

# Pesticide transformation products: a potential new source of interest for drinking water

Laure Pasquini

[laure.pasquini@anses.fr](mailto:laure.pasquini@anses.fr)

Anses Nancy Hydrology Laboratory: Anses Laboratoire d'hydrologie de Nancy <https://orcid.org/0009-0005-0804-4133>

Sophie Lardy-Fontan

Anses Nancy Hydrology Laboratory: Anses Laboratoire d'hydrologie de Nancy

Christophe Rosin

Anses Nancy Hydrology Laboratory: Anses Laboratoire d'hydrologie de Nancy

---

## Research Article

**Keywords:** Pesticides, Pesticide transformation products, Raw water, Drinking water, Monitoring

**Posted Date:** October 1st, 2024

**DOI:** <https://doi.org/10.21203/rs.3.rs-4828947/v1>

**License:**  This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

# Abstract

Pesticide transformation products (TPs) are considered pseudo ubiquitous in aquatic systems, including surface and ground water. They often present higher polarity than parent compounds, are less volatile and less biodegradable, and are therefore more mobile and persistent. These properties make them compounds of main interest in water resources and drinking water. With more than 600 samples collected over two years and nearly 100,000 results available, this study was carried out to evaluate the occurrence of 157 pesticide TPs and certain active substances in raw and drinking water in France. Our study made it possible to assess the potential exposure of the population to pesticides and their metabolites through drinking water consumption, and finally to put forward new TPs of interest for the monitoring of drinking water.

Among TPs, chlorothalonil R471811 and metolachlor ESA were the most frequently quantified compounds, with quantification in more than 50% of raw and drinking water. TPs dimethachlor CGA369873, chlorothalonil R471811 and R417888, terbuthylazine LM2 and LM6, desphenyl chloridazon (DPC) and methyl-desphenyl chloridazon (MeDPC) were monitored for the first time in drinking water in France. Concentrations exceeding the regulatory quality standard of 0.1 µg/L were observed in more than 30% of drinking water samples for chlorothalonil R471811, and a maximum concentration was measured at 9.8 µg/L for DPC in drinking water. The quantification frequencies were relatively similar in raw water and tap water, which appears to indicate poor efficiency of the majority of the currently used drinking water treatment plants. This research confirmed the benefit of focusing on TPs and parent compounds, and also to continue monitoring TPs that originate from compounds already withdrawn from the market for several years that appear to be highly persistent.

## 1. Introduction

Modern food production systems rely on high volumes of chemical pesticides to ensure crop yield stability and quantity, and to maintain food security (EEA, 2017, 2019). It is estimated that less than 5% of applied pesticides are used to kill pests and more than 95% may remain in the environment (Sarker et al. 2024). In the environment, active substances (ASs) of pesticides may degrade depending on their intrinsic properties and the physicochemical conditions encountered in soil, air, water and wildlife. Consequently, pesticide transformation products (TPs), also called metabolites, result from various biotic (metabolisation) and abiotic (hydrolysis, photodegradation) processes (Anagnostopoulou et al. 2022, Barriuso et al. 1996). All of these compounds can seep or leach to ground or surface waters and many studies have highlighted their occurrence in all environmental compartments: water resources, the atmosphere, soil and sediments (Baran et al. 2022, Masiá et al. 2013, Menger et al. 2021, Papadakis et al. 2015, Teyssere et al. 2023, Vulliet et al. 2014).

TPs are often more polar, less volatile and less biodegradable than parent compounds, and are therefore more mobile and persistent. They are considered pseudo ubiquitous in the aquatic system, including in surface and ground water (Buttiglieri et al. 2009, Kolpin et al. 2004). Conventional drinking water

treatment processes, which are designed for the elimination of suspended matter in water and for water disinfection, have poor removal efficiency for some ASs and mainly TPs, considering their large variety of physicochemical properties, especially their polarity.

Polar TPs are considered substances of prime interest and need to be studied to fill knowledge gaps concerning their occurrence and fate in the natural environment and drinking water processes (Harmon O'Driscoll et al. 2022, Mahai et al. 2021). They have consequently become a high concern for health and environment authorities. Importantly, a clear understanding of pollutants, their properties and their concentration levels is a prerequisite for selecting and sizing specific technologies, such as granular activated carbon, nanofiltration or ozonation (Bilal et al. 2019) and organising effective monitoring.

In 2021, 469 pesticide active substances were approved in Europe and 61 were pending a final decision. France is one of the most pesticide-consuming countries in Europe (Baran et al. 2022), with more than 70 000 tons sold in 2021 according to the national database of phytopharmaceutical product sales (EauFrance 2021).

Quality requirements for drinking water are specified in the French Public Health Code in application of European Directive 2020/2184 (European Union 2020). In France, lists of relevant pesticides to be monitored are defined and implemented regionally by regional health agencies according to general guidelines established by the Ministry of Health, considering: historical results, occurrence in other compartments (surface water, ground water), uses and alerts from other administrative regions/territories or other countries, data provided by water suppliers (Direction Générale de la Santé 2015).

Pesticide active substances have for decades been subject to continuous regulatory monitoring in raw water and water intended for human consumption in France. Monitoring of TPs as part of routine supervision of drinking water has been increasing in recent years thanks to improved analytical methods –notably direct injection liquid chromatography-tandem mass spectrometry (LC-MS/MS)– enabling the detection of numerous polar metabolites at low concentrations in water. Nevertheless, many difficulties are still patent because of certain obstacles that are difficult to overcome: i) TPs of interest are very numerous and many of them are not known (pesticide registration data is either not easily accessible or not available at all), ii) analytical standards for TPs are sometimes not commercially available and finally iii) TP analysis often requires dedicated methods, e.g. for small polar compounds. Knowledge is therefore still poor regarding the nature and the concentrations of TPs in raw and drinking waters. Preliminary results nevertheless indicate, as observed in other studies (Buttiglieri et al. 2009, Kiefer et al. 2019, Kolpin et al. 2004, Schuhmann et al. 2016) that TPs occur more frequently and in higher concentrations than corresponding ASs and are therefore responsible for the majority of non-compliance events (Anagnostopoulou et al. 2022, Direction Générale de la Santé 2023).

Environmental monitoring provides an important 'warning system' to supply risk assessment. Accordingly, this study aimed to fill the knowledge gap on the occurrence of a wide range of ASs and TPs through a national campaign covering the entire territory of France, including overseas departments.

The main objectives of this study were: i) to evaluate the occurrence of a large number of pesticide TPs and some ASs in raw and drinking waters, ii) to estimate exposure of the population to pesticides and their metabolites through its consumption and iii) to propose new TPs of interest for the monitoring of drinking water. Multiresidue methods based on gas chromatography (GC) and liquid chromatography coupled with mass spectrometry (MS/MS) were developed and validated to accurately quantify the full set of target compounds. Then, a sampling strategy was deployed to develop an overview contamination of aquifers and surface waters by relevant pesticide ASs and their TPs, including compounds that have been banned for many years.

## 2. Materials and methods

### 2.1. Studied compounds

A list of 145 pesticides as active substances (ASs) and transformation products (TPs) from various chemical families (carbamates, chloroacetamides, phenylpyrazoles, neonicotinoids, triazines, organophosphates, substituted ureas, sulfonamides, etc.) and families of uses (herbicides, fungicides, insecticides and more restricted molluscicides, rodenticides and nematicides) was selected. A total of 44 compounds were ASs (including 17 banned substances), 4 were mixed molecules (ASs and TPs) and 97 were TPs. When certain TPs were deemed of interest, the list of TPs from the same AS was widened in order to develop knowledge on their relative distribution and occurrence through the entire drinking water cycle. The complete list is presented as supplementary information (Table S1). The selection of compounds was based on i) a bibliographic survey, ii) local alerts or alerts from neighbouring countries, iii) contamination of other matrices and iv) expert opinions and peer review. Among selected emerging substances, transformation products of chlorothalonil (R471811, R417888, R182281, R611965, SYN507900), chloridazon (desphenyl- and methyl desphenyl-) or terbuthylazine (LM2 to LM6) that have been found to be of high interest (Kiefer et al. 2019) were included to provide initial data on their occurrence in water systems in France.

### 2.2. Sampling strategy

This national campaign aimed to cover the entire territory of France, covering all departments (including overseas departments and regions) and was carried out in collaboration with Regional Health Agencies and the French Ministry of Health. This sampling plan has shown its effectiveness and relevance in various previously published studies (Bach et al. 2024, Bach et al. 2020, Colin et al. 2014). In order to be representative of a large proportion of the national flow of produced drinking water (20–25% of the French population), the sampling strategy deployed from October 2020 to June 2022 was implemented as described below. For each department, three sample locations were investigated: i) the water catchment producing the greatest flow of drinking water (GF), ii) a randomly selected drinking water source (RS) and iii) a drinking water resource known to present contamination by pesticides (CR). A total of 304 raw water (222 ground waters and 82 surface waters) and 299 drinking water samples were analysed.

All water samples were collected in 40 mL glass bottles containing 0.1% formic acid, shipped at 4°C on cold packs in polystyrene boxes, and received at the laboratory within 24 h to 48 h. In most cases, samples were analysed within 4–5 days of collection. Sodium thiosulfate was added to all drinking water samples to neutralise free residual chlorine and to avoid pesticide degradation after sampling.

## 2.3. Standards and reagents

All native and isotope-labelled compounds ( $^{13}\text{C}$  and  $^2\text{H}$ ) were purchased as pure analytical standards or solutions from Dr. Ehrenstorfer (Augsburg, Germany), Neochema GmbH (Bodenheim, Germany), HPC standards GmbH (Borsdorf, Germany) and Techlab (Metz, France). Some non-commercially available TP standards were obtained from companies such as Bayer, Syngenta, FMC Agricultural Solutions and Dow Agro Science. Water, acetonitrile and methanol were liquid chromatography–mass spectrometry (LC–MS) grade and were obtained from Biosolve (Valkenswaard, the Netherlands).

Two independent batches of individual solutions of the native compounds were prepared when possible: the first for preparation of calibration samples, and the second for spiking of samples. All stock and working solutions were stored in the dark at  $4 \pm 2^\circ\text{C}$ . No instability of compounds in working solutions was detected over a storage period of 12 months. For LC-MS/MS analysis, standard solutions were prepared in a mix of acetonitrile and water (10/90 v/v) according to initial chromatographic conditions. For GC-MS/MS analysis, standard solutions were prepared in methanol.

## 2.4. Analytical methods

Two complementary analytical methods were used to perform analysis of the 157 compounds.

Surface waters were first centrifuged to prevent clogging. The first analytical method was based on direct injection coupled with liquid chromatography hyphenated to tandem mass spectrometry in both negative and positive ionisation modes (DI LC-MS/MS). Two consecutive injections were necessary to monitor the 137 compounds. Accurate quantification was achieved by implementing 31 isotopically labeled standards.

In brief, the second analytical method implemented stir bar sorptive extraction (SBSE) followed by gas chromatography hyphenated to tandem mass spectrometry analysis (GC-MS/MS). In all, 8 compounds of interest and 12 of their isomers were analysed. Three labeled internal standards were implemented to carry out the quantification.

A more complete description of the developed methods (LC and GC parameters, MS/MS transitions) is available in Table S2.

## 2.5. Method performances

Method validation was performed using some of the specific statistical tools provided in the NF T90:210 standard (AFNOR 2018). Therefore, method validation was carried out on a representative matrix. A set of water samples with an extensive range of physicochemical properties was selected as representative

of environmental conditions to which the method will be applied for monitoring in surface, ground and drinking waters.

For both methods, calibrations were performed with 7 to 9 points of concentration range. The quadratic fit of the calibration curves was systematically checked for each sample batch (R-square values from regression analysis  $\geq 0.97$  and maximum bias for each point of the calibration curve below 20%). Quantification of the target compounds was performed using the internal standard method with deuterated or  $^{13}\text{C}$ -labelled internal standards. They were added to each water sample before applying analytical procedures and were used to check the overall recovery of target chemicals during the analytical procedure.

For each compound, limit of quantification (LOQ) and uncertainty were determined (see Table S2). LOQ was defined as the lowest concentration of analyte that can be determined with acceptable accuracy under the stated conditions of the test, e.g. representative real matrix under intermediate precision. In this study, a maximum allowed tolerance of  $\pm 60\%$  was required (XP CEN/TS 16800, (AFNOR 2016)). LOQs, in matrix, were between 0.005 and 0.200  $\mu\text{g/L}$  and maximum relative uncertainties ( $k = 2$ ) around 40% at the LOQ.

## 2.6. Quality assurance/quality control

To check initial system performances and to monitor any prejudicial loss of sensitivity during the analytical runs, a range of quality control tools were deployed. Confirmation of target compound identification was performed, fulfilling the ISO 21253-1:2019 requirements: retention time with a tolerance of 2.5%, monitoring of two distinct transitions and their abundance ratio (based on peak area) with 30% tolerance between samples and calibration samples (International Organization for Standardization 2019).

Standard solution mixtures were injected on average every 10 real samples and a standard solution mixture at the LOQ was injected at the end of each run to prevent analytical drift. To ensure the quality of the data produced, results were interpreted using control charts with tolerances below 30%.

The relative recovery study was carried out by spiking one raw water and one drinking water sample randomly selected in each analytical run. These samples were spiked with the targeted compounds in order to verify the accuracy of the analytical method and to monitor potential matrix effects. These controls were considered valid when recoveries were between 60% and 140%, according to SANTE/11813/2017 guidance document (EURL 2017).

Additional external quality controls were performed by periodic participation (at less twice a year) in inter-laboratory comparisons covering approximately 25% of the targeted compounds. Results of these external quality controls supported the quality of our methods ( $Z$  score  $< 2$ ).

No related cross-contamination was revealed during method validation. However, the absence of contamination up to 1/3 of the LOQ was verified at each sequence by pouring LC-MS grade water into

collection bottles and performing the overall analytical procedures.

The stability of target compounds was investigated before the sampling campaign by conducting spiking experiments in natural water (raw and drinking water) for a period of 3 weeks, under the sampling and storage conditions described above, and after extraction by SBSE and storage at 4°C in amber glass vials for a period of 3 months. All target compounds were stable during this period of time (recoveries within the uncertainty of the analytical method), with the exception of metsulfuron-methyl and pinoxaden, which were stable for 2 and 13 days, respectively in water.

Lastly, 92% of the results were produced under cover of COFRAC accreditation according to NF EN ISO/IEC 17025 requirements (AFNOR 2017) (145 compounds were accredited).

The validated procedures demonstrated their applicability to real samples in relation to the objectives of robust quantification in raw and drinking waters. Finally, the optimised procedures were applied in the national monitoring campaign.

### **3. Results and discussion**

With respect to the overall objectives of the study and considering the limitations of the implemented sampling strategy, a decision was made to aggregate the data from all of France (no regional discussion) in order to highlight the main trends. Furthermore, no paired discussion (raw water / drinking water) at a given site will be shown, and accordingly the efficiency of drinking water process treatment will not be discussed. In fact, treatment processes evaluation can be complex, especially since several resources may be used to provide drinking water.

#### **3.1. Pesticides and their transformation products in raw waters**

This survey involved drinking water networks supplied by ground water and surface water. Due to the sampling strategy, ground water samples were predominant, representing 73% of the 304 raw waters collected, in accordance with the type of water used in France. The results in raw water are given in Fig. 1a. At least one compound was detected above the LOQ in 80% of ground waters and 83% of surface waters. Moreover, 97% of raw water samples coming from vulnerable resources contained at least one of the target compounds above LOQ, while raw waters that were selected randomly exhibited a lower state of contamination, with approximately 60% of them contaminated by at least one of the target compounds above LOQ. This overall picture confirmed the ubiquitous contamination of waterbodies by pesticides and their TPs as a consequence of their mobility via transfer processes, such as runoff, infiltration or leaching into water resources (Guzzella et al. 1996, Hintze et al. 2020, Jorfi et al. 2021, Syafrudin et al. 2021, Verlicchi and Ghirardini 2022).

Among the 145 investigated compounds (44 ASs, 97 TPs and 4 mixed molecules), 84 were quantified at least once in raw water. Among them 27 were ASs and 57 were TPs. Not surprisingly, TPs represented a

substantial proportion of systematically detected contaminants (Hintze et al. 2020, Ulrich 2022), legitimating the critical need to address TPs in routine monitoring programmes.

Herbicides, which were the most commonly represented, were also the most quantified: 77% of the target herbicide ASs and TPs were measured at least once. The broad occurrence of fungicides was also confirmed, with 65% of them quantified at least once. Insecticides, especially neonicotinoids (the main target compounds at 14 of 42), showed the lowest frequency of quantification (17%). These results are consistent with the banning of their use, implemented in France since 2018, and also their uses, especially compared to herbicides as stated by the National Crop Protection Products Sales database (EauFrance 2021). In fact, over the period 2017–2021, considering the selected ASs for this study, fewer than 500 tons per year of insecticides were sold versus more than 12,000 tons for herbicides.

As highlighted in Fig. 1a, ground waters displayed higher frequencies of quantification, regardless of the types of compounds (AS/TP) and chemical classes, compared to surface waters. This may be due to the selection of CR points mainly of ground water origin. Furthermore, as shown in Fig. 2, which presents the 90th percentile of the total concentration ( $\mu\text{g/L}$ ) of quantified substances at a given site, the state of contamination of ground waters by banned ASs and their related TPs was higher than that of surface water, with TP 90th percentile total concentrations of 1.115 and 0.738  $\mu\text{g/L}$ , respectively. Approved substances and related TPs were more concentrated in surface waters than ground waters, at 0.114  $\mu\text{g/L}$  and 0.062  $\mu\text{g/L}$ , respectively. Although an impact of the sampling strategy on this snapshot could not be ruled out, it can be assumed that it reflects the wide persistence and mobility of pesticides. In fact, the fate of pesticides has been recognised to be driven as much by the climate setting and type of aquifer as the use and properties of the compounds (Baran 2021). In France, several studies have demonstrated that compounds can be found in ground water several years after being withdrawn from the market (Baran et al. 2007, Baran et al. 2021, Gourcy et al. 2009, Lopez et al. 2015, Morvan et al. 2006).

Furthermore, the occurrence of approved ASs in surface waters reflects their immediate vulnerability to spray and dust drift during application, or surface runoff (Bonmatin et al. 2014, Ulrich 2022).

Three main phenomena have been put forward to explain the persistence of an AS in ground water: remobilisation from soils, delayed transfer time and the absence of degradation in the saturated zone (Baran et al. 2021). These mechanisms are also affected by hydrology and dynamics of transfer to ground water during the application period (Baran et al. 2021).

This widespread ground water contamination by TPs can also be explained by their physiochemical characteristics. TPs are usually more polar, less volatile and less biodegradable than their parent compounds and show ground water ubiquity scores (GUS) that are greater than ASs, which results in higher leachability from soils and mobility in the general environment (Arp and Hale 2022, Baran et al. 2022, Lapworth et al. 2015, Schuhmann et al. 2016).



With the exception of atrazine (25%), bentazone (16%) and metolachlor (18%), the ASs were quantified at frequencies lower than 10% (Fig. 3). Interestingly, if we compare the most sold ASs in France over the period 2017–2021 (see Figure S1), prosulfocarb, which presents the most significant annual tonnages, was found in only 5% of samples. Flufenacet, chlorotoluron, tebuconazole, metazachlor, dimethenamid, chloridazon, and 2,4 D and 2,4-methyl-chlorophenoxyacetic acid were quantified in 6%, 5%, 3%, 9%, 3%, 1.7%, 2% and 0.7% of samples, respectively. Their median concentrations did not exceed 0.1 µg/L.

Of note, the TPs of chlorothalonil (banned in France since 2020), namely chlorothalonil R4711811 and chlorothalonil R471888, of atrazine (banned in France since 2003), namely desethylatrazine (DEA), desethyldeisopropylatrazine (DEDIA) and 2-hydroxy-atrazine, of metolachlor (withdrawn for its main uses in progress since 2023), namely metolachlor ESA, metolachlor OXA, metolachlor NOA and metolachlor CGA368208, of metazachlor, namely metazachlor ESA and metazachlor OXA were quantified in more than 10% of raw waters. With the exception of chlorothalonil R4711811 (0.140 µg/L) and metolachlor NOA (0.1 µg/L), median concentrations of individual TPs did not exceed 0.1 µg/L. The ratios between the occurrence of ASs and TPs varied, depending on the pesticide.

Herbicides of the chloroacetamide class (metolachlor, metazachlor and flufenacet) and all of their TPs represent a large proportion of the compounds quantified in the water samples studied here. In fact, chloroacetamides, used mainly on maize crops, which represent 11% of the agricultural area in France, and more broadly for pre- or post-emergence weed control, are one of the most widely used groups of herbicides. Certain hotspots events have been observed, as maximum concentrations up to 10 µg/L have been measured for some TPs (data not shown).

For the first time in France, large contamination of raw waters by TPs of chlorothalonil was identified. Chlorothalonil is a fungicide widely used on cereals and potatoes until 2020, date of its end of use, and it was the sixth most commonly used AS in France in 2018. It is therefore not surprising to find these TPs in almost all water bodies.

These results are consistent with recently published findings in Switzerland. In the Swiss study, eight metabolites of chlorothalonil (R611968, SYN507900, SYN548580, SYN548581, R417888, R419492, R471811 and an isomer of R417888) were detected in ground water (Kiefer et al. 2019). Among these metabolites, R471811, R419492 and R417888, which belong to the group of sulfonic acids, tended to have a higher detection frequency and occurred in higher concentrations in Swiss ground water than the phenols SYN548580, SYN507900 and R611968 (Kiefer et al. 2019). Despite the ban of the chlorothalonil in 2020, it is probably justified to include this compound in the routine monitoring programme of waterbodies in France, and to carry out ecological and health safety risk assessment analysis.

Prosulfocarb, the main approved and most commonly used thiocarbamate herbicide in France (in terms of tonnage) is characterised by low solubility in water (13.2 mg/L), high polarity (logP 4.48), potencies for volatilisation and vapour drift, and low leachability (GUS 0.76). The very low contamination observed in our study is consistent with other previously published findings in France (NAIADES database 2024, Slaby et al. 2022), Cyprus (Nikolaou et al. 2017) and Germany (Halbach et al. 2021). To date, to the

authors' knowledge, no published study has addressed the monitoring of its minor soil metabolite prosulfocarb sulfoxide in European raw waters. Despite the potential for ground water exposure via the intended uses above the parametric drinking water limit of 0.1 µg/L for parent prosulfocarb and its minor soil metabolite prosulfocarb sulfoxide, the risk was considered to be low in peer review risk assessment (European Food Safety Authority 2007). Its extensive use has led to the recommendation to include these ASs and TPs in regulatory monitoring.

Raw waters in France still display strong impregnation by triazines, specifically atrazine and its TPs, DEA and DEDIA, as well as terbuthylazine and its TPs. Preferential occurrence of atrazine and its metabolites (DEA, desisopropylatrazine (DIA) and DEDIA) in ground water was highlighted by our results. This appears to reflect a trend towards depletion of AS stocks by leaching migration and transformation processes in deeper soil layers (Bhatti et al. 2022, Buhler et al. 1993, Novak et al. 1998). Terbuthylazine-desethyl and terbuthylazine-hydroxy have been included in regulatory monitoring for many years, but this is not the case for the TPs LM2, LM3, LM4, LM5 and LM6. In our study, eight TPs of terbuthylazine were monitored for the first time in raw waters intended for drinking water production. The results highlight the wide occurrence of LM6 (frequency of quantification (FQ): 7.3% med C = 0.048 µg/L), LM3 (FQ: 1% med C = 0.053 µg/L) and to a lesser extent LM5 (FQ: 4.3% med C = 0.030 µg/L) and LM2 (only one detection, but at a concentration of 0.27 µg/L). Very recently, Kiefer et al. (2019) observed wide contamination of water in Switzerland by LM2, LM3, LM5 and LM6, which were detected in 80–90% of samples, with 90th percentile concentrations ranging from 6.4 to 54 ng/L. These observations are also consistent with certain previously reported results for aquifers in Italy (Valsecchi et al. 2017). The preliminary findings on our work legitimate the recommendation to include LM2, LM3, LM5 and LM6 in regulatory monitoring.

Chloridazon was quantified in fewer than 2% of samples, with a median concentrations 0.006 µg/L. Its two main TPs, MeDPC and DPC, were found in 16.6% and 5% of samples, at median concentrations of 0.041 µg/L and 0.670 µg/L, respectively. Chloridazon is a pyridazinone herbicide characterised by moderate solubility in water (422 mg/L), low polarity (Log P 1.29), moderate persistence in soils and transition state from soils (GUS 2.16). On the contrary, DPC and MeDPC display high leachability from soils, as shown by their GUS (5.46 and 4.39, respectively). Chloridazon, banned in 2021, exclusively applied on beetroot fields and at much lower quantities (300 tons in 2018), had its TP MeDPC quantified in all beetroot-growing departments. DPC was quantified at a lower frequency in these departments, probably due to its LOQ of 0.2 µg/L (LOQ of MeDPC = 0.010 µg/L).

These results are in line with previously published data that demonstrated the prevalence and relevance for routine regulatory monitoring of TPs of chloridazon (Menger et al. 2021).

Importantly, because of scarce results on the contamination of soils by pesticides and their TPs at national scales, it is not possible to establish links between uses, soil contamination and contamination of water resources. The findings supports the conclusion that Froger et al. (2023) arrived at, to consider

pesticides and their residues in the construction of future regulations on soil protection, and particularly the European Soil Health Law currently being discussed.

For better understanding of the occurrence and fate of pesticides, a pairwise correlation matrix of concentrations has been constructed to help identifying the compounds most likely to be found concomitantly in raw waters, and thus potentially identified certain indicators or patterns of substances to be recommended for routine regulatory monitoring. A pairwise correlation matrix for all the concentrations compiled to derive the compounds quantified in more than 20 samples (except for DPC due to its high LOQ) –raw waters type relationships– is presented in Fig. 4. The direction and magnitude of the correlation coefficient is indicated by the colour of the cell: the darker the colour, the stronger the correlation. Blue cells indicate positive correlations, and red cells indicate negative correlations. This represents a total 27 compounds, 22 TPs and 5 ASs.

At first glance, better correlations can be observed in ground water than in surface water. It should also be noted that only surface waters present significant negative correlations.

Whether in ground water or surface water,

- Chlorothalonil TPs (R471811 and 417888) are positively correlated with each other, with a greater correlation in ground water. Chloridazon TPs (MeDPC and DPC) are positively correlated with each other with a greater correlation in ground water. Furthermore, correlation between the metabolites of both ASs is also observed. These compounds correspond to recently banned active substances.
- Metolachlor TPs and metolachlor are positively correlated, with a greater correlation in surface waters. Terbutylazine metabolites and AS are positively correlated, with a greater correlation in surface waters compared to ground waters. These compounds correspond to ASs that are still approved.

In surface waters, negative correlations were observed between TPs from banned ASs (atrazine, chloridazon, alachlor and acetochlor) and ASs and TPs of active substances that are still approved (metazachlor, metolachlor and terbutylazine). Nevertheless, negative correlations are not very significant and may require additional work to better assess the connections between compounds. A positive correlation was observed between dimethenamid ESA, and terbutylazine and its TPs in surface waters, and to a lesser extent with metolachlor and its TPs.

Furthermore, a positive correlation between dimethachlor ESA and terbutylazine and its TPs was observed, and to a lesser extent with metolachlor and its TPs. On the contrary, a negative correlation was observed between dimethachlor CGA369873 and metolachlor and its TPs, and to a lesser extent its terbutylazine TPs.

In ground water, a highly significant positive correlation was found between dimethachlor ESA, dimethachlor CGA 369873, dimethenamid ESA, flufenacet ESA and metazachlor and its TPs. All these ASs are chloroacetanilide herbicides widely used on large crops (wheat, rapeseed, barley, corn and

sunflower), often in rotation. The hypothesis of co-uses of the ASs or co-formulation, such as metazachlor in formulation with dimethenamid-P, and common scheme of degradation, can be made.

No correlations were demonstrated between terbuthylazine and its TPs and metolachlor and its TPs in ground water, while positive correlations were observed in surface water.

A moderate positive correlation between atrazine and its TPs was observed in ground water.

## **3.2. Pesticides and their transformation products in drinking water**

Among the 145 investigated compounds, 73 were quantified at least once in tap water, 19 were ASs and 54 TPs (Fig. 1b). Herbicides were the most frequently quantified in tap water, as observed for raw water. In all, 70% of the target herbicide ASs and TPs were measured at least once in tap water. All compounds quantified in drinking water were also quantified in raw water, and no significant increase in metabolites was observed through treatment processes.

Quantified compounds in tap water can be classified according to different levels of interest. The substances of greatest interest based on this study are highlighted in red squares in Fig. 5. These substances, corresponding to 90th percentile of their concentrations up to 0.100 µg/L and measured in more than 10% of the drinking water samples (n = 30), are all TPs. Among these, 10 TPs, metabolites of chloroacetanilides (acetochlor ESA, alachlor ESA, metazachlor ESA, metolachlor ESA and OXA), are known to be far more mobile, more persistent and more resistant to treatment processes than the parent compounds (Farlin et al. 2018, Gustafson et al. 2003, Verstraeten et al. 2002).

To our knowledge, dimethachlor CGA369873, as well as chlorothalonil R471811 and R417888, have been quantified in this study in drinking water in France for the first time. It should be emphasised that the most frequently quantified metabolites generally correspond to predicted concentrations of high concern, according to EFSA evaluations. This is particularly the case for chlorothalonil R471811, R41788, metazachlor ESA and desphenyl-chloridazon which have predicted concentrations exceeding 10 µg/L in ground water and are considered major TPs in soils. For dimethachlor CGA369873, concentrations are expected to exceed 0.1 µg/L in ground water (European Food Safety Authority 2008). These observations underline the importance in deploying early TP surveillance in connection with EFSA assessments.

The second class, in orange, presents moderate interest. It brings together compounds that have high concentrations (greater than 0.1 µg/L) and low frequencies of quantification (flufenacet ESA, metazachlor OXA, metolachlor NOA and terbuthylazine LM6), or conversely high frequencies of quantification (15–20%) with low concentrations. This is the case for atrazine and its metabolite desethyl-atrazine. Again here, this finding underlines strong persistence and broad contamination by atrazine, a substance banned over 20 years ago. DEDIA, which is an ultimate TP of atrazine and other triazines, is more worrying with high FQ and high concentrations.

The last class, in green, concerns compounds of low interest. They are all TPs, with the exception of metolachlor.

Maximum concentrations in drinking water were measured for DPC (9.8 µg/L), metolachlor ESA (3.1 µg/L) and chlorothalonil R471811 (2.0 µg/L).

A total of 12 TPs that were not part of regulatory control were quantified for the first time in more than 1% of samples. Among them, chlorothalonil SYN507900, metolachlor CGA 357704, metolachlor CGA 368208, sedaxane M02 and terbuthylazine LM5 never exceeded the threshold value of 0.1 µg/L, whereas the other seven TPs (chlorothalonil R471811, R417888, R182281, terbuthylazine LM6, phthalamic acid, phthalic acid and saccharin) exceeded 0.1 µg/L at least once. The guideline value of 0.1 µg/L is taken as a reference, regardless of the relevance of each TP that is evaluated and managed in each country.

Table 1 shows the frequencies of exceeding 0.1 µg/L and the maximum concentrations measured in tap water. Chlorothalonil R471811, metabolite of the fungicide chlorothalonil, banned from use in France since 2020, was the most frequently quantified compound (57% of positive samples) and had the highest frequency of exceeding 0.1 µg/L (34%). AS chlorothalonil was not analysed in this campaign as it requires specific analytical conditions and cannot be included in this type of multiresidue analytical method. However, the AS is regularly monitored through regulatory control in France and does not lead to non-compliance (Direction Générale de la Santé 2022, 2023).

Metolachlor ESA was also quantified in more than 50% of the sample. However, this TP exceeded 0.1 µg/L for only 13% of samples. Other major metabolites of metolachlor, namely metolachlor OXA and metolachlor NOA, were less frequently quantified and were always below the guideline value.

Metazachlor ESA, chlorothalonil R417888, alachlor ESA plus acetochlor ESA, chloridazon-methyl-desphenyl and chloridazon-desphenyl were the next compounds frequently exceeding 0.1 µg/L, for 3–5% of the samples.

Atrazine metabolites DEA and DEDIA, which are also monitored in regular control, presented frequencies of quantification greater than 0.1 µg/L in 2%. These results are consistent with those of Guillon et al. (2019) who highlighted the predominance and ubiquity of these TPs.

Previous studies mentioned that chloridazon TPs are often measured in higher concentrations than the parent compound (Kiefer et al. 2019). In this national campaign, chloridazon was quantified only five times and always under 0.1 µg/L, whereas MeDPC and DPC were quantified in 31 and 10 drinking water samples, respectively with 2.7% and 3.3% exceedance of 0.1 µg/L. These results are convergent with those from Schüle et al. (2008) who revealed frequent quantified results for these compounds among 263 drinking waters. It is worth noting that DPC presents some analytical difficulties and its LOQ was 0.2 µg/L. Thus the FQ exceeding 0.1 µg/L is underestimated for this parameter, as well as for folpel and phosmet TPs phthalic acid, phthalamic acid and phthalimide.

Phytopharmaceutical products containing terbuthylazine were recently re-approved in France. Certain TPs such as desethyl-terbuthylazine, hydroxy-terbuthylazine and desethyl-hydroxy-terbuthylazine are regularly monitored through regulatory monitoring. However, EFSA reports the possible presence of other less well-known metabolites identified with the acronyms LM1 to LM6 (European Food Safety Authority 2011). Only a few recent studies have confirmed, like ours, the presence of LM2, LM5 and LM6 in ground waters in Switzerland and in ground and drinking waters in Italy (Kiefer et al. 2019, Polesello et al. 2017).

Table 1  
Results obtained for drinking water

Compounds	FQ > 0.1 µg/L	Max (µg/L)	LOQ (µg/L)
Chlorothalonil R471811	34.1%	2.000	0.020
Metolachlor ESA	13.0%	3.100	0.005
Metazachlor ESA	5.0%	1.500	0.020
Chlorothalonil R417888	3.7%	0.310	0.020
Alachlor ESA + Acetochlor ESA	3.3%	1.800	0.010
DPC	3.3%	9.800	0.200
Phthalic acid	3.0%	1.100	0.200
MeDPC	2.7%	1.800	0.010
Dimethachlor CGA369873	2.3%	0.460	0.010
DEA	2.0%	0.150	0.010
DEDIA	2.0%	0.210	0.020
Phthalamic acid	1.3%	1.100	0.200
Terbutylazine LM6	1.0%	0.260	0.020
Phthalimide	1.0%	1.900	0.200
Flufenacet ESA	0.7%	0.800	0.005
<b>Metolachlor</b>	0.7%	0.210	0.005
<b>Bentazone</b>	0.7%	0.210	0.005
Chlorothalonil R182281	0.7%	0.200	0.005
<b>Flufenacet</b>	0.7%	1.200	0.005
Flufenacet OXA	0.7%	0.400	0.010
Saccharine	0.3%	0.260	0.020
Terbumeton-desethyl	0.3%	0.230	0.005
<b>Metazachlor</b>	0.3%	0.290	0.005
Terbutylazine-desethyl	0.3%	0.130	0.005
<b>Terbutylazine</b>	0.3%	0.110	0.005
<b>Boscalid</b>	0.3%	0.310	0.005
<b>Active substances - Transformation products</b>			

Compounds	FQ > 0.1 µg/L	Max (µg/L)	LOQ (µg/L)
Epoxyconazole	0.3%	0.150	0.005
Dimethachlor OXA	0.3%	0.430	0.050
Terbutylazine LM2	0.3%	0.190	0.050
<b>Active substances - Transformation products</b>			

Figure 6 focuses on the most quantified ASs and TPs. It summarises the extent of concentrations measured for ASs and for the sum of the produced TPs. In all cases, with the exception of flufenacet, concentrations of TPs were higher than concentrations of associated ASs. Concerning flufenacet, it cannot be ruled out that other TPs, such as TFA, may be present. Clearly, the findings shown in Fig. 6 illustrate the importance of monitoring TPs, which are more frequently detected and in higher concentrations than the corresponding AS.

In this study, the absence of ASs was regularly observed, whereas their TPs were measured at high concentrations. This can be explained by the very low to moderate half-lives (i.e. from a few days to a few weeks) of active substances such as chlorothalonil, chloridazon, metolachlor and metazachlor. These results are consistent with EFSA's peer review of the pesticide risk assessment of these substances (European Food Safety Authority 2008, 2011, 2018, 2023).

### 3.3. Raw water and drinking water balance

The aim of this work was not to study the elimination of pesticides in drinking water treatment plants (DWTP). Further sampling and investigations (understanding of treatment processes) would have been necessary to assess the behaviour of molecules. However, through simultaneous sampling in raw and tap water, an overall estimate was generated. As a first state, it is important to underline that TPs are already formed in raw water, prior to any treatment. No production of TPs during water treatment was observed, while a moderate treatment capacity by DWTPs (Figure S3 and Table 2), with higher FQ in raw water compared to drinking water, can be assumed.



Table 2  
Overall removal efficiency of ASs and TPs

AS or TP	LOQ (µg/L)	XlogP3	n RW	n DW	Overall removal efficiency
<b>Prosulfocarb</b>	0.005	3.9	16	1	94%
Dimethenamid ESA	0.005	0.9	57	15	73%
2-hydroxy-atrazine	0.010	0.1	64	18	71%
<b>Bentazone</b>	0.005	2.8	46	14	69%
<b>Flufenacet</b>	0.005	3.6	19	6	68%
<b>Metolachlor</b>	0.005	3.1	52	18	65%
<b>Chlorotoluron</b>	0.005	2.4	16	6	62%
<b>Metazachlor</b>	0.005	2.7	26	11	57%
<b>Terbuthylazine</b>	0.005	3.1	21	9	56%
Chlorothalonil R182281	0.020	2.5	20	9	54%
Metolachlor CGA 368208	0.010	0.9	34	16	52%
2-hydroxy-terbuthylazine	0.005	-0.4	42	20	51%
DIA	0.010	1.1	23	11	51%
Saccharin	0.020	0.9	33	16	51%
Chlorothalonil SYN507900	0.005	2.6	17	9	46%
Desethyl-terbuthylazine	0.010	2.1	17	10	40%
Metazachlor ESA	0.020	1	81	48	40%
Metolachlor NOA	0.050	2.6	35	21	39%
Alachlor ESA + Acetochlor ESA	0.010	1.8	60	37	37%
DEA	0.010	1.5	102	63	37%
<b>Atrazine</b>	0.005	2.6	74	46	37%
MeDPC	0.010	-0.2	49	31	35%
Metolachlor OXA	0.020	2.5	52	34	33%
Dimethachlor ESA	0.005	0.8	44	29	33%
DEDIA	0.020	-0.1	51	34	32%
Metazachlor OXA	0.020	2	39	26	32%

AS or TP	LOQ (µg/L)	XlogP3	n RW	n DW	Overall removal efficiency
DPC	0.200	-0.3	15	10	32%
Flufenacet ESA	0.005	1.1	27	18	32%
Terbutylazine LM6	0.020	0.1	22	15	30%
Chlorothalonil R417888	0.020	1.1	92	64	29%
Sedaxane CSCD465008	0.010	0.4	17	12	28%
Dimethachlor CGA 369873	0.010	0.8	93	75	18%
Chlorothalonil R471811	0.020	0.3	183	171	5%
Metolachlor ESA	0.005	1.4	170	159	5%

Overall, it can be observed that ASs (in bold) revealed generally lower concentrations in drinking water than in raw water. Prosulfocarb, bentazone, flufenacet, metolachlor, chlorotoluron, metazachlor and terbuthylazine are less polar than TPs and seem to be removed through DWTPs at rates of 59–94% (Figure S2).

On the other hand, for TPs such as chlorothalonil R471811 and metolachlore ESA, poor efficiency of DWTPs was demonstrated (5%), consistent with polarity, and therefore high mobility of these compounds, as reflected in findings reported by Kiefer et al. (2020).

Concerning chlorothalonil or metolachlor TPs, the most frequently quantified compounds, only advanced processes such as reverse osmosis or activated carbon filtration could display some effectiveness (Gustafson et al. 2003, Kiefer et al. 2020, Verstraeten et al. 2002).

Most purification treatment of water in France implements a simple disinfection step (by chlorination) that is recognised to be inefficient to degrade these TPs. However, some compounds could be reactive to chlorine and likely to degrade in drinking water networks or form organo-chlorinated by-products (Pinkston and Sedlak 2004). This is particularly the case for compounds with amine functions, such as DPC, MeDPC and chlorothalonil R471811. This reaction may induce an apparent efficiency of DWTPs, as we occasionally observed in our study. This transformation is likely to occur more frequently in drinking water distribution networks with increasing contact time with chlorine and may require further work. The fate of pesticides and TPs in DWTPs has recently been taken into account through a guideline from ECHA and EFSA (European Chemicals and European Food Safety 2023) and will gradually be integrated into EFSA assessment of pesticides.

Atrazine, banned for over 20 years, is still today the AS most often quantified in drinking water. Moderate removal efficiency is observed for atrazine TPs, and these results are in line with observations from Guillon et al. (2019) who demonstrated elimination of these metabolites with clarification and granular activated carbon treatment.

## 4. Conclusions

This work established for the first time in France an extensive inventory of contamination by pesticide TPs and ASs in drinking waters. With more than 600 samples collected over two years and nearly 100 000 results available, population exposure to pesticides through water consumption could be assessed, even though it may be necessary to track trends over time for compounds with the highest concentrations.

In this type of study, one of the difficulties is the lack of availability of certain commercial analytical standards. This issue was addressed through supply of standard solutions from industrial companies.

Among the 157 TPs and ASs of interest, 89 were quantified at least once. Both ground water and surface water are contaminated by these compounds. The frequencies of quantification were relatively similar in raw water and tap water, which seems to point to poor efficiency of most DWTPs.

TPs are generally more frequently quantified than the corresponding ASs, which confirms the value of focusing on them and not only on the parent compound. Among TPs, chlorothalonil R471811 and metolachlor ESA were the most frequently quantified compounds, with more than 50% quantification in drinking water. It is worth highlighting that the most frequently quantified metabolites generally correspond to predicted scenario according to EFSA evaluation.

To our knowledge, some TPs, such as dimethachlor CGA369873, as well as chlorothalonil R471811 and R417888, were monitored for the first time in drinking water in France in this study. Concentrations exceeding the regulatory quality standard of 0.1 µg/L were observed in more than one of three drinking water samples for chlorothalonil R471811.

Our research also highlights the presence of TPs several years after the parent compounds were withdrawn from the market and illustrates their strong persistence in water systems. More broadly, through this study, the need for more integrative and systematic monitoring of soils and aquatic compartments is underlined, to sustain the characterisation and understanding of pesticide pressure on water resources, especially ground waters, as requested to better characterise the exposome.

Furthermore, the results of this study illustrate the need for an iterative approach to surveillance (regulatory surveillance as well as surveillance by water suppliers) and allow prioritisation of work for health safety risk assessment. This work also revealed the need for a better understanding of the effects of chlorine on certain compounds, and to explore the fate of these compounds in distribution networks. Additional research is underway to assess the efficiency of DWTPs, and to better assess seasonal variations.

Finally, this work advocates for the need to change the paradigm by switching from a posteriori monitoring to early-stage preventive monitoring of TPs from newly approved substances, as Sjerps et al. (2019) did in drinking water sources in the Netherlands.

## **Declarations**

## **Competing interests**

The authors declare no competing interests

### **Ethical Approval**

Not applicable

### **Consent to participate**

Not applicable

### **Consent to publish**

Not applicable

## **Funding**

The authors declare that no funds, grants, or other support were received during preparation of this manuscript. The authors have no relevant financial or non-financial interests to disclose.

## **Authors contributions**

The study was conceptualized and designed by Laure Pasquini, Sophie Lardy-Fontan and Christophe Rosin. Material preparation, data collection and analysis were performed by Laure Pasquini. The first draft of the manuscript was written by Laure Pasquini. and Sophie Lardy-Fontan and Christophe Rosin commented on previous versions of the manuscript. All authors read and approved the final manuscript.

## **Acknowledgments**

This study was supported by the French Ministry of Health. We would also like to thank the departmental and regional Ministry of Health personnel (respectively Délégation Territoriale and Agence Régionale de la Santé) for their invaluable contributions to this work by sampling water, as well as their helpful comments and continued support. This work was carried out through the cooperative efforts of the ANSES staff at the Nancy Laboratory for Hydrology, with a particular mention for Marie-Christelle Clavos, Guillaume Farré, Caroline Hollard, Sophie Lardy-Fontan, Jean-Sébastien Py and Christophe Rosin.

## **Data availability**

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files. Should any raw data files be needed in another format they are available from the corresponding author upon reasonable request.

## References

1. AFNOR (2016) XP CEN/TS 16800 - Lignes directrices pour la validation des méthodes d'analyse physico-chimiques, p. 62.
2. AFNOR (2017) NF EN ISO/IEC 17025 - Exigences générales concernant la compétence des laboratoires d'étalonnages et d'essais, p. 43.
3. AFNOR (2018) NF T90-210 - Qualité de l'eau - Protocole d'évaluation initiale des performances d'une méthode dans un laboratoire, p. 60.
4. Anagnostopoulou K, Nannou C, Evgenidou E and Lambropoulou D (2022) Overarching issues on relevant pesticide transformation products in the aquatic environment: A review. *Sci Total Environ* 815: 152863. <https://doi.org/10.1016/j.scitotenv.2021.152863>
5. Arp HPH and Hale SE (2022) Assessing the Persistence and Mobility of Organic Substances to Protect Freshwater Resources. *ACS Environmental Au* 2(6): 482-509. [10.1021/acsenvironau.2c00024](https://doi.org/10.1021/acsenvironau.2c00024)
6. Bach C, Boiteux V and Dauchy X (2024) Occurrence in France of 1,4-dioxane, an emerging pollutant of high concern in drinking water. <https://doi.org/10.21203/rs.3.rs-3903273/v1>
7. Bach C, Rosin C, Munoz J-F and Dauchy X (2020) National screening study investigating nine phthalates and one adipate in raw and treated tap water in France. *Environmental Science and Pollution Research* 27(29): 36476-36486. [10.1007/s11356-020-09680-6](https://doi.org/10.1007/s11356-020-09680-6)
8. Baran N, Mouvet C and Négrel P (2007) Hydrodynamic and geochemical constraints on pesticide concentrations in the groundwater of an agricultural catchment (Brévilles, France). *Environ Pollut* 148(3): 729-738. <https://doi.org/10.1016/j.envpol.2007.01.033>
9. Baran N, Rosenbom AE, Kozel R and Lapworth D (2022) Pesticides and their metabolites in European groundwater: Comparing regulations and approaches to monitoring in France, Denmark, England and Switzerland. *Sci Total Environ* 842: 156696. <https://doi.org/10.1016/j.scitotenv.2022.156696>
10. Baran N, Surdyk N and Auterives C (2021) Pesticides in groundwater at a national scale (France): Impact of regulations, molecular properties, uses, hydrogeology and climatic conditions. *Sci Total Environ* 791: 148137. [10.1016/j.scitotenv.2021.148137](https://doi.org/10.1016/j.scitotenv.2021.148137)
11. Barriuso E, Calvet R, Schiavon M and Soulas G (1996) Les pesticides et les polluants organiques des sols : transformations et dissipation. *Étude et Gestion des Sols* 3(4): 279-295.
12. Bhatti P, Duhan A, Pal A, Monika, Beniwal RK, Kumawat P and Yadav DB (2022) Ultimate fate and possible ecological risks associated with atrazine and its principal metabolites (DIA and DEA) in soil

- and water environment. *Ecotoxicol Environ Saf* 248: 114299.  
<https://doi.org/10.1016/j.ecoenv.2022.114299>
13. Bilal M, Iqbal HMN and Barceló D (2019) Persistence of pesticides-based contaminants in the environment and their effective degradation using laccase-assisted biocatalytic systems. *Sci Total Environ* 695: 133896. <https://doi.org/10.1016/j.scitotenv.2019.133896>
  14. Bonmatin J-M, Giorio C, Girolami V, Goulson D, Kreuzweiser D, Krupke C, Liess M, Long E, Marzaro M, Mitchell E, Noome D, Simon-Delso N and Tapparo A (2014) Environmental fate and exposure; neonicotinoids and fipronil. *Environ Sci Pollut Res Int* 22. 10.1007/s11356-014-3332-7
  15. Buhler DD, Randall GW, Koskinen WC and Wyse DL (1993) Atrazine and Alachlor Losses from Subsurface Tile Drainage of a Clay Loam Soil. *J Environ Qual* 22(3): 583-588.  
<https://doi.org/10.2134/jeq1993.00472425002200030024x>
  16. Buttiglieri G, Peschka M, Frömel T, Müller J, Malpei F, Seel P and Knepper TP (2009) Environmental occurrence and degradation of the herbicide n-chloridazon. *Water Res* 43(11): 2865-2873.  
<https://doi.org/10.1016/j.watres.2009.03.035>
  17. Colin A, Bach C, Rosin C, Munoz J-F and Dauchy X (2014) Is Drinking Water a Major Route of Human Exposure to Alkylphenol and Bisphenol Contaminants in France? *Arch Environ Contam Toxicol* 66(1): 86-99. 10.1007/s00244-013-9942-0
  18. Direction Générale de la Santé (2015) BILAN DE LA QUALITE DE L'EAU AU ROBINET DU CONSOMMATEUR VIS-A-VIS DES PESTICIDES EN 2013.
  19. Direction Générale de la Santé (2022) BILAN DE LA QUALITE DE L'EAU AU ROBINET DU CONSOMMATEUR VIS-A-VIS DES PESTICIDES EN 2021.
  20. Direction Générale de la Santé (2023) BILAN DE LA QUALITE DE L'EAU AU ROBINET DU CONSOMMATEUR VIS-A-VIS DES PESTICIDES EN 2022.
  21. EauFrance (2021) BNV-D Traçabilité - Données sur les ventes de produits phytopharmaceutiques.
  22. EURL (2017) SANTE/11813/2017 - Guidance document on analytical quality control and method validation procedures for pesticide residues and analysis in food and feed., p. 46.
  23. European Chemicals A and European Food Safety A (2023) Guidance document on the impact of water treatment processes on residues of active substances or their metabolites in water abstracted for the production of drinking water. *EFSA Journal* 21(8): e08194.  
<https://doi.org/10.2903/j.efsa.2023.8194>
  24. European Food Safety Authority (2007) Conclusion regarding the peer review of the pesticide risk assessment of the active substance prosulfocarb. *EFSA Journal* 5(8): 111r.  
<https://doi.org/10.2903/j.efsa.2007.111r>
  25. European Food Safety Authority (2008) Conclusion regarding the peer review of the pesticide risk assessment of the active substance dimethachlor. *EFSA Journal* 6(10): 169r.  
<https://doi.org/10.2903/j.efsa.2008.169r>
  26. European Food Safety Authority (2011) Conclusion on the peer review of the pesticide risk assessment of the active substance terbuthylazine. *EFSA Journal* 9(1): 1969.

<https://doi.org/10.2903/j.efsa.2011.1969>

27. European Food Safety Authority (2018) Peer review of the pesticide risk assessment of the active substance chlorothalonil. *EFSA Journal* 16(1): e05126. <https://doi.org/10.2903/j.efsa.2018.5126>
28. European Food Safety Authority (2023) Peer review of the pesticide risk assessment of the active substance S-metolachlor excluding the assessment of the endocrine disrupting properties. *EFSA Journal* 21(2): e07852. <https://doi.org/10.2903/j.efsa.2023.7852>
29. European Union (2020) Directive (EU) 2020/2184 on the quality of water intended for human consumption., pp. pp. 1-62, *Official Journal of the European Union L 435*, 23 December 2020.
30. Farlin J, Gallé T, Bayerle M, Pittois D, Köppchen S, Krause M and Hofmann D (2018) Breakthrough dynamics of s-metolachlor metabolites in drinking water wells: Transport pathways and time to trend reversal. *J Contam Hydrol* 213: 62-72. <https://doi.org/10.1016/j.jconhyd.2018.05.002>
31. Froger C, Jolivet C, Budzinski H, Pierdet M, Caria G, Saby NPA, Arrouays D and Bispo A (2023) Pesticide Residues in French Soils: Occurrence, Risks, and Persistence. *Environ Sci Technol* 57(20): 7818-7827. [10.1021/acs.est.2c09591](https://doi.org/10.1021/acs.est.2c09591)
32. Gourcy L, Baran N and Vittecoq B (2009) Improving the knowledge of pesticide and nitrate transfer processes using age-dating tools (CFC, SF6, 3H) in a volcanic island (Martinique, French West Indies). *J Contam Hydrol* 108(3): 107-117. <https://doi.org/10.1016/j.jconhyd.2009.06.004>
33. Guillon A, Videloup C, Leroux C, Bertin H, Philibert M, Baudin I, Bruchet A and Esperanza M (2019) Occurrence and fate of 27 triazines and metabolites within French drinking water treatment plants. *Water Science and Technology: Water Supply* 19(2): 463-471. [10.2166/ws.2018.091](https://doi.org/10.2166/ws.2018.091)
34. Gustafson DI, Carr KH, Carson DB, Fuhrman JD, Hackett AG, Hoogheem TJ, Snoeyink VL, Curry M, Heijman B, Chen S, Hertl P and Van Wesenbeeck I (2003) Activated carbon adsorption of chloroacetanilide herbicides and their degradation products from surface water supplies. *Journal of Water Supply: Research and Technology - AQUA* 52(6): 443-454. [10.2166/aqua.2003.0041](https://doi.org/10.2166/aqua.2003.0041)
35. Guzzella LM, Paolis AD, Bartone CR, Pozzoni F and Giuliano G (1996) Migration of Pesticide Residues from Agricultural Soil to Groundwater. *Int J Environ Anal Chem* 65: 261-275.
36. Halbach K, Möder M, Schrader S, Liebmann L, Schäfer RB, Schneeweiss A, Schreiner VC, Vormeier P, Weisner O, Liess M and Reemtsma T (2021) Small streams–large concentrations? Pesticide monitoring in small agricultural streams in Germany during dry weather and rainfall. *Water Res* 203: 117535. <https://doi.org/10.1016/j.watres.2021.117535>
37. Harmon O'Driscoll J, Siggins A, Healy MG, McGinley J, Mellander PE, Morrison L and Ryan PC (2022) A risk ranking of pesticides in Irish drinking water considering chronic health effects. *Sci Total Environ* 829: 154532. <https://doi.org/10.1016/j.scitotenv.2022.154532>
38. Hintze S, Glauser G and Hunkeler D (2020) Influence of surface water – groundwater interactions on the spatial distribution of pesticide metabolites in groundwater. *Sci Total Environ* 733: 139109. <https://doi.org/10.1016/j.scitotenv.2020.139109>
39. International Organization for Standardization (2019) ISO 21253-1:2019 - Qualité de l'eau – Méthodes d'analyse de composés multi-classes – Partie 1: Critères pour l'identification de

- composés cibles par chromatographie en phase gazeuse ou liquide et spectrométrie de masse, p. 60.
40. Jorfi S, Rahim F, Rahmani AR, Jaafarzadeh N, Ghaedrahmat Z, Almasi H and Zahedi A (2021) Herbicide Residues in Water Resources: A Scoping Review. *Avicenna Journal of Environmental Health Engineering*.
  41. Kiefer K, Bader T, Minas N, Salhi E, Janssen EML, von Gunten U and Hollender J (2020) Chlorothalonil transformation products in drinking water resources: Widespread and challenging to abate. *Water Res* 183. 10.1016/j.watres.2020.116066
  42. Kiefer K, Müller A, Singer H and Hollender J (2019) New relevant pesticide transformation products in groundwater detected using target and suspect screening for agricultural and urban micropollutants with LC-HRMS. *Water Res* 165. 10.1016/j.watres.2019.114972
  43. Kolpin DW, Battaglin WA, Meyer MT, Schnoebelen DJ and Kalkhoff SJ (2004) Pesticide degradates: Monitoring and occurrence.
  44. Lapworth DJ, Baran N, Stuart ME, Manamsa K and Talbot J (2015) Persistent and emerging micro-organic contaminants in Chalk groundwater of England and France. *Environ Pollut* 203: 214-225. 10.1016/j.envpol.2015.02.030
  45. Lopez B, Ollivier P, Togola A, Baran N and Ghestem J-P (2015) Screening of French groundwater for regulated and emerging contaminants. *Sci Total Environ* 518-519: 562-573. <https://doi.org/10.1016/j.scitotenv.2015.01.110>
  46. Mahai G, Wan Y, Xia W, Wang A, Shi L, Qian X, He Z and Xu S (2021) A nationwide study of occurrence and exposure assessment of neonicotinoid insecticides and their metabolites in drinking water of China. *Water Res* 189: 116630. <https://doi.org/10.1016/j.watres.2020.116630>
  47. Masiá A, Campo J, Vázquez-Roig P, Blasco C and Picó Y (2013) Screening of currently used pesticides in water, sediments and biota of the Guadalquivir River Basin (Spain). *Journal of Hazardous Materials* 263: 95-104. 10.1016/j.jhazmat.2013.09.035
  48. Menger F, Boström G, Jonsson O, Ahrens L, Wiberg K, Kreuger J and Gago-Ferrero P (2021) Identification of Pesticide Transformation Products in Surface Water Using Suspect Screening Combined with National Monitoring Data. *Environ Sci Technol* 55(15): 10343-10353. 10.1021/acs.est.1c00466
  49. Morvan X, Mouvet C, Baran N and Gutierrez A (2006) Pesticides in the groundwater of a spring draining a sandy aquifer: Temporal variability of concentrations and fluxes. *J Contam Hydrol* 87(3): 176-190. <https://doi.org/10.1016/j.jconhyd.2006.05.003>
  50. NAÏADES database (2024) Données sur la qualité des eaux de surface.
  51. Nikolaou S, Efstathiou P, Tiggiridou M, Arabatzis N, Piera Y and Aletrari M (2017) Monitoring of Pesticides in Drinking, Surface and Ground Water of Cyprus by Liquid-Liquid and Solid Phase Extraction in Combination with GC/MS and UPLC/MS/MS. *Journal of Water Resource and Protection* 9(10). 10.4236/jwarp.2017.910077



52. Novak S, Portal JM, Morel JL and Schiavon M (1998) Pesticide movement through the soil and dynamic of transfer by water - Mouvement des produits phytosanitaires dans le sol et dynamique de transfert par l'eau, pp. 119-132.
53. Papadakis EN, Vryzas Z, Kotopoulou A, Kintzikoglou K, Makris KC and Papadopoulou-Mourkidou E (2015) A pesticide monitoring survey in rivers and lakes of northern Greece and its human and ecotoxicological risk assessment. *Ecotoxicology and Environmental Safety* 116: 1-9. [10.1016/j.ecoenv.2015.02.033](https://doi.org/10.1016/j.ecoenv.2015.02.033)
54. Pinkston KE and Sedlak DL (2004) Transformation of Aromatic Ether- and Amine-Containing Pharmaceuticals during Chlorine Disinfection. *Environ Sci Technol* 38(14): 4019-4025. [10.1021/es035368l](https://doi.org/10.1021/es035368l)
55. Polesello S, Valsecchi S, Rusconi M, Mazzoni M, Sala A, Longoni O and Rusconi M (2017) DIFFUSIONE E VALUTAZIONE DI RISCHIO DI LM6, METABOLITA NON CLORURATO DELLA TERBUTILAZINA, NELLE FALDE ACQUIFERE/DISTRIBUTION AND RISK ASSESSMENT OF LM6, DECHLORINATED METABOLITE OF TERBUTHYLAZINE, IN GROUNDWATER. *Ingegneria dell'Ambiente* 4: 131. [10.14672/ida.v4i2.1144](https://doi.org/10.14672/ida.v4i2.1144)
56. Sarker A, Shin WS, Masud MAA, Nandi R and Islam T (2024) A critical review of sustainable pesticide remediation in contaminated sites: Research challenges and mechanistic insights. *Environ Pollut* 341: 122940. <https://doi.org/10.1016/j.envpol.2023.122940>
57. Schuhmann A, Gans O, Weiss S, Fank J, Klammler G, Haberhauer G and Gerzabek MH (2016) A long-term lysimeter experiment to investigate the environmental dispersion of the herbicide chloridazon and its metabolites—comparison of lysimeter types. *J Soils Sed* 16(3): 1032-1045. [10.1007/s11368-015-1311-3](https://doi.org/10.1007/s11368-015-1311-3)
58. Schüle E, Mack D, Schüler S and Wieland M (2008) Polar pesticide-metabolites in drinking and mineral water, European Pesticide Residue Workshop 2008.
59. Sjerps RMA, Kooij PJF, van Loon A and Van Wezel AP (2019) Occurrence of pesticides in Dutch drinking water sources. *Chemosphere* 235: 510-518. <https://doi.org/10.1016/j.chemosphere.2019.06.207>
60. Slaby S, Le Cor F, Dufour V, Auger L, Pasquini L, Cardoso O, Curtet L, Baudoin J-M, Wiest L, Vulliet E, Feidt C, Dauchy X and Banas D (2022) Distribution of pesticides and some of their transformation products in a small lentic waterbody: Fish, water, and sediment contamination in an agricultural watershed. *Environ Pollut* 292: 118403. <https://doi.org/10.1016/j.envpol.2021.118403>
61. Syafrudin M, Kristanti RA, Yuniarto A, Hadibarata T, Rhee J, Al-Onazi WA, Algarni TS, Almarri AH and Al-Mohaimed AM (2021) Pesticides in Drinking Water-A Review. *Int J Environ Res Public Health* 18(2). [10.3390/ijerph18020468](https://doi.org/10.3390/ijerph18020468)
62. Teyssere R, Barron E, Baldi I, Bedos C, Chazeaubeny A, Le Menach K, Roudil A, Budzinski H and Delva F (2023) Pesticide Exposure of Residents Living in Wine Regions: Protocol and First Results of the Pestiprev Study. *Int J Environ Res Public Health* 20(5). [10.3390/ijerph20053882](https://doi.org/10.3390/ijerph20053882)

63. Ulrich U (2022) Pesticides and Their Transformation Products: Transport, Ecotoxicity and Retention, Christian-Albrechts-Universität zu Kiel.
64. Valsecchi S, Mazzoni M, Rusconi M, Polesello S, Sala A, Longoni O and Rusconi M (2017) Spread and risk assessment of LM6, a non-chlorinated metabolite of terbuthylazine, in groundwater (Diffusione e valutazione di rischio di LM6, metabolita non clorurato della terbutilazina, nelle falde acquifere). *Ingegneria dell'Ambiente* 4(2): 131-141.
65. Verlicchi P and Ghirardini A (2022) *Handbook of Environmental Chemistry*, pp. 225-249.
66. Verstraeten IM, Thurman EM, Lindsey ME, Lee EC and Smith RD (2002) Changes in concentrations of triazine and acetamide herbicides by bank filtration, ozonation, and chlorination in a public water supply. *Journal of Hydrology* 266(3-4): 190-208. 10.1016/S0022-1694(02)00163-4
67. Vulliet E, Berlioz-Barbier A, Lafay F, Baudot R, Wiest L, Vauchez A, Lestremau F, Botta F and Cren-Olivé C (2014) A national reconnaissance for selected organic micropollutants in sediments on French territory. *Environmental Science and Pollution Research* 21(19): 11370-11379. 10.1007/s11356-014-3089-z

## Figures

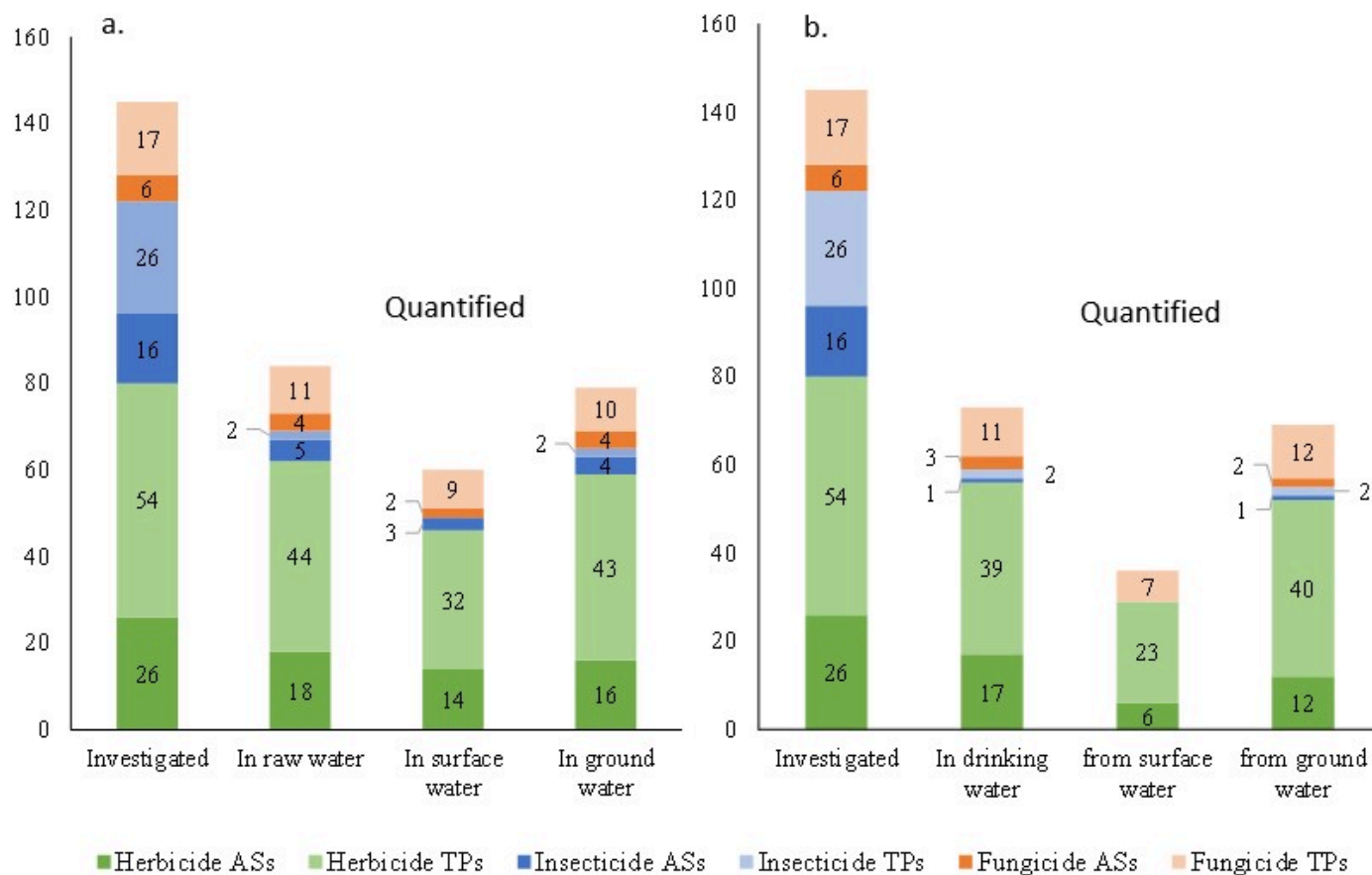


Figure 1

Number of compounds investigated and quantified in raw waters (a) and drinking waters (b), depending on the type of pesticide use.

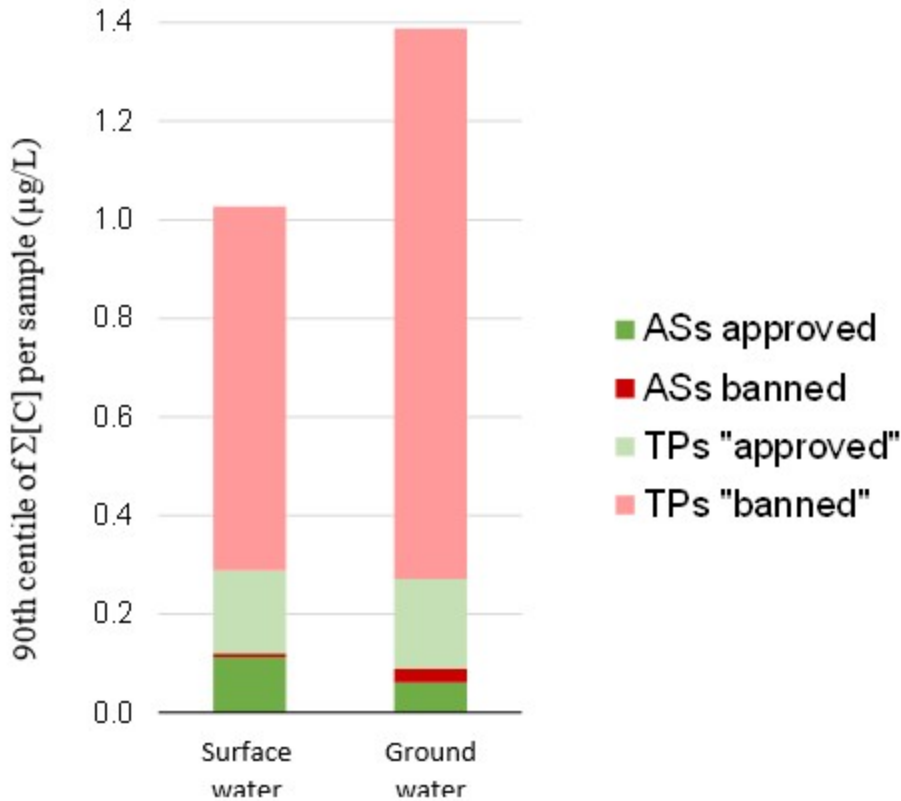


Figure 2

90<sup>th</sup> percentile of the sum of substances, in concentration, per sample according to their type (AS or TP), their regulatory status (approved or banned), and the type of water (surface water or ground water).

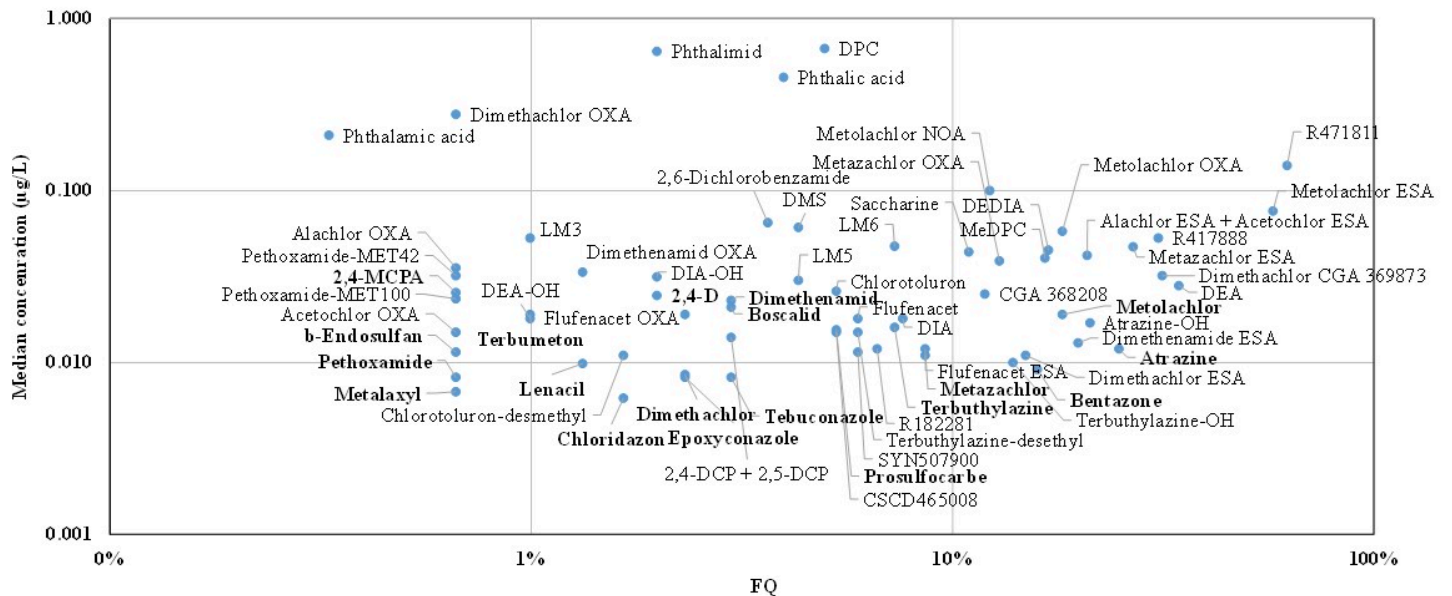


Figure 3

Median concentrations of target compounds in raw water compared to frequencies of quantification.

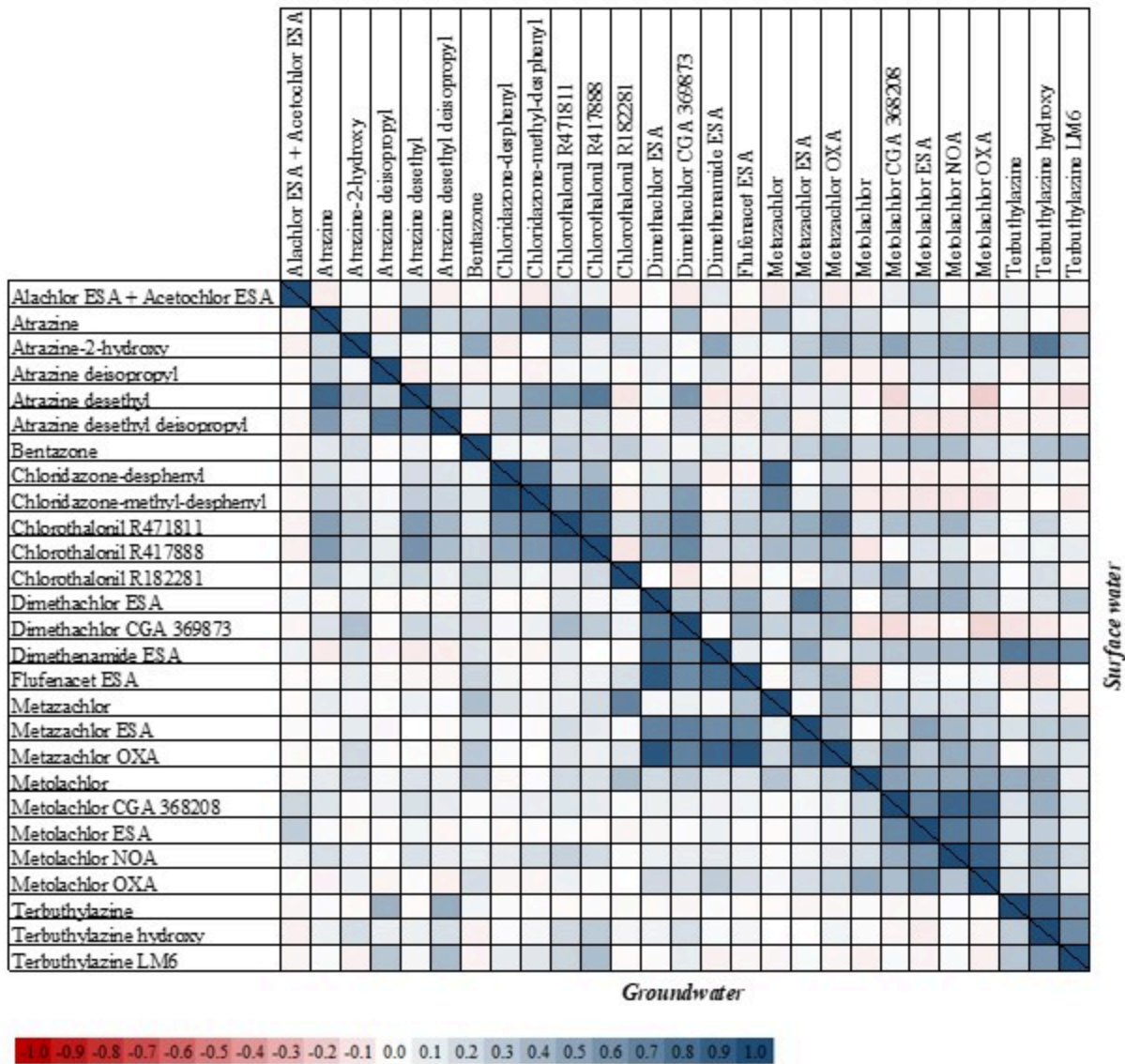
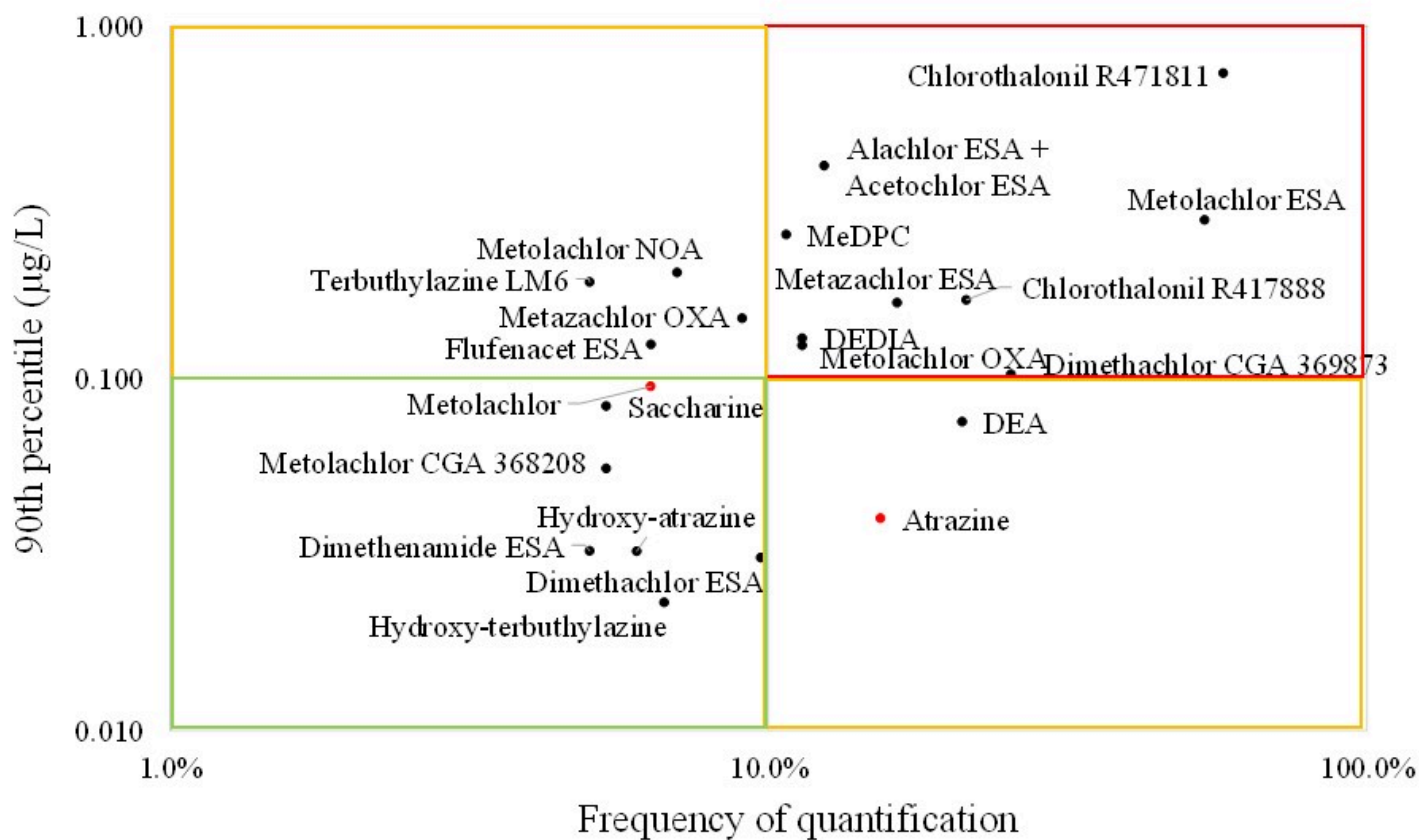


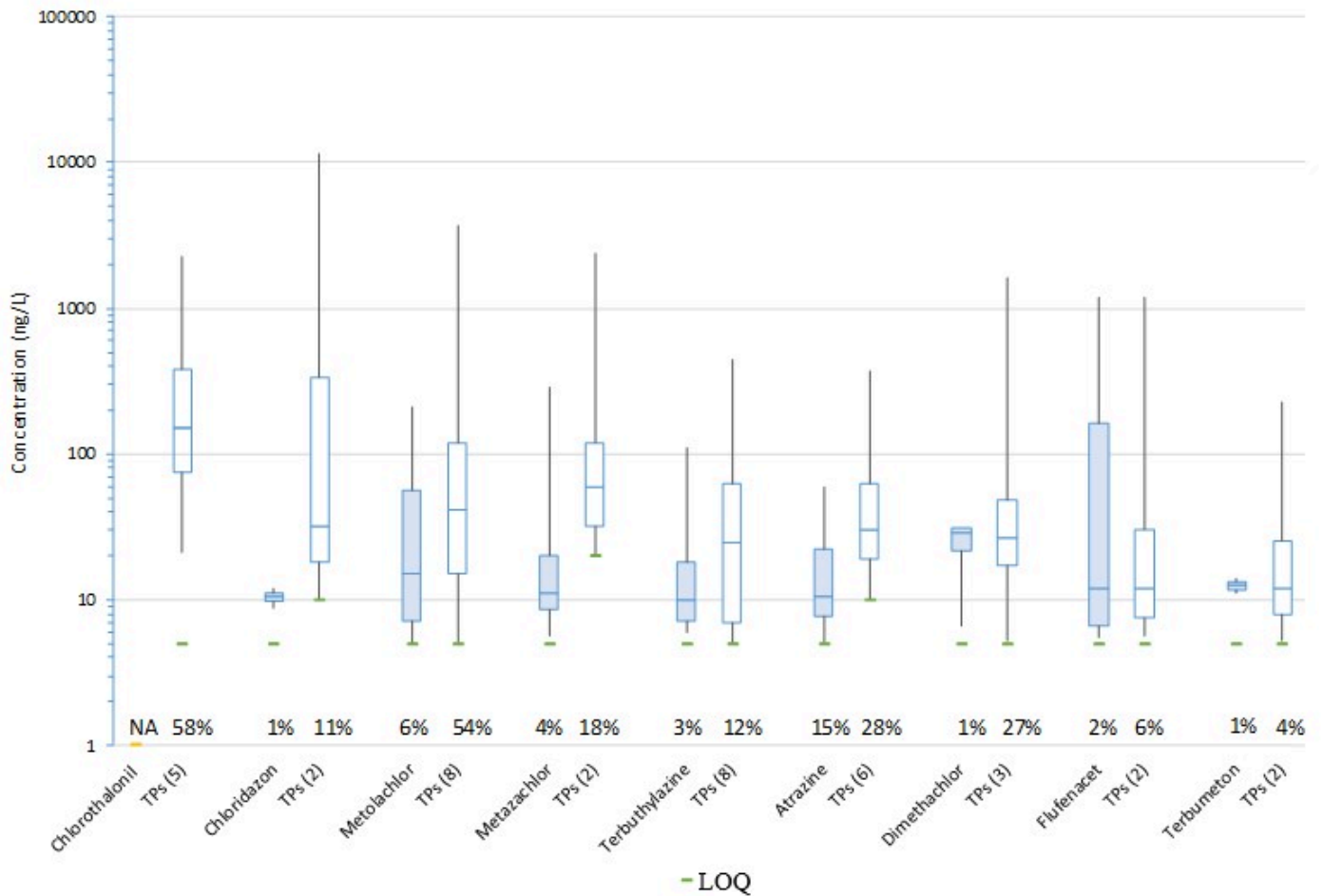
Figure 4

Pairwise correlation between pesticide concentrations quantified in ground water and surface water.



**Figure 5**

90<sup>th</sup> percentile of the concentration of compounds quantified in more than 5% of drinking waters versus frequency of quantification. ASs are represented by red dots.



NA – not analysed

**Figure 6**

Concentrations of ASs compared to the sum of TP concentrations from a same AS in all drinking water samples (the number of TPs is indicated in parentheses). Boxplots define medians, first and third quartiles, and maximum and minimum concentrations. LOQs are shown in green and frequencies of quantification are given on the x axis.

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [FigureS1BNVDDData.docx](#)
- [FigureS2FQflogP1.docx](#)
- [FigureS3FQRWDW.docx](#)
- [TableS1compoundsandmethodperformances.docx](#)
- [TableS2analyticalmethods.docx](#)