Multiyear and seasonal global indicators for French surface waters contamination by WFD substances

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Abstract:

This study offers an unprecedented valuation of the French surface waters WFD chemical monitoring dataset, covering 100 substances (metals, industrial and POPs compounds, PPP and biocides active substances, combustion residues) measured monthly on 4000 sites of the 6 main continental river basins, during 12 years (2009-2020). The concentration data were first made comparable through an original process removing the bias induced by the space-and-time heterogeneity of the monitoring labs performance, to gather a reference workable set of monthly contamination indicators. These were then used to display the substances’ seasonal and interannual timeseries, revealing, e.g., the succession of PPP active substances contamination peaking periods in the 6 basins, or the long-term trends of the concentrations of the various chemicals, sometimes evidencing insufficiencies in the monitoring performance. These statements are put in regard of the knowledge of the substances ban, restriction or reduction measures, to assess how streams’ chemical quality responds to them. Additionally, the observed features and their variations over the years are discussed in terms of changes in their usages, product substitution, emission sources, and linked to environmental processes like runoff, river dilution and physicochemical conditions. We provide some original statements and interpretation on Glyphosate and AMPA wide-scale data inter-relation, and some light is cast on the efficacy of the recent national policies restricting pesticides use in populated areas. For PPPs, our water contamination indicators were compared to tonnage data. We assessed their degree of linear relationship, which we propose to quantitatively express through a substance specific basin-to-river contamination coefficient. The interannual variations of this coefficient appear as nicely correlated to the changes in the water contamination seasonal patterns. We were able to describe and validate the dependency of this coefficient to the molecular properties of the substances, conferring some capabilities for predicting the relative environmental risk induced by non-yet monitored compounds. We finally discuss the relevance of the developed indicators to complement the national chemical pollutants management system currently in place.

Key words: Water Framework Directive (WFD), River basin, Chemical Monitoring, Pollution indicators, Pesticides, Trace elements, Industrial pollutants, Organic contaminants, Surface waters, Trend analysis, Seasonal analysis, Pesticides transfer.
Multiyear and seasonal global indicators for French surface waters contamination by WFD substances

1.1. BACKGROUND AND OBJECTIVES

The Water Framework Directive 2000/60/EC was implemented in France legislation since 2004. For surface waters, it includes the management of “priority substances” and “priority hazardous substances” (PS and PHS, which both define the chemical status of the waterbodies) and regionally-defined “river basin specific pollutants” (RBSP), which contribute to the ecological status), through six-year river basin management plans (called SDAGE in France), associated with dedicated “monitoring programs” (which will be utilized in the present study), as well as “programs of measures” that aim at reducing the anthropogenic pressures threatening the waterbodies.

The quality status of the WFD waterbodies is assessed and reported at European level only every 6-years cycles, which is a very low frequency. Moreover, the substances assessed as well as the Environmental Quality Standards (EQS) used to assess them may change at every cycle. Finally, as stated by the recent Fitness Check Evaluation of the Water Framework Directive (Vermeulen 2019), the “one-out-all-out” principle may mask progress on individual substances, as the good status gets impaired as soon as a single parameter exceeds its EQS. For all these reasons, the WFD status (ecological or chemical) is not in itself a relevant indicator to show the progress obtained through the implementation of the WFD.

Nevertheless, the implementation of the WFD has required significant financial resources, and as such it is a legitimate societal need to have robust indicators to demonstrate the effectiveness of the measures implemented.

Several specific WFD environmental objectives are assigned for the chemical pollutants, namely:

- Maintaining or reaching the good status or good potential for all waterbodies, i.e. having there all substance concentrations under their respective Environmental Quality Standards (EQS) values.
- Ensuring that those of these chemicals with accumulative behavior do not significantly increase in sediment and/or relevant biota
- Progressively reducing pollution from PS and ceasing or phasing out emissions, discharges and losses of PHS.

This last objective is regulatorily verified through the establishment, regular updating and reporting of an inventory of emissions, discharges and losses of all priority substances. This exercise, however, turns out to be very difficult when it comes to have all the involved emission factors reliably mirroring the changes in the driving forces over the years, for all the significant pollution routes, mobilizing very varied sources of data (measured or theoretical) of diverse robustness. This issue is not specific to France, and in 2018, the European Environmental Agency stated poorly comparable data, and that only little information could be gleaned from the WFD emissions inventory (Whalley 2018).

For phytopharmaceutical products, also commonly called plants protection products (PPP), an important predictor of the associated chemical pressure is the French national sold tonnage bank (BNV-d), which provides at various spatial scales the quantity of active substances sold on an annual basis. These data are essential for the WFD inventory of pesticides emissions. They are also a basic component for the French phytopharmaceuticals management plan Ecophyto.
The WFD sediment/biota monitoring of accumulative substances is in place in France, but its spatial and
temporal frequencies are limited (typically one measurement each year), and concerns only a limited number of
substances. Some developments have been achieved recently to optimize the contamination trend
determination methodology in river bed sediment and suspended particulate matter (SPM) samples (Yari 2019).
However, the system is not adapted to the pooling of multiple sites at a given date, as the method refers to some
normalization factors proper to each measurement site in order to account for the interannual variation of matrix
parameters such as sediment granulometry or organic carbon content. Yet, examples of interannual trend
derivation supported by sediment, SPM and biota sampling are progressively developing, either based on
specimen bank infrastructures or on the compilation of monitoring timeseries (Rüdel 2017, Munschy 2019), but
always relying on relatively limited number of samples or sites.

A very significant sediment-based study led in France along the main fluvial corridors has to be highlighted in
this context: the Interpol project, which aimed at reconstructing the polychlorobiphenyls (PCBs) and metallic
pollutions over a very extended time frame, using data from sediment archives and monitoring of surface
sediments started in the 1980s, and informing on chemical pressure dynamics back to 1945 (Dendeviel 2020a,
2020b, 2022a). The obtained general statement for several geographical clusters in France is that for
polychlorobiphenyls (PCBs), and several metals (Cd, Cu, Hg, Pb and Zn), a significant temporal decrease in
levels occurred from the 1960s to the 2010s for most river sections studied, with several of the metals ultimately
reaching values close to the natural regional geological background levels. The observed overall improvement
in sediment quality was linked to several factors over time: (1) the influence of regulations on discharges and
potential source reduction, (2) the increased efficiency of wastewater treatment, and (3) socio-economic
changes that have affected the industrial/metallurgical sector (de-industrialization, ca. -30% in France during the
period 1990-2010). A synthesis of the derived widescale upstream-downstream and 60 years variations in
concentrations was elaborated (Dendeviel 2022b). Due to the internal variability of the available data, the
significant temporal changes for the derivation of trends were only displayable at a time resolution of decades.
This is quite relevant for evidencing the historical dynamics of these contaminations, but inadequate to assess
the progress brought by the WFD since its recent effective implementation in terms of reduction measures in the
various hydrographic districts, as the first programs of measures were engaged in 2009.

THE ADDED VALUE OF THE WFD SURFACE WATER MONITORING FOR MULTIYEAR ANALYSIS

By contrast, the surface water column quality monitoring of WFD chemicals has been running extensively in
France since 2009, on several thousands of sites and about 100 substances. Importantly, this monitoring is
performed on a monthly timestep basis, which offers much finer diagnosis capabilities than the yearly BNV-d
PPP tonnage figures, or sediment/biota WFD data.

One central purpose of the present work will thus be to appraise and evidence to which extent this monitoring
can complement and support this assessment of the progressive reduction in emission, discharge or loss of
WFD chemicals.

To our knowledge, only very few comparable multi-compounds and long-term approaches of the freshwater
column contamination have been undertaken at such large spatial scale. One noticeable related study, though
more restricted in terms of spatial and chemicals perimeters, was recently reported regarding the multiyear
trends (2001-2016) of the Polycyclic Aromatic Hydrocarbons (PAHs) contamination of the river Elbe in Germany,
which used the WFD data to assess and interpret the change in the emission sources of these compounds (Li
2019).

Regarding PPP active substances as measured in surface waters, an important pioneering work was performed
to assess and interpret the multiyear trends (7 to 17 years, from 1990 up to the mid 2000's) of the contaminant
loads for 14 herbicides carried at 7 monitoring sites of the River Rhine (Bach 2012). The work was oriented
toward the identification of the driving factors inducing load reduction, pointing out the product consumption as
the primary cause, but also demonstrating that other contributions, including mitigation measures, could be
statistically evidenced, though in a limited set of situations.

In continental France, 6 water agencies are in charge of producing and organizing the monitoring data for all
water quality elements, aquatic ecosystems and pressure assessments. For this they call on a number of entities
producing data from water and aquatic-environment monitoring systems. Two surveillance programs are now
issued, having covered the six years cycles 2009-2015 and 2016-2021. The water agencies regularly report the
progress in the WFD chemicals management over their territories, the waterbodies status being a central
criterion in this respect. The WFD chemical status is only assessed every six years and relies on the ‘one out all
out’ principle, meaning that a water body is in good status only if all substances meet their environmental quality
standard. Thus, this indicator is relevant as a goal to achieve, but can’t be used to appropriately show annual
progress and assess trends.

In this context, there is room for evidencing in a harmonized manner the overall trends and temporal features of
the French rivers’ contamination by each of these WFD chemicals since the beginning of the first surveillance
programs, and to propose and validate for these datasets some common indicators which could be used to
monitor globally these substances. These indicators would also indirectly reflect the associated pollution drivers
and chemical pressures, would it be agriculture, industry, consumers activities, or emission from legacy pollution
persisting in the environment. They would not refer centrally to the EQS compliance, and provide insight on the
changes in the chemicals pressure even for substances or situations with no chemical-related WFD status
specific stake.

In this line, the current study has set itself as a goal to develop some methodologies to process the now long-
term river contamination 2009-2020 time-series for these substances. More specifically, the following objectives
were pursued:

- Explore and propose non-biased and wide-scale aggregated indicators usable on the long run at the
  national or main basins scales, referring to a single, simple and transparent computation process
  applicable to all substances, in order to assess changes in WFD substances sources, uses and aquatic
  impact (including seasonal insights)
- Reveal and interpret global surface water contamination trends, which could help assessing the WFD
  emission reduction objectives, and more generally the efficacy of banning or mitigation policies.
- Explore predictors for the substance-specific basin-to-river transfer intensity
- Express some specificities for the six main French river basins with respect to the aquatic impacts of
  these chemicals.

In Part I, we provide details on the study parameters (chemicals, samples, basins characteristics, data sources),
and describe the specific monitoring data processing, as well as the building of aggregated indicators that will
support the following results.

In Part II, we share the information revealed by our indicators concerning the seasonal, interannual and risks
aspects related to WFD metals, industrial compounds and persistent organic pollutants (POPs).

Parts III to plant protection products (PPP) and biocide active substances. It details the obtained information and
associated implications regarding seasonal or interannual water contamination variations, and risks
benchmarking in the various basins.

Part IV synthetizes the trend analysis carried out in Parts II and III.

Part V proposes a simple conceptual model to support the quantitative assessment and the prediction of PPP
active substances surface water contamination indicators.

Finally, Part VI summarizes and discusses the whole set of results and proposes some application and follow-
up perspectives.

I.2. CONSIDERED WFD CHEMICALS

GROUPING OF CHEMICALS

This study accounts for 100 substances, representing the vast majority of the parameters considered in mainland France to contribute to the assessment of the surface waterbodies chemical and ecological status. These comprise 7 metallic trace elements, 1 metalloid (Arsenic), 4 PAHs, 30 industrial chemicals - including 6 highly volatile organic compounds HVOCs, 9 brominated flame retardants (BFR), 2 alkylphenols, 1 phthalate plasticizer (DEHP), 3 BTExs (Benzene, Toluene, Xylene) and 1 fluorinated organic compound (PFOS) - , 6 biocide product active substances, and 53 substances related to PPP chemical components, i.e. active substances, and the Glyphosate’s degradation product AMPA.

69 of them are PS or PHS that define the EU surface waterbodies chemical status, for which EQS have been set through the WFD, as well as some emission suppression or reduction objectives. Regarding their EQS, we made the choice to retain the latest annual average EQSs for inland surface waters listed in the EU Commission proposal for the amendment of the WFD issued in October 2022 (EU Commission staff 2022). For metals, however, because the most recent EQSs require to implement some bioavailability correction which we will not consider in our study, we opted for the original values listed in the initial version of the EQS directive 2008/105/EC, which do not include this bioavailability aspect.

The remaining 31 substances are RBSPs, identified at the national or main hydrographic basin scales, together with their EQS, whose values are defined at the national scale (French Ministry of Ecology 2010).

For the sake of the present study, these compounds are grouped by chemicals groups, listed in the tables of Appendix A, together with their EQSs. We also provide in the table dedicated to active substances of PPPs, and for those substances which did receive authorized agricultural use during the studied timeframe 2009-2020, the water/organic carbon partition coefficients Koc, which will be useful in the following. These Koc values were extracted from the PubChem and PPDB web portals, which collate literature values. We report here for each PPP active substance the average, minimum and maximum Koc values found in these two references.

Finally, we append to these tables the values of the “cut-off threshold”, proper to our study, and whose definition will be given in section I.5.

Note that some chemicals were used as both plant protection and biocidal products, so they are present in both groups.

MARKET AUTHORIZATIONS OF THE WFD SUBSTANCES

PPPss

Among the 53 WFD PPP active substances, only 26 have been authorized, at least partially, during the study period 2009-2020. This number may be compared to the about 300 active substances authorized in France as PPP ingredients and subject of a fee for diffuse pollution, in regard of their potential environmental and health impacts. Their number of authorized PPP active substances had increased by 46% between 2008 and 2017 (Salomon 2020).
The 27 WFD PPP active substances that were subject to exclusion from the market ahead of the present study period 2009-2020 includes:

- Herbicides Alachlor, Atrazine, Simazine and Trifluralin
- Fungicides Hexachlorobenzene and Pentachlorophenol.
- All the here considered insecticides, except Cypermethrin, Imidacloprid and Chlorpyrifos-ethyl

In addition, several of the authorized 26 PPPs active ingredients monitored through the WFD in France have been banned and/or substituted during the here studied timeframe (see Table 21 in Appendix A).

This resulted either in some net stops, or in drastic reductions of the sales for the products containing these substances. It was then an opportunity to examine how the river contamination evolved after such situations.

The earliest PPP bans for WFD substances during the studied decade occurred in 2016, for the herbicides Aminotriazole and Isoproturon.

The insecticide Chlorpyrifos-ethyl was banned from the market in France in 2016, except for the spinach growing. It was then excluded from approval at the UE level in 2019. The use of the neonicotinoid Imidacloprid in France as a PPP had been forbidden for open field applications from September 2018 until the latest date of our study (December 2020).

### Other chemicals

Apart from the PPP active substances mentioned above, many of the other WFD substances had been banned before 2009, such as the Chloroalcanes C10-C13, the flame retardants of the BDEs family, or the antifouling agent TBT. The flame retardant HBCDD has been banned since 2011. PFOS and DDTs have already been restricted in the EU for more than 10 years, under the EU’s Persistent Organic Pollutants (POPs) Regulation.

The insecticides Aldrine, Endrine, Isodrine, Heptachlor, Endosulfan, Lindane \( \gamma \)-HCH and its by-products \( \alpha \) and \( \beta \)-HCH, as well as the fungicide Hexachlorobenzene (HCB), the solvent Hexachlorobutadiene (HCB) and the multi-purpose chemical Pentachlorobenzene are all covered by the Stockholm Convention for elimination.

Several halogenated hydrocarbons like Trichlorobenzene, Trichloroethylene, Tertrachloroethylene, Carbon tetrachloride are subject to restricted uses under Reach. So does 4-Nonylphenol, the plasticizer DEHP, the PAH Benzo(a)-pyrene, and most of the WFD metals, with the exception of Copper.

### I.3. STUDY TERRITORIES

#### ANNUAL RAINS IN METROPOLITAN FRANCE OVER THE 2009-2020 PERIOD

Effective rains over the whole metropolitan France varied between 121.5 and 278.8 billion of m\(^3\) respectively in 2017 (driest year) and 2013 (wettest year) during the 2009-2020 period, with a mean value of nearly 200 billion of m\(^3\). 2019 was the second driest year, while 2014 and 2018 were almost as humid as 2013.

The rainfall levels, particularly in late winter/spring, greatly influence the risk of fungal infections of different crops and thus the volumes of fungicides applied.

On a general standpoint, higher precipitations are expected to favor the basin-to-rivers pollutant load transferred at the local scale, but in the meantime, they also increase the river waterflows, and thus the pollutant dilution downstream. The total budget in terms of contaminant concentrations in rivers is thus difficult to predict from the
sole consideration of hydrological conditions.

At the global scale of mainland France, the months with the highest mean precipitations are November, October, December and May.

Human concentration in urban areas generates chronic pollutant discharges, the impact of which is moderated thanks to appropriate facilities (the majority of the population uses collective sanitation). However, there are accidental discharges or discharges in rainy weather. As an example, in urban areas, these discharges during rainy weather represent 760 million m$^3$ per year in the Seine-Normandie basin due to impermeable surfaces (French ministry of ecology 2006). Thus, direct urban discharges per rainy weather represent 30 to 50% of dry weather discharges from wastewater treatment plants on an annual scale.

The artificial agricultural drainage, which can significantly impact the transfer dynamics of PPP compounds from the soils to the surface water, is a common practice in France, covering around 10% of the agricultural area (Vincent 2020). It concerns important areas over the whole territory, with a distinctly smaller relative coverage for the RMC basin.

RIVER BASINS CHARACTERISTICS

There are 6 main river basins in metropolitan France, which are very diverse in term of natural, economic and environmental characteristics (cf. Figure 1 and Table 1).

Figure 1: Map of the continental France, including Corsica, displaying the borders of the 6 main French river basins considered in the study. Also pictured, the artificial (red), agricultural (yellow) and seminatural (green) areas as obtained from Corine Land Cover in 2018.

Table 1 main characteristics of the six mainland France river basins. Data extracted from the water agencies websites and the 2010 French agricultural census. Figures are given with some uncertainty margin as these figures have evolved during the 2009-2020 period.

<table>
<thead>
<tr>
<th>Basins</th>
<th>Basin area km$^2$</th>
<th>Agricultural land area km$^2$ (2010 agricultural census)</th>
<th>% agricultural land (2010 agricultural census)</th>
<th>Population density inh Hab/km$^2$ (ref. INSEE 2018)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artois-Picardie (AP)</td>
<td>20000</td>
<td>13800</td>
<td>69%</td>
<td>239</td>
</tr>
<tr>
<td>Seine-Normandie (SN)</td>
<td>94500</td>
<td>57600</td>
<td>61%</td>
<td>198</td>
</tr>
<tr>
<td>Loire-Bretagne (LB)</td>
<td>157000</td>
<td>87900</td>
<td>56%</td>
<td>84</td>
</tr>
<tr>
<td>Adour-Garonne (AG)</td>
<td>117000</td>
<td>50300</td>
<td>43%</td>
<td>66</td>
</tr>
<tr>
<td>Rhône Méditerranée et Corse (RMC)</td>
<td>131000</td>
<td>39300</td>
<td>30%</td>
<td>130</td>
</tr>
<tr>
<td>Rhin-Meuse (RM)</td>
<td>314000</td>
<td>17900</td>
<td>57%</td>
<td>138</td>
</tr>
</tbody>
</table>
We provide for each of these six basins, in Appendix B, more details of particular interest for the interpretation of our study's results, extracted from the water agencies websites, the Guide de l'eau [https://www.editions-johanet.net/guide-de-eau-2015-2016-o20], and some characteristics of the soils trace elements composition which have been evidenced these recent years from the French soil quality measurement network (RMQS) (Arrouays 2002, Gis-sols 2011, Saby 2011, Marchant 2017).

Chemical pollution pressures upon the surface waterbodies, according to the WFD assessment.

According to the waterbodies WFD assessment performed in 2019 in each of the basins, and summarized in Table 22 (Appendix B), AP, RM and SN basins have the lowest percentage of water bodies without any significant pressure, around 5% of their water bodies, whereas at national level, this percentage is around 20%. RMC has the highest level of pressure-free water bodies (32%).

At national level, the pressures putting at risk the largest number of waterbodies are the diffuse pollutions pressures and the hydromorphological pressures.

The diffuse pollution pressures and the point pollution pressures are the most relevant for this study. More precisely, diffuse pressures due to agricultural activities are significant for 45% of surface water bodies (between 68% of the waterbodies for Rhin-Meuse and 30% for Rhône Méditerranée Corse and around 50% for the 4 other basins). More than 20% of the waterbodies are also concerned by diffuse pollution due to atmospheric deposition (89% of the waterbodies for Artois-Picardie, 66% for Seine-Normandie, 28% for Loire-Bretagne, 0% for Adour-Garonne and Rhône Méditerranée Corse).

PPP USES AND FRENCH PPP SALES DATA BANK

PPPs are used for the prevention, control or elimination of undesirable organisms (plants, animal, bacteria...). They can be classified as herbicides, fungicides, insecticides and molluscicides, depending on their activities and species they fight.

Before the first WFD monitoring exercise, in 2005, cereals accounted in France for 40% of national pesticide consumption, including 60% of fungicides and 35% of herbicides (Aubertot 2005). Arable crops are not the only ones to be heavy consumers of pesticides. Viticulture and arboriculture also consume a lot of it with an average of twenty treatments applied annually due to the significant vulnerability of the vines, in particular to fungal diseases, and the significant use of herbicides such as glyphosate to weed the rows and inter-rows in the vines.

The evolution of agriculture has been accompanied by an increasing diversification of the pesticides placed on the market. These increases are particularly notable for rapeseed, beets, potatoes and corn. Regarding straw cereals, the trends are more contrasted depending on the region. Beetroot and soft wheat are the crops with typically the greatest diversity of molecules used. In 2017, 478 different active substances were sold in France, 285 of which were classified hazardous for the environment or the health (Salomon 2020).

Typical applications of the here studied WFD herbicides involve agricultural uses on cereals (maize, wheat, barley...), sunflowers, peas, vegetables, vines, arboriculture, aromatic plants, as well as non-agricultural functions (road sides, green spaces and lawns, gardens). For fungicides, it is rather about protecting cereals, fruits, vegetables, vines, ornamental vegetation, treatment of seeds, livestock building. The three WFD insecticides having received authorized use during the studied period had very wide ranges of applications.
Since 2009, the BNV-d (National Bank for the Sales of Phytopharmaceutical Products by approved distributors) has collected and processed sales declarations of phytopharmaceuticals products by distributors under the Fee for Diffuse Pollution.

A dedicated internet portal (https://ventes-produits-phytopharmaceutiques.eaufrance.fr/), open on registration, gives access to the sold tonnage figures at various scales, including the six French main river basins considered in our study. The tonnage data used in the present work, relating to the authorized active substances listed in Table 15 and to their sales over the 2009-2020 timeframe, were extracted from this process in June 2022.

It should be noted that the database of distributors who declare on the BNV-d was not constant over the 2009-2015 period and has grown. Thus, the active substances sold for seed treatments were not included in the BNV-d until 2012.

The national sales distribution for different authorized herbicides, fungicides and insecticides monitored through the surface water WFD control in the 2009-2020 period is compiled in Appendix E (Figure 147). Glyphosate was the most sold substance whatever the year. This substance has been used for agricultural weed control and for the maintenance of urban and industrial spaces.

There are strong variations between the years for some substances such as Isoproturon, Aminotriazole, Oxadiazon, Chlorpyrifos-ethyl. As we have seen previously, these substances have been banned for a few years, hence the drop in the sales.

Overall, the monitored PPP active substances used for surface waterbodies WFD status assessment represented one third of the total tonnage sold in metropolitan France during the 2009-2019 period (excluding substances allowed for organic farming and biocontrol). Removing the Glyphosate, this fraction falls to 21%.

Broken down by main usages, the WFD PPPs active substances represented:
- 53% of the total herbicides' tonnages, and 36% without considering Glyphosate
- 16% of insecticides
- 3% of the fungicides/bactericides. This low percentage is largely explained, however, by the fact that Copper and Sulphur-derived products are also accounted as fungicides, with heavy tonnages associated.

Tonnages spatial distribution of the WFD PPP active substances

Looking specifically at the WFD PPP active substances monitored in surface waters, and reporting their sold tonnages (kg) to the main basins areas (km²) where they were sold, we obtained along our study period 2009-2020 the broken down trends displayed in Appendix E (Figure 148 to Figure 151), respectively for insecticides, fungicides, herbicides except Glyphosate, and the last for all herbicides. For these PPPs considered as groups of active substances, AP and SN basins appear as the biggest consumers related to their surface areas. This holds true when only agricultural land areas are considered (cf. Table 1), the four others basins exhibiting some similar overall sales to area ratios.

The most contrasted behavior concerns the WFD insecticides, whose sales sharply increased at the beginning of the period, then stabilized or decreased from 2013 onward, with dramatic dropping until 2019. These variations are in fact mainly driven by the sales of Cypermethrin, Imidacloprid and Chlorpyrifos-ethyl. The sharp increase of reported sale in 2012 is likely imputable to the fact that only from this date the BNV-d started to account for active substances sold for seed treatments. On the other hand, the strong decrease observed at the end of the period is related to the fact that the uses of Chlorpyrifos-ethyl and Imidacloprid have been strongly restricted respectively in 2017 and 2018.
For WFD herbicides (among which Glyphosate represents more than 50% in tonnage) and fungicides, no major change in the sales occurred between 2009 and 2017, followed by a sharp increase in 2018, a drastic drop in 2019, and then a distinct recovery in 2020. The singular increase in 2018, also met for fungicides, is explained by advance purchase by farmers before the increase in the fee for diffuse pollution which occurred in France in 2019. This induced some clear rebalancing lowering in sales in 2019. Another contribution to the sales drop in 2019 was the entry into force of the prohibition of the use of the majority of PPPs by non-professional gardeners.

The BNV-d portal also gives access to the active substance tonnages sold specifically for non-agricultural purpose (use authorized for gardening), at the national scale. Figure 152 in Appendix E delivers the variations of the non-agricultural tonnages fraction along the studied period, for the concerned WFD active substances, i.e. 8 herbicides, and one fungicide. The Aclonifen timeseries was incomplete, and data were apparently missing for some compounds, like Aminotriazole. Nevertheless, as can be seen, this fraction is not negligible for many substances, including the heavy tonnage of Glyphosate. The general trend is a significant drop of these sales. This can be explained by the historically increasing efforts of many French local territories to guarantee pesticide-free environment to their population, relayed by the French Labbé law (French Presidency 2014), which enacted in 2017 and 2019 the prohibition the use of chemical pesticides, respectively in populated areas, and for amateur gardening.

I.4. MONITORING AND STATUS ASSESSMENT OF WATER BODIES UNDER THE WFD

In mainland France, WFD monitoring is the responsibility of the six water agencies, which outsource monitoring to laboratories and engineering offices. The monitoring system, whose description is already available publicly (Eaufrance 2013), comprises two main parts which are relevant for our study:

> Surveillance monitoring network (RCS), which is a permanent network to assess the overall status (qualitative and quantitative) of surface and groundwater. The goal of this network is to monitor the evolution of the status of waterbodies, with a long-term monitoring of water bodies chosen to be representative of the diversity of natural characteristics and anthropogenic pressures in the basin

> Operational monitoring network (RCO), which is a temporary network to assess the status of water bodies at risk of not achieving the environmental objectives and to monitor their evolution in response to the programs of measures

To give a sense on the network dimension, the official French WFD reporting of 2016, which dealt with the first WFD cycle (2009-2015), indicated, for mainland France, 4092 surface water monitoring sites, including 3365 RCO sites, 1883 RCSs, among which 1177 in both networks. We provide a brief about these official French WFD surveillance networks in the Appendix C of the present paper.

Finally, monitoring data are stored in national open databanks, i.e. ADES for groundwater, Naïades for the quality of rivers and lakes, HYDRO for river discharges and QUADRIGE for littoral waters. Data storage must be carried out in compliance with the formats and specifications stipulated by Sandre, the National service for water-data and reference-dataset management, in order to ensure consistency and ease of use by all stakeholders. The data are then made available to the public on the www.eaufrance.fr website.
WATER SAMPLING AND MEASUREMENT PROCESS ATTACHED TO THE STUDIED MONITORING DATASET.

The 2009-2020 measurement dataset which has been used for the purpose of the present study was obtained from the analysis of water column samples collected at the surface water sites of the continental France WFD RCS and RCO networks (including Corsica). For the vast majority of substances (>95%), the samples were collected once a month. The sample collection, transportation, conditioning and analysis protocols are pursuant to the national Ordinance of January 2010 (updated) defining the river basins WFD surveillance programs (French Ministry of Ecology 2010).

More specifically, the analyzed water phase was the whole water (including suspended particulate matter, SPM) for organic chemicals, and the dissolved fraction (filtered at 0.45µm) for inorganic compounds. This aspect is of importance when it comes to data interpretation, as the quantity of organic compounds adsorbed to SPM increases with the compound’s hydrophobicity, and the SPM concentration itself is expected to increase with the river discharge, with seasonal implications (Meybeck 2012, Ody 2022).

The WFD requirement for the limits of quantification values (LoQs) is to target one third of the annual average EQS values. However, this performance was not always achieved for all the substances and all the tenders during the 2009-2020 period. Meanwhile, various monitoring labs also very commonly outreached this limit, improving the sensitivity beyond the minimal requirement, to some variable extents over the study period.

Accredited compliance with methods and protocols is a key factor in obtaining reliable data. To ensure data quality, the analyses must be carried out by laboratories according to the rules contained in the regulations, notably the October 2011 national ordinance concerning certification conditions for laboratories carrying out analyses in the field of water and aquatic environments (French Ministry of Ecology 2011). The procedure for laboratories covers the entire data-production process, i.e. sampling (collection, conditioning, transport and storage of samples), analysis of a parameter or a biological quality element, and transmission of the results.

I.5. ESTABLISHING A REFERENCE DATASET

The workflow of our study is summarized in Figure 2. The three first boxes aim at setting the scene by extracting and processing the WFD chemical monitoring data of the Naïades national surface waters databank (www.naiades.eaufrance.fr), in order to build a reference set of time-and-space-comparable monthly contamination indicators. These steps are extensively described in the first part of the present work.

The three last boxes refer to the analysis of these monthly indicators, in terms of seasonal or interannual timeseries, regarding either metals, polycyclic aromatic hydrocarbons (PAHs), industrial compounds and other persistent organic pollutants (POPs) - in Part II of this work -, or phytosanitary and biocide active substances, in Parts III and V of the present work.

Figure 2 : Work flow diagram of the present study.
The here used original set of WFD monitored concentration data contained 21 million items produced between 2009 and 2020 and corresponding to the above-selected 100 PS and RBSP, from the monitoring sites recorded in the Naïades surface waters databank (metropolitan France). Data relating to the overseas territories were not processed in this study, given the difference in chemical pressures and the low number of data available compared to mainland France.

Concentration data extraction, application of filters, and quality criteria

The Naïades databank is based on the Sandre repository. This repository is made up of technical specifications and lists of free-to-use codes, describes the procedures for exchanging and banking water quality data in France. Thereby, the Sandre guarantees the interoperability of information systems relating to water quality.

To select the useful data for this study, different filters were applied:

- The period: 2009 - 2020
- Sites from Control Network (RCS), Operational Control Network (RCO) and combined RCS/RCO in metropolitan France (cf. Figure 3). 4121 sites were considered. The 6 main river basins where each site is located are identified.
- Water samples and, depending on the chemical, either the whole sample for organic compounds (i.e., with suspended matter) or the aqueous fraction for metals and Arsenic (i.e., filtered samples).
- Data that are qualified “Correct”. Indeed, during data collection, there may be a number of errors that may impact the result, this is why a quality code is associated to each analysis.
- For the data labelled as “quantified”, only those data corresponding to concentrations above the limit of quantification (LoQ), or lower than LoQ but higher than the limit of detection (LoD), were used.
- All values lower than LoD or equal to 0 were discarded.

Moreover, quality filters have been applied. Outliers, i.e., values that deviated significantly from the distribution were removed so as not to bias the results. Depending on the chemical, concentrations larger than 25 to 75 times the 99th percentile of the concentrations were considered as outliers. These outliers probably were input errors, unit errors... A check on the consistency of the data was made. For example, if an analysis was qualified as “unquantified data” and the result was greater than the LoQ, then this value was discarded.

Figure 3: Geographical distribution of the considered 4000 WFD surface water monitoring sites from the mainland France RCS and RCO networks.

Description of the resulting initial study dataset

Once filtered, the dataset contains more than 16 million pieces of data over the 12 years. 8% of these data had been quantified. The distribution of the resulting annual data among the 6 main continental France basins can
be found in Table 23 in Appendix C. The number of data items can vary significantly from one year to another, due to the monitoring calendars of the six corresponding basins' agencies. These yearly variations are however buffered when considered at the national scale. The Rhin-Meuse basin has no data for the year 2020 because the data was missing extraction from the Naïades database at the time of extraction.

We provide in Figure 143 and Figure 144 (Appendix C) the distributions of the number of monitoring sites as functions of, respectively, the number of measured substances and the number of concentration measurements, for each of the six main basins, over the 2009-2020 period. From Figure 143, it turns out that 90% of the 4121 sites had measurements recorded for more than 60 out of the 100 considered substances, and almost half of them have records for 95 of these substances. RMC, AP and SN are those basins where the majority of the substances is being measured on the largest fractions of the sites.

The standardly expected maximal number of measurements for any given compound measured at the monthly WFD frequency, upon the studied 12 years period, is $12 \times 12 = 144$, i.e. 14 400 measurements for the 100 considered substances. Figure 144 tells us that, in reality, only 30% of sites did cumulate more than 5 000 measurements on the period, and only 200 sites had more than 10 000 measurements, mainly in the SN basin. This is because only a fraction of the sites is measured every year, and also because some substances had their monitoring started several years after 2009. Moreover, the measurement frequency minimal requirement for RCO sites is 4 per year, not 12.

THE NEED FOR ADDITIONAL FILTER PROCESSING TO GENERATE A FINAL STUDY DATASET RESTRICTED TO SPACE AND TIME COMPARABLE DATA

Regarding the concentration values extracted from the WFD monitoring datasets, it is important to recall that according to the WFD, and more specifically to the Article 5 of the Commission Directive 2009/90/EC of 31 July 2009 laying down technical specifications for chemical analysis and monitoring of water status, the concentration measurements leading to non-quantification, i.e. when concentration is below the LoQ, are assigned to the value $\frac{\text{LoQ}}{2}$.

It results from this that the average of multiple measurements of a substance will depend on the LoQ values, and this all the more that the rate of quantification is low, with $\frac{\text{LoQ}}{2}$ as a lower limit value for concentrations. As we saw above, 92% of the measurements are non-quantified results, highlighting the importance of managing properly the knowledge of LoQ values when pooling or comparing these data.

Overcoming the issue of the space and time heterogeneity of the chemical analysis capabilities

Variations in the analytical capacity of monitoring laboratories

As explained above, due to the assignment of non-quantified measurement to the $\frac{\text{LoQ}}{2}$ value, the range of observed concentration values primarily depend on the limits of quantification (LoQ) of the labs performing the analyses. Two LoQ-related aspects complicate the comparability of the generated data for a given chemical parameter:

- First, the river basins' water agencies ordering the analyses often choose different labs offering
different LoQs, preventing a direct comparison of data generated a given year in various regions.

- Second, the LoQ performance of a given lab is subject to improvement over time, so that the direct comparison of the mean quantified values generated at several years of interval is not possible.

All along the 2009-2020 period, the monitoring labs have made evolving their analytical methods, improving their LoQs in order to reach the assigned sensitivity criterion (LoQ< EQS/3), and further to gain competitive assets in the frame of the consecutive water agencies’ tenders for WFD surveillance.

Figure 4 expresses the global improvement over the years of the 75th and 25th percentiles of the LoQs annual means, all parameters included, for each of the 6 basins. It demonstrates the important scattering that has existed between among the basins in terms of analytical performance. For parameters with higher LQs (75th percentiles), the years 2011-2012 show a clear improvement in 5 of the basins. For the lower LQs (25th percentiles), the most significant improvements were slower and occurred at different times in different basins.

As illustrations, we provide in Appendix F (Figure 153) a breakdown of this improvement for the considered herbicides, insecticides and metals. Typically, one order of magnitude of improvement over the 2009-2020 was observed for chemical groups like insecticides or metals.

Figure 4: Interannual variation of the 25th (dashed lines) and 75th (continuous lines) percentiles of the mean annual LoQs of the 100 considered WFD compounds in the 6 basins.

Figure 5 quantifies the scattering of the LoQ values across the various substances and all the mainland France monitoring sites, as well as the tightening of values towards improved analytical sensitivities, over the considered period 2009-2020: the displayed curves account for the ratios between the worst annual LoQ values of the parameters, obtained a given year in one of the six basins, and the best ones obtained in 2020 for the same parameters. The top curve (90th percentiles), for instance, expresses that for 10% of the parameters, these ratios were often maintained greater than a factor 70 until 2017, and were still left at best around 10 in 2020. For the most favorable half of the parameters (50th percentiles), the ratios could be as bad as around 10 in 2009, then continuously improved after 2012 down to a value of better than 3 in 2019. In 2020, all the basins had similar performance (within a factor of 3) for 25% of the parameters, but their scattering could still exceed a factor of 10 for 10% of them (cf. last point of the 90th percentiles curve). Overall, the scattering of the LoQ values was quite significant across the study period, biasing any direct comparison of the raw concentration data at the nationwide scale.

Figure 5: Interannual variations of the LoQs distribution among the 100 considered substances at the national scale, as expressed by various percentiles (25th, 50th, 75th and 90th) of the ratio between worst and best LoQs.

Biasing incidence of the LoQ improvements on the averaged quantification rates and measured concentrations

When trying to derive the desired trend information about the actual rivers’ contamination from chemicals monitoring time-series, two types of indicators naturally stand at our disposal:

- The quantification rates (QR) (or quantification frequency), i.e. the ratio of the number of
measurements leading to actual quantification, to the total number of measurements.
- The measured concentrations, as derived from the quantified or detected measurements, would it be mean or percentile values.

However, due to the above change in the analytical performance of the monitoring labs, biasing effects are expected that could hinder the trend derivation objective. In this section we demonstrate the level of distortion which is induced on these indicators by the continuous LoQ improvements.

Quantification rates (QR)

As regards QR, one would expect by principle that it should increase as the LoQ improves, one main purpose of this improvement being precisely to increase the quantification power of the analysis. Knowing, as shown earlier, that the LoQs actually improved significantly over our studied period, this theoretical argument could be considered sufficient to disqualify the quantification rate as a relevant indicator for trend examination. It was however interesting to check the extent of the dependency of QR on LoQ changes, from an empirical standpoint.

An illustrative example is provided by Figure 6, where the consecutive mean annual QR values of the herbicide Atrazine, averaged over the whole mainland France territory, exhibit a distinct increase over time. Knowing that Atrazine was banned from any use in France since 2003 and, as already evidenced by previous studies (Gauroy 2011), one expects a continued decline of the associated contamination in French rivers. As a matter of fact, the observed growth in quantification frequency doesn’t reflect the actual increase in the contamination, but mirrors instead the improvement of the LoQs, which we did picture in the figure by plotting the inverse of the mean annual LoQs for this molecule (the lower the LoQ, the higher the quantifications). The positive correlation between both variables is apparent, with a sharp quantification increase in 2016, associated with a significant LoQ improvement at this time.

Figure 6: interannual variations of the national-scale annually-averaged quantification rates (histogram) and inverse values of LoQ (continuous curve) for Atrazine.

To check how much this situation is generalized over our studied WFD parameters, we selected a set of 24 PPPs and 16 other compounds, and determined for each of them the linear correlation coefficients $R^2$ between QR and the $1/\text{LoQ}$ variable. We also recorded the sign of the associated covariance coefficients for each of these chemicals. According to the Student statistics, the lower significance limit for $R^2$ with a 95% confidence is $R^2=0.27$, considering the 12 couples of values mobilized for each compound.

These $R^2$ values can be found in Appendix F (Figure 154 and Figure 155), as a function of the mean QR values, over the 2009-2020 timeframe, respectively for PPPs active substances, and other compounds. For a majority of compounds, mainly those with high quantification rates, including many PPP active substances, among which the Atrazine case illustrated in Figure 6, and almost all the metals, the covariance is positive (which means that their QRs are increasing over time, as $1/\text{LoQ}$ does) and the correlation is significant, expressing a possible significant dependence of the QRs on the LoQs improvement, which precludes their use as reliable indicators of the contamination trends. Only for a minority of compounds, this dependence could not be evidenced, so that no argument can be put forward against the use of quantification rates as indicators of their contamination trends. Situations with low $R^2$ could be due to the fact that the LoQ improvements were insufficient to increase their quantification rates, or because the actual decrease of the concentrations in the river counterbalances the effects of the LoQ improvements (this is likely the case for PPP active substances whose usages have strongly dropped...
down recently, like Oxadiazon, Iprodione and Linuron in Figure 154, or alkylphenols in Figure 155).

**Concentrations**

With regard to the possible use of the second type of indicators, i.e. the concentration values extracted from the monitoring datasets, it results from the WFD-pursuant assignment of the LoQ/2 value to the non-quantified results that the average of multiple measurements of a substance will depend on the LoQ values, and this all the more that the rate of quantification is low, with LoQ/2 as a lower limit value for concentrations.

This dependency is illustrated in Figure 7, where we have plotted, for various couples of substances (two herbicides, two PAHs, two alkylphenols and two metals), the consecutive values of the mean annual concentrations (2009-2020, pooling for each year the individual measurements from the whole France territory) with respect to the corresponding mean annual LoQ values. The X and Y variables have been normalized to their maximal values in order to allow a joint visualization for all these chemicals. For each couple of substances, we show two very contrasted situations: one substance whose concentrations exhibit a strong dependency on LoQs (fully colored dots), another one independent of LoQs (clear dots).

Figure 7: Correlation diagram between national scale mean annual values of concentration (y-axis) and LoQs (x-axis), both normalized to their maximum values, for 8 different WFD compounds monitored throughout the 2009-2020 period. The continuous line represents the x=y function.

For those substances with strong LoQ dependence, we can then predict that the observed trend in mean concentration time-series will be driven by the LoQ improvement over time, i.e. they will exhibit artificial or exacerbated downward trend, leading to the false or exaggerated conclusion that the water quality improves, and that the pollution sources are decreasing.

The linear determination coefficient $R^2$ between the mean annual concentrations and corresponding LoQs were displayed against the average quantification rates of the individual substances, and can be found in Appendix F (Figure 156 for some of the WFD pesticides, and in Figure 157 for some other of the here studied WFD compounds). $R^2$ values close to 1 were observed for the majority of the substances, corresponding to those substances with strong and biasing LoQ dependence, and about which no conclusion can be driven from direct observation of the mean concentrations regarding the actual river contamination trend.

Noteworthily, very tight dependence on LoQs' changes can be maintained for substances with average QRs up to 20% or more. By contrast, insignificant $R^2$ (<0.27) are observed mainly for some highly quantified compounds (10% to 80% rates), like the main geogenic metals or some widely used herbicides. For these substances only, no argument can be put forward against the direct use of their monitored concentrations to derive conclusion on the multiyear trend, as the LoQs improvement doesn't influence the measured concentration variations on a significant basis.

Intermediate $R^2$ values, typically between 0.9 and 0.3, are found for an important set of compounds with QRs in the 5% to 50% range. For them, it is not possible to conclude about the observed limited correlation with LoQs variations: it could be either some residual dependence on LoQs, or the fact that both LoQs and the actual concentrations are sharing some lessening behavior over the years. For this reason, no reliable conclusion on the river contamination trend can be obtained for these compounds from the direct observation of the interannual concentration time-series.
An illustration of the biasing downward trend distortion in the concentration time-series induced by the LoQ dependence is given by Figure 8, where we plotted the national mean annual concentrations against the sold yearly national tonnages for the two herbicides previously exemplified in Figure 7. One expects a positive correlation between applied PPP tonnage and river contamination. This is indeed observed for the less LoQ dependent times-series (Metazachlor), but the opposite behavior arises for the strongly LoQ-dependent Pendimethalin time-series, giving the false impression of less impact on rivers in spite of increasing tonnages.

Figure 8: National-scale annual means of Metazachlor and Pendimethalin measured concentrations, as a function of the corresponding sold tonnages extracted from the BNV-d databank (2009-2020).

Overall, the LoQs improvement during the 2009-2020 period hinders the direct exploitation of the measured concentrations and quantification rates time series, at serious or hardly predictable levels, for the majority of the WFD compounds. As Figure 5 showed, though progressively reaching in 2020 an improved overall consistency, the LoQs of historically monitored WFD substances were still notably evolving in the end of the 2010’s decade, and some significant discrepancies within the labs performance persist for a good part of them, suggesting the importance of correcting the LoQs variation effects for deriving trends also in the coming years. This will be repeated with equal importance each time we will have to deal with some newly monitored emerging substances included in the regulatory lists, as the labs always go through some progressive method adaptations. Another for LoQ adaptation is the possible change in the EQS values of already regulated substances, as this is about to happen for the future WFD daughter directives (COM 2022).

This situation called for some specific data processing to reliably achieve the here pursued river contamination trend derivation.

Excluding the non-comparable data: application of a “cut-off” threshold strategy

In order to derive reliable conclusion regarding the changes in waters contamination over the 2009-2020 period, it is necessary to get rid of the above-mentioned bias induced by the LoQ variations. One way to do this is to model the values of non-quantified data, according to some hypothesis on their statistical distribution (Huynh 2014, Eumont 2022).

In the present study, we opted for an alternative solution, consisting in sub-sampling the quantified data from original dataset, keeping only those values quantified over a given threshold, set common to all years and basins, but specific to each substance. Thus, we deal with a homogenous measurements’ population over the whole perimeter of our study.

In this line, a cut-off threshold value $\tau_i$ is defined for each substance “$i$”, which will be held constant whatever the year or the basin “$j$”.

For any data related to the substance “$i$”, if LoQ > $\tau_i$, the concentration data is discarded and won’t be used through the presented study.

And for the data that are not discarded, i.e. if LoQ ≤ $\tau_i$, then:

If $C_{i,j} > \tau_i$ (situation of cut-off threshold exceedance), the value of $C_{i,j}$ is used as is

If $C_{i,j} \leq \tau_i$, the value $\tau_i/2$ is used instead of the original $C_{i,j}$ value.
This halving of concentrations below the $\tau$ value was copied from the methodology for chemical quality assessment of water bodies, as specified in Article 5 of the Commission Directive 2009/90/EC of 31 July 2009 laying down technical specifications for chemical analysis and monitoring of water status. This is in order to maintain the consistency of the present study with the WFD regulatory framework.

This process is illustrated in Figure 9.

**Figure 9**: Schematic of the cut-off threshold process implementation on a theoretical concentration timeseries, picturing the situations of data exclusion ($\text{LoQ}>\tau$), concentration-value re-assignment to $\tau/2$ (quantified data $\leq \tau$), and concentration values preservation (quantified data $>\tau$).

One can consider the cut-off threshold $\tau$ as a "virtual LoQ" common to the whole time-series of a given chemical, and wherever were the samples collected. An optimal $\tau$ value is determined (see below), adapted to each substance, according to the characteristics of the corresponding measurement dataset.

It has to be mentioned that a similar approach had already been experimented in France, applied on PPP active substances only, and using measurements collected prior to the WFD RCS/RCO networks activation (Gauroy 2011). In contrast with the present study, however, this work did use a unique cut-off threshold of 0.1µg/L for all the considered compounds. And, instead of the 6 main river basins which we use for our work, the spatial scale at which the derived indicators were aggregated was the "hydro-ecoregion", i.e. 22 territories covering mainland France, and inside which the functioning of running water ecosystems at catchment scale is determined by common patterns in terms of geology, relief and climate (Wasson 2004). Interestingly, these authors tried to desegregate their indicators at even finer spatial scales, but stated that the associated loss in statistics was too important to preserve good data interpretation capabilities. The other outcomes of this preceding study will be discussed in Part III of the present work, dealing with PPP active substances.

It is also worth to be noted that our study didn’t address in a systematic way the possible effects of the change in the labs performance with respect to the measurement accuracy (which is not directly related the LoQ performance), knowing that this accuracy performance is to some extent lab-dependent, and that, for a given set of monitoring sites, different labs might have operated successively over the years. The conservation of the measurement’s accuracy for every substance over the study period is then a strong hypothesis in the frame of the presented work, founded on the fact that the WFD monitoring operators are accredited for their tasks. It is important to keep in mind, then, that the multiyear water contamination trends stated in the following will be based on this assumption.

### Determination of the concentration cut-off thresholds

A determination procedure has been automated for the above cut-off threshold $\tau$.

For a given substance, $\tau$ is tentatively assigned, as separate options, to all the consecutive values of the LoQ
in the original dataset.

Three indicators, each of them reflecting a criterion favoring the representativeness and the statistical richness of the time-series, have been identified to determine the best option, i.e. the optimal $\tau$-value:

- Indicator 1: rank of the option in regard of maximizing the number of quantified concentration data measured above the value $\tau$, with LoQ lower or equal to $\tau$
- Indicator 2: rank of the option in regard of maximizing the number of concentration data, quantified or not, with LoQ lower or equal to $\tau$
- Indicator 3: rank of the option in regard of maximizing the number of months in the 2009-2020 period with quantified data above $\tau$.

The automated search for the optimal $\tau$ consists in finding the option that optimizes the sum of these three ranks. The so-derived optimal cut-off threshold values are available in the tables of Appendix A.

Thanks to the high analytical sensitivity of the WFD monitoring data collected in the various French basins, the obtained $\tau$ values are most (3 cases out of 4) often significantly lower than the EQS values. For 26 parameters, however, the EQS were challengingly low for the monitoring labs, so that our derived $\tau$ values are greater or equal to their EQSs. This concerns 4 herbicides (Diflufenicanil, Metazachlor, Pendimethalin and Bifenox), the fungicide Cyprodynil, half of the insecticides (comprising those with authorized use Cypermethrin, Chlorpyrifos-ethyl and Imidacloprid), the biocide TBT, all the BFRs and the PFOS, 2 PAHs (BaP and Fluoranthene), and the Nonylphenol 4-NP.

Due to the heterogeneity of the LoQs between the basins, it has happened for a few substances that $\tau$ was set at values significantly lower than most of the LoQs of a specific basin. This results in having most the corresponding measurements excluded from our workable dataset, hindering the reliable trend derivation of this substance in this basin. We provide in Table 24 (Appendix D) the (limited) list of substance/basin couples concerned by this problem.

"CUT-OFF PROCESSED" DATASET: DATA REJECTED AND DATA PRESERVED THROUGH THE PROCESS

Total numbers of concentration data

After the above data processing, 13 million data items were preserved, corresponding to concentrations from 4 119 monitoring sites, i.e. only 2 sites were excluded from the above-described input database (for which 4 121 sites had been selected).

The absolute number $N_k$ of concentration data preserved each year $k$ ($k$ ranging from 2009 to 2020) after the "cutoff" data processing described above is illustrated in Figure 10, considering all the parameters. The splitting of the data for the 6 basins is also pictured. Overall, the yearly data numbers ranged from less than 600,000 in 2010 up to more than 1,600,000 in 2018, but the order of magnitude remains similar over the whole period. The Artois-Picardie basin provided significantly less data, in relation to its smaller dimension and lower number of sampling sites. The Loire-Bretagne and Adour-Garonne basins exhibited the strongest increases in data number over time.
Figure 10: Interannual variations of yearly cumulated numbers of concentration data (reassigned to $\tau/2$ or not) available after the cut-off threshold processing, in the 6 basins, 2009-2020.

Figure 11 informs us that, after the data exclusion process related to the LoQ values described above, 60 of the 100 considered substances have fit for purpose measurements left on 83% of the 4119 sites, to be compared with the no so different 90%-figure initially recorded before the data exclusion (cf. Figure 143 in Appendix C). For the remaining 40 substances, the situation is more contrasted, especially in the AG basin where only a few sites remain with valid measurements on more than 80 substances, at variance with Figure 143. This is due to the higher LoQ values observed in this basin for a significant part of the compounds, resulting in more data rejection by our cutoff processing.

Also, as Figure 12 shows, after the above-mentioned data exclusion, that almost half the sites still provide at least 2500 usable measurements, which is a situation similar to the original dataset previously depicted in Figure 144 (Appendix C). However, the set of monitoring sites left with higher number of measurements is more severely reduced: less than 20% of the usable sites have more than 5 000 comparable concentration data, compared to the 30% from Figure 144, mainly due to LoQ-related data exclusion in AG and LB basins. And almost no site is left with more than 10 000 usable measurements.

Figure 11: Distribution of the considered 4092 monitoring sites throughout the 6 basins, according to the number of substances for which they yielded data during the 2009-2020 period, after the cut-off threshold filtering.

Figure 12: Distribution of the considered 4092 monitoring sites throughout the 6 basins, according to the 2009-2020 total number of measurements per site which were preserved after the cut-off threshold filtering.

Informational richness of the concentration datasets for the various parameters and chemical groups

With the labs progressively developing their analytical methods, and some substances having been identified as PS or PHS only after the 2013 daughter WFD Directive 2013/39/EC, or some others identified as RBSP only for the 2015-2021 WFD cycle, not all the WFD parameters have been monitored with the same intensity over the studied period. Moreover, the cut-off threshold process described in §I.5 resulted in the selection of various proportions of quantified data, according to the parameter-specific LoQ variabilities and associated initial quantification rates.

The informational richness embedded in the data depends, for parameter “$i$” and year “$k$”, on the amount of “over-the-threshold” concentration data $N_{l,k}^{c>\tau i}$ among the data that were preserved after the cut-off determination process. The distribution of the $N_{l,k}^{c>\tau i}$ values can be found in Appendix D (Figure 145), for those
substances for which the mean $N_{i,k}^{C>T_i}$ exceeds 100, i.e. more than 1200 individual data for the whole 12 years chronicle. Figure 146 of Appendix D informs on the remaining substances.

The highest yearly amounts ($N_{i,k}^{C>T_i} > 1000$) are obtained for some metals, herbicides (including Glyphosate and its degradation product AMPA) as well as some PAHs. The amplitude of these numbers for a given parameter sometimes reaches several orders of magnitude, due to sometimes very few data generated at the beginning of the studied period. The second figure pictures the parameters with poorer data numbers, with one quarter of the substances showing less than 10 “over-the-threshold” data per year in average. These are mainly banned flame retardants, industrial solvents and insecticides, present in water at very low concentrations, and for which LoQ (and thus the associated cut-off thresholds) are typically insufficient to permit high detection rates. The statistical quality of the resulting chronicles will be low, possibly preventing any reliable trends determination.

The Figure 13 displays the number of parameters of each chemical group, broken down according to four classes of data richness, considering the annual means of the $N_{i,k}^{C>T_i}$ values, $N_i$: from more than 1000 to less than 10. Metals, PAHs, Biocides and Herbicides are the most informed chemical groups. Insecticides, BTEX, BFRs and HVOCs are the least ones.

**Figure 13**: Distribution, for the 100 considered substances, of the 2009-2020-averaged numbers of concentration data per year ($N_k$ mean), classified according to their value ranges (>1000, 100-1000, 10-100, <10) and their chemical groups.

### I.6. DERIVED TIME-SERIES OF MONTHLY INDICATORS, AND ASSOCIATED BASIC STATISTICAL PARAMETERS

For the sake of the present study, the month was opted as the basic time unit. This choice corresponds to the standard monitoring frequency through the WFD implementation. The monthly time-step also allows to explore the seasonal variations of the river concentrations.

A central goal for our study was then to build a time-and-space consistent nationwide dataset of monthly-defined river chemical contamination indicators, for the 100 studied WFD substances, based on the above-described individual measurements. This dataset contains indicators either related to all monitoring sites, or to subsets of sites with upper contamination profiles (higher local substance use).

**AGGREGATION OF THE DATA AT THE MONTHLY TIME UNIT**

All the data, being the number of measurements or the concentration values, were aggregated within each monthly time period “m” of each year “k” (k=2009 to 2020).

For each substance “i” and each of the six basins, the workable dataset used in this study basically contains the variables defined hereafter.

**Numbers of sites and measurement data**

The built dataset of monthly variables contains:
- The total numbers of measurements $N_{i,m}$ recorded within each consecutive month “m” of the 2009-2020 period, as well as the associated numbers $N_{i,m}^{c>\tau_i}$ of measurements yielding concentrations greater than the cut-off threshold $\tau_i$.

- The total number of sites $n_{i,m}$ with measurements on substance “i” each consecutive month “m” of the 2009-2020 period, as well as the associated numbers of sites $n_{i,m}^{c>\tau_i}$ with measurements exceeding the threshold $\tau_i$.

An examination of the full dataset showed that for 95% of the sites only one measurement was recorded per month (consistently with the WFD monitoring requirements). As a consequence, $N$ and $n$ have very close values.

- The mean values and some percentile values (50%, 95%) of all the concentrations measured during each of these months.

**Monthly rates of cut-off threshold exceedance**

Considering a given period and a given set of monitoring sites, the **rate of cut-off threshold exceedance** $\rho_i$ is simply the ratio between the number $N_{i,m}^{c>\tau_i}$ of concentration measurements of a substance “i” exceeding the cut-off value $\tau_i$, and the associated total number of measurements $N_{i}$ for this same substance.

$$\rho_i = \frac{N_{i,m}^{c>\tau_i}}{N_{i}}$$

For the present study, this quantity was calculated for every substance and each month $m$ of the 2009-2020 period, at the French metropolitan scale, and complementarily at the scales of each of the six mainland basins described in §I.3.

These compiled $\rho_{i,m}$ data are thus spatially averaged monthly values. Figure 14 exemplifies a time series of $\rho_{i,m}$ values (grey bars) for the herbicide Bentazone, covering the six basins areas.

Because the measured sites most often produced a single measurement per month, $\rho$ is also a very good indicator of the proportion of sites with concentration exceeding the cut-off threshold on month $m$.

In this sense, it characterizes the spatial extent of the exceedances.

The more a substance will be widespread over the territory, the more it will have some opportunities to contribute to some mixture effects when associated to other compounds or environmental stressors (Malaj 2014, Gustavsson 2017, Posthuma 2019, Finckh 2022, Weisner 2022). For this reason, even if it doesn’t explicitly refer to some ecotoxicological aspect, $\rho$ is a relevant indicator to contribute to the global assessment of the ecological risks associated to a substance.
Figure 14: Display of the full 2009-2020 timeseries of the national scale monthly exceedance rate $\rho$, and concentration indicators $\chi$ (mean value of the cut-off processed concentration data), $\chi^{95\%}$ (95th percentile) and $\chi^\tau$ (mean of the concentrations exceeding $\tau$), for the WFD monitored herbicide Bentazone.

Throughout the text following, the term “Exceedance” will always refer to the above-defined Cutoff threshold exceedance rate ($\rho$), unless explicitly mentioned (e.g. “EQS exceedance”).

Monthly concentration means

Considering a given set of monitoring sites, the monthly mean concentration $\chi_{i,m}$ of a substance “$i$” measured during month “$m$” stored in our present work dataset is the average of the $N_{i,m}$ concentrations $C_{i,m}(p)$ ($p$ ranging from 1 to $N_{i,m}$), keeping in mind that the $N_{i,m}^{c<\tau_i}$ pieces of data with values lower than the cut-off threshold $\tau_i$ were set to the value $\tau_i/2$ during the preliminary dataset processing step described above (cf. §0).

$$\chi_{i,m} = \frac{\sum_{p=1}^{N_{i,m}} C_{i,m}^{c<\tau_i}(p)}{N_{i,m}} \quad (2)$$

The minimum value for $\chi_{i,m}$ is then $\tau_i/2$.

Figure 14 illustrates such a mean concentrations $\chi_{i,m}$ time-series for the herbicide Bentazone (orange dots). The associated cut-off threshold is $\tau = 0.02 \, \mu g/L$, so the minimum $\chi$ values are 0.01 $\mu g/L$.

The monthly mean value $\chi_{i,m}^{\tau}$ of the sole concentration values exceeding $\tau_i$, $C_{i,m}^{>\tau_i}(p)$, which refers to a restricted number of sites where the local substance use is higher, can be calculated; from eq. ($1$) and ($2$), it is linked to $\chi_{i,m}$ and $\rho_{i,m}$ as follows:

$$\chi_{i,m}^{>\tau_i} = \frac{\chi_{i,m} - \tau_i/2}{\rho_{i,m}} + \tau_i/2 \quad (3)$$

The corresponding time series is pictured in blue diamond dots in Figure 14.

As the minimal value for $\chi$ is $\tau/2$, the varying part of $\chi$ is in fact:
\[ \chi'_{i,m} = \chi_{i,m} - \frac{\tau_i}{2} \]  

(4)

Considering equation (3), this is also written as:

\[ \chi'_{i,m} = \rho_{i,m} \cdot (\chi_{i,m}^{\tau_i} - \frac{\tau_i}{2}) \]  

(5)

Equation (5) tells us that \( \chi' \) (as well as \( \chi \)) is a complete contamination indicator, that aggregates both the variable spatial information, through \( \rho \), and the variable concentration information, through \( \chi^{\tau_i} \).

50% and 95% percentiles of concentrations

Our study database also compiles the monthly medians \( \chi^{50\%} \) and 95th percentiles \( \chi^{95\%} \) values of all the concentration data (below and above the threshold). Figure 14 illustrates a 95th percentiles time-series (black triangles curve curve).

Typically, as exemplified in Figure 14, \( \chi^{95\%} \) can be lower than \( \chi_{i,m}^{\tau_i} \), as a large part of the original set of concentrations are often situated below the \( \tau_i \) threshold.

\( \chi^{95\%} \) even remains equal to the minimum \( \tau_i/2 \) as long as less than 5% of the concentration data do exceed the cut-off threshold \( \tau_i \).

The built database also contains the monthly median and 95 percentile values \( \chi^{50\%}, \chi^{95\%} \) of the sole data exceeding the cut-off threshold (not shown in Figure 14).

Annually averaged indicators

In order to give a visual of the interannual trends, we will display in the following the variations of the annual averages of the above monthly indicators.

Each of these annual values will be the result of the above-described cutoff thresholding, the incidence of which will vary according to the LoQ changes over the years. Indeed, as compared to the number of data exceeding the actual LoQ in the original raw database values (quantified data, cf. colored upper-part of the histogram in Figure 9), the processing described in Figure 9 selects only a reduced number of concentrations data values (cut-off threshold exceedances, cf. part of the histogram bars included in the upper-right rectangle in Figure 9).

The ratio between these two numbers, i.e. \( \rho/QR \), mostly depends on how \( \tau_i \) compares with LoQs.

The whole process is illustrated in Figure 15 for the herbicide Pendimethalin, picturing both the changes in the ratio of the annually averaged \( \rho \) and the corresponding QR values, for each consecutive year of the 2009-2020 period, considering the whole mainland France monitoring sites. For the sake of qualitative comparison, the changes in the LoQs (also mean annual values) are also displayed in the figure. The cut-off threshold for this...
compound ($\tau_i = 0.02$ µg/L) is significantly lower than the average LoQ values for the first part of the period (until 2011). As explained in §I.5, concentration data acquired with LoQ > $\tau_i$ are automatically excluded from the study dataset. For Pendimethalin this resulted in about 50% of the initial data being discarded from 2009 to 2011. In 2012, the average LoQ comes close to the Cut-off threshold, which is an optimal situation, and about 90% of the quantified data are kept to contribute to the set of data exceeding $\tau_i$. From 2013 onward, the LoQ continues to improve but falls below $\tau_i$, so that more and more data are quantified, but with an increasing number of them having values below $\tau_i$, which are finally converted to the value $\tau_i/2$ through the data processing mentioned above. This means that more data are lost for feeding the number of cutoff exceedances, inducing the lessening of the plotted ratio. This doesn’t mean however that the absolute number of cutoff exceedances decreases, as the number of quantifications also increases when LoQs go down. This is illustrated in the figure by the numbers attached to the ratio curve giving the amounts of preserved cut-off exceedances every year for Pendimethalin, which reaches the range of several hundred for the end of the studied period.

Figure 15: For the herbicide Pendimethalin, display of the national-scale interannual variation of the ratio between the yearly averages of the exceedance rate $\rho$ and the original quantification rate QR (blue curve). The figures attached to this curve indicate the absolute annual numbers of measurements exceeding the cut-off threshold ($\tau=0.02$ µg/L). Also displayed in parallel, the national-scale mean annual LoQ values (black curve).

Multiyear integrated indicators

Finally, the environmental risk level associated to river contamination by the various chemicals is a central concept for WFD, and is an important way to diagnose and prioritize the environmental management of the activities taking place over the territories. In this line, our multiyear concentration dataset can readily be employed in order to establish some comparisons between the six main French river basins, and identify some regional specificities attached to the various uses or releases of the WFD chemicals over their areas.

To simplify these comparisons, we define here for the chemical \textit{i} in basin \textit{j}:

- a time-integrated contamination indicator $X_{c_{i,j}}$ gathering the available information on the spatial frequency of the river contamination (using the cut-off exceedance rate $\rho$ for that purpose)

- a time-integrated risk indicator $X_{r_{i,j}}$ gathering the available information on the spatial frequency of the river contamination (using the cut-off exceedance rate $\rho$ for that purpose), on the concentration level, as expressed through the 95th percentile value of the concentrations measured over the cut-off threshold, $\chi_{95\% > \tau}$ (cf. §0), and finally on the environmental quality standard EQS, as follows:

\[ X_{c_{i,j}} = \bar{\rho}_{i,j} \]  
\[ X_{r_{i,j}} = \frac{\bar{X}_{i,j,95\% > \tau_i}}{EQS_t} \]
With $\bar{\rho}$ and $\chi_{95\%}>\tau$ representing respectively the averages over the considered time period of the cut-off exceedance rates and 95th percentile of concentration values.

**GENERAL MEANING OF THE PROPOSED INDICATORS**

Conceptually, the indicators $\rho$ and $\chi$ simply can be viewed, respectively, as some generalization of the usually employed measured QR, and mean concentration, for those situations when the LoQs significantly vary throughout the considered dataset. Indeed, if the LoQs could have been considered as sufficiently constant, then we would simply have used $\tau = \text{Mean LoQ}$, with equations (1) and (2) leading us back to the usual quantification rate and mean concentration indicators.

The spatially aggregated indicator $\chi$ is conceptually the same that was proposed earlier by Gauroy et al. for pesticides (Gauroy 2011). It can be viewed as the substance concentration in the surface water of a fictitious "basin-representative monitoring site", representing the average contamination characteristics of all the monitoring sites of the considered territory, would it be the whole mainland France, or one of its 6 main basins. This fictitious, unrealistic site, corresponds to the one which would be exposed to the combined spatially averaged chemical pressures, associated to each of the monitoring sites catchments, for all of the here considered 100 compounds.

On the one hand, the authors are aware that such a simple average of chemical signals from various sites, sometimes corresponding to superimposed or overlapping catchment areas along the rivers, which to an unknown extent induce redundancies in the considered spatial areas, cannot claim to represent a real situation.

On the other hand, the fact remains that this resulting averaged fictitious site integrates the signals from all the considered territory, in a statistically consistent manner over the whole studied period for a given territory. This is the main required indicator’s characteristic that is looked for when trying to assess trends and variations over time, central purpose of the present work.

**I.7. SPECIFICITIES IN THE ANNUAL MONITORING CALENDARS OF THE 6 STUDIED BASINS, FOR THE VARIOUS CHEMICAL GROUPS**

In order to properly interpret the seasonal patterns of the monthly contamination indicators, a prerequisite is to understand how the various water agencies have set up the annual planning of the monitoring intensity over their territory, and how this is reflected at the scale of the mainland France.

To perform this analysis, we considered four chemical families: Arsenic and metals (8 parameters), PAHs (4 parameters), and Industrial and POPs compounds (30 parameters), and finally PPP + biocide actives substances (53 substances). For each of these families, we compiled the mean monthly number of measurements "N", as well as the mean monthly number of monitoring sites with measurements "n". This was done by averaging these numbers over all the parameters of each chemical family, the whole mainland France,
and the whole 2009-2020 timeframe. For a given month, the ratio $N/n$ may exceed 100% if several measurements are performed during this month at some of the sites.

Figure 16 to Figure 19 present, for each of chemical family, the resulting seasonal variations of $n$, as well as of the $N/n$ ratio.

**Figure 16**: Average monthly numbers $n$ of monitoring sites in mainland France providing data for a WFD industrial or a POP compound (histogram), and ratio between the monthly number of measurements $N$, and $n$ (curve).

**Figure 17**: Average monthly numbers $n$ of monitoring sites in mainland France providing data for a WFD PAH compound (histogram), and ratio between the monthly number of measurements $N$, and $n$ (curve).

**Figure 18**: Average monthly numbers $n$ of monitoring sites in mainland France providing data for a WFD trace element (histogram), and ratio between the monthly number of measurements $N$, and $n$ (curve).

**Figure 19**: Average monthly numbers $n$ of monitoring sites in mainland France providing data for a WFD PPP or biocide active substance (histogram), and ratio between the monthly number of measurements $N$, and $n$ (curve).

A common observation is that somewhat lower spatial investigation intensities are made in February, June, August and December, the highest figures being manifested in May July and November. Overall, the ratio between the number of measurements and the number of monitoring sites recorded each month is pretty constant, varying between 103 and 106%, meaning that only a limited fraction the sites were monitored more than once each month.

PAHs and PPP/Biocide active substances have somewhat higher monitoring coverage, with monthly figures varying between 800 and 1200 sites, whereas they stand between 600 and 800 for the other compounds.

For PPP and biocide active substances, distinctly higher spatial coverage of the monitoring was achieved during spring (from March to July), and autumn (September to November), with figures upper than 1000 sites being observed in average. The ratio between the number of recorded measurements and number of sites exceeds unity only by 5 or 6%, indicating that the "one measurement per month" frequency was applied in most situations.

Overall, at the national scale, the monthly variations of the monitoring intensity remain limited, so that we can expect that the spatial representativity of the seasonal analysis and associated statistics are maintained all over the year.
In all cases, only about one fourth or one fifth of the total number of the more than 4000 considered national sites are investigated in average every month, reflecting the fact that the basins monitoring networks are covered by fractions every consecutive year (rotating network strategies).

We provide, in the Appendix C of the present work, a breakdown of these data at the scales of each of the 6 basins (cf. the section there called “Specific monitoring annual calendars of each basin”).

I.8. PRELIMINARY USE OF THE PROPOSED INDICATORS FOR GLOBAL EVOLUTION ASSESSMENT

We initiate the implementation of the proposed indicators by displaying how they could answer two very generic questions about the WFD implementation in France between 2009 and 2020.

1. DID THE FRENCH SURFACE WATERS CONTAMINATION BY WFD COMPOUNDS DECREASE, GLOBALLY?

Considering the whole set of the here studied 100 WFD chemicals, the multiyear trends of both the average quantification rate (before cut-off processing) and cut-off exceedance rate are shown in Figure 20. The overall cut-off exceedance rate $\rho$ indicates, as expected from the WFD implementation, a continuous improvement/reduction of the overall river contamination. In average, the exceedance rates have diminished by a factor 2 between 2009 and 2020, reflecting, in average, a very significant decline in the water contamination by these chemicals.

This is at variance with the increasing QRs, induced by the biasing effect of the LoQ improvement.

The ratio between the two global indicators, cut-off threshold exceedance rate $\rho$ and original quantification rate, is depicted by a dotted curve in the same figure, which - very similarly to the above specific case of Pendimethalin previously depicted in Figure 15 - first grows from 2009 to 2012, due to less and less data being rejected (criterion LoQ>$\tau$), and then decreases as the LoQs improve, due to proportionally more and more quantified data having values lower than $\tau$. Altogether, the mean cut-off exceedance rates remain around 40 to 50% of the original QRs, preserving a rich set of data and associated statistical power.

Figure 20: Compared interannual variations of the exceedance rates $\rho$ (grey-coloured histogram) and original quantification rate QR (blank histogram), all 100 considered substances included, over the 2009-2020 period. Also displayed, ratio $\rho$/QR (blue curve). The figures attached to this curve indicate the absolute annual numbers of measurements exceeding the cut-off thresholds.

2. DID THE MEASUREMENT QUALITY IMPROVE, GLOBALLY?
One way to assess the quality of the measurement processes, referring to both sampling and laboratory steps, is to control the scattering of the results: for a given set of samples, measurement processes improving over time will lead to decreasing internal deviations of the data.

The improvement in the mean LoQs already described above (cf. Figure 4 and Figure 5) is in itself a relevant sign that the monitoring labs have progressively reach better control of some of their process. But this is only one aspect of the measurement quality, which doesn't account for the sampling, nor for other possible factors that could affect the comparability of the outputs from different laboratories.

Moreover, starting from the above finding that the contamination of the French waters by the WFD compounds has itself significantly diminished between 2009-2020, we expect that their actual concentrations in samples have lessened over the years. On a statistical standpoint, this means higher challenge for the measurement operators, with higher risk of increased relative standard deviation (RSD) of the results.

In Figure 21 we make a first use of the mean concentration indicator $\chi$ (annually averaged) to display the change over time of the distribution of the relative standard deviations associated to the consecutive yearly concentrations measured on the whole set of the studied monitored sites. In order to optimize the statistics involved and reveal at best the influence of the measurement quality, we considered here only those 41 parameters having in average more than 100 "over-the-threshold" concentrations per year.

![Figure 21](image)

**Figure 21**: Interannual variation of the distribution of the relative standard deviations (RSD) of the national-scale yearly $\chi$ values, considering the 41 substances exhibiting mean annual numbers of cut-off exceedances $> 100$. The annual distributions are characterized by the 25th, 50th, 75th and 90th percentiles of the RSDs among the 41 parameters.

The first observation from this figure is that there exists a strong discrepancy in terms of concentration relative scattering among the various compounds: there is one order of magnitude between the 25% chemicals showing the lowest RSDs (25th percentile curve) and the 10% with the highest RSDs (90th percentile). This is no surprise, as the monitoring sites exposure to the chemicals' pressures can vary quite differently in space, depending on the considered compound.

More interestingly, the figure shows an overall decline of the RSDs. For instance, it tells that for 75% of the 41 considered parameters (75th percentile), the relative standard deviation (RSD) improved by falling persistently after 2014 below 70%. In 2014, this indicator falls below 40% for half of the parameters (50th percentile), and below 20% for the most favorable quarter of them (25th percentile). For the 10% less favorable cases (90th percentile), however, the RSD remains mostly above 80% over the whole period, though some improvement also occurred in the second part of the decade.

The observed decrease of the scattering among the measurements during the 2009-2020 timeframe suggests that, consistently with the LoQ improvements described above, some unwanted and initially significant variability sources in the metrological process have successfully been more and more controlled by the monitoring personnel, samplers and labs included. And this despite the above-mentioned challenge associated to the progressive decrease of the compounds' concentrations in the samples.

Referring to the definition of $\chi$ in equation (2), the variability expressed in the standard deviation entirely comes from those measurements exceeding the threshold value $\tau$. There is good reason to believe that the revealed metrological improvements also benefited the measurements resulting in values than $\tau$.

Credit for these improvements should be given to the monitoring operators themselves, to the water agencies which continuously adapted the technical part of their tenders, but also in large part to the French National
Reference Laboratory for the monitoring of aquatic environments, AQUAREF, that provides, since its creation in 2007, support to public authorities for the implementation of the WFD especially on thematic related to quality of data (analysis and sampling methods) (AFB 2018, Chauvin 2021).

I.9. INTERMEDIATE CONCLUSION AND INTRODUCTION TO THE RESULTS’ PARTS II to V

We have established and statistically characterized a workable dataset of time- and space-comparable surface water contamination monthly indicators, for the continental France WFD monitoring data collected between 2009 and 2020. This dataset is scheduled to be made publicly available from the French water data website https://data.eaufrance.fr.

It is ready for being used in order to express the seasonal and interannual behaviors of these indicators at both the national and main river basins scales, and interpret these results in regard of other indicators related to chemical products uses and emissions (whenever available), and according to the above described river basins characteristics.

As will be shown in parts II, III to follow, from our monthly-variables dataset, it will be readily possible to derive monthly indicators integrating the information over the study period 2009-2020, whose variations reveal the average/typical seasonal profiles of the river contamination over the considered territories. As in the exemplified situation of Figure 14, three monthly concentration indicators will be considered (mean concentration $\chi$, 95% percentiles $\chi_{95\%}$, and concentrations in sites showing threshold exceedances $\chi^{\geq \tau}$), and the associated cutoff exceedance rate $\rho$.

All the seasonal profiles that we show in the following integrate several years of measurements (typically 12 years, 2009-2020), and the displayed indicators for each month will always be the average of their consecutive annual values. The error bars in all the figures drawing the seasonal profiles correspond to twice the standard deviation of the considered annual indicators.

Regarding the exploration of inter-annual variations, we will present in parts II and III of this work our data as yearly indicators, i.e. for each year “k” of the study period 2009-2020, the mean values of the 12 monthly data (those already used for the above seasonal exploration) will be displayed in the various following figures. In order to apprehend the statistical quality of the time series, we will also display error bars corresponding to twice the intra-annual standard deviations (considering 12 monthly values) attached to each yearly indicator.

In all the seasonal and interannual variations figures displayed in the following, we will display the two independent indicators $\rho$ and $\chi^{\geq \tau}$, that respectively account for the spatial and concentration aspects, thus providing a complete picture of the extent of contamination.

The comparison of the 6 basins specificities using the time-integrated indicators $X_{Ci,j}$ and $X_{rf,i,j}$ will also be presented in parts II and III of this work.

TREND DERIVATION PROCESS

Two types of effects can contribute to the variation of our contamination indicators, which have to be distinguished:
Some changes in the overall level of contaminating pressures, typically resulting from changes in the anthropic activities, or in the environmental conditions, affecting the transfer of contaminants from the catchments to the receiving waters. The very purpose of the present work is to infer and propose hypothesis regarding these types of causalities.

Some changes in the considered set of monitoring sites, which can modify the representativity of some specific contaminating contexts. As Figure 10 already illustrated, the number of sites has actually significantly evolved over the years, especially in some basins, like in 2018 for the LB basin. The assumption which will be made in the present study is that, given the fact that we are dealing with numerous sites, the change in the sites number within a basin, if not too drastic, does not modify the representativity of the corresponding pressures. However, when trying to derive a national scale trend, it will be necessary to check that the change in the weight of a given basin, whose proper contamination levels could be significantly different from the national averages, does not induce a bias. This point will be of particular importance for trace elements, as the geological background concentrations might significantly differ among the basins.

To compute trends and slopes of the contamination indicators, we used the non-parametric Mann-Kendall approach (Hirsch 1982), and the Theil-Sen method (Theil 1950, Sen 1968).

In close relation to our study, a particularly significant example of the Mann-Kendall approach for the trend derivation from large-scale contamination indicators, as applied to surface water contamination multi-year timeseries, is available for the River-Rhine case (Bach 2012). This particular work went through the additional complexity that it concerned pollutant loads assessment, i.e. mixing both concentration and river discharge data.

The Mann-Kendall test tests the existence of a monotonic trend in a series of time data. It is applied to a non-stationary chronic and is based on a rank test.

The Mann-Kendall S test statistic is defined as:

\[ S = \sum_{m=1}^{M-1} \sum_{q=m+1}^{M} \text{sign}(y_q - y_m) \]

With: \( \text{sign}(y_q - y_m) = 1 \) if \( y_q - y_m > 0 \)

\( \text{sign}(y_q - y_m) = 0 \) if \( y_q - y_m = 0 \)

\( \text{sign}(y_q - y_m) = -1 \) if \( y_q - y_m < 0 \)

\( y_q \) is the contamination indicator value of one month, and \( M \) is the number of observations.

If the sample contains more than 10 analyses, the law of Z-test statistics can be approached by a normal centered-reduced law (where \( \alpha \) is the standard deviation of S).

The slope computation is performed by the Sen method. It corresponds to the median \( Q \) of all the calculated slopes \( Q_{qm} \) between each pair of points, with:
\[ Q_{qm} = \frac{y_q - y_m}{q - m} \]

In the frame of the present work, the interannual trends will be numerically assessed and discussed considering only the variation of the cutoff threshold exceedance \( \rho \), reflecting the spatial extension/lessening of the surface waters contamination, over the years.

By default, trends have been calculated over the last 6 years (2015-2020). Furthermore, as long as there was no change in derived trend, previous years were also explored to extend the considered period (20xx-2020). The derived trends will then be displayed associated with an initial year \( K=20xx \), which will depend on both the substance and the considered basin/territory. Starting years later than 2015 (2016, 2017) were also explored in the few cases when 2015 was not sufficiently supplied with data.

Once the slope \( Q \) is determined, one can access the relative variation on \( \rho \) induced by the trend, as follows:

\[
\Delta \frac{\rho}{\rho^K}^{[K\rightarrow 2020]} = \frac{(2020 - K) \cdot Q}{\rho^K}
\]

\( \rho^K \) being the mean annual cutoff threshold exceedance rate at the trend starting date \( K \).

When seasonal variations were detected in the timeseries, the STL (Seasonal Trend decomposition using LOESS method) was applied in order to remove their incidence over the trend derivation (Cleveland 1990).

The statistical significance of every trend estimates was checked according to its \( p \)-values. In the trend results tables to follow we will indicate the level of significance, from high to low, with the following symbolistic: \( p < 0.001 = *** \), \( p < 0.01 = ** \), \( p < 0.05=\ast \).

As an illustration, Figure 22 echoes with Figure 14, presenting the de-seasonalized timeseries of the national \( \rho \) monthly values for the herbicide Bentazone, over the 2012-2020 period. The derived median slope was estimated non-significantly differing from zero, resulting in no trend identified.

Conversely, the Loire-Bretagne (LB) basin \( \rho \) values 2009-2020 timeseries of the herbicide Atrazine presented in Figure 23 resulted in a significant downward trend (negative slope), with a high significance level, as indicated by the "***" symbol in the figure.

**Figure 22**: Illustration of the multiyear trend derivation process for the monthly \( \rho \) values averaged at the national scale (blue dots), for the herbicide Bentazone. The continuous red line indicate the median \( Q \) of the calculated slopes, the dashed ones the lower and upper slopes. The absence of "***" symbol in upper part of the figure indicates non-significance of the derived slopes, i.e no trend.
Figure 23: Illustration of the multiyear trend derivation process for the monthly $p$ values averaged at the AG basin scale (blue dots), for the herbicide Atrazine. The continuous red line indicates the median $Q$ of the calculated slopes, the dashed ones the lower and upper slopes. The "***" symbol indicate high significance of the derived negative slopes, i.e downward trend.

To calculate trends, for the sake of representativeness, we considered only those months with at least 15% of the average monthly data number. For the national trends, only such months represented in at least 4 basins are used.

Sometimes trends have not been calculated because of too many missing years with data (less than 3), or because of a high number of missing data within the period, which prevented the imputation of missing data. In the following, uncalculated trends will be noted "n.c" in the trend results tables.
II.1. METALS AND ARSENIC

As a remainder (cf. Table 17 in Appendix A), 8 trace elements are considered:
- four PSs: Lead (Pb), Nickel (Ni), Mercury (Hg), Cadmium (Cd)
- four RBSPs: Arsenic (As), Chromium (Cr), Copper (Cu), Zinc (Zn)

In the following, we will refer to the French soil quality measurement network (RMQS) for the sake of comparison between our water indicators and excising information on trace elements soil contamination (Arrouays 2002, Gis-sols 2011, Saby 2011, Marchant 2017).

TEMPORAL VARIATIONS OF THE CONTAMINATION INDICATORS

Contrary to organic compounds for which both dissolved and some suspended matter fractions are measured, the WFD monitored metal concentrations represent the dissolved fraction of the samples (samples are filtered at 0.45µm). This fraction is highly sensitive to the metal speciation and soluble/particulate partition, which depend on the physicochemical conditions (dissolved organic matter, temperature, pH), themselves varying along the seasons, e.g. according to the dilution of anthropogenic effluents or hydrobiological processes, and as a function of relative contribution the geological background to the river flow (Bourg 1995; Priadi 2011).

Considering this complexity, we expect particular difficulties in interpreting the observed seasonal patterns.

Most toxic trace metals occur in solution as cations (e.g. Pb 2+, Cu2+, Ni 2+, Cd 2+, Co 2+, Zn 2+) which generally become increasingly insoluble as the pH increases (Smedley 2002). In contrast, most oxyanions, including arsenate, tend to become less strongly adsorbed as the pH increases (Dzombak 1990).

Regarding the interannual variations, not all the basins have started intensive WFD monitoring of these elements in 2009, sometimes delaying their generalized routine monitoring until 2012 or later. For this reason, the timeframes of the various nationwide indicators timeseries shown below can vary depending on the considered metal.

Moreover, when trying to derive interannual trends from the monitoring data at the national scale, we will need to account for the possible bias associated to the changes in the number of monitoring sites in the various basins over the years. Indeed, as will be seen, the overall geological background concentration can be very different among the 6 basins, so that our indicators could become sensitive to variations of the weighing of these basins for the national average computation. In particular, we paid attention to the influence of the year 2018 in the LB basin, which corresponds to a drastic increase if the sites number (cf. Figure 10).
Arsenic

Arsenic (As) was monitored extensively over the continental France only since 2015, and only since 2017 do we have comparable complete timeseries of monthly values, from 4 of the main basins.

Figure 24 and Figure 25 respectively illustrate the seasonal profiles of the cut-off exceedance rate ($\rho$) and the mean of the concentration values exceeding $\tau$, $\chi^{\text{ex}}$.

The first observation is the important offsets between the four basins, reflecting the overall geological background of each basin, with LB and RM exhibiting the highest backgrounds.

The seasonal distributions cap during summer. This can be associated with some continuous geogenic emission to rivers, through groundwater contributions, exacerbated in low-flow periods. It is also known, however, that seasonal changes in the physicochemical conditions in the river themselves, like redox condition changes of iron-oxide particles of the sediment, which is temperature driven, may contribute to the release of diluted arsenic from the riverbed sediments (Mok 1989). It has also been suggested in the literature that bacterial reduction of As(V) to more soluble species As(III), favored by warmer temperature, may be a main process controlling the seasonal variations of dissolved As concentrations (Masson 2007, Wang 2023).

Figure 24: Seasonal variations of the basin-averaged exceedance rates for As, in 4 basins, integrating the 2017-2020 measurements.

Figure 25: Seasonal variations of the basin-averaged concentrations at the sites exhibiting cutoff exceedance for As, in 4 basins, integrating the 2017-2020 measurements.

The Arsenic's national interannual $\rho$-values timeseries is displayed in Figure 26, plotting both the full set of data, and those values excluding the LB basin, in order to check if the important change in the sites number in this basin influences the whole picture. In both cases, there is a limited but rather regular upward tendency since 2015 for the exceedance rate indicators, with no impact of the LB basin on the qualitative trend assessment.

At the basins scale, some upward trends were detected in RM and SN basins, respectively since 2015 and 2012, explaining the national slope.

Figure 26: Interannual variations of the annually averaged As cut-off exceedance rates $\rho$, considering separately the national scale (grey histogram), and the national scale without the LB basin (white histogram). The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Metals
As a preliminary, it is important to note that the above-described top position of the LB basin for Arsenic contamination turned out to be reproduced for the majority of the here-considered trace elements (Hg, Pb, Ni, Zn), due to its geology (crystalline and volcanic rocks, basalts and ultrabasic rocks) and the numerous related historical mining sites present in this territory. An opposite situation was met for Cr, where LB appeared as the least contaminated basin, overall. In this regard, we systematically conducted the checking of the national interannual variation against the same set of data with LB exclusion, as shown above for As, with a focus on year 2018 and its drastic change in the number of LB’s monitoring sites. The result of this exercise was that, even though the LB exclusion resulted in some visible change in the national $\rho$ values, the qualitative conclusion on the national trend was preserved in all cases but Hg, strengthening confidence in the assumption that the main driver for the trends in the studied timeseries are actual contamination variations, rather than aspects linked to the level of activation of the monitoring networks.

As of Zinc, the contamination seasonal pattern was obtainable consistently over the 2012-2020 timeframe, from RM, AP and SN basins. The resulting profiles are the reverse of Arsenic’s: the highest contamination indicator values are found in fall and winter, and this in spite of higher river dilution (cf. Figure 27 and Figure 28, respectively for $\rho$ and $\gamma^{\infty}$). A secondary peak is observed during the spring season. A quite similar profile could also be verified in the LB basin from 2016-2020 measurements.

Figure 27: Seasonal variations of the basin-averaged exceedance rates $\rho$ for Zn, in the AP, RM and SN basins, integrating the 2012-2020 measurements.

Figure 28: Seasonal variations of the basin-averaged concentrations at the sites exhibiting cutoff exceedance for Zn, in 3 basins, integrating the 2012-2020 measurements.

These findings might suggest a prominent role of the runoff during the rainy seasons, Zinc being a common component of the urban and road materials, as well as a veterinary-sourced component of the manure dispersed on agricultural soils (SOGREAH 2007).

Similar $\rho$ value winter maxima were similarly observable for Cadmium, in all basins, except AP. As for Zinc, Cadmium-enriched particles have actually also been evidenced as associated with road runoff waters (Lerat-Hardy 2021). For Cadmium, diffuse input from soil-leached contaminated phosphate fertilizers are also to be considered as significant source (Carne 2021).

The possible influence of the in-river physicochemical processes should not be underestimated, however, as exemplified by some former research performed in French river waters (Moatar 2009). Indeed, the seasonal biological activity in the rivers induces pH variations, associated to photosynthetic and respiration processes (Moatar 1999). pH thus increases during warm season and produces the precipitation of dissolved Zn and Cd, whereas the pH depletion in winter releases them back into the water column, in relation to their desorption from Manganese oxide particles (Bourg 2000).

In terms of interannual variations, for Zinc, only in AP was it possible to evidence some long-term downward changes: the AP surface waters slightly improved since 2012. Some upward trends could also be diagnosed since 2015 in LB and RM basins, feeding the nationally-derived increasing trend.
For Cadmium, as Figure 29 illustrates, the national river contamination indicators pointed out some global degradation from 2014 onward. The main driver for this observed overall contamination increase is in fact the contribution from the SN basin, where the Cd mean exceedance rate slowly inflates since 2012 and until 2020, though showing smaller figures than the average national contamination. The calculated trends were rather contrasted in the other basins, with exceedance rates varying up in AG and RM, or down in AP.

**Figure 29**: Interannual variations of the annually averaged Cd cut-off exceedance rates $\rho$, considering separately the national scale (grey histogram), and the sole SN basin (green histogram). The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

With regards to Lead, for which we have consistent seasonal data in all basins since 2015, similar to Zinc, we were able to observe two kind of behaviors:

- in the western basins LB, AG and SN (cf. Figure 30), we found bimodal distributions in the seasonal profiles, with contamination indicators peaking both in June and in winter. Some very clear early spring and early-fall depletions are observed, halving the fraction of sites with exceedances.

- In the eastern basins AP, RM and RMC (cf. Figure 31), the distributions are much flatter, with one wide peak centered around summer, and a secondary maximum in early winter. The observed AP trimestral frequency of peaking values (February, May, August and November) is very likely related to the higher spatial monitoring coverage performed there during these months.

Actually, the observed east-west gradient well echoes the modelled spatial distribution of annual Pb deposition flux over Europe which were established by the Convention on long-range transboundary air-pollution (EMEP 2012), with twice higher quantity of deposited Pb in the eastern part of mainland France. We could then hypothesize that more “natural” dynamics of Pb occurrence are reflected by the western profiles (**Figure 30**), with the same seasonal features - yet more contrasted - as previously observed for Zn and Cd, associated with the bio-physicochemical conditions of the rivers. On the other hand, a more disturbed dynamic would be reflected by the eastern time series (**Figure 31**), with higher influence of atmospheric-sourced Pb (mainly originating from metal and energy production facilities in eastern Europe), which reinforces the spatial contamination, especially in summer and autumn. This would, obviously, deserve further confirmation.

**Figure 30**: Seasonal variations of the basin-averaged exceedance rates $\rho$ for Pb, in the LB, AG and SN basins, integrating the 2015-2020 measurements.

**Figure 31**: Seasonal variations of the basin-averaged exceedance rates $\rho$ for Pb, in the AP, RM and RMC basins, integrating the 2015-2020 measurements.

It was possible to identify a significant long-term upward trend for our Lead indicators at the national scale. A distinct upward signal appeared in the end of the timeseries, but mainly related to some very recent contamination upward offsets in the RM basin (2019) and SN basin (2020). AP was the only basin that recurrently exhibited improvement of its Lead contamination over the full 2012-2020 duration.

For Copper, only three basins did maintain some consistent spatial coverage every month on a long-term
timeframe (2012-2020), i.e. AP, RM and SN. The examination of their Copper seasonal contamination profiles revealed some faints but reproducible patterns. Indeed, consistently with what was observed for Zn, Cd and Pb, the Cu cut-off threshold exceedance ($\rho$) appeared to be maximal in cold seasons (February-March and November-December), while the lowest figures are observed during summer. The same patterns could also be verified for the LB basin after 2015. By contrast, full year AG basin seasonal profiles were accessible only for the years 2012 and 2015. Interestingly, the statement there was inverse from the above basins, with the highest contamination exceedance occurring between May and August. This could be related to the high level of vines sulphating in this viticultural region, which usually begins in mid-May and ends in mid-August. As a matter of facts, the department of Gironde, situated in the AG basin, is by far the highest consumer of copper-based plant protection compounds in France (ANSES 2022).

With regards to Copper pluriannual trends, our river contamination indicators indicate a slightly increasing exceedance rate at the global scale, with concentrations temporarily elevated in the 2018-2019 years, essentially driven by some unidentified process occurring in the SN basin.

For Nickel, as for Zn, Cu, Pb or Cd, some faint but distinct maximum in the $\rho$ values could also be observed nationally during the fall and winter months, which became even more noticeable at the basin scale in LB, SN and RM., with for all of them a secondary maximum also observable in June.

The tendency for higher $\rho$ values of Chromium in winter was even more clear, especially for RM, LB and AP basins, mainly in the second part of the studied period (2015-2020): cf. Figure 32, where the seasonal patterns are very exacerbated and match surprisingly well in the 3 basins. Such seasonal features didn’t appear in the three remaining basins. The dissolved Chromium in normally oxygenated natural waters is mainly found under its hexavalent form Cr VI, with the most common reduced form Cr III being prone to precipitate and adsorbed on sediment particles, except when associated with high quantity of dissolved organic matter in acidic conditions (Saputro 2014, Gorny 2016, Fan 2019). The particularly low exceedance frequencies observed in summer and early fall for these 3 basins could then be tentatively explained by the combination of reductive conditions in eutrophicated streams, and substantially lower diffuse runoff contribution from the catchments of the monitoring sites. Interestingly, AP, RM and LB basins are actually those with the highest fraction of WFD waterbodies degraded by phosphorus eutrophication. In such a scenario, the eutrophication could be viewed as an attenuation factor for the ecotoxic Cr VI contamination of the aquatic ecosystems. For the other 3 basins, consistently, we did not observe any systematic depletion of the $\rho$ values in warm seasons.

Figure 32: Seasonal variations of the basin-averaged exceedance rates $\rho$ for Cr, in the LB, AP and RM basins, integrating the 2015-2020 measurements.

The Cr indicators’ multiyear timeseries of the basin RMC is showing some long-term improvement (2012-2020). The evolution of the indicators is unclear for AP end AG, while in LB there appears to be some worsening from 2015 to 2020. In SN and RM, the most recent exceedance rates (2018-2020) are also going up. Summing up, rising contamination occurrences could be diagnosed for Cr at the national scale, from 2013 onward. Figure 33 illustrates this, as well as the result of the checking that was done upon the incidence level of the LB data, as already described for As in Figure 26, with the reverse situation of LB Cr value being notably lower than the national average. Here again, the LB data didn’t change the conclusion about some upward trending.
Figure 33: Interannual variations of the annually averaged Cr cut-off exceedance rates $\rho$, considering separately the national scale (grey histogram), and the national scale without the LB basin (white histogram). The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

For Nickel, a global nationwide trend could be derived, from 2015 onward. At the basin scale, a rather continuous 2010-2020 contamination increase appeared in RMC (though maintaining values notably under the national average).

Regarding Mercury, in spite of weak statistics, we were able to observe somewhat higher $\rho$ values in winter and spring, especially in the southern RMC and AG basins. In the most recent LB basin data (2019 and 2020), however, both the concentration and cut-off threshold exceedance indicators indicate a broad contamination peak, topping during summer, with a secondary peak in early winter.

For the interannual variations, the national Hg indicators exhibit small values ($\rho<1\%$), and high variability. Only the RMC basin has a consistent multiyear timeseries (since 2011), but no conclusive trend could be derived from it. Some upward trend was initially derived from the calculation at the national scale, but it was invalidated because it was mainly due to some LB monitoring sites suddenly yielding high exceedance rates in the last two years only (2019 and 2020), possibly related, according to LB water agency, to some change of Hg analytical service supplier.

OVERALL STATEMENTS FOR CONTAMINATION TRENDS OF METALS AND ARSENIC

From these results, it is possible to distinguish two big kinds of seasonal behaviors for the river contamination by the WFD metals and Arsenic:

- A first set of metals often exhibiting maximal values of river contamination indicators in high-flow season (Zn, Pb, Cu, Ni, Cd, Cr), some of them also peaking secondarily in the late-spring season. The relatively higher values in wet seasons might be associated with higher inputs due to runoff, or to relatively lower pH values during limited photosynthetic activities, inducing high dissolved metal fraction. The temporary spring inflation (May-June) followed by the summer downward trend could tentatively be interpreted as resulting from some diminishing dilution effect in late spring, competing against some growing metal precipitation effect due to the pH increasing with the summer eutrophication of many water courses, the latter phenomenon taking the lead from July up to early fall.

- A second set gathering As (all basins) and Hg (only in LB), with a wide contamination peak topping during summer. For Arsenic, this might at least partly be related to warmer water temperature favoring the microbial degradation of oxide particles carrying adsorbed Arsenic.

Nevertheless, as compared with the other chemical groups which will be considered in the following, metallic river contaminations provide weakly contrasted seasonal profiles, in relation to the prominent role of a permanent concentration background, with a large part of it imputable to the hydrogeology of the various catchments.
Overall, the long-term contaminations dynamics appears to be very region-dependent, with some important contribution of the geochemical background emissions. As Table 2 shows, most of the significant trends that could be derived from the inspection of the exceedance rates multiyear variations are signing upward water contaminations, which questions the global efficiency of the anthropogenic metal emission control in France, in spite of some long-lasting progress achieved for some metals in some basins (AP, RMC), possibly in relation to actions undertaken by the industry sector.

Considering in Table 2 the Sen’s slopes $Q$, and especially those established at the national scale with the highest confidence (i.e. those elements with slopes marked “****”), we can apply eq. (8) to assess the relative changes of the exceedance rates induced until 2020 since the trends’ starting years $K$. Doing so, the strongest relative changes could be stated for Cd and Pb, with about 60 to 70% increases versus the 2010-2012 period. These extensions are more limited for As and Zn (about 20%, respectively since 2015 and 2012), and even less for Cu (about 10% since 2012), but are concerning much more sites.

Table 2: Summary of the identified trends of the exceedance rates $\rho$ for WFD metals and As. Statistically significant upward trends are indicated in pink-coloured cell with an $\uparrow$ symbol. Downward in green with an $\downarrow$. Trend significance are as follows: **** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data.

<table>
<thead>
<tr>
<th></th>
<th>LB</th>
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<td>1.1 (***)</td>
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<td>Starting year of trend, K</td>
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<td>-1.5(***)</td>
<td>0.5(*)</td>
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<td>0.2(*)</td>
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</table>
Figure 34 averages the annual exceedance rates and associated concentrations of those metals which exhibit higher wet seasons contamination (Zn, Pb, Cu, Ni, Cd, Cr), and indicates that the observed upward trends for the spatial extension indicator $\rho$ have been increasingly influenced by fall and winter values, notably during the four latest years (2017-2020). The contribution of increasing contaminated runoffs in rainy weather should then be mentioned as a possible cause. Actually, every year, France loses 20 to 30,000 hectares of natural, agricultural or forestry of natural, agricultural or forest land, mainly to the benefit of the urban fabric, buildings and linear transport infrastructures, all of them known sources of metallic contaminants. This globally induces enhanced sealing of the soils, and thus, potentially higher spatial frequency of runoff-related leakage of these elements to surface waters.

**Figure 34**: Interannual variations of the national scale annually-averaged cut-off exceedance rates $\rho$, averaging the signals from Cd, Cr, Cu, Ni, Pb and Zn metals, considering separately the spring-summer data (red-coloured histogram) and the fall-winter ones (blue-coloured)

**RISK AND CONTAMINATION INDICATORS: RIVER BASINS COMPARISONS AND SPECIFICITIES**

Concerning metals and Arsenic, we present in Figure 35 and Figure 36 the 2016-2020 integrated contamination indicators $X_c$ and risk indicators $X_r$. As regards the risk indicator $X_r$, it has to be said that, for the metals, it refers to worst-case EQS values, i.e. situations where all the measured metal is bioavailable.

$X_c$ stands high (typically $> 50\%$) in the various basins for some major elements like Zinc and Copper, as well as for Arsenic, largely related to their geochemical backgrounds. For Arsenic, the highest values are observed in LB (likely linked to geology and mineralization process occurring in the Massif central region), RM (likely due to former mining and industrial activities), and AG, with some possible historical inputs from Arsenic being used in the formulation of pesticides. These observations for surface waters are spatially quite consistent with the national soils contamination maps recently established through the French soils quality measurement network (RMQS). For Nickel, the situation is more contrasted, with distinctly higher values met in LB, AP and SN basins, which, on a qualitative standpoint, also could be consistently related to the top soils map from RMQS.

**Figure 35**: Multiyear (2016-2020) integrated indicators of contamination ($X_c$) and risk ($X_r$) for As, Cu, Ni and Zn. $X_c$ values of each basin are presented through the cumulative histograms (linear scale), and $X_r$ values by the round dots (log scale).

Lead contamination indicators (Figure 36) are somewhat similar in all basins, with the exception of a significantly lower value in RMC.

Cadmium exhibits its higher contaminations in the AP basin, consistently with its elevated soils Cd content.
imputable to both intensive use of contaminated phosphate fertilizers and historical industrial pollution, while RM and SN appear as the less impacted.

For Chromium, the SN gets the highest $X_c$ figures. Finally, Mercury shows distinctly higher contamination in LB than the other regions, consistently with the soils contamination results of the RMQS, and likely linked to the presence of volcanic rocks, as well as of ancient gold mining activities (some hot spots in the Massif central).

In terms of risk, the obtained $X_r$ indicator stands high in all basins (upper than 1 typically) for Arsenic (heading in LB), Copper (notably in SN and LB) and Zinc (especially in AG). Other high $X_r$ values are met for Cadmium, in AG and RMC. LB also exhibits a significant $X_r$ value for Hg.

**Figure 36**: Multiyear (2016-2020) integrated indicators of contamination ($X_c$) and risk ($X_r$) for Cd, Cr, Hg and Pb. $X_c$ values of each basin are presented through the cumulative histograms (linear scale), and $X_r$ values by the round dots (log scale).

Generally speaking, the $X_c$ values in Figure 35 and **Figure 36** offer an interesting integrated large-scale vision over the average concentrations associated to these 8 elements in the main French 6 basins, which could advantageously be discussed in regard of the existing knowledge of the influence of the geological backgrounds levels in these areas.

### II.2. PAHs

**SEASONAL PATTERNS**

Four PAHs monitored through the WFD implementation are considered in the present study: Anthracene, Benzo(a)pyrene (also called BaP), Fluoranthene and Naphthalene. The seasonal profiles for 3 of these molecules, integrated over the full 2009-2020 period, are exemplified in **Figure 37** to **Figure 39**. As these figures show, these compounds share the characteristic of distinctly inducing contamination peaks during the winter season, in relation with their atmospheric emission by the domestic heating systems and thermic power plants, vehicle and transportation activities, and with the abundant winter runoff on contaminated soils or urban areas (Ravindra 2008). The reduced volatilization of these compounds and their enhanced adsorption to atmospheric particles during the cold season may also contribute to the observed profiles, as these particles are easily washed-off after deposition. All these water-based wide-scale observations are consistent with former ones collected by Gateuille et al. (Gateuille 2014) regarding the seasonal variations of PAHs atmospheric fallouts of PAHs at a French river basin scale.

**Figure 37**: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^\tau$ for BaP, integrating the 2009-2020 measurements.
Figure 38: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{*r}$ for Anthracene, integrating the 2009-2020 measurements.

Figure 39: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{*r}$ for Naphthalene, integrating the 2009-2020 measurements.

The Benzo(a)pyrene (BaP) profile also exhibits a secondary contamination maximum around June. As of Fluoranthene, it is closely resembling to the BaP. This strong similarity indicates that the main sources for both these compounds are probably identical.

Anthracene is the least quantified of these PAHs, mainly detected in AP and RM basins, at one order of magnitude lower than BaP, but with a similar annual profile.

Naphthalene, which records the most contrasted winter to summer contamination figures, suggests an important contribution of the wet seasons’ runoff. The volatile property of Naphthalene (classified as volatile organic compound) is also likely to contribute to the much lower contaminations measured in the warm seasons, when water temperature is higher.

Figure 39 indicates that Naphthalene concentrations, at the limited number of sites exceeding the cut-off thresholds, exhibit higher variability than BaP or Fluoranthene. This suggests that, aside from the above-mentioned diffuse pollution, local sources of incidental Naphthalene emissions, like wastewater effluents or polluted urban/industrial runoffs, may also contribute significantly to the river contamination, whatever the season.

The breaking down of the analysis at the six main basins scales revealed that the shapes of these national seasonal variations are maintained quite similarly at the regional scales.

INTERANNUAL VARIATIONS INDICATORS, TRENDS OF CONCENTRATIONS AND RATES OF EXCEEDANCE

As can be seen from our indicators in Figure 40 to Figure 41, the river contamination trend for the three major PAHs of our study, i.e. Benzo(a)pyrene, Fluoranthene and Naphthalene, have been globally favorable since 2009, with very similar patterns for the two firsts compounds, and a more erratic but still significant decline for Naphthalene. The mean concentrations in the sites with cut-off exceedances, however, remain pretty steady over the whole study period, at least for BaP and Fluoranthene, indicating that these pollutions are spatially shrinking, but without any significant reduction in average for the residual highly polluted sites.

Breaking down the examination at the six main basin scale, these highly contaminated rivers are mostly located in the northern basins AP, RM and SN.

Figure 40: Interannual variations, for the BaP PAH, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{*r}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.
Figure 41: Interannual variations, for the Fluoranthene PAH, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^c$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

More insight is brought when considering the changes in the seasonal profiles of our indicators for these molecules over the years, as exemplified for Benzo(a)pyrene in Figure 42. Indeed, this figure demonstrates that winter months like February or March are those when no contamination reduction is observed globally, unlike the other three seasons, where clear gains were achieved. This supports the idea that the contribution of the heating systems to the PAH water contamination didn’t diminish between 2010 and 2020, if not worsened, whereas the other PAH sources - like vehicles emissions, or economic activities effluents -, which express themselves distinctly when the heating emissions cease, seem on the contrary to have significantly improved.

Such an explanation would be consistent with the recent literature (Keyte 2016), and with the statement made by Paris region air quality center Airparif, which indicated a significant reduction over the recent years of the BaP contamination in the vicinity of the road infrastructures, related to the renewal of the vehicles. One can also mention that, since the beginning of 2010, the use of high aromatic process oils in tire manufacturing has been banned under the REACH regulation. As a matter of fact, the runoff flowing from urban surfaces is a known PAH source for river pollution (Motelay-Massei 2006, Markiewicz 2017).

The same change in the seasonal pattern over the years was observed for the Fluoranthene contamination of the French surface waters, reinforcing the hypothesis that BaP and Fluoranthene share common major emission sources.

Figure 42: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^c$ for BaP, separately integrating the measurements from the 2009-2013 and 2016-2020 periods.

These findings and conclusions are quite consistent with those of a recent study which used the PAHs WFD data of the river Elbe in Germany over the 2001-2016 period (Li 2019). In this study, the 16-year period, the average PAH concentration of all the PAHs in the River Elbe was reduced by around 38%. The authors identified vehicle emissions from petrol- and diesel- powered engines as the main contributors of PAHs (contributing approximately 42% of the total mass). Coal combustion made a lower but significant contribution (27% on average).

Repeating the same exercise with the Naphthalene revealed a very different situation. As shown in Figure 43, the seasonal pattern and the observed reduction in the exceedance rates is this time maintained to a similar level all over the year. This suggests that the achieved progress is likely imputable to emission reduction affecting a major type of sources, active all over the year. One significant hypothesis explaining the observed reduction is the now long-lasting and continued replacement of coal tar (which contained important quantities of Naphthalene) as road building material by modified bitumen, concrete, and resins or binders from synthetic chemistry.
Figure 43: Seasonal variations of the national scale-averaged exceedance rates \( \rho \) and concentrations at the sites exhibiting cutoff exceedances \( \chi^{c} \) for Naphtalene, separately integrating the measurements from the 2009-2013 and 2016-2020 periods.

Regarding the fourth PAH included in our study, Anthracene, the exceedance rates \( \rho \) are much lower (<2.5%), and it was not possible to derive any overall national trend on the studied period.

Table 3 summarizes the visually identified trends in the exceedance rates \( \rho \) over the 2009-2020 timeframe. The overall budget is quite positive, with occurrences of PAHs river contamination continuously and significantly decreasing in most of the basins, and a reflection of this at the national scale for 3 out of the 4 studied compounds. In most cases the downward slope was initiated in the early years of the study period. These progresses are even more obvious in the most contaminated northern basins (RM, SN), though AG and RMC exhibit also nice improvements.

Table 3: Summary of the identified trends of the exceedance rates \( \rho \) for WFD PAHs. Statistically significant upward trends are indicated in pink-coloured cell with an \( \uparrow \) symbol. Downward in green with an \( \downarrow \). Trend significance are as follows: *** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data.
Considering in Table 3 the Sen’s slopes Q, and especially those established at the national scale with the highest confidence (i.e. those elements with slopes marked ‘***’), we can apply eq. (8) to assess the relative changes of the exceedance rates induced until 2020 since the trends’ starting years K. Doing so, it turned out that for BaP, Fluoranthene and Naphthalene, quite important relative reductions were achieved, ranging between 60 and 80% of the original exceeding rates recorded for 2009-2010. This represents the highest reductions among all the 100 compounds considered in this study.

### Table 3: Sen’s slopes Q (%/an)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting year of trend, K</th>
<th>Trend</th>
<th>Absolute Sen’s slope Q (%/an)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>2014</td>
<td>nc</td>
<td>-0.05(*)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>2015, 2014</td>
<td>nc</td>
<td>-0.3 (<em><strong>), -0.5(</strong></em>), -2.4(<em><strong>), -1.7(</strong></em>), -0.5(**<em>), -1.4(</em>)</td>
</tr>
</tbody>
</table>
of the PAHs deposition associated to the changes in the contemporary emission sources.

As already observed above in terms of seasonal patterns and interannual variations, Figure 44 confirms, this time in terms of regional distribution, that Benzo(a)pyrene and Fluoranthene have very similar fingerprints, strengthening the hypothesis of common major emission sources.

Naphthalene, however, is regionally distributed differently, with RMC contamination approaching the AP and RM's, while SN stands relatively low compared to BaP and Fluoranthene. The singular contamination level of Naphthalene in RMC compared to the other PAHs could hypothetically be associated to some specific industrial emissions (chemical and petrochemical industries along the Rhône valley), but one could also mention the role of forest and brush fires residues that contain significant quantity of Naphthalene (Jia 2010), as such events regularly affect the south-east of France. Further spatially-resolved investigation would help in diagnosing this.

In terms of risk indicator Xr, BaP and Fluoranthene exhibit the highest values among all the chemicals considered in the present study, with maximal scores reaching 20 to 60 for the northern basins. This is fully in line with the regulatory WFD assessments historically carried out in France, that highlighted the prominent role of these PAHs in the degradation of the surface water chemical status. This statement has to be tempered, however, as the here-adopted water-EQS paradigm for risk indication related to these two PAHs is no longer the privileged approach in the recent version of the WFD. Indeed, biota-EQSs, indicating risk to human health via food consumption, have been promoted instead since the 2013 WFD daughter Directive, and the first risk assessments using this new approach seem to raise much attenuated alerts for both these compounds, with apparently no observed correlation between water and biota concentrations (UK Environmental Agency 2019). Water monitoring of PAHs remains useful to check that exposure to contaminant levels in water does not present a risk to the organisms themselves.

Figure 44: Multiyear (2016-2020) integrated indicators of contamination (Xc) and risk (Xr) for Anthracene, BaP, Fluoranthene and Naphthalene. Xc values of each basin are presented through the cumulative histograms (linear scale), and Xr values by the round dots (log scale).

II.3. INDUSTRIAL AND POP COMPOUNDS

TEMPORAL VARIATIONS OF THE CONTAMINATION INDICATORS

With regards to Nonylphenol (4-NP), as Figure 45 illustrates, there is a general diminution of the exceedance rate ρ, which used to reach values as high as 10% in some basins (especially SN and RM) in 2012-2013, whereas the latest years values approach 1% in almost all the basins. This downward trend is consistent with the regulation of this chemical which no longer receives authorized use in marketed products. Indeed, following their inclusion as a priority hazardous substance, nonylphenols and nonylphenol ethoxylates have been subject to a ban/restriction of use and placing on the market for a large number of sectors (directive 2003/53/EC of June 18, 2003) such as industrial and institutional cleaning products, household cleaning products, leather and textile processing, or papermaking (Berryman 2012, Rusconi 2015).

We identified the AG basin as an exception, in which the river contamination at the end of the study period indicates persistent contamination, contributing significantly to the final rise of the concentration curve in Figure 45.
Figure 45: Interannual variations, for the 4-NP Nonyphenol, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^r$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Looking at the national scale seasonal profiles (cf. Figure 46), both indicators exceedance rate $\rho$ and mean concentration $\chi$ expressed higher contaminations during the dry seasons of the 2012-2016 period. A known contribution to 4-NP higher concentrations in the summer is the increase in microbial activity with warmer temperatures (Priac 2017), leading to an enhanced degradation of Nonylphenol ethoxylates, which used to be an abundant parent compounds of the 4-NP in the environment.

Figure 46 also shows that this seasonality seems to have vanished in the late period 2017-2020, once the overall usages had considerably decreased.

Concerning Octylphenol (4tOP), though occurring with lower contamination figures, there is a similar overall decrease of the exceedance rates as for Nonlyphenol since 2012, with the same exception for the AG basin, experiencing some upper values in 2019-2020. These correlations might not be incidental, as octylphenols impurity in nonylphenols is one of the top three sources of 4tOP emissions to the environment (COHIBA 2011).

The seasonality aspect of DEHP displayed in Figure 47 is seemingly similar to the 4-NP situations described above, with high rates of exceedance and a summer peaking profile in the 2012-2016 period, followed by much lower $\rho$ values and the disappearance of seasonality afterward.

Actually, the phthalates family, including DEHP, is known to strongly challenge chemical analysis sensitivity, because of parasite contamination from both measurement equipment and ambient air (Fankhauser-Noti 2007). In this respect, one hypothesis to be formulated in this case is that the seasonality of the 2012-2016 indicators could have been influenced by the presence of DEHP in ambient air, with higher contamination of the sampling instruments and materials in summer. Indeed, previous studies have reported DEHP ambient air concentration about 10 times higher in summer compared to winter (Moreau-Guigon 2013).
This parasite contamination effect is supported by the examination of the interannual data shown in Figure 48. The global rates of cut-off exceedance from all the mainland France exhibit an apparent nice and strong decrease from 2014 until 2020. Looking deeper in the data and examining the contributions of every basin, it turned out that this global behavior was mainly driven by the SN and AG data, such a sharp downward trend being actually occurring in both of them, and them only. When subtracting their contributions from the overall national indicator, one obtains a completely different picture (Figure 48), with much lower $\rho$ values, and no longer any distinct interannual trend. Such huge differences in river contaminations figures, averaged at big basins scales, cannot be real, and supports the hypotheses of mismanaged measurement blanks in some labs before 2016. Figure 47 shows that the seasonality did vanish in the recent 2017-2020 period, likely due to a better management of this parasite contamination through the sample measurement protocol. Adapted QA/QC processes have been only progressively implemented in the labs in the early years of the WFD monitoring, in some cases with delays. As a matter of fact, the SN and AG values finally got consistent with the other basins' values after 2016.

**Figure 48**: Interannual variations, for DEHP, of the annually-averaged cut-off exceedance rates $\rho$, considering separately the national scale (grey-coloured histogram) and the national scale without AG and SN basins (blank histogram). The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

All in all, one should refer only to the four other basins averages to look for a trend in the DEHP during the 2012-2020 period. In this respect, Figure 48 indicates that, contrarily to what could initially be expected from a first visual inspection of the national indicators, the indicators pooled from the remaining four most reliable basins no longer express any clear global trend, with rather steady figures since 2017. This suggests that DEHP contamination persisted over the whole study period, or at least could not be properly controlled at such wide scale, although its various uses have been drastically restricted in the meantime.

Regarding industrial solvents, Dichloromethane (DCM) is a WFD compound that underwent a drastic reduction of its entry into surface waters. The use of this substance in paint strippers was regulated through the Reach restriction process in 2010. According to the information available by INERIS in 2015, DCM was still important in industrial applications, but was becoming less important in professional and consumer uses. In industrial applications, it is generally used in closed systems, where possible (INERIS 2015).

**Figure 49** shows the reduction that resulted in the SN basin – i.e. the basin where the main DCM pollution have been identified through the WFD- essentially before 2014. No further significant trend could be detected afterward for $\rho$ (due to low statistics), but Figure 49 shows that the high concentration values (> 20µg/L) still met in the 2012-2016 were ultimately terminated in the end of the timeseries.

**Figure 49**: Interannual variations, for Dichloromethane solvent, of the SN basin annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $c^r$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.
Comparing the seasonal profiles of DCM between 2009-2012 in the SN and AG basins, (Figure 50) it turned out that they exhibited very different seasonal patterns. In SN the river pollution mainly occurred between July and January, whereas in AG this happened in February and May. This substance has received many industrial applications, and the observed seasonal specificities very likely reflected the diversity of this solvent’s usages in different economic sectors implemented in these different regions. This is at variance with substances receiving mainly domestic applications, where the temporal patterns are expected to be similar whatever the location, at least within the France mainland territory.

Figure 50: Seasonal variations of the basin-averaged exceedance rates for the solvent Dichloromethane, in the AG and SN basins, integrating the 2009-2012 measurements.

For Trichloromethane (Chloroform), by contrast, no such obvious trend could be derived. The \( p \) values are persistently varying in the 0.5 to 1% range at the nationwide scale. Yet, in the RMC it was possible to detect that the exceedance rates were typically higher in the latest years 2017-2020 compared to the previous 2009-2013 period (cf. Figure 51). This finding could be of significance as one of the main applications of the Trichloromethane is the synthesis of polytetrafluoroethylene PTFE (INERIS 2014), with some specific pollution issues having been raised during the recent years regarding the release of perfluorinated compounds by some industries of the Rhône chemical valley (Mourier, 2019). In the RM basin instead, a slight decrease could be hypothesized from the 2014-2020 timeseries.

Figure 51: Interannual variations, for Trichloromethane, of the RMC basin annually-averaged cut-off exceedance rates \( p \) and the mean concentrations at the sites exceeding cut-off threshold \( \chi^* \). The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Regarding the Tributylphosphate, as for DCM, after a clear reduction until 2014, the surface water contamination seems to have stabilized to \( p \) values about 0.5%.

For Tetrachloroethylene, with \( p \) values typically <1%, there is no overall trend at the national scale. Some seasonality aspects were identified in RMC and RM basins, with more frequent exceedances met in summer and fall.

Regarding the Tetrachlorocarbide solvent, it was essentially quantified in the SN basin. Overall the contamination indicators in these basins are slowly lowering since 2012, but this concerns very few sites (less than 10 sites with exceedances, \( p < 0.1\% \)).

Three Trichlorobenzene (TCBs) compounds have been measured in France through the WFD surface waterbodies assessment monitoring: 1,2,3 TCB, 1,2,4 TCB, and 1,2,5 TCB. The RMC multiyear timeseries in
Figure 52 reports the indicators for the sum of these 3 TCBs, in regard of the Rhône valley petrochemical sector, which has been a major emitter of the TCBs. As shown, it seems that a significant reduction of the exceedance sites has been obtained over the studied period. Our Mann-Kendall trend analysis could not confirm this, however, due to poor statistics. The TCB concentrations in the residual sites showing exceedance do not indicate any clear trend either.

Figure 52: Interannual variations, for the 3 considered Trichlorobenzenes species, of the RMC basin annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^*$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Regarding the flame retardants, it was only possible to successfully assess some faint downward trends in the SN basin, summing-up the signals of the two most quantified BDEs, i.e. BDE 28 and 99, whereas the national values were also identified as decreasing.

Some seasonality is observed for Biphenyl compound. This compound has very diverse uses, and industrial plants are potentially significant contributors to it (INERIS 2018). Threshold exceedances are more widespread (yet limited to a few %) in the RM and SN basins. It tends to exhibit higher exceedance rates during the winter to early spring periods. Distinctly higher concentrations are incidentally found in the RM and RMC basins, possibly due to the detection of some punctual releases from industries.

Two other regional particularities regard the Hexachlorobutadiene HCBD and the Pentachlorobenzene solvents’ occurrence in the RMC basin, whose concentrations - in the few sites where they were quantified over the cut-off value - recurrently peaked during the fall/winter seasons.

Table 4 summarizes the trends identified for all these industrial chemicals. With the exception of the alkylphenols, no significant trend could be derived for most of the remaining situations, with only isolated cases of upward variations. The RMC basins was the most concerned by identifiable trends, probably in relation with the important industrial plants located in some parts of this region.

Table 4: Summary of the identified trends of the exceedance rates $\rho$ for WFD industrial and POP compounds. Statistically significant upward trends are indicated in pink-coloured cell with an ‘$\uparrow$’ symbol. Downward in green with an ‘$\downarrow$’. Trend significance are as follows: *** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data.

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1.2 (***): Significant trend.
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Considering in Table 4 the Sen’s slopes \( Q \), and especially those established at the national scale with the highest confidence (i.e. those elements with slopes marked "***"), we can apply eq. (8) to assess the relative changes of the exceedance rates induced until 2020 since the trends’ starting years \( K \). Doing so, some significant relative changes could be stated for the alkylphenols 4-NP and 4OP, with respectively about 60% decrease since 2009 and 40% decrease since 2012.

For those industrial or legacy POP compounds not mentioned in Table 4, no seasonal concentration patterns nor any significant interannual trend could be identified.

### RISK AND CONTAMINATION INDICATORS: RIVER BASINS COMPARISONS AND SPECIFICITIES

Regarding industrial chemicals, as shows Figure 53 reporting values integrated from the 2016-2020 period, the highest contamination indicators \( X_c \) stand for DEHP and 4-Nonylphenols, though remaining limited to a few percent. A notable contamination is observed in the AP basin for 4-NP (\( X_c \) about 7%), distinctly above other basin’s figures, likely related to the high population and industrial densities in this region, as alkylphenols are known to originate from both domestic and industrial sources (Moilleron 2019). Relatively extended contaminations (>2%) are also observed for DEHP in SN, possibly related to high population density, and less expectedly in LB.

AP shares with AG the highest \( X_c \) values for Octyphenol, and Xylene.

With respect to the risk indicator \( X_r \), the highest values are observed for DEHP in LB, SN and RM basins. Somewhat lower values (close to 0.1) are met for 4-NP in AP, Octylphenol in AG or Pentachlorobenzene in RMC.

**Figure 53**: Multiyear (2016-2020) integrated indicators of contamination (\( X_c \)) and risk (\( X_r \)) for the considered industrial compounds. \( X_c \) values of each basin are presented through the cumulative histograms (linear scale), and \( X_r \) values by the round dots (log scale).

For the WFD legacy POPs (cf. Figure 54), the contamination indicators are all very low. This is sufficient, however, to induce high \( X_r \) values for the PFOS compound, exceeding 0.1 in all basins, and even 1 in SN and LB.

**Figure 54**: Multiyear (2016-2020) integrated indicators of contamination (\( X_c \)) and risk (\( X_r \)) for the considered
II.4. DISCUSSIONS

From the above described information brought by our indicators (combining data on contamination, risk and trends), several general statements can be driven for the studied WFD metals, PAHs and industrial compounds.

On the one hand, considerations can be made regarding the compounds studied that are currently of growing or persistent ecological concern, despite their long-term management under the WFD, including:

- Metals and Arsenic is a first chemical group justifying a high level of concern for surface water chemical quality, due to the combination of their trends (most often increasing or left undefined), associated to their concentrations approaching the EQSs. This is especially true for Arsenic, similarly at stake in every of the six basins, but also for Cadmium (in AG), Copper (in SN) and Zinc (in LB). It must be noted, however, that the risk indicators accounted for in this study didn’t consider the bioavailability aspect of these trace elements, which is, by contrast, embedded in the most recent WFD EQS, and which would probably moderate the here highlighted risk statements. In terms of trends of the exceedance \( \rho \) indicators, the elements having undergone the highest relative increase in 2020 compared to 2010 were Cd and Pb, with 60 to 70% more monitoring sites presenting exceedances in mainland France.

- Two PAHs compounds, namely Benzo(a)pyrene and Fluoranthene, in spite of their downward contamination trends successfully evidenced by our indicators, maintain preoccupying risk profiles when compared to their water EQS (especially in AP, RM and SN basins). It is likely, however, that the more recent biota EQS approach promoted by the WFD will significantly moderate the regulatory risk statements for these compounds.

- Regarding legacy compounds, residual hot spots of PFOS are expected to continue damaging the water quality, at least in the LB and SN basins, but also in AG and RMC.

- A final negative general statement is the fact that for a large part of the compounds, in spite of many monitoring points and multiyear data collection, it was not possible to derive trends at the basin or at the national scales. This is true for metals in a large part of the basins, as the natural variations of their important geological backgrounds are big enough to hide the anthropogenic influence. This is not entirely surprising when one considers the results of preceding large-scale studies which did show that in the recent decades, metals concentration in French sediments had gone down to values close to their natural regional geological background levels (Dendeviel 2020b). The quantification capabilities in the water matrix was also a limiting factor for some of them, like Cadmium or Mercury, the latter certainly being more appropriately handled by aquatic biota monitoring. Nevertheless, when considering the national indicators \( \rho \), it appeared that for most of the metals the spatial frequency of threshold exceedance was going up, which was not expected a priori considering the emission reduction actions undertaken since the beginning of the century at the basins’ scales. The influence of the runoff on the growing fraction of the French lands made impervious was questioned, in relation to the recent specific increase of exceedance rates of the metals met during the wet seasons.

- Undefined wide-scale trends were often met also for many industrial HVOC and BTEX compounds, as well as for most of the legacy POPs, in spite of their expected long-term dissipation, due to their low concentrations that challenge the analytical capabilities of the monitoring labs.
On the other hand, the results of the present study have objectivated the clear capability of the WFD chemical surveillance to evidence the reduction since 2009 of some contaminants inputs affecting the French surface waters quality.

Nice improvements were thus evidenced at the national scale for PAHs, for 3 of the 4 studied compounds, and reflected by decreasing contamination occurrences observed in one third of the basin/compound trend analyses, with zero associated increase occurrence. Compared to the earliest years of the studied period, their 2020 national exceedance rates was lowered by 60 to 80%, which represents the best identified achievements among all the 100 considered WFD compounds.

Significantly diminishing contamination indicators were also reported for some of the HVOCs (Dichloromethane, Trichloromethane, Trichloroethylene), and even more clearly for the two monitored alkylphenols (4-NP, 4tOP), confirmed at the national scale and in some of the basins, especially RMC.

As of metals, significant improvements since 2012 were detected in the historically polluted AP basin, for species that characterized the waters of this basin as particularly contaminated, i.e. Cd, Zn and Pb. Such success could not be confirmed in the other basins, with the exception of Cr in RMC.

Finally, this study was an opportunity to derive unequalled information on the seasonal patterns of the chemicals' emission and use, through the variation of the cutoff threshold exceedance rate indicator $\rho$ and surface water mean concentrations. Indeed, the monthly sampling frequency of the WFD monitoring, when associated to the rich statistics of the multiyear integration, permits the extraction of fine temporal features, which may in turn be related to the dynamics of the pollution sources, i.e. to the most significant products use, or to the main emission process or sources of the chemicals.

With respect to metals, although the seasonal contrasts were sometimes rather weak and difficult to interpret, we were able to derive general similarities between several of the WFD trace elements, e.g. the typically higher dissolved contamination indicators found in wet seasons for most of them (excepting Arsenic), which may be imputed to exacerbated surface runoff from both urban and agricultural areas, as well as to river pH values or Redox conditions more favorable to speciation in dissolved forms. For Arsenic instead, the indicators do rise in warm/dry seasons, possibly related, in part, to the thermal activation of the bacterial reductive desorption of its most soluble form (arsenite), and/or to the reduced the low-flow dilution. In general, our trace element indicators proved to be a good - and rare - opportunity to confirm at large-scale some previous theoretical or experimental studies, in terms of the influence of bio-physical-chemical river conditions on dissolved fraction concentrations.

Concerning PAHs, we revealed very distinctive seasonal patterns, featuring high winter river contamination peaks. Benzo(a)pyrene and Fluoranthene both presented very similar profiles, either in terms of seasonal, interannual and regional distributions, strongly suggesting common emission sources, at least when it comes to surface water contamination. Comparing different periods along the 2009-2020 timeframe, we were able to decouple some steady winter components in the BaP and Fluoranthene river contamination profiles, corresponding to the heating system contribution, and another components regressing in the rest of the years, likely reflecting the improvements brought by continuous emission reduction from the renewal of the vehicle fleet, that explained the overall decline of these PAHs in water. Reduction in industrial emissions to water might also have contributed. Given the high rate of these PAHs interannual decrease in water, and despite some similar spatial patterns between water and soils PAH contamination at the national scale, we discarded the idea that the erosion from the historically contaminated soils could be a country-wide primary contribution to the measured surface water PAHs levels.

The Naphthalene seasonal fingerprint was shown as very different from the BaP and Fluoranthene's, clearly involving other emission sources, and exhibiting the highest seasonal contrasts, likely related to its strong linkage to runoff enhancement in wet seasons, and to its volatility exacerbated in warm conditions.

Finally, the seasonal variations of several industrial compounds were also characterized, with some significant
changes in these distributions over the years (e.g. Nonylphenol), or with specificities according to the considered river basins (e.g. Dichloromethane, Biphenyl, HBCD or Pentachlorobenzene).
Ill.1. AUTHORIZED PPPs

SEASONAL DYNAMICS OF THE SURFACE WATER RESPONSE TO AGRICULTURAL ACTIVITIES

Contamination peaks and river basins specificities

The seasonal contamination of rivers by PPPs is directly linked to the products application periods in the fields. This, in turns, depends on various factors, like the crop types or the climate conditions.

Many studies have reported PPP active substances contamination peaks in streams at the local scale, subsequent to rain events occurring upon the treated fields (Castle 2018, Belles 2019). These “flushes” may occur through very limited time periods (e.g. a few hours or days) according to the size of the studied catchment.

As was done previously for other compounds in Part II, it is of interest to aggregate PPP active substance concentration data from many sites, over several years, in order to obtain statistical relevance for the description of seasonal aspects of agricultural pressures and their related impacts on water. This approach had already been investigated in France (Gauroy 2011), suggesting that some active substance specificities (e.g. concentration peaking times, and catchment-to-river transfer intensities), associated to their use in different hydro-ecoregions, could be satisfactorily reflected through their monitoring in surface water.

Regarding the present work, we have been dealing with some even stronger aggregation, concerning hundreds or thousands of sites scattered over even larger territories, i.e the whole mainland France, or the 6 large continental river basin districts. This implies that we expect much wider peaks as compared to local studies, due to the contribution of sites where the substance is used at various dates for a large range of crops. The peaking times through our study will then be representative only of the dominant PPP application periods, and will not be able to efficiently reveal the less widespread usages.

As illustrations of how this converts into the WFD monitored river contamination, Figure 55 and Figure 56 display the cases of the two herbicides Chlorotoluron and 2,4 MCPA, which exhibit very different profiles, peaking respectively in fall/winter and in spring periods. The curves showing the concentrations in sites with threshold exceedance cover only the sites with the highest contaminations (i.e. likely the catchments with the strongest substance uses). In the case of 2,4 MCPA, whereas the fraction of sites with cutoff exceedances get strongly attenuated in the winter period, as shown by the profile, it appears that the sites with significant product use remain instead significantly contaminated over the whole year. As a matter of facts, this herbicide actually received, aside of its main use in spring on cereal crops, usages in autumn for grassland dandelion weeding, or lawns treatment.
The same phenomenon is observed with the fungicide Azoxystrobin, in Figure 57, associated with a flatter profile, widening from April up to autumn. This larger time window can be understood due to its multiple applications, as Azoxystrobin is part of the strobilurins class of post-emergence broad-spectrum systemic fungicides, preventing and/or curing foliar diseases caused by several major groups of pathogenic plant fungi. It is registered for use in a lot of different crops and can control soil-borne and foliar diseases (Bartlett 2001, Rodrigues 2013). Compared to the 2,4 MCPA herbicide, we have the additional observation that the sites with the major uses exhibit a distinct time-profile: for these "high-use" sites, the maximum concentrations are observed in August, in spite of having overall more sites exceeding in May. This suggests specific and more intensive use of this molecule in August, but on a more restricted number of sites. Deeper investigations revealed that the highest August concentrations were found in RMC and LB basins, possibly related to Azoxystrobin applications in viticulture and arboriculture.

In Figure 58 we illustrate the case of the molluscicide active substance Metaldehyde, our indicators witnessing the fact that two distinct major application periods typically occur in France during the year, i.e. spring and fall. These observations are very consistent with the results of a recent English study (Castle 2018), which imputes the autumn and winter peaks to the usual applications of Metaldehyde to protect cereals, oilseed rape and potatoes against molluscs that thrive in the wet weather conditions, and spring peaks to horticultural use in the growing period for summer plants.
the case of the herbicide Chlorotoluron, of which the $\rho$ values reflect that this substance has very similar application calendars over the whole metropolitan territory, i.e. mainly uses during fall and early winter. A consistent seasonal behavior is offered in Figure 60, regarding the concentration values. Chlorotoluron is, indeed, traditionally used in autumn, for pre-emergence or post-emergence, but it is also effective in late applications, especially to manage grassy weeds at the end of winter.

**Figure 59**: Seasonal variations of the basin-averaged exceedance rates $\rho$ for the herbicide Chlorotoluron, integrating the measurements from 2009-2020.

**Figure 60**: Seasonal variations of the basin-averaged concentrations at the sites exhibiting cutoff exceedances $\chi^c$ for the herbicide Chlorotoluron, integrating the measurements from 2009-2020.

This is at variance with the fungicide Boscalid, shown in Figure 61 and Figure 62, which display opposite patterns: the spatial extension of the exceedance ($\rho$) is maximal in spring and summer, whereas the concentration is much more erratic, due to very diverse applications depending on the regions.

**Figure 61**: Seasonal variations of the basin-averaged exceedance rates $\rho$ for the fungicide Boscalid, integrating the measurements from 2015-2020.

**Figure 62**: Seasonal variations of the basin-averaged concentrations at the sites exhibiting cutoff exceedances $\chi^c$ for the fungicide Boscalid, integrating the measurements from 2015-2020.

Figure 63 and Figure 64 summarize the seasonal patterns of the exceedance rate $\rho$ determined from the integration of the 2016-2020 data, respectively for the herbicides, and the fungicides (+ molluscicide Metaldehyde) that were still authorized as PPPs in 2016 and after, at the full mainland France scale, as well as for every of the 6 main basins. This synthesis provides a visual of the varieties and the similarities between the various substances’ profiles in France, with distributions reflecting either wide applications periods (e.g. Glyphosate, or some fungicides), or unimodal and bimodal peaking periods (spring and autumn typically).

These figures also provide the time windows, for each basin, during which it would be potentially relevant to increase the monitoring frequency of the different active substances.

The AP basin gathers the maximal exceedances for most of the active substances, consistently with its higher agricultural area density, and higher pesticides areal consumption (cf. Appendix E, Figure 148 to Figure 151).
Noteworthy also are some relatively high values in other basins, many of these concerning substances related to cereal and maize cropping, or receiving non-agricultural usages, i.e.:

- In SN: Diflufenicanil, Chlorotoluron, Bentazone, Métazachlor, Glyphosate, Aclonifen, and Tebuconazole
- In RM: Metazachlor, 2, 4D, Nicosulfuron, Thiabendazole, Tebuconazole
- In AG: Metaldehyde and Nicosulfuron
- In RMC: Glyphosate
- In LB: Nicosulfuron

**Figure 63**: Seasonal variations global mapping of the 2016-2020-averaged monthly exceedance rates $\rho$ (red-coloured histograms), for all the considered herbicides that were authorized as PPPs in 2016 and after, at the national scale (first column), and in the 6 basins (following columns). The percentages figures in each red histogram bar provide to the $\rho$-values. The annual means of $\rho$ are given in **bold font** for each basin/compound pair, aside of the December bars. The round symbols ranging from ● to ○ and those of intermediately filled qualitatively indicate the ranking of the basin in terms of contamination: highest contamination= ●, lowest = ○.

**Figure 64**: Seasonal variations global mapping of the 2016-2020-averaged monthly exceedance rates $\rho$ (red-coloured histograms), for all the considered fungicides and molluscicides that were authorized as PPPs in 2016 and after, at the national scale (first column), and in the 6 basins (following columns). The percentages figures in each red histogram bar provide to the $\rho$-values. The annual means of $\rho$ are given in **bold font** for each basin/compound pair, aside of the December bars. The round symbols ranging from ● to ○ and those of intermediately filled qualitatively indicate the ranking of the basin in terms of contamination: highest contamination= ●, lowest = ○.
Considering all these WFD PPP residues, May and June appear as the most impacting months for the surface waters, both in terms of variety of active substances, and in terms of number of basins concerned. Glyphosate, Metaldehyde are the PPP residues that most often exceed the cut-off levels throughout the year. Tebuconazole is the most common fungicide contaminant.

The annual variations of the average exceedance indicators, considering all these substances together, is displayed in Figure 65, for each basin. It highlights the upper position of the AP basin. Figure 66 complements this picture by considering the number of substances for which the 2009-2020 averaged monthly exceedance rates exceed 5%. It suggests that mixtures of WFD PPP active substances are likely to occur at more numerous monitoring sites during these spring and fall seasons.

Figure 65: Seasonal variations of the basin-averaged exceedance rates $\rho$, mixing the 16 PPP active substances that were authorized in 2009 and after, integrating the measurements from 2016-2020, for the 6 basins.

Figure 66: Seasonal variations of the number of substances which exhibit $\rho$ values >5%, considering the 16 PPP active substances that were authorized in 2009 and after, integrating the measurements from 2016-2020, for the 6 basins (curves), and the 6 basins altogether (histogram).

In this regard, the already discussed increase of activated monitoring sites in spring and autumn, which is already in place in four of the six main basins (cf. Part II.7), is consistent with this pesticide pressure reality. The measurement frequency at each site in these high PPP use periods, however, could probably be reconsidered in various basins, as it still often stands close the minimal requirement of a single occurrence per month. The success in improving the capture of pesticide’s risk to surface waters with such an adaptation of the sampling strategy has been emphasized by earlier studies (Weisner 2022).

Detecting changes in the PPP use over the years

The richness of the gathered dataset allows to breakdown the seasonal contamination profiles with respect to some specific period of time over the studied period 2009-2020. The Figure 67 to Figure 70 reveal how the WFD river contamination monitoring permits to disclose some significant changes in the use of some of the considered PPPs.

In Figure 67 for instance, the fungicide Azoxystrobin profiles ($\rho$ and $\chi^{-1}$) extracted from the earlier period 2009-2012 appear quite different as compared to the ones obtained between 2016 and 2020, with a distinct shift toward dominant spring uses.

A similar shrinking of the application periods toward spring is also observed after 2011 for herbicide Nicosulfuron, from Figure 68, associated with lower induced-concentrations, even in spring. This could be explained by the fact that Nicosulfuron has been recognized as a strong resistance promoter in corn weeds, with recommendations to limit its application periods.
Figure 67: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{\text{c}}$ for the fungicide Azoxystrobin, separately integrating the measurements from the 2009-2012 and 2016-2020 periods.

Figure 68: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{\text{c}}$ for the herbicide Nicosulfuron, separately integrating the measurements from the 2009-2011 and 2017-2020 periods.

Other pictures are offered by the herbicides Pendimethalin and Diflufenicanil (DFF), which are typically present in PPPs as complement to Chlortoluron, extending its anticotyl spectrum and increasing its activity on grasses. They found extended application when Isoproturon went being banned in 2017. DFF has been used as an early application in pre- or post-emergence of cereals, but can also be used until the end of winter. It was also often used for the weeding operations in roads sides, green spaces or gardens.

By contrast with Nicosulfuron, Figure 69 and Figure 70 for Pendimethalin and DFF indicate recent significant increases of their use during fall (November and December).

Figure 69: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{\text{c}}$ for the herbicide Pendimethalin, separately integrating the measurements from the 2009-2012 and 2017-2020 periods.

Figure 70: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{\text{c}}$ for the herbicide Diflufenicanil (DFF), separately integrating the measurements from the 2009-2014 and 2015-2020 periods.

INTERANNUAL VARIATIONS

Trends in river contamination

Herbicides
The inter-annual variation of our contamination indicators for some high volumes/sales herbicides are exemplified in Figure 71 to Figure 73, featuring Bentazone, Pendiimethalin and Oxadiazon, i.e. three contrasted situations, reflecting respectively steady, increasing and decreasing usage trends.

Bentazone shows no obvious contamination trend since 2012. On the contrary, a continuous and significant increase is observed for Pendiimethalin values, capping during the last 3 years.

Figure 71: Interannual variations, for the herbicide Bentazone, of the national scale annually-averaged cut-off exceedance rates and the mean concentrations at the sites exceeding cut-off threshold . The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Figure 72: Interannual variations, for the herbicide Pendiimethalin, of the national scale annually-averaged cut-off exceedance rates and the mean concentrations at the sites exceeding cut-off threshold . The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

For Oxadiazon, its presence in French rivers has been collapsing during the studied decade, as represented by the exceedance rate continuous downward variation. The river concentration at the sites maintaining threshold exceedances (sites with local uses of the molecule) slowly declined between 2012 and 2017. After 2018, very few sites were left with cut-off exceedances, but it seems that they were kept with high induced concentrations, though the statistics became bad for robust interpretation.

Figure 73: Interannual variations, for the herbicide Oxadiazon, of the national scale annually-averaged cut-off exceedance rates and the mean concentrations at the sites exceeding cut-off threshold . The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Overall, as shown in Table 5 describing the trends identified from the exceedance rates timeseries , among the 15 WFD herbicides having received authorized uses during the study period, 8 demonstrate some distinct decreasing behaviors at the national scale, while only one (Pendiimethalin) exhibits a distinct increase. For the remaining ones, a rather steady behavior is recorded, at least during the latest years of the studied period.

As of their variations in the six main basins scales, they generally fit quite well with the national trend (though their appearances may differ in time), indicating shared practices changes over the whole territory, which is largely explained by the fact that the active substances ban or restriction apply with the same severity to all the region. A few diverging trends between basins are observed, however, resulting in some national undefined trends, as happening for Bentazone, Chlorotoluron or Aclonifen.

Table 5: Summary of the identified trends of the exceedance rates for WFD herbicides. Statistically significant upward trends are indicated in pink-coloured cell with an symbol. Downward in green with
Trend significance are as follows: *** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data.

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As a synthesis, the interannual change in the average of the threshold exceedance rates of these authorized WFD herbicides is shown in Figure 74. As expected, a continuous decline over the study period is observed, ultimately lowered to half the level of the earliest years. At the residual sites showing
exceedances (the exceedance occurrence numbers per year are given in blue types within the histograms), the corresponding average herbicides concentration, however, tends to increase at the end of the period, reflecting the fact that these locations are also those with the most intensive PPP uses.

**Figure 74**: Interannual variations, mixing all the considered herbicides that were authorized in 2009 and after, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{>\tau}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

**Fungicides**

Interannual timeseries of the authorized WFD fungicides concentrations and cut-off threshold exceedance rates are exemplified in Figure 75 (Boscalid), **Figure 76** (Tebuconazole) and **Figure 77** (Azoxystrobin).

Boscalid exhibits the most obvious $\rho$ decrease, but on a more general standpoint, after a progressive inflation until 2015, $\rho$ appear to have been declining for most of these molecules during the 2016-2020 period. For Azoxystrobin, we show a comparison between the national and the AG basin $\rho$ values, for which the decline occurred after on long-lasting growth, and only since 2019, so that our Mann-Kendall trend assessment process indicates an upward trend.

**Figure 75**: Interannual variations, for the fungicide Boscalid, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{>\tau}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

**Figure 76**: Interannual variations, for the fungicide Tebuconazole, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{>\tau}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

**Figure 77**: Interannual variations, for the fungicide Azoxystrobin, of the annually-averaged cut-off
exceedance rates $\rho$, considering separately the national scale (grey-coloured histogram) and the sole AG basin (orange-coloured). The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

As of Thiabendazole, the BNV-d figures indicated that it was significantly used as a fungicide PPP only in the AP basin (Thiabendazole, as a pre- and post-emergence fungicide, is used extensively on potatoes, on tubers, or during storage to prevent dry rot by Fusarium species). The exceedance rate $\rho$ approaches 10% there, and some significant decrease was detected since 2013.

All in all, as shown in the Table 6 reporting the trends derived from the $\rho$ timeseries, 4 the 7 fungicides having received authorized use during the study period demonstrate distinct reduction of the exceedance occurrences at the national scale, at least during the five latest years of the studied period. As a reminder Iprodione and Quinoxifen had been banned during the studied timeframe. Only a few contrasting behaviors are observed in some basins, e.g. regarding the upward trends of Azoxystrobin in RM and AG, or Cyprodinil in SN.

Table 6: Summary of the identified trends of the exceedance rates $\rho$ for WFD fungicides. Statistically significant upward trends are indicated in pink-coloured cell with an $\uparrow$ symbol. Downward in green with an $\downarrow$. Trend significance are as follows: *** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data

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Figure 78 pictures the average of concentrations and cut-off exceedance rates for all these WFD.
fungicides. A downward global trend showed up since 2016 for the exceedance spatial extension ($\rho$), while the overall concentration remained rather steady over the period. Interestingly, whereas fungicide use is known to be very dependent on pluviometry, we were not able to distinguish any specific signal from the wettest years, i.e. 2013, 2014 and 2018, neither in terms of threshold exceedances, nor concentrations. This is likely due to the fact that, at the large spatial scale of our indicators, in times of increased PPP loads (during wet years), the concentration values are counterbalanced by increased dilution by river flows.

*Figure 78:* Interannual variations, mixing all the considered fungicides that were authorized in 2009 and after, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{\geq}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

**Insecticides and molluscicides**

*Figure 79 to Figure 81* display the river contamination timeseries for the three WFD insecticides having benefited from use authorizations during our study period. The neonicotinoid Imidaclopid is the one benefiting from the best statistics, indicating a slight but continuous river contamination increase until 2018, followed by a drastic drop in 2019-2020, as most of the applications of this molecule were phased out in France in 2019.

*Figure 79:* Interannual variations, for the insecticides Imidaclopid, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{\geq}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

By contrast, Chlorpyrifos-ethyl, and Cypermethrin (widely monitored since only 2013), suffer from low quantification rates, translating into low cut-off exceedances (in the 0.1% range, typically less than 20 sites per year contributing over the cutoff threshold), complicating any reliable trend identification, although a rather distinct collapse of the cut-off exceedance rate can be observed for Chlorpyrifos-ethyl since 2014.

*Figure 80:* Interannual variations, for insecticide Chlorpyrifos-ethyl, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{\geq}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.
**Figure 81**: Interannual variations, for the insecticide Cypermethrin, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^{**}$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

With regard to the molluscicide Metaldehyde, in spite of elevated exceedance rates (10% in average) it underwent strong variations from year to year since 2015, so that it wasn’t possible to derive a reliable interannual trend. Peculiarly high contamination values were observed, though, in 2019 and 2020, especially in the LB and AP basins, which were surprising, considering that the sold tonnages had been decreasing continuously in all basins between 2013 and 2019.

The Table 7 summarizes the trends visually observed from the exceedance rates timeseries for these molecules, reflecting the Chlorpyrifos-ethyl and Imidacloprid bans in 2014 and 2016 respectively. The Cypermethrin data were too scarce to derive any trend, and only one trend could be diagnosed for the Metaldehyde indicator, in LB.

**Table 7**: Summary of the identified trends of the exceedance rates $\rho$ for WFD insecticides and molluscicides. Statistically significant upward trends are indicated in pink-coloured cell with an $\Uparrow$ symbol. Downward in green with an $\Downarrow$. Trend significance are as follows: *** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data points.

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Rivers and farmers responses to products bans or restriction

PPP bans are reflected in the BNV-d data, through a drastic decrease in the tonnage sold in France and in the various basins.

This is exemplified below, in Figure 82 to Figure 88, where we report for 2 herbicides, and 2 insecticides the national annual means of the cut-off threshold exceedance rates $\rho_k$, together with the cumulated yearly tonnage figures $T_{j,k}$ of the six basins.

For each of these molecules, after the extinction of the tonnages, it can be seen from the residual values expressed by $\rho$ that the contamination in rivers typically takes several years to disappear. Two main reasons can explain this:

1. Product owners used up their product stocks in the years following their bans. This could be verified for Isoproturon (intensively used in cereal crops regions like SN and LB basins, with 2 application periods for this pesticide, at the winter cereal sowing and at the vegetation regrowth). Figure 83 shows that before and after the ban, which produced its effect on sales in 2017, the $\rho$ seasonality profiles were kept similar. The same phenomenon could be observed for Linuron after its ban in 2018, with sharp May-June contamination maxima being maintained until 2020. For Aminotriazole (ban year 2016), the situation was more complex, as this molecule was used both as a PPP herbicide (typically in vineyards and orchards, all over the year) or as a biocide herbicide (typically in urban context, or along linear infrastructures like roads and railways), with different application periods. The seasonal profiles displayed in Figure 85 reflect this complexity during the authorized used period 2009-2015, with a large exceedance peak in spring, generating relatively high concentrations in waters. After the extinction of the sales in 2016, the residual concentration profile is fully free of the former springtime peak, but the wider feature peaking in July and continued until December appears to be maintained, inducing during these months some moderated concentrations, similar to the authorization period. Considering that the use of herbicides in

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urban context, where they used to be intensively applied in spring period on young
erbaceous vegetation, was gradually eliminated since the enactment of the 2014 Labbé law
in France (French Presidency 2014), one likely explanation for the observed change after the
ban is that the residual water contamination after 2016 was mainly imputable to the
progressive disposal of agricultural product stocks. The high concentrations before 2016 were
then associated with urban uses, during spring.

Figure 82: Compared interannual variations of the BNV-d-registered yearly tonnages (histogram
cumulating the tonnages of the 6 basins) and of the national-scale annually-averaged exceedance rates
ρ, for the herbicide Isoproturon.

Figure 83: Seasonal variations of the national scale-averaged exceedance rates ρ and concentrations
at the sites exhibiting cutoff exceedances χ⁺ for the herbicide Isoproturon, separately integrating the
measurements from the 2009-2016 and 2017-2018 periods.

Figure 84: Compared interannual variations of the BNV-d-registered yearly tonnages (histogram
cumulating the tonnages of the 6 basins) and of the national-scale annually-averaged exceedance rates
ρ, for the herbicide Aminotriazole.

Figure 85: Seasonal variations of the national scale-averaged exceedance rates ρ and concentrations
at the sites exhibiting cutoff exceedances χ⁺ for the herbicide Aminotriazole, separately integrating the

2. A second cause for remnant river contamination after the ban can be the persistency of the
molecule in the soils and in the sediments. This could have happened with Imidacloprid, for
which the sales were stopped in 2018 (cf. Figure 86). Indeed, as Figure 87 shows, the
seasonality profile of the river contamination after 2019 is quite different from the 2009-2017
authorization period. The post-2018 profile no longer exhibits the former November-
December compound leakage peak, showing instead a wide distribution which is more typical
of the legacy persistent molecules (cf. section III.3). As a matter of fact, the literature assigns
to Imidacloprid some very high in-field DT50 values (174 days), classifying it as a persistent
contaminant. One should also mention, however, some remaining authorized uses of
Imidacloprid as veterinary insecticide and as biocide, which could contribute also significantly
to the observed residual water contamination (Perkins 2021a, Perkins 2021b, Dipens 2023).
Interestingly, the use of Imidacloprid-containing spot-ons for dogs (products applied directly
to the animal skin) was recently found to be most frequent in the months of July and August
in the UK, and in September and October for cats (Anthe 2020), which, though not proving anything, well correspond to the 2019-2020 residual contamination seasonal signals of Figure 87.

**Figure 86**: Compared interannual variations of the BNV-d-registered yearly tonnages (histogram cumulating the tonnages of the 6 basins) and of the national-scale annually-averaged exceedance rates $\rho$, for the insecticide Imidacloprid.

**Figure 87**: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi_{\text{cut}}$ for the insecticide Imidacloprid, separately integrating the measurements from the 2009-2017 and 2019-2020 periods.

Chlorpyrifos-ethyl was used to control insects (aphids, caterpillars) in wheat, oilseed rape, vineyards, vegetable crops (potatoes, turnips) and fruit crops (apple, pear and peach trees). It is a semi-persistent molecule in soils (in-field DT50=27 days), so that its observed remanence in water after the 2017 ban is expected to be due to residual use (cf. **Figure 88**). As a matter of fact, its seasonal $\rho$ profile was found to be peaking around summer both before and after its ban, so that it is not possible to discard the possibility of a continued residual usage until 2019. Moreover, the **Figure 88** indicates that this molecule has been subject in 2016 to high rate of anticipated sales before its ban the following year, especially in SN, which suggests that it was planned to use it afterward.

**Figure 88**: Compared interannual variations of the BNV-d-registered yearly tonnages (histogram cumulating the tonnages of the 6 basins) and of the national-scale annually-averaged exceedance rates $\rho$, for the insecticide Chlorpyrifos-ethyl.

In other situations, however, like fungicide Iprodione, the market termination in 2018 translated into a direct disappearance of the molecule in the rivers. For the herbicide Oxadiazon, in spite of its high persistency in open fields (DT 50= 165 days), sales and river contamination have also been vanishing altogether rather tightly.

**Comparison of river contamination indicators with yearly PPP sales/tonnage figures**

In this section, we want to check in a more systematic way the empirical consistency between our two main datasets:

- the national and main basins river contamination indicators previously processed to ensure space and time consistency, annually averaged, $\chi_{ij,k}$ and $\rho_{ij,k}$, and their national-scale...
equivalents $\chi_{i,k}$ and $\rho_{i,k}$

- and the annual tonnages of PPP active substances sales over the six main river basins, $T_{i,j,k}$, and their national-scale equivalents $T_{i,k} = \sum_{j=1}^{6} T_{i,j,k}$

For this we explored the linear correlations between these two sets of indicators for the WFD active substances having had authorized use at minimum during the 2009-2017 timeframe.

Examples of satisfactory relationships are provided in Figure 89 to Figure 92, for both contamination indicators $\chi$ and $\rho$, and for two herbicides whose sold tonnages underwent contrasted scenarios between 2009 and 2020: Pendimethalin sales continuously increased, while 2,4 MCPA tonnages was globally trending downward.

**Figure 89**: Correlation diagram between the national-scale annual means of the concentration indicator $\chi$ and the total BNV-d extracted tonnage figures, for the herbicide Pendimethalin, over the 2009-2020 timeframe. The correlation line is pictured in dotted-blue and the $R^2$ value refers to the correlation coefficient.

**Figure 90**: Correlation diagram between the national-scale annual means of the exceedance rate indicator $\rho$ and the total BNV-d extracted tonnage figures, for the herbicide Pendimethalin, over the 2009-2020 timeframe. The correlation line is pictured in dotted-blue and the $R^2$ value refers to the correlation coefficient.

**Figure 91**: Correlation diagram between the national-scale annual means of the exceedance rate indicator $\rho$ and the total BNV-d extracted tonnage figures, for the herbicide 2,4 MCPA, over the 2009-2020 timeframe. The correlation line is pictured in dotted-blue and the $R^2$ value refers to the correlation coefficient.

**Figure 92**: Correlation diagram between the national-scale annual means of the concentration indicator $\chi$ and the total BNV-d extracted tonnage figures, for the herbicide 2,4 MCPA, over the 2009-2020 timeframe. The correlation line is pictured in dotted-blue and the $R^2$ value refers to the correlation coefficient.

As regards Pendimethalin, it is noteworthy that, by contrast with the uncorrected concentration timeseries presented above in Part I (cf. **Figure 8**), the $\chi$ indicator in Figure 89 reflects quite nicely the tonnage increase over the years, and in particular the 2016 upward offset associated with the replacement of Isoproturon by PPPs containing Pendimethalin for winter crops management.

The linear correlation coefficients $R^2$ between our indicators and the tonnage data, as well as the sign of the associated covariance coefficients, were determined for each of these 25 active substances. The $R^2$
values were considered significant when exceeding 0.27, which the significance limit for a set of 12
couples of independent data with a 95% confidence interval, according to the Student statistics.

Figure 93 reports, for each studied territory (mainland France and the six main basins) the fraction of the
25 compounds for which significant R² values were obtained, distinguishing the expected positive
covariances (tonnage and contamination are expected to vary together in the same direction) and the
observed negative ones.

**Figure 93**: Fraction of the considered 25 PPP active substances which were of authorized use in 2009 or after, whose annual contamination indicators $\rho$ (fully coloured histograms) or $\chi$ (hatched histograms) significantly correlate with annual BNV-d tonnage figures. Blue coloured histograms refer to positive covariance between the indicators, red ones to negative.

As can be seen from **Figure 93**, compared to the contamination indicator $\chi$, the cut-off threshold
exceedance indicator $\rho$ is a better predictor of the tonnage incidence on river contamination. This can be understood because, as equation (5) recalls, $\chi$ integrates the variability of both $\rho$ (relative number of sites showing exceedances) and $\chi^+$ (concentration at these sites). The good correlation of tonnages with $\rho$ values is particularly true at the national scale with half of the compounds concerned.

At the basin scale, the tonnage correlation to $\chi$ gets higher, which is also understandable, as one could expect that the tonnage figures become more relevant to explain the contamination when the considered area gets smaller and less diverse. A reverse effect is observed, however, for $\rho$. This could be due to the fact that, compared to the nationwide scale, for an increased amount of weakly quantified substances, the restricted number of contributing sites at basin-scale gets statistically insufficient to express a significant correlation to tonnage.

Nonetheless, overall, the occurrence of significant positive covariances (27% of the situations) is much stronger than the negative ones (2.5%), especially for $\rho$ to T associations, confirming the intuitive expectation that the sold tonnage is actually a dominant driver for river contamination.

The active substances that were still authorized in 2020, and for which the river contamination showed the best correlation to their sold tonnages, were Pendimethalin, Bescid, 2,4D, 2,4MCPA, Azoxystrobin, and Metazachlor.

Significant negative covariances are observed at the national scale for only a few compounds: Nicosulfuron, Diflufenicanil and Thiabendazole. As regards Thiabendazole, its alternative use as a biocide hindered the chances to observe simple relationship with PPP sale figures. At the basin level, significant negative covariances were only observed for Diflufenicanil, and secondarily for two compounds that were banned during the period (Iprodione and Chlorpyrifos), as well as once for the low occurrence insecticide Cypermethrin.

These observed negative covariances should also be compared to the above-described findings, where it was suggested from the display of seasonal contamination changes that the main Nicosulfuron and Diflufenicanil usages underwent significant modifications over the studied years, resulting in disturbed basin-to-river transfer potentialities. The apparent contradictory findings of increasing tonnages and decreasing surface water contamination for Diflufenicanil was already made by the French agency for food environmental and occupational health & safety, with a decreasing proportion of measured concentrations exceeding the EQS between 2009 and 2016 (Anses 2019a).
Figure 94 provides deeper understanding of the Diflufenicanil case: comparing the exceedance rates timeseries with a differentiation between the Spring-Summer periods (natural spontaneous vegetation periods) and the Fall-Winter ones, there is a clear discrepancy, with a progressive decline of the warm seasons contamination indicator, and a reverse trend for the cold seasons. This must be put in regard of the fact that Diflufenicanil, aside of its agricultural use for winter cereal protection, also used to be employed extensively for the weeding in non-agricultural contexts (road sides, green spaces, gardens…). As a matter of fact, the downward variations of the tonnage sold for non-agricultural purposes, shown in Figure 94, fully match with warm seasons contamination indicator decline.

**Figure 94**: Interannual variations, for the herbicide Diflufenicanil (DFF), of the national scale annually-averaged cut-off exceedance rates $\rho$, considering separately the spring-summer data (red-coloured histogram), and the fall-winter ones (blue-coloured). Also pictured, the yearly tonnage BNV-d data for DFF associated to non-agricultural usages (black curve).

This is further demonstrated by Figure 95 which clearly correlates the respective proportions of non-agricultural and agricultural tonnages to the ratio between warm and cold seasons water contamination indicators. This reflects that Diflufenicanil received its most river-impacting applications in urban contexts during the warm seasons, while its cold seasons uses are actually essentially restricted to agricultural purposes. The progressive abandonment of pesticides uses in French populated environments during the last decade strongly favored the surface water quality in spring and summer for this substance, in spite of the moderated fraction of the total tonnage dedicated to nonagricultural use (lower than 7% of the cultivated land uses). These findings are very consistent with the diagnostic made above for Aminotriazole, for which the warm season urban use turned out to be the most impacting for the river’s quality.

All this corroborates earlier results that pointed to a much higher potential for leakage to watercourses for pesticides used on impermeable grounds than for uses in the field. For instance, Wittmer et al. indicated loss rates for urban-use compounds up to an order of magnitude higher than those of agricultural-use compounds (Wittmer 2011).

**Figure 95**: Correlation diagram between the warm seasons to cold seasons ratios of the annual exceedance rates (y-axis) and the BNV-d non-agricultural to agricultural annual tonnage ratios (x-axis), for the national scale Diflufenicanil figures (2009-2020).

### III.2. SPECIFIC CONSIDERATIONS ON GLYPHOSATE AND AMPA

The herbicide Glyphosate has been extensively used in France for several decades. Glyphosate is essentially a grass control agent. It receives many applications in agriculture. The major agricultural uses are in field crops, viticulture and arboriculture.
In field crops, these uses cover the destruction of intercultural plant cover, crop regrowth, or perennial, annual and woody weeds, in order to sow or plant a new crop by limiting competition with weeds.

Examples of applications are preparation of spring and autumn seedlings, use after harvest on stubble of all crops, before the harvest of cereals (soft winter wheat, durum wheat, triticale, spelt, spring barley, winter barley), or destruction and limitation of the growth of fallow land and cover crops. It is used for weeding of vineyards and orchards, or devitalization of vine stocks.

It has also applications for market gardening crops, or weeding of forests.

Glyphosate also has received many non-agricultural applications, for the management of weeding in urban context, road and infrastructure management, and by private gardeners. As already mentioned in Part I (cf. Figure 152 of Appendix E), these non-agricultural uses amounted for up to 20% of the sales, before they were considerably restricted in 2017 and 2019 under the French legislation (French Presidency 2014).

This multiplicity of applications induced a permanent and extended contamination of the surface waters, throughout the 6 main French basins, as reflected by the seasonal profiles in Figure 63.

Tightly associated with the Glyphosate occurrence in the environment, the surface waters are also extensively contaminated by its main degradation product AminoMethylPhosphonic acid, also named AMPA (Botta 2009, Grandcoin 2017, Poigier 2017). The relative amounts of Glyphosate and AMPA in the freshwaters are governed by various processes, some of which having been empirically elucidated by recent studies. It has been for instance evidenced that the water phosphorus content was a determining factor to understand the AMPA accumulation resulting from the Glyphosate degradation by the riverine biofilms (Carles 2019). The ratio between Glyphosate and AMPA concentrations (G/A) was also found to be conditioned by the distance between the glyphosate source in the catchment and the monitoring site (Medalie 2020): the shorter the travel-time of Glyphosate from the source, the lesser the quantity of AMPA generated, and the higher G/A. This allowed to evidence that the use of Glyphosate in urban/developed contexts, where the pollution transportation by runoff is more effective than in agricultural fields (Hanke 2010), results in higher G/A values.

In this respect, interesting findings could be made by comparing the seasonal variations of the Glyphosate with those of AMPA. As can be seen in Figure 96, which compiles the contamination indicators $\rho$ and $\chi^{x'}$ from the whole mainland France during the 2009-2020 period, out of the fact that AMPA contamination is in the average much higher (G/A<1), there is a distinct offset between the two species' profiles. Glyphosate indicators peak in May, consistently with its main herbicide applications. AMPA, instead, is very distinctly peaking in August. These observations are similar to those made in previous seasonal variations studies (Poiger 2017, Carles 2019). Several hypotheses can be formulated at this stage to explain this shifted AMPA profile:

- either the AMPA concentration is influenced by continuous inputs to surface waters, like urban effluents, with some dilution effect diminishing in summer/low flow period (Botta 2009, Poiger 2017).
- or the AMPA is generated from the Glyphosate degradation in the river basins’ soils, and then progressively transferred to streams with a lag time of a few months. This last hypothesis qualitatively complies with some recent in-field Glyphosate to AMPA degradation studies (Carretta 2021), which indicated that the soil concentration of the generated AMPA is peaking about one month after the Glyphosate application, and that AMPA remains in the field surface for several months (DT50 varying between 110 and 250 days).

- The last hypothesis is the above-mentioned effect of the phosphorus availability in water, with eutrophication by phosphorus favoring the incomplete degradation of Glyphosate by natural river biofilms, and promoting the accumulation of AMPA (Carles 2019). The phosphorus concentration in rivers being most often significantly higher in dry periods (Abbott 2018), this might also contribute to the observed AMPA summer-peaking.

In theory, all these processes may cumulate, obviously. Further insights will be provided below in this respect, by comparing the relative behaviors of the two species each of the 6 basins.

**Figure 96**: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{-2}$ for the Glyphosate (blue-colored features) and AMPA (red-colored features), integrating the measurements from the 2009-2020 period.

**EXAMINATION OF THE GLYPHOSATE AND AMPA MULTIYEAR TIMESERIES**

Glyphosate is also among the active substances for which it was not possible to establish a good correspondence between the sold tonnage figures and our river contamination indicators. Figure 97 allows to easily visualize this discrepancy between the rather steady total annual tonnages (till 2018) and the contrasting variations of the $\rho$ exceedance indicator.

**Figure 97**: Compared interannual variations of the BNV-d-registered yearly tonnages (histogram cumulating the tonnages of the 6 basins) and of the national-scale annually-averaged exceedance rates $\rho$, for the herbicide Glyphosate.

Three “regimes” can be distinguished in **Figure 97**:  
- a declining and relatively low contamination period 2012-2014  
- second, a high contamination timeframe 2015-2018  
- finally, a second low contamination period 2019-2020, following the 2019 tonnage drop (which has been jointly observed for most of the PPPs, cf. section I.3).

The interannual comparison between the concentration indicators $\chi$ of the Glyphosate and its degradation
product AMPA is displayed in Figure 98. The three regimes observed in Figure 97 for ρ values are consistently reflected in these concentration timeseries. These steep variations probably mark some significant successive changes among the Glyphosate’s usages over the duration studied period.

It appears clearly there that Glyphosate has been a predominant contributor to the AMPA concentration values in French rivers during the study period, as both curves mostly reflect very similar variations. The cooccurrence of both species had already been stated at large scale in France on a qualitative standpoint (Carles 2019), but Figure 98 provides the additional evidence of some high quantitative consistency, which supports the major Glyphosate causality of AMPA’s presence in surface waters. This statement is of importance, as it had been suggested in many other studies that AMPA may also arise from the degradation of polyphosphonates which are components of various household and industrial products, particularly detergents (Jaworska 2002, Botta 2009, Struger 2015).

Figure 98: Interannual variations, for Glyphosate (blue curve) and AMPA (red curve), of the national scale annually-averaged mean concentrations χ.

Possible interpretations for the observed transition between the 2011-2014 and 2015-2018 regimes

Regarding the observed significant and surprising oscillations of the indicators, it first has to be noted that the 2015 upward offset in Figure 98 had also been previously documented independently by the French agency for food environmental and occupational health & safety, considering AMPA quantification frequency data, but could not be evidenced for the Glyphosate (Anses 2019b).

Looking, thanks to Figure 99, at the details in the seasonal profiles of the rivers’ contamination for these three regimes, it appears that the strongest relative differences between the indicators of the two regimes are observed in the October to January wet season periods, i.e. when PPP transfer induced by runoff or drainage is more likely to occur.

Figure 99: Seasonal variations of the national scale-averaged exceedance rates ρ for the herbicide Glyphosate, separately integrating the measurements from the years 2012-2014 (grey-colored histogram), 2015-2018 (blue-colored) and 2019-2020 (golden-colored).

A possible interpretation for the wet season Glyphosate river contamination rising after 2015 may be related to the fact that the place of intercropping had become more important in France, as incentivized by the 2015-2020 EU Common Agricultural Policy, through the “green payment” of farmers. Indeed, Glyphosate is the privileged chemical method to manage the destruction of intercrops, which typically has to be done in late fall and beginning of winter.

Another part of the explanation for the 2015 contamination offset could be that it was the year when the herbicide Aminotriazole sales collapsed (it was banned in December 2015), and Glyphosate was its main alternative as a broad-spectrum systemic post-emergence control agent (Reboud 2017). Indeed, looking at the six main river basins scales, we were able to find out that the main contribution to this steep upward change of the national exceedance rate between 2014 and 2015, though being common to all basins,
primarily came from RMC, with the SN basin also exhibiting a similar but smoother behavior. In RMC the exceedance rate growth between the two periods was general all over the year, whereas for SN this happened mainly in May-June and November-December. As a matter of facts, we could check that the SN and RMC basins were also those recording the highest Aminotriazole tonnages per area unit before 2015, i.e. where the most intense transitions to Glyphosate could be expected.

Looking now at the equivalent display for the Glyphosate’s degradation product AMPA (Figure 100) we observe very similar features for the 2012-2018 timeframe: the 2012-2014 period is characterized by particularly depleted ρ values between October and January, compared to 2015-2018. This strong similarity between the two compounds stated at the monthly timestep comes to confirm the tight filiation linking the largest part of the AMPA contamination to the Glyphosate’s in French surface waters, as already strongly suggested by the joint interannual behaviours of their annual indicators in Figure 98.

Figure 100: Seasonal variations of the national scale-averaged exceedance rates ρ for AMPA, separately integrating the measurements from the years 2012-2014 (grey-colored histogram), 2015-2018 (blue-colored) and 2019-2020 (golden-colored).

Finally, we have to remind that 2013 and 2014 were overall the most humid years in France during the studied period. On the one hand one could have expected higher concentrations due to higher overland and drainage runoff these years. On the other hand, the dilution in higher river flows might have played a role in the other direction, contributing to the contamination depletion recorded in the 2012-2014 timeframe. This precipitation-related explanation remains unlikely, however, as no such 2013-2014 singularity could be evidenced in any of the other WFD PPP active substances timeseries.

Transition between the 2015-2018 and 2019-2020 regimes: unravelling the effect of the French pesticide regulation

Regarding the 2019-2020 Glyphosate national data, the decreased annual Glyphosate indicators recorded in Figure 97 and Figure 98 are detailed at the monthly time step in Figure 99: lower ρ values are observed compared to 2015-2018, such a lessening being widely distributed throughout the year, except for winter. This observation is contrasting with the above described 2014-2015 transition, which was mainly occurring in wet seasons.

Moreover, regarding the 2019-2020 AMPA national data, contrary the preceding regime transition in 2014-2015, the similitude with Glyphosate is no longer as obvious: while the Glyphosate rates markedly dropped for the largest part of the year (cf. Figure 99), the AMPA’s very closely kept the same levels as in the previous 2015-2018 period (cf. Figure 100). This could also independently be verified in every of the 6 basins.

Figure 101 transposes these observations for the concentration indicator, displaying the monthly ratios of Glyphosate and AMPA values (G/A). The observed patterns are there consistent with the expectations
from Figure 96, with the highlighting of a significant depletion of G/A in spring and summer seasons.

**Figure 101**: Seasonal variations of the ratio between the national scale-averaged exceedance rates $\rho$ of Glyphosate and AMPA, separately integrating the measurements from the years 2015-2018 (blue-colored histogram), 2019-2020 (golden-colored).

These findings about the G/A variation can be put in regard of the above-mentioned relationship linking G/A values with the Glyphosate use context, i.e. urban or agricultural, as recently reported in the literature (Medalie 2020), and demonstrating that a G/A reduction can generally be interpreted as reflecting a decreasing Glyphosate in urban context. This would make sense considering that, indeed, two successive legislations entered into force in 2017 and 2019 to prohibit the use of pesticides in populated areas, forbidding their use for the maintenance of green spaces, walks and roads accessible or open to the public, and by amateur gardeners (French Presidency 2014). Moreover, the warm seasons were the periods of non-agricultural Glyphosate use, so it is logical to see G/A lowered more intensively in these timeframes.

Figure 102 strengthens this hypothesis by depicting the association, during the 2011-2020 period, between the progressive diminution of the Glyphosate tonnage used in non-agricultural context - reflected in abscissae by its quotient versus agricultural tonnage - with the mean annual national Glyphosate/AMPA concentrations ratio, both of them decreasing over time.

Also pictured in this figure, the relative proportions of exceedance rates in the spring-summer season - which cumulates both agricultural and non-agricultural applications, and in fall-winter seasons, which essentially relates to cultivated land Glyphosate use.

**Figure 102**: Correlation diagram between the Glyphosate BNV-d non-agricultural to agricultural annual tonnage ratios (x-axis) and: – 1. The warm seasons to cold seasons ratios of the Glyphosate annual exceedance rates (blue dots) – 2. The ratios of the Glyphosate and AMPA's mean annual concentrations (orange dots). National scale. 2009-2020 timeframe.

As previously observed for Diflufenicanil (cf. Figure 95), the French rivers' contamination related to the Glyphosate use in warm seasons has been progressively decreasing over time. These periods of the year correspond to when the Glyphosate used to receive its major non-agricultural applications (and also to when the river vulnerability is maximal due to low dilution and high biological activity).

In parallel, the decrease in urban Glyphosate uses occurred while the AMPA generated by the degradation of wastewater-related polyphosphonates was maintained or increased, likely resulting in even lower G/A ratios at the outlet of urban catchments, especially in warm seasons when wastewaters are weakly diluted in receiving streams.

The sensitivity of the observed water contamination decreases related to non-agricultural product sales
emphasizes the high significance of the Glyphosate contamination related to its urban usages, as was already stated from more local studies (Hanke 2010, Poiger 2017).

Overall, these clearly observed trends, shown in the present work at a full country scale, here for Glyphosate and above for Difluflenicanil and Aminotriazole, are consistent with the fact that, in France, there has been since 2009 various incentives to promote pesticide-free urban and inhabitation territories, which culminated in 2017 and 2019 with laws prohibiting their use in these areas. Prior to this, Glyphosate was indeed heavily used as a total herbicide biocide, its non-agricultural use summing up to 20% of its sales, and likely more in terms of environmental impact.

BENCHMARKING THE GLYPHOSATE AND AMPA IN THE 6 MAIN FRENCH BASINS

Figure 103 materializes the correlations between the two species Glyphosate and AMPA, as dispatched through the six main basins. As can be seen, though there exists some variability, both annual concentration indicators positively covary. The ranges of concentrations, however, are quite distinct between the basins, with notably smaller values recorded in the AG basins, and distinctly higher ones for AP. Interestingly, these ranges are not consistent with the expected hierarchy that would arise from the sole information on the spatially normalized Glyphosate tonnages sold in the various basins (cf. Figure 104), AG appearing as yielding much lower contamination in spite of medium tonnages, while AP exhibits contaminations way higher, despite not so higher tonnage figures.

A first consideration to be made here, is that there seems to be a gradient in the Glyphosate contamination which qualitatively corresponds to the population density of the 6 basins (cf. Table 1), AP and SN exhibiting the highest figures, and AG, LB the lowest. This brings us to back to the above-discussed significance of the urban use of Glyphosate as a strong promoter of the surface water contamination.

Moreover, the ability of the in-field sprayed Glyphosate to migrate easily through the fields is known to be strongly conditioned by the phosphorus content of the soil: the more phosphorus, the less adsorption on soils particles, with higher surface waters contamination potency (Carles, 2019). The highest phosphorus soil contents in metropolitan France are found in the northern France area, i.e. at the AP basin location (GIS-sols 2011, Delmas 2015). Conversely, the phosphorus-rich locations occupy only a limited fraction of the AG territory. These knowledge inputs are qualitatively consistent with the observed spatial gradient of water contamination levels by Glyphosate shown in Figure 103. More globally, they highlight how the river basins specificities do impact the PPP transfer potentials.

Figure 103: Correlation between the mean annual concentration indicators $\chi$ of AMPA (y-axis) and Glyphosate (x-axis), for each of the 6 considered basins. Each dot corresponds to one of the 2009-2020 years.

Figure 104: Average Glyphosate tonnage per km² of each basin, from BNV-d 2009-2020 figures.
In Figure 105 we display the 2009-2020 interannual variations of the yearly average values of the G/A ratio, for the 6 main French river basins. Several main observations can be derived from it:

- The G/A ratios are always lower than 1, i.e. AMPA concentrations are typically higher than Glyphosate’s, consistently with the existing literature statements and with what was observed above at the national scale.

- The values of the G/A ratio are sometimes distinctly differing between the basins, with the AG basin exhibiting the highest figures, especially in the first part of the chronicle, followed by SN, while RM, and AP show the lowest, notably in the second part of the timeseries. To explain these differences, as mentioned above, one can hypothesize the role of the phosphorus-induced water eutrophication, which in various basins favors some higher AMPA accumulation. This is highly supported by Figure 106 which compares the average 2015-2017 G/A ratios with the percentage of surface waterbodies degraded by the Phosphorus WFD criterion in the 6 basins, based on Phosphorus monitoring data from the same time window.

- Finally, Figure 105 also reveals that the Glyphosate/AMPA ratios tend to progressively decrease over the years for 3 of the basins (AP, RMC and AG), while none of the others show any ratio increase. In line with the above recalled interpretation of this ratio in the literature, this would suggest that, at least in the first 3 basins, there is a progressive relative reduction of the processes that favor rapid Glyphosate leakage to water, i.e. reduction of non-agricultural usages. For the three other basins (LB, SN, RM), no distinct downward trend of the G/A ratio can be observed, but, with regard to the findings displayed in Figure 106, one could hypothesize that this is due to a competition with a hidden inverse upward trend associated to the progressive decrease of the surface water phosphorus contamination in the French rivers, which has been independently documented (Abbott 2018).

All in all, the gathered information from such a long-term Glyphosate & AMPA WFD monitoring permits to confirm the dominant causality of the Glyphosate use to explain AMPA river contamination, and the interest of the Glyphosate/AMPA concentrations ratio to diagnose changes in the profile of the Glyphosate sources: high Glyphosate/AMPA ratios indicates more use in non-agricultural, typically urban and road infrastructure contexts. Reciprocally, the downward interannual trend observed in France for this Glyphosate/AMPA ratio suggests a progressive relative increase of the Glyphosate use in cultivated land - consistently with the local and national policies regulating the pesticides use in populated areas - and a lessened overall Glyphosate spring-summer usage compared to fall and winter ones. In the meantime, the contemporary reduction of phosphorus inputs in French surface waters likely attenuates the observed
G/A decrease, to some various extents according to the considered basins.

### III.3. LEGACY PPP ACTIVE SUBSTANCES

#### SEASONAL PATTERNS

Among the numerous legacy WFD PPP active substances, Atrazine and Simazine are those inducing the highest residual river contamination. These triazines are known to be extremely persistent in the environment, and 20 years after their ban, together with their degradation products, they are still ubiquitously quantified in soils, surface waters and groundwaters (Jablonowski 2011, Vonberg 2014, Belles 2019).

Figure 107 and Figure 108 show their average annual contamination profiles over the 2009-2020 period. The observed similar wide distributions for the exceedance rates of the two compounds could easily be put in regard of the river dilution effect: as the rivers discharges get lower in summer, lesser dilution increases the fraction of monitoring sites where the contaminant transfer can result in concentrations higher than $\tau$.

The difference between the two intra-annual behaviors, with Atrazine showing less relative variation between dry and wet seasons than Simazine, supports this dilution hypothesis. Indeed, the national Atrazine seasonal profile happens to be highly biased by the contribution of the northern basins, AP and SN exhibiting by far the highest Atrazine contaminations. This is also where the yearly river flow variations are the less severe. By contrast, the Simazine profile integrates higher contribution from the southern basins, where dry summers and river discharge variations have higher amplitude.

**Figure 107** : Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{\tau}$ for the legacy herbicide Atrazine, integrating the measurements from 2009-2020.

**Figure 108** : Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^{\tau}$ for the legacy herbicide Simazine, integrating the measurements from 2009-2020.

The above regular dilution-related seasonal profiles are favored by the relatively high mobility in soils of the triazine compounds, their reported Koc values ranging in the tens to hundreds L/Kg range, according to literature. For less mobile compounds, like the Lindane isomer $\beta$-HCH exemplified in Figure 109, whose reported Koc values range in the thousands L/Kg range, one no longer observes anything suggesting a river dilution effect on the contamination indicators, with instead an apparent higher contamination activation of the water column in winter (December to March). Actually, for such high Koc values, the contaminants are expected to be tightly adsorbed on the sediment particles, and the measured concentrations are likely to be more determined by the amount of suspended matter, which is known to
increase with the river discharge, i.e. more frequently during the wet season (Meybeck 2012).

Figure 109: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^c$ for the by-product $\beta$-HCH of legacy insecticide Lindane, integrating the measurements from 2009-2020.

INTERANNUAL TRENDS

We give below a picture of the long-term residual river contamination by legacy pollutants, as monitored through the WFD in mainland France, and considerations on the most-often limited interpretability of their time-series, due to their low detection rates (e.g. insecticides).

Herbicides

Four of the herbicide molecules monitored through the WFD implementation on French rivers were banned before 2009, namely: Alachlor, and the 3 triazines Trifluralin, Atrazine and Simazine. Diuron and Terbutryn were also banned before 2009 for agricultural herbicide uses, but still receive some applications as biocides, so they will be considered as biocidal compounds in the following.

As shown in Figures 108 and 109, which show the successive average annual values of monthly exceedance rates and monthly concentration values, the very high persistence of triazine residues in the environment is confirmed by a very slow decline over the study period 2009-2020, which could, however, be confirmed by robust statistics for atrazine in almost all basins (with the exception of the RM) and on a national scale. For Simazine, downward trends could be detected since 2009 in AP and RMC only, resulting into a national decrease since 2015, but with a low level of significance, as if it would have reached a semi-permanent “background level”. Too few quantified data have been collected for Trifluralin, Alachlor and Bifenox for any trend derivation.

Figure 110: Interannual variations, for the legacy herbicide Atrazine, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^c$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Figure 111: Interannual variations, for the legacy herbicide Simazine, of the national scale annually-
averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^*$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

Fungicides

Two molecules monitored in France through the WFD implementation had been banned for agricultural fungicide usage prior to 2009: Hexachlorobenzene and Pentachlorophenol. The amount of data exceeding the cut-off thresholds was very limited for these molecules and it hasn't been possible to reveal any long-term trend in contamination.

Insecticides and molluscicide

Most of the WFD regulated insecticides compounds had been banned before 2009. They include organochlorides like Aldrine, Isodrine and Endrine, two isomers of Endosulfan, or 4 isomers of the Lindane (HCH), 4 degradation products of DDT, as well as Heptachlor and 2 of its degradation products. The organophosphorus Chlorfenvinphos and Dichlorvos can also be considered as legacy compounds.

These highly ecotoxic molecules need to be monitored at very low concentration levels, challenging the analytical capabilities of the laboratories. This results in only a few quantified data available for trend derivation. Moreover, due to the associated analytical complexity, their monitoring has often been delayed several years after 2009 by the various agencies, so that the national consistency of the chronicles since 2009 is obtained only for few of them. The general statement is then that no global trend could be derived for most of these compounds, with the exception of Dichlorvos, for which a recent significant increase could be observed, almost entirely driven by SN data, and some recent rise of some Lindane isomers (beta and delta HCH) exceedances, in LB, leading in both cases to weakly significant upward trend derivation at the national scale. A unique downward trend could be detected among legacy insecticides, for Endosulfan in the SN basin, again with limited statistical significance.

Table 8 reports the trends which could be derived from the inspection of the $\rho$ indicator timeseries for all these legacy molecules.

<table>
<thead>
<tr>
<th>Atrazine</th>
<th>Starting year of trend, K</th>
<th>LB</th>
<th>AG</th>
<th>AP</th>
<th>RM</th>
<th>RMC</th>
<th>SN</th>
<th>National</th>
</tr>
</thead>
</table>

**Table 8**: Summary of the identified trends of the exceedance rates $\rho$ for WFD legacy PPP active substances. Statistically significant upward trends are indicated in pink-coloured cell with an $\uparrow$ symbol. Downward in green with an $\downarrow$. Trend significance are as follows: *** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Starting year of trend, K</th>
<th>Trend</th>
<th>Absolute Sen's slope Q(%/an)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simazine</td>
<td>2014 2012 2009 2011</td>
<td>↓</td>
<td>-0.4(<em><strong>), -0.1(</strong></em>), -5.6(<em><strong>), -0.1(</strong></em>), 0.9(<em><strong>), -0.5(</strong></em>), 0.1(<em><strong>), -0.07(</strong></em>), -0.1(**<em>), -0.03(</em>)</td>
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<tr>
<td>Trifluraline</td>
<td>2010 2016 2014 2015 2014 2016 2014</td>
<td>-</td>
<td>-0.07(<em><strong>), -0.1(</strong></em>), -0.03(*)</td>
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<tr>
<td>Bifenox</td>
<td>2014 2016 2014 2009 2014 2009 2012</td>
<td>-</td>
<td>-0.07(<em><strong>), -0.1(</strong></em>), -0.03(*)</td>
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<tr>
<td>Alachlor</td>
<td>2012 2010 2009 2011 2014 2009 2009</td>
<td>-</td>
<td>-0.07(<em><strong>), -0.1(</strong></em>), -0.03(*)</td>
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<tr>
<td>HCB</td>
<td>2016 2016 2017 2014 2014 2016 2016</td>
<td>-</td>
<td>-0.07(<em><strong>), -0.1(</strong></em>), -0.03(*)</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
<td>2009 2012 2011 2015 2009 2009 2010</td>
<td>-</td>
<td>-0.07(<em><strong>), -0.1(</strong></em>), -0.03(*)</td>
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<tr>
<td>Absolute Sen’s slope Q(%)</td>
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<tr>
<td><strong>Endosulfan a+b</strong></td>
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<td>Starting year of trend, K</td>
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<td>Absolute Sen’s slope Q(%)</td>
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<tr>
<td><strong>HCHs (b+d)</strong></td>
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<td>Starting year of trend, K</td>
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<td>Trend</td>
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<td>Absolute Sen’s slope Q(%)</td>
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<tr>
<td><strong>DDT PTs</strong></td>
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<td>Absolute Sen’s slope Q(%)</td>
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<tr>
<td><strong>Hep-tachlore’s</strong></td>
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<td>Absolute Sen’s slope Q(%)</td>
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<td><strong>Dichlor-fos</strong></td>
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<tr>
<td>Trend</td>
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<td>nc</td>
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<td>Absolute Sen’s slope Q(%)</td>
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### Aldrine + Dieldrine +Isodrine

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### Chlorfenpyrifoos

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### III.4. BIOCIDES

Various biocides are monitored through the surface water WFD:

- 3 compounds are both construction material and film preservatives (the latter including preservation of surfaces for paints, plastics, papers, ...): Diuron, Terbutryn and Thiabendazole. These compounds are known to undergo significant leaching from building surfaces under rain events (Wittmer 2011, Buckhardt 2012).
- 2 wood preservative: Tebuconazole and Thiabendazole.
- 2 antifoulings for vessels, aquaculture equipment or other structures used in water: Cybutryn, and Tributyltin (the latter being a legacy contaminant).

### SEASONAL PATTERNS

With regards to the active substances used to protect construction materials and surfaces, their monthly variations are displayed in Figure 112 (Diuron), Figure 113 (Terbutryn), and in Figure 64 for Thiabendazole, as this compound is also a PPP fungicide. Interestingly, Diuron and Terbutryn have very similar seasonal profiles: a wide structure peaking in July, with a secondary peak in October. Due to their common types of application, we could interpret their observed common river contamination seasonal pattern as a fingerprint of the trade-off between the river dilution (high in winter, low in summer) and the rains and runoffs that wash the chemicals from urban surfaces. Also, a rise in temperature tends to increase the release of biocides from façades, possibly due to faster diffusion (Buckhardt 2012), and could contribute to the observed summer peak.

Generally speaking, the wide distribution of our contamination indicators is consistent with what was
already observed in previous studies, i.e. urban biocide loss to river occurs all over the year (Wittmer 2009, Wittmer 2011), contrary to situations typically resulting from agricultural pesticides uses where it happens in limited time windows.

Figure 112: Seasonal variations of the national scale-averaged exceedance rates \( \rho \) and concentrations at the sites exhibiting cutoff exceedances \( \chi^+ \) for Diuron, integrating the measurements from 2009-2020.

Figure 113: Seasonal variations of the national scale-averaged exceedance rates \( \rho \) and concentrations at the sites exhibiting cutoff exceedances \( \chi^+ \) for Terbutryn, integrating the measurements from 2011-2020.

The Thiabendazole case is a bit different, because it receives usages both as biocide and as fungicide PPP. Actually, the BNV-d figures indicate that this compound was significantly used as a PPP only in the AP basin. Looking at the seasonal profiles at the basin scale, we were able to clearly distinguish the AP monthly distribution from the five other basins. Indeed, Figure 64 shows that, contrary to the other basins, the \( \rho \) values profile in AP depletes in summertime and reflects high use in wet seasons, likely mostly related to the potatoes production, which is predominantly carried-out in northern France.

Tebuconazole is a long-term wood preservative biocide, whose application isn’t restricted to a given period of the year, although there could exist some preferred use conditions, with respect to natural fungi’s occurrence. It is also, however, a fungicide in various PPPs, with an important use in agriculture, as the BNV-d indicates, with high tonnages recorded in all of the six main French basins (especially in AP and SN when related to their areas). As a matter of fact, the seasonal distribution of exceedance rates exhibits a rather sharp peak in May-June (cf. Figure 114), suggesting that the rivers respond to a dominant spring use on their catchments. Interestingly, this observation is very consistent with recent ones concerning the seasonality of the contamination in French vineyards of ambient air, and birds, by azole compounds, including Tebuconazole (Angelier 2023). It is likely then that the global scale environmental effects of the Tebuconazole uses as biocide are actually masked by its dominant application as PPPs, including vine growing.

Figure 114 also shows a faint increase of the indicator in October, recalling the similar pattern observed in the above-described profiles of the material and surface protection biocides Diuron and Terbutryn which leads us not to rule out the possible influence of Tebuconazole leaching from wooden materials during the autumn rains. It was shown for instance that the Tebuconazole depletion from painted window frame sections amounted to ~20% of the originally sorbed quantity, when exposed for six months to harsh environmental conditions (Kukowski 2017). Similarly, a year-long leaching study on treated spruce showed the percentages of leached Tebuconazole to be up to 25% in the first 7 months and up to 30% in 12 months (Woo 2010).

Figure 114: Seasonal variations of the national scale-averaged exceedance rates \( \rho \) and concentrations at the sites exhibiting cutoff exceedances \( \chi^+ \) for Tebuconazole, integrating the measurements from 2011-
The seasonal profiles of the antifouling biocides Tributyltin (TBT) and Cybutryn are displayed in Figure 115 and Figure 116. The first one was banned from any use since 2008, while the second was halted only in 2018. TBT is extremely persistent in sediments (DT50 >10 years). The observed seasonal profile is quite noisy, but more cut-off exceedances are observed in winter. This might be imputed to the sediment remobilization in high river discharge regimes. Cybutryn has been the favored TBT substitute for boat hull coating during the studied period. Its apparent contamination seasonal profile, very weakly informed statistically and driven essentially by LB and RM data, is reverse of the TBT’s, with higher occurrence in the middle of year, when touristic boating activities are higher and river flows stand lower. Another interpretation could come from the fact that Cybutryn also receives some applications as preservative biocides of construction materials, and as a matter of fact, the observed profile features (May and October maxima) echo with those of Diuron and Terbutryn discussed above.

In both cases, however, the exceedance rates are low, with too poor associated statistical quality to infer reliable general conclusion.

**Figure 115**: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^\tau$ for the Tributyl Tin biocide (TBT), integrating the measurements from 2009-2020.

**Figure 116**: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^\tau$ for Cybutryn, integrating the measurements from 2018-2020.

**INTERANNUAL VARIATIONS**

The multiyear timeseries of the national Diuron contamination indicators is presented in Figure 117. It shows a clear continuous decreasing trend, at least until 2015, after what a stabilization seems to occur. Meanwhile, the concentration at the most impacted sites (those exceeding the cut-off threshold) underwent only a slight lessening.

The actual definite ban of Diuron as an herbicide PPP occurred only in 2008, i.e. only one year before the start of the river monitoring here accounted for. Consistently with what is observed after the ban of other PPPs (cf. § 0), several years might be necessary to see the products stock being actually consumed. Moreover, Diuron is a very persistent contaminant in soils (DT50 of 229 days in field), so its dissipation from agricultural environment could have taken years as well, with residual chances to leak to rivers. This would provide a scenario for the river contamination decline observed at the beginning of the timeseries, inducing significant continuous downward contamination trends since 2009 in the AP and AG basins. After 2015, the biocide use of the Diuron in urban context would account for the most recent and rather steady overall levels of contamination.
Figure 117: Interannual variations, for Diuron, of the national scale annually-averaged cut-off exceedance rates $\rho$ and the mean concentrations at the sites exceeding cut-off threshold $\chi^c$. The figures in the histograms refer to the corresponding annual absolute numbers of measurements exceeding the cut-off threshold.

A finer examination of the change in the seasonal Diuron annual profile between the beginning and the end of the chronicle is given by Figure 118. We observe that the initial contamination indicators distribution (2009-2012) express a sharp increase during the March-April window, which corresponded to the main Diuron application period when it was authorized as a PPP herbicide. By contrast, in the most recent lowered distribution (2017-2020), this increase is quite flatter, no longer suggests any specific spring time pressure, but rather recalls the river dilution-driven profile of Atrazine (cf. Figure 107), with an enhanced “October-rain” feature, like for the biocide Terbutryn (Figure 113). This would support the above hypothesis of a contamination downward trend due to a transition of Diuron from an historical residual - but still dominant - PPP use, to a present single use as biocide.

Figure 118: Seasonal variations of the national scale-averaged exceedance rates $\rho$ and concentrations at the sites exhibiting cutoff exceedances $\chi^c$ for Diuron, separately integrating the measurements from 2009-2012, and 2017-2020.

For Terbutryn, which receives very similar urban material preservative biocidal functions as Diuron, the contamination indicators are notably smaller ($\rho$ values typically below 1%), and only faintly significant trends could be derived (upward in SN basin, downward in LB and the national scale). Such close to steady chemicals’ leakages are expected from constructed areas exposed to rain events, as these substances are still in use in products, and are long-duration components of the slowly-degrading urban surfaces.

As regards Thiabendazole, it is used as both a fungicide PPP, almost exclusively in the AP basin, and also an urban material preservative biocide. For this reason, it is not possible to interpret our river indicators in regard of its use trends as a biocide in the AP basin. In the other basins, the Thiabendazole sales as PPP are marginal, and the rivers contamination is expected to be mainly associated to its biocide uses. The contamination indicators in these basins are low ($\rho<1\%$), and a consistent trend (downward) could be derived only in LB (cf. Table 6).

Regarding the legacy antifouling biocide TBT, we could only formulate the hypothesis that our river contamination indicators timeseries reflect a noisy background level, associated with the historical pollution stored in the surface water sediments, and occasionally remobilized in higher discharge periods.
No distinct trend could be derived at the national scale, but it has been persisting high in AP, and some surprising increase in exceedance occurrences happened in RMC in the most recent years.

Finally, the Cybutryn antifouling compound was not monitored long enough (2015-2020 only), and too scarcely, to derive any relevant interannual information.

Table 9 delivers the overall trend investigation results for the biocides. Only few trend assertions could be made, in large part due to limited statistics.

**Table 9**: Summary of the identified trends of the exceedance rates $\rho$ for WFD biocide active substances. Statistically significant upward trends are indicated in pink-coloured cell with an $\uparrow$ symbol. Downward in green with an $\downarrow$. Trend significance are as follows: *** high significance (p-value<0.001), ** medium significance (p-value<0.01), * low significance (p-value<0.05). White cells indicate the absence of identifiable trend since the indicated starting date. When no starting date is specified, and the trend is marked “nc”, it means that the trends computation was not performed, due to insufficient number of data.

<table>
<thead>
<tr>
<th></th>
<th>LB</th>
<th>AG</th>
<th>AP</th>
<th>RM</th>
<th>RMC</th>
<th>SN</th>
<th>National</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Diuron</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Trend</td>
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</tr>
<tr>
<td>Absolute Sen's slope Q(%/an)</td>
<td>-</td>
<td>-0.1(***</td>
<td>-2.6(***</td>
<td>-</td>
<td></td>
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</tr>
<tr>
<td><strong>Terbutryn</strong></td>
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<tr>
<td>Trend</td>
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<tr>
<td>Absolute Sen's slope Q(%/an)</td>
<td>- 0.1(**)</td>
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<td>0.05(*)</td>
<td>- 0.06(*)</td>
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<tr>
<td><strong>Cybutryn</strong></td>
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<tr>
<td>Starting year of trend, K</td>
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<td>2016</td>
<td>-</td>
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<td>2016</td>
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<td>Trend</td>
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<td>Absolute Sen's slope Q(%/an)</td>
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</tbody>
</table>
The multiyear indicators $X_c$ and $X_r$ have been integrated over the 2016-2020 timeframe to compare and reveal the specificities of the basins regarding the pesticide and biocide active substances.

**Figure 119** exemplifies this indicator for the WFD PPPs and biocides having had authorized uses during this period. The highest contamination indicator $X_c$ values are by far observed for herbicides, headed by Glyphosate. According to the use figures gathered by the French agency for food environmental and occupational health & safety, 26,000 km² in France received at least one Glyphosate application in 2014, i.e. 5% of the metropolitan France area (ANSES 2019b). After Glyphosate come Metaldehyde, followed by the cereal and corn crops herbicides Bentazone, Chlorotoluron, Nicosulfuron, 2,4 M CPA, 2,4 D, then by the fungicide Tebuconazole or the biocide Diuron.

The relative contribution of the 6 basins are visible for each molecule, except Cypermethrin and Cybutrin which have much smaller $X_c$ values. It can be seen that the AP basin often exhibits the highest contributions (11 situations out of 17 here displayed), reflecting either the proportionally high PPP usage of these chemicals in this highly cultivated territory, or its strong population density (i.e. heavy urbanization, likely explaining the dominant AP value for the biocide Diuron indicator).

For Thiabendazole, AP is the only basin with significant BNV-d figures, i.e. with agricultural use of this molecule. In the other basins, the observed contamination likely results from use as biocide. For Metazachlor however, the RMC basin rivers appear as the most impacted, and high values also happen for Chlorotoluron in SN, or 2,4 D in RM.

With regard to the risk indicator $X_r$, the highest values show up for the insecticide Cypermethrin hot spots (all basins exceeding $X_r=0.1$, while SN, AG and LB exceed 1), as well as for the herbicides Diflufenicanil (in the 3 northern basins), Chlorotoluron in SN and AP, Metazachlor in all basins except AG, Pendimethalin in AP and RM, and Cyprodinil in AP. Among the biocides, Diuron is the most problematic, with $X_r$ values exceeding 0.1 in most basins (except AG).
**Figure 119**: Multiyear (2016-2020) integrated indicators of contamination (Xc) and risk (Xr) for the considered PPP and biocide active substances that were authorized in 2009 and after. Xc values of each basin are presented through the cumulative histograms (linear scale), and Xr values by the round dots (log scale).

The same approach was applied for legacy PPPs and biocides (Figure 120). In spite of their ban decided years before the studied period, significant contamination indicators Xc are still met for Atrazine (10 to 20%), especially in SN and AP basins, and for the boat hull antifouling agent TBT in the AP basin. This converts into a rather high risk indicator Xr in AP for TBT, which is consistent with the fact that fluvial navigation has historically been especially intense in this basin.

**Figure 120**: Multiyear (2016-2020) integrated indicators of contamination (Xc) and risk (Xr) for the considered legacy herbicide, fungicide and biocide active substances. Xc values of each basin are presented through the cumulative histograms (linear scale), and Xr values by the round dots (log scale).

For all the legacy insecticides, we choose to limit the indicator calculation to the 2018-2020 timeframe, i.e. after the entry into force of the sales restrictions concerning Chlorpyriphos and Imidacloprid, in order to be representative of the most recent period (cf. Figure 121). Both indicators Xc and Xr stand low (maximum 5%, typically much lower). Imidacloprid, however, shows some significant residual contaminations, which are sufficient to induce Xr values close to 1, especially in LB and RM. This molecule still has applications as a biocide to controls fleas and ticks in domestic pets, with ability to leak in the environment of induce effects on non-target organisms (Perkins 2021, Dipens 2023). Noteworthy also is the significant residual contamination met in RMC and LB when cumulating the four Lindane isomers (HCHs), here again many years after their ban. The highest (but limited) risk indicator refers to some Dichlorvos hot spots in the SN basin.

This being said, it has to be reminded that the here indicated contamination and risks refers to water column samplings, which are not the most appropriate to assess substances having affinity for sediments. Many legacy pesticides exhibit such affinity, and recent research results have shown than when it comes to agricultural streams sediment sampling, these molecules contribute much more to the ecological risk, especially for macroinvertebrates with benthic life traits (Rasmussen 2015).

**Figure 121**: Multiyear (2016-2020) integrated indicators of contamination (Xc) and risk (Xr) for the legacy insecticide active substances that were authorized in 2009 and after. Xc values of each basin are presented through the cumulative histograms (linear scale), and Xr values by the round dots (log scale).
III.6. DISCUSSION

From the above described information brought by our indicators (combining data on contamination, risk and trends), several general statements can be driven regarding the PPP and biocide active substances monitored through the French WFD in surface waters.

On the one hand, about the studied compounds which are presently left with rising or persisting ecological concern, despite their long-term management through the WFD, and notably:

- The cereal crops herbicides Chlorotoluron, Diflufenicanil (both of them largely used on winter cereals), Nicosulfuron (main use in Maize), and the urban surface biocide Diuron, combine high contamination and risk profiles. The herbicides Metazachlor (typically used on colza, sunflowers, aromatic plants...) and Pendimethalin (used on large cultures, vegetables, arboriculture, vines... and increasing in several basins, notably LB and AP), the insecticide Cypermethrin, the biocide Imidacloprid, and the fungicide Cyprodinil in the AP basin, also exhibit elevated risk indicator. The molluscicide Metaldehyde (most notably in the AG basin), and the herbicide Glyphosate produce the most widespread contaminations. Some increasing exceedance occurrences were also detected for the herbicide Bentazone (LB), and the fungicide Azoxytrobin (AG and RM).

- Regarding legacy compounds, the antifouling TBT also keeps some impact potency, especially in the AP basin. Atrazine remains a significantly occurring compounds in the SN and AP basins.

- A final negative general statement is the fact that for a large part of the compounds, in spite of many monitoring points and multiyear data collection, it was not possible to derive trends at the basin or at the national scales. This is true for most of the legacy PPP active substances, especially insecticides, in spite of their expected long-term dissipation, due to their low concentrations that challenge the analytical capabilities of the monitoring labs.

On the other hand, the results of the present study have objectivated the clear capability of the WFD chemical surveillance to evidence the transfer reduction, since 2009, of some important active substances, benefiting the French surface waters quality.

The most significant progress relates to the downward trend at the national scale of the exceedance rates for about 50% of the 26 PPP active substances having received use authorization during the studied period (authorized either partially or over the whole 2009-2020 timeframe): this could be verified for 4 out of 7 fungicides, 7 out of 15 herbicides, and 2 of the 3 insecticides. These overall progresses were also reflected at the six basins scales, with downward trends observed for 44% of the trend analyses made on the various basin/compound combinations. Only 6% of these analyses concluded to some net increases, and a single one at the national scale (i.e. for the herbicide Pendimethalin).

These contamination declines can be characterized by various starting dates, some initiated as early as 2009, others only since 2015. This sometimes depended directly on the active substance bans that occurred during the studied period (Aminotriazole, Isoproturon, Linuron, Oxadiazon, Ipodione, Imidacloprid, Chlorpyrifos-ethyl), but could also be related to some changes in the substances use, either in terms of applied tonnage or of application seasons/targeted crops, or mitigation measures.
National scale exceedance rates declines were also observed for 2 out of the 7 WFD legacy active
substances of banned herbicide and fungicide PPPs, i.e. Atrazine and Simazine, with, as expected, zero
associated increase occurrence.

For authorized substances, the dependence on the sold active substances tonnage figures of the here-
developed contamination indicators was checked empirically by assessing the linear correlation between
these variables, with actual correlations validated for various substances. Further implications and
application of this statement will be discussed in Part V.

For the situations with low correlation between tonnage figures and contamination indicators, we were
able to diagnose the observed non-linearities as associated to some changes in the water contamination
seasonal profiles over the years, itself indicating significant changes in the substances use. As an
example, the interannual variations of the Glyphosate contamination were successfully associated to such
changes in the seasonal profiles.

It was also possible to associate some important change in the French surface water contamination by
Glyphosate and AMPA that occurred between 2014 and 2016 with the coinciding ban of the Aminotriazole
herbicide, especially in some regions where vineyards and orchards are intensively grown, which
exemplifies well the environmental effects of PPP substitution.

The study also provided the opportunity to investigate, for the first time at such spatiotemporal scale, the
cocurrence of Glyphosate and its degradation product AMPA. It was evidenced from the tightly related
interannual variations of their contamination indicators that the annual river content AMPA is indeed mainly
generated by the Glyphosate transferred to waters the same year, although some offset exists in the
seasonal dynamics of both species, AMPA typically peaking in mid-summer, i.e. 3 months after its parent
compound. Our large-scale contamination indicators were also able to successfully reflect and support
the recent findings of the strong interaction which exists between Glyphosate/AMPA concentrations and
the phosphorus contents in both soils and waters.

Additionally, a distinct long-term decreasing trend in the Glyphosate/AMPA concentration ratio was also
observed in some basins, which expresses itself mainly in the spring and summer periods. Supported by
the recent literature, we argued that the lowering of this ratio, which was especially noticeable at the
national scale in 2019-2020, likely reflects the progressive abandonment of the Glyphosate use in
urbanized contexts, which culminated with the recent French legislations (2017 and 2019) prohibiting the
use of pesticides in public places, and by amateur gardeners.

Similarly, to Glyphosate, we were able to demonstrate that the apparent discrepancy between the
increase over time of the herbicide Diflufenicanil sales and the decrease of its contamination indicators
was in fact imputable to the progressive abandonment of this substance for non-agricultural purpose.
Indeed, in spite of the limited share of its non-agricultural sales (<5%), these activities were shown to be
a major contributor to the surface waters Diflufenicanil contamination in the spring and summer periods,
this contribution vanishing as the non-agricultural tonnages finally collapsed. Similar conclusions could
also be drawn regarding Aminotriazole. Factually, this converted in downward trends of the exceedance
occurrences for Diflufenicanil and Glyphosate in some of the basins, especially in RMC. In other basins,
the cereal cropping is more important, with fall-winter uses of these molecules, counterbalancing the
decrease of urban uses.

Regarding biocides, a generalized decrease was observed over the 2009-2020 period in the Diuron
contamination indicators, with a stabilization since 2015. The associated change in the seasonal behavior
was shown consistent with the expression of a transition when the spring-time agricultural use of Diuron
was progressively abandoned, while its urban biocide function was maintained. We also highlighted that some vigilance is required regarding the residual water contamination of the neonicotinoid Imidaclopid after its recent ban as a PPP component, possibly associated to its still authorized veterinary biocidal use, which might continue to induce significant risks due to its high ecotoxicological potency.

This study was also an opportunity to derive unequalled information on the seasonal patterns of the PPP and biocide active substances emission and use, through the variation of the cutoff threshold exceedance rate indicator $\rho$ and the surface water concentrations $\chi^\tau$. Indeed, the monthly sampling frequency of the WFD monitoring, when associated to the rich statistics of the multiyear integration, permits the extraction of fine temporal features, which may in turn be related to the dynamics of the pollution sources, i.e. to the most significant products uses, or to the main emission sources of the chemicals. In this sense, our study is a demonstration that the WFD monitoring offers much more insight on the global PPP use, as compared to what the annual sales figures can provide, although indispensable, when used alone.

It has thus been possible for us to map the large spatial scale-averaged peaking seasons of most of the WFD PPP active substances among the six main France river basins, over the 2016-2020 period. The May-June, followed by the November-December periods were identified as the most impacted by contamination peaks, with seasonal nuances according to the basins (fewer exceedances occurring in autumn in the southern basins AG and RMC). Some substances like Glyphosate, Metazachlor, Boscalid or Metaldehyde presented high occurrences, both in space and time.

It was also possible to express the wide-scale seasonal behavior of legacy active substances, like the mobile compounds Atrazine and Simazine, whose wide summer-centered temporal distributions were shown to be consistent with their expected dilution-driven in-river concentration. By contrast, the levels of more hydrophobic and sediment-adsorbed compounds like the Lindane isomers or the antifouling TBT didn’t reflect any dilution-like variations, and were hypothesized as reflecting more the re-suspended particles concentration variations, themselves influenced by the river discharge, typically in winter.

Finally, the seasonal distributions of the biocide surface water contamination were also investigated. The construction material and surface preservatives Diuron, Terbutryn showed very similar patterns, consisting in a bimodal distribution of the threshold exceedance rates, with one broad peak reaching its top in summer, suggesting a river dilution effect induced by low-flows, followed by a second peak in October, likely imputable to the urban surface wash-off at the beginning of the wet season. Similarities and differences with the wood preservative Tebuconazole were also debated.
The initial primary purpose of the presented study was to check out if the chemical data from the surface water monitoring networks could help in assessing the pollution reduction achievements of the 2009-2020 period, at the scales of mainland France and its 6 main river basins, and in regard of the WFD’s environmental objectives. In this respect, capitalizing on the numerous concentration measurements produced by the water agencies, we studied 100 compounds, and were able to apply our trend calculation process in at least one basin for 75 of them, the 25 remaining ones presenting too few data. Figure 122 summarizes the identified trends for these compounds in the various basins.

For 58% of the 7*75= 525 compound/basin situations (including the national scale), it was not possible to reveal any trend, either because the interannual variations were too limited, or, most often, because the amount of quantified data was too poor, due to the insufficient sensitivity of the analytical techniques to detect low dissolved concentrations contaminants. These unfavorable situations mainly correspond to legacy insecticides, fungicides, of industrial pollutants.

On the other hand, significant trends could be diagnosed of 32% of the basin/compound combinations, splitting into 25% downward trends (pollution reduction) and 7% upwards.

The trends obtained at the national scale were the most numerous. The basins recording the highest rates of pollution reduction are AP, RMC and SN. Worsening situations, although few in number, are most numerous in the SN and RM basins. The LB and AG basins stand intermediate.

Finally, for 10% of the combinations, the trend calculation was not even possible, due to too many missing data in some parts of the timeseries, with the AP basin being highly represented here, due to its limited absolute number of monitoring sites.

**Figure 122**: Overall results of the $\rho$ values trend computations made throughout the study, distinguishing, for each of the 6 basins and at the national scale, the number of substances with trends identified as downwards, upwards, the situations when the trend algorithm resulted in no significant trend, and finally the situations for which the trend calculations were not possible.

The durations of the calculated trends are reflected by the Figure 123, showing the starting years $K$ of the concerned $K\rightarrow2020$ timeframes. In 90% of the cases it was possible to trace the trends back to the first WFD cycle (2009-2015). One third of the trend could be assessed over more than 10 years. The LB and AG basins were those with the shortest durations in average. This has to do with the fact that, in these basins, the number of monitoring data strongly increased late in the studied period, i.e. from 2015-2016 onward, as previously reported in Figure 10.

**Figure 123**: For each year of the studied timeframe (x-axis), number of computed significant trends covering $\rho$ data up to 2020 in each basin, and which started this particular year (y-axis).
Figure 124 details the identified downward and upward trends in the various investigated areas, according to their levels of significance. Highly significant slopes (*** ) were characterized the most often. This is especially true for downward ones, whatever the basin (upward trends are too few for asserting much about the significance distribution).

Figure 124: Fractions of the downward and upward computed significant trends, according the 3 levels of significance, for each basin and at the national scale.

Table 10 gives the breakdown of these trends according to the chemical groups.

Table 10: Summary of the identified trends of the exceedance rates $\rho$ for all the considered WFD substances. Upward trends are indicated in pink-coloured cell. Downward in green. The number of compounds benefiting from high trend significance (p-value<0.001) are marked after the *** symbol.

<table>
<thead>
<tr>
<th>Chemical Group</th>
<th>Number of compounds for which trend computations were possible</th>
<th>Number of compounds with downward trends at the national scale (*** with high significance)</th>
<th>Number of compounds with upward trends at the national scale (*** with high significance)</th>
<th>% of compound /basin pairs with downward trends</th>
<th>% of compound /basin pairs with upward trends</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trace elements</td>
<td>8</td>
<td>0 (***0)</td>
<td>7 (***6)</td>
<td>10%</td>
<td>50%</td>
</tr>
<tr>
<td>PAHs</td>
<td>4</td>
<td>3 (***3)</td>
<td>0 (***0)</td>
<td>40%</td>
<td>0%</td>
</tr>
<tr>
<td>Industrial and POPs</td>
<td>18</td>
<td>5 (***4)</td>
<td>0 (***0)</td>
<td>17%</td>
<td>2%</td>
</tr>
<tr>
<td>Authorized herbicides</td>
<td>15</td>
<td>8 (***6)</td>
<td>1 (***1)</td>
<td>51%</td>
<td>7%</td>
</tr>
<tr>
<td>Authorized fungicides</td>
<td>7</td>
<td>4 (***2)</td>
<td>0 (***0)</td>
<td>32%</td>
<td>4%</td>
</tr>
<tr>
<td>Authorized insecticides and molluscicides</td>
<td>4</td>
<td>2 (***0)</td>
<td>0 (***0)</td>
<td>32%</td>
<td>0%</td>
</tr>
<tr>
<td>Biocides</td>
<td>4</td>
<td>1 (***0)</td>
<td>0 (***0)</td>
<td>15%</td>
<td>4%</td>
</tr>
</tbody>
</table>
Overall, the best reduction achievements were observed for the PAHs (3 compounds), the alkylphenols (2 compounds subjects to ban and restrictions), the herbicides (14 compounds, among which 5 banned during the period) and fungicides (4 compounds, among which one banned during the period).

For pesticides, all PPP active substances included, downward trends were detected in 44% of the basin/substance pairs, with some part these decreases imputable to the abandonment of non-agricultural uses. Decreases at the national scale were recorded for 3 still authorized fungicides and 4 still authorized herbicides, including Glyphosate. Upward trends were found in 6% of the situations.

Conversely, the main degradations were observed for the trace elements (for 7 out of the 8 elements, among which 5 with high significance upward trends), and the herbicide Pendimethalin.

<table>
<thead>
<tr>
<th>Legacy PPP and biocide active substances</th>
<th>14</th>
<th>2 (***)</th>
<th>2 (**0)</th>
<th>11%</th>
<th>3%</th>
</tr>
</thead>
</table>

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Part V. PREDICTIVE INDICATORS FOR THE LARGE-SCALE BASIN-TO-RIVER CONTAMINATION OF PPP ACTIVE SUBSTANCES

In this second part of our study related to PPP active substances, we aim at quantifying the relationship between the annual tonnage figures provided by the BNV-d databank, and the surface water integrated concentration indicator $\chi$. The obtained relationship would allow to predict, to a certain level of accuracy, the variations of the contamination indicator according to those of the tonnage. Moreover, we will also aim at explaining the difference between these relationships for the various active substances here considered, according to their physicochemical properties, in particular their Koc values, in order to extrapolate the prediction of the concentration indicator to PPP active substances not yet monitored.

V.1. QUANTITATIVE CHARACTERIZATION OF THE BASIN-TO-RIVER TRANSFER OF ACTIVE SUBSTANCES

HYPOTHESIS AND CONCEPTUAL MODEL

Making the first-approach assumption that the tonnage spread over each of the main river basins a given year “k” equals the tonnage sold in the basin this same year (no storage, nor import or export of the substance out the considered basin), the basic concept underlying the relationship between the sold substance quantities and the expected load of substance emitted from the whole basin “j” to its surface waters, can be expressed through the following equation:

$$L_{i,j,k} = T_{i,j,k} \cdot \Gamma_{i,j,k} \quad (9)$$

$L_{i,j,k}$: Load of the chemical $i$ emitted during year k” to the surface waters from the whole basin area $A_j$ of basin “j”

$T_{i,j,k}$: Tonnage of substance $i$ sold and hypothetically applied on basin $j$ area’s during year “k”. In the present approach, we will assume that $T_{i,j,k}$ actually corresponds to the annual tonnage extracted from the BNV-d databank for the year $k$ and considered basin. We will ignore, for instance, the “edge effects” possibly induced by the transportation of some PPP bought in one basin and used in another. The very large sizes of the considered basins favor such a hypothesis.

$\Gamma_{i,j,k}$: A basin-to-river transfer factor, accounting for the specific soil-molecule interactions. This coefficient also embeds all the spatial features of basin “j” and temporal variabilities during year “k”, including the pedo-hydro-climatic conditions which affect the contaminants mobility, as well as the spatial characteristics of the monitoring networks (e.g. sizes and nesting of the individual watersheds collected at the monitoring sites). In this sense the $\Gamma$ value only represents an average situation and cannot be directly transposed to other locations or spatial scales, nor to other time frames.
This rough and globalized approach is conceptually the same as the one proposed recently by the European Environmental Agency for computing the pesticide load to surface water for preparing the WFD inventory of emissions (Roovaart 2022).

Defining $f_{j,k}$ the average surface water flow per area unit of the basin $j$ during year "k", and assuming moreover that the whole emitted PPP active substance load transferred to water ends up dissolved in the water column, we can estimate the averaged concentration in the surface waters as follows:

$$C_{i,j,k} = \frac{L_{i,j,k}}{A_{j} \cdot f_{j,k}} = \frac{\Gamma_{i,j,k}}{A_{j} \cdot f_{j,k}} \cdot T_{i,j,k} = \frac{\gamma_{i,j,k}}{A_{j}} \cdot T_{i,j,k}$$  \hspace{1cm} (10)

with $\gamma_{i,j,k} = \frac{\Gamma_{i,j,k}}{f_{j,k}}$ a basin-to-river contamination coefficient, which accounts for both the active substance transferability in the river basin (through $\Gamma$) and its surface water dilution in this basin (through $f$). In a first approach, $\Gamma$ and $f$ are expected to covary positively with the basin’s pluviometry.

This latter formula provides a basic conceptual framework to account for the relationship empirically reported in Part III.1 between yearly concentration indicators $\chi$ and sold tonnages $T$: the close to linear relationships that were observed for some favorable situations indicate that the coefficient $\gamma$ might be rather constant over time for a given territory and a given active substance, whatever the tonnage applied.

More specifically, these correlated “$T-\chi$” situations suggest that, at such large scales, both the variations induced by the pluviometry for the substances mobility within the catchments and for the surface water flow do, to a certain extent, compensate each other to yield a close to constant contamination rate, i.e. insignificantly differentiated concentration levels. This hypothesis is supported by a study carried out about the herbicides loads in the River Rhine (Bach 2012), which indicated that, at the scale of a large river basin, and on the basis of some multiyear monthly monitoring, the substance concentration in rivers was not statistically correlated with the river discharge at the dates of sampling.

However, as was already shown in III.1 for substances like Glyphosate, Diflufenicanil or Nicosulfuron, the quantitative relationship between tonnage and water contamination will be maintained only provided the substances keep being used for the same main agricultural purposes over the study period.

**EMPIRICAL DERIVATION OF THE CONTAMINATION COEFFICIENTS**

According to formula (10), the $\gamma$ values can be derived empirically from the measured concentration and the knowledge of the active substance tonnage supposed to be applied, as follows:
\[ \gamma_{i,j,k} = \frac{C_{i,j,k}}{A_{j}T_{i,j,k}} \]  \hspace{1cm} (11)

\( \gamma \) may then be used to quantify, on a relative basis, the overall transfer potential of the various PPPs active substances.

In this section, we apply the above-defined \( \gamma \) concept to characterize the transfer properties of the WFD PPP active substances in the six main French basins, capitalizing on the above described time and space consistent concentration database.

With this in mind, and mirroring the above equation, we define the proxy coefficient \( \gamma' \) as follows:

\[ \gamma'_{i,j,k} = \frac{\chi'_{i,j,k}}{A_{j}T_{i,j,k}} \]  \hspace{1cm} (12)

With \( \chi' \) being the varying part of the concentration indicator \( \chi \), already defined in equation (5). Like the true concentration \( C \) of eqs. (10) and (11), and contrary to \( \chi \) whose lower limit is \( \tau/2 \), \( \chi' \) has the asset of theoretically taking a null value when the tonnage \( T \) itself is null (i.e. when the active substance "i" is not used on the considered territory "j").

Equation (12) means that \( \gamma' \) only accounts for the transfer of the active substances applied during the considered year \( k \), i.e. we hypothesize that the emission of molecules sprayed the years before is considered as negligible compared to the those of the freshly applied substance.

One has also to bear in mind that the comparison of the derived \( \gamma' \) values between the 6 basins will not be straightforward, as the 6 factitious representative sites of each basin do not embed comparable realities, in particular due to the differences between the monitoring network spatial configurations. This question is reflected in equation (12) by the association of \( \chi' \) with the territory area \( A_{j} \), whereas \( \chi' \) partly aggregates concentrations from nested catchments, whose cumulated areas actually exceed \( A_{j} \) by an unknown factor which depends on each basin. In the ideal situation where all the 6 basins would have adopted similar monitoring sites spatial distributions, this factor could be considered constant, but this is not the case. As a consequence, any direct quantitative comparison of the \( \gamma'_{ij} \) values between the basins will have to be questioned in this respect.

**Derivation of the \( \gamma' \) coefficients**

Having extracted the \( \chi' \) values from our monthly indicator dataset, and computed the corresponding yearly means \( \chi'_{i,j,k} \), we determined the \( \gamma'_{i,j,k} \) using formula (12).
This being done, averaged values of $\gamma'_{i,j}$ over the full period k=2009->2020 can be calculated, by weighting the annual $\gamma'_{i,j,k}$ coefficients according to the number $N_{i,j,k}$ of yearly data in basin j, and normalizing to the total number of these data over the whole period, $N_{i,j}$:

$$\gamma'_{i,j} = \frac{\sum_{k=2009}^{2020} N_{i,j,k} \cdot \gamma'_{i,j,k}}{N_{i,j}}$$  \hspace{1cm} (13)$$

Note that for this calculation, in order to preserve at best the possibility of getting expressed the expected consistency between river contamination and substances tonnages, the concentrations indicators collected from years with insufficient number of measured sites, as well as data collected during periods when an active substance went being banned, were excluded.

In Figure 125 we display the resulting $\gamma'$ values derived for the whole mainland France territory. The vertical bars extremities refer to the min and max $\gamma'$ values observed among the six river basins, and the dots express the mean of the six basins values.

As can be seen in this figure, the contamination coefficient $\gamma'$ varies by more than 3 orders of magnitude among the various PPP active substances, and typically by less than one order of magnitude among the six river basins. These findings put strong prevention against using too simplistic approaches for concentration or load prediction based on a single transfer factor, which would be valid whatever the considered substance or territory. We believe that this aspect is of particular relevance concerning, for instance, the method promoted to calculate the pesticides transfer to waters through the WFD inventory of emission exercises, as discussed recently in the Technical Report of the European Topic Centre on Inland, Coastal and Marine Waters (Roovaart 2022).

In view of considering also the acute risks involved by the PPP contamination peaks, the same exercise was repeated using this time the annual maxima of the 95 percentiles concentrations $\chi_{95\%}$ (i.e. best approximation of the annual peak concentration) instead of the mean concentrations $\chi$. In a first rough approach, assuming that the whole tonnage is typically applied during a single month in the year, one would expect a calculated contamination coefficient rising a factor 12 higher than when using the annual mean.

As shown in Figure 125, the contamination coefficients $\gamma'_{95\%}$ obtained this way for the full range of the WFD PPP substances follow a behavior rather similar to the one derived from mean concentrations, indicating that the transfer conditions are consistently described using either the mean or peak concentrations indicators. And actually, there exists around one order of magnitude difference between both curves, this observation being consistent with the above mentioned theoretically expected factor 12.
Figure 125: Values of the $\gamma'$ contamination coefficients for each of the considered WFD active substances that were authorized as PPPs in 2009 or after. Blue dots = values derived from mean annual concentration indicators $\chi$. Orange dots = values derived from the maxima of the $\chi^{95\%}$ indicators (95th concentration percentiles).

In Figure 126, we display the relative values (% of the sum of coefficients) of the averaged contamination coefficients $\gamma'$ established from the annual mean concentrations, for each of the studied WFD PPP substance in the six main river basins.

In a theoretical world, where all basins would have the same agricultural and environmental patterns, and identical PPP use, and monitoring sites spatially distributed in comparable ways with respect to individual catchments sizes, one would expect each basin relative contribution to be equals, i.e. 100%/6 ~ 15%, for every PPP, reflecting identical basin to river transfers.

Figure 126: Contamination coefficients of the 6 basins normalized to their sum for each considered substance.

As expected, because of the heterogeneity between the regional situations, the Figure 126 shows more variability between basins. Several qualitative observations can be made here:

- First, for most of the substances, the transfer coefficient values are similar among the basins (most values differing by no more than a factor 3 from the above 15% theoretical target), which indicates that the effects of the heterogeneity among the basins' characteristics are not such that they would induce drastic variability in the basin-to-river contamination coefficients.

- For certain active substances, however, the river contamination coefficient is much higher for one basin as compared to the others. This happens for instance for Aminotriazole, Metaldhehyde or Linuron in the AP basin, for Thiabendazole, Chlorpyrifos-ethyl, Tebuconazole, Imidacloprid in RMC, Oxadiazon or Cypermethrin in LB.

- Finally, the SN and AG basins appear as those associated to the smallest contamination coefficient values for the majority of the considered PPPs. This is further illustrated by Figure 127, where it can be seen that for 90% of these PPP substances, the ratio between basin's and national $\gamma'$ values is maintained under 100% for these two basins. This is at variance with AP, RMC or LB basins, where the mean national $\gamma'$ values can be significantly exceeded, some ratios close to 200% or more showing up for them in this figure. The diversity of the cropping conditions and agricultural practices in the various basins, as well as of environmental conditions, are likely to explain these discrepancies. According to the assessment of the state of the soil in France performed in 2011 (GIS-Sols 2011), strong erosion hazards exist in AP, RMC and AG basins, as well as in the Bretagne region part of
the LB basin, which is subject to important precipitation along the year. In this line, for the
RMC basin, one can put forward the combination of dominant erosion-vulnerable cultures like
vineyards, with important slopes and humid weather in some areas. For AP, the low vegetal
coverage of soils in some parts of the years also favors precipitation-induced soils erosion.
We also noticed that some distinctly high $\gamma'$ values were observed in some basins where the
sold areal tonnages were especially low, so there exist also a probability that the
incompleteness in some consumption figures induce some overestimation bias in the $\gamma'$
computation via eq. (12).

One has to keep in mind, finally, that the $\gamma'$ values are also sensitive to the monitoring network spatial
configuration, e.g. the distribution of the watersheds sizes viewed by the monitoring sites. These
configurations are varying among the 6 basins, and could explain some significant part of the observed
discrepancies in the $\gamma'$ values.

Figure 127: For each of the 6 basins, representation of the distribution of the active substances’ ratios
between basin’s and national $\gamma'$ values: the diamond dots represent the median ratios, and the min and
max value of the histograms refer respectively to the 10th and 90th percentiles of the ratios.

V.2. OBSERVED CHANGES IN THE BASIN-TO-RIVER TRANSFER OF THE WFD
PPP SUBSTANCES OVER THE STUDY PERIOD, AND CONNECTION WITH
CHANGES IN PPP USE, OR IN CROPS MANAGEMENT

Using the monitoring data to differentiate the effects of the pesticide consumption from the other possible
factors which could induce some water contamination reduction, including mitigation measures, is a
challenge. At least one interesting approach in this respect is available in the literature (Bach 2012),
concerning the interpretation of some herbicide loads reduction in the River Rhine.

As a matter of facts, because the $\gamma'$ value is by definition normalized to the applied tonnage - cf. equation
(12) – it is theoretically appropriate to reflect the contribution of the other factors affecting the
effectiveness of the contamination, independently of changes in substance consumption.

Looking at the successive annual values of $\gamma'$, we were able to distinguish various behaviors according
to the studied PPP substance.

For certain PPPs, this coefficient was rather steady over the years, indicating that the variations in the
active substance uses, as well as in the transfer and river flow conditions, remained within limits that
maintained at a similar level the surface water contamination. A good illustration of these situations is
given by the herbicide 2,4 MCPA (Figure 128), where only a limited increase of $\gamma'$ might be noticed, in
spite of a significant change in terms of tonnage over the years (the 2019 singular value is an artifact due
to the sudden drop of sold PPP tonnages in France this particular year).

Figure 128: Interannual variations, for the herbicide 2,4 MCPA, of the national scale annually-averaged contamination coefficient \( \gamma' \) (red curve). Also pictured, the national-scale yearly tonnage values for 2,4 MCPA extracted from the BNV-d (black histogram).

This is at variance with the observation made for Pendimethalin (Figure 129). Here the \( \gamma' \) coefficient varied sharply, with an upward trend, signing a significant change in the dominant basin-to-transfer route. This finding has to be debated in regard of the change in the seasonal contamination profile, which we had already diagnosed in Part III. Indeed, Pendimethalin gradually received new usages during our studied period, with a shift toward winter usages in the recent years, in particular due to its capacity to substitute the Isoproturon herbicide, which was retrieved from the market in 2017. The high-volume use of this molecule in these new application conditions likely affected its propensity to leak to the river systems, explaining the observed increase of the contamination coefficient. This worsening in the substance management is all the more of significance that the tonnages sold also strongly grew in the meantime, as depicted in Figure 129.

Figure 129: Interannual variations, for the herbicide Pendimethalin, of the national scale annually-averaged contamination coefficient \( \gamma' \) (red curve). Also pictured, the national-scale yearly tonnage values for Pendimethalin extracted from the BNV-d (black histogram).

An opposite situation is revealed for the herbicide Diflufenicanil. Indeed, as shown in Figure 130, one states a distinct overall decline of the \( \gamma' \) coefficient through the early part of the study period, followed by a stabilization. This observation relates to the singular and unexpected relationship already noticed for this substance between increasing tonnages and decreasing river contamination (cf. Part III). Here again, one has to get back to the previously made observation regarding the important change of the seasonal profile for this substance over the studied timeframe, with a shift of the use from spring to fall period, signifying a significant modification of the molecule application, coupled with an upward trend in the tonnages. This time the application change benefited the river quality, with the \( \gamma' \) coefficient decreasing. The explanation was given in Part III, i.e. relating to the progressive abandonment of the Diflufenicanil usage in non-agricultural areas, where it was associated to high leakage rate to surface waters.

Figure 130: Interannual variations, for the herbicide Diflufenicanil (DFF), of the national scale annually-averaged contamination coefficient \( \gamma' \) (red curve). Also pictured, the national-scale yearly tonnage values for DFF extracted from the BNV-d (black histogram).
A similar variation in the basin-to-river coefficient was observed for the herbicide Nicosulfuron (cf. Figure 131), but a reversed modification of the seasonal profile occurred during the study period: the monthly-resolved river contamination profile (cf. Part III) revealed a strong regression of the Nicosulfuron fall-winter use, further restricting its recent use to early summer. This apparently influenced favorably the river quality, in spite of the increasing tonnages sales in the first half of the studied period.

**Figure 131**: Interannual variations, for the herbicide Nicosulfuron, of the national scale annually-averaged contamination coefficient $\gamma'$ (red curve). Also pictured, the national-scale yearly tonnage values for Nicosulfuron extracted from the BNV-d (black histogram).

A synthesis of the contamination coefficient variations for all the here considered in-use WFD PPP substances is proposed by Figure 132, picturing the ratio of the 2015-2020 average $\gamma'$ values to a reference 2009-2014 values. When this ratio exceeds 1, the corresponding intrinsic transfer capacity of the substance is likely to have worsened over the study decade, due to less favorable agricultural practices. On the contrary, the lower this ratio under unity, the better the change in the substance use typology over the study period, with respect to rivers contamination.

One should be cautious, however, as for some substances which ended up to be banned during the 2015-2020 period, farmers likely made some anticipation storage, producing an underestimation bias of the quotient between the mean annual river concentration and the yearly sold tonnage, translating into artificially low $\gamma'$ in this period. This could be part of the explanation for the low ratios observed in Figure 132 for Linuron and Isoproturon.

These precautions considered, the uses of the molluscicide Metaldehyde and of the herbicides Pendimethalin, Aclonifen, Glyphosate and Metazachlor, and to a lesser extent 2,4 MCPA, appear to have shifted toward detrimental practices, overall. For Glyphosate, this worsening occurs in spite of that fact that, as diagnosed in Part III, it has been less and less used in non-agricultural areas. Its increased use in wet seasons from 2015 onward is likely the reason for the observed $\gamma'$ upward variation. As a matter of fact, the examination of the Pendimethalin, Aclonifen and Metazachlor seasonal profiles also showed relative increase of waters contamination in November-December in the latest years of the studied period, signing a shift towards more use in wet conditions, favoring the basin-to-river transfer.

These substances and their agricultural application should be subject to specific considerations at the national scale, in this regard.

On the other hand, the use of herbicides like Nicosulfuron and Chlorotoluron, or Diflufenicanil, as well as the practices associated to three of the WFD-monitored fungicides (Cyprodinil, Tebuconazole, Ipredione), seem to have shifted toward less detrimental profiles in terms of river contamination. Here again one can associate this to seasonal profile changes, with Nicosulfuron and Chlorotoluron seeing the weight of their winter exceedance rates lowered in the 2015-2020 period, compared to the earlier one. Diflufenicanil was an exception, with a favorable ratio in Figure 132, due to some drastic limitation of the spring-summer uses related to its prohibition as a non-agricultural herbicide (cf. Part III), and despite some relatively higher exceedance rates in wet seasons at the end of the timeseries.
We believe that this kind of ratio could be suggested as a national PPP substance-specific progress indicator, reflecting the global efficacy in management of the transfer to rivers. This indicator is independent of tonnages but depends on usages or mitigation practices, and it is based on the relative changes in the basin-to-river contamination coefficient over the years.

V.3. BASIN TO SURFACE WATER CONTAMINATION AS A FUNCTION OF THE PPP SUBSTANCES MOLECULAR PROPERTIES

One important aspect driving the transfer of the PPPs from the basin to the aquatic system is the contaminant’s mobility in soils, which is known to be well described by the partition coefficient between water and organic carbon, i.e. Koc.

The idea of trying to correlate the Koc values of PPP active substances with associated large-scale streams contamination indicators was explored in some previous study (Gauroy 2011), mobilizing there the concept of Groundwater Ubiquity Score (GUS), which accounts for both Koc and DT50 to predict soil leaching effects on groundwater contamination (Gustafson, 1989), in the absence of equivalent surface water-dedicated approach. No correlation could be found, however, due to the lack of associated quantitative data on the substances’ consumption in the considered territories.

By contrast, as shown in Figure 133 for the illustrative case of the river basin RM, thanks to the tonnage normalization embedded in the definition of $\gamma'$ - cf. equation (12) - we have been able to clearly evidence such a correlation. Indeed, for those active substances which were essentially used in agricultural pesticide products, and for a given basin $j$, it is satisfactorily possible to link the empirically derived average contamination coefficients $\gamma'_{i,j}$ computed in section V.1, to the corresponding soil-water partition coefficients Koc (cf. Table 15 in Appendix A), through a simple linear relationship:

$$\log \gamma'_{i,j} = \beta_j - \alpha_j \cdot \log (Koc_i)$$ (14)

with $\alpha_j$ and $\beta_j$ characterizing the transfer specificities of basin $j$ for the considered period.

Figure 133: For all the considered PPP active substances which are mainly used in agricultural contexts, correlation diagram between the Log values of their $\gamma'$ coefficients determined for the RM basin, and those of the Koc. The red-dotted line expresses the optimal linear correlation, according to eq. (14) ($R^2=0.75$).
The empirical values of $\alpha$ and $\beta$ found for the six main basins are given in Table 11, together with the associated linear correlation coefficient $R^2$.

Table 11: Empirical values of the $\alpha$ and $\beta$ parameters of eq. (14) for the 6 main French basins, and for the national scale, and the associated linear correlation coefficients $R^2$

<table>
<thead>
<tr>
<th>Basin</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB</td>
<td>0.51</td>
<td>-1.00</td>
<td>0.58</td>
</tr>
<tr>
<td>AG</td>
<td>0.60</td>
<td>-0.92</td>
<td>0.67</td>
</tr>
<tr>
<td>AP</td>
<td>0.53</td>
<td>-0.89</td>
<td>0.66</td>
</tr>
<tr>
<td>RM</td>
<td>0.70</td>
<td>-0.45</td>
<td>0.75</td>
</tr>
<tr>
<td>RMC</td>
<td>0.63</td>
<td>-0.43</td>
<td>0.54</td>
</tr>
<tr>
<td>SN</td>
<td>0.68</td>
<td>-0.82</td>
<td>0.70</td>
</tr>
<tr>
<td>Mainland France</td>
<td>0.57</td>
<td>-0.77</td>
<td>0.74</td>
</tr>
</tbody>
</table>

Equation (14) readily converts into:

$$\gamma'_{i,j} = \frac{10^\beta_j}{(Koc_i)^{\alpha_j}}$$  \hspace{1cm} (15)

The Figure 134 displays, as a function of Koc values, all the basin-to-river contamination coefficients which we derived from the mean concentrations, all basins considered. The vertical error bars represent the amplitude of variations between the 6 studied basins. The horizontal bars account for the range of Koc values found in the PPDB and PubCHEM databases (cf. Table 15 in Appendix A).

As can also be seen in the figure, in line with equation (15), a power law (pictured by the red line, $\alpha=0.57$, $\beta=-0.77$) can actually be used to approximate the dependency of $\gamma'$ on Koc. The obtained correlation coefficient $R^2=0.74$ is significant.

The figure also accounts for the ranges of degradability for the various substances: the red dots refer to compounds whose DT50s in the field (again according to the PPDB database) are higher than 100 days (persistent compounds), green dots refer to DT50s lower than 20 days (readily degraded compounds), and blue dots are intermediate situations. It appears from this plot that, at the large scale of the present study where pollution sources are widely scattered spatially and temporally, there is no distinct clustering or consistent behavior of the empirically derived contamination coefficients according to these degradability ranges. However, one can note that those compounds situated in the lowest part below the regression line, like 2,D, 2,4MCPA, Metazachlor or Chlorpyrifos-ethyl, i.e. those with contamination coefficients lower than predicted, have their main usages occurring in spring or summer. These seasons
are also when the biodegradation in soils is favored by the thermal conditions. In the case of Chlorpyriphos, previous studies also indicated its high propensity to volatilize either from the crop foliage or from the water column, which could explain the observed low contamination coefficient (ATSDR 1997).

This is to the point that Chlorpyriphos can be considered as a long range transported pollutant (Mackay 2014).

Nevertheless, at the national or great basin scales, the Koc predictor for the $\gamma'$ coefficients appears as prevalent over the compound degradability aspect.

**Figure 134**: Correlation diagram between the national scale contamination coefficients $\gamma'$ and Koc values of the considered PPP active substances. Round dots: substances with mostly agricultural uses. Squared dots: substances with significant non-agricultural uses. Red dots= substances with open field DT50>100 days; green dots= DT50<20 days; blue dots= intermediate DT50s. The vertical error bars correspond to the min-max range of the $\gamma'$ values among the 6 basins. The horizontal error bars refer the Koc range of Table 15 (Appendix A). The black-dotted line expresses the optimal linear correlation, according to eq. (15) ($R^2=0.74$), considering only those substances with main agricultural applications (round dots).

Compared to Figure 133, we also displayed in Figure 134 the data corresponding to active substances widely used as biocides in non-agricultural products (square dots): Aminotriazole, Oxadiazon, Glyphosate and Thiabendazole.

For those substances, the river contamination responded very diversely to the recorded sold compound tonnages (e.g. Aminotriazole, with a factor 20 between basin AG – lowest coefficient- and basin AP – highest one, in Figure 134). This could, at least partly, be imputed to the variety of use of this substance according to the region. Actually, Aminotriazole did receive uses in vineyards and open fields, but was also significantly used in urban contexts, for the weeding of parks and gardens, as well as sidewalks and roadways. It might have had some major use in some urbanized areas, like in the AP basin, with extensive application on low permeability surfaces, hastening the transfer to waters, and biasing the relationship to Koc, as the adsorption to soil particles is there minimized. The Figure 135 very well reflects the specificity of this substance, with a high contamination seasonal profile in AP basin, despite low tonnage figures, whereas the AG basin exhibits much lower concentrations, with a different time distribution, and this in spite of much higher tonnage figures compared to AP, related to the formerly heavy application of this substance in vineyards.

**Figure 135**: Seasonal variations of the basin-averaged concentrations $\chi$, for Aminotriazole in AG and AP basins, integrating the measurements from 2009-2015.

The same holds true for the biocide Thiabendazole, which specifically received significant agricultural use in the AP basin, with comparable water contamination in the other basins in spite of much lower PPP tonnages recorded there.

This holds true also for Oxadiazon, the last upper hand outlier in Figure 134, which also used to receive many urban applications before it was banned.
Finally, a similar statement can be made about Glyphosate, which, in spite of its high degradability, also
stands in the upper part of the mean line in Figure 134. This may again be linked to the relatively high
usage of Glyphosate in non-agricultural/urban contexts (representing typically 20% of its sales in the first
years of the studied period), which, as already discussed and verified in Part III.2, is known to involve high
loss rate to river (Hanke 2010).

Figure 136 shows that a similar log-linear law between the contamination coefficients and Koc could also
be derived from the peak concentrations, using the maximum annual values of the concentrations 95th
percentiles and the associated $\gamma^{95\%}$ values previously exemplified in Figure 125. The correlation is
however somewhat weaker ($R^2=0.48$), with less compounds and less basins per compound represented
compared to Figure 134, as only those compounds exhibiting exceedance rates $\rho>5\%$ could be
associated with 95th percentile concentration values.

Table 12 provides the parameters of equation (14), applied for the six basins, regarding the concentration
95th percentile dependence on Koc. No identifiable correlation could be derived for the RMC basin, due
to a too low number of PPP active substances exhibiting exceedance rates $\rho>5\%$ in this region.

Table 12: Empirical values of the $\alpha$ and $\beta$ parameters derived when applying eq. (14) to describe the $\gamma^{95\%}$ dependence on Koc, for the 6 main French basins, and for the national scale, and the associated linear correlation coefficients $R^2$

<table>
<thead>
<tr>
<th>Basin</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LB</td>
<td>-0.60</td>
<td>0.37</td>
<td>0.47</td>
</tr>
<tr>
<td>AG</td>
<td>-0.21</td>
<td>-0.47</td>
<td>0.24</td>
</tr>
<tr>
<td>AP</td>
<td>-0.45</td>
<td>0.056</td>
<td>0.54</td>
</tr>
<tr>
<td>RM</td>
<td>-0.40</td>
<td>0.13</td>
<td>0.61</td>
</tr>
<tr>
<td>RMC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SN</td>
<td>-0.44</td>
<td>-0.12</td>
<td>0.49</td>
</tr>
<tr>
<td>Mainland France</td>
<td>-0.40</td>
<td>0.045</td>
<td>0.48</td>
</tr>
</tbody>
</table>
Meanwhile, these data tend to produce an empirical demonstration of the primary dependence of the basin-to-river coefficients \( \gamma \) on the physico-chemical properties of each PPP substance, i.e. its soil adsorption propensity as expressed by the water/organic carbon partition coefficient Koc.

To strengthen this assertion, the validity of the above equation (15) could be tested further on an extra dataset of WFD monitoring data (Assoumani 2022), collected between 2016 and 2019 from hundreds of sites (the number of individual measurements varies between 1200 and 1700, depending on the considered parameter), on 8 PPP substances for which we have consistent tonnage data from the BNV-d, but which were not part of our initial compounds list because they are neither priority substances nor river basin specific pollutants.

Table 13 delivers their PPP functions and the Koc values obtained from the PPDB database, covering a wide range of applications and physicochemical properties.

**Table 13**: Identification and Koc values of the 9 PPP active substances extracted from Assoumani et al. 2022

<table>
<thead>
<tr>
<th>Function</th>
<th>CAS number</th>
<th>Parameter</th>
<th>Koc (L/Kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Herbicide</td>
<td>51218-45-2</td>
<td>Metolachlor</td>
<td>120</td>
</tr>
<tr>
<td>Herbicide</td>
<td>23950-58-5</td>
<td>Propyzamid</td>
<td>840</td>
</tr>
<tr>
<td>Fungicide</td>
<td>67306-00-7</td>
<td>Fenpropidin</td>
<td>71790</td>
</tr>
<tr>
<td>Herbicide</td>
<td>2164-08-1</td>
<td>Lenacil</td>
<td>165</td>
</tr>
<tr>
<td>Herbicide</td>
<td>61213-25-0</td>
<td>Flurochloridone</td>
<td>700</td>
</tr>
<tr>
<td>Insecticide</td>
<td>23103-98-2</td>
<td>Pyrimicarb</td>
<td>388</td>
</tr>
<tr>
<td>Herbicide</td>
<td>5915-41-3</td>
<td>Terbutylazine</td>
<td>231</td>
</tr>
<tr>
<td>Herbicide</td>
<td>1918-00-9</td>
<td>Dicamba</td>
<td>5.28</td>
</tr>
</tbody>
</table>

Figure 137 summarizes the average concentrations and quantification rates determined for each of the six basins during the 2016-2019 period. Here again a wide range of situations are covered.

*Figure 137*: Combined display of the mean quantification rates (QR, y-axis) and averaged quantified concentrations of 8 additional PPP active substances measured in France over the 2016-2019 period.

The robustness of equation (15) and its parameterization in Table 11 can be tested by comparing, for each compound i:

- on the one hand, the average BNV-d-recorded tonnage assumed to be applied per area unit, i.e. the value of \( \frac{T_{ij}}{A_j} \), in each of the six main basins j
- on the other hand, the values of $\frac{T_{i,j}}{A_j}$ predicted according to equation (12).

Indeed, according to equations (12), we have:

$$\frac{T_{i,j}}{A_j} = \frac{\chi'_{i,j} \cdot \tau_i/2}{\gamma'_{i,j}} = \frac{\rho_{i,j} \cdot (\chi''_{i,j} - \tau_i/2)}{\gamma'_{i,j}} \quad (16)$$

In the present situation, we will assume that the LoQs in each basin were close to constant along the 2016-2019 duration, and that they can then be used as proper cut-off threshold values for the considered basin. In this condition we can set the $\tau_i$ values for each basin to the average values $\overline{LoQ}_{i,j}$.

Moreover, $\rho_{i,j}$ and $\chi''_{i,j}$ simply represent respectively the mean quantification rates QR and the mean value of the quantified concentration measurements, i.e. the data already represented in Figure 137.

Applying equation (15) to determine the contamination coefficients $\gamma'_{i,j}$, and using the dataset of Figure 137, we obtained the comparison of BNV-d recorded and predicted $\frac{T_{i,j}}{A_j}$ depicted in Figure 138.

Figure 138: Correlation diagram between the eq. (16) predicted and BNV-d registered areal tonnages for the 8 additional substances in the 6 basins.

As can be seen, for a majority of the 48 considered compound/basin situations, there is a pretty good agreement between recorded and predicted tonnages, with no distinct differences among the six considered basins. Some outlier situations are observed, however, for those active substances named in the graph (Propyzamide, Fenpropidin, Dicamba, Flurochloridone, Pyrimicarb, Lenacil). The only systematic bias concerns the herbicide Dicamba, which yield predicted tonnage far lower than BNV-d values, whatever the basin. This can be put in regard of its very low Koc value, actually lower than any of the WFD substances considered in this study, and thus standing out of the original application domain of equation (15). Another hypothesis would be that, due to this very polar molecular behavior, the analytical techniques of the monitoring labs might have been challenged, resulting in only a limited part of the actual Dicamba concentration being quantified, inducing weaker tonnage prediction. This, however, would need specific checking.

Another noticeable set of outliers regards the lowest part of the tonnage range (around 0.01 kg/year/km²), where it is likely that the measurements capabilities were also significantly challenged.

Excluding the 6 basins Dicamba’s values, Table 14 summarizes the remaining matching performance of the left 42 predicted vs. BNV-d registered tonnage comparisons, with the ratio of both these variables exhibiting a median value close to unity (0.90), and 60% of the ratios ranging between 0.43 and 1.72. This is quite satisfactory in regard of the variability which characterizes the matching between the measured data and the theoretical log-linear relationship in Figure 133 and Figure 134. We conclude that this validation dataset strengthens the predictability of equation (15).
Table 14: Percentile analysis of the 42 values of the Predicted to Registered tonnage ratios

<table>
<thead>
<tr>
<th>42 ratio values</th>
<th>Ratio Predicted/BNV-D Tonnages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentile 90</td>
<td>2.61</td>
</tr>
<tr>
<td>Percentile 80</td>
<td>1.72</td>
</tr>
<tr>
<td>Percentile 50</td>
<td>0.90</td>
</tr>
<tr>
<td>Percentile 20</td>
<td>0.43</td>
</tr>
<tr>
<td>Percentile 10</td>
<td>0.11</td>
</tr>
</tbody>
</table>

In the end, we consider that the fact that the contamination coefficients derived from two independent empirical datasets, namely the WFD chemical monitoring data bank and the BNV-d for PPP tonnage, ultimately appears to be ranked in a consistent way in regard of a third set of empirical data, i.e. Kocs, is quite reassuring. It brings confidence on the global quality of the three datasets, and to the general approach described through this study.

V.4. PRACTICAL USE OF THE DEPENDENCE OF THE CONTAMINATION COEFFICIENT ON TONNAGE & Koc

Moving further, the above considerations could invite the authorities in charge of controlling the river quality to modulate their predictive indicators founded on PPP tonnage data with a Koc dependent coefficient. Possible examples of such indicators for assessing the interannual variations of the contamination pressure and risk on stream waters are given below:

- one referring to the assessment of the active substance pressure on surface waters (equation (17)):

\[ PPP \text{ pressure}_{j,k} = \frac{10^{\beta_j}}{A_j} \sum_{\text{substances } i} \frac{T_{i,j,k}}{(Koc_i)^{a_j}} \]  

(17)

- and the other converting it into risks through the EQS accounting (equation (18)):

\[ PPP \text{ risk}_{j,k} = \frac{10^{\beta_j}}{A_j} \sum_{\text{substances } i} \frac{T_{i,j,k}}{EQS_i \cdot (Koc_i)^{a_j}} \]  

(18)
Figure 139 and Figure 140 provide illustrations of such predictive indicators, computed for the here studied WFD herbicides, over the 2009-2020 period. Figure 139 can readily be compared with Figure 151 (Appendix E), which accounts for the sole tonnage data. The contamination pressure indicator shows the effect of the Koc differentiation between the various herbicides, with some enhanced deviation between AP basin and the others, and an overall downward trending which wasn’t that clear when considering only the tonnage. This is because in eq. (17) more weight is given to easily-transferred low Koc substances, weakening the influence of the high tonnage Glyphosate.

Figure 139: Interannual variations, for the considered herbicides that were authorized in 2009 and after, of the pressure indicator calculated by eq. (17), for each of the 6 basins

Switching to the predicted risk indicator, Figure 140 offers a somewhat different picture: the downward trend no longer exists for the AP basin, and the gradation between the various basins is more distributed. The strong behavior difference between the two indicators for the AP basin is due to the increased usage overtime of some low tonnage but highly ecotoxic compounds, like Diflufenicanil or Pendimethalin. Such upward trends also exist in the other basins, but are counterbalanced by some sharper decline in the Metazachlor contamination.

Figure 140: Interannual variations, for the considered herbicides that were authorized in 2009 and after, of the risk indicator calculated by eq. (18), for each of the 6 basins

Figure 141 and Figure 142 provide an equivalent picture for the insecticides’ family, to be compared with the tonnage data given in Figure 148 (Appendix E). For the considered timeframe, there has been only 3 authorized insecticides included in the surface water WFD assessment: Imidacloprid, Chlorpyrifos-ethyl and Cypermethrin. The tonnage data are driven essentially by the Imidacloprid, which was banned for most of its application in 2018, and this is exacerbated in Figure 141 as this substance has the lowest Koc (highest contamination coefficient) of all the 3 compounds. The risk indicator of Figure 142, however, displays a completely different picture, as the Cypermethrin, in spite of far lower tonnages, comes with a very low EQS, ruling the overall risk prediction, and indicating much less obvious progress in terms of impact of the surface waters’ quality.

Figure 141: Interannual variations, for the considered insecticides that were authorized in 2009 and after, of the pressure indicator calculated by eq. (17), for each of the 6 basins
Figure 142: Interannual variations, for the considered insecticides that were authorized in 2009 and after, of the risk indicator calculated by eq. (18), for each of the 6 basins

Such curves could obviously have also been derived directly from the monitoring data. They are shown here to highlight the capability to have them, instead, predicted by the simple access to the tonnage, Koc and ecotoxicological data, with the extra opportunity to supervise, and possibly to manage, the contamination pressure and the risk associated to yet non-monitored compounds.

Such easily computable indicators could, for instance, be used either in retrospective mode to analyze the historical impact of PPPs in the surface waters, or in prospective mode to assess the effects of various agronomical scenarios, implying non-yet monitored active substances.

Moreover, from equations (12) and (15), it is possible to extrapolate and derive a theoretical value for the mean yearly concentration indicator $\chi'_{i,j}$ for any non-monitored PPP “$i$” in basin “$j$”, given the corresponding value $\chi'_{WFD,j}$ of any WFD-monitored PPP “$i_{WFD}$” in the same basin “$j$”, provided the associated tonnage and Koc values are known for both PPPs, as follows:

$$\chi'_{i,j} = \chi'_{i_{WFD},j} \cdot \frac{T_{i,j}}{T_{i_{WFD},j}} \cdot \left( \frac{Kc_{i_{WFD}}}{Kc_{i}} \right)^{\alpha_j}$$

This could be of use, for instance, when trying to assess the relative river impact of substituting a WFD PPP active substance another substance, for the same crop applications... More generally, the ratio between $\chi'_{i,j}$ and EQS could readily be used to define a criterion contributing to the risk prioritization of compounds not benefiting from enough monitoring data.

V.5. DISCUSSION

On the basis of a simple conceptual contaminant transfer model, we proposed to quantify the linear correlations between the active substance tonnage data and our surface water contamination indicators, through the quantification of a basin-to-river contamination coefficient $\gamma'$. The distribution of the $\gamma'$ values among the six mainland France basins were examined for 22 PPP active-substances. Probably due to the variations in crop types, agricultural practices and pedo-hydro-climatic conditions, and also maybe in regard of the monitoring sites network specificities, some basins like RMC, AP and LB exhibited, overall, higher basin-to-river transfer figures, whereas SN and AG showed significantly lesser apparent leakage to surface water.

Building on the correlations between PPP annual tonnages and our contamination indicators, we were led to propose the quantification of the change in the multiannual coefficient $\gamma'$ as a relevant, active
substance-specific indicator, mirroring the long-term progress/regression in the substance use/management, regardless of the tonnage aspect. This indicator theoretically sensitive to the change in substance uses (e.g. new crop applications when a substance comes to replace a former banned compound, or new applications associated to new agricultural practices, ...), to hydroclimatic conditions, but also to the transfer mitigation measures, and could thus potentially receive interesting application in the field of environmental or crop management policies.

We went further, and demonstrated that the contamination coefficient $\gamma'$ could be reasonably well predicted knowing the Koc partition coefficient, thanks to a simple log-linear regression. This prediction was further improved by discarding those active substances having received significant non-agricultural applications, like Aminotriazole, Glyphosate or Oxadiazon, as the adsorption to soil particles is a less relevant property in nonpermeable contexts. The nice correspondence thus obtained, linking three independent data sources (WFD chemical monitoring, active substance tonnages, and Koc values) tends to validate the whole system, including the associated simple transfer conceptual model, at least when dealing with wide spatial scales like mainland France or large river basins areas. Additionally, we were able to challenge the soundness of the established $\gamma'$ vs. Koc dependence by applying it to predict the recorded tonnages of eight new active substances of various functions and physicochemical properties in the six main French river basins. The predictions went satisfactorily matching the BNV-D tonnages for most these substances, confirming the relevance of the proposed empirical relationship.

Finally, we proposed some practical use of the predicted basin-to-river contamination coefficient in order to derive contamination pressure and ecological risk indicators from the sole access to tonnages, Koc and ecotoxicological thresholds. These indicators could be used either in retrospective mode to analyze the historical impact of PPP in the surface waters, or in prospective mode to assess the effects of various agronomical scenarios, implying non-yet monitored active substances.
Part VI. CONCLUSIONS

Throughout this work, we aimed at developing, and demonstrating the interest of big-data-founded, statistically optimized indicators, dedicated to the revelation of the anthropogenic and natural processes that rule the chemical contamination of surface waters in continental France. Exploring beyond the regulatory compliance check exercise of the waterbody’s status, we showed that the WFD monitoring and the resulting data allow to build such indicators, and to obtain a finer assessment of the surface water aquatic contamination evolution over the 2009-2020 period, when occurring.

More specifically, we first showed that, due to the time and space heterogeneity of the chemical analysis capabilities, the French WFD monitoring data couldn’t be used directly to show meaningful large-scale trends. We then used an original methodology to constitute a set of data comparable through time and space, and be able to demonstrate some reliable trends in the contamination of various WFD substances, at national or at basin level. For this, we addressed the issue of time and space variation of the analytical capabilities of the monitoring laboratories. We established and statistically characterized a workable dataset of monthly indicators, for the continental France WFD monitoring data collected between 2009 and 2020. This dataset is scheduled to be made publicly available from the French water data website [https://data.eaufrance.fr](https://data.eaufrance.fr).

We believe that this approach should be more often applied for future similar studies, because, as shown in the present study, this variability can have great impact on concentration trends.

This monthly indicator dataset being built-up, and assisted by the large and permanently growing amount of scientific literature related to the interpretation of the chemicals’ occurrence in the environment, we have set ourselves several objectives related to the implementation of the indicators:

- Secure the comparison between the 6 main continental French basins, in order to provide a coherent national picture of some societal, economic and environmental developments, mirrored by the surface water chemical contamination, and reported by the WFD monitoring.

- Allow an un-biased evaluation of the contamination trends, in particular with a view to assessing the effects of public policies that address the use of the WFD chemicals. This implied the consideration of the product ban decisions, and the reflection of their actual efficiencies through the water contamination data in the following years, be it about PPP stocks disposal, persistence related to the use of banned PPP substances due to other fields of application (e.g. as biocides), or follow up of industrial compounds after regulatory restrictions (e.g. alkylphenols, HVOC solvents, etc.). Legacy substances, like Atrazine, Simazine, Lindane pesticides, or BFR like BDEs were also covered. Public policies related to the prohibition of pesticide use in some non-agricultural areas, or the impact of some CAP incentives on the Glyphosate use, could also be considered to interpret the observed trends.

- Highlight and value the use of monthly-resolved seasonal information on water contamination, as a diagnostic tool to disclose either the signature of the various dominant uses of a substance (e.g. biocide vs. PPP, as for Diuron, Imidacloprid or Thiabendazole), or to provide the time window in which the water quality managers should optimally intensify - or decrease – the monitoring efforts. Last but not least, use this information to track the change in the seasonal patterns, so as to reveal the modifications in the practices over the basins, as diverse as the effects of PPP substitutions (e.g. after banning herbicides like Isoproturon or Aminotriazole), the incidence of improved technology on some pollution sources - like the
PAHs emission by the vehicles - or the industrial management of some HVOCs.

Another benefit of the developed indicators has been the restoration of the consistency between sales and water contamination figures for PPPs, and by extension, the provision of a reliable tool to assess comparatively, for a given substance and thanks to the WFD data, the levels of associated basin-specific pollution pressures.

Our indicators also proved to be useful for evidencing the metrological progress made by the French monitoring operators (sampling and labs) along the 2009-2020 study period, allowing the observation of a reduction in the internal deviation of the measured data, yet with challenging problems still to overcome, e.g. for DEHP or hydrophobic compounds.

When it came to explain or hypothesize the causality of the observed chemicals aquatic occurrences and trends, we had to consider a wide variety of factors, reflecting the relevance of the WFD to potentially encompass the regulation of a large range of societal aspects. The involved direct anthropogenic drivers were manifolds, including:

- Atmospheric-deposition aspects, either referring to distant contaminant transportation, like for Lead, or to regional/local influence for PAHs (heating systems, vehicles, industrial exhausts), or to even closer influences, like the measurement quality impairments associated to the ubiquitin presence of DEHP in the atmosphere surrounding the metrological process.

- Effect of navigation and boating (TBT, Cypermethrin)

- The use of various products in urban/populated areas, would it regard the outdoor or indoor practices of professionals or consumers, inducing wastewater or stormwater contaminations by biocides, detergents, metals, or other compounds involved in the industrial processes of sewer-connected plants.

- Last but not least, agricultural substances use. For PPPs, we were able to demonstrate that large-scale contamination of waterways reflects rather well, quantitatively and at first order of approach, the records of the active substances’ sales national databank BNV-d, once these had been normalized to the respective basins’ areas. We were also able to show, however, that the relationship between our contamination indicators and tonnages can be strongly challenged by variations in the use of the substance, i.e. the balance between agricultural and non-agricultural uses, as well as by changes in the seasonal applications. Wet seasons were shown, or hypothesized, as important drivers to explain the occurrence of enhanced aquatic contaminations, related to the effect of spreading herbicides, or metals associated to fertilizers materials.

The role of the soil/PPP substance interaction was investigated through a quantitative approach, in order to integrate our observations into both some descriptive and predictive schemes. The development of a simple conceptual allowed us, through the definition of a basin-to-water contamination coefficient $\gamma$, to evidence the wide range of transfer potentials attached to the various WFD PPPs, this coefficient varying by 3 order of magnitudes depending on the compound. We suggest to use the temporal variation of $\gamma$ as an indicator of progress in the large-scale management of substances. Moreover, we made the empirical demonstration that adsorption on soil particles (expressed via the Koc) could be a relevant predictive driver of the large-scale surface water contamination, ahead of the degradability of the molecule. We propose a formulation that allows the prediction of some large-scale indicators of surface water contamination and associated risks, including for substances not yet monitored, based on Koc and
Finally, the influence of the environmental parameters was also mobilized to interpret the seasonal patterns of the contamination indicators. In particular, our observations did match satisfactorily with recent knowledge advances concerning the influence on the Glyphosate and AMPA occurrence in rivers of the soil and water phosphorus contents. The seasonality of the biological activity in the surface waters and its implication on pH or Redox potential also appeared as relevant to explain our observed large-scale annual variability for several WFD trace elements. The river dilution effects were well reflected in the seasonal profiles of some mobile groundwater originated contaminants, like Atrazine or Simazine, while more hydrophobic legacy substances (Lindane or TBT) found their variability better explained by the particulate matter resuspension during high flows.

Regarding specifically the 8 considered WFD trace elements, our investigations have provided an integrated large-scale vision over the average concentrations in the main French 6 basins, which could advantageously be discussed in regard of the existing knowledge of the influence of the geological backgrounds' levels in these areas.

All this being said, the processing which we applied to the original measurement data, however, does not compensate for the shortcomings linked to some too limited analytical sensitivity, as it is the case for insecticides, BFRs and HVOCs.

More generally, building on the long-term and large spatial coverage of the here presented results, it would probably be possible to rethink the national and basin’s monitoring efforts in an optimized way. For instance, is the monthly frequency really required to monitor banned compounds, for which reduction options are lacking, and that are known to induce only very limited risks to the aquatic ecosystem or water resources? Monitoring optimization could be reasoned for instance in view the statements of the present study, either in terms of low concentration-to-EQS ratios (via the Xr indicator) combined with no increasing trend detection, or because the considered compounds are detectable in only a few localized contexts (cf. the Xc indicator), i.e. with limited risk to contribute to widespread mixture effects. The European Commission recently proposed some amendments to the WFD which go in this direction and are fully consistent with our study results (COM 2022), e.g. considering the suppression of the legacy compound Alachlor, Chlorfenvinphos and Simazine, or Carbon tetrachloride from the priority substance list.

By contrast, even when the spatial frequency of the compound detection stands low, if the risk indicator is popping up high, and especially when this doesn’t come up associated with a clear downward trend, then one should consider to invest more in the improvement the measurement process. Good illustrations of such situations are given in the present study by PFOS or Cypermethrin, and these examples should be a strong argument to extend the monitoring to other compounds of their chemical families, i.e. respectively PFAS and Pyrethroids, given that adapted analytical methods already exist (Rösch 2019). Here again the above-mentioned EU Commission proposal of WFD amendments fits quite well with these orientations, setting options for the inclusion of 24 PFAS, and nine new priority insecticides (4 pyrethroids and 5 neonicotinoids). For such situations, one should also seriously consider the use of integrative passive samplers instead of the usual grab sampling strategy, in order to improve the quantification limits and have the WFD monitoring representing the actual risk in a more appropriate way (Moschet 2014, Mathon 2022).

In addition, as we have been able to evidence at the France scale throughout our study, the May-June, and November-December periods were those when the surface waters are the most heavily impacted by
the PPP active substances. Because, at the local scale, the contamination peaks are known to occur in very tight time windows, it would be reasonable to increase the sampling frequency during these periods where up to now it stayed at the minimal requirement of a single measurement per month, so that those peaks are better detected and accounted for.

All these current limitations, added to the fact that the present regulatory waterbody assessment accounts only for a very limited fraction of the contaminants that are generated by the terrestrial activities, clearly call for some further improvements in the WFD chemical surveillance, considering better analytical techniques, and the use of integrative sampling (passive samplers, bio-monitoring), and more integrated approaches, like previously promoted through some UE projects (Brack 2017), and which we couldn’t extensively discuss in the present work.

PROSPECTS

- Based on the developed set of indicators, and the on the scientific background which we gathered to assist their interpretation, it is intended (and encouraged) to continue and extend the study of the chemical contamination trends at nation and river basin scales. In this line, we intend to extensively share this work and the developed indicators with the French ministry of ecology, and the water agencies, see if it could contribute to better diagnose, report and promote the WFD achievements, in particular with regard to the substance reduction objectives. Also explore if it could contribute to adapt the local monitoring, and help put in place specific or more efficient management measures for contamination reduction.

- In the same vein, the many signals, hypothesis or questions detected throughout our study often need to be confirmed at finer spatial scales, in order to convert the information into relevant actions in terms of pollution reduction. These activities would be best carried out by professionals acting in the river catchment areas, within the framework of WFD management plans.

- For PPPs, we hope that the developed indicators will provide opportunities to have the WFD monitoring activities further appropriated by the actors of the French pesticides’ management plan, especially in the perspective of continued progress towards a more integrated and systematic steering of the PPPs’ impacts on the water-dependent biodiversity.

- It would also be interesting to implement the proposed approach related to the predicted basin-to-river contamination coefficients, in order to derive contamination pressure and ecological risk indicators from the sole access to tonnages, Koc and ecotoxicological thresholds. These indicators could be used either in retrospective mode to analyze the historical impact of PPP in the surface waters, or in prospective mode to assess the environmental effects of various agronomical scenarios, including those implying non-yet monitored active substances. Possible interaction with the phyto-pharmacovigilance activities coordinated by the French Agency for food environmental and occupational health & safety (ANSES) could be envisioned in this respect.

- Finally, the developed indicators could benefit the comparison of WFD results beyond the sole France boundaries, and exploratory exchanges with other UE member states or with the Environment Directorate of the Commission could be envisaged.
Appendix A: Lists of the considered WFD chemicals, and associated information

Table 15: Identification of the considered surface water WFD active substances of plants protection products, their possible ban situation, their WFD status (PS, PHS or RBSP), their Koc ranges, their EQSs, and the Cut-off thresholds (τ values).

<table>
<thead>
<tr>
<th>Function</th>
<th>Parameter</th>
<th>CAS number</th>
<th>Legacy compound (banned before 2009)</th>
<th>WFD status</th>
<th>Koc (L/Kg) (Average, Min, Max)</th>
<th>EQS water (µg/L)</th>
<th>Cut-off threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fungicides</strong></td>
<td>Hexachlorobenzene</td>
<td>118-74-1</td>
<td>Yes</td>
<td>PHS</td>
<td>0.01</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Iprodione</td>
<td>36734-19-7</td>
<td>RBSP</td>
<td>(1521;223;3927)</td>
<td>0.35</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pentachlorophenol</td>
<td>12155-2-61-2</td>
<td>RBSP</td>
<td>(2789;1618;4393)</td>
<td>0.026</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cyprodinil</td>
<td>10753-4-96-3</td>
<td>RBSP</td>
<td>(1718;102;6000)</td>
<td>1</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tebuconazole</td>
<td>148-79-8</td>
<td>RBSP</td>
<td>(4242;1200;11000)</td>
<td>1.2</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thiabendazole</td>
<td>13186-0-33-8</td>
<td>RBSP</td>
<td>(453;207;594)</td>
<td>0.95</td>
<td>0.02</td>
<td></td>
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<tr>
<td></td>
<td>Quinoxyfen</td>
<td>12449-5-18-7</td>
<td>PHS</td>
<td>0.15</td>
<td>0.02</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Boscalid</td>
<td>18642-5-85-6</td>
<td>RBSP</td>
<td>(796;507;1110)</td>
<td>11.6</td>
<td>0.03</td>
<td></td>
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<tr>
<td><strong>Herbicides</strong></td>
<td>Alachlor</td>
<td>15972-60-8</td>
<td>Yes</td>
<td>PS</td>
<td>0.3</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aminotriazole</td>
<td>61-82-5</td>
<td>RBSP</td>
<td>(74;11.6;202)</td>
<td>0.08</td>
<td>0.05</td>
<td></td>
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<tr>
<td></td>
<td>Atrazine</td>
<td>1912-24-9</td>
<td>Yes</td>
<td>PS</td>
<td>0.6</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bentazone</td>
<td>25057-89-0</td>
<td>RBSP</td>
<td>(54;3;158)</td>
<td>70</td>
<td>0.02</td>
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<tr>
<td></td>
<td>Bifenox</td>
<td>42576-02-3</td>
<td>PS</td>
<td>(7148;2658;23000)</td>
<td>0.012</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2,4 D</td>
<td>94-75-7</td>
<td>RBSP</td>
<td>(46;12;136)</td>
<td>2.2</td>
<td>0.02</td>
<td></td>
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<tr>
<td></td>
<td>Isoproturon</td>
<td>34123-59-6</td>
<td>PS</td>
<td>(131;36;241)</td>
<td>0.3</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Linuron</td>
<td>330-55-2</td>
<td>RBSP</td>
<td>(680;484;987)</td>
<td>1</td>
<td>0.02</td>
<td></td>
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<tr>
<td></td>
<td>2,4 MCPA</td>
<td>94-74-6</td>
<td>RBSP</td>
<td>(88;9;4;157)</td>
<td>0.5</td>
<td>0.02</td>
<td></td>
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<tr>
<td></td>
<td>Pendimethalin</td>
<td>40487-42-1</td>
<td>RBSP</td>
<td>(19694;8942;43863)</td>
<td>0.02</td>
<td>0.02</td>
<td></td>
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<tr>
<td></td>
<td>Simazine</td>
<td>122-34-9</td>
<td>Yes</td>
<td>PS</td>
<td>1</td>
<td>0.02</td>
<td></td>
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<tr>
<td></td>
<td>Trifluralin</td>
<td>1582-09-8</td>
<td>Yes</td>
<td>PHS</td>
<td>0.03</td>
<td>0.005</td>
<td></td>
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<tr>
<td></td>
<td>Glyphosate</td>
<td>1071-83-6</td>
<td>RBSP</td>
<td>(4152;1424;9615)</td>
<td>28</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Insecticides</td>
<td>Formula</td>
<td>CAS Number</td>
<td>Structure</td>
<td>Pesticide</td>
<td>Environmental Fate</td>
<td>Breaking Down</td>
<td>Half-life</td>
</tr>
<tr>
<td>--------------</td>
<td>---------</td>
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<td>----------</td>
<td>-----------</td>
<td>-------------------</td>
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<tr>
<td>Oxadiazon</td>
<td>19666-30-9</td>
<td>RBSP</td>
<td>(2358, 676, 3236)</td>
<td>0.09</td>
<td>0.01</td>
<td></td>
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<tr>
<td>Metazachlor</td>
<td>67129-08-2</td>
<td>RBSP</td>
<td>(72, 54, 83.5)</td>
<td>0.019</td>
<td>0.025</td>
<td></td>
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<tr>
<td>Aclonifen</td>
<td>74070-46-5</td>
<td>PS</td>
<td>(7685, 5318, 10612)</td>
<td>0.12</td>
<td>0.02</td>
<td></td>
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<tr>
<td>Diflufenican</td>
<td>83164-33-4</td>
<td>RBSP</td>
<td>(4170, 1531, 7431)</td>
<td>0.01</td>
<td>0.04</td>
<td></td>
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<tr>
<td>Nicosulfuron</td>
<td>11199-109-4</td>
<td>RBSP</td>
<td>(123, 7.9, 567.1)</td>
<td>0.035</td>
<td>0.01</td>
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<tr>
<td>Chlorpropham</td>
<td>101-21-3</td>
<td>RBSP</td>
<td>(497, 245, 816)</td>
<td>4</td>
<td>0.05</td>
<td></td>
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<tr>
<td>AMPA</td>
<td>1066-51-9</td>
<td>RBSP</td>
<td>452</td>
<td>0.05</td>
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<tr>
<td>Chlorpyrifos-ethyl</td>
<td>2921-88-2</td>
<td>PHS</td>
<td>(8070, 995, 31000)</td>
<td>0.00046</td>
<td>0.01</td>
<td></td>
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<tr>
<td>Aldrine</td>
<td>309-00-2</td>
<td>Yes PHS</td>
<td>0.01</td>
<td>0.001</td>
<td></td>
<td></td>
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<tr>
<td>Cypermethrin</td>
<td>52315-07-8</td>
<td>PS</td>
<td>(297274, 20800, 574360)</td>
<td>0.00008</td>
<td>0.02</td>
<td></td>
<td></td>
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<tr>
<td>DDD 44’</td>
<td>72-54-8</td>
<td>Yes PS</td>
<td>0.025</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>DDE 44’</td>
<td>72-55-9</td>
<td>Yes PS</td>
<td>0.025</td>
<td>0.001</td>
<td></td>
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<tr>
<td>DDT 24’</td>
<td>789-02-6</td>
<td>Yes PS</td>
<td>0.025</td>
<td>0.001</td>
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<tr>
<td>DDT 44’</td>
<td>50-29-3</td>
<td>Yes PS</td>
<td>0.01</td>
<td>0.001</td>
<td></td>
<td></td>
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<tr>
<td>Dichlorvos</td>
<td>62-73-7</td>
<td>Yes PS</td>
<td>0.0006</td>
<td>0.001</td>
<td></td>
<td></td>
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<tr>
<td>Dieldrine</td>
<td>60-57-1</td>
<td>Yes PHS</td>
<td>0.01</td>
<td>0.001</td>
<td></td>
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<tr>
<td>Endosulfan alpha</td>
<td>959-98-8</td>
<td>Yes PHS</td>
<td>0.005</td>
<td>0.002</td>
<td></td>
<td></td>
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<tr>
<td>Endosulfan bêta</td>
<td>33213-65-9</td>
<td>Yes PHS</td>
<td>0.005</td>
<td>0.0015</td>
<td></td>
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<td>Endrine</td>
<td>72-20-8</td>
<td>Yes PHS</td>
<td>0.01</td>
<td>0.005</td>
<td></td>
<td></td>
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<tr>
<td>Heptachlore</td>
<td>76-44-8</td>
<td>Yes PHS</td>
<td>0.00000007</td>
<td>0.005</td>
<td></td>
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<td></td>
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<tr>
<td>Hexachlorocyclohexane alpha</td>
<td>319-84-6</td>
<td>Yes PHS</td>
<td>0.02</td>
<td>0.005</td>
<td></td>
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<tr>
<td>Hexachlorocyclohexane beta</td>
<td>319-85-7</td>
<td>Yes PHS</td>
<td>0.02</td>
<td>0.001</td>
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<tr>
<td>Hexachlorocyclohexane delta</td>
<td>319-86-8</td>
<td>Yes PHS</td>
<td>0.02</td>
<td>0.001</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Hexachlorocyclohexane gamma</td>
<td>58-89-9</td>
<td>Yes PHS</td>
<td>0.02</td>
<td>0.006</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Isodrine</td>
<td>465-73-6</td>
<td>Yes PHS</td>
<td>0.01</td>
<td>0.001</td>
<td></td>
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<td>Chlorfenvinphos</td>
<td>470-90-6</td>
<td>Yes PS</td>
<td>0.1</td>
<td>0.02</td>
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<td></td>
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<tr>
<td>Heptachlore epoxide exo cis</td>
<td>1024-57-3</td>
<td>Yes PHS</td>
<td>0.00000007</td>
<td>0.015</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heptachlore epoxide endo trans</td>
<td>28044-83-9</td>
<td>Yes PHS</td>
<td>0.00000007</td>
<td>0.02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>13826</td>
<td>RBSP</td>
<td>(340, 109, 800)</td>
<td>0.0068</td>
<td>0.02</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 16: Identification of the considered surface water WFD active substances of biocide products, their possible ban situation, their WFD status (PS, PHS or RBSP), their Koc ranges, their EQSs, and the Cut-off thresholds (τ values).

<table>
<thead>
<tr>
<th>Product types</th>
<th>Parameter</th>
<th>CAS number</th>
<th>Legacy compound (banned before 2009)</th>
<th>WFD status</th>
<th>EQS water (µg/L)</th>
<th>Cut-off threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Construction material and film preservatives</td>
<td>Diuron</td>
<td>330-54-1</td>
<td>PS</td>
<td>0.049</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Construction material and film preservatives</td>
<td>Terbutryn</td>
<td>886-50-0</td>
<td>PS</td>
<td>0.065</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Antifoulings for vessels, aquaculture equipment or other structures used in water</td>
<td>Cybutryn</td>
<td>28159-98-0</td>
<td>PS</td>
<td>0.0025</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Construction material and film preservatives</td>
<td>Thiabendazole</td>
<td>148-79-8</td>
<td>RBSP</td>
<td>1.2</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Wood preservative</td>
<td>Tebuconazole</td>
<td>107534-96-3</td>
<td>RBSP</td>
<td>1</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Antifoulings for vessels, aquaculture equipment or other structures used in water</td>
<td>Tributyltin cation (TBT)</td>
<td>36643-28-4</td>
<td>Yes</td>
<td>0.0002</td>
<td>0.0002</td>
<td></td>
</tr>
</tbody>
</table>

### Table 17: Identification of the considered surface water WFD trace elements, their WFD status (PS, PHS or RBSP), their EQSs, and the Cut-off thresholds (τ values).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CAS number</th>
<th>WFD status</th>
<th>EQS water (µg/L)</th>
<th>Cut-off threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arsenic</td>
<td>7440-38-2</td>
<td>RBSP</td>
<td>0.83</td>
<td>0.5</td>
</tr>
<tr>
<td>Lead</td>
<td>7439-92-1</td>
<td>PHS</td>
<td>7.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Zinc</td>
<td>7440-66-6</td>
<td>RBSP</td>
<td>7.8</td>
<td>1</td>
</tr>
<tr>
<td>Nickel</td>
<td>7440-02-0</td>
<td>PS</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Mercury</td>
<td>7439-97-6</td>
<td>PHS</td>
<td>0.05</td>
<td>0.025</td>
</tr>
<tr>
<td>Cadmium</td>
<td>7440-43-9</td>
<td>PHS</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Chromium</td>
<td>7440-47-3</td>
<td>RBSP</td>
<td>3.4</td>
<td>1</td>
</tr>
<tr>
<td>Copper</td>
<td>7440-50-8</td>
<td>RBSP</td>
<td>1</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Table 18: Identification of the considered surface water WFD Polycyclic Aromatic Hydrocarbons (PAHs), their WFD status (PS, PHS or RBSP), their EQSs, and the Cut-off thresholds ($\tau$ values).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CAS number</th>
<th>WFD status</th>
<th>EQS water (µg/L)</th>
<th>Cut-off threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo (a) pyrene (BaP)</td>
<td>50-32-8</td>
<td>PS</td>
<td>1.70E-04</td>
<td>0.005</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>206-44-0</td>
<td>PHS</td>
<td>7.62E-4</td>
<td>0.01</td>
</tr>
<tr>
<td>Anthracene</td>
<td>120-12-7</td>
<td>PHS</td>
<td>0.1</td>
<td>0.005</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>91-20-3</td>
<td>PS</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

It has to be noted that we didn’t consider here all the PAHs initially considered by the WFD. In particular, we aligned our restricted list on the fact that the Daughter Directive EC 2013/39 assigned Benzo(a)pyrene as a representative marker for Benzo(b)fluoranthene (CAS 205-99-2, EU 205-911-9), Benzo(g,h,i)perylene (CAS 191-24-2, EU 205-883-8), Benzo(k)fluoranthene (CAS 207-08-9, EU 205-916-6), Indeno(1,2,3-cd)pyrene (CAS 193-39-5, EU 205-893-2).

Table 19: Identification of the considered surface water WFD industrial compounds, their WFD status (PS, PHS or RBSP), their EQSs, and the Cut-off thresholds ($\tau$ values).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CAS number</th>
<th>WFD status</th>
<th>EQS water (µg/L)</th>
<th>Cut-off threshold (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene (BTEX)</td>
<td>71-43-2</td>
<td>PS</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Toluene (BTEX)</td>
<td>108-88-3</td>
<td>RBSP</td>
<td>74</td>
<td>1</td>
</tr>
<tr>
<td>Xylene (BTEX)</td>
<td>1330-20-7</td>
<td>RBSP</td>
<td>1</td>
<td>0.03</td>
</tr>
<tr>
<td>Tributyle phosphate</td>
<td>126-73-8</td>
<td>RBSP</td>
<td>82</td>
<td>0.1</td>
</tr>
<tr>
<td>Pentachlorobenzene</td>
<td>210-172-0</td>
<td>PHS</td>
<td>0.007</td>
<td>0.002</td>
</tr>
<tr>
<td>Biphenyle</td>
<td>92-52-4</td>
<td>RBSP</td>
<td>3.3</td>
<td>0.02</td>
</tr>
<tr>
<td>Trichloromethane (HVOC)</td>
<td>67-66-3</td>
<td>PS</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>1,2-dichloroethane (HVOC)</td>
<td>107-06-2</td>
<td>PHS</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>Dichloromethane (HVOC)</td>
<td>75-09-2</td>
<td>PS</td>
<td>20</td>
<td>5</td>
</tr>
<tr>
<td>Tetrachloroethylene (HVOC)</td>
<td>127-18-4</td>
<td>PS</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Carbon Tetrachloride (HVOC)</td>
<td>56-23-5</td>
<td>PS</td>
<td>12</td>
<td>0.5</td>
</tr>
<tr>
<td>Trichlorobenzene-1,2,4</td>
<td>120-82-1</td>
<td>PS</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Trichloroethylene (HVOC)</td>
<td>79-01-6</td>
<td>PHS</td>
<td>10</td>
<td>0.5</td>
</tr>
<tr>
<td>Trichlorobenzene-1,3,5</td>
<td>108-70-3</td>
<td>PS</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Trichlorobenzene-1,2,3</td>
<td>87-61-6</td>
<td>PS</td>
<td>0.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Nonylphenols (4-)</td>
<td>84852-15-3</td>
<td>PHS</td>
<td>0.037</td>
<td>0.1</td>
</tr>
</tbody>
</table>
### Table 20: Identification of the considered surface water WFD legacy Persistent Organic Pollutants (POPs), their WFD status (PS, PHS or RBSP), their EQSs, and the Cut-off thresholds ($\tau$ values)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CAS number</th>
<th>WFD status</th>
<th>EQS water ($\mu$g/L)</th>
<th>Cut-off threshold ($\mu$g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perfluorooctanesulfonate (PFOS)</td>
<td>1763-23-1</td>
<td>PHS</td>
<td>0.00065</td>
<td>0.05</td>
</tr>
<tr>
<td>Hexachlorobutadiene (HCBD)</td>
<td>201-765-5</td>
<td>PHS</td>
<td>0.44</td>
<td>0.02</td>
</tr>
<tr>
<td>Chloroalcanes C10-C13</td>
<td>85535-84-8</td>
<td>PHS</td>
<td>0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>BDE154</td>
<td>207122-15-4</td>
<td>PHS</td>
<td>0.0005</td>
<td>0.001</td>
</tr>
<tr>
<td>BDE153</td>
<td>68631-49-2</td>
<td>PHS</td>
<td>0.0005</td>
<td>0.001</td>
</tr>
<tr>
<td>BDE100</td>
<td>189084-64-8</td>
<td>PHS</td>
<td>0.0005</td>
<td>0.001</td>
</tr>
<tr>
<td>BDE99</td>
<td>60348-60-9</td>
<td>PHS</td>
<td>0.0005</td>
<td>0.0005</td>
</tr>
<tr>
<td>BDE47</td>
<td>5436-43-1</td>
<td>PHS</td>
<td>0.0005</td>
<td>0.001</td>
</tr>
<tr>
<td>BDE28</td>
<td>41318-75-6</td>
<td>PHS</td>
<td>0.0005</td>
<td>0.0005</td>
</tr>
<tr>
<td>Alpha 1,2,5,6,9,10-HBCDD</td>
<td>134237-50-6</td>
<td>PHS</td>
<td>0.0016 (4.6 E-4)</td>
<td>0.05</td>
</tr>
<tr>
<td>Beta 1,2,5,6,9,10-HBCDD</td>
<td>134237-51-7</td>
<td>PHS</td>
<td>0.0016 (4.6 E-4)</td>
<td>0.0016</td>
</tr>
<tr>
<td>Gamma 1,2,5,6,9,10-HBCDD</td>
<td>134237-52-8</td>
<td>PHS</td>
<td>0.0016 (4.6 E-4)</td>
<td>0.05</td>
</tr>
</tbody>
</table>

### Table 21: Considered WFD PPP active substances having been banned during the 2009-2020 period

<table>
<thead>
<tr>
<th>Category</th>
<th>Substance</th>
<th>Status</th>
<th>Year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fungicides</td>
<td>Iprodione</td>
<td>Exclusion</td>
<td>2017</td>
</tr>
<tr>
<td></td>
<td>Quinoxyfen</td>
<td>Exclusion</td>
<td>2018</td>
</tr>
<tr>
<td>Herbicides</td>
<td>Aminotriazole</td>
<td>Exclusion</td>
<td>2016</td>
</tr>
<tr>
<td>Insecticides</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----------------------</td>
<td>------------------</td>
<td>---------</td>
<td></td>
</tr>
<tr>
<td>Chlorpyrifos ethyl</td>
<td>Exclusion</td>
<td>2019</td>
<td></td>
</tr>
<tr>
<td>Imidacloprid</td>
<td>Restricted to green house uses only</td>
<td>2018</td>
<td></td>
</tr>
</tbody>
</table>
Appendix B: Complementary information on the considered six main continental French basins

Table 22: Percentages of surface waterbodies for which each pressure is assessed as significant in 2019 (meaning putting the waterbody at risk of not achieving the good status)

<table>
<thead>
<tr>
<th>Basins</th>
<th>Point Pollution Pressures</th>
<th>Diffuse Pollution Pressures</th>
<th>Water Abstraction Pressures</th>
<th>Hydromorphological Pressures</th>
<th>Other pressures</th>
<th>No significant pressures</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP</td>
<td>61%</td>
<td>96%</td>
<td>3%</td>
<td>90%</td>
<td>41%</td>
<td>4%</td>
</tr>
<tr>
<td>RM</td>
<td>59%</td>
<td>93%</td>
<td>6%</td>
<td>41%</td>
<td>29%</td>
<td>5%</td>
</tr>
<tr>
<td>RMC</td>
<td>27%</td>
<td>30%</td>
<td>19%</td>
<td>59%</td>
<td>2%</td>
<td>32%</td>
</tr>
<tr>
<td>AG</td>
<td>28%</td>
<td>50%</td>
<td>22%</td>
<td>51%</td>
<td>1%</td>
<td>23%</td>
</tr>
<tr>
<td>LB</td>
<td>45%</td>
<td>58%</td>
<td>48%</td>
<td>62%</td>
<td>6%</td>
<td>18%</td>
</tr>
<tr>
<td>SN</td>
<td>17%</td>
<td>81%</td>
<td>5%</td>
<td>51%</td>
<td>8%</td>
<td>4%</td>
</tr>
<tr>
<td>Metropolitan France</td>
<td>31%</td>
<td>54%</td>
<td>22%</td>
<td>55%</td>
<td>6%</td>
<td>20%</td>
</tr>
</tbody>
</table>

Short description of the six main French river basins characteristics of significance with regards to water pollution.

The Artois-Picardie (AP) basin represents 3.6% of the area of metropolitan France, or 20,000 km².

Nearly 19,000 farms, including more than 10,000 livestock farms, use around 1,400,000 ha of useful agricultural area, i.e. 70% of the area of the Artois-Picardie basin. Compared to the rest of the national territory, agriculture in this basin is characterized by more arable land and less grassland. Organic farming has been progressively reaching 2.2% of the agricultural area in 2023.

Regarding the industry sector, the weight of the turnover of the basin compared to the national is 22% for textiles, 14% for glass/metal/packaging, 13% for chemicals/pharmaceuticals, 12% for wood/paper and 11% for agri-food – even though the basin represents only 4% of the territory's surface, but 8% of the French population.

In the past, the hairy streams that drain the basin have too often served as an outlet for water polluted by domestic or industrial uses. The relief is not very marked, making the flow rates of the rivers very low: they cannot ensure a significant dilution of the pollutant load, causing the self-purification capacities of many rivers to be exceeded.

Although the basin receives relatively moderated amounts of annual precipitation compared to continental France average, arable land is particularly vulnerable to precipitation-induced erosion, due to low vegetation cover during part of the year.

In 2013, only 14 surface water bodies out of 66 achieved good chemical status, and as many did so for good ecological status. Recent WFD management plans have devoted significant resources to reducing
the release of toxic substances, and to implementing alternative practices to the use of pesticides.

The soils of some Artois-Picardie areas have been characterized as containing elevated trace elements contents, like Cadmium from diffuse agricultural (mineral fertilizers) and industrial pollution, plus Lead and Zinc (mines, industry, agricultural spreading, road traffic, roofs, etc.). The basin also contains wide areas of very high Phosphorus soil concentrations, in relation to the ancient use of slag, and by-products of the elaboration of metallurgical items.

The Seine-Normandie (SN) basin is made up of the Seine River and its tributaries, and the small rivers of the Normandy coast. It has 55,000 km of rivers and extends over 94,500 km², i.e. 18% of French continental territory. It is an extremely flat basin, with very slow flow speeds and subject to very high evaporation. Groundwater constitutes vast reservoirs and contributes to the regulation of flows.

The Seine estuary receives discharges from 30% of the French population, from 40% of the national industry, and diffuse pollution from 25% of the national agriculture.

The Seine valley is a major centre of establishment and industrial attraction in France both for processing industries (petrochemicals, specialty chemicals, paper mills) and for manufacturing industries (automotive construction, aeronautics, mechanical industry). Each year, 50 million euros from industrial pollution fees are redistributed to industrial initiatives aimed at protecting water in the Seine-Normandie basin.

With a useful cultivated area of nearly 6 million hectares, i.e. 63% of the total area of the basin in 2012, the water resources of the Seine-Normandie basin are subject to strong agricultural pressures. The density of forests is low there, while agricultural activity and urbanization are strongly present around the major rivers. The area still under grass in the basin decreased by 18% between 2000 and 2016, in particular to the benefit of field crops.

The Seine-Normandie basin is a major national producer of cereals and sugar beets. Several areas of high phytosanitary pressure can be highlighted, such as the Beauce cereal region, the plain of Caen (intensive cereal growing area), the viticultural and large industrial crop areas of the Hauts de France and Grand Est regions as well as than the vineyards of Champagne, Auxerrois and around Chablis. The most contaminated areas are located in the Île-de-France region and in particular in Seine-et-Marne, characterized by crops of soft wheat, winter barley, corn and oilseeds.

The quantities of phytosanitary active ingredients observed in the regions of the basin are generally higher than those observed on the scale of France, in particular for rapeseed and common wheat, the two most common crops in the basin.

The soils of some Seine-Normandie areas have been characterized by elevated trace elements contents. This is true for Cadmium (alteration of rocks evolution of soils resulting from Jurassic chalk and limestone of the Champagne area), Chromium (argillaceous limestones, marls and clay from the Lower Jurassic), Mercury (industry and the historical contribution of spreading sludge from the largest urban water treatment plant in the northwest of Paris), and Lead (contact between sedimentary basins and crystalline massifs in Morvan region).

The Loire-Bretagne (LB) basin is a contrasted geographical territory. It extends over 155,000 km², i.e. 28% of the continental France territory and is characterized by, 6,654 km of coastline, i.e. nearly 38% of the country's coastline, 135,000 km of waterways, two ancient mountain ranges located at both ends: the Massif Central and the Massif Armorican, and a vast central plain crossed by the Loire, the longest river in France, which is over 1,000 km long.
Precipitation is between 500 mm of water and 1,800 mm of water per year, thus creating very contrasting situations in the basin (oceanic, Mediterranean and continental influences). The heaviest precipitation is observed on the two old mountain ranges, at the ends of the basin. The coastal fringe is generally wetter than the hinterland. The vast plains, crossed by the Loire, receive lower rainfall, from 500 to 900 mm per year.

The territory has a marked rural footprint (average density of 75 inhab/km²), with more than 2,700 municipalities having less than 400 inhabitants. The basin concentrates two-thirds of French livestock, and 50% in the Bretagne region alone, which creates there a major challenge for water quality. It also supports 50% of national cereal production, with the Centre Val de Loire and Nouvelle Aquitaine regions. The industrial activity reflects this agricultural characteristic, with agri-food production dominating in the west and centre of the basin.

The soils of some regions of the Loire-Bretagne basin have been characterized by elevated contamination by several trace elements. This is especially true for the Massif Central mounts, with hotspots of Arsenic (geological or mineralization origins), Zinc, Chromium and Nickel (crystalline rocks, basalts and ultrabasic rocks), Mercury (volcanic rocks, ancient gold mining activities), and Lead (contact zones with sedimentary basins). The Bretagne region also holds high soils contamination related to agricultural spreading (Zinc from food supplements used in cattle, pig or poultry farming, which also induces high Phosphorus contents).

The Rhine-Meuse (RM) basin, with a surface area of 32,700 km², including 12,000 km of forest, represents approximately 6% of the continental territory for a population of some four million inhabitants. The population is mainly concentrated along the economic axes of the Rhine, Moselle and Meuse valleys. The basin owes its main characteristic to its cross-border character, upstream part of the international basin of the Meuse and the Rhine, this hydrological basin is located on the central axis of Europe, in an area of very strong economic activity between the North Sea and Switzerland.

Actually Rhin-Meuse, together with Artois-Pacardie, are international districts part of the International River Basin District of the Scheldt (Artois-Picardie), of the International River Basin District of the river Meuse (Artois-Picardie and Rhin-Meuse) and of the International Rhine River Basin District (Rhin-Meuse).

At the industrial level, the automotive and capital goods sectors are those that generate the highest turnover in the sector. The agri-food and chemical industries also generate significant turnover.

The agricultural activities include arable crops (cereals, soft wheat, oilseeds, grain corn and seed corn,) viticulture (quality viticulture, orchards), as well as the breeding of cattle, sheep and goats.

Some soils in the Rhin-Meuse basins are characterized by elevated trace elements contents. This is true for Cadmium (residues from mineral fertilizers in cereal regions in Alsace), Chromium (from crystalline rocks in the Vosges area), but also for Arsenic or Lead. The basin also contains wide areas of high Phosphorus soil concentrations, in relation to the ancient use of slag, and by-products of the elaboration of metallurgical items.

The Adour-Garonne (AG) basin covers 1/5th of the continental territory (116,000 km²) and is home to nearly 7 million inhabitants. Its population density is low. It has a few medium-sized towns and two regional cities: Toulouse and Bordeaux.

The basin has a strong agricultural vocation at the base of a diversified agri-food industry. The traditional industrial fabric (heavy chemicals, leather, textile and paper industry, metallurgy, etc.) rather declines, and...
neighbours with high-tech industries such as electronics and aeronautics.

Metals are detected downstream of artisanal or industrial centres for surface treatment, leather or metallurgy.

There is also significant contamination of some Pyrénées mountain streams by former mines or industrial sites. Finally, the presence of cadmium and zinc in the waters and sediments of the Lot River is an important issue in the basin because the impact is felt even in the coastal oyster farming sector.

The soils of some Adour-Garonne basin areas contain elevated trace elements concentrations. This was identified for Cadmium (residues from mineral fertilizers in cereal regions, alteration of rocks evolution of soils resulting from Jurassic chalk and limestone of the Causses area), Copper (from recurrent fungicide vineyard treatments, based on copper sulphates, in the Gironde area), Nickel (Jurassic rocks of the Charente area), Lead (ferralitic soils of the Poitou region), Zinc from Jurassic rocks in the Causses region, and some Arsenic anomalies.

The Rhône-Méditerranée et Corse (RMC) basin is made up of the Rhône and its tributaries which, with their branches – the diversion channels of Provence and Languedoc – concern approximately 130,000 km², i.e. 3/4 of the Mediterranean French catchment area. On an annual average, water is relatively abundant in the basin, given the presence of large mountain ranges (Vosges, Jura, Cévennes, Alps, Pyrénées-Orientales, mountains of Corsica) which favour precipitation; in total, the annual flow is around 70 billion m³, i.e. 37% of the flow of the national territory, but it should be noted that the distribution over time nevertheless remains very irregular, particularly in the southern regions which often experience long periods of drought.

The basin includes the catchment areas of the Rhône, its tributaries and Mediterranean coastal rivers. It has more than 15 million inhabitants, for an area of 121,600 km², i.e. nearly 20% of the continental territory. Covering 6.7 million hectares or 33% of the continental territory, the forest is the primary mode of occupation of the RMC basin;

Some areas of high urban and industrial concentrations (regions of Lyon, Marseille, Grenoble, etc.) are present along the navigable Rhône and near major seaports.

The industrial activity includes several major sectors (chemicals, petrochemicals, pharmaceuticals). The RMC basin is also the leading electricity producer in France with 2/3 of national hydroelectric production and 1/4 of nuclear production. Finally, tourist activity is a source of strong seasonal demographic variation, mainly in the southern part of the basin and the mountain areas.

The basin provides 15% of the agricultural production in value of the metropolitan France. The dominant agricultural activity is twofold: in the plain, in the Rhône valley and all around the Mediterranean, activity is dominated by viticulture. Vines are also present in the Saône catchment, with notably Burgundy and Beaujolais which have a strong impact on the quality of the rivers. To a lesser extent, the Jura vineyards also have an impact. With more than 400,000 hectares, vines represent half of the metropolitan wine-growing area. On the western and eastern fringes - foothills of the Massif Central, the Pyrénées and the Alps - more than 80% of the agricultural area is made up of fodder land. The main activity here is dairy farming.

After wine-growing farms, arable farms are the most numerous. They are present in all plain areas: in the north, in the Saône and Bresse valleys, in the centre in Bas-Dauphiné and in the south in the Durance valley and the Rhône delta. The basin also concentrates 61% of metropolitan tree farms. The RMC has the highest rate of biological agriculture in France, representing up to more than 10% of the agricultural
area in some important districts.

Some parts of the basin, especially the Alpin Arc region, is subject to the combination of important slopes and heavy rains, with risk of high precipitation-induced soils erosion.

In 2021, 530 different substances were quantified at least once in RMC, including 280 pesticide substances. Measurements taken at a Rhône outlet site showed that significant flows of pesticides reach the sea.

The soils of some RMC basin areas contain high trace element contents, like Chromium from Corsican schists, Copper from recurrent fungicide treatments, based on copper sulphates, in the Languedoc-Roussillon area, but also some Nickel and Zinc (Jura massif) or Lead and Arsenic (Cévennes) anomalies.
Appendix C: complementary information on the WFD monitoring networks.

**Table 23**: Summary of the annual numbers of measured data available for our data analysis, in each of the 6 main French basins, over the 2009-2020 timeframe.

<table>
<thead>
<tr>
<th>Year</th>
<th>Loire-Bretagne</th>
<th>Adour-Garonne</th>
<th>Artois-Picardie</th>
<th>Rhin-Meuse</th>
<th>RMC</th>
<th>Seine-Normand</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Number of analyzes</td>
<td>Quantification frequency(%)</td>
<td>Number of analyzes</td>
<td>Quantification frequency(%)</td>
<td>Number of analyzes</td>
<td>Quantification frequency(%)</td>
</tr>
<tr>
<td>2009</td>
<td>314 332</td>
<td>4.5</td>
<td>185 342</td>
<td>3.6</td>
<td>18 513</td>
<td>7.1</td>
</tr>
<tr>
<td>2010</td>
<td>133 244</td>
<td>4.4</td>
<td>32 345</td>
<td>3.9</td>
<td>18 930</td>
<td>8.1</td>
</tr>
<tr>
<td>2011</td>
<td>140 637</td>
<td>4.7</td>
<td>51 952</td>
<td>4.1</td>
<td>49 789</td>
<td>7.0</td>
</tr>
<tr>
<td>2012</td>
<td>136 880</td>
<td>6.3</td>
<td>210 001</td>
<td>4.5</td>
<td>17 259</td>
<td>12.2</td>
</tr>
<tr>
<td>2013</td>
<td>141 478</td>
<td>6.2</td>
<td>120 528</td>
<td>3.8</td>
<td>19 906</td>
<td>19.3</td>
</tr>
<tr>
<td>2014</td>
<td>181 810</td>
<td>6.1</td>
<td>115 390</td>
<td>4.2</td>
<td>48 047</td>
<td>15.8</td>
</tr>
<tr>
<td>2015</td>
<td>258 215</td>
<td>6.4</td>
<td>302 279</td>
<td>3.3</td>
<td>18 559</td>
<td>17.5</td>
</tr>
<tr>
<td>2016</td>
<td>328 028</td>
<td>10.1</td>
<td>206 160</td>
<td>3.3</td>
<td>42 886</td>
<td>14.7</td>
</tr>
<tr>
<td>2017</td>
<td>328 419</td>
<td>10.8</td>
<td>228 554</td>
<td>3.7</td>
<td>80 123</td>
<td>15.5</td>
</tr>
<tr>
<td>2018</td>
<td>579 388</td>
<td>10.8</td>
<td>423 694</td>
<td>3.4</td>
<td>44 268</td>
<td>13.1</td>
</tr>
<tr>
<td>2019</td>
<td>387 825</td>
<td>9.2</td>
<td>209 077</td>
<td>4.2</td>
<td>44 838</td>
<td>13.3</td>
</tr>
<tr>
<td>2020</td>
<td>323 879</td>
<td>10.4</td>
<td>240 296</td>
<td>4.1</td>
<td>60 493</td>
<td>18.3</td>
</tr>
</tbody>
</table>
Figure 143: Distribution of the considered 4092 monitoring sites throughout the 6 basins, according to the number of substances for which they yielded monitoring measurements during the 2009-2020 period.

Figure 144: Distribution of the considered 4092 monitoring sites throughout the 6 basins, according to the 2009-2020 total number of monitoring measurements per site.

Brief about the official French WFD surveillance network RCS and RCO

RCS for surface water was deployed in 2007 at about 2000 permanent monitoring points covering all of France (continental and overseas territories). Monitoring points were selected to acquire general knowledge on aquatic environments and not specifically to monitor pollution. The criteria used to define the network dealt essentially with the size of the river basin, taking care to cover all types of water bodies and to avoid sites close to pollution sources and installations. A majority (82%) of surveillance monitoring points are located on rivers. If calculated in terms of river lengths, national surveillance-monitoring network has a monitoring point every 137 kilometers. The ratio is one monitoring point for 10 square kilometers of lake, one for 245 km² of coastal waters and one for 46 km² of transitional waters. Monitoring frequencies and cycles are calculated to provide sufficient data for a reliable assessment of water status. Measurement parameters and minimal frequencies are defined in the 25 January 2010 national ordinance (regularly modified), setting up a water-status monitoring program (French Ministry of Ecology 2010).

Monitoring covers all quality elements:

> biological quality elements, i.e. fauna (fish, crustaceans, etc.), flora (e.g. algae);
> hydromorphological quality elements, i.e. discharge, bank condition, width of the river bed, continuity of flow, etc.;
> general physical-chemical (temperature, oxygen, nutrients, etc.) and chemical quality elements (various substances).

RCO started gradually in 2008 and 2009. Rivers account for 92% of the monitoring points and lakes for 5%. If calculated in terms of river lengths, the national operational-monitoring network has a monitoring point every 54 kilometers. Operational monitoring covers the quality elements most sensitive to anthropogenic pressures (abstractions, pollution, point or nonpoint-source agricultural and industrial releases, etc.) that often result in good status not being reached. For example, in addition to measurements of chemical concentrations, benthic macroinvertebrates are also monitored because they are highly sensitive to toxic substances and are thus the biological element best suited to detecting this type of pressure. Among the operational-monitoring points, 25% are already included in the surveillance-monitoring system.
Specific monitoring annual calendars of each basin

Regarding metals, PAHs and industrial/POP compounds:

- In the AP basin, some supplementary sites are monitored every 3 months, (February, May, August and November) for PAHS and metals, so that a factor 2 can be observed between minimal and maximal monthly sites numbers. This is not observed for the other compounds. The monitoring frequency per site remains there very close to one per month.

- In the AG basin, the monitoring coverage strongly varied every two months for PAHS, industrial and POPs chemicals. Higher figures are thus met in January, March, May, July, September and November, which can range up to twice the lower monthly-values. For metals and Arsenic, overall, the frequency of one measurement per month is tightly respected. However, the monitoring spatial coverage is very different depending on if the metal is a priority substance (Hg, Cd, Pb and Ni) or a RBSP (Zn, As, Cr, and Cu). In the first case, the coverage is extended by a factor of about 2 every two months, from January onward. In the second case, the monitoring intensity is distinctly higher in March, May, September and November, and was even abandoned after 2016 for the other months (except June). This complicates the seasonality analysis for these four elements in AG.

- In the LB basin, the monitoring coverage is significantly higher in spring and autumn seasons for, industrial and POPs chemicals (up to a factor of 2). The monthly measurement frequency is very close to 1, except in November (ratio Measurements/Sites reaching 112%). For metals, the highest spatial coverages are met in April, June, October and December, with figures upper by 40% than the lowest. Measurement frequencies upper than 1 per month are met between November and April.

- In the RM basin, the spatial coverage is increased between April and November for the three chemical groups (up 3 times more than December, lowest month). Frequencies significantly higher than once per month are met for metal (measurements/sites ratio values up to 125%), and also for the other compounds (up to 114%).

- In the RMC basin, the spatial coverage is rather constant over the year for the PAHs, industrial and POPs chemicals, with a monthly measurement frequency tightly sticking to 1. For metals, the monitoring coverage is completely different depending on if the metal is a priority substance (Hg, Cd, Pb and Ni) or a RBSP (Zn, As, Cr, and Cu). In the first case, the spatial monitoring coverage if kept high and constant over the year, mostly with a once-a-month frequency. In the second case, this same monitoring strategy is performed, but only every 3 months (January, April, July and October). The remaining months, only very few sites are monitored, though with higher frequency (around twice a month). This complicates the seasonality analysis for these four elements in RMC.

- Finally, in the SN basin, the monitoring coverage is somewhat constant over the year for PAHs. For metals, industrial compounds and POPs, the monitoring coverage is slightly extended (around 20% change) every two months (from January onward). Overall, a limited fraction of the sites is measured twice a month (ratio around 105%).

Regarding PPP and biocide active substances:

- In the AP and RMC basins, there is no important seasonal variation in the monitoring intensity for pesticides: the number of sites remains similar for every month. Moreover, the “one measurement per month” appears as strictly applied in any situation.
- In the **AG basin**, some months are gathering distinctly more spatial information, i.e. one can observed up to 8 times more sites being measured in spring, September and November, compared to winter months. April, August and October are also relatively very limitedly monitored. Moreover, in intense spatial coverage periods, the measurement frequency often exceeds the “once per month” routine (measurements to sites ratios ranging between 114% to 119%).

- In the **LB basin**, the spatial monitoring coverage is in the spring and autumn up to 3 times more extended than in winter. The once per month measurement frequency is mostly respected, except in November when it is higher (ratio = 112%).

- In the **RM basin**, the spatial coverage is increased between April and November by a factor of about 2. Frequencies significantly higher than once per month are met (measurements/sites ratio values up to 113%).

- In the **SN basin**, the monitoring coverage appears as increased by about 30% between July and November compared to the rest of the year. The “one measurement per month” rule is only rarely exceeded (ratio = 104%).
Appendix D: Complementary information on the expected relevance of the considered substances for trend derivation.

Table 24: Basin/Compound combinations for which trend derivation will not be possible due to $\tau$ values higher than most of the LoQs.

<table>
<thead>
<tr>
<th>LB</th>
<th>AG</th>
<th>AP</th>
<th>RM</th>
<th>RMC</th>
<th>SN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichlorvos,</td>
<td>TBT, Dichlorvos,</td>
<td>Beta-HBCDD,</td>
<td>Xylene</td>
<td>Xylene, Beta-</td>
<td>Beta-HBCDD</td>
</tr>
<tr>
<td>Hexachlorobutadiene</td>
<td>Pentachlorobenzene,</td>
<td>Cybutryn,</td>
<td></td>
<td>HBCDD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Métaldehyde, Xylene</td>
<td>DDT 24'</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 145: Ranges of the mean annual numbers $N_k$ of concentration data exceeding the cut-off threshold (orange bars), for those substances which benefit from $N_k$ whose averages is higher than 100 over the 2009-2020 period.

Figure 146: Ranges of the mean annual numbers $N_k$ of concentration data exceeding the cut-off threshold (orange bars), for those substances having $N_k$ averages values lower than 100 over the 2009-2020 period.
Appendix E: Complementary information on PPP active substance sales

**Figure 147**: Ranges annual BNV-d sold tonnages figures over the 2009-2020 timeframe, for the considered PPP active substances which were authorized in 2009 and after. Green substances are herbicides, blue are fungicides, and orange are insecticides.

**Figure 148**: Sold tonnages of the 3 authorized insecticides active substances monitored for the French surface waterbodies WFD status assessment.

**Figure 149**: Sold tonnages of the 7 authorized fungicides active substances monitored for the French surface waterbodies WFD status assessment.

**Figure 150**: Sold tonnages of the 15 authorized herbicides active substances (Glyphosate excluded) monitored for the French surface waterbodies WFD status assessment.

**Figure 151**: Sold tonnages of the 15 authorized herbicides active substances (Glyphosate included) monitored for the French surface waterbodies WFD status assessment.

**Figure 152**: Interannual variation of the fraction of some WFD PPP substance's tonnages dedicated to non-agricultural applications.
Appendix F: Complementary information on the LoQs variation and its correlation with monitoring results

**Figure 153**: Interannual variations of the mean annual LoQs for 3 groups of WFD chemicals (Metals, Insecticides and Herbicides). The error bars correspond to the min and max values within each chemicals group.

**Figure 154**: Linear correlation coefficients $R^2$ characterizing the observed relationship between the national scale average annual quantification rates QR and the corresponding mean annual values of $1/\text{LoQ}$, plotted against the QR values, for PPP active substances, along the 2009-2020 timeframe. Blue dots correspond to positive covariance between QRs and $1/\text{LoQ}$, red dots to negative covariance.

**Figure 155**: Linear correlation coefficients $R^2$ characterizing the observed relationship between the national scale average annual quantification rates QR and the corresponding mean annual values of $1/\text{LoQ}$, plotted against the QR values, for PPP active substances, along the 2009-2020 timeframe. Blue dots correspond to positive covariance between QRs and $1/\text{LoQ}$, red dots to negative covariance.

**Figure 156**: Linear correlation coefficients $R^2$ characterizing the observed relationship between the national scale average annual concentrations and the corresponding mean annual values of LoQ, for PPP substances, plotted against the QR values, along the 2009-2020 timeframe.

**Figure 157**: Linear correlation coefficients $R^2$ characterizing the observed relationships between the national scale average annual concentrations and the corresponding mean annual values of LoQ, for substances other than PPPs, plotted against the QR values, along the 2009-2020 timeframe.
Declarations

**Ethic approval**

- Disclosure of potential conflicts of interest: No potential conflicts of interest to declare
- Research involving Human Participants and/or Animals: None
- Informed consent: Not applicable as our research involve neither Human Participants nor Animals

**Consent to Participate**

Not applicable (no human participants involved)

**Consent to Publish**

All authors and their institutions consent to publish this work.

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**Competing Interests**

The authors have no relevant financial or non-financial interests to disclose.

**Authors contributions**

All authors contributed to the study conception and design. Material preparation and contextual information were gathered by all the authors. Adeline Blard-Zakar ensured the proper integration of the study within the WFD regulatory framework. Input data collection, validation and fit for purpose filtering were performed by Morgane Salomon and Azziz Assoumani. Trend computations were performed by Morgane Salomon. Data analysis, interpretation formulation, dedicated bibliographic survey and conceptual developments were coordinated by Pierre-François Staub. The first draft of the manuscript was written by Pierre-François Staub and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.
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The scatter plot shows the relationship between KoC (L/Kg) and $\gamma'$ (All basins, m²/L) for various chemical compounds. The trend line equations are:

1. $y = 0.17x^{0.57}$ with $R^2 = 0.74$
The graph shows a scatter plot with a linear regression line. The equation of the line is given as $y = 1.11x^{-0.40}$ with a $R^2$ value of 0.48. The x-axis represents KoC (L/Kg) and the y-axis represents $\gamma^{95\%}$ (All basins), m$^2$/L. The scatter plot includes points labeled with various chemical names such as Nicosulfuron, Bentazon, Metaldéhyde, Imidaclopride, Isoproturon, and others.
Predicted pressure indicator, all authorized WFD Herbicides
Predicted risk indicator, all authorized WFD Herbicides

- LOIRE-BRETAGNE
- ADOUR-GARONNE
- ARTOIS-PICARDIE
- RHIN-MEUSE
- RHONE-MEDITERRANEE-CORSE
- SEINE-NORMANDIE
Predicted pressure indicator, all authorized WFD Insecticides
Distribution of WFD PPPs tonnages sold between 2009-2020
One point represents the sales of one year
Extraction of the 2000-2020 data for the targeted chemicals from WFD surveillance and operational control networks of the 6 main metropolitan basins.

Quality-filtered concentrations and LoQs.

Determination of cut-off thresholds $\tau$ for each chemical, exclusion data with LoQ < $\tau$, allocation of the value $\tau/2$ to concentrations < $\tau$.

Workable set of time and space comparable data.

Averaging of the data within monthly variables, aggregated at the 6 main river basins scales, and at national scale.

**Analysis of seasonal variations of contamination and associated sources**

**Display of time-series of monthly concentrations and rates of cut-off threshold exceedance**

**Grouping of monthly data per year**

**Analysis of inter-annual trends; comparison with yearly PPP sales.**

**Display of time-series of yearly concentrations and rates of cut-off threshold exceedance**

**Information integration over periods of several years**

**Comparison with chemicals physicochemical properties (Koc,...)**

**Chemical's specific multiyear-integrated indicators (Basin-to river transfer coefficients, etc..)**

**Integrated national and basin rivers contamination & risk statements**
The graph shows the quarterly rolling standard deviation (RSD) for pH at sampling stations from 2009 to 2020. The 90th percentile is represented by a solid black line, the 75th percentile by a dashed black line, the 50th percentile (median) by a dash-dot black line, and the 25th percentile by a dotted black line. Over the years, the RSD values fluctuate, with some years showing higher variability compared to others.
Slope Q: -0.143 [-0.186, -0.105] units/year
A bar graph showing the percentage of Fluoranthene ($\rho$) and Fluoranthene concentration ($\chi > \tau$) from 2009 to 2020. The percentage values range from 0% to 40%, and the concentration values range from 0.000 to 0.040 µg/L. The data points for each year are represented with error bars, indicating the variability or uncertainty in the measurements.