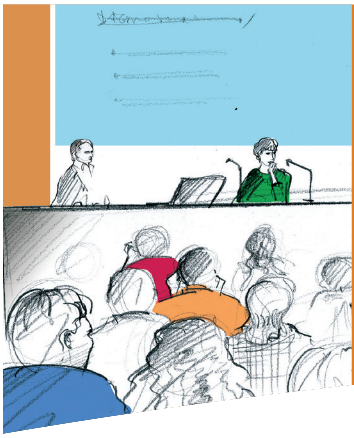
N°23
DECEMBER
2013



ONEMA
Meetings

Reducing chemical contamination of aquatic environments: five years of progress and results

A symposium organised with Ineris

The national symposium on monitoring and reducing chemical contamination of aquatic environments, held in Paris on 17 and 18 June 2013, brought together almost 200 participants, including water managers, stakeholders and scientists. An array of results and techniques, produced over five years of intensive efforts by BRGM, Ifremer, Ineris and Irstea, were presented.

Pesticides, polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), metals and metalloids, dioxins and furans, phthalates, etc. are some of the 950 substances for which the document on micropollutants in aquatic environments, published in 2011 by the Ecology ministry, presented the monitoring results for French freshwater resources between 2007 and 2009. Pesticides were found at 91% of the monitoring points on French rivers and 70% of the monitoring points for groundwater. If pesticides are excluded, 40% of the monitoring points on rivers detected pollutant concentrations exceeding environmental quality standards[1]. PAHs resulting from combustion (transportation, incineration, heating) and PBDEs (flame retardants) are the cause of most of the overruns. PCBs are still highly present in the sediment of some rivers and chlorinated solvents are regularly found in groundwater.

Driven by the Water framework directive, an unprecedented R&D effort in France has been undertaken over the past five years to reduce this virtually omnipresent contamination. In conjunction with a number of specific action plans (for pesticides, PCBs, medicinal residues in water, collective sanitation), the national Micropollutants 2010-2013 plan, under management by the Ecology ministry, launched several proactive projects. The objective is to reduce emissions at their source, improve assessments of water status and gain new knowledge, notably concerning «emerging pollutants». The symposium organised in June by Onema and Ineris was an occasion to review the significant progress made in preserving aquatic environments and human health.

1 MONITOR

Develop innovative tools and methods to detect and/or measure contaminants.
Study the new substances and new parameters.

More information +

2 CHARACTERISE THE STATUS and ASSESS RISKS

Develop indicators of environmental quality, tools, criteria, standards to interpret chemical data.
Assess risks of not achieving environmental objectives.

More information +

3 CONTROL

Manage emissions and transfer of contaminants to aquatic environments.

More information +

The three main fields in which the Onema R&D partners work on aquatic contaminants. Results achieved in these fields may be consulted at http://www.onema.fr/contaminants-et-pollutions-aquatiques.

[1] At least once during the years 2007 to 2009.

Identify and control the sources of pollution

Extensive research and studies in France have been put into nonpoint-source pollution from farms (pesticides and nitrates) because it is a major source of contamination in aquatic environments. A symposium organised by Onema and Astee, held in Paris on 18-20 September 2013, presented research results concerning these substances and a document on the symposium will soon be published. The origin of other types of contaminants is highly varied, e.g. industrial sites, wastewater, urban run-off, etc. Just 1% of the sources is thought to represent 90% of the overall emissions, hence the **absolute need to set priorities**. In this context, Ineris has developed a promising method to detect and list sources discharging to surface waters, for use by the Water agencies. The method (*A. Gouzy, Ineris*) is based on statistical processing of data covering large catchments. Total amounts are calculated for each source, based on the available data on discharges (databases, bibliographies, etc.) and on equations when no data is available. Inventories are now being calculated by the Water agencies and offices using this method that will be enhanced in the future by developing the discharge factors, improving the integration of nonpoint sources, etc. In the years to come, these inventories will serve to develop strategies targeting a reduction in discharges. Examples of method application were presented for the Saône River (Figure 1).

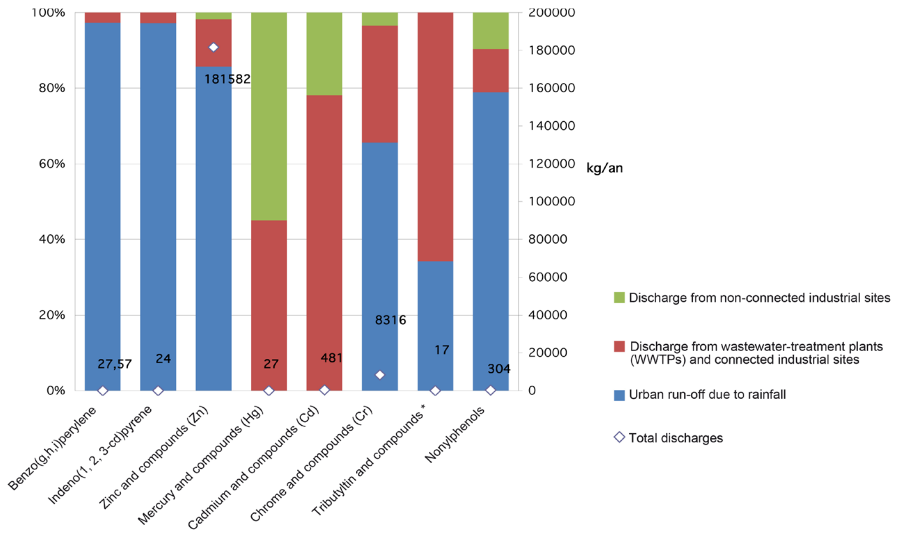


Figure 1. Example of results obtained by the Ineris discharge inventory method. Sources of discharges in the Saône River basin for eight contaminants (*A. Gouzy, Ineris*).

Ineris has also provided in-depth documentation on the most worrisome substances (*J.-M. Brignon, Ineris*) and a set of precisely targeted studies has been carried out to gain more knowledge on contaminant discharges by different economic sectors. Since 2009, discharges by **regulated installations** for environmental protection (ICPE) have been monitored very carefully in the framework of the RSDE2 project managed by the Ecology ministry. As of mid-2013, 3 077 sites, ranging from chemical industries to slaughterhouses and dry-cleaners, have been subjected to over 600 000 analyses in the campaign to detect precise substances (*E. Ughetto, Ineris*). Of the approximately 100 listed substances, 35 have been quantified on over 25% of the sites. This initial examination will be followed by long-term monitoring and, if significant flows are detected, corrective action plans will be launched. The potential reductions in micropollutant flows achieved by these efforts are significant. For example, in one sector where 23 sites were studied to reduce discharges of nickel, over 3.6 kg of the metal will now no longer be released to aquatic environments every day. In addition, a "sector study" on mechanical metal treatments was carried out by the Technical centre for the mechanical industries. A questionnaire filled out by 495 industrial companies made it possible to identify dozens of correlations between the substances detected and the processes employed (*J. Kirmann, CETIM*). For example, surface preparation using the vibratory-grinding technique results in quantifiable discharges of nickel.

Finally, a study addressed the detection of dangerous substances in **discharges from artisanal businesses** (*M. P. Fischer, CNIDEP*). The first phase of the study looked at four sectors of activity, namely automobile mechanics and body work, printing, dry- and wet-cleaning, and the painting business. In the 22 businesses audited to date, various samples have been taken, depending on the sector, e.g. water used to wash floors, oil changes from machines, water or solvents used to clean tools, etc. The analyses identified approximately 30 dangerous substances quantified at levels over 100 times the

Claire Riou,
Rhin-Meuse water agency

"Our knowledge on point-source discharges has made great strides thanks to the project to find dangerous substances in water (RSDE2). In our river basin, virtually all isolated industrial discharges have now been characterised using measurement data from the RSDE campaign and from regular monitoring by the industrial companies themselves and by the Water agency. Concerning wastewater treatment, we have analysed the treated water released by approximately 80 urban plants of various types. The results enabled us to calculate emissions factors that will be used in national studies on pressure quantification and priority setting. Unfortunately, there are still difficulties in quantifying discharges resulting from urban run-off. The current method, which most likely produces overestimates, is nonetheless a signal informing us on the importance of this source of pollution."

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).

quantification limit, including a majority of metals (zinc, iron, aluminium, lead, etc.), but also nonylphenols, formaldehyde and seven WFD priority substances. This study will be continued in 2013 for six other economic sectors.

Another major source of progress lies in **wastewater treatment**, a sector in which Onema has funded numerous projects. A study by Irstea characterised the quality of untreated wastewater from small towns, through statistical processing of data provided by the Water agencies. The results revealed that behind "standard" average values, there were major discrepancies in terms of both quality and composition (*C. Boutin, Irstea*). Given the wide range of innovative treatments for wastewater, a work group was set up to structure and assess the processes. More precisely targeted studies were also carried out, for example to improve the effectiveness of sludge drying beds planted with reeds or to adapt certain techniques to the overseas territories.

The Armistiq[2] partnership project consists of assessing and improving our knowledge of and control over treatment technologies for priority and emerging substances present in urban sludge and wastewater. Primary goals include obtaining operational data on these substances when processed by several treatment techniques and improving knowledge on the optimum conditions to reduce the substances during secondary and tertiary water treatment and sludge treatment (*M. Coquery, Irstea*). A symposium and publications in 2014 will present the Armistiq project in greater detail.

Improve the water-status assessment system

Since the year 2000, contamination monitoring of surface and groundwater in Europe has been governed by the WFD and in France, the WFD network comprises several thousand monitoring points. Assessment of the chemical status of surface water bodies is based on detecting and quantifying 41 WFD priority substances at each monitoring point of the RCS surveillance-monitoring network. For surface and coastal waters, assessment of the ecological status requires that the RCS network also scan for a series of specific pollutants (metals and pesticides) set by each country. For groundwater, in addition to micropollutants, the qualitative assessment must also take into account salinity levels (natural and/or anthropogenic). This issue was the topic of a detailed report by BRGM, which revealed that only 22 aquifers, of the 534 used for drinking water in continental France, showed significant and recent increases in salinity levels (*W. Kloppman, BRGM*). In general, the establishment of water-quality assessment systems is preceded by significant R&D work and the symposium presented a panorama of the recent work.

Quantification of pollutants in environments is a challenge because the statistical significance of traditional monitoring systems, based on repeated sampling, is limited due to the variability of concentrations over time. The use of passive samplers, which continuously collect pollutants over a given time period, may represent a useful solution for WFD monitoring networks. In 2008, 2009 and 2012, Ifremer tested three complementary techniques (POCIS/SBSE sensors for hydrophilic/hydrophobic organic contaminants and DGT sensors for trace metals) in the framework of the large-scale WFD campaigns for coastal

Jean Prygiel, Artois-Picardie water agency

In our river basin, 79% of water bodies have been ranked as having "good chemical status", if PAHs are excluded. But these overall results must not mask the actual situation in the field. Assessment of the chemical status via the water compartment alone is not sufficient because long-standing metals and PCB pollution (not monitored by the WFD) in sediment is significant in some cases. In channelled environments, navigation stirs up sediment that can affect the chemical and ecological status. Studies have also revealed the virtual omnipresence of chemical activity similar to endocrine disruptors and/or PAH and dioxin-like substances in the tested sediments. As a result, there may be little relevance between the chemical status of water bodies and their ecological status. A great deal of work is still required to better understand the pressure-impact relationships and the effects of substance mixtures.

[2] Improving the elimination of micropollutants in treatment plants for household wastewater.

environments. The sampling campaigns confirmed the technical feasibility of these techniques (*J.-L. Gonzalez, Ifremer*), at acceptable cost levels for routine monitoring, for both fresh and saltwater. The results presented for the Mediterranean coast informed on the presence or absence (trace levels) of over 140 chemical contaminants in coastal waters. In the Mediterranean lagoons, they revealed concentrations of insecticides, herbicides and copper often higher than the applicable quality standards. On the other hand, for hydrophilic organic compounds, no exceedances were noted.

Setting of relevant **environmental quality standards** (EQSs) is also a major factor in view of achieving correct assessment of environmental status. Defined by the WFD as a "concentration of a particular pollutant in water, sediment or biota, which should not be exceeded in order to protect human health and the environment", EQSs are set on the European level for substances determining the chemical status and on the national level for those determining the ecological status. They are regularly updated in step with progress in understanding the risks caused by contaminants for organisms. Since 2008, Ineris has drafted 181 proposals for new guide values, based notably on toxicity tests in the lab or in mesocosms (artificial ecosystems). One major line of work in this field concerns enhancing our understanding of the "cocktail" effect, i.e. combinations of substances (*S. Andres, Ineris*). Another is the attempt to determine the relationships between pollutant concentrations measured in the environment and those measured, following transfer, in the tissues of organisms (biota).

Statistical models have been created (*M. Babut, Irstea*) to link PCB concentrations in sediment and those noted in fish in order to determine intervention thresholds for sediment management (see the Onema Meetings no. 18 on the PCB plan). Dissolved metals are also widely present in aquatic environments and have been the topic of specific research. The goal is to better assess the risks they represent for aquatic organisms by taking better into account their "bio-available" fraction, i.e. the part likely to be toxic for organisms, depending on different parameters such as the pH and the concentration of dissolved organic carbon and of dissolved calcium. A research partnership (L. Geoffroy, Ineris) has developed a progressive approach for assessments at a given monitoring point involving first a comparison with a generic "bio-available" EQS and, secondly, if an exceedance is observed, use of a mechanistic model to determine the toxicity of the metal depending on the local parameters of the environment and to identify sites requiring restoration work.

New substances and new tools for the future

To date, over 100 000 chemical substances have been or are still produced industrially worldwide. The list of substances that must be monitored for the WFD, the result of difficult priority setting on the European level, is regularly updated and another 12 substances were added in 2013. But above and beyond the regulatory requirements, enhanced awareness of emerging substances is an absolute necessity in order to protect the environment and public health. Numerous substances, whether actually released or simply a potential source of concern, are likely to damage aquatic environments, e.g. organotins, phthalates, perfluorinated compounds, chlorinated biocides, nano particles, medicinal residues, etc. Since 2005, the Norman network of laboratories (www.norman-network.net) have provided a watch and information-exchange service on the European level for emerging substances (*V. Dulio, Ineris*). The French Norman mirror group to set priorities for emerging substances was created in 2010, namely the expert committee for substance priorities in aquatic environments (CEP). The committee is managed by Onema and Ineris and includes among its members Aquaref, Irstea, BRGM, Ifremer, CNRS, representatives from the water-treatment companies and from the Ecology and Agriculture ministries. It has developed a procedure to regularly update the list of substances for which research is required.

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.

Pierre Boissery,
Rhône-Mediterranean-Corse
water agency

"The lists of substances that must be monitored grow continuously, which is quite good, and the Water agencies must now scan for up to 150 substances. Unfortunately, regulations progress faster than we can organise and we have steadily smaller budgets for monitoring. Given the above, a reduction in pollutant discharges is more important than ever. We have placed great hope in the tools now being developed to identify the sources of contaminants and that will enable us to set priorities for our pollution-management work."

In 2012, on the basis of the priorities set, a national prospective study on continental and coastal waters, including the overseas territories, attempted to detect over 180 substances in water and sediment, primarily pesticides, medication and multiple-use products. In 2011, another exceptional measurement campaign on emerging micropollutants was carried out on groundwater, under management by BRGM and the Water agencies. Using samples from 494 aquifers, the partner labs looked for a total of 411 substances, including 133 pharmaceutical products as well as phytosanitary, industrial and household products. The two campaigns, unprecedented in Europe, produced over 400 000 useful data points on pollutants that have not been extensively studied in those waters, notably certain types of medication and body-care products, gasoline additives, dioxins and furans, etc. The initial results (*F. Botta, Ineris, and B. Lopez, BRGM*) contained important information, summarised in Figures 2a and 2b.

Detailed reports on these studies and a document for the general public will be published in the beginning of 2014. The collected data will be used to update the lists of contaminants requiring monitoring during the upcoming WFD management cycles. More generally, the data served to identify priority substances in view of developing ecotoxicological knowledge and analytical techniques.

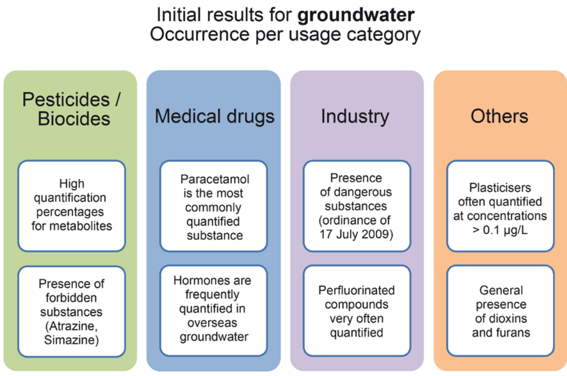


Figure 2a. Detection of emerging substances in groundwater (2011). Summary of the initial results per usage category.

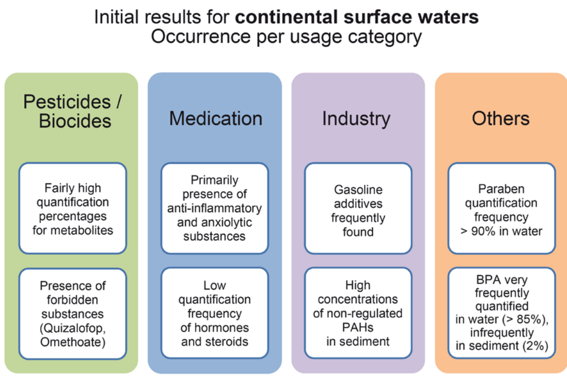


Figure 2b. Detection of emerging substances in surface and coastal waters (2012). Summary of the initial results per usage category.

Figure 2. Substances were quantified in over 90% of water samples and "contamination profiles were similar for both continental France and the overseas territories" (*F. Botta, Ineris, and B. Lopez, BRGM*).

Measurements of pollutant concentrations in the tissue of certain species selected for their integrative capacity provide both a reliable image of local contamination and solid information for the study of the impacts on organisms. This type of approach is used for routine monitoring by Ifremer, which analyses each year the concentrations of persistent organic pollutants (PCBs, PBDEs, etc.) and various emerging substances in the tissue of mussels and oysters at 25 sites along the entire coast of continental France (C. Munschy, Ifremer). The results constitute a map of contamination levels in seafood. The highest concentrations are located near industrial centres, such as the estuaries of the Seine River and of the Nivelle River (Pyrénées-Atlantiques department).

Pollutants produce impacts on aquatic environments through complex mechanisms, e.g. chronic toxicity caused by very low doses, the combined effects of mixes of chemical substances having different toxic processes, etc.

Other approaches, such as biomarkers and bioassays on entire organisms, have been developed over several decades and constitute excellent tools to reveal the exposure and/or the effects of contaminants on natural environments (*O. Perceval, Onema*). A number of biomarkers have been selected in France to provide information on contamination levels of coastal environments, for implementation of the Marine strategy framework directive[3].

[3] Directive 2008/56/EC (17 June 2008).

© O. Geffard - Irstea

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.

For example, measurements on the stability of the lysosomal membrane provide an indication on the general level of stress in fish or mussels and the observation of anomalies in the gonads of fish signals reprotoxic contamination in an environment (*T. Burgeot, Ifremer*). For freshwater environments, this type of tool is also available, notably for fish, and is used for multi-biomarker approaches in environmental investigations (*W. Sanchez, Ineris*). The Gammarus bioindicator (O. Geffard, Irstea) provides quantitative information on environmental toxicity, based on parameters measured on a population caged in situ, notably feeding and reproduction rates, and energy metabolism. “Bioanalytical” approaches, combining chemical analyses and in vitro bioassays (*N. Creusot, Ineris*) have been developed to detect, among other aspects, the activity of endocrine disruptors in aquatic environments. These methods could be used in the future for systematic assessments and monitoring of contamination in aquatic environments, notably for WFD monitoring systems.

© Michel Chantrelle, Ineris

Five years of R&D work, notably the Micropollutants 2009-2013 plan and the specific national plans, have produced considerable scientific knowledge and operational advances for monitoring and reducing chemical contamination in aquatic environments. However, the progress made also highlights the extent of the efforts and work still required. One of the major sources of future progress will certainly be better control over micropollutants in urban waters, one of the primary causes of contamination in water bodies. What are the best techniques to identify and rank the priority pollutants? What changes in practices, what innovations can be developed to avoid or reduce their release to collection systems and their effects on aquatic environments? These questions will be the topic of a call for projects launched by Onema and the Water agencies. All the details on the requested three to five-year studies are available on the Onema site at http://www.onema.fr/Appel-a-projets-Micropolluants-dans-les-milieux-aquatiques. ■

For more information

Slides from the symposium:
http://www.onema.fr/Retour-sur-le-seminaire-contaminants-chimiques-des-milieux-aquatiques-2013

A Meeting Recap will be available in 2014 at www.onema.fr, in the Resources section (Meeting Recap series).

Symposium organisation:

Onema :
Pierre-François Staub, Research and development department, and Céline Piquier, Information and communication department

Ineris :
Christine Feray, Chronic risks department, and Aurélie Prévot, Communication department

ONEMA
Meetings

Publisher: Elisabeth Dupont Kerlan
Coordination: Véronique Barre, Research and development department, and Claire Roussel, Information and communication department, Onema
Rédaction: Laurent Basilico, Pierre-François Staub and Olivier Perceval
Editorial secretary: Béatrice Gentil, Information and communication department, Onema
Translation: Bartsch & Cie (info@bartsch.fr)
Layout design: Eclats Graphiques
Production : Bluelife
Printed on paper from sustainably managed forests
Onema - 5 Square Félix Nadar - 94300 Vincennes
Document available at:
http://www.onema.fr/Les-rencontres-de-l-Onema

INERIS maîtriser le risque pour un développement durable

Ministère de l'Écologie, du Développement durable et de l'Énergie

ONEMA French national agency for water and aquatic environments