River Conservation
Challenges and Opportunities

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Chapter 5 Offprint

The River Drugstore: The Threats of Emerging Pollutants to River Conservation

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Chapter 5

The River Drugstore: The Threats of Emerging Pollutants to River Conservation

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Due to the rapid growth of population, industrialization and change in life style, water contamination has become one of the major environmental concerns faced by the world today. This chapter focuses on pollution by organic micro-contaminants, giving an overview of the main sources and routes of entry of specific classes of contaminants, such as pesticides, pharmaceuticals, perfluorinated compounds, endocrine disrupting compounds, etc. Potential effects on aquatic organisms and humans are also discussed.

5.1. What is pollution?

Since early in history, people have dumped sewage into waterways, relying on natural purification by dilution and by biodegradation. However, the rapid growth of population, and change in life style resulted in a greater volume of domestic and industrial wastewater generated and subsequently discharged into the aquatic environment. Consequently water contamination became one of the major environmental concerns faced by the world today. Water quality has a direct impact on citizens and economic sectors that use and depend on water, such as agriculture, tourism, industry, energy and transport. It also affects river-associated ecosystems and the biodiversity they host. The effects of water contamination on humans are many, including disruption of the natural food chain, diseases, as well as serious harm to aquatic ecosystems.

There are many different types of water pollution and all have specific adverse effects on the environment and humans. The following types of water contaminants are usually distinguished:

— nutrients (nitrogen and phosphorus) and organic matter causing an increase in algal production and depletion of oxygen from the water column,
— inorganic compounds (salts, such as chlorides, sulphates and metals) that are toxic to aquatic organisms and can affect the rest of the food chain,
— organic (micro-) pollutants that can affect the health of aquatic organisms and those who eat them,
— microorganisms (virus, bacteria, protozoa) producing infectious diseases in aquatic life or terrestrial life through drinking water,
— suspended particles that reduce the amount of sunlight penetrating the water, and the oxygen transport into the sediments,
— physico-chemical pollution, such as thermal pollution (increase in water temperature due to hot water discharges) or change in the pH (i.e. acidification),
— radionuclids.

This chapter focuses on the pollution by organic micro-contaminants, a large group of compounds differing in their toxicity, mobility and behaviour in nature, and one that is constantly increasing in numbers, as new products are being synthesized and used in the industry. The chapter also gives an overview of the main sources and routes of entry of specific classes of contaminants, as well as potential effects on aquatic organisms and humans.

5.2. Sources

Generally, pollution of the aquatic environment originates from point or diffuse (or non-point) sources. *Point source pollution* enters a water body at a specific site, such as a sewer, and can generally be readily identified. Potential point sources of pollution include effluent discharges from wastewater treatment plants (WWTP) and industrial sites, power stations, landfill sites, fish farms, and oil spills from pipelines. Amongst them, WWTP deserve special attention as their effluents are the main source of many organic contaminants as shown in Box 5.1. Point source pollution generally can be prevented or at least reduced, since it is possible to identify where it is coming from. Therefore, the responsible person or agency can take immediate remedial action or invest in preventive measures such as longer-term investment in treatment and control facilities.

Diffuse pollution occurs where substances are widely used and dispersed over an area as a result of land use activities such as agriculture, farming and forestry.

Box 5.1

Point source – Wastewater treatment plants (WWTP)

WWTP effluents are the principal source and route of entry of many contaminants into the environment. Sewage is generated by residential, commercial and industrial establishments. It includes household waste liquid from toilets, baths, showers, kitchens, sinks and so forth that is disposed of via sewers. In many areas, sewage also includes liquid waste from industry and commerce. Sewage may include stormwater runoff in the case of combined sewer systems. These systems are usually avoided because precipitation causes widely varying flows reducing sewage treatment plant efficiency. With increasing urban population, changing lifestyles and industrialization, the quality of wastewater has deteriorated over the years, and hence requires treatment before it can be discharged into the aquatic environment or recycled for any purpose. In addition, the cost of water increases and environmental regulations for wastewater discharge become more stringent, thus making it necessary to implement more efficient treatment, including different physico-chemical and biological steps. Since the early 1970s until about 1980, aesthetic and environmental concerns were mainly considered, and wastewater treatment facilities were designed to reduce organic matter and nutrients such as nitrogen and phosphorus, and suspended solids. Since 1980, focus on health concerns related to toxics has driven the development of new treatment technology. However, in spite of advanced treatment options, not all organic contaminants are removed during treatment, resulting in degraded receiving water quality. Many toxic substances can

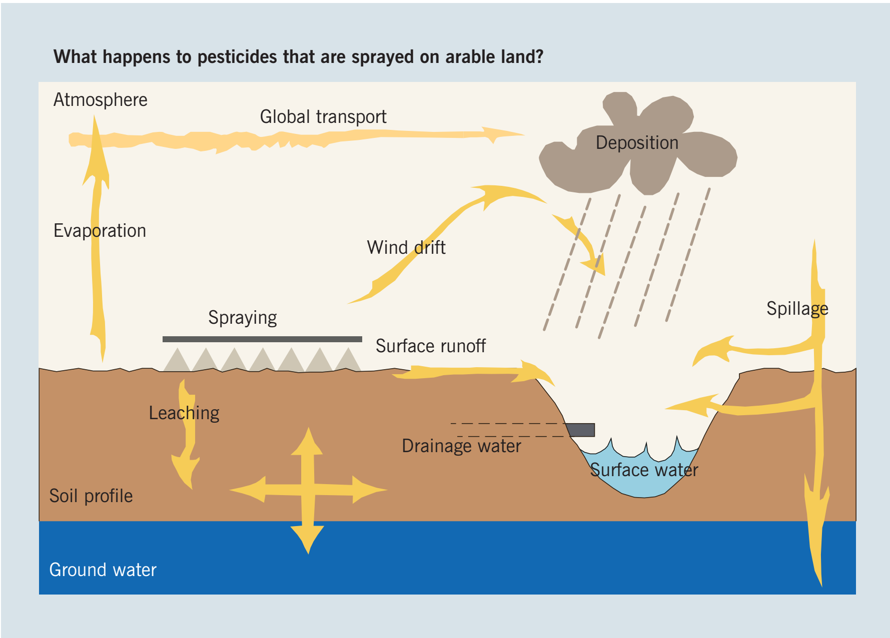
Figure 5.1:
Discharge pipe

Box 5.1 ***(cont.):*** **Point source – Wastewater treatment plants (WWTP)**

pass through conventional treatment systems (based on activated sludge treatment). These are designed and dimensioned to achieve the prescribed removal of organic matter and nutrients, and their discharge is regulated on a national level to limit the total load to the recipient systems, thereby minimizing potential problems with oxygen consumption and eutrophication. However, no such regulations exist regarding organic micropollutants in the effluents from WWTPs. Most concerning are polar compounds that may occur in WWTP effluents because they are truly persistent under these conditions. The occurrence and removal of many polar chemicals has been studied, but still it is often not clear whether a certain class of compounds is widespread in municipal wastewaters, to which extent they are removed in WWTP and whether yet unknown polar metabolites are being formed.

Examples of diffuse pollution include the leaching to surface water and groundwater of contaminants from roads, manures, nutrients and pesticides used in agriculture (Figure 5.2) and forestry, and atmospheric deposition of contaminants arising from industry and combustion. It is often difficult to identify specific sources of such pollution, and prevention often requires major changes to land use and management practices.

Figure 5.2: *Diffuse source – Agriculture. Pesticides sprayed on fields can be transported to nearby surface water by run-off of rainfall or to groundwater by leaching of water through the soil. They can also be transported away in the air through wind drift and evaporation and then carried back to soil or water*



Source: Adapted from Swedish University of Agricultural Sciences.

5.3. Main classes of organic microcontaminants

Current use of chemicals by our technological society can be estimated in some hundreds of thousands of compounds (most of them organics) and this number is continuously growing (Figure 5.3). Depending on their properties and extent of use, a large amount of different chemicals can potentially reach the environment, their environmental and health effects being hard to predict in the long term.

The use of several products of unknown environmental impact was widespread after the Second World War, most used as products against agricultural pests, others applied as industrial products. Amongst them, DDT, aldrin, or parathion, but also heavy metals such as mercury, cadmium, or lead were used without any environmental protection. Public awareness of the effects of these products on the environment and human health was slow, it came by the hand of activists such as Rachel Carson and her renowned book *Silent Spring*. Non-polar hazardous compounds, i. e. persistent organic pollutants (POP) and heavy metals were in the focus of the administrations' interest and some of these products were

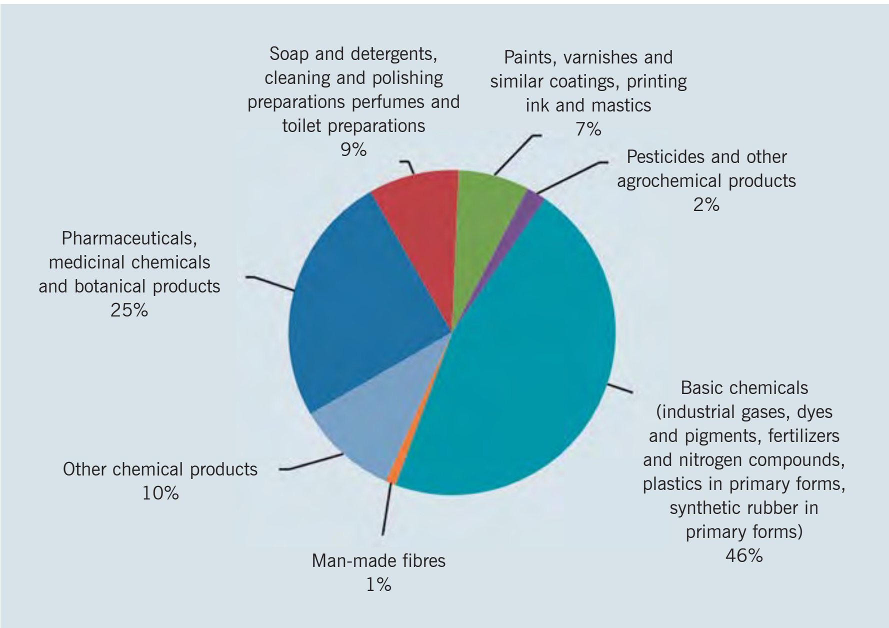


Figure 5.3: *Use of chemicals in our technological society. Manufacturing of chemicals and chemical products by production value in EU-27*

Chemical Abstracts Service (CAS): ~8,400,000 registered compounds.
European Union: ~100,000 compounds available.
REACH (EU Regulation on Registration, Evaluation, Authorisation and Restriction of Chemicals): ~30,000 compounds (10,000 already registered).
Source: Eurostat.

banned. The main concern is related to their persistance in the environment since they are resistant to environmental degradation through chemical, biological, and photolytic processes. Consequently, they can bioaccumulate in human and animal tissue and biomagnify in the food chain having significant impacts on human health and the environment. Their definition as priority pollutants came together with intensive monitoring and control programs. The global concern of these pollutants was finally defined by the United Nations treaty, signed in Stockholm, Sweden, in May 2001. Under the treaty, known as the Stockholm Convention, countries agreed to reduce or eliminate the production, use, and/or release of an initial twelve chemicals or chemical groups, the so called "the dirty dozen" (Table 5.1).

Today, the pressure of increasingly strict regulations, the adoption of appropriate measures and the elimination of the dominant pollution sources has resulted in a drastic reduction of emissions as well as a decrease in their arrival to the aquatic ecosystems. In the industrial sector, the reduction in discharges of POPs, particularly characteristic of the chemical, paper, textile and food processing sectors, was initiated in the 1970s with reductions at source combined with the implementation, made compulsory by legislation, of efficient wastewater treatment plants.

However, the so-called "emerging" or "new" unregulated contaminants have emerged as an environmental problem and there is a widespread consensus that this kind of contamination may require additional legislative intervention. A wide

Table 5.1: *The* dirty dozen

Aldrin – Pesticide widely used on corn and cotton until 1970. Closely related to dieldrin
Chlordane – Pesticide on agricultural crops, lawns, and gardens and a fumigant for termite control
DDT – Pesticide still used for malaria control in the tropics
Dieldrin – Pesticide widely used on corn and cotton until 1970. A breakdown product of aldrin
Endrin – Used as a pesticide to control insects, rodents, and birds
Heptachlor – Insecticide in household and agricultural uses until 1988
Hexachlorobenzene – Pesticide and fungicide used on seeds, also an industrial by product
Mirex – Insecticide and flame retardant
Toxaphene – Insecticide used primarily on cotton
Polychlorinated biphenyls (PCB) – Widely used in electrical equipment and other uses
Polychlorinated Dioxins and Polychlorinated Furans – Two classes of "unintentional" pollutants, by-products of incineration and industrial processes

range of man-made chemicals designed for use in industry, agriculture and as consumer goods, as well as chemicals unintentionally formed as by-products of industrial processes or combustion, are potentially of environmental concern. The term "emerging contaminants" does not necessarily correspond to "new substances", i.e. newly introduced chemicals and their degradation products/ metabolites or by-products, but refers also to compounds with previously unrecognised adverse effects on the ecosystems, including naturally occurring compounds. Therefore, "emerging contaminants" can be defined as contaminants that are currently not included in routine monitoring programs and which may be candidates for future regulation, depending on research on their toxicity, potential health effects, public perception and on their occurrence in the environment. Their concern has been raised as a consequence of the progress achieved in analytical chemistry. Increased sensitivity in mass spectrometry, as a result of more efficient ionization techniques and better detectors, has enabled detection of virtually any contaminant at a very low level.

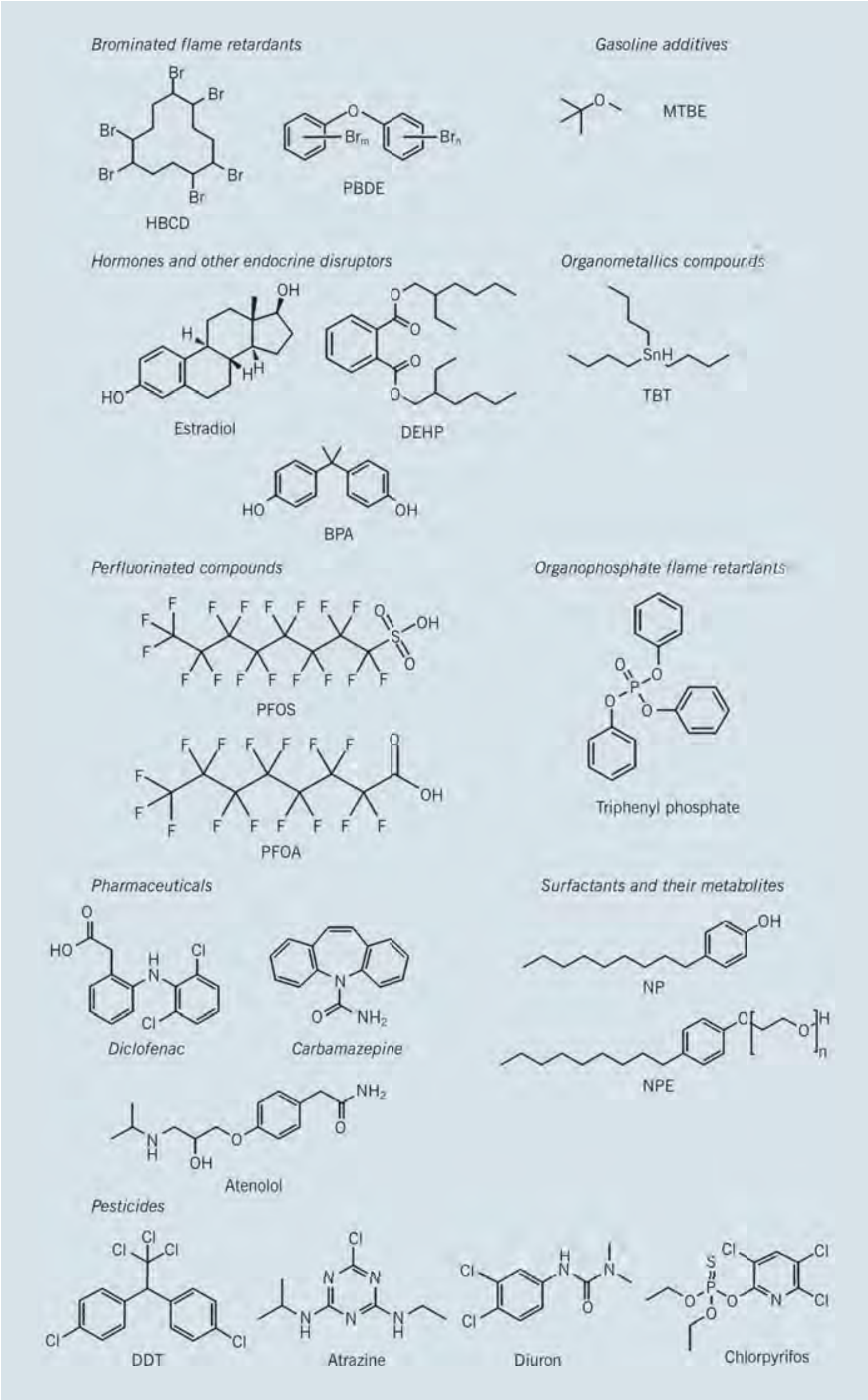
Particularly relevant amongst these emergent pollutants are several groups of compounds including brominated flame retardants, disinfection by-products, gasoline additives, hormones and other endocrine disrupting compounds, nanomaterials, organometallics, organophosphate flame retardants and plasticisers, perfluorinated compounds, pharmaceuticals and personal care products, polar pesticides and their degradation products, siloxanes, surfactants and their metabolites.

Some representative examples of common pollutants of the aquatic environment are shown in Figure 5.4. For most emerging contaminants, data on their occurrence and effects in the environment are not available and, therefore, it is difficult to predict what effects they may have on human health and on aquatic organisms. Numerous field studies are being conducted to identify the sources and points of entry of these contaminants into the environment, and to determine their concentrations in both wastewaters and the receiving environment.

5.3.1. Pesticides

Pesticide pollution in waters usually occurs from diffuse sources (runoff after application in agriculture), with minor point-type pollution from industrial emissions caused during production. Over the years the pesticides used have changed, from persistent compounds, hardly degradable, such as organochlorines (DDT, lindane, cyclodienes type aldrin, endrin, dieldrin, endosulfan, etc.) to more polar (water soluble) compounds that are degradable, such as N-methylcarbamate. However, their use has not stopped growing.

Figure 5.4: *Some representative examples of common pollutants of the aquatic environment*



Pesticides have been regulated and studied for decades. The current priority list of the EU Water Framework Directive (WFD) includes several individual compounds from different chemical classes, such as alachlor (aniline), atrazine and simazine (triazine), the chlorofenvinfos and chlorpyrifos (organophosphate), diuron and isoproturon (phenylurea), endosulfan (organochlorine), and trifluralin (dinitroaniline). All the above compounds are active ingredients of the phytosanitary formulations and their levels in the aquatic environment are certainly disturbing. However, the concern about pesticides is now focused mainly on their degradation products, which are often more ubiquitous and toxic than the parent compounds.

5.3.2. Pharmaceuticals and personal care products

The term "pharmaceutical" encompasses all prescription, non-prescription and over-the-counter therapeutic drugs, in addition to veterinary drugs and nutritional supplements. Personal care products include all consumer chemicals typically found in fragrances, lotions, shampoos, cosmetics, sunscreens, soaps, etc.

In the EU around 3,000 different pharmaceutically active compounds are used in human medicine. Most of modern drugs are small organic compounds, which are moderately water soluble, but still lipophilic, which permit them to be bioavailable and biologically active. They are designed to have specific pharmacologic and physiologic effects at low doses and thus are inherently potent, often with unintended outcomes in wildlife. Their consumption has increased recently and will continue to increase due to the expanding population, general ageing, increase of per capita consumption, expanding potential markets, new target age groups, etc. After they are administrated, pharmaceuticals are excreted via liver and/or kidneys as a mixture of parent compounds and metabolites that are usually more polar and hydrophilic than the original drug. Thus, after their usage for the intended purpose, a large fraction of these substances is discharged into the wastewater, unchanged or in the form of degradation products, that are often barely eliminable in conventional WWTPs. Depending on the efficiency of the treatment and chemical nature of a compound, pharmaceuticals can reach surface and ground waters.

Pharmaceuticals have been found in treated sewage effluents, in surface waters, in soil, and in tap water. Although the levels are generally low, there is rising concern about their potential long-term impacts to both humans and aquatic organisms as a result of the continuous environmental exposure to these compounds. These levels are unable to induce acute effects in humans, i.e. they are

Box 5.2

Case study: Occurrence of pharmaceuticals in the Ebro River basin

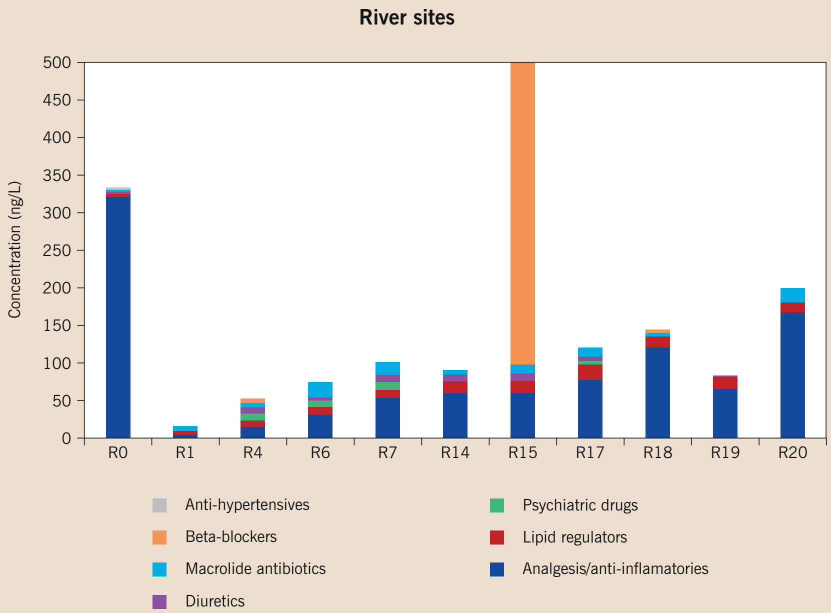
The Ebro River basin (northeast of Spain) drains an area of approximately 85,000 km^2, ending in the Mediterranean Sea and forming a delta of more than 30,000 ha. The most relevant economic activity in the region is agriculture (vineyards, cereals, fruit, corn, horticulture and rice production), but there are also some highly industrialized regions, mainly located in the northern-central part, close to the cities of Zaragoza, Vitoria, Pamplona, Logroño, Monzón and Lleida. Around 2,800,000 inhabitants live in the area.

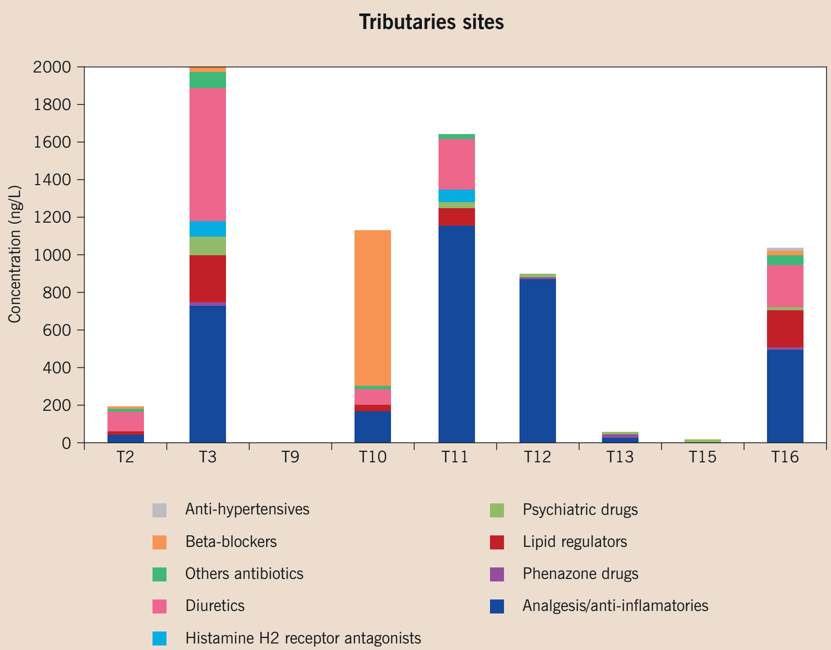
Pharmaceuticals were commonly found in the river water. The highest concentrations were detected in small tributary rivers adjacent to WWTP discharges (T3, T10, T11, T16), with low river flow rates and therefore low dilution of discharged effluents. The highest levels were found for anti-inflammatory drugs and analgesics such as acetaminophen, ibuprofen and ketoprofen. Other pharmaceutical classes showing high concentrations were the β-blocker atenolol and the diuretics hydrochlorothiazide and furosemide.

The hazard posed by pharmaceuticals in both surface and effluent wastewaters was assessed toward different aquatic organisms (algae, daphnids and fish). Studies showed that no significant risks exist in the Ebro River associated with the presence of pharmaceuticals, which indicate that reduction of compound concentration after wastewater treatment as well as dilution in the receiving river water efficiently mitigate possible environmental hazards. However, studies were only focused on the toxicity that individual compounds may cause to aquatic organisms, while toxicity of mixtures of pharmaceuticals (and also mixtures of other contaminants) was not taken into account. Therefore, in the absence of definitive data we should not relax our vigilance.

Figure 5.5: *The Ebro River basin, in N Spain, and the location of the sites in this case study*

Figure 5.5 *(cont.)*





far below the recommended prescription dose, but have been found to affect aquatic ecosystems. Antibiotics and estrogens are among the many pharmaceuticals suspected of persisting in the environment either due to their resistance to natural biodegradation or to continuous release.

5.3.3. Natural and synthetic hormones

Female sex hormones and synthetic estrogens are considered the most potent endocrine disrupting compounds (compounds that interfere with the hormonal (endocrine) system in animals, including humans). Synthetic estrogens and progestogens are commonly administered in contraceptive formulations and for treatment of certain cancers and hormonal disorders as common as the menopause. Both natural and synthetic steroids, in either a conjugated (as glucuronides and sulfates, principally) or an unconjugated form, are excreted in the urine of mammalians and enter the aquatic environment via wastewater treatment plant effluents or untreated discharges. These potent estrogenic compounds have been shown to induce estrogenic responses in fish at concentrations in water (0.1-1 ng/L) (Purdom et al. 1994), concentrations often exceeded in the environment, and have been associated with certain alarming effects on reproduction and developmental processes, such as feminization, decreased fertility, or hermaphroditism (Colborn et al. 1993).

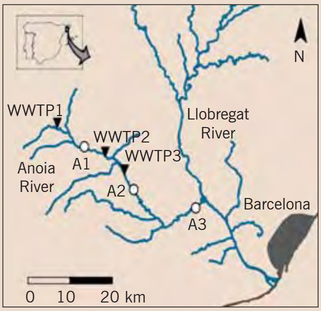
5.3.4. Alkylphenols

Alkylphenols, including nonylphenol (NP) and octylphenol (OP), are degradation products of surfactants alkylphenol ethoxylate type (APEOs). With a global production of about 500,000 tons per year, this type of surfactants are primarily used as detergents in both domestic and industrial sectors, especially in the textile, leather and paper industry, and as adjuvants for pesticides, paint ingredients, and wetting agents, among others. The concern lays in the fact that approximately 60% of APEOs entering WWTPs are released into the aquatic environment, 85% of them in the form of degradation products. Levels detected in the environment are in the range between ng/L and µg/L in water, sometimes approaching or exceeding those deemed to be sufficient to produce estrogenic effects, which are estimated in the case of the NP and NPEO1 between 1 and 20 µg/L. The most alarming and best studied effects are those that link exposure to these compounds in the aquatic environment with phenomena of feminization and intersex (the simultaneous presence of male and female reproductive organs) in fish (Solé et al. 2000; Petrovic et al. 2002, Box 5.4). This activity as endocrine disrupting compounds led to restrictions on their use in various countries, and the addition of NP and OP to the list of priority

Box 5.3

Case study: Occurrence of nonylphenolic compounds in the Anoia River (Llobregat River basin, NE Spain) and their effect on feminization and intersex of male carp

The Anoia River is a tributary of the Llobregat River and is situated in Catalonia, NE of Spain. The river receives effluents from several WWTP and is characterized by rather high levels of nonylphenolic compounds originating from WWTP treating effluents from several tannery and textile plants that use nonylphenolic compounds as surfactants. The study conducted in 2000 revealed a correlation between the presence of nonylphenolic compounds in water and sediment downstream of WWTP and plasma VTG concentration in male carp was observed. In female fish the synthesis of vitellogenin (VTG – an oviparous female egg yolk precursor) is regulated by estradiol (natural female hormone) levels in the plasma. In males, as a consequence of exposure to substances that mimic natural estradiol (in this case nonylphenolic compounds), VTG can also be synthesized inducing feminization in male fish and resulting in pathological intersex gonads formation (containing both male and female tissue).



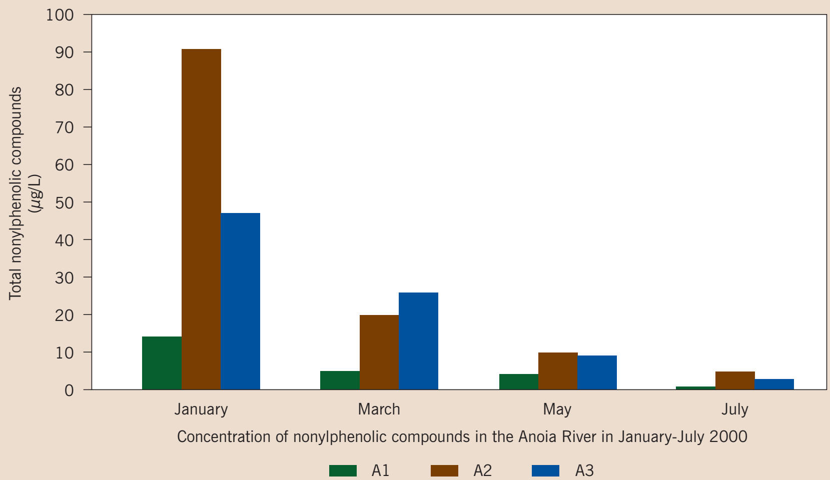
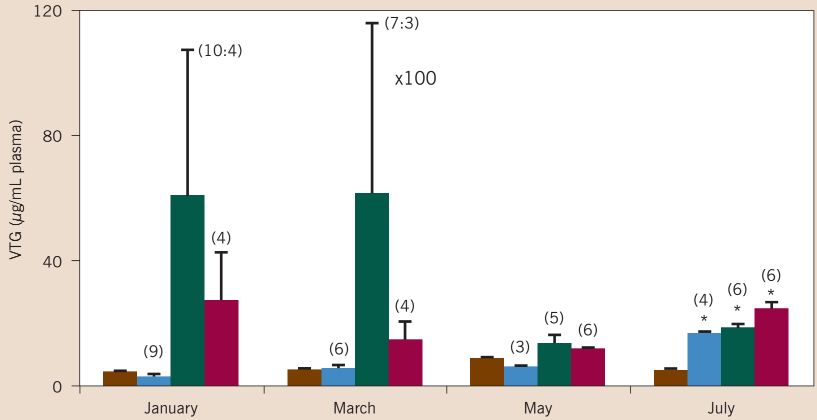


Figure 5.6: *Nonilphenolic compounds in the Anoia River and effects in carps*

Box 5.3 *(cont.)*: Case study: Occurrence of nonylphenolic compounds in the Anoia River (Llobregat River basin, NE Spain) and their effect on feminization and intersex of male carp

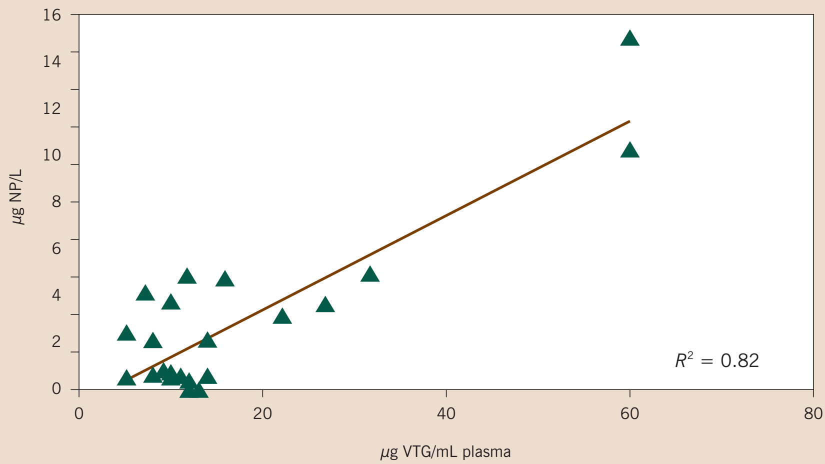
Figure 5.6 *(cont.)*



Vitellogening levels in µg/mL plasma of male carp *(Cyprinus carpio)* in the Anoia River

Control A1 A2 A3

Numbers in paretheses correspond to the number of fish analysed and the number of intersex fishes out the total



Correlation between VTG concentration in plasma an NP concentration in river water

substances in the EU. The average annual concentration of NP in surface water should not exceed 0.3 µg/L and the maximum should not exceed 2 µg/L. In the case of OP the maximum allowable concentration is not set, but the annual mean concentration should not exceed 0.1 µg/L in inland surface waters and 0.01 µg/L in other surface waters.

5.3.5. Perfluorinated compounds

Perfluorinated compounds comprise a large group of compounds characterized by a fully fluorinated hydrophobic linear carbon chain attached to one or more hydrophilic head. Perfluorinated compounds repel both water and oil, and are therefore ideal chemicals for surface treatments. These compounds have been used for many industrial applications including stain repellents (such as Teflon), textile, paints, waxes, polishes, electronics, adhesives, and food packaging (Clara et al. 2008). They are resistant to breakdown, and therefore persistent and bioaccumulative in the environment. They also biomagnify through the food chain.

There are many perfluorinated compounds, but some of the most studied are the following:

— PFOA or perfluorooctanoic acid, used to make fluoropolymers such as Teflon, among other applications.
— PFOS or perfluorooctanesulfonic acid, used in the semiconductor industry, and fire-fighting foam mixture.
— PFNA or perfluorononanoic acid, used as surfactant in the emulsion polymerization of fluoropolymers, like PFOA.
— PFBS or perfluorobutanesulfonic acid, used as a replacement for PFOS.
— POSF or perfluorooctanesulfonyl fluoride, used to make PFOS-based compounds.
— PFOSA or perfluorooctanesulfonamide.

The main direct routes of exposure of perfluorinated compounds to humans are in their diet and drinking water. They have been found in rivers, precipitation water, soils and sediments and biota samples. Perfluorinated compounds enter the environment through direct (directly from manufacture wastes or direct application) and indirect sources (due to their decomposition or disposal through product life cycle). WWTPs have been also identified as relevant pathway of their releases into the environment.

5.4. Effects on aquatic organisms and biodiversity

A fundamental characteristic of most biological systems is their diversity. The rapid loss of genetic, specific, and functional diversity resulting from anthropogenic disturbances (e.g. chemical stressors) is a significant environmental problem with global consequences (Chapter 6). Researchers and policy makers are becoming increasingly aware that species provide ecosystem goods and services that are essential for human welfare (Chapters 7 and 11). Contaminants exert their effects at all levels of biological organization, from molecules to ecosystems. Most research in environmental toxicology focuses on effects on lower levels of biological organization (molecules, cells, individuals) and is based in laboratory studies. This research improves our understanding of mechanisms of toxic action and exposure assessment, but must be linked with changes in communities and ecosystems. Following direct exposure to chemicals, sensitive individuals may die (i.e. lethal effect) or they may suffer sub-lethal consequences such as physiological, behavioural changes or impaired reproduction. Indirect effects may also occur, usually derived from direct effects on other species that induce changes in processes such as competition or changes in resource-consumer relationships. Direct toxic effects are easier to interpret than indirect effects, which received little attention.

Water contamination by man-made chemicals, chemicals unintentionally formed as by-products, nutrients and microorganisms, is one of the major environmental concerns faced by rivers today

One of the most important entry ways of contaminants into ecosystems is by ingesting organic materials. Materials and energy are processed and flow in ecosystems throughout food webs. Bioconcentration is defined as the uptake of contaminants directly from water, and bioaccumulation is the uptake of chemicals from either biotic (food) or abiotic (sediment) compartments. In aquatic organisms, bioconcentration describes the process which leads to higher concentration of a toxicant in the organism than in water. In the same way, bioaccumulation produces higher concentrations of a chemical in an organism than in its immediate environment, including food. Biomagnification refers specifically to the increase of contaminant concentration with trophic level. If biomagnification occurs, the concentration of contaminants increases with trophic level, i.e. concentrations in a consumer or predator exceed concentrations in the consumed prey. For example, periphyton and attached algae in streams concentrate contaminants several orders of magnitude above water levels. Organisms grazing these materials, such as several insect larvae (e.g. mayflies or midges), are exposed to significant concentrations that can be accumulated. Fish feeding on these contaminated insects may present elevated levels of a contaminant in tissues and consequently suffer a significant reduction in growth. The extent to which compounds accumulate and the routes that they are taken up and excreted may differ depending on the type of organism and chemical involved. These concepts are widely recognized as useful indicators of a biological exposure to toxicants.

Pesticides are designed to kill undesired organisms or pests, but these compounds also have direct and indirect (through trophic links) effects on non-target organisms. Herbicides target primary producers, such as algae, mosses or flowering plants, but they can also have effects on animals. Both algae and invertebrates suffer a loss in diversity and abundance, whereas species tolerant to pesticides can spread in rivers. For example, the herbicide diuron changes algae abundance and species composition in rivers, but at higher concentrations also produce lethal effects on invertebrates, tadpoles and fish. Additionally, sub-lethal effects can also occur at lower concentrations, close to those found in the environment. Diuron shows antiestrogenic and antiandrogenic activities in yeast, and these endocrine disrupting effects could change the fecundity of organisms and consequently have an ecologically significant impact on population dynamics. Similar studies with other herbicides also found changes in the community, from primary producers to herbivores and predators. Atrazine has negative effects on macrophytes, algae, and on the diversity and abundance of herbivore insects. In an experiment with the herbicide glyphosate at environmental concentrations, algal biomass increased as the herbicide killed herbivore tadpoles, and predator populations decreased as their prey died. Continuous exposure to pollutants can generate genetic adaptation in aquatic organisms and convert biological communities to be tolerant if sensitive species or genotypes are replaced by resistant ones. This phenomenon has been reported in both experiments and field studies with pesticides and also with heavy metals. These changes usually drive to a simplification of the community composition and function and a loss of natural biodiversity.

The potential ecological effects associated with the presence of emerging contaminants in the environment has been largely ignored, and there is a lack of data regarding long-term low-dose exposure

Recent reviews analyzed the potential risk of pharmaceuticals to freshwater biota, and summarized the results of bioassays (e.g. Fent et al. 2006). Pharmaceuticals introduced into the environment may affect animals like they do humans. However, as hundreds of different medical drugs are regularly used, when released into the environment they may interact, producing unknown effects. At least sub-lethal effects have been reported for mixtures of pharmaceuticals at concentrations similar to those found in the environment, pointing to a risk for the biota. For instance, the heart rate and fecundity of the freshwater crustacean *Daphnia magna* are sensitive to beta blockers, the psychiatric drug fluoxetine affects reproduction in the freshwater snail *Physa acuta*, the anti-inflammatory indomethacin produces changes in insect larvae growth, and antidepressants, lipid regulators, steroids, non-steroidal anti-inflammatory drugs, lipid regulators or antibiotics, induce sub-lethal effects on the reproduction, physiology and behaviour of fish (Corcoran et al. 2010). Ultra violet radiation absorbing chemicals (UV-filters) are added to sunscreens and a wide variety of cosmetics, and thus have been detected in freshwater systems. They bioaccumulate in invertebrate, fish and fish-eating birds. To date, quite a lot of information has been generated about the effects of emerging pollutants on single organisms, but community approaches are very scarce (see an example in 5.4, Ginebreda et al. 2010), highlighting the necessity of future investigations. Experimental investigations on communities are difficult because of the long-term studies required and because endpoints are inconspicuous. In field studies it is difficult to predict the effects of emerging pollutants on communities because the effects of these substances on animals are poorly known (e.g. feminization or changes in behavior), and because other stressors often act simultaneously.

A review of the available information on the toxicity and bioaccumulation of alkyphenols and their metabolites reveals toxicity to fish, invertebrates and algae. Effects have been observed on the growth of testicles, alterations in steroid metabolism, disruption of smoltification (internal metabolic process when a fish adapt from freshwater to marine waters, e.g. salmons) and cause

Box 5.4

Case study: Effect of pharmaceuticals on the macroinvertebrate biodiversity in the Llobregat River (NE Spain)

The Llobregat river (NE Spain; see Figure 5.7) is 156.5 km long and covers a catchment area of about 4,948 km^2. Its watershed is heavily populated (3,089,465 inhabitants in 1999), especially in its lower part, which is located in the metropolitan area of Barcelona. Together with its two main tributaries, the Cardener river and the Anoia River, the Llobregat is a paradigm of overexploited Mediterranean river suffering from urban, industrial and agricultural pressures. The river has a mean annual discharge of 693,000,000 m^3 and near 30% is used for drinking water. The Llobregat receives extensive urban and industrial waste water discharges (137,000,000 m^3/year; 92% comes from the waste water treatment plants) that cannot be diluted by its natural flow (0.68-6.5 m^3/s basal flow).

Among other compounds, pharmaceuticals resulting from domestic use are present in relevant quantities in the wastewater effluents discharged into the river. The potential ecotoxicological effect of these pharmaceuticals can be characterised using the so called **hazard quotients** or **hazard indexes** (HQ). For a single compound HQ is defined as the ratio between its environmental concentration to its long term (chronic) toxicity concentration. If more than one compound occurs simultaneously (as is the case), an overall HQ is obtained by summing up all the single HQ's for every compound present. The most relevant contributing compounds to HQ among those analyzed are shown in the attached figure.

Ginebreda et al. (2006), studied the relationship between the HQ's associated with the presence of pharmaceuticals in different points of the Llobregat River basin with the biodiversity of the macroinvertebrates (measured using an appropriate metric, i.e. the Shannon index), which is a measure of the river ecological status. An inverse relation was found (see Figure 5.7) indicating that the presence of pharmaceuticals can be associated with a loss of macroinvertebrate diversity.

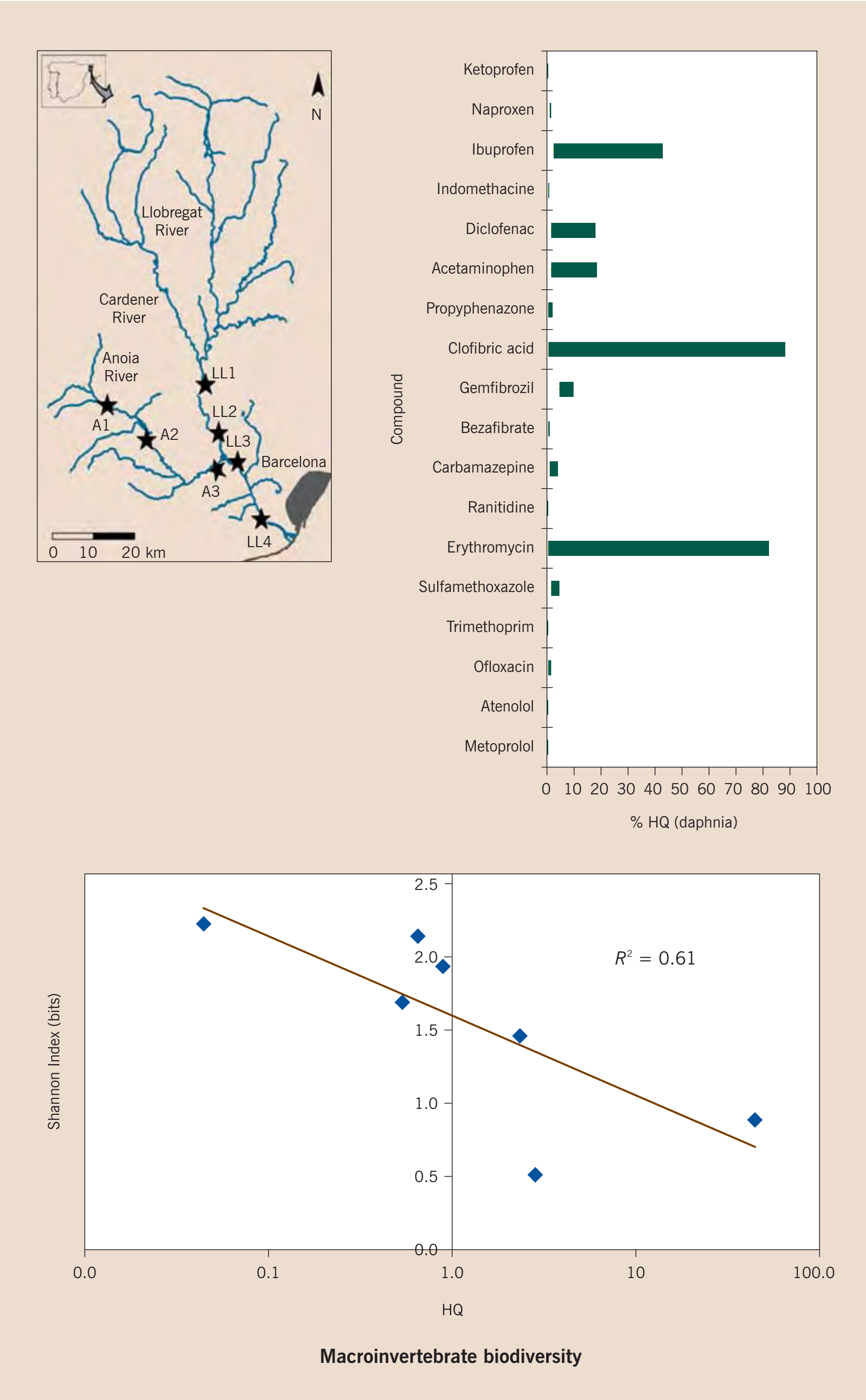


Figure 5.7: *Llobregat River (NE Spain). Relationship between the Risk Quotient (HQ) associated with pharmaceuticals and the aquatic macroinvertebrate biodiversity (expressed as Shannon Index)*

intersex in fish. In rivers, worms and midges are the groups most resistant to alkylphenols. Sub-lethal effects in invertebrates are detected in high concentrations, however, in European rivers, an increase in reproduction of the invasive snail *Potamopyrgus antipodarum* is observed in sediments from sites with high concentrations of xenoestrogens, including alkylphenols. The ability of alkylphenols to bioaccumulate in aquatic biota in the environment is low to moderate. However, high concentrations of perfluorinated compounds are detected in invertebrates, fish, reptiles in aquatic ecosystems, and marine mammals worldwide. More studies have demonstrated the bioaccumulation and biomagnification potential of these compounds in both freshwater and marine food webs. Mortality in sediment dwelling organisms such as the nematode *Chaenorhabtidis elegans* has been observed and decline in fecundity at lower concentrations.

5.5. Present threats and future challenges

Today, one of the major objectives for environmental scientists is to establish causal links between stressors and the quality of ecological systems. The potential ecological effects associated with the presence of emerging contaminants in the aquatic environment have been largely ignored, and there is a lack of data regarding effects on the aquatic ecosystems resulting from long-term low-dose exposure. Such analysis of chronic toxicity of emerging contaminants on organisms is essential to obtain a realistic environmental risk assessment, especially in the case of biologically active pharmaceuticals, because these substances were designed to exert distinct effects. Direct estimation of effects caused by environmental pollutants on ecosystems is not a straightforward task. In real-world scenarios, contaminants rarely exist alone. Instead, they usually appear as mixtures of many compounds, and their combined effects are difficult to predict (i.e. synergies or antagonisms may take place). Furthermore, many other stressing confounding factors (i.e. hydrology, climate change etc.) may take place at the same time, thus giving rise to a very complex situation, especially on Mediterranean rivers. Understanding the respective contribution and reciprocal feed-back of each one on a common integrated picture constitutes a tremendous scientific challenge in which the concurring interdisciplinary efforts of environmental chemists, biologists, hydrologists, engineers and even social scientists are needed.

On the other hand and beyond pure scientific interest, the deployment of adequate management actions at river basin scale as required by the Water framework Directive, such as the elaboration of River Basin Management Plans and the associated Programs of Measures can only succeed if they are supported on a solid scientific basis.

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