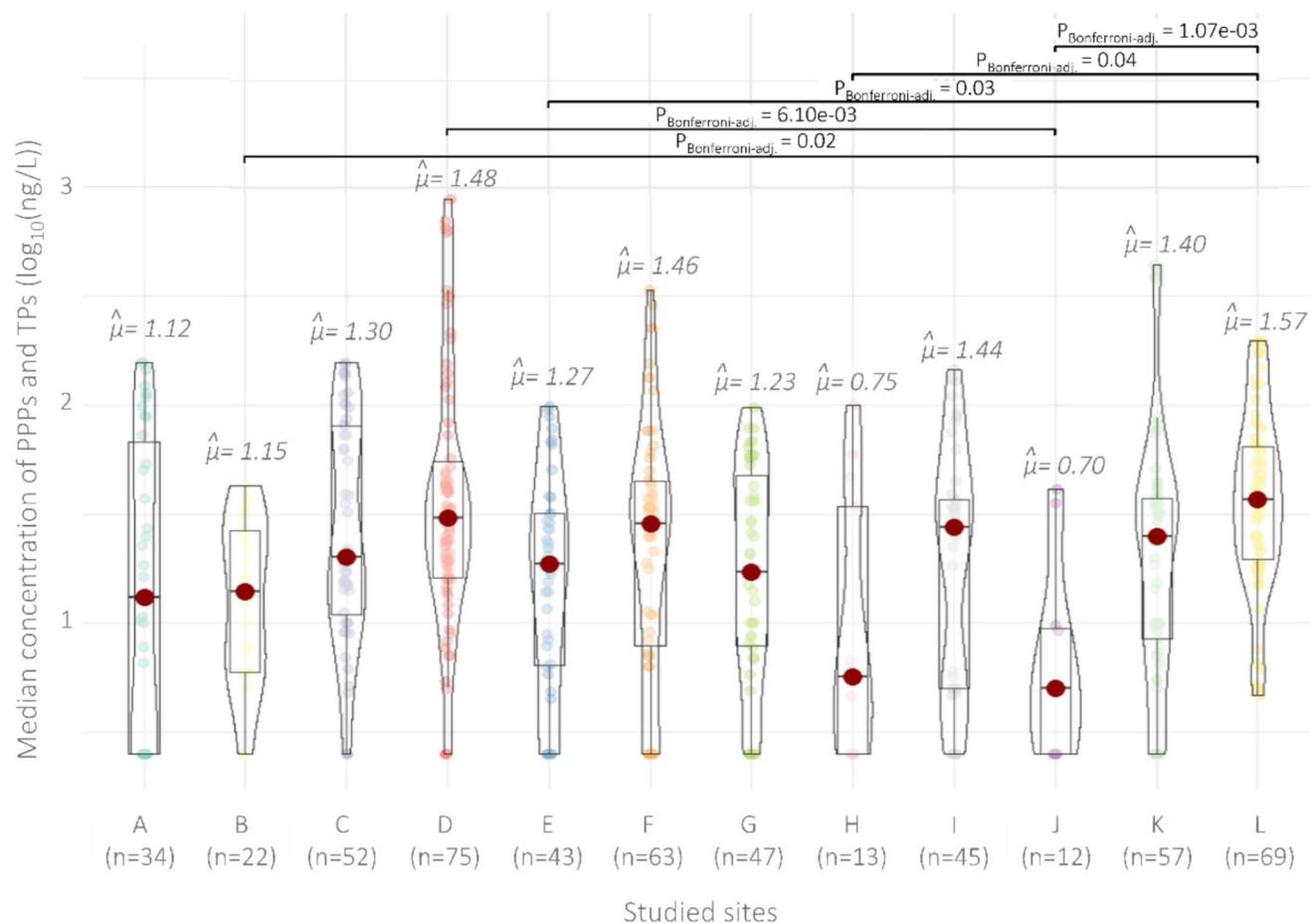


Fig. 4 Median pesticide concentrations within the studied sites. Median concentrations (in ng/L) are log-transformed and represented on a logarithmic scale for better readability. A Kruskal–Wallis test (p -value = 2.7×10^{-7}) was followed by a Dunn post hoc test. The Bonferroni correction was used to obtain an adjusted significance level ($P_{\text{Bonferroni-adj.}}$). Significant differences between rank sums are indicated by bars. Large red circles represent the median concentrations of all plant protection products (PPP) and transformation products (TPs), with the values displayed above the plots. The “ n ” below each pond’s corresponding letter indicates the number of non-zero concentrations measured for each pond and used in median calculations

ated by bars. Large red circles represent the median concentrations of all plant protection products (PPP) and transformation products (TPs), with the values displayed above the plots. The “ n ” below each pond’s corresponding letter indicates the number of non-zero concentrations measured for each pond and used in median calculations

series. This was consistent with the activities carried out in their catchment areas. However, the surrounding land use can vary and depends on other molecules, even in forested areas (Holmes and MacQuarrie 2016), sometimes leading to adverse effects (Tissot et al. 2022).

The integration of ponds within the PCA (Fig. S5) shows, through biplot visualization, that ponds have different patterns when transposed into dimensions 1 and 2, which together explain 43.2% of the analysis. Pond L was primarily defined by the triazine consortium, and pond D was defined more by the chloroacetanilides. The remaining ponds, due to their lower quantity and diversity of pesticides, were less distinguishable from each other.

Environmental risk assessment applied to ponds

Derivation of effect concentrations and PNECs

The ERA was exclusively conducted on the molecules quantified above their limit of quantification. Consequently, 30 molecules were able to be considered, comprising 10 PPPs and 20 TPs, with a comprehensive analysis focused on both groups and special attention given to the toxicity of the TPs. Table S7 provides ecotoxicological data utilized in the following *PNEC* calculations for all PPPs and TPs and across each taxonomic group (S7. A. for algae, S7. B. for invertebrates, and S7. C. for vertebrates). This listing includes organisms that need to be considered in a regulatory manner (e.g., *Daphnia* sp. for invertebrates) but also non-classic/standard species. The subsequent derived *PNEC* are compiled in Table S8, providing a precise overview of the *PNECs* for quantified molecules.

It is important to note that, for some TPs, data were either unavailable (non-reported: NR) or unusable. Here, “unusable” refers to data expressed in databases or literature with an upper limit (for example in the following form: > 100 mg/L) rather than a precise value. The 11 molecules concerned were deethylhydroxyatrazine (DEA-OH), deisopropyl-hydroxy-atrazine (DIA-OH), dimethachlor-ESA, dimethenamid-ESA and OXA, flufenacet-ESA and OXA, metolachlor-ESA, OXA and NOA, and terbuthylazine-desethyl-2-hydroxy. For these molecules, based on the work of Sinclair and Boxall (2003), which concluded a lower toxicity of TPs in 70% of cases, we considered TPs as less toxic than their precursor PPPs. A *PNEC* ten times higher than that of the precursor was then assigned to the TPs.

This choice was made to avoid being perceived as overly protective and can be regarded as reasonable in light of the results of Sinclair and Boxall (2003). Thus, within the scope of this work, a highlighted risk situation is not the result of excessive precaution but rather a field situation requiring particular attention. The decision to consider the toxicity of metabolites as lower than that of their precursor PPPs, due

to the lack or absence of toxicological information on some TPs, was made to avoid being overly conservative and to balance the risk appropriately, aiming for environmental realism. This assumption is deeply ingrained in the assessment of TPs' toxicity, where their ecotoxicity could be inferred from that of the parent compounds (precursor PPPs) or by applying a multiplicative factor (2, 5, or 10) to the *PNEC*, especially if a specific ERA needs to be conducted (Munaron et al. 2023).

The *PNEC* data concerning dimethachlor-ESA were sourced from the ecotoxicological studies section of the notification on the active substance dimethachlor issued by the supplier (Syngenta, 2019). It should be noted that for priority substances (e.g., atrazine) defined within the framework of EU regulation (Annex X of Directive 2000/60/EC), the threshold values (*PNEC*) used correspond to regulatory EQS. Regarding all other molecules, the conventional approach described above was favored. The final *PNEC* selection is conducted and can be found in Table S9.

Risk quantification and identification of key risky contaminants

For the identification of molecules posing the highest risks to aquatic ecosystems, the *RQs* associated with maximum observed environmental concentrations (*MaxECs*) across all 12 ponds are presented in Table 2. This risk quantification allows us to discern the most concerning molecules and their potential impacts on the aquatic ecosystems under study. $RQ > 1$, indicating an alert situation, was observed for 8 pesticides, including 4 PPPs (chlortoluron, dimethenamid, MCPA, and imidacloprid) and 4 TPs (2-hydroxy-atrazine, desethylterbuthylazine, flufenacet-ESA, and terbuthylazine hydroxy). These values result, depending on the molecule, either from relatively high concentrations in the environment—slightly below 1000 ng/L, as in the case of flufenacet-ESA—or from a relatively low *PNEC*, leading to a high risk at low concentration (imidacloprid), or a combination of both factors (high *MaxECs* and low *PNEC*), as is the case for MCPA. For this latter molecule, the RQ_{max} reached 2931.33, revealing an MCPA contamination level likely to induce deleterious effects on organisms. Indeed, the concentration (880 ng/L) measured in our study was nearly three times higher than the EC_{50} 48 h of *Gomphonema* sp. (i.e., $EC_{50} = 300$ ng/L; Wood et al. 2016), a diatom commonly used as a bioindicator. Such concentrations measured within a water body rich in biodiversity, such as microphytobenthos, are very concerning. This finding is even more concerning for headwater aquatic ecosystems, as pond concentrations are often much lower than those of their tributaries due to dilution and degradation processes within the water body. This is confirmed by the MCPA values measured by Le Cor et al. (2021), reaching 21,200 ng/L in one of the pond

Table 2 Maximum environmental concentrations (MaxECs) of the pesticides quantified in the sampled pond water, with their respective PNEC, along with the derivate $RQ_{\max} = \frac{MaxECs}{PNEC}$

Class	Molecule name	Concentration (ng/L)		RQ _{max}
		MaxECs	PNEC	
<i>Anilide herbicides</i>	Flufenacet	22.79	44.00	0.52
	Flufenacet ESA ¹	695.30	440.00	1.58
	Flufenacet OXA ¹	337.00	440.00	0.77
<i>Anilide fungicides</i>	Boscalid	9.32	12500.00	0.00
<i>Conazoles</i>	Tebuconazole	20.72	98.70	0.21
<i>Chloroacetanilides</i>	Dimethachlor ESA ¹	21.19	100000.00	0.00
	Dimethenamid	47.97	28.00	1.71
	Dimethenamid ESA ¹	38.64	280.00	0.14
	Dimethenamid OXA ¹	41.04	280.00	0.15
	Metazachlor ESA ¹	157.46	93800.00	0.00
	Metazachlor OXA ¹	215.88	100000.00	0.00
	Metolachlor	57.05	70.00	0.81
	Metolachlor ESA ¹	153.61	15400.00	0.01
	Metolachlor OXA ¹	63.91	400000.00	0.00
	S-metolachlor NOA ¹	102.53	700.00	0.15
	<i>Organophosphorus</i>	TCP ¹	23.36	290.00
<i>Phenoxy</i>	MCPA	879.40	0.30	2931.33
<i>Pyridazinone</i>	Me-DPC ¹	38.12	18600.00	0.00
<i>Pyridylmethylamine</i>	Imidacloprid	18.60	0.0386	481.92
<i>Sulfonylureas</i>	Saccharin	29.45	5400.00	0.01
<i>Thiocarbamates</i>	Prosulfocarb	12.20	1500.00	0.01
<i>Triazines</i>	Atrazine-2-hydroxy ¹	156.91	6.60	23.77
	DEA-OH ¹	18.53	6000.00	0.00
	DIA ¹	11.59	12.00	0.97
	DIA-OH ¹	113.04	6000.00	0.02
	Terbuthylazine	48.35	60.00	0.81
	Terbuthylazine desethyl ¹	84.50	18.00	4.69
	Terbuth-desethyl-OH ¹	61.76	600.00	0.10
<i>Ureas</i>	Chlorotoluron	23.702	8.5	2.79

Corresponding color code for RQs: light green: no risk (RQ<0.01), green: minimal/low risk (0.01<RQ<0.1), orange: moderate/medium risk (0.1<RQ<1), red: high risk (RQ>1). ESA, ethane sulfonic acid; OXA, oxalinic acid; TCP, trichloropyridinol; DEA-OH, deethylhydroxyatrazine; DIA, deisopropylatrazine; DIA-OH, deisopropyl-hydroxy-atrazine; MCPA, 4-chloro-2-methylphenoxy) acetic acid; Me-DPC, methyl-desphenyl-chloridazon; S-metolachlor NOA, N-(2-Ethyl-6-methylphenyl)-N-(2-sulfoacetyl)-L-alanine. ¹Transformation products (TPs)

tributaries and exceeding the value of 300 ng/L (i.e., EC_{50} 48 h) for several days in the upstream creek.

In addition to these high risks, there were moderate risks associated with 10 molecules, including 6 representatives of chloroacetanilides (flufenacet and its OXA form, dimethenamid ESA and OXA, and metolachlor and its NOA form),

3 representatives of triazines (DIA, terbuthylazine, and its TP desethyl-OH), and one of the two fungicides in this study, tebuconazole. The risks induced by these contaminants, especially the triazines, mainly result from their relatively high toxicity. Chloroacetanilides, on the other hand, although presenting lower toxicity, are still prone to posing

a risk to organisms dependent on these water compartments due to the relatively high concentrations at which they were quantified in the water bodies. After MCPA, flufenacet-ESA and OXA were the two contaminants quantified at the highest concentrations in the studied ponds, with *MaxECs* of 695 and 337 ng/L, respectively (Table 2).

Risk profiles across sites

In order to characterize the risk profiles of the 12 ponds individually, RQ_{mean} and RQ_{max} were derived for each one. This allowed for an in-depth analysis, focusing on specific situations that could reveal variations in ecotoxicological risk depending on the unique characteristics of each pond or its watershed. Different contamination profiles are discernible among the ponds, as shown in Fig. 5, which displays the RQ_{max} , RQ_{mean} , and also the mixture RQ (RQ_{mix}), which

considered the co-occurrence of pesticides and their potential combined toxicity based on the assumption of additivity. The details of the RQ specific to each pond are presented in Table S10.

Based on the maximum RQ_{mean} values, all the ponds except H and I could be considered high risk. Conversely, pond I was classified as medium risk, and H as low-risk. In the worst-case scenario (maximum values of RQ_{max}), this ranking was maintained. As for the moderate risk, it applied to the RQ_{max} values of ponds H and I, with 0.14 and 0.76, respectively.

The RQ_{mix} values suggest a near-total risk contamination for all the studied ponds, except for H, which, it is worth noting, is one of the “pristine” ponds of this study, with a catchment primarily constituted of a forest environment with presumably limited PPP application. The act of summing individual RQ values explains these hazardous exceedances

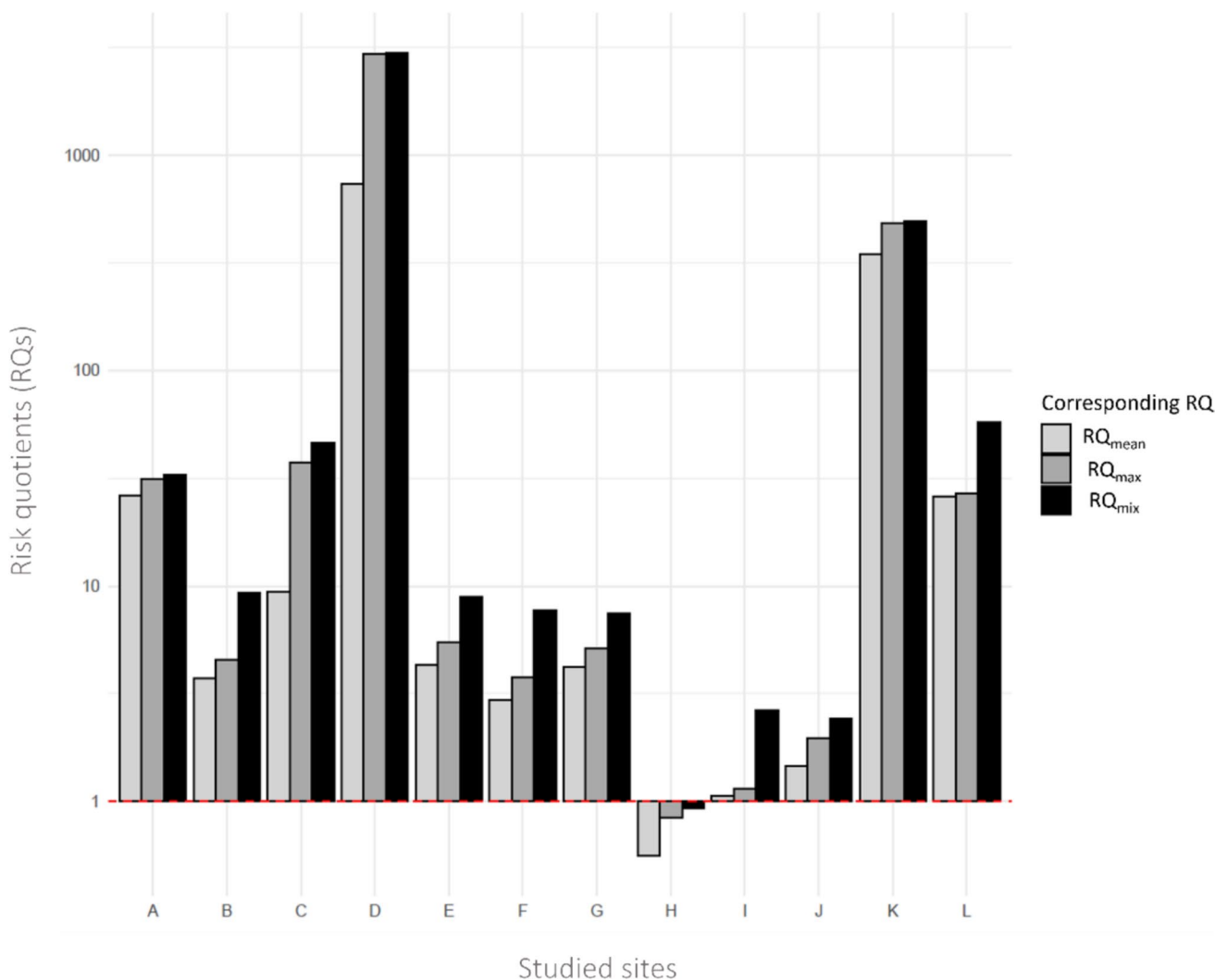


Fig. 5 Maximal risk quotients (RQs) for each site, representing three scenarios: a general (RQ_{mean} , in light gray), worst-case (RQ_{max} , in gray), and cumulative (RQ_{mix} , in black) scenario. The scale has been converted to logarithmic format for better readability

but remains within the realm of simple additivity. There is no consideration here for potential synergistic effects that could pose even greater risks, or conversely, for antagonistic effects that could reduce the risk through the simultaneous presence of molecules with co-suppressive effects.

In this latter context, the relative contribution of a pesticide's RQ (RQ_i) to the RQ_{mix} , namely the PRQ_i , was studied (see Table S11 for details). For ponds A, B, E, and J, it was primarily atrazine-2-hydroxy that contributed markedly to the toxicity among the mixture (95%, 79%, 84%, and 81%, respectively). MCPA predominated in ponds C and D, while imidacloprid was most common for pond K. For the remaining ponds, pairs or trios of molecules contributed more or less equally, as was the case for ponds F and L, which were predominantly characterized by a sharing of ecotoxicity by atrazine-2-hydroxy and terbuthylazine-2-hydroxy (50%/18% and 23%/58%, respectively). The ecotoxic status of pond H was mainly due to the presence of terbuthylazine-2-hydroxy and metolachlor, herbicides from different chemical classes. For other sites (ponds G and I), more than 5 molecules contributed jointly. These potential joint effects or sharing of toxicity among molecules support the argument for conducting studies considering combined effects, as has been the case in recent years, especially around the issue of pesticides (Belden et al. 2007; Martin et al. 2021; Pistocchi et al. 2023), although integrating this approach into risk assessment remains challenging (Weisner et al. 2021).

Limitations of current approaches and future directions

In the pursuit of comprehensiveness, some studies complement the regulatory tests required for the market approval of pesticides and go beyond them by employing other biological models and exposure protocols. They also explore co-exposures that could correspond to such environmental co-occurrences (Silva et al. 2018; Tóth et al. 2019; Rozmánková et al. 2020). It is essential to acknowledge the limitations of the current approaches while considering the potential for future advancements in ERA methodologies. Our study is one of the first to conduct an ERA of this type on continental LSWBs. It is worth noting similar work on the risk of pesticide mixtures in French lagoon waters (Munaron et al. 2023). As a complementary approach to ERA, active biomonitoring methods are also employed. A recent study by Slaby et al. (2023) conducted a biomarker analysis to compare and provide insights into the health status of caged fish in ponds D and A from the present study. Combining the results of these studies, pond D, which is located in the vicinity of conventional agriculture, exhibited a higher concentration of contaminants despite its biomarker responses not differing sharply with those of pond A, an organic-agriculture-adjacent pond. This supports the fact that many contaminants, forming the distinct profiles of each of these

ponds, remain toxic and thus impact toxicity analyses conducted through a biomarker approach. A biomonitoring study involving a greater number of ponds with distinct profiles would therefore allow for a more comprehensive analysis to obtain tangible comparison elements.

Returning to ERA, it should be noted that this work is not set in stone, since there may be enrichment of the ecotoxicological data set and therefore a reduction in extrapolation factors, leading to changes in $PNEC$ values and therefore RQ s. When many decision-making processes are based on a risk approach, it is important to use appropriate data to support the decisions that could be made. Most of the time, we tend to be more conservative than the reality (in applying safety factors, for example), making overprotective decisions. For new compounds such as contaminants of emerging concerns (CECs) that are TPs, the trend is reversed due to the fact that there is little or no evidence of their occurrence or toxicity. Moreover, we have to bear in mind that safety factors can be referred to as uncertainty factors, showing the complexity of being sure of what we demonstrate. Hence, there is a need to bridge the gap between key studies and their use in a regulatory context, such as by avoiding the misuse of non-standard studies that may be of high quality and reliability. However, such studies may be unusable or only marginally usable because they are quite specific and do not meet all the criteria for the use of their data. Nevertheless, this argument could potentially reverse the trend and modify the selected ecotoxicological values, ultimately impacting the overall ERA. The legislation evolves, meaning that regulated substances could be retired, but sometimes in favor of another with similar properties or leading to common metabolites (like dimethenamid and dimethenamid-P), further complicating the work on TPs.

Conclusion

This study presents new data on the occurrence of pesticides, particularly focusing on their transformation products (TPs). A total of 86 molecules were investigated, and up to 32 molecules were detected simultaneously within a single pond. Our findings reveal that even water bodies fed by predominantly forested watersheds can exhibit multi-contamination, with up to 10 detected molecules, underscoring the pervasive nature of pesticide contamination. This study highlights that this phenomenon occurs across watersheds subjected to a wide range of agricultural pressures. Among the quantified contaminants, the herbicides atrazine-2-hydroxy and metolachlor were the most prevalent, the latter belonging to the chloroacetanilide class and reflecting known agricultural practices in the surrounding watersheds. Notably, some ponds displayed distinct contamination patterns, primarily influenced by specific pesticide families. The majority of

these pesticides were found in degraded form, highlighting the importance of investigating these products, especially since the parent molecule was rarely found (e.g., as in the case of flufenacet). The lower levels of flufenacet in our samples can be attributed to various physicochemical parameters, such as its significant lipophilicity (LogP of 3.5), which limits its solubility in water (Table S2.B.). Pesticides banned for about two decades remain problematic due to the traces they leave, such as atrazine and its hydroxy TP, found ubiquitously and likely to pose a risk across all studied aquatic ecosystems. The ecological risk assessment (ERA) further nuances these observations, demonstrating the necessity of comparing concentration levels to ecotoxicity to objectively evaluate risks to the living organisms inhabiting the ponds.

The potential for cocktail effects, indicated by the co-occurrence of multiple contaminants, warrants further investigation through laboratory testing of realistic mixtures, alongside acquiring new data for poorly documented TPs. It is important to note that we have opted to regard pesticide TPs as potentially less toxic than their parent compounds. This decision was made because there is a real lack of data regarding the toxicity of these contaminants. If future ecotoxicological studies were to challenge this a priori choice (i.e., that TPs are more toxic than parent compounds), the risk to aquatic ecosystems would need to be re-evaluated upwards. Despite the absence of such ecotoxicological data concerning those TPs detected very frequently in the field, and although we did not wish to consider them as potentially more toxic than their parent compounds, several concentrations detected are already worrying for the fauna and flora of these ecosystems.

This work owes its novelty to the study of ecosystems that are widespread in Europe but remain understudied, with a focus on contaminants that are still too little considered, allowing for detailed concentration levels and a realistic ERA. Although this assessment includes TPs from pesticides, which are not always considered, it represents a small fraction of the multiple substances present in the environment and does not properly incorporate the real impact of their simultaneous occurrence. Furthermore, majority of substances found here are not part of the EU “priority” list and therefore are not considered in the current global quality assessment of water bodies. This extensive detection of untargeted molecules within regulatory frameworks shows that pollution induced by pesticide use is greatly underestimated, and that regular updates of lists of contaminants to be monitored in water bodies would be necessary. Such updates should include those TPs found at concentrations higher than their parent compounds to obtain a more precise picture of chemical pollution in these systems and to assess the actual and future environmental impacts of our choices in pesticide use.

Finally, if this original study on ecosystems (i.e., small lentic water bodies) and contaminants (TPs) that are understudied has highlighted the importance of these contaminants from the headwaters, it is worth noting that multiple other stressors to biodiversity have not been considered in this work. Additionally, these small water bodies typically have longer hydraulic residence times than streams, exposing their biota to pesticides for extended periods, an aspect often overlooked in routine ecotoxicological tests conducted for regulatory purposes, ultimately influencing the methodologies employed in ERA studies.

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Data availability Data will be made available on request.

Declarations

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Consent to participate Not applicable.

Consent for publication Not applicable.

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