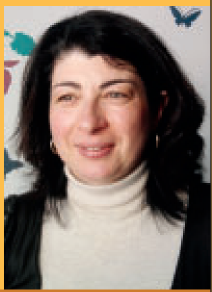
Water quality: a major challenge

Water resources are over-exploited. The management of this element essential for life on Earth is crucial for the future of humanity.



>>> Claire ALBASI, CNRS researcher in the Laboratoire de Génie Chimique (LGC, UPS/CNRS/INP lab)

The use and the conservation of surface water quality as a resource for water production for domestic use (in particular, drinking water) or industry (water of a lesser quality) is important for modern society. The complete water cycle is thus an important part of long-term water resource management.

Drinking water, waste water

Domestic use requires treatment to make water drinkable, that is to say, water that complies with quality standards compatible to human health. Once used, this water is discharged from our houses and offices. «Used» means that the water now carries molecules that include cleaning products, medicines, fats, ions (metals) and solid materials and micro-organisms that might be pathogenic. In order to avoid any sanitary and environmental risk, domestic waste water is "cleaned" either in collective networks or by systems of autonomous purification (called also "non-collectives»). Industrial usage requires a lower-quality water to begin with but discharges a much more varied water with a more complex composition. It is generally bad for the environment. This water must comply to discharge standards and undergo compulsory treatments by the user before the water can be allowed to return to the collective sewer system. Water for agricultural use is probably the one that raises the most questions concerning its re-use and sometimes one can end up with the ridiculous situation of drinking-quality water being used to wash public roads or water green spaces. The re-use of waste water has today become a political and socio-economical topic.

>>> Aeration tank of a small waste water treatment plant (Brax).

Water competitive pole

Understanding the quality of water we use is thus crucial. Research at Toulouse brings together various disciplines in areas as diverse as characterizing what it contains, to elimination and transformation of substances. The researchers are skilled in understanding the chemistry of water and treating it to rid it of pollutants, such as medical drugs. The different teams in the Midi-Pyrnées are involved in the "Water Competitive Pole", in collaboration with the Languedoc-Rousillon and Provence-Alpes-Côte d'Azur regions. Several months after its launch, this competitive pole has already certified several projects stemming from laboratories in Toulouse.
The work presented in this dossier addresses the question of water quality from three angles. The first concerns analysis and how current techniques allows us identify and quantify pollution. The second is concerned with purifying water to make it drinkable using membrane-based processes that have been developed at Toulouse and better understanding biofilms. The third angle is dedicated to better understanding the quality of water discharged into the natural environment, or one that is destined for re-use after treatment.

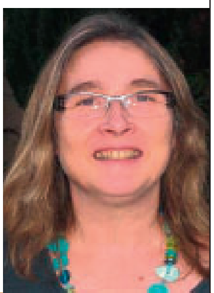
Contact: claire.albasi@ensiacet.fr

LGC: Laboratoire de Génie Chimique/ Chemical Engineering Laboratory
LISBP: Laboratoire d'Ingénierie des Systèmes Biologiques et Procédés/ Laboratory of Engineering of Biological Systems and Processes
LIMRCP: Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique / Laboratory of Molecular Interactions and Chemical and Photochemical Reactions

Pharmaceutic in waste water

Hormones, antidepressants, and antibiotics, to name a few. So many powerful pharmacological molecules are found in waste water. Several research teams in Toulouse are looking at how to eliminate these molecules before they permanently pollute the environment.

>>> Dépollution des Eaux Contaminées Group at the département BioSym of the Laboratoire de Génie Chimique (LGC, UPS/INP/CNRS lab).



>>> Corinne CABASSUD, professor at INSA, member of the Laboratoire d'Ingénierie des Systèmes Biologiques et des Procédés (LISBP, INSA/CNRS lab).

>>> Photobiologie Environnement and Photochimie Group of the Laboratoire IMRCP (UPS/CNRS lab).

Pharmaceutical products in urban waste water and water surfaces could pose risks for human health and for aquatic biodiversity. More than 150 ules, from various therapeutic classes – for example, analgesics, hormones, lipid regulators, antibiotics, anticancer drugs and other cytotoxics, and antiepileptics – have been detected in concentrations of ng/L in diverse environmental matrices (effluents of water-treatment plants, surface waters and groundwater and water sources for the production of drinking water). Faced with this problem, researchers at the Laboratoire de Génie Chimique, the Laboratoire d'Ingénierie des Systèmes Biologiques et Procédés, the Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique are studying diverse treatments - chemical, physical or biological - aimed at limiting the pollution caused by these pharmaceutics.

Membrane bioreactors

Membrane bioreactor technology (which involves coupling biological degradation with membrane separation) is particularly being studied to estimate its potential for eliminating diverse medicines. The objectives are, on one hand, to estimate the potential of bioreactors at membranes for eliminating drug molecules, and, on the other hand, to look for the effects of these molecules on the global performance of the processes.
We have shown that molecules contacting with micro-organisms responsible for the biodegradation can induce stress in these micro-organisms. This behaviour can then lead to physico-chemical changes in the biological environment. It has been shown, on laboratory scales, that under certain conditions, the concentration levels of many of these molecules can drop by around 80%. With the goal of complete elimination of contaminants in mind, the studies at Toulouse are now concerned with implementing tertiary treatments, finalizing the degradation after passage through the membrane bioreactor, either by nanofiltration, or by photochemical treatment.

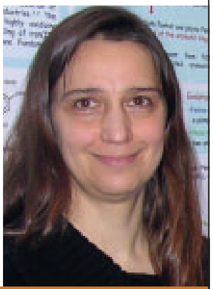
Nanofiltration or photochemical

Nanofiltration or osmotic membranes retain molecules that will be sent back into the bioreactor. The impact of this extended contact time, as well as the quality of the retention (depending on the properties of the water matrix), are being studied. The choice of the tertiary process membrane also turns out to be a decisive factor in determining the quality of the water produced in the end, with a view to re-use or re-introduction into the natural environment.
The photochemical methods are part of processes known as advanced oxidation. They allow to obtain the total mineralized content of organic matter present (by total conversion of the target compound into carbon dioxide, water and inorganic ions). These techniques have the advantage of producing, at ambient temperatures and pressures, a powerful oxidizer -the hydroxyl radical. This species, in spite of its short lifetime, is capable of oxidizing a wide variety of organic compounds (medicines, pesticides and colouring agents, for example), by tearing (wrenching) hydrogen or by addition in double links. Trapping by the dioxygen of the organic radicals so formed starts oxidizing degradation reactions in chain that eventually lead to the mineralization of the organic matter. Trials on the experimental scale have demonstrated the efficiency of some of these methods to decrease the concentration of certain anti-cancer or antiepileptics to below their threshold of detection.

Contacts: claire.albasi@ensiacet.fr, corinne.cabassud@insa-toulouse.fr and florence@chimie.ups-tlse.fr

Toxic molecules in the water, better and better analyzed

Metals, hydrocarbons, pharmaceutical molecules, pesticides and nitrates. The majority of streams and subterranean springs in France contain such unwanted elements, or at least traces of these elements. Toxicological analysis allows us to draw up a balance sheet of the quality of the water and how to improve it. Here we present a short review of the analytical methods currently being used.



>>> Florence BENOIT MARQUIE, assistant professor in Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique (IRMCP, UPS/CNRS lab).

Minimize the risks that humans take when drinking water and the damage that polluted water does to the environment. These are the objectives of water quality controls. The European water framework directive aims at obtaining a good state of water resources by 2015, and improve its chemical quality, in particular by reducing the discharge of «priority» substances and eliminating the discharge of substances deemed to be dangerous. A preliminary list of such substances has been adopted. These include pesticides, xenobiotics, metals and hydrocarbons. Chemical pollutants in water are of two types: organic pollutants and inorganic and metallic pollutants. For each, specific and very successful methods of analysis have been developed on the Toulouse campus.

Millions of toxic molecules

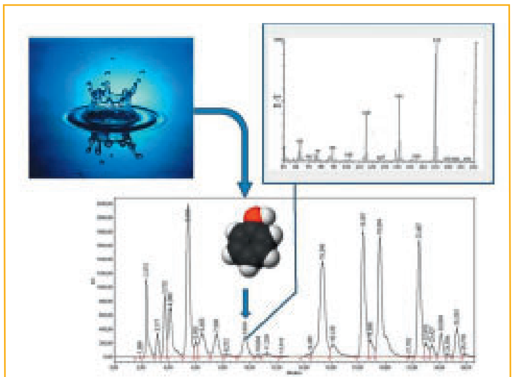
Organic micropollutants in water are usually chemical and very varied. They include cleaning solutions, phenols and their by-products, residues of phytosanitary products or medicines, synthetic hormones, hydrocarbons and haloforms.

Potentially, there are several million organic molecules that can be discharged into water and which can be toxic, even at very low concentrations. We thus look specifically for a molecule or a family of compounds by using a normalized method of analysis involving chromatographic separation. According to the chemical nature of the compounds to be separated, we can use chromatography in gaseous phase (CPG), ionic or liquid high-performance (HPLC) or ultrahigh performance (UPLC-UHPLC). Coupling GC-MS and LC-MS together leads to very powerful analytical tool, which allows for fast identification of compounds. The selectivity of the systems LC/GC-MS is very high, and allows us to isolate co-eluted compounds (those that are transported simultaneously). These analyses allow us to determine the masses of compounds and their fragmentation (by MS/MS mode). MS/MS allows to study fragments produced during the collision between an ion and a neutral gas like argon in a controlled cell.

Unknown micropollutants

For unknown micropollutants, it is possible to create a chemical «imprint» corresponding to all chromatographic peaks of specific masses and fragments of a sample. Databases can be established and compared to follow the evolution of these unknown compounds. In high-resolution systems, it is possible to realize an elementary analysis of the compound - that is, to propose a raw formula from its exact mass and from its isotopic profile. This information can generally be obtained in mass spectrometers.

The sensitivity of current systems allows to obtain limits of quantification (LOQ) that are 1000 times lower than those obtained by UV detection. For the analysis of trace (concentrations lower than 10-6 mol/L) and of ultratrace (c < 10-9 mol/L) it is possible to concentrate the compound to be studied by adsorbing it on a solid support in an organic solvent that can then be evaporated. Such systems can also be coupled to a liquid chromatography system for a complete and totally automated analytical tool. All these techniques are used by the Toulouse teams working in the field of water pollution for various research projects, like, for example, the analysis of xenobiotics.



>>> Analysis of the organic compounds by the LC-MS.

Accumulation of metals

Water pollution can also result from the accumulation of metals. Indeed, metals are present naturally in the Earth's crust and are crucial to life on Earth. However, they can also be highly toxic to living organisms depending on their quantity.

There are several techniques to measure the concentrations of metals in varied matrices (natural waters, ground and rocks), but since the beginning of the 1980s these concentrations are generally obtained by ICP-MS (Inductively Plasma Mass Spectrometry).

headline

This analytical technique revolutionized the measure of metal concentrations because it allows for fast analyses (40 elements in five minutes), huge precision while having a limit of very low detection - on the order of micrograms per litre. These state-of-the-art techniques developed by the Toulouse teams are used in numerous research projects - for example, for dosing metals such as copper or zinc accumulated in biomass, seaweed and bacteria, present in Garonne (by the LMTG/ECOLAB team), or the evaluation of various metal concentrations in sediments transported by streams in Gascony (ECOLAB/ENSAT).

Alarm systems

Because of the vital importance of water quality, in particular for the preservation of the environment, it is crucial to have biological alert systems that allow to assess how harmful pollutants are. Until a few years ago, we essentially worried about the dangers of massive amounts of pollution and the ability of rivers, seas and oceans to recover from acute toxicity. Nowadays, we are not only concerned about general toxicity, which affects living organisms - be they terrestrial or aquatic in direct contact contact with the effluent (for example zebra fish, water plants and seaweeds) - we also study genotoxicity (impact of pollution on genetic material). Indeed, the genotoxicity of aquatic pollution in water (whose effects are much more insidious and often pass unnoticed in the short-term) must be taken into account because of the fatal repercussions that it can have on living organisms (including man). The genotoxic character of micropollutants thus makes up a major part of long-term toxicity. It is worrisome in many respects because of mutagenic and/or teratogenic effects that can affect individuals or their offspring by modifying the genetic heritage of the concerned species and by possible carcinogenic effects that can develop in the exposed individual.


>>> Xenope larvae used for the toxicity tests.

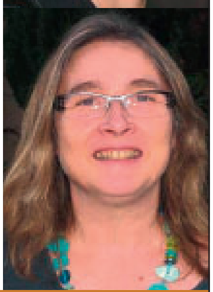
The Toulouse teams ECOLAB and LGC have developed various biological tools to measure the visible effects of genotoxic pollutants in water, including drinking water, using several approaches. The first are in vitro studies on various types of cells (hepatic or renal, for example), or in vivo studies on zebra fish or on amphibian larvae (xenope). In this last case, the sensitivity of these vertebrates was used by the researchers to develop a simple, fast and robust biological test. The method, particularly relevant for aquatic animals, turned out to be sensitive enough to reveal genotoxic effects in water, where we expected, a priori, not to find them. This biological tool is the object of a standard ISO (International Standard Organization) since 2006 as well as of the AFNOR standard (French National Organization for Standardization). Its use, within the framework of numerous curricula, has contributed in improving treatment processes of water (for instance, purification of drinking water and the control of the formation of by-products of purification as well as understanding how these products act). It has also allowed the in-depth study of surface and underground water that needs to be purified, waste water during the various stages of treatment before return to the natural environment, as well as urban or industrial water-treatment plants (in particular within the framework of their use in agriculture).

Contributed to this article: Jean Christophe Garrigues, Laboratoire des Interactions Moléculaires et Réactivité Chimique et Photochimique (UPS/CNRS lab); Cathy Claparols, Mass Spectrometry Unit of the Toulouse Institute of Chemistry; Laury Gauthier and Eric Pinelli, Ecolab (UPS/CNRS lab); Jerome Viers, Geosciences Toulouse Environment (UPS/CNRS/IRD lab); Annie Leszkowicz, Laboratoire de Génie Chimique (UPS/INP/CNRS lab)

Contact: florence@chimie.ups-tlse.fr

Membranes, the right choice for removing biological contaminants from water

To rid water of microbes, bacteria, viruses or fungi responsible for disease transmission, nothing is cleaner than a membrane. But it must have pores fine enough to retain tiny viruses or bacteria that can change their shape.



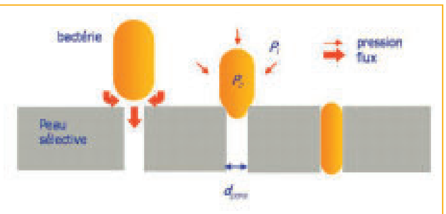
>>> Christel CAUSSERAND, professor at Paul Sabatier University, researcher at the Laboratoire de Génie Chimique (LGC, UPS/INP/CNRS lab) and Corinne CABASSUD, professor at INSA, researcher at the Laboratoire d'Ingénierie des Systèmes Biologiques et des Procédés (LISBP, INSA/CNRS lab).

In treatments for producing drinking water, the conventional techniques of disinfection (chemical or physical) present a certain number of disadvantages. In particular, these processes often only partially inactivate microorganisms. In this context, ultrafiltration which allows the removal of microorganisms present in water using a physical barrier, is an alternative or complementary process to these techniques. The advantages of the membrane-based process are numerous. In particular it doesn't require the use of chemical oxidants and thus avoids the formation of disinfection by-products. Moreover, as long as the integrity of the membrane is not compromised, the quality of water produced by this process is independent of the quality of the source. Nevertheless, the presence of imperfections in the membrane structure likely to be generated during the manufacture or use can lead to an unexpected transfer of microorganisms.

The work carried out by the researchers of the LGC and the LISBP at Toulouse aims at developing, together with membrane manufacturers and water companies, protocols for assessing membrane processes safety. These studies have led to the use of tracers, which may be biological (bacteria or viruses) or artificial (virus surrogates), in suspension preparation, in tests at laboratory or pilot scales, and in quantification methods used for the analysis of samples.

Deformable bacteria

Concerning biological tracers, work conducted on the study of the behavior of bacteria during filtration allowed us to interpret the leakages observed under certain conditions as a result of the presence of defects in the membrane structure (abnormally large pores, for example) linked to the ability of some organisms to deform under stress. It appears that gram-negative bacteria are deformable and thus likely to pass through the membrane pores with diameter less than their size at rest. Gram-positive bacteria, for which the ability to deform is more limited, are totally retained. A new method for characterizing membranes has thus been proposed. It is based on selective transfer that occurs by the deformation of bacteria and is designed to detect larger pores present in the membrane structure (in the range of 0.05 to 1.2 µm) that can lead to contamination of the permeate.



>>> The passage of bacteria through membranes.

Virus behavior during filtration has also been investigated to propose a protocol for determining the reduction of virus number by ultrafiltration membranes in conditions close to those encountered in water treatment. Here, the most relevant viruses proved to be the bacteriophage MS2. On the other hand, three phenomena have been taken into account that can affect the apparent elimination of viruses: aggregation, adsorption and viral inactivation. These can lead to an overestimation of the system's effectiveness.

Virus surrogate

Concerning artificial tracers, a new virus surrogate has been developed to characterize retention dynamics (ANR Precodd Program POME). This surrogate is a bacteriophage modified by grafting enzymatic probes that then allows it to be detected and quantified directly in solution and online. Moreover, it is representative of a native virus in terms of size, molecular weight and surface charge. While the first filtration tests have helped to validate the similarity of behavior between surrogate and native bacteriophage MS2, optimizing the detection method has allowed for a dynamic monitoring of membranes. This new characterization tool could be really helpful for the rapid detection of integrity problems in membrane filtration systems.

Contacts: *causserand@chimie.ups-tlse.fr and corinne.cabassud@insa-toulouse.fr*

How to treat industrial effluents?

Pollutants present in industrial effluents hardly degrade in the environement. Specific treatments are required to remove them.

>>> Mathieu SPERANDIO, professor at INSA Toulouse, researcher at the Laboratoire d'Ingénierie des Systèmes Biologiques et des Procédés (LISBP, INSA/CNRS lab) and Marie-Hélène MANERO, professor at the IUT/UPS, researcher at the Laboratoire de Génie Chimique (LGC, UPS/INP/CNRS lab).

Industrial activities contribute to water pollution and are thus a priority for the European water framework directive as substances requiring drastic discharge standards. In Toulouse, researchers from the Laboratoire de Génie and the Laboratoire d'Ingénierie des Systèmes Biologiques et des Procédés have developed specific treatments that can be used to treat this pollution.

Petroleum products

The treatment of some xenobiotic organic molecules, particularly those from petroleum products, is the subject of several research projects. For poorly biodegradable pollutants, one solution is to adsorb the pollution on porous solids. But what to do with the partially saturated adsorbent? Proposed solutions consist of chemical oxidation of adsorbed pollutants or biological regeneration.

One way is to combine a chemical solution with activated carbon or zeolite in the same reactor and regenerate the adsorbent in situ using either catalytic wet air oxidation under pressure (AD-OX process with activated carbon) or ozonation under ambient conditions (AD-OZ process with zeolite). In the first case, the catalytic effect of the activated carbon allows us to operate at moderate temperatures.

In the second case, the solid can decompose ozone into hyper-reactive species destroying the molecules trapped in the pores of the zeolite. Ongoing studies are focusing on the influence of both the adsorbent and pollutant properties on the overall process performance, the evolution of the adsorption capacity, as well as the optimization of cycle time. In the context of sustainable development, the efficiency of non-conventional activated carbons made from sewage sludges is also being investigated. Moreover, advanced oxidation techniques, such as the photo-Fenton reaction, photocatalysis and electrochemistry, are being evaluated for regenerating exhausted activated carbons.

>>> Ozonation reactor.

Bioremediation

Researchers are also assessing the efficiency of a process alternating adsorption on granular activated carbon and bioremediation by biofilms, especially in the case of naphthalene or toluene. Encouraging results have been obtained: the molecules adsorbed on meso- and macro-pores can then be biodegraded by the biofilm. Membrane bioreactors with activated carbon injection have been also evaluated for the elimination of aromatic molecules, such as dimethyl-phenol. Another project aims to model microbial diversity to improve the resistance and resilience of a bacterial community in these bioreactors.

The most hydrophobic micropollutants (such as PAHs) cause particular difficulties: these substances are adsorbed very quickly on solids and flocs, which limits their accessibility to bacteria, reduces biodegradation rates and leads to their accumulating in sludge. One proposed solution is to test various physical and chemical stresses to modify the properties of biological suspensions and minimize the immobilization of PAHs. These tests have reduced the accumulation of certain molecules (phenanthrene and fluoranthene, for example) in sludges issued from two laboratory-scale biological processes from 60 to 70%.

Also contributed to this text: Carine Julcour (CNRS researcher, LGC), Caroline Andriant Siferana (assistant professor, LGC) and Jean-Stéphane Pic (assistant professor, LISBP)

Contacts: Mathieu.sperandio@insa-toulouse.fr and marie-helene.manero@iut-tlse3.fr

Microbial biofilms in water pipes

In water pipes, pathogenic bacteria form colonies, or biofilms, that are difficult to eradicate.

>>> The Biofilm et Adhésion Bactérienne team from UFR de Pharmacie joins the bioSYM Department of the Laboratoire de Génie Chimique (LGC, UPS/INP/CNRS).

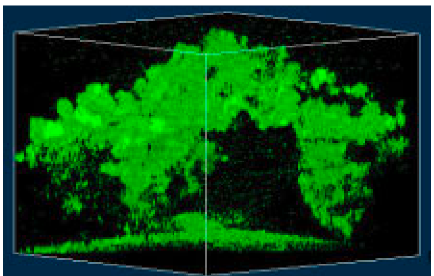
A low concentration of chlorine is the traditional way to control microbial populations in drinking water as a preventative method. But when a curative treatment is necessary, that is, in hospitals or industrial systems, thermal and/or chemical shocks (circulating solutions of highly concentrated disinfectant solutions) are utilized. The effectiveness of these processes has been demonstrated against planktonic (free-swimming) micro-organisms. However, bacterial structures known as biofilms can develop at the interface between water and a solid substrate. These structures consist of sessile micro-organisms forming aggregated colonies and are considered to be the major bacterial form of life. Biofilms can include bacteria, fungi, microscopic algae and protozoa, adhering to each other or to a surface.

Microcolonies

In biofilms, micro-organisms are able to proliferate in micro-colonies embedded in a matrix of extracellular polymeric substances like polysaccharides, proteins, or nucleic acids (sometimes associated with minerals). This matrix is partly responsible for the weak effect of biocides in biofilms (due to limited biocide diffusion and the neutralization or consumption of the biocide). Also, adhering micro-organisms present specific phenotypical and genotypical characteristics leading to a modification of potential targets for antimicrobial molecules. These two phenomena explain the eventual loss of sensitivity to treatments of bacteria in biofilms. They also help us to understand the ubiquity of biofilms, which are found not only in water pipes but also on medical devices, mucous membranes or teeth.

Legionella

In water systems, biofilms can harbour potential pathogens (like Legionella and some species of Vibrio) that can be released into the water flow. Hence, biofilms represent an important health risk via the degradation of drinking water quality. Understanding how biofilms work is a major health issue and, in the last decade, an increasing number of studies have been developed concerning both fundamental and functional aspects of biofilms. Various approaches are being developed on the Toulouse campus. Macroscopical behaviour of biofilms is being evaluated according to physical and chemical parameters (fluid hydrodynamics, composition of the liquid phase and of the matrix) aimed at rational control (LISBP, IMFT). Other teams (LGC-BioSYM) are interested in physiological and physiopathological aspects. Recently, we demonstrated the capacity of Legionella pneumophila to form biofilms in the absence of other micro-organisms and protozoa and this work led to the development of a relevant model for studying sessile L. pneumophila behaviour. This model, also available for studying other species (such as Pseudomonas aeruginosa) allows fundamental and applied approaches: evaluation of the loss of sensitivity and modification of pathogenicity factors.



>>> L. pneumophila biofilm (height > 300µm).

From cosmetics to aeronautics

This developing research domain concerns various industries, specifically in the Midi-Pyrénées region. Not only is it attractive to water producers but also to pharmaceutical and cosmetic industries or food plants that need to control their production processes as well as the cleaning and disinfection of their water systems. Even aeronautics (cutting fluids systems) and hospitals will benefit from these studies.

~~(1) : LISBP : laboratoire d'Ingenierie des Systèmes Biologiques et des Procédés (unité mixte INSA/CNRS/INRA).~~
~~IMFT : Institut de mécanique de fluides de Toulouse (unité mixte UPS/INP/CNRS)~~

A traduire

Contacts: christine.roques@cict.fr and sophie@pecastaings.net