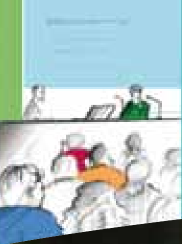
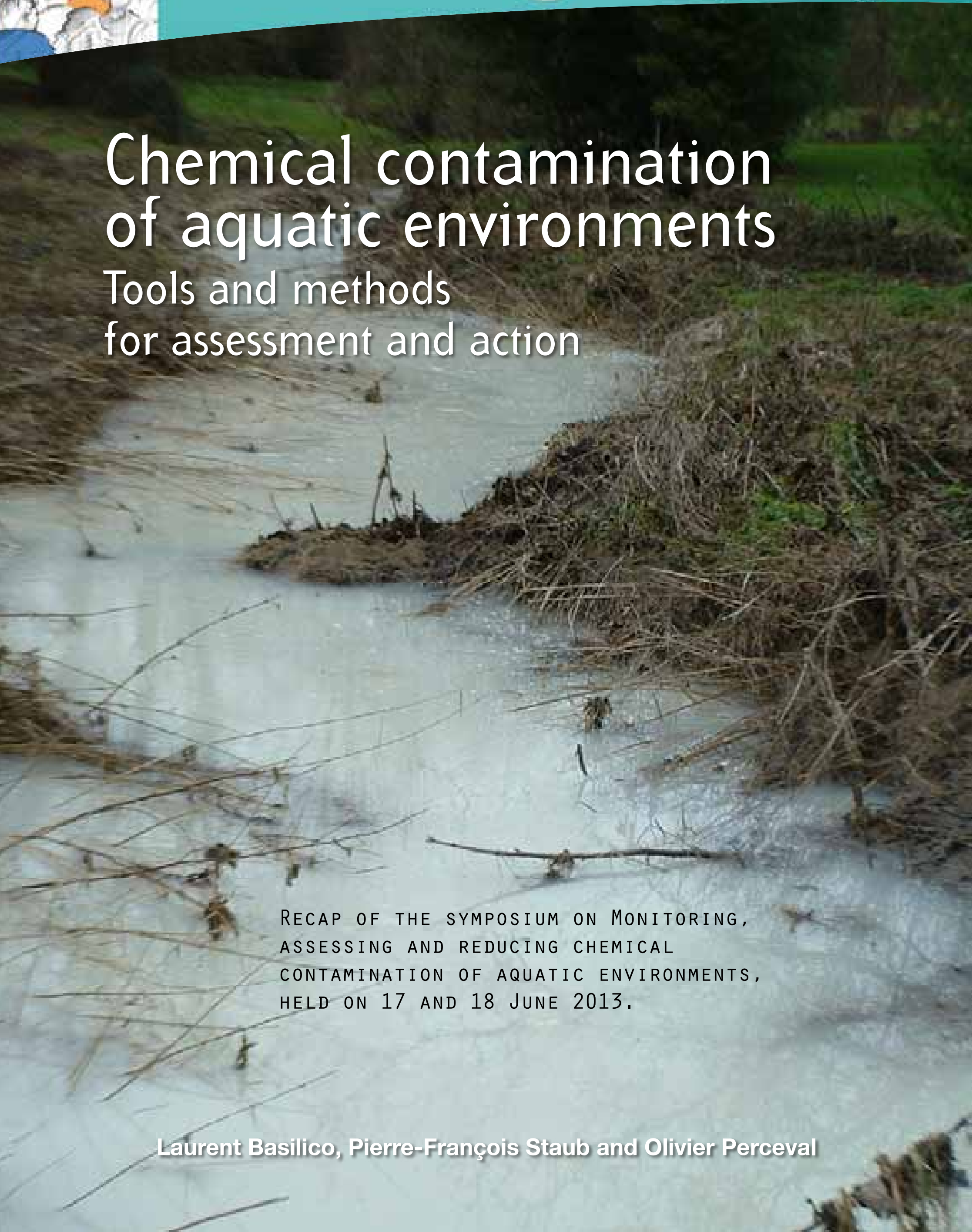


ONEMA Meeting

Recap



Chemical contamination of aquatic environments

Tools and methods for assessment and action

Recap of the symposium on Monitoring, assessing and reducing chemical contamination of aquatic environments, held on 17 and 18 June 2013.

Laurent Basilico, Pierre-François Staub and Olivier Perceval

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The symposium on Monitoring, assessing and reducing chemical contamination of aquatic environments was organised by Onema and Ineris. The symposium was held in Paris, on 17-18 June 2013.

This document may be consulted on the Onema site (www.onema.fr), in the Resources section, and on the Ineris site (www.ineris.fr). It is also listed at the national portal for "Water technical documents" (www.documentation.eaufrance.fr).

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Foreword

Each day, humans release a wide array of chemical contaminants to natural environments in the form of wastewater from towns and pollutants from industrial activities and intensive farming practices. Surface waters and water tables are particularly affected by these point-source and nonpoint-source forms of pollution. Over the last decades and increasingly ever since the adoption of the Water framework directive (WFD) in the year 2000, the assessment and reduction of chemical contamination in water have become major issues throughout Europe in the effort to preserve aquatic ecosystems and human health.

Confronted with the vast array of polluting substances and the complexity of their effects on both ecosystems and lifeforms, water managers and stakeholders have expressed growing needs for operational knowledge, tools and methods. How can the sources of pollutants be better identified and how can emissions be reduced? How can the presence of pollutants be linked to the observed ecological impacts and how can the assessment of water status be improved? Finally, how can the “emerging compounds of most concern” be identified in order to start working immediately on regulating them and attenuating their impacts?

Over the past five years in France, these questions were the focus of an unprecedented R&D effort in the framework of the national 2010-2013 Micropollutants plan and a number of more specific action plans targeting PCBs, plant-protection products, pharmaceutical residues, urban wastewater management, etc. The national symposium, organised by Onema and Ineris on 17 and 18 June 2013, was an occasion to review the work undertaken. The symposium brought together in Paris over 200 participants, including water managers, scientists, elected officials, associations, experts, managers of river contracts, etc., for a progress report on the available tools and methods, on current projects and on the outlook for current research. This document recapitulates those discussions.

Contents

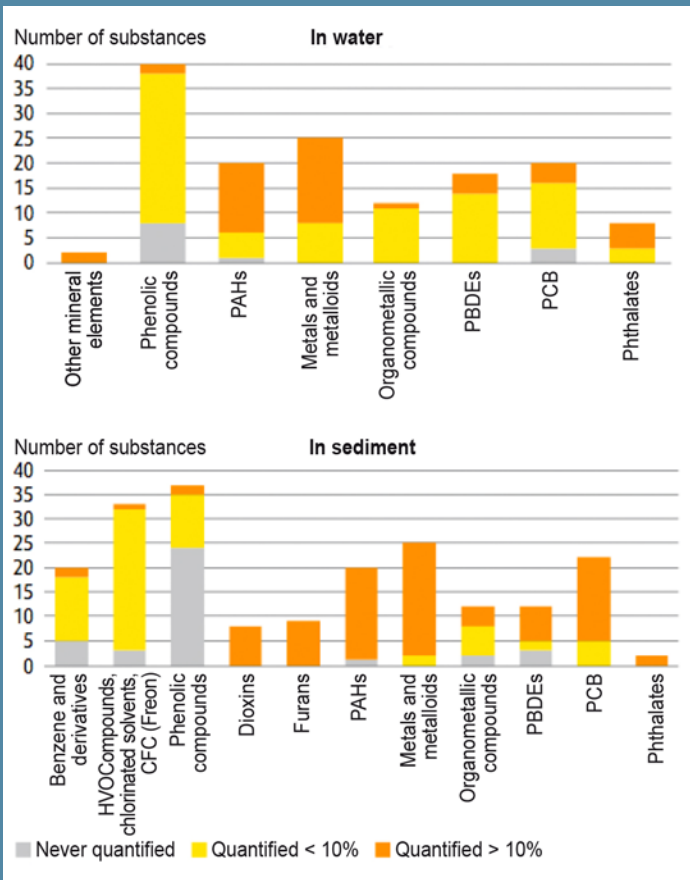
Since the mid 1800s, human activities have produced a vast array of chemicals for industry, agriculture, metallurgy, transport systems, consumer goods, medicine, building materials, electronics, etc. The American Chemical Society has listed 65 million substances produced worldwide in its database, of which 100 000 are or have been produced on an industrial scale. Released to the atmosphere and to soil, transported by sanitation networks, a high percentage of these substances and their by-products end up, via run-off or infiltration, in rivers, water tables and even littoral waters.

Widespread presence of micropollutants in French waters

The study on micropollutants in French aquatic environments, published in 2009 by the Ecology ministry, revealed the virtual omnipresence of the targeted micropollutants in freshwater resources in both continental France and the overseas territories. During the years 2007 to 2009, efforts were made to detect almost 950 micropollutants at 2 880 monitoring points throughout France in rivers, lakes and groundwater. The sediment of surface waters was also analysed for contaminants. Pesticides were detected at 91% of the monitoring points on French rivers, with total concentrations higher than 0.5 µg/L at 21% of the monitoring points. Of the 516 pesticides for which analyses were run, 413 substances were detected at least once in rivers. The most commonly detected was glyphosate, a widely used herbicide, and AMPA, its by-product, respectively present at one-quarter and one-half of the monitoring points on rivers. Pesticides were also found at 75% of the monitoring points on lakes and 70% of the monitoring points for groundwater. In addition to pesticides, efforts were made to detect over 400 contaminants from some 20 families of products in surface waters and 300 contaminants in groundwater. The presence of metals and metalloids, partially of natural origin, is also widespread. Polycyclic aromatic hydrocarbons (PAHs), produced by various types of combustion (transportation, incineration, heating) were commonly found in rivers in continental France. Persistent pollutants such as polybrominated diphenyl ethers (PBDEs), used in industrial products as flame retardants, and polychlorinated biphenyls (PCBs), produced from 1930 to 1970 for various electrical applications, are today present in the sediment of many rivers. River sediments also contain phenolic compounds, dioxins, furans and phthalates. Contamination of groundwater, though less significant in absolute terms, is characterised by the regular presence of chlorinated solvents and dissolved hydrocarbons.

All these chemical contaminants, also called micropollutants, are likely to produce toxic effects and disturbances

Figure 1. Number of substances, both quantified and non quantified, by group of micropollutants not including pesticides, in rivers in continental France. (Source: Water agencies, 2010 - Processing by SOeS, 2011)



in aquatic environments, even at very low concentrations (e.g. µg/L or ng/L) in water or sediment. Their diffuse or localised presence in rivers, lakes and groundwater represents a major pressure on these environments and can have occasionally formidable consequences on biodiversity as well as affecting water quality, thus creating risks for human health.

Increasing recognition in European and national policies

Ever since the incidents of high fish mortalities in a large number of European rivers in the 1970s and 1980s, public opinion has become increasingly aware of the need to restore and preserve the quality of aquatic environments. Acknowledgement of this need by European policies resulted in the adoption of the Water framework directive (WFD) and its daughter directives that since 2000 have laid the groundwork for EU efforts to **monitor and protect aquatic environments**. The WFD instituted the concept of good chemical and ecological status of water bodies and made the restoration and/or preservation of that status an official objective. WFD implementation requires that the Member States undertake long-term R&D efforts in numerous fields, ranging from environmental chemistry to modelling of pollutant transfers in river basins and from ecotoxicology to sanitation engineering. Assessment of the chemical status of water bodies is based in particular on systematic analyses to detect and quantify, at each monitoring point in the monitoring networks, “priority substances” (the number was increased from 33 to 45 in April 2013), of which 21 have been declared “priority hazardous substances”.

These efforts to monitor and restore the chemical status of environments were filled out with a system to **regulate the sale of the substances**. Since 2006, the European REACH regulation has organised the risk assessment and the authorisation (or restriction) of all chemical products manufactured or used in the EU. Specific regulations were also adopted for plant-protection products (EC 2009/1107), biocides (EU 2012/528) and veterinary and human medicines (EC 2001/82 and EC 2001/83).

The third pillar of EU policy concerns the **prevention and reduction of pollution**. This aspect is implemented notably by the directive on industrial emissions (EU 2010/75) and the regulation (2006/166) requiring that the operators of industrial installations (industrial sites, wastewater-treatment plants) file an annual report on their polluting emissions and waste.

All of these legal stipulations, reinforced over the past 30 years by proactive policies on the part of the various economic sectors (industry, agriculture, local governments) and by the increasing awareness of citizens, have already produced visible results. That is notably the case concerning the reduction in discharges to the environment of certain contaminants (formerly used pesticides such as DDT, triazines, lindane, as well as PCBs and pollutants that are becoming increasingly rare due to the use of clean technologies in industry and improved standards in wastewater-treatment plants, etc.).

An unprecedented R&D effort in France

Over the last five years in France, a number of coordinated action plans have been launched by public authorities in accordance with the WFD schedule, but often targeting objectives exceeding regulatory requirements. The national action plan against pollution in aquatic environments, a.k.a. the 2010-2013 **Micropollutants plan**, managed and funded by the Ecology ministry, initiated 22 operational and research programmes in three major fields, i.e. reducing emissions at their source, improving the assessment of water status and gaining new scientific knowledge, notably concerning “emerging” pollutants. Numerous organisations worked closely together on implementing the plan, notably Onema and the Water agencies, with scientific and technical support from Ineris, Irstea, Ifremer and BRGM. The cross-cutting plan, addressing all water bodies (surface and littoral waters, groundwater, in continental France and the overseas territories) and all pollutants (with the exception of pesticides), was filled out with a number of R&D programmes in specific fields, most of which are still in progress:

- the Ecophyto 2018 plan, launched in 2008, to reduce pesticide use and impacts on the environment;
- the National plan for medical residues in water (2011-2015), to improve the assessment and management of medicinal substances in aquatic environments and drinking water;
- the National action plan for PCBs (2008-2010), that produced considerable progress in our understanding of PCB transfers from sediment to fish and of the degree to which consumers of fish are exposed;

The Micropollutants plan.

- finally, the 2012-2018 action plan for sanitation policy contributing to quality objectives for aquatic environments.

Following the 2010-2013 Micropollutants plan and in spite of the fact that many R&D projects in specific fields have not yet been terminated, new knowledge, tools and methods are already available for water managers and stakeholders. They were the topic of discussions during the national symposium organised by Onema and Ineris in Paris, on 17 and 18 June 2013, with over 200 participants. This document briefly presents the scientific and operational progress discussed during the two days of meetings, looking successively at the three major fields addressed by the 2010-2013 Micropollutants plan, namely knowledge of and control over the sources of pollution, improved assessments of the status of aquatic environments and, finally, research on emerging substances and the new biological tools used for assessments and to guide further action.

Spotlight

Obtaining information on existing knowledge and tools in a few clicks

As a central factor of French water policy, chemical contaminants in aquatic environments have been the topic of abundant literature, including regulatory documents, scientific summaries, spatialised data, operational guides, reference information on substances, etc. Many of the documents are available on-line and a panorama of the various platforms was presented *(P.-F. Staub, Onema; Christine Féray, Ineris)* during the symposium.

- An introduction to **French national policies and regulations** is available on the site of the Ecology ministry (www.developpement-durable.gouv.fr), under the “Water and biodiversity” and the “Risk prevention” tabs. Topics range from implementation of the WFD and the European Reach (listing and assessment of chemical substances) regulations to presentations of the national action plans.

- The Onema site (www.onema.fr/contaminants-et-pollutions-aquatiques) provides access to an array of **summary documents on current scientific and technical knowledge**. The pages on “Contaminants and pollution” comprise three sections, namely Monitoring (sampling and analysis

1 Knowledge and action at the source

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to control micropollutant transfers and reduce overall pollution

The first step in improving the chemical status of aquatic environments is to take action at the source of the pollution, e.g. point-source discharges from industrial sites and other regulated installations for environmental protection (ICPE), agricultural nonpoint-source pollution (nitrates and pesticides), urban run-off following rainfall and discharges from wastewater-treatment plants (WWTP).

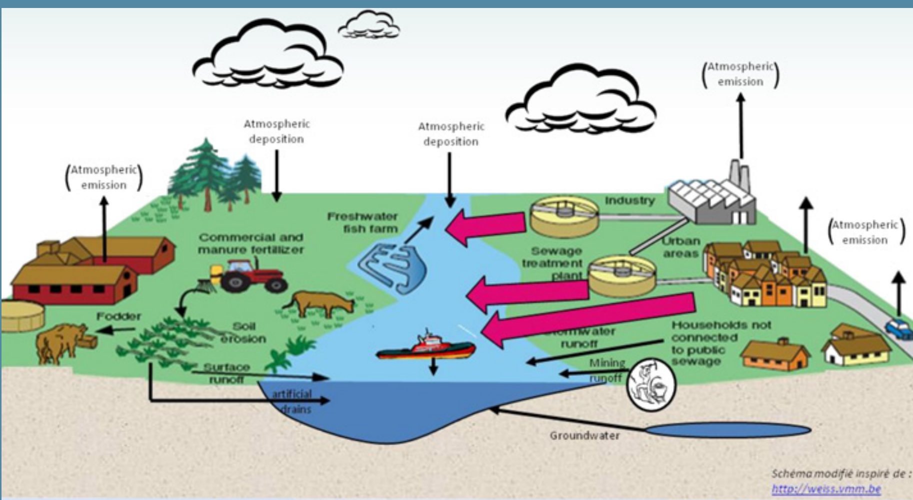
Identifying these sources over entire river basins, characterising their emissions and implementing measures to reduce emissions and their transfer to the environment (changes in industrial processes, new treatment methods) are the three main parts of the 2010-2013 Micropollutants plan. Several R&D projects for each type of source (excluding agriculture) were presented during the June 2013 symposium and constitute the topic of this first section.

1.1 – Setting priorities for multi-source pollutants

In a given region, many sources of pollution (see Figure 2) are likely to affect the chemical quality of water... to widely varying degrees. It has often been estimated that 1% of the discharge points represent 90% of total emissions. That is why the identification of the sources, the activities and the transfer channels contributing most to overall pollution is an essential factor in efforts to set priorities for the preservation and restoration of the chemical status of water. With that in mind, Onema has supported Ineris since 2010 in formulating a simplified method to draw up inventories of emissions to surface waters, intended initially for the Water agencies. This method *(A. Gouzy, Ineris)* produces emission inventories for each substance, expressed as annual flows. The method consists of adding two types of emission values for entire regions.

The first type is for emissions for which measured values are available. That is the case for most point-source emissions (industrial sites not connected to treatment plants and WWTPs), listed in the annual reports required by the EC 2006/166 regulation or measured during specific monitoring campaigns (see section 1.3.). This data is collected and compiled.

Figure 2. Diagram showing the various channels by which micropollutants reach surface waters. ***(Source: A. Gouzy, Ineris, diagram modified from original by http://weiss.vmm.be)***



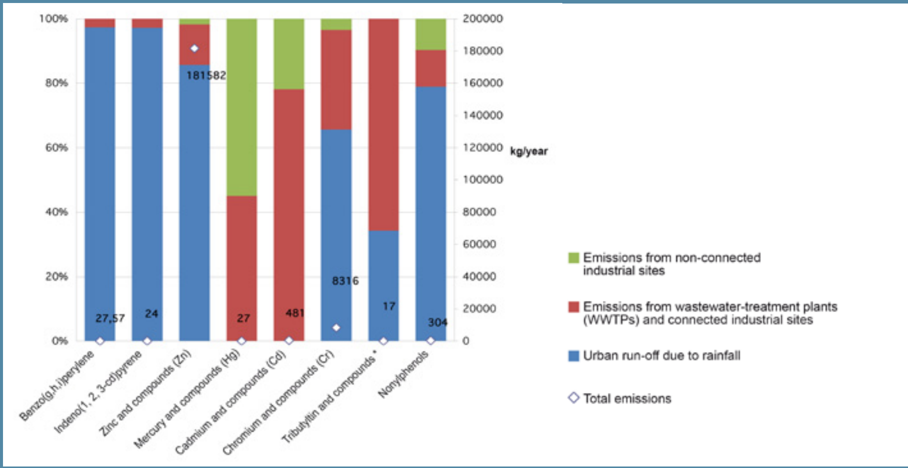


Figure 3. Example of results obtained by the Ineris emission-inventory method. Sources of emissions in the Saône River basin for eight contaminants. ***(A. Gouzy, Ineris)***

Estimates are made for emissions for which no *in situ* measurements are available:

- either via a very general approach, e.g. for run-off rainwater, it is possible to run calculations using the quantities of run-off water and the median concentrations of pollutants observed in this type of sample;
- or using statistical correlations (called emission equations), to calculate the flow of substances on the basis of known emission data (e.g. the value of suspended matter in a point-source emission) for a given site (industrial site or WWTP).

The entire method and its inherent limits are presented in detail in a technical report published by Ineris in April 2012.

Based in part on statistical processing of emissions, this type of method must be used on sufficiently large geographical areas, e.g. river-basin districts or large river basins. A few examples of method results for the Saône River basin were presented during the symposium (see Figures 3 and 4).

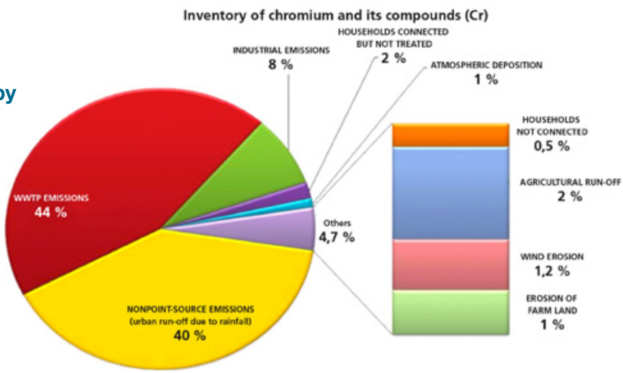


Figure 4. Example of results obtained by the Ineris emission-inventory method. Origin of emissions containing chromium and its compounds in the Saône River basin. ***(A. Gouzy, Ineris)***

At this point in its development, the method is operational. The initial surveys are being run by the Water agencies and will serve later in defining strategies to reduce pollutants. A number of improvements to the method are currently under study. They will deal with more precise identification of nonpoint sources, notably due to rainfall, with refinements in the emissions equations and with the inclusion of new sources, e.g. run-off of rainwater in non-urbanised areas, soil erosion, non-treated household emissions, etc.

1.2 – More work required on transfers of polluted water in urban areas

Urban areas comprise a wide array of human activities, e.g. households, transportation, hospitals, industry, trades, etc., and an equal number of potential sources of chemical pollution. Ranging from organic matter to heavy metals, from plasticisers to hydrocarbons, a wide variety of substances are emitted to the atmosphere of the city or deposited in the soil, on roads and roofs. During rainfall, the substances are rapidly carried away by run-off water and generally removed via drains where they mix with wastewater if the networks are not separate. Following a heavy rainfall, this excess load of pollutants made up of wastewater and rainwater saturates the networks and treatment plants which let it simply overflow to aquatic environments without any treatment. In such cases, it constitutes a major source of water pollution, as was shown by the pollutant inventories for the Saône River basin, presented in section 1.1.

Control over urban emissions, a major factor in the preservation of aquatic environments, has been regulated since May 1991 by directive EC 91/271 on urban wastewater treatment, which requires the use of rigorous treatments for towns with more than 10 000 population equivalents discharging to a sensitive area (areas stipulated by ordinance on 31 August 1999) and secondary or simply appropriate treatment for other towns. Since 1992, its implementation has absorbed almost half of all the subsidies granted each year by the Water agencies (information supplied by the Ecology ministry). The directive targets carbon pollution, nitrogen and phosphorus, i.e. it does not

directly concern micropollutants, but certain substances may be eliminated in the process.
However, a great deal of work is still required to better identify the different sources of chemical contaminants in urban areas, their transfer channels to natural environments and, above all, the technical and political means to improve their management.

An in situ campaign on emissions from the trades

In the framework of the 2010-2013 Micropollutants plan, a study by the CNIDEP (National innovation centre for sustainable development and the environment in small companies) attempted to characterise the emissions of hazardous pollutants released by artisanal companies. Launched at the end of 2011, this study *(M.-P. Fischer, CNIDEP)* focussed on ten sectors selected in conjunction with the Water agencies, namely auto shops, printing, the painting business, dry- and wet-cleaning, careening, denture manufacturers, hair dressers and animal groomers, cleaning services, façade cleaning and stripping, and finally the wood industry. The study consisted of attempting to detect *in situ* 68 hazardous substances in the emissions of a group of companies representing each sector. The study was financed by Onema. A report on the first phase of the study, addressing the first four sectors mentioned, was presented during the symposium. For example, in the auto-repair shops, samples were taken of the water used to wash floors, wash cars, and of the water and solvents used to clean paint sprayers in four different companies. Among printers, six small to mid-sized companies were audited, of which some were equipped with chemical-free prepress units, others with "low chem" or "high chem" units. Samples were taken of water used to wash floors and for prepress and wetting operations.

During the first phase, a total of 22 companies were audited and 52 samples were taken, of which 41 had been analysed before the symposium. The initial results provided useful information. Of the 68 substances for which analyses were run, approximately 50 were quantified at concentration levels greater than ten times the limit of quantification (LOQ). Hydrocarbons were quantified in 97% of the samples. Other frequently quantified substances included phenols (84% of samples), phthalates (79%) and organohalogenated compounds (76%). Some 30 substances were quantified at over 100 times the LOQ. The study continued in 2013, notably for the six other economic sectors, and a complete report is expected in the beginning of 2014.

A call for projects in 2013

Going beyond this highly targeted study, a systematic effort must be made to identify and set priorities for critical micropollutants in water from cities, but also to devise solutions to avoid or reduce their discharge into collection systems and the resulting effects on water resources. That is the objective of the call for projects titled Innovation and changing practices, launched jointly by Onema and the Water agencies in June 2013 *(P.-F. Staub, Onema)*. With a total funding envelope of up to ten million euros, the goal of the programme is to create a dynamic networking effect on the national level through the creation of "project" consortia bringing together locally for periods of up to five years various stakeholders, including local governments, industrial companies, the trades, laboratories, engineering firms, competitiveness clusters and other entities capable of contributing to putting the project together. The desired solutions span all aspects of the problem spectrum, ranging from changes in the habits of consumers and professionals to urban systems for the management of rainwater run-off, from methods to measure the flows of micropollutants to proposals for substitution products. Applications and all the necessary information are accessible on the Onema site (www.onema.fr/Appel-a-projets-Micropolluants-dans-les-milieux-aquatiques).

The calls for projects on the Onema site.

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1.3 – Ways and means to improve treatment of wastewater

Approximately 18 600 wastewater-treatment plants (WWTPs) exist in France. In 2008, they treated over 7 billion cubic metres of wastewater, i.e. untreated household wastewater, effluents from connected industrial sites and rainwater run-off (data from SOeS, 2008). Following treatment, 88% of the water is discharged to surface waters. Characterising the pollutants in emissions and improving treatment systems thus constitute important factors in reducing the pollution of aquatic environments and are the topics of a major public R&D effort in France, undertaken notably at Irstea. This section sums up a panorama of that work presented during the symposium.

Very incomplete elimination of micropollutants

A majority of French WWTPs were constructed after 1970 and over half after 1995. They differ significantly in their treatment capacities with 6% having a capacity greater than 10 000 PE (population equivalents) and handling over 80% of the treated volumes, whereas over 50% have capacities of less than 500 PE. They also differ in design and offer different treatment levels. Primary treatment eliminates mechanically (filters or decantation) certain types of suspended matter and oils. Secondary treatments (biological and physical-chemical) further reduce organic matter and mineral substances suspended in the water. Finally, tertiary treatments implement more or less sophisticated techniques such as sand filtration, natural basins, ozonation, activated-carbon filtration, reverse osmosis, etc.

Current WWTPs are designed to treat macropollutants (nitrogen, phosphorous, etc.) and their results in eliminating micropollutants vary considerably. The Ampères study, run by Irstea and Suez-Environnement in 2007 and 2008, looked at the performance of 21 WWTPs of different designs in eliminating 127 substances (WFD priority and emerging substances). The results are available on a special internet site (https://projetamperes.cemagref.fr/). On the whole, 50% of the substances quantified at input were significantly eliminated (over 70%) by the secondary treatments, notably metals, hormones, analgesics and PAHs. On the other hand, several substances (polar pesticides, certain pharmaceuticals, nonylphenol ethoxyacetic acid) were not affected by standard treatments. Elimination rates of over 70% are however achieved for certain difficult substances by additional, advanced techniques such as ozonation, activated-carbon filtration and reverse osmosis. Launched on the heels of the Ampères study, the national ARMISTIQ project *(M. Coquery, Irstea)* consists of assessing and improving our knowledge of and control over treatment technologies for priority and emerging substances present in the sludge and water discharged from WWTPs. This partnership programme, funded by Onema and managed by Irstea, in conjunction with the University of Bordeaux and Suez-Environnement, assesses the elimination of micropollutants by test installations in certain WWTPs or by full-scale WWTPs. A number of aspects are addressed, namely *in situ* and lab trials on different combinations of **"intensive"** (sand filtration, activated-carbon filtration, ozonation, etc.) and **"extensive" tertiary treatments** (planted discharge zones, filtration using adsorbent materials), optimisation of existing processes for **activated sludge**, and finally an assessment of different **techniques to reduce hydrophobic micropollutants in sludge** so that it can be used as fertiliser.

This important programme produced a number of scientific and technical advances, as well as progress in the methods employed. Two PhD thesis are currently being completed and a number of scientific and technical articles have been submitted for publication, a feedback symposium will be held in February 2014 in Lyon and practical guides will also be edited. All the work undertaken, the methods employed and the documents produced are presented in detail on a special internet site (http://armistiq.irstea.fr/armistiq/).

Irstea is working on adapting sophisticated water-treatment techniques to the overseas context. The photo shows a planted filter (reeds) at a wastewater-treatment plant in Macouria (Guiana).

Specific work on non-collective sanitation systems in the overseas territories

In addition to the ARMISTIQ project, a set of studies *(C. Boutin, Irstea)* is currently under way to characterise the quality of untreated wastewater, assess the effectiveness of different existing treatment processes and develop new processes suited to an array of situations. Particular attention is paid to small and mid-sized local governments whose WWTPs often do not offer high performance levels. One study looked at the quality of untreated wastewater in areas with less than 2 000 PE (83% of WWTPs). Using a database comprising 20 000 data points supplied by the Water agencies, statistical analysis showed that untreated wastewater varies considerably, in terms of both its composition and quality. In light of the growing number of innovative techniques, the EPNAC work group assesses new sanitation processes for small and mid-sized local governments and produces guides on water and sludge treatments to assist them in making a selection among the new processes. All of the guides are available on the internet (http://epnac.irstea.fr/).

Further work produced improvements in drying beds planted with reeds that have been used since 1990 to treat biological sludge. They were modified for treatment of septage by setting up and monitoring over

a period of six years a set of semi-industrial pilot systems *(Vincent, 2011)*. Another study looked at the possibility of using the above techniques in the very specific context of the overseas territories with their particular topographies and climates, and the sensitivity of their ecosystems, to say nothing of their long overdue implementation of European wastewater policies. A set of technical decisions was validated on the basis of *in situ* monitoring systems in full-scale installations. Non-collective sanitation systems, which in 2008 concerned over one-third of all French towns and five million homes, were also studied *(Portier* et al.*, 2012)* in view of transferring and adapting techniques used for collective sanitation. A network of partners addressing this topic was set up, including the SPANC (public non-collective sanitation service), the Water agencies and the departmental councils. The results of this work will be presented in a guide comparing the authorised systems.

Finally, it is interesting to note that homes without any sanitation system, i.e. where the wastewater is discharged directly to the environment, have practically ceased to exist in France in that they represented only 1% of the population in 2008, compared to 17% in 1998 (Source: SOeS).

1.4 – Enhanced monitoring of aqueous discharges from industrial sites

Over the last century, industrial sites, both those connected and not connected to a WWTP, represented a major source of the micropollutants released to water, which led to acute cases of pollution that were still frequent in the 1980s. At about the same time as the launch of the WFD, particular attention was paid to monitoring and reducing industrial emissions of pollutants via campaigns (RSDE) to detect hazardous substances in water. An initial five-year national campaign (RSDE1) was launched in 2002 by the public authorities to detect 106 chemical substances or groups of substances in the emissions of over 3 000 industrial sites. The campaign resulted in an improvement in the work of the analysis labs for the concerned substances and produced new knowledge on the sources of point-source emissions, notably by identifying the main economic sectors releasing each type of substance. The report on the campaign was published in

January 2008 and may be found on the special RSDE internet site (www.ineris.fr/rsde/).

The above efforts were pursued and amplified in the framework of the 2010-2013 Micropollutants plan. The RSDE2 programme, carried out with Ineris for the Ecology ministry, is taking an in-depth look at the point-source emissions of chemicals from approximately 3 500 regulated installations for environmental protection (ICPE) that require special authorisations. Approximately 40, highly diverse economic sectors are involved, e.g. agri-food companies, chemical firms, metallurgy, paper mills, waste treatment, glass manufacturers, pharmaceuticals, power stations for electrical generation, etc. The process involves three steps. “Initial monitoring” comprises six monthly measurement campaigns to detect a set of substances determined in advance and depending on the economic sector of the site. If necessary, the monitoring becomes “long term” and a measurement is carried out each quarter for the substances actually detected in the emissions from the site. If the flows are deemed significant, an action plan is set up to reduce the emissions in conjunction, where necessary, with a technical-economic study of the site.

A progress report on the programme was presented during the symposium *(E. Ughetto, Ineris)*. In March 2013, 3 077 sites had undergone the initial monitoring (out of 3 492 listed in the official documents), representing 22 239 samples and approximately 600 000 analyses run by 147 laboratories. All sectors included, a total of 35 substances were quantified on over 25% of the sites, notably eight WFD priority hazardous substances and 11 priority substances (see Figure 5). For example, nonylphenols were quantified in the emissions of over 90% of the sites. Fluoranthene, naphthalene and chloroform were quantified on at least 60% of the sites.

At this stage in the programme, the number of sites placed under long-term monitoring for at least one substance varies widely between the economic sectors, with 54% of the audited sites in the paper-cardboard sector, 35% in the surface-treatment and coatings sector, but only 4% in the wine-growing sector. For the same sectors, the percentages of sites subjected to a study in view of reducing emissions were 28%, 17% and 2% respectively.

The benefits that may be expected from this programme are numerous and important. By providing countrywide

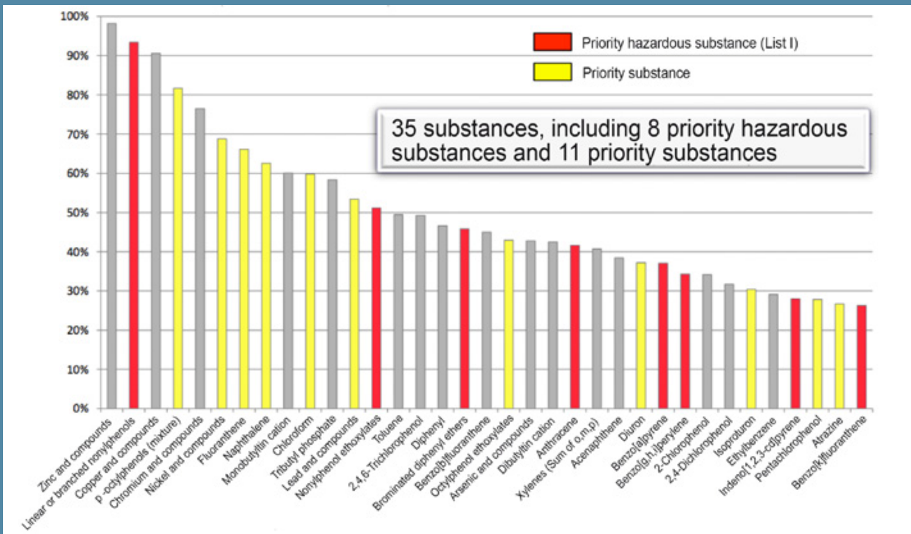

Figure 5. Preliminary results of initial monitoring in the RSDE2 programme showing the substances quantified on over 25% of the inspected sites, all economic sectors included *(E. Ughetto, Ineris)*.

data on the contribution of each industrial sector, it will be possible to set priorities for reducing emissions on the scale of each river basin and nationally. The simultaneous progress made in characterising non-ICPE (regulated installations) contributions will also be of help in setting priorities (by better determining the relative shares of emissions to the environment, in conjunction with the emissions inventories discussed above). Studies on reducing emissions, organised by the April 2011 ministerial document, and implementation of the corresponding action plans will constitute a more direct means of avoiding the discharge of significant quantities of pollutants to aquatic environments. For example, in one of the economic sectors, the flow of metals (Zn, Ni, Cu, Cr) that could be avoided amounts to 8.5 kilogrammes per day. For the same sector, it has been estimated that the release of 16 kilogrammes of organic substances (primarily chloride and methylene) to the environment could be avoided each day.

Other studies on individual industrial sectors (by the professional federations and/or technical centres) attempt to identify the processes in which the quantified substances are used and to devise solutions to reduce or eliminate them, notably by using other processes.

The goal is to provide relevant data to each industrial sector that must then carry out the necessary technical-economic studies. This type of study has already been run by CETIM (technical centre for the mechanical industries) on two sub-sectors, i.e. the metal-working sector and the surface-treatment and coatings sector. With funding from the Water agencies, the basic data for the study *(P. Sire, J. Kirmann, CETIM)* consisted of the initial RSDE monitoring and the answers made to a questionnaire by almost 500 industrial companies. The study identified 150 correlations between industrial processes and substance discharges. Concerning nickel, for example, several surface-treatment processes would appear to have caused emissions, e.g. aqueous degreasing by chemical means (acid), chemical pickling (HF, HF- NO3), tribofinishing and vibratory grinding, non-conventional machining with products containing the corresponding substances.

Some of these correlations will be confirmed by further questioning of the industrial companies and their suppliers, others will require *in situ* studies, similar to those already launched for seven sites in order to determine the origin of quantified discharges of chloroform, nonylphenols and octylphenols.

The Descartes paper mill, Indre-et-Loire department, France.

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2 Improving the assessment of


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environmental contamination and its impacts

Upstream efforts to reduce the sources of pollution go hand in hand with better information on the presence of micropollutants in water, their fate in ecosystems and their impacts on aquatic environments, on the species dependent on those environments and on human health.

Over the past ten years, WFD implementation has been a source of significant progress in this field. The legal assessment system for the chemical status of water bodies is based on systematic efforts in the monitoring networks to detect a set of substances for which the list (WFD Annex X and the daughter directives) is periodically updated (the last update took place in mid-2013).

In France, analyses focus on 53 substances or groups of substances, namely 21 WFD priority hazardous substances, for which emissions must be eliminated by 2018 or 2021, 24 priority substances for which emissions must be reduced (initially by 30% in 2015 compared to 2004), finally eight “Annex I” substances for which emissions must be reduced by 50% by 2015. In addition, France also decided to systematically monitor nine “specific pollutants for ecological status”.

In step with its upgrades, this system for systematic monitoring has come to represent a significant scientific and technical effort, with the development of field protocols and analysis methods, progress made on understanding the effects of substances on environments, the formulation of environmental quality standards (EQS, for concentrations in water, sediment or biota that should not be exceeded in order to protect human health and the environment) (see section 2.2.), etc. The work to improve assessments of water status will continue for years to come. Recent progress in this field was presented during the symposium and is the topic of this second section.

2.1 – The contribution of passive samplers to measuring concentrations

The first challenge in assessing the chemical status of water bodies lies in measuring the concentrations of each substance, in water, of course, but also in sediment and in the tissue of living beings (the biota), as the case may be. For the WFD, measurements are carried out in different monitoring networks spread throughout the country for surface waters (rivers, lakes), groundwater and littoral waters. In France, two networks for surface and littoral waters play different roles. The RCS surveillance-monitoring network comprises over 1 900 monitoring points and informs on the general status of water, whereas the RCO operational-monitoring network comprises 4 553 monitoring points located at spots where good status is at risk of not being reached. It monitors the status of these water bodies and the effectiveness of the corrective measures. For groundwater, the RCS network comprises 1 800 monitoring points and the RCO network 1 500 (including 860 serving both networks). In addition, there are 1 700 quantitative measuring points (piezometric sensors).

Periodic measurements for all the monitored substances at each monitoring point represent a considerable effort in terms of sampling and analysis. Given the volumes involved, routinely obtaining quality data at an acceptable cost represents a major challenge. Traditional analysis methods based on discrete samples may lack in reliability due to the high variability over time of concentrations of certain substances. For example, the results at a given monitoring point may differ depending on whether the measurement took place just before a storm causing high urban run-off or just after. Similarly, for agriculture, pesticide concentrations in aquatic environments are closely linked to spraying dates.

To avoid these difficulties, the use of passive samplers, which continuously integrate even minute quantities of pollutants, over a given time period, may represent a useful solution for monitoring networks. A number of passive sampling devices have long been used for specific research projects. From 2008 to 2012, Ifremer tested their potential usefulness in a series of large-scale WFD campaigns in coastal waters along the Mediterranean coast, off Corsica and in the overseas territories *(J.-L. Gonzalez, Ifremer)*. Three complementary techniques were used. **POCIS (polar organic chemical integrative sampler)** units, originally developed by the U.S. Geological Survey and adapted by University of Bordeaux, are based on the adsorption of pollutants in a microporous membrane. When submerged in water, they provide an integrated measurement over time of hydrophilic organic contaminants (certain pesticides, pharmaceutical and veterinary compounds, etc.). Hydrophobic organic contaminants (PAHs, PCBs, PBDEs, certain pesticides, etc.) were measured in a lab using the **SBSE (stir bar sorptive extraction)** technique where the dissolved molecules are extracted by a polymer-coated magnetic bar. Finally, concentrations of trace metals (cadmium, cobalt, copper, nickel, lead, zinc, etc.) were measured using the **DGT (diffusion gradient in thin-films)** technique.

Passive sampling consists of placing membranes in the water column that trap micropollutants over periods ranging from a few days to several weeks. The samplers are then transported to the lab for analysis to determine the contamination level of the environment. The results represent the actual situation better than discrete samples.

The campaigns run from 2008 to 2012 using these three techniques measured concentrations of hydrophilic and hydrophobic contaminants and of trace metals in over 200 different water bodies along the Mediterranean coast, in Guiana and on the islands of Réunion, Mayotte and Martinique. The analyses targeted contaminants affecting the chemical and ecological status of water as per the WFD, as well as other metals and organic contaminants (pharmaceutical residues, PCBs, emerging substances, etc.), i.e. a total of approximately 140 substances. The results revealed, for the first time in coastal and lagoon environments, the presence of certain herbicides, fongicides, pharmaceutical products and alkylphenols. Metals and organic compounds were also measured at very low concentrations on the ng/L level. For example, the SBSE sensors used along the Mediterranean coast revealed that, at virtually all the monitoring points, naphthalene (originating primarily from heating systems using wood or forest fires) represents almost all the measured PAHs and that no measurements exceeding quality standards were noted for this group of substances. On the other hand, concentrations of hexachlorocyclohexane isomers exceeded quality standards (EQS, 2 ng/L) in one-half of the water bodies analysed (see Figure 6). Concentrations of endosulfan exceeded EQS values at 14 of 34 monitoring points. In general, the risks of water bodies not achieving good status were due to four types of contaminants, namely copper, endosulfan, cyclodien insecticides and lindane isomers. The results of the 2012 campaign are still being processed.

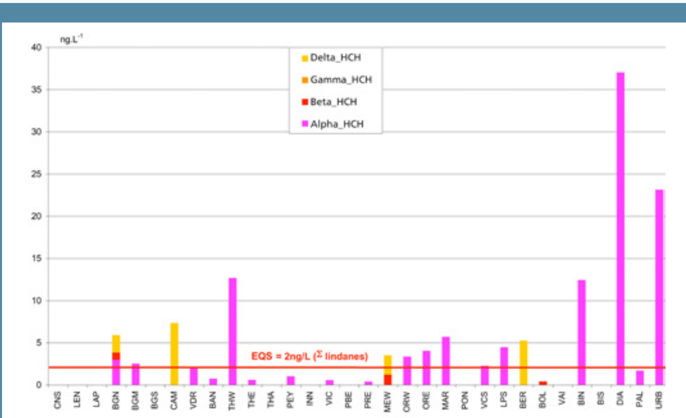


Figure 6. Example of results from the Ifremer measurement campaign using passive samplers showing the concentrations of hexachlorocyclohexane in lagoons along the Mediterranean coast *(J.-L. Gonzalez, Ifremer)*.

In terms of the methods employed, these campaigns confirmed the value of continuing to work on the technical-economic feasibility of passive samplers for routine monitoring, notably for the WFD monitoring networks. Passive samplers are suited to both freshwater and saltwater environments, however they are still undergoing additional development work to make them easier to use in the field, to limit certain biases and to make progress toward partial automation of data processing. Work must also be put into increasing the number of measurable contaminants, particularly among the priority substances, e.g. mercury quantification using the DGT and/or SBSE techniques, tributyltin quantification using the SBSE technique, etc. Finally, another important aspect concerns expanding the use of passive samplers to detect pollutants in other environments and above all in sediment.

2.2 – Better threshold values to assist in interpreting monitoring data

At what concentration in water or sediment does the presence of a given substance (or group of substances) constitute a danger for aquatic environments and for human health? More generally, how should the monitoring data on water bodies be interpreted for assessments of chemical status? For surface waters, the WFD made EQSs (environmental quality standards) the key factor in assessments. these legally-binding threshold values are defined as "the concentration of a particular pollutant or of a group of pollutants in water, sediment or biota which should not be exceeded in order to protect human health and the environment". EQSs are formulated on both European and national levels according to EU rules (see *Technical Guidance for Deriving Environmental Quality Standards under the Water Framework Directive*, 2011) and regularly revised. The EQS for a given substance must cover five protection objectives:

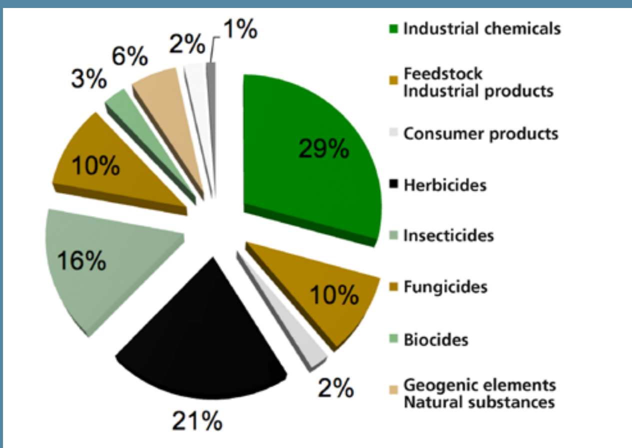
- protection of pelagic organisms (open waters) in conjunction with acceptable concentration limits in water, determined by ecotoxicity tests;
- protection of benthic organisms living in or on sediment in conjunction with acceptable concentration limits for this compartment. Concentration limits are determined by ecotoxicity tests or through modelling using the partition equilibrium coefficient of substances in the solid and dissolved phases;

- protection of higher predators against “secondary poisoning” (by consuming contaminated preys), which requires a concentration limit in the prey;
- protection of human health for people consuming fish and seafood, which requires another concentration limit in the animals consumed;
- finally, protection of human health for water consumption, in conjunction with standards for drinking water.

For each of the above five protection objectives, the concentration limits determined by the data on substance effects are lowered by an extrapolation factor to compensate the lack of knowledge on the ecotoxicity of the considered substance, e.g. its toxic effects over the long term, toxic effects on other, potentially more sensitive species, extrapolation of effects to the natural environment based on data acquired in the lab, lack of information on the food web as a whole, etc. The final EQS corresponds to the lowest of the five concentration limits.

Assessment of the chemical status of surface water then takes place according to the “one out - all out”

Figure 7. Breakdown by usage of all proposed EQS values (i.e. not yet adopted) suggested by Ineris to date for major chemical substances.



rule, whereby if one substance exceeds the applicable EQS, the status of the water body is judged “bad”. The system is different for groundwater where threshold values for each substance are set nationally and are based on standards for drinking water or, failing that, on WHO standards.

Setting more relevant EQSs

In France, applicable EQSs are listed in the ordinance dated 8 July 2010 for priority substances and in the ordinance dated 25 January 2010 for pollutants affecting specifically the ecological status. All validated values are listed on the Ineris Chemical substances internet portal, under the Environment tab. However, the monitoring system is undergoing constant changes. The lists of substances requiring monitoring and assessment methods are regularly updated while, in parallel, research work is carried out to improve our understanding of the effects of substances on ecosystems and organisms in order to produce more relevant EQSs. For the period 2008-2013, Ineris provided Onema with 181 EQS proposals *(S. Andres, Ineris)*. These values are called “EQS proposals” as long as they have not been transposed into law. They are validated by groups of experts and cover substances for which monitoring has produced useful results in France (they are listed notably in the ordinance dated 30 June 2005 concerning the “national action plan against pollution of aquatic environments by certain hazardous substances”).

Among the main lines of work in view of improving the relevance of EQSs, **the conversion of threshold values from one compartment to another**, e.g. water to biota or sediment to biota, is a major management issue and a complex scientific challenge. What is the relation between a substance concentration measured in sediment and that measured in the muscular tissue of fish? Starting at what threshold values in sediment is there a risk of exceeding applicable health standards for the consumption of fish by humans? Progress has been made in this field in the framework of the national PCB action plan and is presented in section 2.4.

Other work carried out by Ineris targets better assessment of the toxic risks caused by certain metals dissolved in aquatic environments.

The metals are present in different forms in water, depending on the physical-chemical conditions in the environment, and only some can have a toxic effect on organisms. The objective is therefore to formulate EQSs for the "bioavailable fraction" and not for the total concentration of dissolved metal. This work is presented in section 2.3.

Finally, though still emergent, an essential line of work concerns the **effects of mixtures of chemical substances** on the environment and organisms. Current EQSs generally address the effects of a substance taken individually, however it is now widely acknowledged that contaminants do not produce toxic effects independently of each other, but rather via numerous interactions and synergies, known as the "cocktail" effect. To enhance assessments, Ineris now produces EQS proposals for groups of chemical substances and for metabolites (by-products of degraded substances in the environment), notably pesticides. Integrative tools, e.g. bioassays and biomarkers, are also being developed to characterise the effects of mixtures of chemicals on living beings (see section 3.3.).

2.3 – Targeting the bioavailable fraction of metallic contaminants

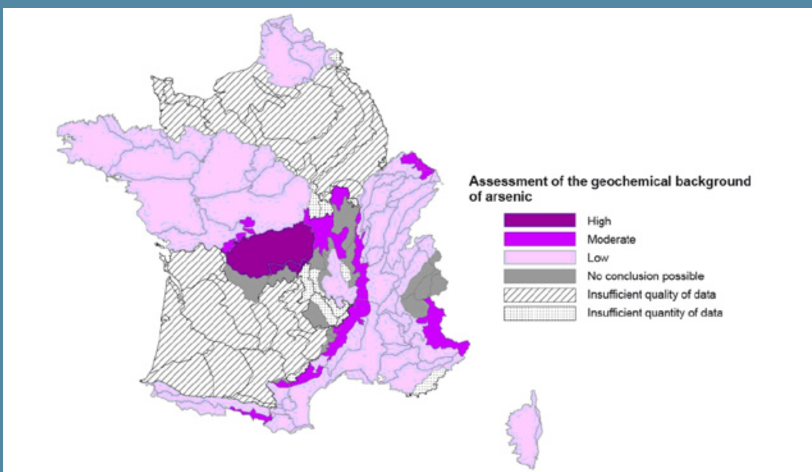
Metallic trace elements, notably cadmium, chromium, copper, lead, zinc, nickel, tin, mercury, etc., are present naturally in minute quantities in the Earth's crust and in natural environments. Many are indispensable for certain biological processes, similar to iron which is a component of hemoglobin. However, these elements have been massively released to the environment by human activities and also have negative effects on organisms. In some forms, they can be assimilated by living beings and produce a toxic effect. For example, hexavalent and trivalent chromium are much more toxic than other forms of the metal.

It follows that in efforts to assess the chemical status of environments, the formulation of relevant EQSs for trace elements is confronted with a two-fold difficulty *(L. Geoffroy, Ineris)*, namely it must take into account the **geochemical background** (the natural presence of metals in the environment) and target the **bioavailable fraction** of the metals (the part of the total concentration likely to produce toxic effects).

Over the past five years, Onema has funded and coordinated a number of research projects on these two topics. For example, BRGM developed an assessment method for the geochemical background of trace metals in the groundwater of continental France. Ifremer carried out measurement campaigns in the coastal waters of the overseas territories and determined the background values for the four priority metals targeted by the WFD, namely cadmium, lead, nickel and mercury. Finally, Irstea recently started work to assess qualitatively the impact of the geochemical background on the quality of continental surface waters in France (see Figure 8).

In parallel, new EU regulations were adopted in view of taking into account only the bioavailable fraction of trace elements. New "generic" EQSs, corresponding to high levels of bioavailability, have since been adopted (EU 2013/39) for nickel and lead. The threshold values for nickel were reduced from 20 µg/L to 4 µg/L and for lead from 7.2 µg/L to 1.2 µg/L.

Figure 8 : Map showing the geochemical background of arsenic. *(A.Chandesris* et al., *Irstea-Onema 2013)*.



However, these set values are not suitable for a precise assessment of the contamination of aquatic environments because the bioavailability of a trace metal for aquatic organisms (algae, small pelagic crustaceans and fish) and its toxicity vary depending on the physical-chemical parameters of each site. For some metals, bioavailability is determined by "simplified BLM" models (biotic ligand models, see Figure 10) integrating information on the speciation of the dissolved metal and its reaction on the surface of biological membranes (e.g. the gills of fish) in order to predict the toxicity of the metal. For nickel, zinc and copper (see Figure 9), these models are used to calculate ecotoxicity on the basis of the pH, the dissolved organic carbon (DOC) and the calcium concentration (due to competitive interactions on the surface of the gills, see Figure 10). For lead, ecotoxicity can be roughly calculated on the basis of the dissolved organic carbon alone. For other metals such a chromium, BLM models are not useful given the complexity of the phenomena involved.

The new regulatory framework offers the Member States the option of adopting a progressive approach to assessing water status for trace metals. If the monitoring data indicate an exceedance with respect to the generic EQSs, the BLM models may be used to obtain a more precise assessment by taking into account the influence of the physical-chemical conditions in the environment, which may, to a certain degree, attenuate the toxicity of the metal (the protective effect of the DOC, the calcium and the H^+ protons). If the overrun is manifest, restoration measures must be taken.

To prepare implementation of this progressive approach in France, Ineris reviewed the literature for all the existing BLM models and has, since 2008, tested their use on the national monitoring data. On the basis of the above work, a guide was published presenting detailed information on good practices and on the changes in monitoring techniques required for routine use of the models. For example, measurements of the parameters required for BLM models (DOC, pH, calcium) must be carried out more frequently and synchronised with efforts to detect the trace metals. These changes will result in more relevant monitoring results for water status because the trace metals for which models are available (zinc, copper, nickel) are currently among those most often leading to "bad" status of water bodies.

Figure 9. Prediction of variations in the toxicity of copper (PNEC = predicted no-effect concentration, in Cu mg/L) as a function of the pH and the dissolved organic carbon (DOC) in fresh water. The higher the PNEC, the lower the ecotoxic potential of the substance *(L. Geoffroy, Ineris)*.

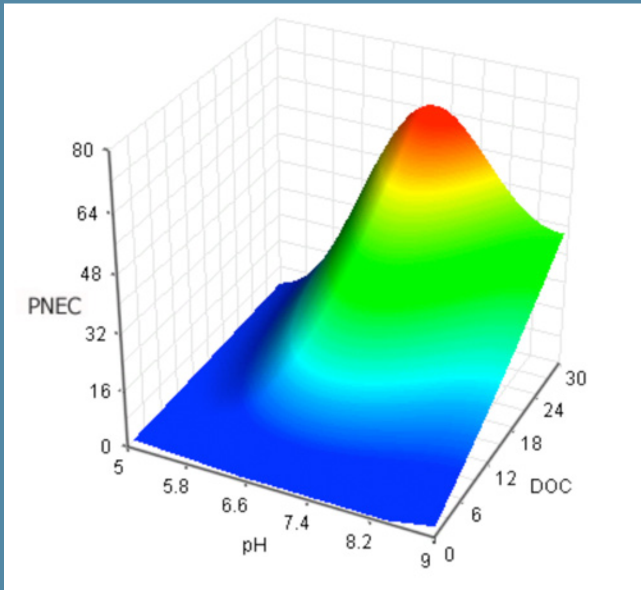
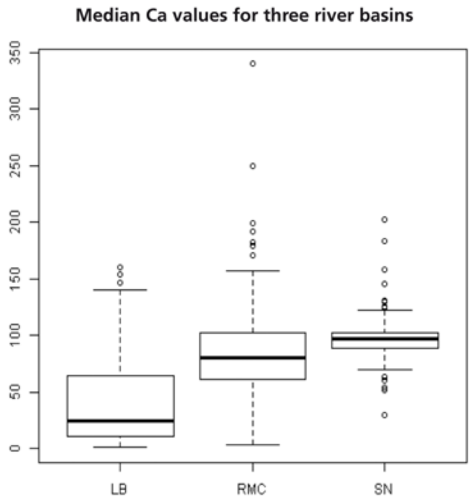


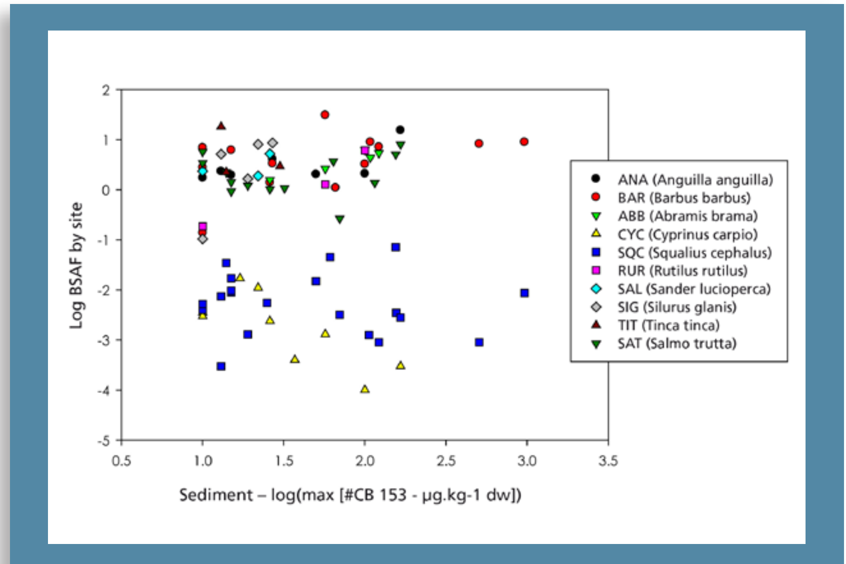
Figure 10. BLM models (biotic ligand models) may be used to take into account protective parameters that vary depending the hydrochemical context, e.g. dissolved calcium whose concentration depends on the geology of river basins. In the graph below, the prevalence of sedimentary zones in the Seine-Normandie basin (SN) results in high calcium concentrations, compared to the Loire-Bretagne basin (LB) where basement formations are more common.



2.4 – Better threshold values to assist in interpreting monitoring data

PCBs (polychlorinated biphenyls) have been forbidden in France for over 20 years, but were used for various industrial applications up to the 1980s and are still present in the sediment of many rivers. These persistent, organic pollutants have clear carcinogen and endocrine effects and contaminate organisms primarily via their food. The national PCB action plan, launched in 2008 following adoption by the EU of new health standards governing the consumption of freshwater fish, has resulted in significant progress in understanding the links between contamination of sediment and that of fish, and the risks involved in the consumption of fish by humans. One of the main objectives of the plan concerned the establishment of thresholds values for PCB concentrations in sediment, above which fish are no longer suitable for consumption. The results of several studies by Irstea in view of setting threshold values were presented during the symposium *(M. Babut, Irstea)*.

Figure 11 : Biota-sediment accumulation factors (BSAF) for species of freshwater fish by site, as a function of PCB 153 concentrations measured in sediment. Species showing high accumulation values are represented by eels (ANA) and river barbel (BAR), those showing low accumulation values are represented by chub (SQC) and common carp (CYC).



High error rates for BSAFs

Between 2008 and 2010, 2 300 samples of freshwater fish were drawn from 300 sites throughout France and the concentrations of 18 PCB congeners were measured in each specimen. This study, the most complete to date in France, confirmed that PCBs contaminate virtually all freshwater fish because they were detected in every batch analysed. However, there were major variations in concentrations from one site to another and between species. Some species have high potential for bioaccumulation (eels, Wels catfish, bream, barbels) while other have fairly low potential (pike-perch, pike, roach, chubs). Using this data, a large-scale effort was made to link PCB concentrations in sediment to concentrations measured in the tissues of fish using biota-sediment accumulation factors (BSAF, see Figure 11). Defined as the ratio between the contaminant concentration in the biota (standardised as the percentage of lipids in tissues) and that in sediment (standardised as the concentration of total organic carbon), the BSAFs were calculated for each species and each site. The result was a distribution of BSAF values for each fish species. This simple approach was used to propose (based on the third quartile of BSAF values for barbel, for all sites) a concentration limit in sediment corresponding to the legal maximum values in the biota. This method was applied to the data in the national database for PCB contamination of freshwater fish. It correctly predicted “edibility” for only 55% of the fish when the PCB threshold value in sediment was set at 50 ng/g (dry weight) for the sum of the indicator PCBs. A few changes in the method may be undertaken to reduce the error rate, however, it would appear unlikely that reliable threshold values could be set using this approach.

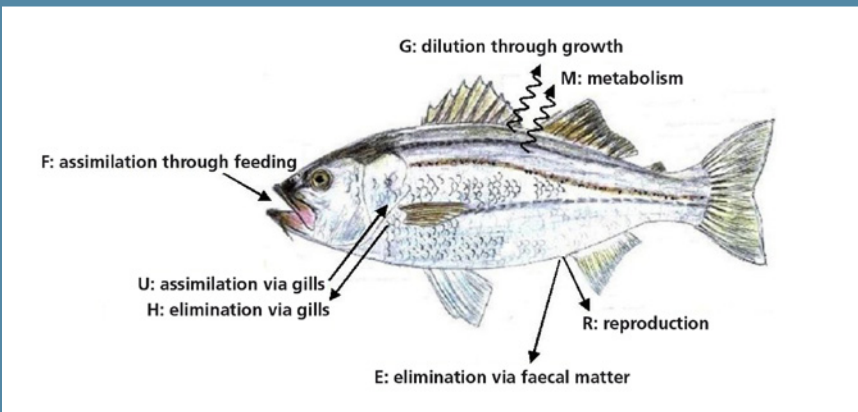
Conclusive modelling results

Another study by Irstea, with support from Onema and the Rhône-Méditerranée-Corse Water agency in the framework of the Rhône plan, analysed the contamination of 135 fish of three species (bream, barbel, chub) and sediment samples from three sites in the Rhône River. Two complementary approaches were used.

The first was a statistical model to link fish contamination to a number of different variables such as the size, mass, sex and age of the fish, the percentage of fatty tissues, the proportion of detritic carbon in its food and, finally, the maximum PCB levels in the sediment to which the fish was exposed during its life. Processing of the data showed that 78% of the total variability could be traced to only three variables, namely the size, proportion of detritic carbon in the food and the maximum PCB concentration in sediment. This method made it possible to back-calculate, for each fish, a maximum concentration in sediment compatible with the legal threshold for human consumption. On the basis of this data, EQS proposals were made. For example, if it is decided that at least 75% of fish must comply with the legal threshold for consumption, then the sum of indicator PCBs in sediment must not exceed 12.7 ng/g (dry weight). To obtain a 90% compliance rate, concentrations must not exceed 5.9 ng/g.

In parallel, using the same data from the field, the research teams developed a physiologically based model for PCB accumulation (see Figure 12). The point of this work was to describe bioaccumulation processes in view of understanding why, on a given site, fish of the same species had different PCB-contamination levels.

Figure 12. Physiological model of PCB accumulation with a diagram of mechanisms involved *(M. Babut, Irstea)*.



The model was formulated to produce a maximum PCB concentration in sediment such that no fish exceeded, at any time, the legal threshold. Depending on the site and the species in question, the resulting values ranged from 2.6 to 14 ng/g (dry weight).

Toward useful values for managers

The three-pronged approach to the PCB action plan made it possible to propose a set of maximum PCB-concentration values in sediment complying with consumption standards for fish. A few values are shown in Table 1.

The simplified approach using the BSAF values would appear to produce an excessively high percentage of type II errors (high concentrations not predicted). The two other methods (statistical and physiological) produced values that were consistent between the two methods. Their results are of great value in view of establishing sediment EQSs that can be used by water managers. They must, however, be tested with other data sets and expanded to include other species and other river basins.

Limited impact of dredging on pollutant mobilisation

In addition to the issue of sediment-to-biota transfer, the national PCB action plan produced results in other fields as well. A study by ANSES

Table 1. Sediment-based threshold values for PCBs derived for the national action plan on PCBs *(M. Babut, Irstea)*.

Approach	Maximum value for sediment (indicator PCB µg/kg, dry weight)	Remarks
Statistical model	5.9 (90% compliance in fish) 12.7 (75% compliance in fish)	10% permissible type-II error 25% permissible type-II error
Physiological model	2.6	100% compliance required at all times
Accumulation factor (BSAF) in the Rhône-Méditerranée basin	26.6	62% accurate predictions. High percentage of type-II errors
Accumulation factor (BSAF) used on national database	50	55% accurate predictions. High percentage of type-II errors

(Agency for food, environmental and occupational health & safety), in conjunction with INVS (National institute for health monitoring), revealed the level of PCB impregnation in the blood of adults consuming river fish in view of identifying the main factors involved in the impregnation. In Lyon, the Axelera competitiveness cluster worked on treating and reusing on land sediment contaminated by PCBs and a technical feedback symposium was organised in July 2012. Another study *(F. Rebischung, Ineris)*, not focussed precisely on PCBs, looked at the effects of dredging operations in rivers and canals. Dredging is required to remove accumulated sediment blocking navigation and may also be used to improve the status of an aquatic environment if the sediment is contaminated. However, it can produce negative effects by churning the toxic substances in the sediment. To determine the impact of mechanical dredging operations on the quality of surface waters, *in situ* monitoring was carried out over the summer of 2010 on dredging in the Lens canal. A set of physical-chemical parameters (turbidity, pH, suspended matter) was measured at various distances (0 to 3 000 metres) downstream of the work. Analyses were run on the concentrations of eight trace metals and on two groups of emerging contaminants, DEHPs and PBDEs. The results showed that the dredging operations had limited impact. Concentrations of suspended matter and contaminants increased significantly (up to 20 times the initial values) at a short distance downstream, however EQS thresholds were not exceeded. Concentrations then decreased rapidly with the distance, due to the deposition of the suspended matter. At one kilometre downstream, the measured values corresponded to the average values of the canal. Though limited in its spatial and temporal coverage, this study would suggest that the risk of pollution caused by dredging is fairly limited compared to the potential benefits of removing contaminated sediments for the chemical status of water.

Spotlight

Limited impact of salinity on groundwater

In addition to organic micropollutants, WFD assessments of the quantitative status of groundwater take into account a range of physical-chemical parameters, from the pH to ion concentrations (Cl-, Ca2+, Mg2+, etc.) and from suspended matter to turbidity. Particular attention is paid to the salinity of groundwater because it is a major cause of degraded water quality throughout the world. The natural mechanisms causing the phenomenon (seawater intrusion, precipitation and infiltrations along coasts, etc.) may be amplified or modified by human activities such as pumping, mining waste, salting of roads, geothermal systems, infiltrations from farms, etc. A study *(W. Kloppmann, BRGM)*, co-funded by Onema, used the data stored in the ADES database between 2005 and 2010 to draw up a status report on aquifers in continental France. The study (see Figure 13) revealed that only 22 water bodies (of the 594 supplying drinking water, i.e. less than 4%) are confronted with troublesome salinity levels, that is those having more than seven wells with chlorinity levels higher than 100 mg/L during the study period. Among the 22 water bodies, 15 were continental, i.e. far from the saltwater wedge. Their salinity levels may be caused by the dissolution of evaporites in sedimentary basins, old sources of seawater or brine, localised industrial sources or other anthropogenic sources. A number of geochemical assessment tools (isotopic methods, radiocarbon dating, etc.) were used on these water bodies to determine the geometry of the water salinity and the age structures of the salt and fresh water in aquifers, in order to produce hypotheses on the causes (natural or anthropogenic) of the salinity. The study also proposed an operational method to assess the salinity and, where necessary, management techniques. A total of three detailed reports were produced and are available on the Onema site.

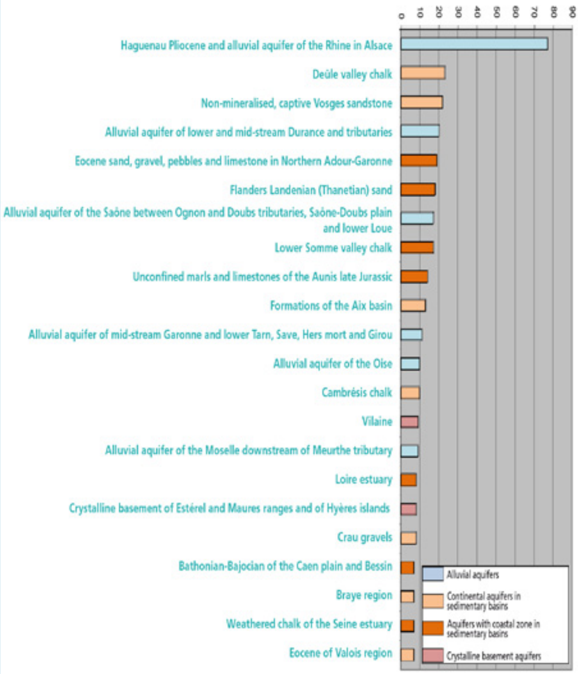
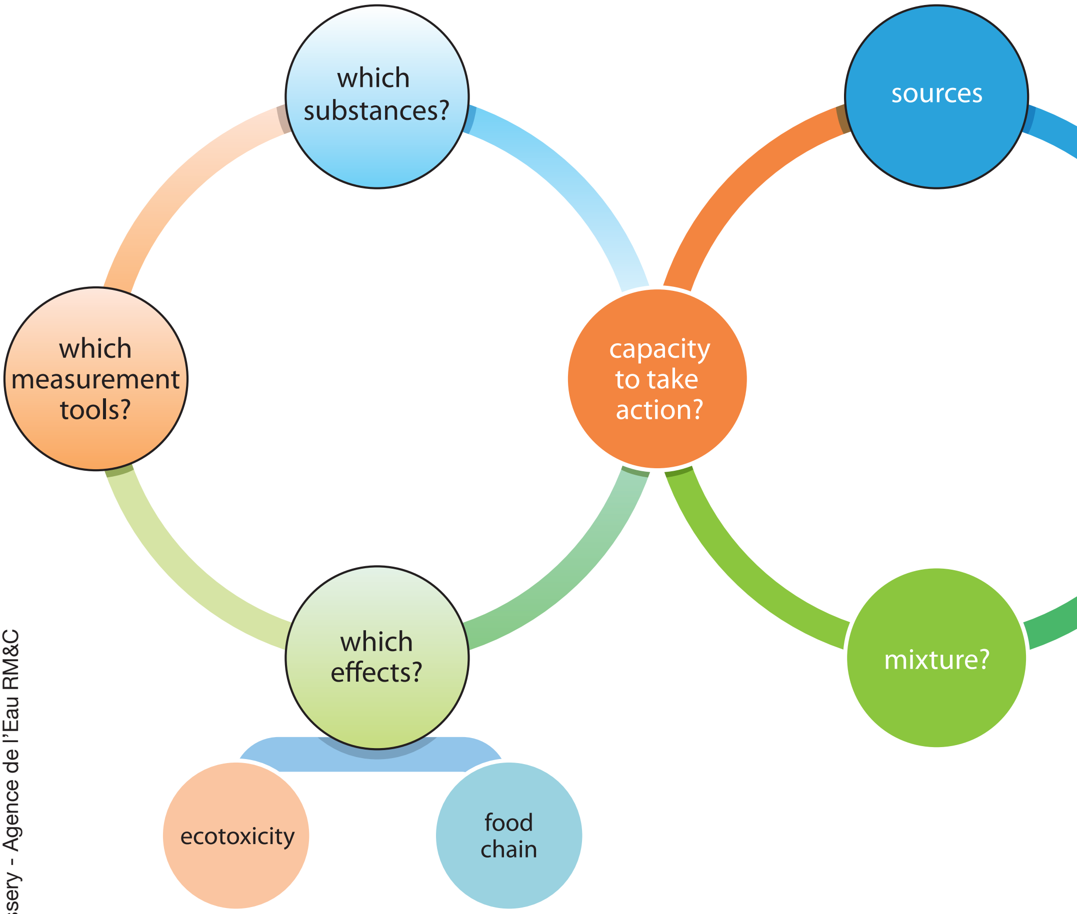


Figure 13. The 22 groundwater bodies confronted with high salinity levels in continental France *(W. Kloppmann, BRGM)*.

3 New substances and new tools to



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prepare for the future

Thanks to the WFD, over the past ten years the Member States have made a considerable effort to systematically monitor chemical substances in aquatic environments. However, this regulatory system is necessarily focussed, for technical and economic reasons, on a limited number of priority substances, currently 52 substances for surface waters in France.

Periodic updating of the lists implies a difficult task of setting priorities on the European level. Over 50% of the candidate substances were refused during the last selection procedure, often due to a lack of information concerning their effects or of sufficiently conclusive exposure data.

In comparison, over 100 000 chemical substances have been or are still produced industrially worldwide. Europe currently produces 30% of those substances and over 3 800 new substances have been registered since 1981 in the European inventory of existing commercial chemical substances (EIECCS).

In light of the threats to biodiversity, the increases in cancer, diabetes, behavioural troubles and endocrine disorders observed over the past 40 years, enhanced attention is now paid to substances termed “emerging” or of “emerging importance”. These relatively ambiguous concepts may apply to very different situations, including 1) substances present for years in environments, but for which analytical methods are not (or were not) available, e.g. PBDEs and phthalates, 2) newly synthesised chemical substances intended notably to replace banned substances, 3) substances whose environmental and/or health impacts are a source of new concern, e.g. nanoparticles, pharmaceutical residues, perfluorinated compounds, chlorinated biocides, etc.

Over the past five years in France, increasing awareness of the risks represented by these substances for human health and aquatic environments has resulted in sustained research efforts, the results of which are presented in this third section. A national committee of experts was set up to identify, using an iterative approach, the emerging substances requiring special attention. For the first time on such a large scale, exceptional campaigns were launched to detect dozens of new substances in continental waters. In parallel, an array of innovative biological tools (biomarkers and bioassays) were developed and used to assess the effects of substances, both individually and in mixtures, on organisms and ecosystems.

3.1 – An iterative approach to identifying and monitoring priority substances

For a given contaminant, the obtention of scientific knowledge on its characteristics and potential effects in the environment is a prerequisite to creating regulations in view of limiting emissions and setting up a monitoring strategy. But in a context of limited resources and given the number of chemical substances likely to affect aquatic environments, research efforts must target those substances representing the greatest health and environmental risks (see Figure 14).

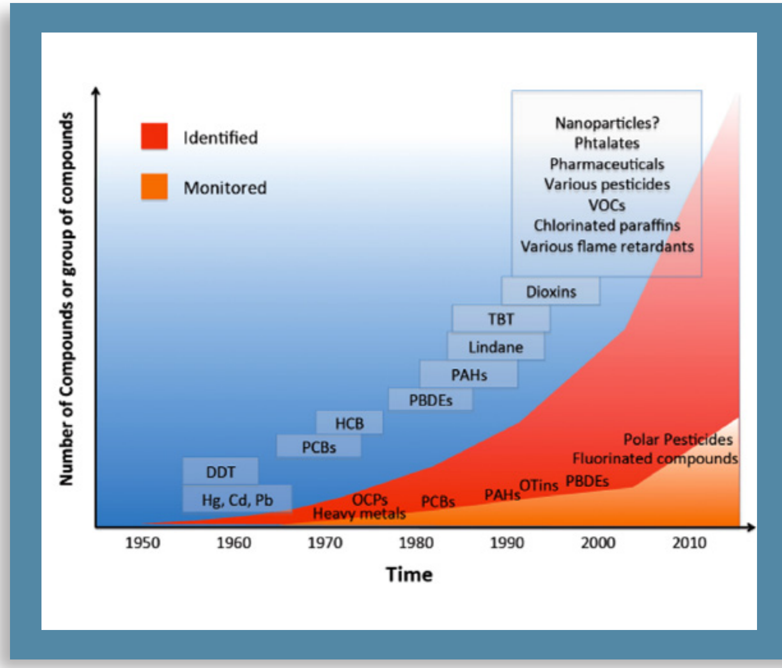


Figure 14. Change over time in the number of monitored pollutants compared to the number of identified pollutants *(O. Perceval, Onema, excerpt from Marine Board-ESF)*.

For the EU as a whole, the Norman network (www.norman-network.net) has since 2005 worked to detect and set priorities for chemical contaminants. Comprising 46 reference labs from 19 countries, the network ensures the exchange of information by creating shared knowledge bases and organising workshops, and working to harmonise the data and methods used.

Created in 2010 in the framework of the 2009-2013 Micropollutants plan, the French equivalent is the CEP (committee of experts on setting priorities), a national organisation charged with selecting the most impressing issues concerning aquatic micropollutants. Among other members, it includes Ineris, Onema, BRGM, Irstea, Ifremer, Anses, University of Bordeaux and the Ecology and Agriculture ministries. In April 2013, the CEP published a method to update the lists of substances (see Figure 15) for which national monitoring is required before determining whether they may be of use for WFD assessments of water status *(V. Dulio, Ineris)*.

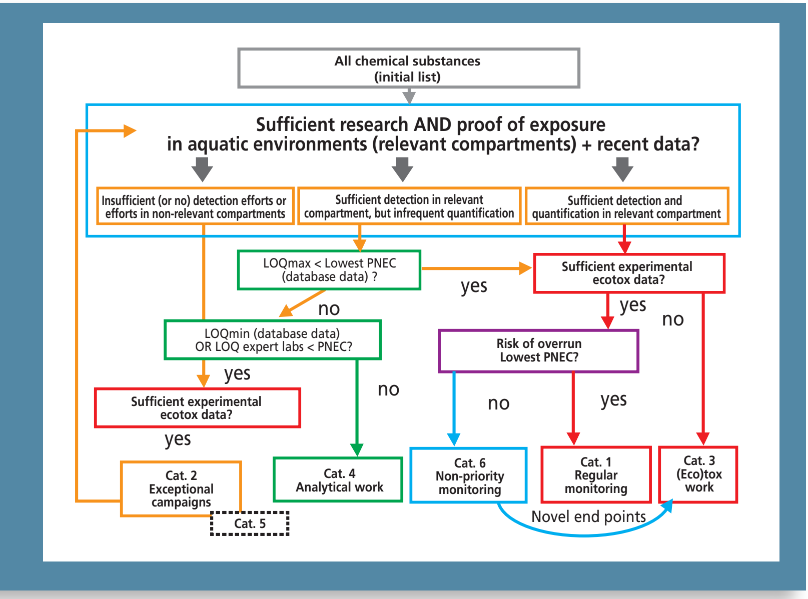


Figure 15. The CEP has developed a procedure to regularly update the list of substances for which research is required. (CEP)

This process produces categories of substances based on the information that is currently not available. A total of six situations are identified. Category 1 (proven exposure of aquatic environments and known risks) groups in particular the substances for which continuous monitoring should be instituted, e.g. the contaminants specific to the ecological status for which lists are established by each country. Category 2 comprises the substances representing a potential risk of pollution, but whose presence in aquatic environments has not been precisely determined in spite of the fact that the necessary analytical tools are available. Exploratory measurement campaigns are required to characterise the exposure level of these environments. Category 4 concerns the substances for which the exposure level of aquatic environments has not been precisely determined because suitable measurement techniques are not available. In this case, work must be put into improving analytical techniques.

This iterative method enabled the CEP in 2011 to draw up the list of substances for the measurement campaign carried out in 2012 (see section 3.2.), the results of which will in turn serve to determine the substances most in need of monitoring (category 1). This transparent procedure, which will be progressively improved, serves as the European model for improvements in knowledge on emerging contaminants and for determining future monitoring needs.

3.2 – Initial assessment of emerging substances in water bodies

Knowledge on the chemical status of water, above and beyond the mandatory monitoring, made considerable progress in France through two national campaigns, in 2011 and 2012, to gain an overview on the presence of emerging substances in all types of water bodies, both surface water and groundwater. The **exceptional campaign in 2011**, managed by the six Water agencies and the Ecology ministry, addressed groundwater. Efforts were made to detect 411 emerging substances at 494 abstraction points from aquifers in continental France. Over 393 000 useful analysis results were produced by the participating laboratories, a successful analysis rate of 96%.

The following year, the **forward-looking study in 2012** analysed surface waters in continental France and the overseas territories, as well as groundwater in the overseas territories. The study, run by Onema with coordination from Ineris, was the first effort to detect an array of emerging contaminants in water (82 substances in continental France) and in sediment (134 substances), ranging from gasoline additives to plasticisers and from medicines to body-care products. All types of surface water bodies were covered, notably rivers (115 measurement points), lakes (18) and littoral waters (20). Over 50 000 useful analysis results were produced by the participating university laboratories. Another 30 000 results came in from five overseas territories for both surface and groundwater. Samples were drawn from 20 littoral measurement points using the POCIS and SBSE techniques (see section 2.1.). The data of these two ambitious campaigns are still being processed, however initial results were presented *(F. Botta, Ineris)* for the first time during the symposium.

Information on groundwater

The 411 targeted emerging substances in groundwater in continental France may be divided into five categories, i.e. pharmaceutical products (133), plant-protection products (101), industrial substances (127), household products (24) and multiple-use substances (26). The first (reassuring) result is that 56% of the substances were not quantified in any of the samples. The substances most frequently quantified in continental France were pharmaceutical products (61), ahead of industrial substances (48) and plant-protection products (41).

For the overseas territories, the percentage of non-quantified substances was 59% (112 out of 189 targeted substances). The most frequently quantified substances were plant-protection products, followed by pharmaceutical products. Analysis of the data according to the sectors of use has produced initial qualitative results that are summarised in Figure 16.

Processing is also run to identify the types of substances most frequently quantified for the type of environment (and thus representing the dominant pressure) at the measurement points, e.g. agricultural, industrial, urban/household or reference environments (only slightly impacted by anthropogenic pressures). For example, industrial substances have been quantified fairly evenly in agricultural, industrial and urban environments. In comparison, plant-protection products are found primarily in agricultural environments, followed by urban environments.

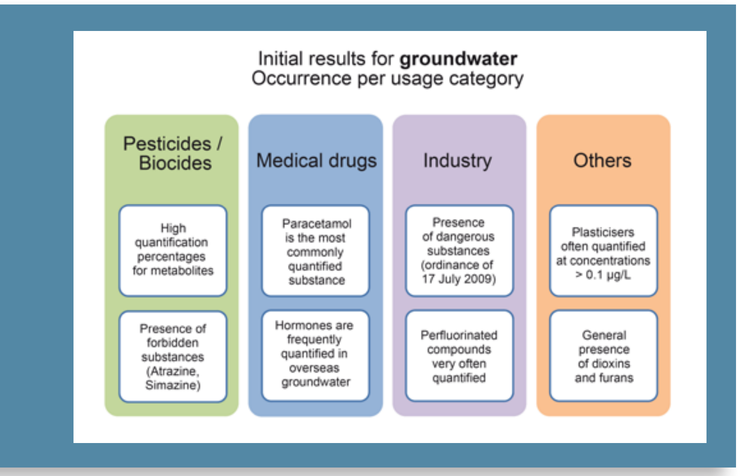


Figure 16. Emerging substances quantified in groundwater, per usage category. Initial qualitative results. ***(F. Botta, Ineris)***

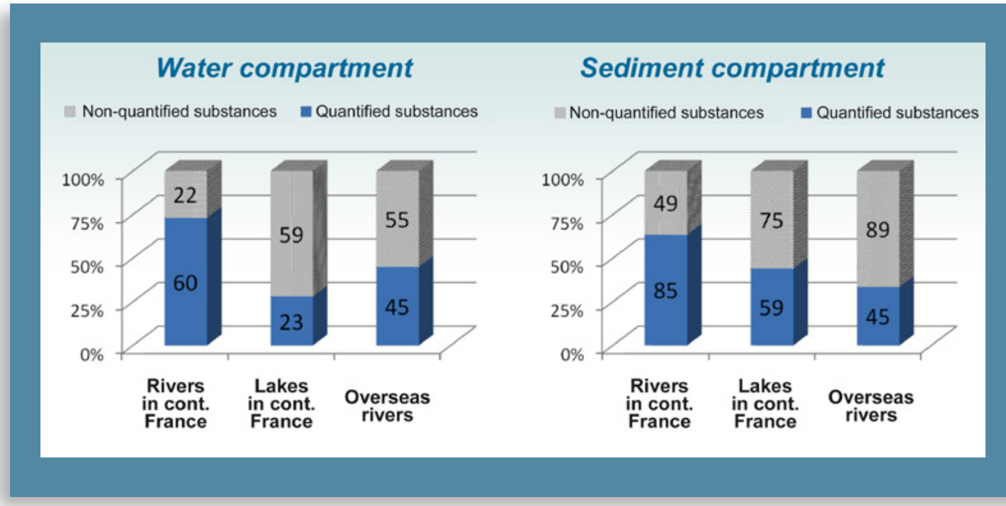
Information on surface water

In surface waters, quantification rates for emerging substances differ widely depending on the compartment (water or sediment) and the type of water body (river, lake, coastal waters). In general, the greatest number of quantified substances is found in rivers in continental France (see Figure 17).

Here as well, data processing will identify the emerging substances most frequently quantified for the type of environment (i.e. the dominant pressure) at the measurement points, e.g. agricultural, industrial, urban/household or reference environments.

At this point, certain substances would appear to be closely linked to a certain type of pressure, e.g. metolachlor, the active ingredient of a herbicide, is much more frequently found in agricultural areas than in other environments, whereas other substances, said to be ubiquitous, are found in all types of environments. That is the case of carbofuran, a banned insecticide that is found in trace quantities (a few ng/L) in all samples, including those from reference sites.

Figure 17. Presence of emerging substances in surface waters (in the different compartments). ***(F. Botta, Ineris)***



Further qualitative results from the 2012 campaign are summed up, by usage category, in Figure 18.

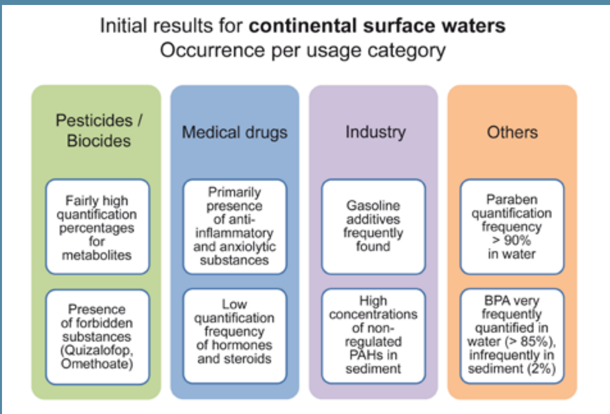


Figure 18. Emerging substances quantified in surface waters, per usage category. Initial qualitative results. ***(F. Botta, Ineris)***

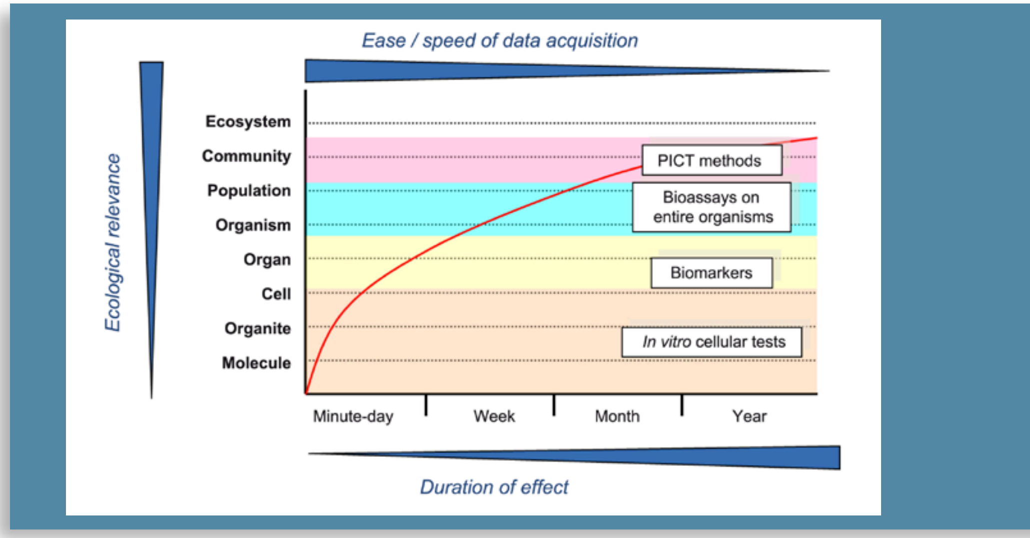
These two campaigns, unprecedented in Europe given the variety of substances and the number of water bodies sampled, represent a vital source of information to understand the origin and sources of emerging substances in aquatic environments. In the framework of the iterative approach instituted on the national level (see section 3.1.), they contribute to identifying important substances in terms of increasing our toxicological and ecotoxicological knowledge, and developing analytical techniques. The results will be used in updating the list of substances requiring monitoring in aquatic environments and selected for the monitoring programme to be launched in 2014, and the list of substances requiring monitoring in groundwater over the WFD management cycle 2015-2021. In addition, the results will serve to prepare precise recommendations for later campaigns. The Ecology ministry now plans to run this type of study every six years, in step with the WFD management cycles. Finally, detailed reports on these campaigns and a document for the general public will be published in the beginning of 2014.

3.3 – Innovative biological tools for monitoring and assessment

Going beyond the quantification of new substances in aquatic environments, efforts to assess the environmental risks posed by these substances represent a complex scientific challenge. Chemical contamination, whether acute or chronic, is likely to affect various biological functions of the exposed organisms, including toxic effects on reproduction and neurotransmission, endocrine disruptions, mutagenic and immunotoxic effects. It would appear critically important to better understand the toxic effects of mixtures of contaminants. To date, they have not been extensively addressed by regulations in spite of the fact that numerous studies have shown the impact of mixtures of interacting substances, even at very low individual concentrations. The need to go beyond "substance-by-substance" risk assessments is now widely acknowledged in the scientific community.

To that end, various biological tools (see Figure 19) have been developed

Figure 19. Types of biological tools available for the assessment of chemical contamination of aquatic environments. ***(O. Perceval, Onema, adapted from Braunbeck 1993 et Kase et al. 2009)***



over the past 20 years that may represent useful elements in an integrated assessment of the chemical quality of aquatic environments, namely *in situ* monitoring of contaminants in the tissues of organisms (selected for their qualities as bioaccumulators), biomarkers (functional measures of exposure to stressors expressed at the sub-organismal, physiological or behavioural level) and bioassays (studies on living organisms to measure the effects of substances or groups of substances), and ecological assessment tools (informing on the effects of contaminants on the scale of living communities).

Though these integrative tools may suffer from as yet insufficiently standardised interpretation, they nonetheless represent useful approaches in conjunction with traditional chemical analyses *(O. Perceval, Onema)*. When used under controlled conditions (*in vitro* cellular tests or bioassays) and/or in the natural environment (biomarkers, ecological assessment tools), they are a means to take into account the active and bioavailable fraction of contaminants. Their combined used also paves the way to characterising the effects of a wide range of contaminants in the environment and the combined effects of contaminant mixtures. Biomarkers that are specific to a given group of contaminants sharing a similar mode of action also inform on the links between exposure and effects.

These tools have long been used for research on precise topics and in the future will prove highly useful in assessing water status by identifying the substances causing effects observed in the environment, assessing the effects of representative mixtures, launching alarms for new pollutions (early-warning signals) and, more generally, providing support for the assessment of the chemical status. A number of projects presented here illustrate the usefulness and the feasibility of employing these tools for management purposes.

Molluscs signal changes in emerging pollutants in littoral zones

The molluscs are sampled yearly on 25 sites along French coasts (English Channel, Atlantic Ocean and Mediterranean Sea). Analyses are carried out in soft tissues to detect organohalogenated pollutants (chlorinated, brominated, fluorinated substances) characterised by their high toxicity and persistence. Examples are persistent organic pollutants such as PBDEs and various emerging contaminants for which very few data are yet available concerning the French coasts. The monitoring has provided information on the geographic distribution of the substances in littoral zones *(C. Munschy, Ifremer)*. Temporal trends have also been studied thanks to samples stored in the Ifremer Environmental Specimen Bank of marine bivalves since 19811. The results for PBDE-47 are an example of how useful monitoring of biota can be for assessments of the chemical status of the environment (see Figure 20).

This brominated flame retardant is regulated in Europe and its emissions have decreased sharply since 1995. The average concentrations in mollusc tissues are significantly higher near industrial centres such as the Seine estuary or the Nivelle estuary (Pyrénées-Atlantiques department). However, the temporal trends closely follow the trends in emissions, i.e. the strong increases in concentrations in biota between 1975 and 1995 have since given way to a clear reduction to the point that the pollutant should have virtually disappeared from the French coasts by 2015 (see Figure 21).

Figure 20. Average concentrations (2010) of PBDE-47 in the tissue of oysters and mussels along French coasts. ***(C. Munschy, Ifremer)***

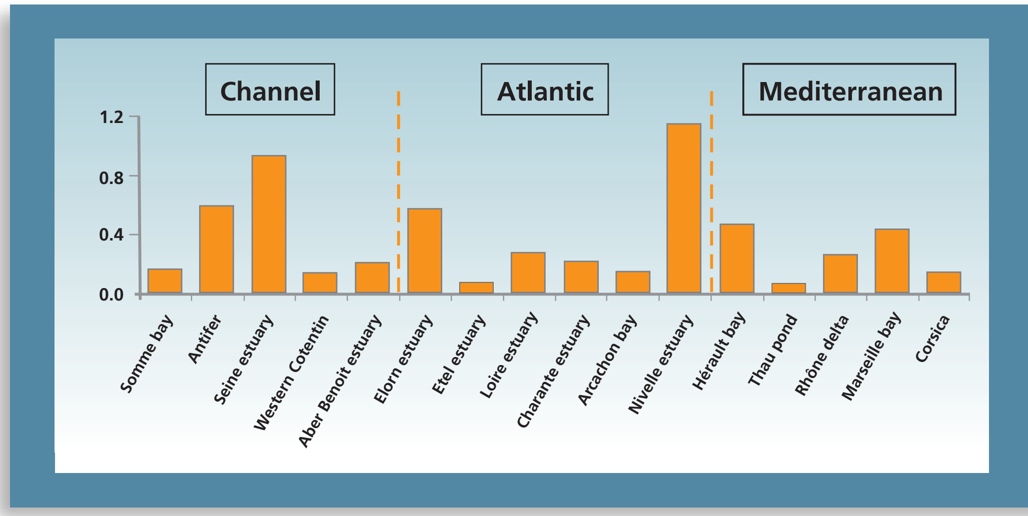
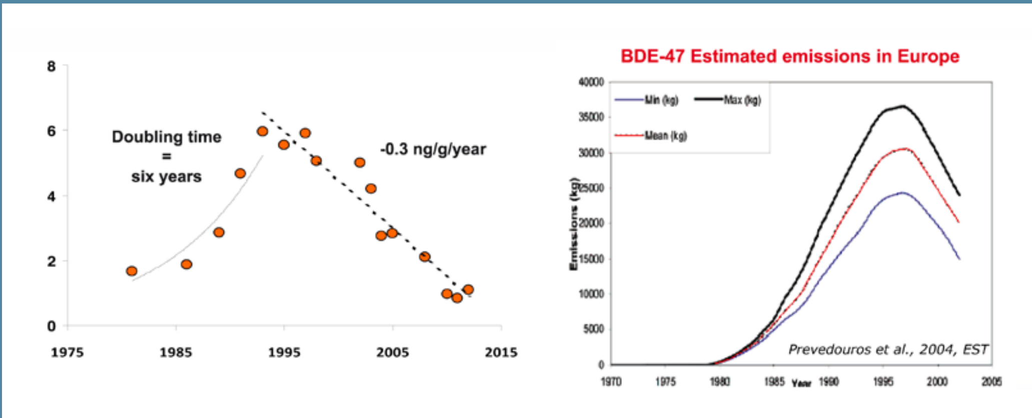


Figure 21. Temporal trends of PBDE-47 concentrations measured in the tissue of oysters and mussels in the Seine estuary (ng/g, dry weight), reflecting the trends of estimated emissions in Europe. ***(C. Munschy, Ifremer)***



In comparison, the results for hexabromocyclododecane (HBCDD), a non-regulated flame retardant, show a similar geographic distribution, but no sign of a reduction over time (see Figure 22).

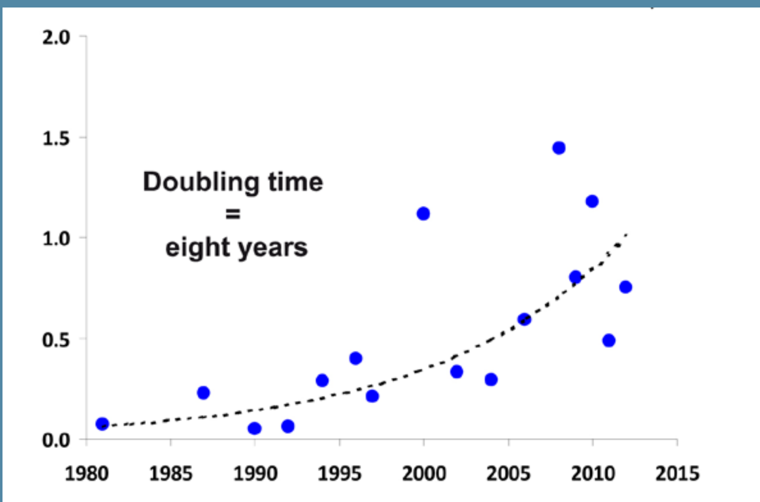


Figure 22. Temporal trends of HBCDD concentrations measured in the tissue of oysters and mussels in the Seine estuary (ng/g, dry weight). ***(C. Munschy, Ifremer)***

These observations confirm the rapid effects produced by restrictions on emissions, for certain substances, on the contamination of living organisms. In terms of methods, they illustrate the value and feasibility of detecting emerging substances in biota, including on a routine basis, in the framework of efforts to monitor the status of environments and the effectiveness of restrictions on polluting emissions. Large-scale application of this approach, supported by Onema, was recently the topic of recent publications and presentations to international conferences. The data also contributed to the report titled *Levels of emerging contaminants in the marine environment*, PCDD/F, PBDE, HBCD in marine molluscs, that is available on the Onema site.

Biomarker and bioassay techniques validated in coastal environments

On the EU level, the development of ecotoxicological assessment tools for the assessment and monitoring of chemical pollution has made significant progress thanks to the OSPAR convention. This system of intergovernmental cooperation to protect the marine environment of the North-East Atlantic was launched in 1992 and, via a network of study sites including the Seine estuary, has driven the validation of a set of bioassay and biomarker methods. The R&D work, carried out nationally by Ifremer, has resulted to date in the validation of 19 biomarkers and four bioassays, all standardised *(T. Burgeot, Ifremer)*. For each tool, e.g. the stability of the lysosomal membrane of mussels or the vitellogenin level in European flounder and cod, quantitative interpretation thresholds were set by groups of experts. In most cases, two distinct thresholds were set (for a given species and geographic sector). The first corresponds to a “base” response of the biomarker or the bioassay (BAC, background assessment concentration), i.e. no effect calculated using data series from only slightly contaminated sites. The second corresponds to an “effect” threshold determined on the basis of contaminated sites. A description of the bioassessment tools and the corresponding interpretation thresholds is provided in the report titled *Integrated marine environmental monitoring of chemicals and their effects* (ICES, 2012).

Following validation by the long-term monitoring carried out on the study sites, these tools are now operational for routine use in the monitoring networks established for the

Marine strategy framework directive (EC 2008/56), the equivalent of the WFD for marine waters. As a result, the ordinance dated 17 September 2012 listed five biomarkers and bioassays for quantitative analysis of chemical contaminants in coastal waters. They are shown in Table 2.

Table 2. Biomarkers and bioassays selected in France for monitoring of coastal environments (MSFD) and the corresponding biological effects. ***(T. Burgeot, Ifremer)***

Biological effect	Biomarkers and bioassays
1. General stress index for mussels and fish	Stability of the lysosomal membrane
2. Genotoxicity for mussels and fish	Micronucleus assay and Comet assay as methods for assessing DNA damage
3. Embryotoxicity for true oysters (Crassostrea) and reproductive toxicity for fish	Anomalies in oyster larvae and fish gonades
4. Imposex in gasteropods	VDS (Vas Deferens Sequence) index
5. Fish pathologies	Index for hepatic and external pathologies

Gammarus reveals pressures in fresh water

The use of standardised biomarkers and bioassays is just as useful for continental waters as for coastal environments, however their deployment does not benefit from the highly structured framework provided by the OSPAR convention. Promising tools are nonetheless available. In France, one of the tools for which the most progress has been made uses the Gammarus, a small freshwater shrimp that is both common and abundant in most rivers in continental France. Developed by Irstea, the tool consists of *in situ* caged Gammarus used as indicators of environmental contamination by toxic substances *(O. Geffard, Irstea)*. On a given site, six to eight exposure chambers, each containing 20 male Gammarus, are submerged for two to four weeks in the monitored environment. Following the exposure, contamination measurements are run on the organisms and various biological responses are assessed, corresponding to different types of toxic effects. For example, measurement of acetylcholinesterase, an enzyme involved in neurotransmission, informs on the neurotoxicity of the chemical mixture present in the environment.

Measurement of vitellogenin, a protein normally synthesised by females, in the male Gammarus informs on the presence of endocrine disruptors. Similarly, the genotoxic effects (impacting the genetic material) of contaminants can be quantified using a very simple visual test called the "comet" assay. It consists of using a microscope to estimate the percentage of damaged cells, i.e. those in which the fragmented DNA takes on a characteristic "comet" shape. Researchers also observe the life history traits of Gammarus (feeding rates, fecundity, fertility), which provide other indications used to identify disturbances in the physiological functions of the organisms in response to local exposure to toxic substances. All these biological responses are determined quantitatively using relatively simple measurements, e.g. observation under a binocular microscope, image analysis or molecular analysis using a spectrophotometer. For each parameter, the researchers proposed standardised threshold values for use in WFD monitoring networks.

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The Gammarus *bioindicator is being used to develop a method based on organisms caged* in situ *to provide information on the toxicity of their environment.*

Table 3. Biomarkers developed for the fish model by Ineris and measured during the study on fish mortality in the Loue River.

Physiological function	Biomarker	Organ	Method
General health	Lysosomal stability	Spleen	Cytometry
	Lipid peroxidation	Liver	Fluorometry
Energy management	Condition factor		Biometry
Neurotoxic alterations	Acetylcholinesterase	Muscle	Colorimetry
Immunity	Phagocytosis	Spleen	Cytometry
	Respiratory burst activity	Spleen	Cytometry
	Lucocytary formula	Spleen	Cytometry
Reproduction	Gonadosomatic index	Gonads	Biometry
	Vitellogenin	Blood	ELISA
	Thickness of kidney epithelium	Kidney	Histology
	Intersex	Gonads	Histology
Defence against pollutants (biotransformation)	EROD	Liver	Fluorometry
	CYP3A	Liver	Fluorometry
	Glutathione S-transferase	Liver	Colorimetry
Genotoxic disturbances	Chromosomal damage	Blood	Cytometry

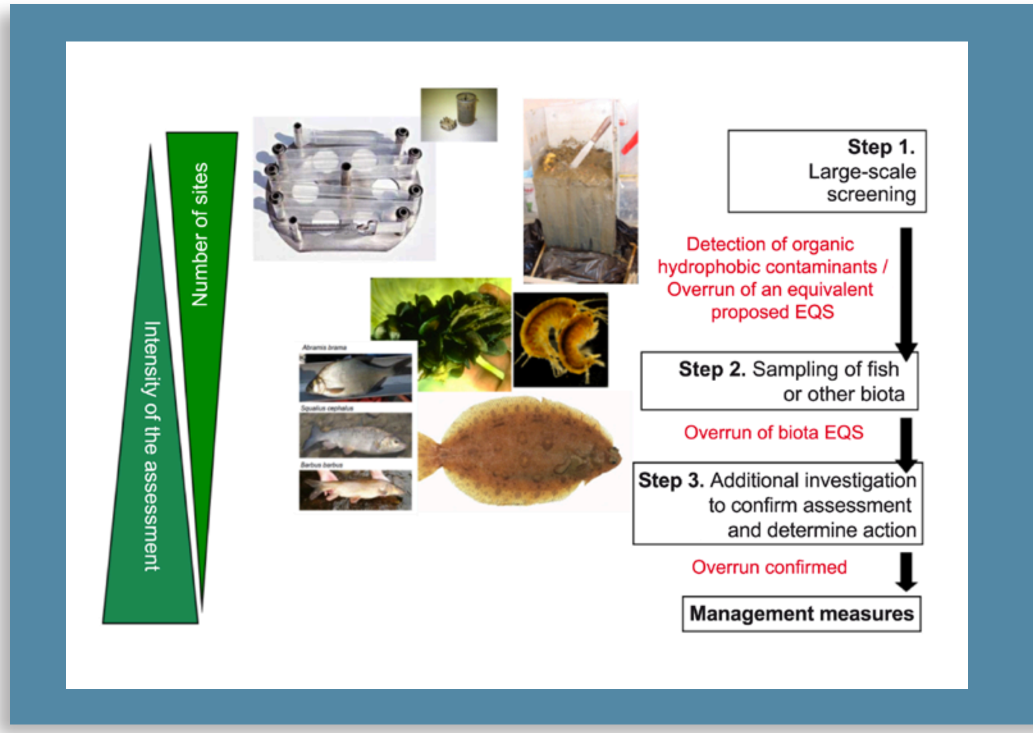
In addition to *Gammarus*, other approaches employing freshwater biomarkers have also been developed by Ineris *(W. Sanchez)* based on observations of wild fish, notably sticklebacks and roach (see Table 3). Analysis of the liver, spleen and gonades, as well as measurements of the vitellogenin and the acetylcholine all provide information on the toxic pressures in the environment. These approaches are used to acquire data for environmental studies, characterise the toxic effects in the vicinity of an industrial site or to identify the origin of local disturbances observed in fish populations. They will be of particular use for an in-depth assessment of the Loue River, in which serious ecological malfunctions have been observed for several years.

Tiered assessment strategies

The development of biological tools is important for water management and has paved the way for progressive assessment strategies combining chemical analysis and biological approaches all in one set of tools *(O. Perceval, Onema)* (see Figure 23).

This type of strategy, whose usefulness is acknowledged by numerous public and private stakeholders, is a component in the policy that now guides the entire monitoring and assessment system for the chemical status of water, i.e. the priority is routine monitoring using fast and inexpensive techniques, complemented with further analysis if necessary. On sites where a significant disturbance has been confirmed, an in-depth environmental study is carried out to identify the sources of the pollution and set up the necessary counter measures.

Figure 23 : Diagram showing the progressive assessment strategy for hydrophobic contaminants. ***(O. Perceval, Onema)***



Spotlight

A bioanalytical method to identify endocrine disruptors

Endocrine disruptors belong to a highly diverse set of chemical groups used for very different purposes (chemistry, medicines and veterinary products, cosmetics, agri-food industry, etc.) and impact environments via complex mixtures at very low concentrations.

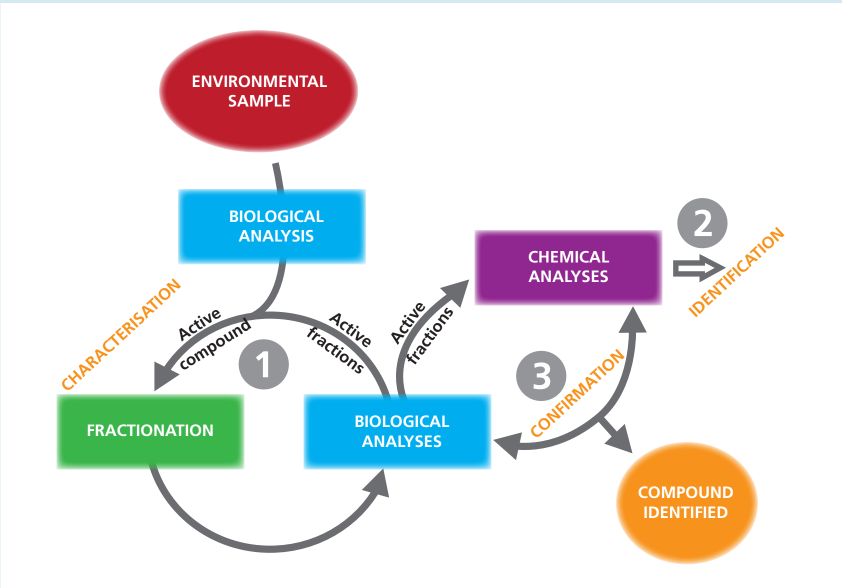
They can have major effects on ecosystems by affecting organisms both individually and via entire populations (impacts on reproduction and development, feminisation of populations). Assessment of these effects and identification of the causal pollutants is currently a major issue for research.

Ineris has developed a three-step bioanalytical approach (*N. Creusot and S. Aït-Aïssa, Ineris*, see Figure 24), combining bioassays and chemical analyses according to the EDA (effect-directed analysis) principle. On the basis of samples (drawn from passive samplers or sediment) taken from the studied environment, a set of in vitro cellular tests is used to identify the mechanisms occurring in the environment and to propose an initial diagnosis on the chemical properties of the substances involved. For example, a mixture of xenobiotics and steroids would indicate pharmaceutical compounds. The second step consists of targeted chemical analyses to quantify the contribution of various known pollutants to the measured biological phenomena. Finally, if the targeted pollutants cannot fully explain the phenomena, sample fractionation is carried out to isolate and identify the active compounds not initially targeted using sophisticated chemical-analysis techniques.

This innovative analysis method was used for the forward-looking study in 2012 (see section 3.2.) to determine the toxicological profiles of study sites prior to their selection, as well as for environmental studies targeting precise goals, e.g. identification of the compounds causing visible endocrine disruptions in fish (gonadal hypertrophy, intersex) downstream of an industrial plant. In addition to steroids, this type of approach can also characterise environmental contamination by dioxin-like compounds.

These methods remain relatively expensive and complicated to implement, but are currently being standardised by European research programmes in order to expand their use.

Figure 24. Principle behind the EDA (effect-directed analysis) approach.
(N. Creusot, Ineris, based on Brack, 2003)



After five years of R&D work, the 2009-2013 Micropollutants plan and the specific national plans (PCBs, pharmaceutical residues in water, collective sanitation), have produced considerable scientific knowledge and operational advances for monitoring and reducing chemical contamination in aquatic environments. The strategies to reduce polluting emissions, an essential first step toward restoring water quality, have been reinforced by an array of targeted research projects involving notably the research teams of public stakeholders in water policy.

Knowledge on the sources of industrial pollutants has improved thanks to the national research programme on dangerous substances in water. Emission measurements were carried out in thousands of companies, a number of which are currently undergoing analysis to reduce emissions (by modifying or completely replacing processes). This work will avoid the release to aquatic environments of pollutant flows that, in some cases, represented considerable volumes. Other more targeted studies have produced new knowledge on the contaminants released by various industrial sectors, e.g. metallurgy, and artisanal sectors. All of this new knowledge contributes to identifying the sources of pollution having the greatest impact on the environment. In particular, this knowledge is folded into the work to inventory sources required by the WFD, in view of setting priorities for corrective action in each major river basin. This work to identify and reduce polluting emissions will be a long-term effort and considerable progress in techniques can still be made. That is particularly the case for urban rainwater run-off, which today represents a major, though difficult to quantify, contribution to the chemical pressures exerted on aquatic environments.

What changes in habits by the professional sector, what changes in household and health products could be implemented to reduce and/or better manage urban emissions? What changes in urban management could contribute to progress? These questions are the topic of a call for projects launched by Onema and the Water agencies in 2013.

Conclusion

In the field of wastewater treatment, a number of joint research programmes have studied how to assess and improve different treatment techniques. This work will be of considerable help in improving the performance of collective-sanitation systems in reducing certain micropollutants.

In parallel, the systematic monitoring and assessment of the chemical status of water bodies, boosted over the past ten years by the WFD, has continued to make progress thanks to the development of new tools designed for large-scale use. Detection and quantification of contaminants in water now benefits from techniques such as passive samplers, which may provide more representative results on the actual situation than spot sampling. These integrative methods, used notably by Ifremer for chemical monitoring of coastal waters, are now available at a reasonable cost and their potential for routine use is now being studied for the WFD monitoring system. Measurement of contaminants in the tissues of animals used as pollutant integrators, e.g. mussels and oysters, also used on a routine basis by Ifremer, as well as freshwater Gammarus, provides further information taking into account the physiology of the organisms and the bioavailability of substances.

Environmental quality standards (EQS) constitute a vital component in interpreting monitoring and assessment data on the chemical status of water bodies and constant R&D work is put into them on the EU level. Over the past five years, an array of projects have been carried out in France to improve our understanding of the effects of substances on organisms and on human health, and to propose increasingly relevant threshold values for pollutant concentrations in the environment. In the case of metallic trace elements, the work funded by Onema attempted to better take into account the geochemical background (the natural presence of the metals) in the assessment. Operational models were developed to assess the bioavailable fraction of the metals as a function of the physicochemical parameters. When used with progressive assessment strategies, they provide more precise information on the impact of the contaminants when generic threshold values are overrun and serve to identify the sites where risks are high and corrective action is urgent.

Another important field of work concerns converting EQSs from one compartment (water, sediment, biota) to another. Thanks to the national PCB action plan, equivalences between threshold values for sediment and concentration limits for fish tissues have been made available to water managers. Further work has targeted enhanced understanding of the toxic effects of mixtures of substances.

Going beyond regulatory requirements, public authorities and the scientific community have put extensive effort into the crucial issue of emerging substances, i.e. recently created molecules, medicinal residues, endocrine disruptors, etc. Identification of the most worrisome substances and knowledge on their behaviour in the environment are essential conditions for their effective monitoring. In France, the CEP (committee of experts on setting priorities), created at the end of 2010, published a method to categorise substances and identified the priority knowledge required for each. The work by this committee contributed notably to the preparation of two research campaigns on emerging contaminants, unprecedented in their scope, the first for surface waters and the second for groundwater. The results are currently being analysed, but have already produced valuable information. They will be made public in 2014. On a parallel track, the shared desire to push risk assessments beyond a simple "substance-by-substance" approach has resulted in the development of in vitro and in vivo biological tools. Bioassays and biomarkers have the acknowledged potential to enhance our knowledge on the toxic effects of mixtures of substances and on their different processes, e.g. endocrine disruptors, mutagenic and neurotoxic effects, etc. They have long been used for research programmes, but are now being adapted to more operational applications and, following further experimentation, will be available for assessment and management purposes. These tools are already used on a voluntary basis in the monitoring programme for coastal waters (OSPAR convention) and will soon be employed for the Marine strategy framework directive.

Active biomonitoring approaches using caged organisms such as gammarus, that are based on the analysis of the biological responses, are also available for freshwater environments. Innovative approaches combining biological tools and analytical techniques are now making it possible to identify the compounds producing a toxic effect (e.g. endocrine disruptions) on a given site and consequently to track down the sources.

The development of these biological tools has initiated a transition in the assessment system for water bodies with the introduction of progressive assessment strategies where initial monitoring data can signal the need for additional analysis using the biological tools and, in some cases, an in-depth environmental investigation. This trend provides a glimpse of future monitoring systems that will better integrate chemistry and biology.

The results and progress obtained over the five-year period in identifying and reducing sources of pollution and in improving the chemical status of water are the product of an intense collective effort on the part of scientists and managers, both public and private, national and local stakeholders, combining field data and research in the lab. This proactive effort must be maintained over the long term. A wide array of projects will be pursued, notably in the action plans for medicinal residues in water, collective sanitation and urban run-off. A further important issue concerns the process by which water managers and stakeholders, both public and private, learn to use the available tools. The technology transfer must be accompanied by a political transition, i.e. integration of social-economic aspects that to date are not sufficiently taken into account in decisions on major issues, e.g. how can links be established between costs of monitoring programmes and their benefits for the environment and public health? What means are available to induce changes in the practices of local governments, industrial companies and households? More generally, the decision to address these issues by society will condition our capacity to act collectively in favour of water quality and the preservation of aquatic environments.

Introduction to national policy and regulations
www.developpement-durable.gouv.fr

Important documents:
- 2010-2013 Micropollutants plan
  www.developpement-durable.gouv.fr/IMG/pdf/plan_micropolluants_dv.pdf
- 2012-2018 action plan for sanitation policy contributing to quality objectives for aquatic environments
  www.developpement-durable.gouv.fr/IMG/pdf/2011_09_27_Plan_daction_assainissement_version_finale.pdf
- National PCB action plan
  www.developpement-durable.gouv.fr/IMG/pdf/plan_PCB.pdf
- National plan for medicinal residues in water
  www.developpement-durable.gouv.fr/IMG/pdf/PNRM-2.pdf
- Ecophyto plan
  www.agriculture.gouv.fr/IMG/pdf/PLAN_ECOPHYTO_2018-2-2-2_cle8935ee.pdf

Background documents on scientific and technical knowledge
www.onema.fr

Important documents:
- Call for projects on "Micropollutants in urban waters"
  www.onema.fr/Appel-a-projets-Micropolluants-dans-les-milieux-aquatiques
- Formulating environmental quality standards
  www.onema.fr/QUALIFIER-Normes-Qualite-Environnementales
- Other quality indicators, trend indicators
  www.onema.fr/QUALIFIER-Autres-indicateurs-qualite-tendance
- Report on "Observing and assessing salinisation of water bodies in France"
  www.onema.fr/IMG/pdf/2011_031.pdf
- Salinisation of water bodies in continental France and the overseas territories, final report
  www.onema.fr/IMG/pdf/2010_057.pdf

Reports on water contamination in geographical regions
www.statistiques.developpement-durable.gouv.fr

Important documents:
- Report on micropollutants in continental aquatic environments 2007-2009
  www.statistiques.developpement-durable.gouv.fr/publications/p/1808/1108/bilan-presence-micropolluants-milieux-aquatiques.html
- Micropollutants in the Artois-Picardie river basin (2009)
  www.eau-artois-picardie.fr/Les-micropolluants-des-eaux.html
- 2010 report on monitoring water status in the Seine-Normandie river basin
  http://www.eau-seine-normandie.fr/fileadmin/mediatheque/Expert/Etat_des_Lieux/Bilan_2010_de_surveillance_qualite_des_eaux_AESN.pdf

Bibliography

Practical guides on water monitoring
www.aquaref.fr

Reference data on chemical substances
www.ineris.fr/substances/fr/

Key-word search function for all on-line documentation
www.eaufrance.fr

Important documents:
- Method for drafting inventories of emissions, discharges and losses of chemical substances in France
  http://www.reseau.eaufrance.fr/webfm_send/2782
- Data produced by the national PCB action plan
  http://www.pollutions.eaufrance.fr/pcb/

Other useful links...

... on collective sanitation
- AMPERES project
  https://projetamperes.cemagref.fr/
- ARMISTIQ project
  http://armistiq.irstea.fr/armistiq/
- EPNAC (assessment of new treatment processes for small to mid-sized local governments) work group
  http://epnac.irstea.fr/).

... on industrial emissions
- Report on the national RSDE 1 plan (2008)
  http://www.ineris.fr/rsde/doc/docs%20rsde/DRC-07-82615-13836C.pdf

... on emerging substances
- NORMAN network in the EU
  www.norman-network.net
- Levels of emerging contaminants in the marine environment, PCDD/F, PBDE, HBCD in marine molluscs, final report
  www.onema.fr/IMG/pdf/2010_B004.pdf

... on new monitoring tools
- Principles and contributions of in vitro bioanalytical tools for monitoring organic contaminants in aquatic environments
  http://www.ineris.fr/centredoc/R_08_16732A_Action28_final.pdf

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