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Monitoring micropollutants in French aquatic environments: recent advances

Some substances produced by human activities require particularly close monitoring, due to their dispersal in the environment and their potential effects on living organisms, even at low doses. A key issue in risk prevention is to improve our understanding of their presence and level in the environment and their effects on human health and on aquatic environments. For several decades, measures have been taken to monitor and evaluate the quality of ecosystems in order to drive forward the necessary conservation actions. Significant efforts have been made over the last few years, under three national plans¹, and individual citizens have become increasingly aware of these issues. All this has led to real progress, in particular in the monitoring of so-called “emerging substances”. The exploratory monitoring campaigns in 2011 and 2012 on rivers, lakes, littoral waters and groundwater throughout mainland France and its overseas territories showed that substances such as plasticisers, drugs and pesticides are among those most often found in these environments.

Need for monitoring of aquatic environments

There is a long list of human activities that use or produce chemicals, including micropollutants - manufacturing, transport, construction, agriculture, consumer goods, pharmaceuticals and many more². A report by the Ecology Ministry covering the period 2007-2009³ highlighted the very widespread presence of chemicals such as pesticides, metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and phthalates in freshwater, in mainland France and its overseas territories. Awareness of these substances has grown among the public authorities, business stakeholders and citizens, due to

their potential dangers for the environment (toxicity for aquatic organisms, loss of biodiversity) but also for human health (quality of drinking water resources).

Since the early 1970s, aquatic environments have been monitored, particularly for their chemical content. Through this monitoring and other research projects:

- > the quality of aquatic environments is better understood;
- > pollution sources and the substances of concern have been identified;
- > risks related to the effects of each individual substance on environments and species have been assessed;
- > their use has been brought under better control, through emissions reductions and risk prevention, to contribute to resource protection and environmental conservation.

1. Plan national d'actions sur les PCB, MEDAD/MAP/MSJS, 2008. Plan micropolluants 2010-2013 de lutte contre les pollutions des milieux aquatiques, MEEDDM, 2010. Plan 2011-2015 sur les résidus médicamenteux dans les eaux, MEDDTL/MTES, 2011.

2. Chemicals with effects even at microgram or nanogram per litre concentrations.

3. Based on 950 micropollutants sought. MEDDE/CGDD/SOeS, Bilan de présence des micropolluants dans les milieux aquatiques continentaux - période 2007-2009, 2011.

Main categories of micropollutants

- > pesticides and biocides: acetamides, amides, anilines, carbamates, organochlorides, organophosphorous compounds, organotin compounds, triazines, ureas, amino acids (including glyphosate, for example), etc.;
- > drugs: amides, carbamates, sterols and steroids, etc.;
- > detergents: alkylphenols, etc.;
- > plasticisers: phtalates, bisphenol, etc.;
- > flame retardants: polybrominated diphenyl ethers (PBDEs), etc.;
- > electrical insulators: polychlorinated biphenyls (PCBs), etc.;
- > combustion products: polycyclic aromatic hydrocarbons (PAHs), dioxins, furans, etc.;
- > miscellaneous industrial or domestic chemicals (plastics, adhesives, fuel additives, antibacterial substances): aldehydes, anilines, benzenes, ketones, perfluorocarbons (PFCs), phenols, etc.



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In 2000, the Water Framework Directive⁴ (WFD) set out environmental objectives to be met according to specific timetables for all European Union Member States, including ensuring no deterioration of resources and achieving “good status” for all waters. Good status for surface water covers chemical status (substance concentrations, in particular micropollutants) and ecological status (fauna and flora species, habitat quality, physico-chemical quality). For groundwater, good status covers quantitative status (water level) and chemical status.

In 2007, in order to meet these requirements, historical monitoring mechanisms for surface freshwater (rivers and lakes), littoral waters and groundwater were reorganised into “monitoring programmes” in each of the major river basins.

The monitoring programme is one of the four key documents under the common working method for Member States established by the WFD:

- > the Article-5 report presents a snapshot of the various activities and water uses in a country, with data on the resulting impacts on aquatic environments, in order to identify the issues to be tackled;
- > the monitoring programme describes the system set up to monitor the status of the environments. A detailed report on this subject was drafted in 2013⁵;
- > the management plan for each basin sets the environmental objectives: in France this type of plan became mandatory under the 1992 Water Act⁶, referred to as strategic water management plans (in France, SDAGE);
- > the programme of measures lists the measures designed to reach the set objectives.

WFD implementation is organised in six-year cycles: 2010-2015, 2016-2021, 2022-2027 and so on.

Monitoring aquatic environments: key stakeholders

In France, the role and responsibilities of each participant in water monitoring are stipulated in the National master plan for water data⁷ (SNDE):

- > the production of monitoring data is organised on the river-basin district level, under the joint responsibility of the basin DREAL⁸ and the Water agency (or Water office in overseas territories):

- the Water agencies are in charge of producing and organising monitoring data for all water quality elements, and for data on aquatic ecosystems and pressure assessment. The regional Ecology Ministry services are responsible for producing quantitative data (aquifer levels, river flowrates, etc.);
- the Water agencies and the regional Ecology Ministry services (basin DREALs) work with other bodies that produce data - BRGM⁹, Ifremer¹⁰, Onema¹¹, DREAL, DDT(M)¹², etc.;

- > measurement methodologies (sampling and analysis methods) are proposed by various expert bodies, including the French national reference laboratory for the monitoring of

aquatic environments (Aquaref)¹³. Strict compliance with the methods and protocols is one of the key points for obtaining reliable data. To ensure the quality and validity of data, the results must be provided by approved laboratories according to the rules contained in the regulations¹⁴;

- > data produced is stored in national data-banks administered by national bodies: the “Ades¹⁵” database for groundwater (BGRM), river basin databases for the quality of rivers and lakes (water agencies), the “Hydro¹⁶” database for river discharge (Schapi¹⁷), and the “Quadrige²¹⁸” database for littoral waters (Ifremer). Data must be stored in compliance with the formats and specifications stipulated by the French national service for water data and reference dataset management (Sandre¹⁹) in order to ensure consistency and ease of use by all stakeholders;

- > finally, data is made available to the public on www.eaufrance.fr, a website coordinated by Onema.

4. Directive 2000/60/EC of the European parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, transposed into French law by Law 2004-338 (21 April 2004) and by Law 2006-1772 (30 December 2006).
 5. Onema, *La surveillance des milieux aquatiques et des eaux souterraines*, 2013.
 6. Law 92-3 (3 January 1992)
 7. Ordinance (26 July 2010) approving the national water data framework
 8. Regional Ecology Ministry services
 9. French geological survey
 10. French research institute for research and exploitation of the sea
 11. French national agency for water and aquatic environments
 12. Departmental Ecology ministry services
 13. Aquaref, French national reference laboratory for the monitoring of aquatic environments.
 14. In particular by the Decree of 27 October 2011. The accreditation given to laboratories covers the whole data production process, i.e. sampling (sampling, packaging, transport and storage of the sample), analysis (of a parameter or a biological quality element) and delivery of the result.
 15. www.ades.eaufrance.fr
 16. www.hydro.eaufrance.fr
 17. Hydrometeorology and flood-prevention support group.
 18. www.quadrigue.eaufrance.fr
 19. www.sandre.eaufrance.fr
 20. And amended by the Directive 2013/39/EU of the European Parliament and of the Council of 12 August 2013 amending Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy.
 21. Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy.



For surface water (rivers, lakes, transitional waters and coastal waters), the WFD defined a list of chemicals²⁰ that had to be monitored during the 2010-2015 management cycle:

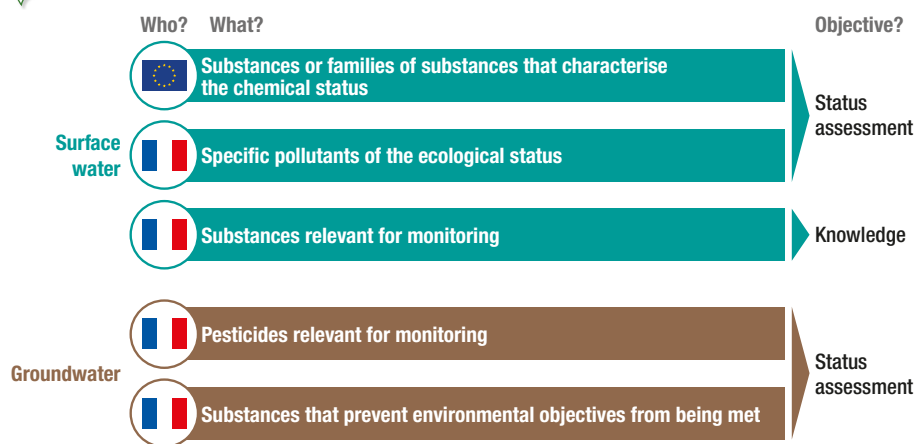
> substances or families of substances that characterise the chemical status (defined for all Member States), including priority substances that pose a potential risk for or via the aquatic environment. Some of these substances are considered to be hazardous, i.e. persistent, bioaccumulative and toxic²¹;

> specific pollutants of the ecological status (defined by each Member State, specific to each river basin): in France, metals and pesticides;

> substances referred to as “relevant for monitoring of aquatic environments” (defined in France), which do not specifically contribute to the status assessment required by the WFD: an initial list had been drawn up on the basis of an exceptional inventory study²³ performed in 2005.

For groundwater, the monitoring requirements under the WFD are less detailed. Water monitoring must, at the least, focus on²⁴:

Chemicals monitored under the monitoring programmes²²



> pesticides, their metabolites and decay/reaction products considered as relevant for water monitoring;

> substances or families of substances that prevent environmental objectives from being met.

For groundwater, France carries out the following:

> an analysis (snapshot) once every six years, based on a precise list of substances or groups of chemicals, in order to provide a comprehensive picture of the quality of groundwater;

> more regular surveillance (once or twice a year) of a smaller list of substances, and of substances that are indicators of local pressures.

Enhanced proactive monitoring of micropollutants

In order to meet the challenges of public health, protection of natural resources and biodiversity, France has implemented a forward-looking system of chemical monitoring for aquatic environments and preventive actions, which are embodied in three national plans:

> the *National PCB Action Plan*, which is based on six areas for action: intensifying the reduction of PCB releases, improving scientific knowledge on PCB pathways in aquatic environments, enhancing the monitoring of fish for human consumption, improving knowledge of the human health risk, adopting risk management measures relating to these various points and supporting professional and amateur fisherman anglers affected by these measures;

> the *2010-2013 Micropollutant Plan for Combating Pollution of Aquatic Environments*, which is organised into three areas for action: improving diagnosis of water status, reducing emissions of the micropollutants of concern, and acquiring knowledge on so-called “emerging” substances²⁵ in particular;

> the *2011-2015 Plan on Drug Residues in Water*, which is also based on three areas for action: developing knowledge, assessing environmental and human health risks and defining appropriate management measures, enhancing and structuring research actions.

The monitoring strategy has been improved through large-scale studies over the last few years in order to develop sampling protocols, analysis methods to measure low-level concentrations and interpretation tools, etc.

The chemical surveillance monitoring programme includes a prospective aspect comprised of exploratory measurement

campaign for groundwater and surface water²⁶, with the following objectives:

> gathering statistical information on the presence in aquatic environments of emerging or unregulated substances that have not been sufficiently monitored up to now;

> contributing to upgrade the list of substances for regular monitoring under the national programme;

> anticipating the emergence of new risks to aquatic resources and identifying substances for which further knowledge gathering actions will be required.

These prospective studies cannot be used for assessing the risk for the aquatic environments related to specific substances at a given location. The exploratory measurements are performed on a limited number of molecules and monitoring sites, and do not provide a comprehensive perspective on micropollutant contamination of aquatic environments in France.

22. Order (25 January 2010) as amended, setting up a water-status monitoring programme.

23. MEDDE/INERIS, *État des lieux de la contamination des milieux aquatiques par les substances dangereuses – Campagne exceptionnelle 2005*, 2006.

24. Directive 2006/118/EC of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration.

25. Substances whose effects are ignored or underestimated, or new substances.

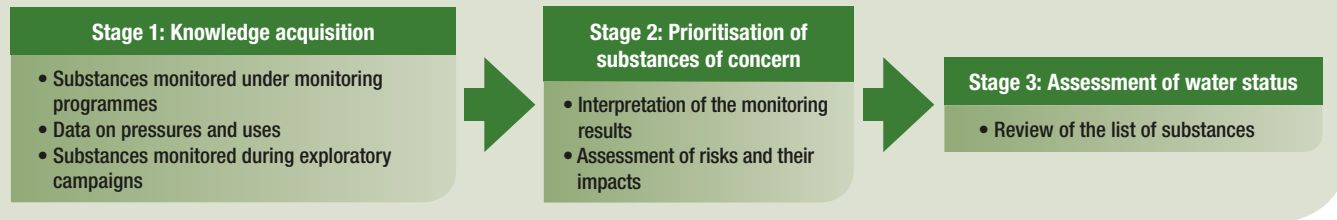
26. <http://www.onema.fr/2campagnes-d-analyse-sur-des-certaines-de-molecules-emergentes>.

Reviews of the list of substances for monitoring

On a European level, the list of “priority” and “priority hazardous” substances is reviewed every six years according to the Water Framework Directive implementation cycles (2010-2015, 2016-2021, 2022-2027). In each cycle, the river basin monitoring programmes have to be updated, which includes reviewing the list of substances for monitoring.

In France, a three-stage method is used to prepare for this review:
 > firstly, knowledge acquisition: measurements performed during exploratory campaigns or under the monitoring programme for a national list of substances are used to confirm the level of substances in aquatic environments;
 > secondly, prioritisation of substances of concern:

scientists interpret the results and issue recommendations concerning the selection of relevant substances for monitoring;
 > finally, assessment of water status: stakeholders in water policy study the recommendations and review the list of substances for regular monitoring to assess water status, in line with territorial realities (e.g. mainland France vs overseas territories).



A broadly shared framework for exploratory monitoring campaigns

Two exploratory campaigns were initiated by the Ecology Ministry and performed in 2011 and 2012, with involvement from many stakeholders in water policy:

- > the campaigns were led and supervised by the Ecology Ministry;
- > a close partnership was established between government and research bodies, with the involvement of key people from a range of public institutions - water agencies and offices, BRGM, Ifremer, Ineris, Onema

- along with public-sector research and private laboratories.

The campaigns covered both mainland France and overseas territories - Martinique, Guadeloupe, French Guiana, Réunion, Mayotte - and spanned different categories of water:

- > one campaign in 2011 for groundwater in mainland France, run by the water agencies with technical support from BRGM; the focus in this campaign was on the spatial representativity, with nearly 500 monitoring sites selected;
- > one campaign in 2012 for surface fresh-water (rivers and lakes) and the littoral waters of mainland France and overseas territories, as well as groundwater in overseas territories. These actions were coordinated by Ineris²⁷ and performed by the

water agencies and offices, Ifremer and BRGM respectively, in conjunction with Aquaref. This campaign represented real progress from the previous campaign, with a focus on analytical sensitivity - research laboratories were commissioned to perform the analysis work.

The campaign involved five steps:

- > definition and organisation: objectives, choice of commissioning authority, financial issues;
- > selection of substances and locations for monitoring, definition of technical specifications (sampling and analysis techniques);
- > measurement performance: sampling and analysis;
- > incorporation and storage of results in databases;
- > examination, interpretation and dissemination of results.

Samples were taken from rivers at three different periods - spring, summer and autumn - in order to take account of seasonal hydrological variability. Because of their lower variability over time, only one sampling period was required for lakes and other static bodies of water. For groundwater, samples were taken, wherever possible, over two periods - high and low water - depending on local hydrogeological features.

The cost of the campaigns (€4.5 million) was shared between fifteen public bodies, primarily Onema and the water agencies. The resources used were divided almost evenly between groundwater and surface water monitoring. However, in proportion to the number of samples, significant resources were required for transporting the samples from overseas territories to laboratories in mainland France.

Organisational arrangements and costs incurred for the campaigns

| Area | Groundwater | | Littoral surface water | | Continental surface water (rivers, lakes) | |
|------------------------------|---|-------------------------------------|---|------------------------------|---|---------------------------|
| | Mainland France | Overseas territories | Mainland France | Overseas territories | Mainland France | Overseas territories |
| Year | 2011 | | 2012 | | | |
| Lead partner | Ecology Ministry | | | | | |
| Steering committee | Ecology Ministry, Onema, water agencies and offices, BRGM, Ifremer, Ineris, Aquaref | | | | | |
| Coordination | Water agencies | | Ineris | | | |
| Lead funding partner | Water agencies | | Onema | | | |
| Operators | BRGM | Water offices, DEAL, BRGM | Water agencies, Ifremer | Water offices, DEAL, Ifremer | Water agencies | Water offices, DEAL, BRGM |
| Analysis | Private laboratories | Public-sector research laboratories | Public-sector research laboratories, private laboratories | | Public-sector research laboratories | |
| Costs (€k) | 1,729 | 615 | 190 | 75 | 1,326 | 542 |
| Number of sampling campaigns | 2 | | 1 | | 3 (rivers) or 1 (lakes) | |

27. French national competence center for industrial safety and environmental protection



Forward-looking aspects of monitoring

These measurement campaigns are an opportunity to take on new challenges by testing innovative methods and tools.

> Enhancing knowledge of the chemical quality of aquatic environments

Traditional analysis methods, based on grab sampling, reflect the situation for a predefined list of substances at a given place and a given time. However, concentrations vary in space and over time, in particular depending on environmental releases and climate conditions. It is therefore difficult to comprehensively assess contamination. Innovative monitoring techniques, developed in research programmes, were tested during these campaigns, with the aim of taking such variations into consideration, along with the effects of contaminants on organisms. For instance:

> use of passive samplers: the principle of this technique is to leave sensors in the water for periods of a few days to several weeks, for micropollutants to fix and accumulate on. These sensors are then analysed in laboratories in order to assess the level of environmental contamination incorporated over time, which is more representative than a one-off sample and provides higher sensitivity. This technique was used especially for littoral waters, where occasional monitoring using conventional systems is most difficult;

> use of biotools such as biotests to identify toxicity in laboratory organisms and biomarkers to monitor sensitive biological parameters in species in the wild; these approaches can identify the effects on these species of general chemical contamination in their environment.

The campaigns were also an opportunity to use analytical methods developed by expert laboratories, with the aim of subsequently transferring knowledge to laboratories that usually perform measurements for the monitoring programme.

> New methods to select substances for investigation

A panel of experts²⁸ determined which substances were to be monitored, as part of a formal national strategy²⁹. From an initial list of approximately 2,400 proposals, 190 were eventually selected:

> substances with little research or poor-quality research to date (including under regular monitoring programmes), and whose level of occurrence in the aquatic environment is poorly known;

> substances whose characteristics indicate a potential transfer to the aquatic environment or a worrying level of ecotoxicity;

> out of these two groups, substances for which the analytical sensitivity in a laboratory environment enable toxicity threshold measurements to be performed.

For the 2011 campaign (groundwater in mainland France), some substances that were already monitored but considered hazardous were also selected³⁰, alongside pesticides, drugs and drug residues that

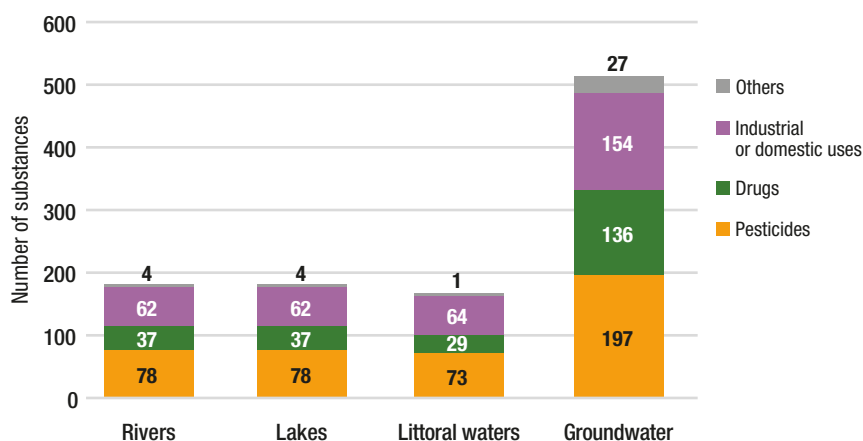
are not monitored extensively or consistently, in order to supplement current knowledge in a variety of contexts (human activities, geology, etc.). The list of substances investigated varied according to the environment. Depending on their properties, different substances may be more likely, for instance, to be found in surface water or groundwater. There were also differences between mainland France and the overseas territories, where local practices may require the use of different molecules - for instance chlordecone (or kepone), an insecticide used in Guadeloupe and Martinique on the banana weevil.

38% of the substances were primarily used³¹ as pesticides, 33% for industrial or domestic uses, 25% as drugs and 4% for other uses (personal hygiene products, caffeine, etc.).

> Better consideration of the diversity of sites used in national campaigns

Although the aim of the campaigns is to investigate substances throughout the country, the number of sites selected was limited, for budgetary and logistical reasons. In the end, 735 sites were selected, 650 in mainland France and 85 in the overseas territories. Almost all of the sites were already monitored under the national monitoring programme, in order to optimise sampling rounds and to leverage on historical data logs.

Number of substances investigated by water category and primary usage (mainland France and overseas territories)



28. Experts Prioritisation Committee (CEP), created in 2010, co-led by Onema and Ineris.

29. MEDDE, *Plan Micropolluants 2010-2013*, 2010.

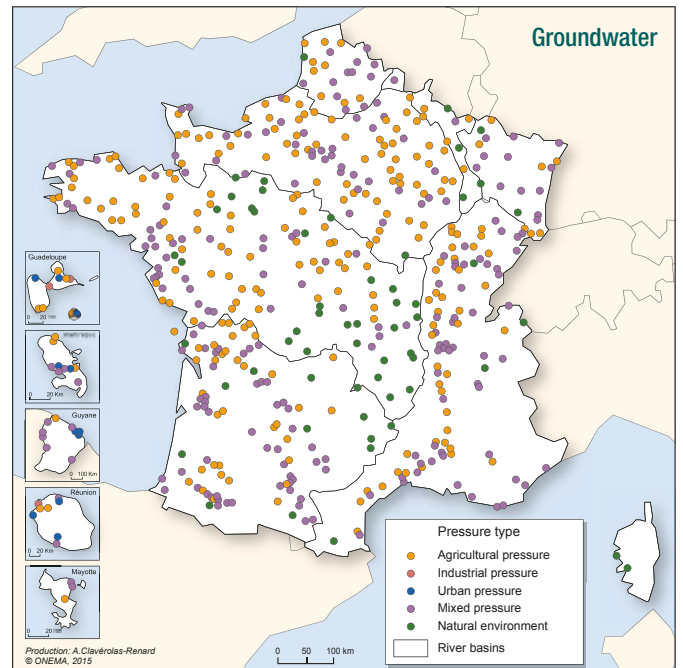
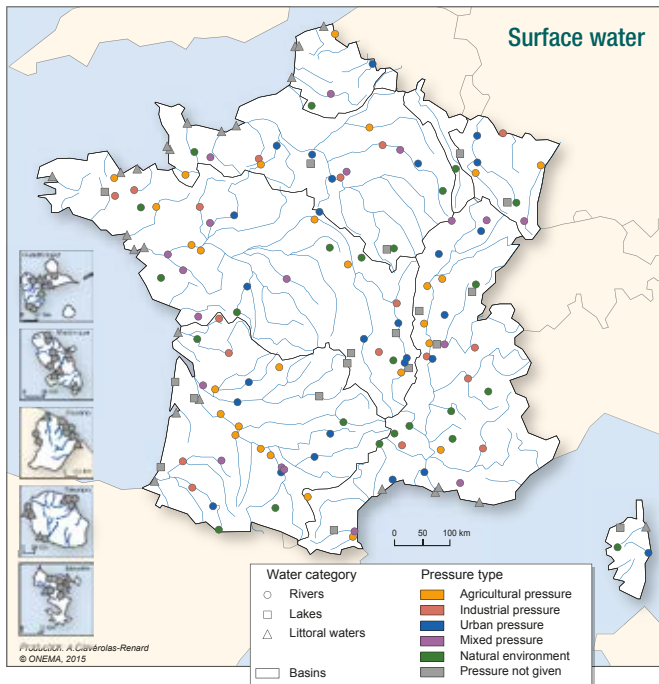
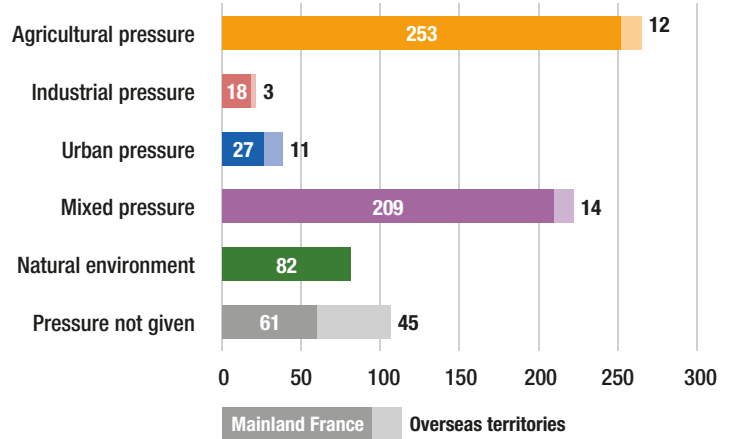
30. Order (17 July 2009) on measures to prevent or limit inputs of pollutants into groundwater.

31. A substance may have various uses, but only one main use was considered for this analysis.

These sites are representative of the different types of pressure (agricultural, industrial or urban) and 11% of them are areas of low human pressure (referred to as "Natural environment").

79% of investigation sites focus on groundwater (2011 campaign, which targeted high levels of spatial representation), 19% on rivers, 6% on littoral waters and 3% on lakes.

Distribution of selected sites, by pressure type (broad categories)



Number of substances, sites and analyses by water category

| | Rivers | | Lakes | | Littoral waters | | Groundwater | |
|-----------------------------------|-----------------|----------------------|-----------------|----------------------|-----------------|----------------------|-----------------|----------------------|
| | Mainland France | Overseas territories | Mainland France | Overseas territories | Mainland France | Overseas territories | Mainland France | Overseas territories |
| Number of substances investigated | 168 | 181 | 168 | 181 | 167 | 166 | 412 | 188 |
| Number of sites | 115 | 24 | 18 | 1 | 24 | 20 | 493 | 40 |
| Number of analyses | 39,921 | 8,879 | 3,883 | 234 | 4,083 | 3,729 | 352,634 | 14,894 |



When interpreting the results, it is important to bear in mind the fundamental differences in the way the two campaigns were organised. One focused solely on groundwater in mainland France (2011) and the other on surface water in mainland France and overseas territories as well as groundwater in the overseas territories (2012):

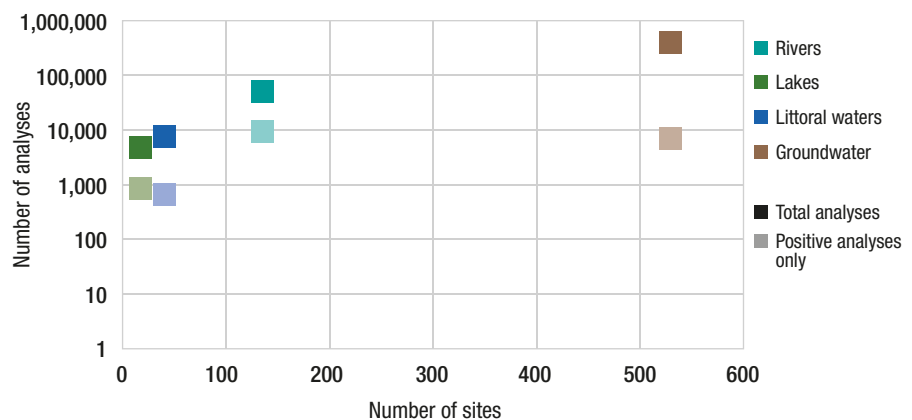
- > in 2011, the focus was on spatial representation with a large number of investigation sites;
- > in 2012, the priority was analytical sensitivity, with fewer monitoring sites and fewer investigated substances, but more advanced testing by expert research bodies.

Analyses were declared "positive" when the substance was detected by the laboratory. A substance was described as "quantified" if its concentration could be measured in a statistically robust manner. The "quantification frequency" of a substance is the number of times it was quantified, as a ratio of the number of times it was sought. However, if a substance is described as "frequently quantified", this does not necessarily mean that it was present in high concentrations.

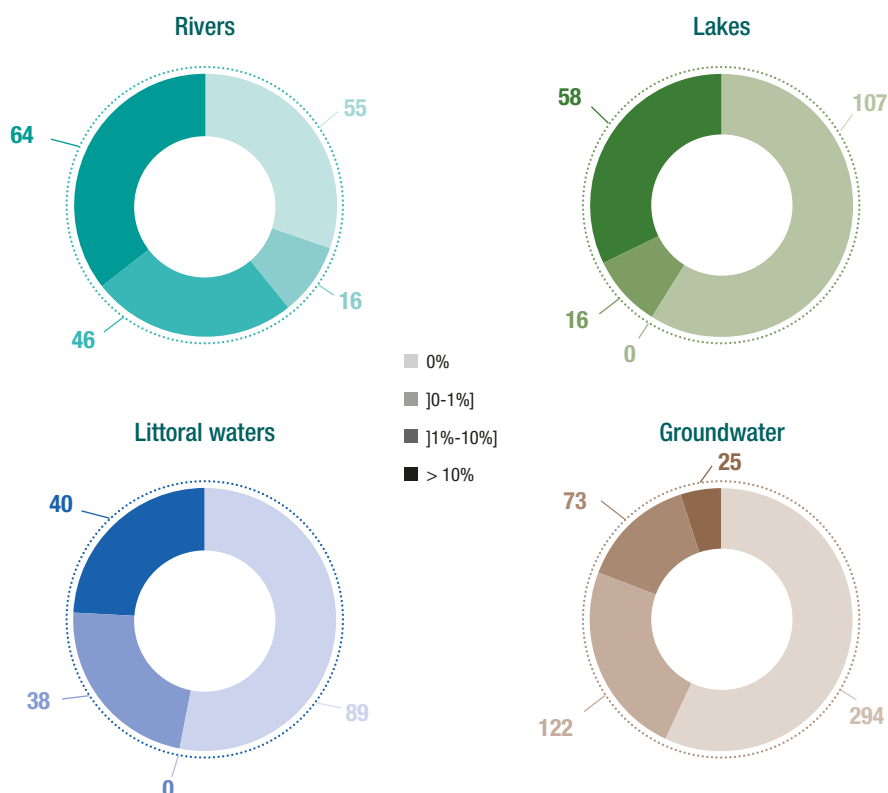
Key figures on prospection results

The number of positive analyses as a proportion of the total number of analyses varies according to the water category. It is, for instance, higher for samples taken from continental surface water (rivers and lakes). There are two reasons for this: firstly, different levels of contamination in different environments, and secondly, the difference in analytical sensitivity between the two campaigns in 2011 and 2012. Overall, 4% of the 428,257 analyses were positive.

Number of analyses, by water category (for all substances - mainland France and overseas territories)



Number of substances quantified, by quantification frequency (mainland France and overseas territories)



Of the 637 substances investigated for all categories of water, almost half (49%) were not quantified on any site. However, the fact that a substance is not quantified does not necessarily mean that it is not present. The result is related to the analytical sensitivity of the test method used by the laboratory.

Rivers were the category in which the highest number of investigated substances was observed (70%), since they are more closely connected with pollutant pressures.

The most frequently quantified substances were drugs (56%), followed by industrial or domestic substances (53%).

Of the 326 substances quantified, the following were the most frequently identified:

> in rivers and lakes: preservatives used in cosmetics and beauty products (parabens), plasticisers (diisobutyl phthalate and bisphenol A), a surfactant (p-nonylphenol diethoxylate), but also combustion products (PAHs) in sediments;

> in littoral waters: plasticisers (phtalates) and, in sediments, PAHs and organometallic compounds (biocides from ship anti-fouling paints);

> in groundwater: drugs (e.g. acetylsalicylic acid, better known as aspirin), compounds used in industry, pesticides (including atrazine metabolites, which have been banned since the early 2000s or imidacloprid, a neonicotinoid) or caffeine.

The level of environmental contamination is estimated from the measured concentration values. To give an idea of the level of concentration, one nanogram per litre (ng/l) means one billionth of a gram per litre, which is the active substance concentration you would get if you dissolved an aspirin tablet in a 25-metre swimming pool³². The measured concentration levels must then be compared with the toxicity of each substance (1,000 ng/L is the same as 1 µg/L).

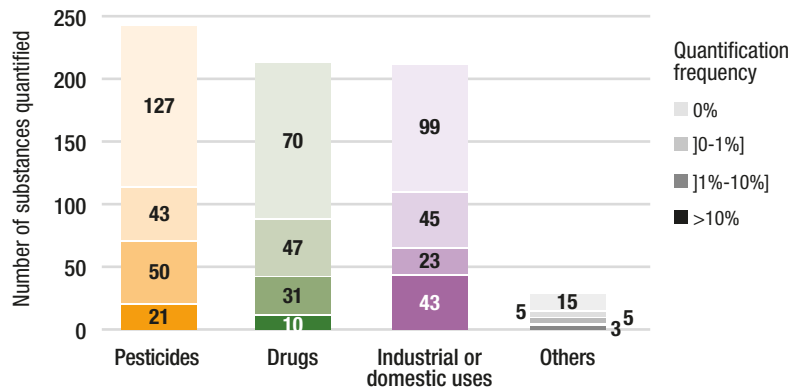
In groundwater, some industrial molecules were at times found at high concentrations (up to tens of µg/l). Some furans and dioxins were frequently measured but at very low concentrations (one thousandth of a ng/L). Some drugs and pesticides were found very frequently, but at concentrations most often below 1 µg/L.

In rivers and lakes, the gradients were longer and flatter. Unlike for groundwater, the concentrations of drugs were often higher than pesticide concentrations. In littoral waters, the most commonly identified substances, both for mainland France and overseas territories, were plasticisers and pesticides.

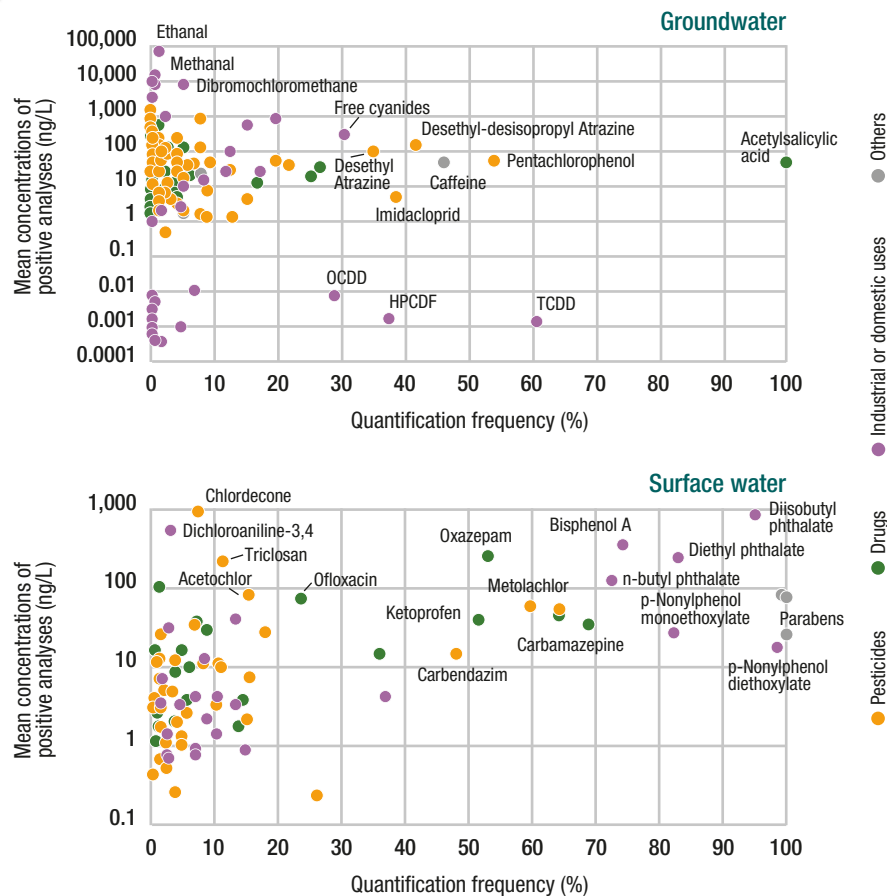
High concentrations of certain pesticides in water (metolachlor metabolites) were specifically observed in areas with agricultural pressure. Other pesticides found in sediments (e.g. metabolites of DDT, an insecticide that was banned in France in 1971) were seen in areas of urban pressure.

Plasticisers and parabens were observed in all contexts, even where there was no anthropogenic pressure. Some “rogue”

Number of substances quantified, by primary usage (mainland France and overseas territories)



Concentration and quantification frequency of substances identified in positive analyses (mainland France and overseas territories)



contamination may however have taken place during sampling. Plasticisers, in particular, are very widely used in many types of sampling equipment, and beauty products may have been present on the

skin of the people responsible for sampling. It is therefore possible that their presence has been overestimated. Further studies³³ are under way in order to detect and estimate the significance of any bias related to these substances.

32. Eawag, *Questions fréquemment posées sur les micropolluants dans le milieu aquatique*, 2010.
 33. 2015-2016 Aquaref work programme.



Special attention required for certain substances

The campaigns highlighted various substances or groups of substances of concern, because of their widespread presence at national level, sometimes in high concentrations or with a potential risk for environments. The potential risk was identified by comparing the concentrations with the threshold values above which the substances may be toxic or ecotoxic. The substances requiring vigilance include the following:

> pesticides: one insecticide (imidacloprid), one herbicide (terbutryn) and one biocide used in beauty products and textiles (triclosan), that were present in significant

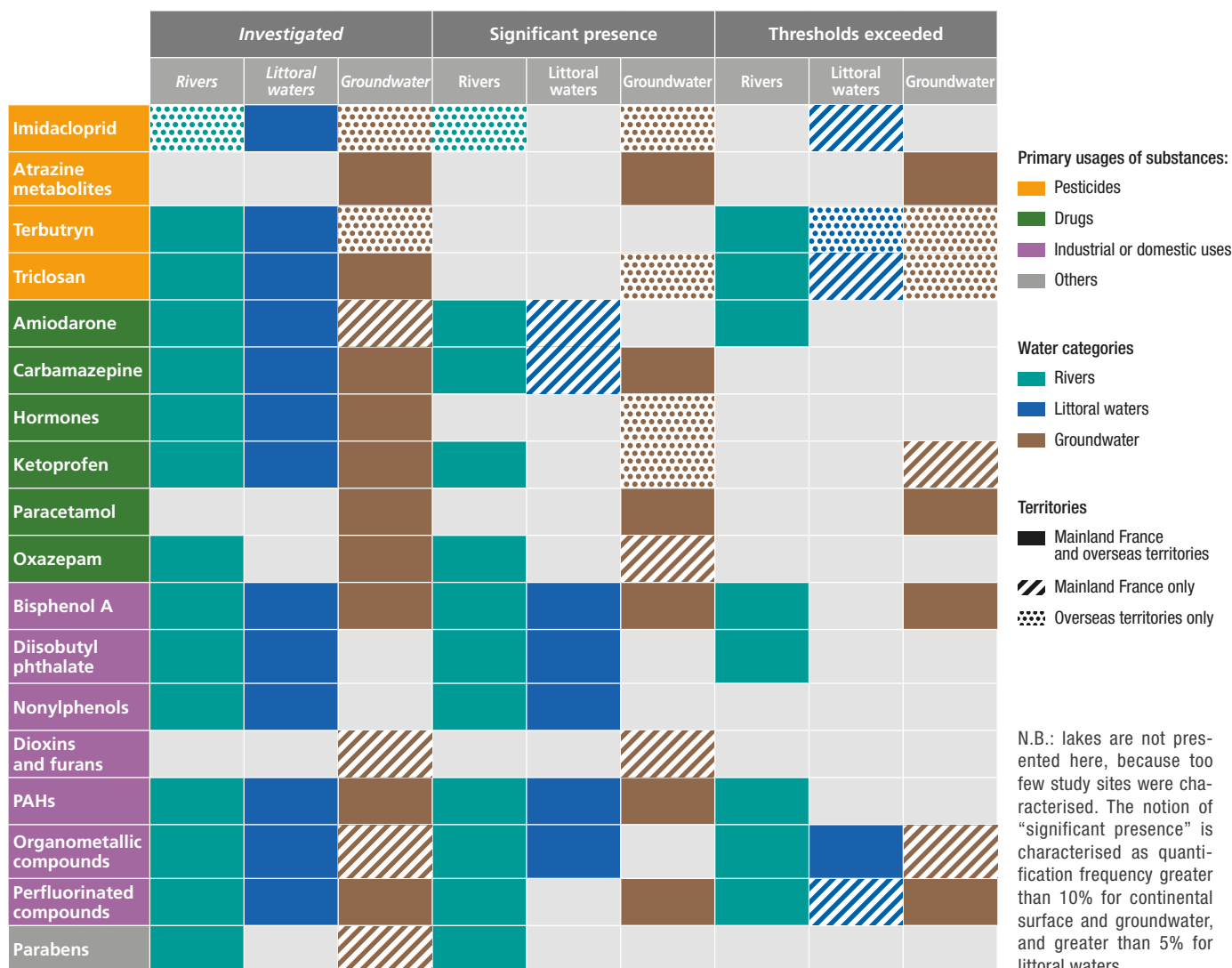
levels in groundwater and some overseas rivers, with a potential impact in some rivers, littoral waters and groundwater supplies. Atrazine decay products (atrazine is a herbicide that was widely used on crops between 1960 and 2001) were recurrent in groundwater at concentrations often above 100 ng/L;

> several drugs: amiodarone, which is used to prevent and treat cardiac dysrhythmias, the anti-anxiety treatment oxazepam, anti-epileptic treatment carbamazepine and the anti-inflammatory ketoprofen - thresholds were exceeded for amiodarone in rivers and lakes and for ketoprofen and paracetamol in groundwater; significant levels of hormones were also detected in overseas groundwater supplies;

> substances from industrial or domestic uses: dioxins and furans produced from combustion (waste incineration,

metallurgy), which were very recurrent in groundwater in mainland France (but at quite low doses); nonylphenols (often from cleaning products), which affected surface water widely, PAHs produced by combustion (heating, transportation, industry) and organometallic compounds contained in anti-fouling paints, which were found in terrestrial and littoral sediments; and perfluorinated compounds (surfactants or flame retardants), which were recurrent in groundwater in industrial areas, and also in littoral sediments;

> parabens (biocides used in cosmetics, for example) and plasticisers (bisphenol, diisobutyl phthalate) were found in almost all samples taken in rivers, including in natural contexts, sometimes at high levels of concentration (but these samples may have been affected by rogue contamination as explained above).



Monitoring updated in 2015

Results from these exploratory campaigns, alongside another analysis campaign by the Ministry of Health in 2009-2010³⁴, provided the information required for a review of the list of substances for monitoring over the next WFD cycle (2016-2021). The method was used to prioritise substances based on three independent and complementary issues: the data collected on frequency of occurrence, potential danger and the risk of exceeding a threshold of concern. Recommendations³⁵ have been submitted to the Ecology Ministry and the river basin stakeholders who will be responsible for implementing monitoring. 129 substances are included, including 49 active substances (or metabolites) that are used in agricultural products or biocides, 30 industrial chemicals and 23 drug residues. Alongside the WFD updates on priority substances, these recommendations contributed to a revision of the 2015 monitoring programmes³⁶, with the following implications:

- > for surface water: 12 supplementary priority substances or groups of substances have been added (insecticides, herbicides, PCBs, perfluorinated compounds); 21 supplementary pesticides and industrial substances have been added for characterisation of the ecological status (with specific lists for each river basin, in order to reflect the unique features of each territory); and the additional list of “relevant substances for monitoring” has been substantially amended;
- > for groundwater: the list of substance for snapshot monitoring and regular monitoring testing has been supplemented with a number of pesticides, industrial and domestic substances, and drug residues. Moreover, intermediate surveillance testing for 55 substances shall be performed on one quarter of sites from the monitoring programme.

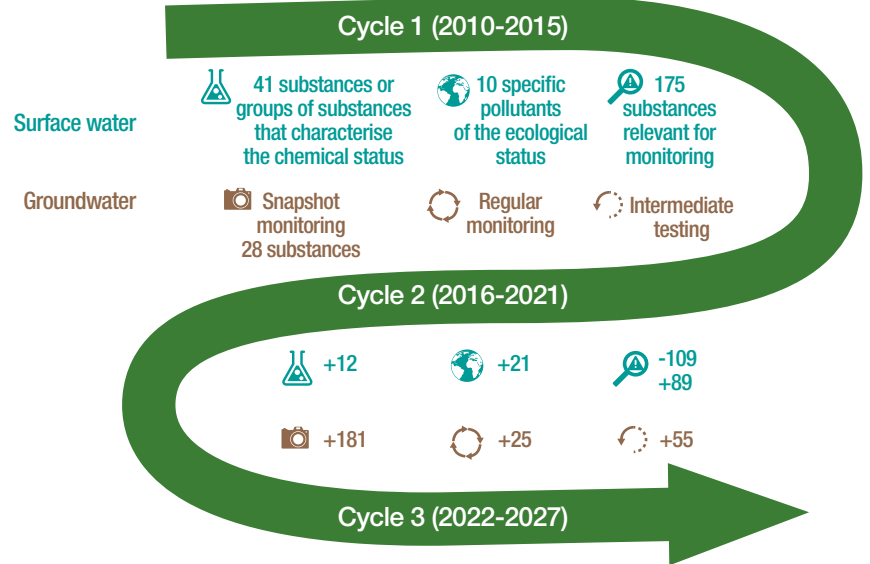
34. ANSES, *Campagne nationale d'occurrence des résidus de médicaments dans les eaux destinées à la consommation humaine*, 2011.

35. Aquaref/Ineris, *Recommandations du CEP auprès du MEDDE pour la sélection des Substances Pertinentes à Surveiller dans les Milieux Aquatiques pour le Second Cycle de la DCE (2016-2021)*, 2014.

36. Order (7 August 2015) amending Order (25 January 2010) setting up a water-status monitoring programme.

37. Decision 2015/495 of 20 March 2015 establishing a watch list on substances subject to monitoring in water policy.

Comparison of substances for statutory monitoring in WFD cycles 1 and 2



European watch list of substances for close monitoring

The European Commission, seeking to gather evidence for future selection of priority substances, recently added new requirements from 2015³⁷ (notably in the 2016-2021 management cycle), with a watch list of 17 new substances that that may potentially present a significant risk for the aquatic environment and for which there is currently a lack of knowledge:

- > drug residues: one anti-inflammatory (diclofenac), three hormones (17-alpha-ethinyl estradiol EE2, 17-beta-estradiol E2 and oestrone) and three antibiotics (erythromycin, clarithromycin and azithromycin),
- > one anti-UV filter used as an ingredient in cosmetics (2-ethylhexyl 4-methoxycinnamate),

- > one food additive (2,6-di-tert-butyl-4-methylphenol),
 - > agricultural chemicals: one molluscicide (methiocarb), two herbicides (oxadiazon, triallate) five neonicotinoid insecticides (imidacloprid, thiacloprid, thiamethoxam, clothianidid, acetamiprid).
- Each Member State must monitor surface water in representative areas for a period of at least 12 months. In France, monitoring will take place across at least 26 stations. A similar exercise is being carried out on a European scale for groundwater, with a specific watch list planned for 2017.



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Ongoing exercises

The data collected and scientific advances lead to regular improvements in chemical monitoring of aquatic environments. As these efforts continue, results from the second WFD cycle (2016-2021) will supplement the knowledge that is required for assessing the risks from micropollutants in aquatic environments, and will help to identify the most appropriate management measures. The results will help to identify which substances should be taken into account in the third cycle (2022-2027) and fine-tune assessments of the water status. Prospective monitoring thus contributes to updating management plans every six years, a time interval that is aligned with the WFD cycles. This iterative process will provide a framework for periodic reviews of lists of substances and investigated mediums (water, sediment) as new knowledge is acquired. It will also give an opportunity to assess the role that innovative tools such as passive samplers and biotests should play in forthcoming monitoring cycles.

Furthermore, data gathered in the 2011 and 2012 campaigns was used to establish substance lists under other frameworks outside of the WFD. For instance, the list of emerging pollutants for the *2012 Roadmap to Ecological Transition*³⁸ or the list of marker substances for work on sediments (from dredging and immersion operations) and the consolidated substance list covered in the *Ecophyto plan*³⁹.

Questions about sampling practices and analytical performance also fed into the 2013-2015 work programme of Aquaref, the French national reference laboratory. Aquaref has started work on potential sample contamination in analyses for substances, such as plasticisers, that are widely used in sampling equipment. Over the next few years, Aquaref will pay special attention to the development, validation and transfer to statutory monitoring bodies of methods used by the research laboratories during prospective campaigns of testing for emerging contaminants.

Further work will also be carried out over the next few years to:

- > improve understanding of the combined effects of different chemicals (often referred to as the “cocktail effect”), improve understanding of ecotoxicity, enhance knowledge of contamination pathways within the food chain and improve characterisation of pollutant flows towards the sea;

- > deal with emissions at source, to reduce the transfer of micropollutants to aquatic environments. 13 pilot projects have been launched over a five-year period (2014-2018) with this aim, under a call for projects on methods for combating micropollutants in urban wastewater. Four topics will be covered by these projects: dealing with drug residues and domestic cosmetics, dealing with hospital releases, integrated micropollutant management in communal sanitation networks, and management of pollution drained by rainwater.

38. Ministère chargé de l'Environnement, *Feuille de route pour la transition écologique*, 2012.

39. Ministère chargé de l'agriculture, *Plan Ecophyto 2018*, 2008.

40. <http://www.onema.fr/LUTTE-CONTRE-LES-MICROPOLLUANTS>



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Note on methods

The information presented in this document was generated through a methodology shared between Onema, IOWater and members of a national working group (GVI), comprising water agencies and offices, the Water and biodiversity directorate of the Ecology ministry, basin DREALs, the Statistics and observation service (SOeS), alongside research bodies such as BRGM, Ifremer or Ineris. The figures and charts are all taken from the results of exploratory campaigns led by the Ecology Ministry:

- > the *exceptional campaign* focusing on substances in groundwater in mainland France, run by the water agencies with technical support from BRGM and a focus on the spatial dimension;
- > the *prospective study* on emerging

contaminants in continental and coastal surface water in mainland France and overseas territories and in groundwater in overseas territories, coordinated by Ineris, and carried out by the water agencies and offices, Ifremer and BRGM respectively in 2012, in conjunction with Aquaref, with a focus on analytical sensitivity (in particular by using expert research laboratories to carry out the analyses).

In producing this summary document, Ineris and BRGM have also issued complementary analysis reports on continental surface water and groundwater respectively. They consolidated some data, which explains the discrepancies in some figures. The overall conclusions remain unaffected.

For more information

Data on the exploratory campaigns can be found at: www.data.eaufrance.fr

For detailed reports on the different campaigns: www.onema.fr/SURVEILLER-Contaminants-dinteret-emergent#Resul

Find this document on the internet at: www.eaufrance.fr/IMG/pdf/campex_201603_EN.pdf or www.documentation.eaufrance.fr

eaufrance The French water-information portal: www.eaufrance.fr

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This document was drafted under the national master plan for water data and was submitted to the relevant water information system partners for consultation.

