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Water Scarcity in the Mediterranean

Perspectives Under Global Change

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Water Scarcity in the Mediterranean

Perspectives Under Global Change

Volume Editors: Sergi Sabater · Damià Barceló

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This volume is dedicated to the memory of Prof. François Brissaud.

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Aims and Scope

Since 1980, *The Handbook of Environmental Chemistry* has provided sound and solid knowledge about environmental topics from a chemical perspective. Presenting a wide spectrum of viewpoints and approaches, the series now covers topics such as local and global changes of natural environment and climate; anthropogenic impact on the environment; water, air and soil pollution; remediation and waste characterization; environmental contaminants; biogeochemistry; geoecology; chemical reactions and processes; chemical and biological transformations as well as physical transport of chemicals in the environment; or environmental modeling. A particular focus of the series lies on methodological advances in environmental analytical chemistry.

Series Preface

With remarkable vision, Prof. Otto Hutzinger initiated *The Handbook of Environmental Chemistry* in 1980 and became the founding Editor-in-Chief. At that time, environmental chemistry was an emerging field, aiming at a complete description of the Earth's environment, encompassing the physical, chemical, biological, and geological transformations of chemical substances occurring on a local as well as a global scale. Environmental chemistry was intended to provide an account of the impact of man's activities on the natural environment by describing observed changes.

While a considerable amount of knowledge has been accumulated over the last three decades, as reflected in the more than 70 volumes of *The Handbook of Environmental Chemistry,* there are still many scientific and policy challenges ahead due to the complexity and interdisciplinary nature of the field. The series will therefore continue to provide compilations of current knowledge. Contributions are written by leading experts with practical experience in their fields. *The Handbook of Environmental Chemistry* grows with the increases in our scientific understanding, and provides a valuable source not only for scientists but also for environmental managers and decision-makers. Today, the series covers a broad range of environmental topics from a chemical perspective, including methodological advances in environmental analytical chemistry.

In recent years, there has been a growing tendency to include subject matter of societal relevance in the broad view of environmental chemistry. Topics include life cycle analysis, environmental management, sustainable development, and socio-economic, legal and even political problems, among others. While these topics are of great importance for the development and acceptance of *The Handbook of Environmental Chemistry,* the publisher and Editors-in-Chief have decided to keep the handbook essentially a source of information on "hard sciences" with a particular emphasis on chemistry, but also covering biology, geology, hydrology and engineering as applied to environmental sciences.

The volumes of the series are written at an advanced level, addressing the needs of both researchers and graduate students, as well as of people outside the field of "pure" chemistry, including those in industry, business, government, research establishments, and public interest groups. It would be very satisfying to see these volumes used as a basis for graduate courses in environmental chemistry. With its high standards of scientific quality and clarity, *The Handbook of*

Environmental Chemistry provides a solid basis from which scientists can share their knowledge on the different aspects of environmental problems, presenting a wide spectrum of viewpoints and approaches.

The Handbook of Environmental Chemistry is available both in print and online via www.springerlink.com/content/110354/. Articles are published online as soon as they have been approved for publication. Authors, Volume Editors and Editors-in-Chief are rewarded by the broad acceptance of *The Handbook of Environmental Chemistry* by the scientific community, from whom suggestions for new topics to the Editors-in-Chief are always very welcome.

Damià Barceló
Andrey G. Kostianoy
Editors-in-Chief

Volume Preface

Water scarcity is a structural, persistent drought affecting resources and aquatic ecosystems, with implications in water quality and societal needs. Scarcity results in repeated drought episodes. While drought is a temporary (and often normally associated to climatic patterns) decrease in water resources, water scarcity occurs when water demand exceeds the water resources exploitable under sustainable conditions.

Terrestrial ecosystems (plants and animals) under water scarcity suffer from water stress, and aquatic ecosystems of intermittency in water flow. Water scarcity has implications on hydrologic resources and systems connectivity, as well as negative side-effects on biodiversity, water quality, and river ecosystem functioning. Finally, water scarcity has also direct impacts on citizens and economic sectors that use and depend on water, such as agriculture, tourism, industry, energy and transport.

The effects of water scarcity on drainage networks extend from its associated hydrological irregularity to variations in geomorphological dynamics (higher channel incision, habitat simplification). Water chemical quality is affected; higher nutrient and pollutant concentrations are expected under lower water flows. Biological communities respond to harsher environmental conditions with lower diversity, arrival of invasive species, as well as lower efficiency of biological processes (nutrient uptake, primary production, decomposition, etc.). The increased pressure on water resources will cause additional effects on aquatic ecosystems, some direct and some indirect, where the stress being produced by scarcity may sum up others, physical or chemical. Because freshwater ecosystems deliver services to society, water scarcity affects both the ecosystem and human beings.

The Mediterranean Basin is one of the regions most vulnerable to climate changes, as well as one of the most impacted because of human water demand. Most climate change models conclude that Mediterranean regions will be more affected by summer drought, higher flood frequency and higher temperatures. Further, overpressures on water resources are associated to water scarcity, thereby triggering stress on water quality and ecosystems. The two associated effects demand careful diagnoses that allow reliable predictions. These two should be at the base of wise management of water resources and ecosystems.

This book unites visions on the particular problems of water quality and resource scarcity in the regions belonging to Mediterranean climate. Some of the chapters were presented at the conference "Water scarcity and management under Mediterranean climate", which was held in Girona (NE Spain) from 24 to 25th November 2008. Other chapters include invited visions related to this particular topic.

This book provides an in-depth view of the water quality and quantity implications of water scarcity. It provides a diagnosis of the causes, and describes the effects of water scarcity in the Mediterranean Basin. This Basin encompasses the common history and common problems of all the neighbouring countries in the Mediterranean region. However, the observations are not applicable only to this region, but also to those other parts of the world with Mediterranean climate, such as California, Australia, South Africa and Chile, where issues regarding water scarcity are the common concern. We hope that this book will provide an adequate overview on the climate effects, water resources (use, storage, new sources), water quality (chemical, microbiological), and effects on the ecosystems under water scarcity. The book should be useful to people interested in this topic, students and scientists, but also to managers involved in the necessary decision-making process to face future drought episodes. It is well-known to all of us living in Mediterranean areas, that drought will return every 4–7 years, the next being even worse than the previous one. The more the scientific and technical clues provided, the more likely that solutions can be found by water managers to cope with water supply of the required quality to the whole population, as well as making water available for the ecosystems.

We thank all the contributors of the book for the quality of their chapters, and their patience. Special thanks are due to the editorial staff of Springer and especially to Andreas Schlitzberger, who helped us during the process.

Girona and Barcelona, Spain
February 2010

Sergi Sabater and Damià Barceló

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Possible Climate Change Scenarios with Specific Reference to Mediterranean Regions

Josep Calbó

Abstract The Mediterranean basin is one of the most sensitive areas of the world regarding possible consequences of the present, anthropogenic-induced climate change. Besides temperature increase, most models consistently project rainfall decreases both on annual basis and for all seasons. On the basis of results from general circulation models (as presented in the recent Fourth Assessment Report of the IPCC) and also from results of several downscaling studies applied to Europe and the Mediterranean areas, some quantitative projections are summarized in this chapter. On average for the region, temperature is projected to increase about 3.5°C on an annual basis by the end of this century, with remarkable differences among specific areas. Precipitation could be reduced more than 10% (annual and regional average), the decrease being larger in summer and in the southern areas of the region. There are many uncertainties involved in these projections; basically, they derive from the unknown future emissions of greenhouse gases and aerosols, from the knowledge gaps of the complex climatic system, and from limitations of models and downscaling techniques. Despite these uncertainties, it is highly probable that water availability will be reduced in the Mediterranean areas as a consequence of increased temperatures and decreased and more variable precipitation. This result should be taken into account by water management agencies, concerned stakeholders and society in general.

Keywords Climate change, Climate projections, Downscaling, Mediterranean, Uncertainties

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1 Introduction

Recent climatic change is a phenomenon of planetary scale, which has its effects at regional and local scales also. Given the dimension of the phenomenon and its causes, that is the introduction into the atmosphere of greenhouse gases as a result of the human activities, the study of climatic projections needs to derive from this same global scale. The recent Fourth Assessment Report (AR4) of the Intergovernmental Panel on Climate Change (IPCC) presents its conclusions first, on the global scale projections, followed by regional projections [1]. In discussing about climate projections, it should be understood that they are estimations about the future climate, in the next decades. These projections depend mainly on three factors: first, the future emissions of greenhouse gases (which depend on demographical, economical, and technological evolutions, and on future regulatory efforts that might be implemented); second, the understanding of the climate system, which continuously improves as a result of basic research efforts; third, the ability of numerical models in reproducing this climate system, in close connection with the capabilities of computation technologies.

Climate projections are mostly obtained as a result of climate models, in particular the so-called Atmospheric Oceanic General Circulation Models (AOGCM). These models are numerical tools that incorporate most of the knowledge about the climate system to produce climate scenarios depending on factors that affect the climate (i.e., climate “forcings”). These forcings are one of the main sources of uncertainty in climate projections, and are strongly linked with the emissions of greenhouse gases and aerosols; the diversity of possible future evolution of emissions is addressed through the use of the so-called emission scenarios.

Indeed, the most important factor that affects the future estimates of climate is the (anthropogenic) emissions of greenhouse gases and all kind of aerosols. The amount of these products released into the atmosphere depends upon the socio-economical and technological development of humankind. Thus, different hypotheses about these evolutions are assumed, resulting in several emission scenarios. The scenarios used in the IPCC AR4 derive from a Special Report on Emission Scenarios (SRES) published earlier [2]. All these scenarios can be grouped in four families (storylines) that are named A1, A2, B1, and B2.

All predicted scenarios show that greenhouse gases emissions will keep growing, at least until the middle of the present century. Among these scenarios, A2 produces the maximum emissions along the twenty-first century, while B1 is the most optimistic, i.e., forecasts the lowest emissions. In general, most climate projections are based on intermediate scenarios, such as B2 or A1B (a particular case within the A1 scenarios that assumes that energy will be obtained from a variety of sources, including fossil fuels and renewable). Despite the assumption that emissions would start to decrease by the middle of the century in some scenarios, atmospheric concentrations would increase further, in all cases, until reaching a new equilibrium state. In scenario B1, CO_2 concentration reaches 500 ppm by 2100; in scenario A1, this concentrations is reached by 2050, and by 2100 the concentration is more than 800 ppm, i.e., far more than double the preindustrial amount of 280 ppm.

This chapter summarizes climate projections presented by the recent Fourth Assessment Report (AR4) of the IPCC, both for the global scale and for the so-called European and Mediterranean region. Besides the IPCC projections, other results regarding the Mediterranean area will be reviewed as well. The emphasis will be mostly placed on temperature and precipitation projections, while other variables, such as wind, solar radiation, or sea level, will not be commented in depth. Some attention will be paid to methodologies used to develop projections, and the corresponding uncertainties will be commented. In general, projections will be given for the end of the current century.

2 Global Projections After the IPCC AR4

As a consequence of the continuous increase in concentration of greenhouse gases, global mean temperature will increase in the future [3], as it has been doing in recent years. Figure 1 shows this projected increase, for several emission scenarios and relative to the period 1980–1999 (recall that the average temperature in this period is at least 0.5°C higher than the mean temperature by the end of the nineteenth century). Depending on the emission scenario and on the model used, the temperature increase ranges between 1.1 and 6.4°C by the end of the twenty-first century. The best estimate for the most optimistic scenario included (B1) is an increase of 1.8°C, and the best estimate for the most pessimistic scenario (A1FI) is an increase of 4.0°C. For the most immediate decades, all scenarios show very similar temperature increases: for example, about 1.2°C by 2040.

Most models indicate a global increase of precipitation. Nevertheless, given the great disparity among models, and the great heterogeneity and variability of precipitation across the Earth, the AR4 does not produce global average values of precipitation changes. In general, most AOGCM generate precipitation increases within the intertropical area, and also at higher latitudes of both hemispheres, as well as precipitation decreases at subtropical latitudes. On the other hand, the AR4 indicates that an increase in the frequency of heavy precipitation events is very

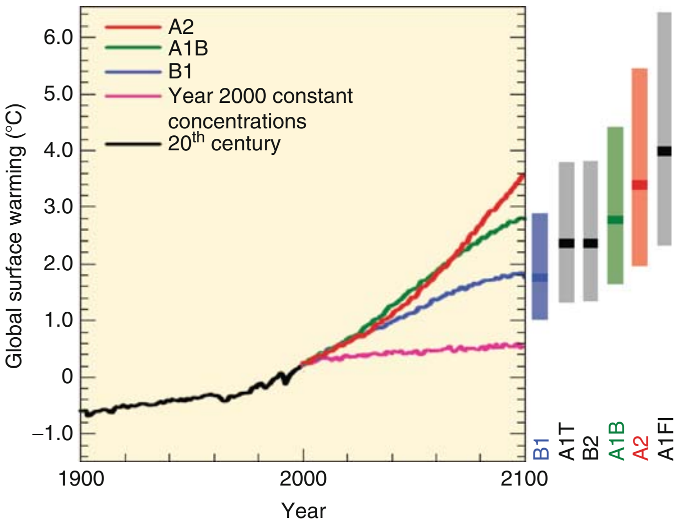

Fig. 1 Global mean surface temperature evolution during the last century (observed) and projected for the next century. Bars on the right show the possible range of temperature increases from different AOGCM, and also from Simple Climate Models (SCM) and Earth Models of Intermediate Complexity (EMIC). Figure taken from IPCC [1]

likely over most areas, while the length and frequency of dry spells may likely increase in areas where they are currently usual.

According to the AR4, it is very likely that some currently semiarid areas will suffer a clear decline of water availability. Among these areas, the Mediterranean region is particularly highlighted. To illustrate this fact, Fig. 2 shows changes in surface runoff as a result of changes in precipitation and temperature (that induce evapotranspiration increases). It is apparent that the Mediterranean regions may suffer a significant decline of between 20 and 40%. These results, however, are not particularly robust: surface runoff models deviate from measurements in the present climate, so these projections must be taken with caution.

Figure 3 shows temperature and precipitation changes for Europe and the Mediterranean, according to the results of 21 global models included in the Program for climate models diagnostic and intercomparison (PCMDI) that produced the so-called “multimodel data set” (MMD). These results correspond to the A1B emission scenario and are given for the end of this century (2080–2099) with respect to the end of the previous century (1980–1999); values plotted are calculated as the average of the variations produced for each model. Results are presented both for the annual basis and for seasonal basis (summer, June–July–August; and winter, December–January–February).

On an annual basis, temperature increase will be between 2.5 and 3.5°C for this scenario, lower on the sea itself and in coastal areas, higher in the interior of Iberian and Balkan peninsulas and in Northern Africa. These increases are slightly lower in winter, and remarkably higher in summer, when temperature increases of more than

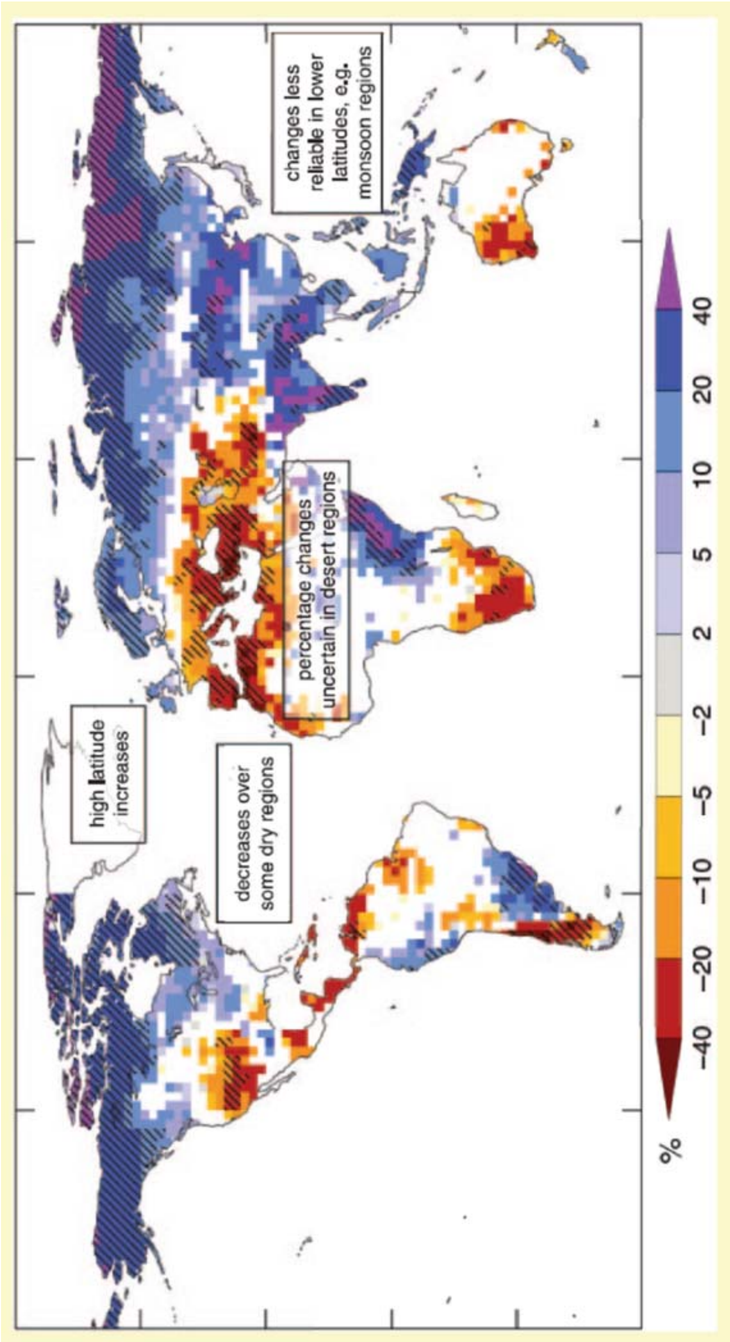

Fig. 2 Relative changes (between 2080–2099 and present, 1980–1999) of annual surface runoff on the globe, from results of several climate models forced by emissions of scenario A1B. Dashed areas indicate that more than 90% of models agree with the sign of change. Taken from IPCC [1]

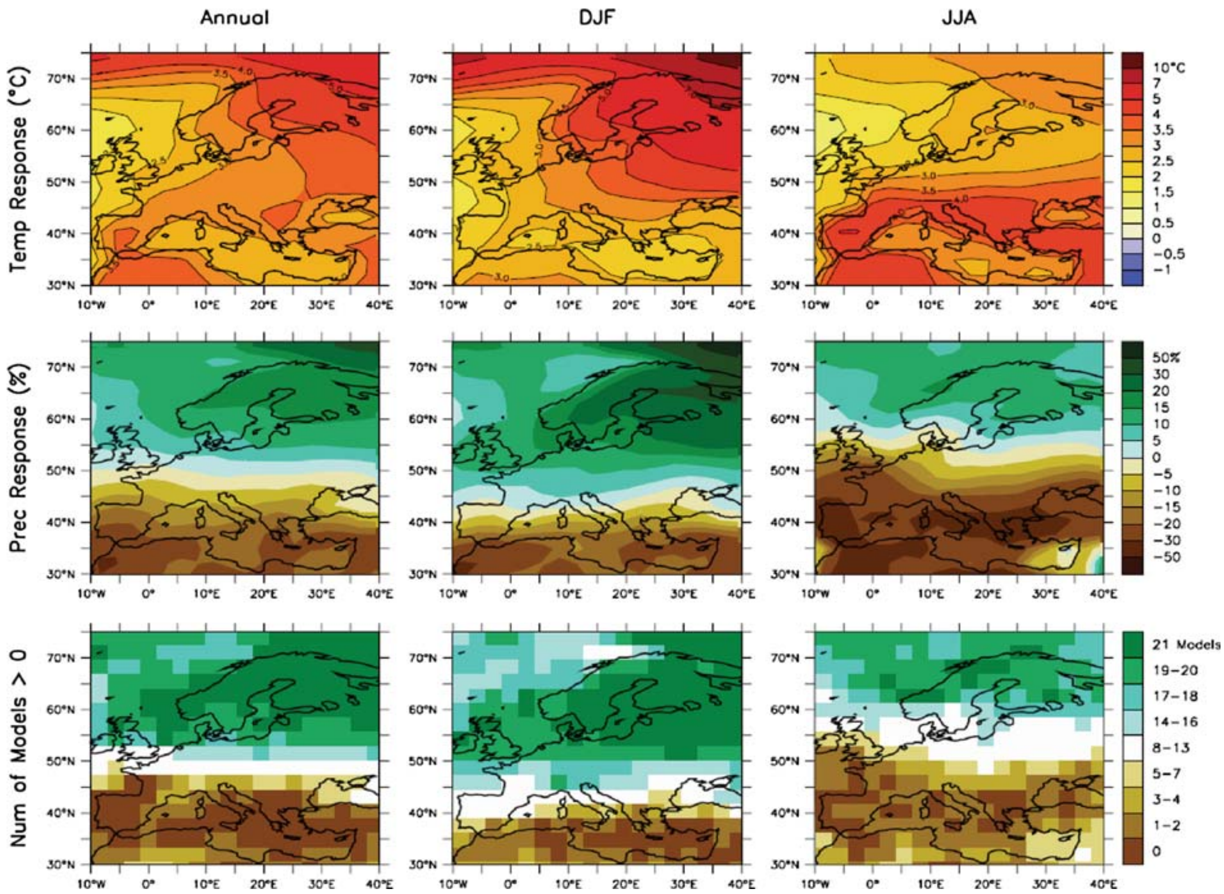

Fig. 3 Temperature changes (top) and precipitation changes (middle) in Europe and the Mediterranean, from the simulations performed by 21 global models, for the A1B scenario. Values are differences between 2080–2099 and 1980–1999. Left column, annual mean; middle column, winter mean; right column, summer mean. An assessment of the uncertainty of precipitation changes is given in the bottom row, by indicating the number of models that give the same sign of change. Taken from Christensen et al. [4]

4°C are projected for most land areas in the Mediterranean region. Regarding precipitation, there is a clear latitudinal gradient within the analyzed area. Thus, in the South of the Mediterranean region (including part of the Iberian Peninsula and most of Northern Africa), the average precipitation decline in annual basis might be as large as 20%. All Mediterranean countries would suffer this or even stronger precipitation declines in summer, while in winter the change is lower, particularly in the northern half of the Mediterranean. Although these results carry some uncertainty, the Mediterranean region is one of the few areas in the World where most models, for all seasons, agree in the decreasing trend in rainfall [4].

3 Downscaling Projections to Mediterranean Regions

3.1 Downscaling Techniques

Global models used so far to estimate climate projections such as those presented above,are based on numerical computations on a grid that typically has sizes of 2–3° both in latitude and longitude. Therefore, global models do not include a good description of orography or coastal lines, at least, not at the level required to obtain a reliable climate description for Europe or the Mediterranean. A possible solution for this issue would be to increase resolution of global climate models, but this is limited by the computing capabilities in practical applications. Therefore, as long as global models cannot work at finer resolutions (about 50 km or better), some technique for "regionalization" or "downscaling" is required to obtain more spatial detail of climate projections. Researchers have already established several downscaling methodologies in recent years; all of them, however, rely on results of global climate models, since downscaling methods do not really project the climate into the future, but convert global results into higher resolution results.

Broadly speaking, there are two main downscaling techniques, and some methodologies that are variations or combinations of these two. Firstly, dynamical downscaling consists in the use of regional climate models nested within global models. That is, a high resolution model is applied in a limited area of the world, while low-resolution AOGCM is applied globally and supplies the necessary boundary conditions to the former. Secondly, statistical downscaling consists in multivariable statistical regressions (or other statistical techniques) between climatic variables at a particular point (or small region) and the values obtained in one or several cells of a global model. Sometimes, the relationship is established between a particular point and some index that summarizes the synoptic state of the atmosphere. For example, several indices relative to the behavior of a low frequency synoptic pattern or a teleconnection mechanism are commonly used: the North Atlantic Oscillation (NAO), the Arctic Oscillation (AO), the El Niño-Southern Oscillation (ENSO), the Western Mediterranean Oscillation (WeMO) indices, among others. The analogues methodology is still a statistical technique, which is founded upon the clustering of all possible synoptic situations in a few typical cases; knowing the frequency (that might be changing) of each of these cases and the local behavior of the weather for each situation allows estimating the local climate.

Whatever is the methodology used, a regional climate projection is the result of combining a) an emission scenario, b) the output of a global model forced with these emissions, and c) a particular downscaling technique. Therefore, note that the number of uncertainties involved is huge: some arise from the human behavior (emissions), some from limitations in knowledge (for example, cloud physics) and due to the chaotic nature of the climate system, and some are a result of computing limitations or of the statistical method (for example, it is assumed that current relations between synoptic state and local weather will remain valid in the future). In this sense, some authors advocate for recognizing the fundamental, irreducible uncertainties that limit the accuracy of climate predictions [5].

As an attempt to provide climate projections for Europe and to assess the implicated uncertainties, the PRUDENCE project (Prediction of Regional scenarios and Uncertainties for Defining European Climate change risks and Effects, Christensen [7]) involved, during 2002–2005, more than 20 European research groups. The specific goal of the project was to obtain climate scenarios with high resolution, for Europe and for the end of the twenty-first century, by using dynamical downscaling. Experiments performed in the frame of PRUDENCE consisted of a control simulation for the period 1961–1990 (which was used to evaluate the ability of the regional models, i.e., to validate them) as well as other simulations for the future period 2071–2100. Most simulations were performed for the A2 scenario, and used the output of an atmospheric model (HadAM3H) which in its turn was initialized by the output of the HadCM3 AOGCM. Other simulations were performed for the B2 scenario or forced by the output of another global model (ECHAM4/OPYC3) [6]. Regarding the regional models, PRUDENCE used ten different models developed at several European institutions. All of them were run with a resolution of around 50 km, and applied for an area that covered most of Western Europe. The project produced a number of reports and peer-reviewed papers that may be considered the state-of-the-art regarding climate projections for Europe ([7–9]). More recent projects, however, are producing new results. In particular, the ENSEMBLES project deals with developing an ensemble prediction system for climate change based on the principal state-of-the-art, high resolution, global and regional Earth System models developed in Europe. The goal is to produce for the first time an objective probabilistic estimate of uncertainty in future climate at the seasonal to decadal and longer timescales [10].

3.2 Results for the Mediterranean Area

On the basis of results from GCM (Fig. 3) the AR4 summarizes the projected changes for the Mediterranean region (Table 1, regarding temperature changes; Table 2 for precipitation), the moderate emission scenario A1B having been

Table 1 Summary of projections from the 21 models included in the *MultiModel Data set*, for the Mediterranean region (30°N, 10°W–48°N, 40ºE) and the A1B emission scenario. Temperature differences (°C) between 2080–2099 and 1980–1999. The table shows the minimum, maximum, median (50%), and 25 and 75% quartile values. The frequency of extremely warm, averaged over the models, is also shown. From Christensen et al. [4]

Season	Min.	P25	P50	P75	Max.	Warm seasons (%)
DGF	1.7	2.5	2.6	3.3	4.6	93
MAM	2.0	3.0	3.2	3.5	4.5	98
JJA	2.7	3.7	4.1	5.0	6.5	100
SON	2.3	2.8	3.3	4.0	5.2	100
Annual	2.2	3.0	3.5	4.0	5.1	100

Table 2 As in Table 1, but for precipitation differences (%)

Season	Min.	P25	P50	P75	Max.	Wet seasons (%)	Dry seasons (%)
DGF	−16	−10	−6	−1	6	3	12
MAM	−24	−17	−16	−8	−2	1	31
JJA	−53	−35	−24	−14	−3	1	42
SON	−29	−15	−12	−9	−2	1	21
Annual	−27	−16	−12	−9	−4	0	46

considered in both cases. On annual basis, the temperature is projected to increase in the range of 2.2–5.1°C (median of the 21 models, 3.5°C). Note that unlike most areas in the world, in the Mediterranean, the largest temperature increment is expected in summer. The average precipitation projected decrease, for the whole area and on annual basis, is in the range −16%, −9% (median of the 21 models, −12%); summer is the season with the largest expected precipitation decreases.

Combining an analysis of these results from GCM with results from the PRUDENCE project, the AR4 also [4] presents some clear facts about the future climate in Europe and the Mediterranean:

- Annual mean temperatures in Europe are likely to increase more than the global mean. Seasonally, the largest warming is likely to be in northern Europe in winter and in the Mediterranean area in summer.
- Maximum summer temperatures are likely to increase more than the average in southern and central Europe.
- It is very likely that the mean annual precipitation will decrease in most of the Mediterranean region. The annual number of precipitation days is very likely to decrease in the Mediterranean area.
- It is likely that the risk of hydrological drought (as a result of precipitation and evaporation trends) will increase, in particular in summer in Southern Europe and the Mediterranean.
- It is very likely that the snow season will shorten in most of Europe. It is also very likely that the winter accumulation of snow will decrease.

Besides the IPCC AR4, several specific works make reference to climate projections for Europe and/or the Mediterranean, some being related with the PRUDENCE project also. One particular study is that of Sánchez et al. [11] where they use one regional climate model (PROMES) to analyze and show changes of temperature and precipitation and their related extreme events by the end of this century for the scenario A2. They conclude that it is convenient to use a set of diagnostic indices for a correct analysis of climate extreme events, trends and changes, since frequency or intensity parameters separately cannot represent all the aspects of extreme processes. Intensity of extreme daily maximum temperatures will increase more than the average maximum temperatures. On the other hand, extreme daily minimum temperatures will increase less than the average of minimum temperatures. In terms of temperature ranges in the projected climate for the Mediterranean region, daily temperature range will be greater than current climate values. Changes in precipitation extremes are much more varied than maximum and minimum temperature extremes. Though a moderate to high decrease of annual precipitation in most of the Mediterranean region is projected, important seasonality changes are also possible [11]. An increasing trend in projected extreme precipitation events is expected in many Mediterranean areas. That increase of extreme events is mainly expected in the warmest seasons (summer and early autumn).

Gao et al. [12] utilized a regional model with a resolution of 20 km to analyze the changes of periods without precipitation (dry spells, DS) and with intense rainfall (defined as the maximum accumulated precipitation in five consecutive days, 5DP). They also used scenario A2 and gave results for the end of the twenty-first century. They found substantial (and seasonally dependent) fine scale topographically-induced structure in the climate change signal over a number of regions of the Mediterranean area (i.e., the Alpine and Balkan regions, the Iberian, Italian and Hellenic peninsulas, and the Northern African coastal regions). Similar to the changes in mean precipitation, the changes in extreme events also exhibit topographically induced fine scale structure. Gao et al. [12] also indicated that an increase in maximum 5DP and a decrease in maximum DS length over western and central European areas are to be expected in winter, implying stronger and more frequent storms. In summer and intermediate seasons, as well as in winter in some Mediterranean areas, increases in maximum DS length and areas of both increase and decrease for maximum 5DP can be expected. In general, the areas of increased maximum 5DP are more extended than the areas of increased mean precipitation, and the areas of increased DS length are more extended than those of decreased mean precipitation. This implies a widening of the precipitation distribution, with increased probability of both flood and drought events.

Beniston et al. [13] presented an overview of changes in the extreme events that may affect Europe in next decades, on the basis of regional climate model simulations produced by the PRUDENCE project. They concluded that the frequency, intensity and duration of heat waves will increase over Europe. They also found that in both winter and summer, intense precipitation may decrease in south Europe, while Mediterranean droughts may start earlier in the year and last longer. Diffenbaugh et al. [14] combined temperature and relative humidity to define a heat index, and assess the probability that a certain warming threshold be reached in the future climate. Diffenbaugh et al. [14] determined that days with high values (dangerous or extremely dangerous heat index) are projected to increase under an A2 emission scenario, in particular in the coastal areas of northern Africa, the Iberian Peninsula and south Italy. Christensen and Christensen [15] analyzed the summer precipitation, and concluded that a decrease of mean precipitation may be compatible with an increase in extreme precipitation events. Lehner et al. [16] analyzed the risk of both droughts and floods, and obtained reduced return periods for both phenomena in many areas in Europe, from simulations of global models (HadCM3 and ECHAM4) and the scenario A1B.

4 Discussion and Conclusions

Climate projections, in particular regarding mean or extreme precipitation over limited areas of the World, carry remarkable uncertainty. This is reflected in some contradictory results mentioned in the previous section. The uncertainty has many different causes, the future evolution of the climate forcings (greenhouse gases emissions, land use changes,...) being the most relevant. There are, however, several physical mechanisms of the climate system that are not yet fully understood. Most of them concern feedback mechanisms, which are processes that may amplify or reduce the response of the climate system for a given forcing. The main positive climate feedback is the water vapor feedback: when temperature increases, water vapor content also increases in the atmosphere, which produces an enhanced greenhouse effect. This mechanism is nowadays much better understood than in previous IPCC reports. Contrarily, feedbacks involving clouds and aerosols are still poorly described, and mean an important cause of uncertainty in the climate projections by global models.

Therefore, as it is mentioned in the AR4, climate projections for the end of the century depend on the scenario and the particular model used to develop them. Temperature changes, and especially precipitation changes, show, for such temporal horizon, a broad range of values. On the other hand, projections for the next 2–4 decades are quite robust, since they depend less on long-term feedbacks and also on future greenhouse gases emissions. In fact, the climate of the next few years is tightly determined by past and recent emissions (climate commitment).

Regional climate models use high resolution grids (20–50 km) to simulate the evolution of the atmosphere in a particular region of the Earth by applying the output of a global model as boundary condition. This methodology, however, increases the number of uncertainties involved; besides the already mentioned emission scenario and global model uncertainty, regional models carry their own issues related with the parameterization physical processes and other approximations. For example, the PRUDENCE project has shown that several regional models, even if forced by the same global model and by the same emission scenario, produce quite diverse results. This is an interesting fact, since the range of results may be understood as a measure of the uncertainty over the significant signal [17]. In fact, the European project ENSEMBLES, still under development, is trying to perform climate projections of a probabilistic nature, based upon an ensemble of simulations obtained by combining several scenarios, global models, and regional models and downscaling techniques. This methodology is expected to produce a remarkable improvement in the regional climate projections. In fact, there is a general consensus among the scientific community that a step further in climate modeling is necessary, particularly for regional scales [18].

Despite the uncertainties discussed in previous paragraphs, it is highly probable that water availability can be reduced in the Mediterranean areas as a consequence of increased temperatures and decreased and more variable precipitation. Specifically, besides the lowered precipitation, higher temperatures will enhance evaporation rates from reservoirs and the potential evapotranspiration rates from land areas in general, thus further reducing available water for human uses. This result is confirmed by the recent IPCC technical paper on climate change and water [19], where it is stressed that many semiarid and arid areas (e.g., the Mediterranean Basin, among others) are projected to suffer a decrease of water resources due to climate change. These projections are to be taken into account by the water management agencies, the concerned stakeholders and the society in general.

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Effects of Hydrologic Alterations on the Ecological Quality of River Ecosystems

Sergi Sabater and Klement Tockner

Abstract In most of the world's watercourses, dramatic modifications have occurred as a consequence of intensive use by human societies. The simplification of the channel network and the alteration of water fluxes have an impact upon the capacity of fluvial systems to recover from disturbances, because of their irreversible consequences. However, human impacts on river hydrology, such as those that derive from regulating their flow or by affecting their channel geomorphology, affect the functional organisation of streams, as well as the ecosystem services that derive from them, and lead to the simplification and impoverishment of these ecosystems.

Keywords Biodiversity, Biogeochemistry, Drought, Intermittent, Stream

Contents

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1 Water Scarcity, Water Stress and Drought, Expressions of Change in River Ecosystems

In most of the world's watercourses, dramatic modifications have occurred as a consequence of their intensive use by human societies [1]. Pollution, water abstraction, riparian simplification, bank alteration, straightening of watercourses, dam construction, and species introduction are widespread perturbations in river ecosystems. These human-driven alterations are part of *global changes*. The simplification of the channel network and the alteration of water fluxes reduce the capacity of fluvial systems to recover from natural disturbances. Hydrologic alterations affect the functional organisation of streams and rivers, and lead to a simplification and impoverishment of the biota within these ecosystems.

These effects add to the ongoing *climate change*, which results in altered temperature and rainfall in all biomes [2]. Though mostly human-driven, these changes do refer exclusively to the climate. The direct implications of climate change on flow regime are certain. Barnett et al. [3] documented a decrease in water flow of the NW America watercourses and related it to the increase in late winter temperature as well as to the associated lower thickness of the snow pack. Globally, the Mediterranean Basin is one of the regions most vulnerable to climate changes. The Mediterranean climate is subject to complex planetary scale processes and teleconnections, but also to local processes, which are induced by the complex physiography of the region and the influence of the Mediterranean Sea. Consequently, the Mediterranean basin is one of the most prominent "hot spots" for potential changes [4]. Most climate change models indicate that Mediterranean regions will be affected by summer drought and high temperatures. These changes will probably not be limited to the catchments draining into the Mediterranean Sea, but will affect all Mediterranean-type regions worldwide. The relation of these climate alterations to the fate of Mediterranean-type aquatic ecosystems will be expressed in altered flow regimes, increasing frequency and magnitude of floods and enduring and unexpected droughts [99] which will affect the distribution and survival of unique biota, and the associated ecosystem functions.

Nevertheless, the response of water resources will be more complex, as human activities will also change in response to altered climates. The intensity of the pressure put on water resources and aquatic ecosystems by external drivers is related to higher economic income (e.g. expressed by electricity production and consumption) of human societies [5]. The limitation of resources can be qualified by a diversity of terms, varying somewhat in intensity: drought, temporality, and

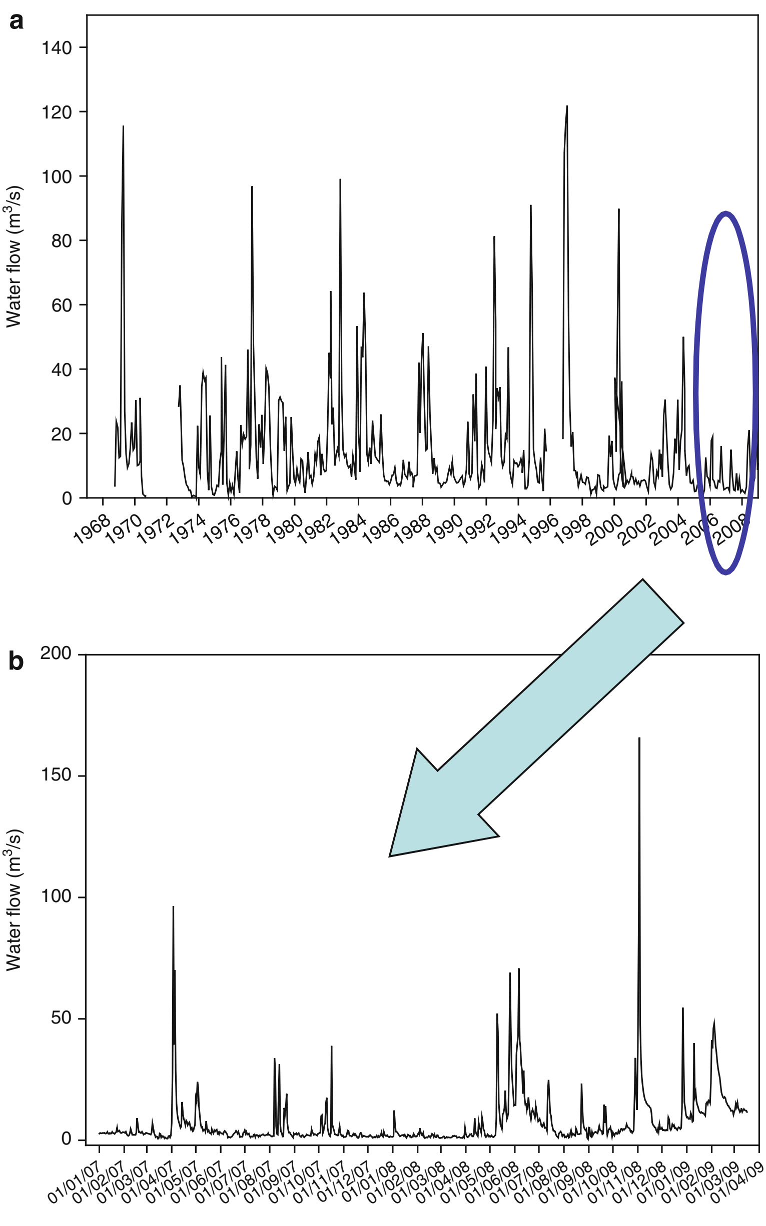

Fig. 1 Water flow dynamics in the Llobregat River (NE Spain) close to its mouth. (**a**) Monthly average flow rates between 1968 and 2008. (**b**) Daily average flow rates in 2007–2008 during a remarkably dry period (data: Catalan Water Agency data base)

water scarcity. Droughts are here defined as persistent periods when the river discharge is below a reference minimum. Droughts can be characterized by the time of occurrence, duration, the minimum flow recorded, and the deficit volume during that episode [6]. Water scarcity is a more structural, persistent drought; it can be properly defined only on the basis of reliable records of drought situations, as well as consistently establishing a drought threshold line. This is a relevant issue to define repetitive drought situations that therefore can be indicative of structural effects. Drought varies in space and time, and therefore the rainfall threshold used to define drought is dependent on the location [7]. Available long-term records can be particularly useful to define these thresholds. Long-term records are available in Mediterranean countries because these events have affected daily life for a long time. Several indicators can be useful to derive this information: tree ring chronology, documentary data (administrative, from local government institutions, both civil and ecclesiastical [8], and even data from rogation ceremonies [7]. To sum up, while *drought* means a temporary decrease in water availability, due for instance to rainfall deficiency, *water scarcity* means that water demand exceeds the water resources exploitable under sustainable conditions (COM2007-414 final).

A mixture of natural and human-driven components causes water temporality. It is obvious that natural influences may be particularly relevant in systems where the seasonal and interannual variability is high, as in the Mediterranean systems; [9]. In the Mediterranean Basin, as well as in many arid or semi-arid areas, temporality naturally associated to the climate leads to drought most usually in summer, followed by extreme autumnal flood episodes (so-called first flush events). For example, the Llobregat River (NE Spain) has an average mean annual discharge of 14 $m^3\ s^{-1}$ (Fig. 1a), but a monthly range from <2 to 130 $m^3\ s^{-1}$. The diel water flow rate is even more variable (Fig. 1b). The hydrological year 2007–2008 was one of the driest years recently recorded, and during 86% of the time the river carried less than the average water flow. During that year, flashy episodes reaching 100–180 $m^3\ s^{-1}$ occurred, and flow returned very quickly to baseflow afterwards. Catastrophic flood events with 1,500–2,000 $m^3\ s^{-1}$ can occur on average every 9–20 years in the Llobregat River [10]. The most painful event occurred on 25th September, 1962 and caused 441 human casualties. These drought–flood patterns have been documented over a long period of time. Thorndycraft et al. [11] analysed paleoflood deposits in the Llobregat River and described that the largest flood in a mid-river location ever recorded in modern times (1971; 2,300 $m^3\ s^{-1}$) was exceeded on five occasions in the past 2,700 years, reaching maximum discharges of 3,700–4,300 $m^3\ s^{-1}$. Therefore, the Llobregat flood events exceed baseflow by up to a factor of 100–300.

2 The Alteration of Water Flows in the Context of Climatic and Global Changes

Global change is an expression of the human footprint on resources, energy and soil uses, directed to larger and less efficient agglomerations, higher use of resources, and a potential higher pressure towards natural ecosystems. As an expression of this global change, ecosystem and societal requirements compete for water resources,

Table 1 Spatial extent of temporary watercourses. Data: Larned et al. (in review), among other sources

Global		~20%
USA	3.2 mill km	~60%
France	70,000 km	25–35%
Tagliamento	1,300 km	~50%
Chatooga	2,800 km	70%
Albujon	820 km	99%
Val Roseg	26 km	80%

and this competition increases with increasing water scarcity. Aquatic ecosystems are impacted in a nonlinear way with increasing water withdrawal. The effects of drought and water scarcity on river ecosystems are evidenced by an extended duration of dry periods as well as by a growing proportion of watercourses being affected (Table 1).

Current estimates predict that on average, the global annual runoff is increasing [12]. However, remarkable variations occur at the regional and local scales. While high-latitude catchments may experience an increase in runoff, tropical and mid-latitude watercourses are expected to experience a reduction in flow. The predictions of the Intergovernmental Panel on Climate Change [2, 13] indicate that annual average river runoff might increase by 10–40% at higher latitudes, and may decrease by 10–30% in dry regions. An increase in flow has already been noticed for Scotland [14]. In Europe, the southern and south-eastern regions already suffer most from water stress and will see a further increase in the frequency and intensity of droughts [15].

The potential impact of water withdrawal on river ecosystems is indicated by the ratio between water demand and available water resources. Though the ecological relevance of this ratio could be stronger if the Q_{90} was used instead of the more general estimate of total resources, it is a simple index easily applicable, using public data sets. For the Iberian Peninsula, the potential ecological effects are demonstrated in Fig. 2. The northern part of the Peninsula exhibits an Atlantic climate with sufficient water supply; the use of water accounts for 4–7% of the total resource available, though this does not prevent severe local shortages in large cities. However, demands increase to 30–80% of the total resource in the remaining catchments of the Peninsula, following the gradient of decreasing precipitation from NW to SE. In the Segura basin, located in the SE corner of the Iberian Peninsula, current demands exceed the supply by 224%, which requires an interbasin transfer of water (especially from the Tajo River). The downstream channel network of the Segura River dries up for several months during summer. When water flows, it consists of treated sewage effluents and, hence, is of poor chemical and biological quality. Figure 2 shows that the quantity attributed to the river (the so-called *minimum flow*) is far from being reasonable where water demand is high [16]. The application of a minimum flow (also called *ecological flow)* regime requires guaranteeing resources to make the ecosystem function. In short, very low water flow implies the inability to carry on with essential ecosystem processes, and complete water absence inhibits even minimum ecosystem function.

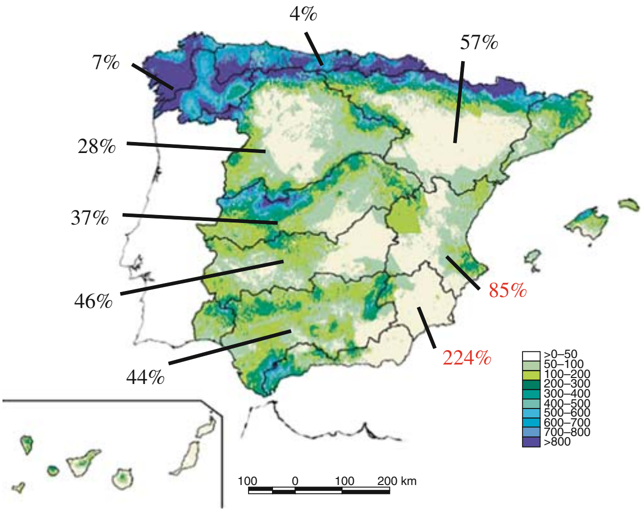

Fig. 2 Relative proportion (%) of water demand in relation to available resources in the main catchments of the Iberian Peninsula (data: derived from Libro Blanco del Agua en España, Spanish Ministry of Environment 2000)

Water withdrawal and scarcity are related to water flow regulation and dam construction. The regions suffering most from water scarcity are those which have a large number of big dams and reservoirs [17]. The global figures are also impressive. About 15% of the world's total runoff (40,000 km^3 yr^{-1}) is retained in 45,000 large dams higher than 15 m [18]. From this retained volume, a further 10% is abstracted [19]. As a result of these manipulations and subsequent irrigation, up to 6% of the resources evaporate [20]. A total of 52% of the surface area connected by large river systems (with a discharge of over 350 m^3 s^{-1}) is heavily modified, Europe containing the highest fraction of altered river segments.

Arid and semi-arid regions are particularly water-thirsty, further increasing the pressure on water resources and causing extended dry river networks. However, this is already a global phenomenon. The Yellow River in China, for example, ceases to flow along extensive reaches [21]. In 1997, during a particularly dry year, more than 700 km of river channel remained dry for 330 days. Similarly, sections of the Lower Colorado and Rio Grande Rivers in SW USA remain dry at the surface for extended periods [22], thereby affecting the ecosystem viability. In the former water-spotted area of Central Spain (La Mancha), the only option for the Tablas de Daimiel wetlands to survive is to transfer water from the distant Tajo River that is hydrologically disconnected from these wetlands. The Tablas de Daimiel wetlands were once fed by ground water that is now exploited for corn production. The steadily increasing water abstraction has caused a decline in the aquifer by up to 35 m [23]. Legal regulations are difficult to enforce because of the resistance by the farmers who exploit ground water for irrigation.

2.1 Potential Effects in Temperate Systems

A recent assessment by the European Environmental Agency indicated that high levels of water stress, both in quantity and quality, exist in many areas throughout Europe, and identified several significant ongoing pressures on water resources. The annual water withdrawal in Europe is projected to rise from 415 km^3 today to ~660 km^3 by 2070 (for comparison: the total annual discharge of the Rhine River is 73 km^3). Overall, the area with severe water stress is predicted to increase from 19% today to 34–36% of entire Europe by 2070. At present about 45% of this water is used for industry, 41% for agriculture, and 14% for domestic needs [24–27]. High water stress and an increase in temporary water are already characteristic phenomena in the Mediterranean area. In Turkey, for example, a significant decrease in discharge has been detected during the past 30 years [100]. The minimum flow during the dry summer months (July to September) is particularly affected by increasing water demands and climate change [28]. Many Balkan rivers have undergone even more dramatic annual discharge reduction during the past 40–45 years; e.g. a 79% discharge reduction for the Evrotas, a 57% reduction for the Axios, and a 48% reduction for the Sperchios [29].

However, the spatial and temporal extent of temporary rivers will not only increase in regions where water is already scarce, but this increase will become a more global phenomenon, mainly as a consequence of climate and land-cover change, increased demand for freshwater for agriculture, and of increasing hydropower generation. Permanent water bodies are shrinking even in areas devoid of human population. Smol and Douglas [30], for example, showed that many shallow ponds in the Arctic region are disappearing, mainly because of increased evaporation/precipitation ratios. For natural ecosystems such as the Yellowstone National Park (USA), Mcmenamin et al. [31] have shown that during the last 16 years the number of permanently dry ponds has increased fourfold, leading to dramatic declines in amphibian population density and species richness. Shallow water bodies and headwater streams are particularly sensitive to small changes in flow alterations; at the same time they are hot spots of biodiversity [32], and their desiccation will have severe ramifications for their structure and function.

In many parts of Europe, dramatic hydrological modifications have occurred during the last few centuries. In the central and eastern plains, for example, the total river network length has increased mainly due to the creation of artificial drainage canals. In addition, a 35,000 km long network of navigation canals in the EU (www.inlandnavigation.org/en/factsandfigures.html) now connects most large rivers across all Europe, from the Rhone River in the west to the Volga River in the east, thereby facilitating the rapid spread of nonnative species. While river basins remain hydrologically separated, they become ecologically more and more connected. At the same time, former permanent rivers are becoming temporary, mainly as a consequence of increasing variation in precipitation and domestic and agricultural use. The Spree River in NE Germany, for example, exhibited a sharp decrease in mean and low discharge during the last decade because of an increase in

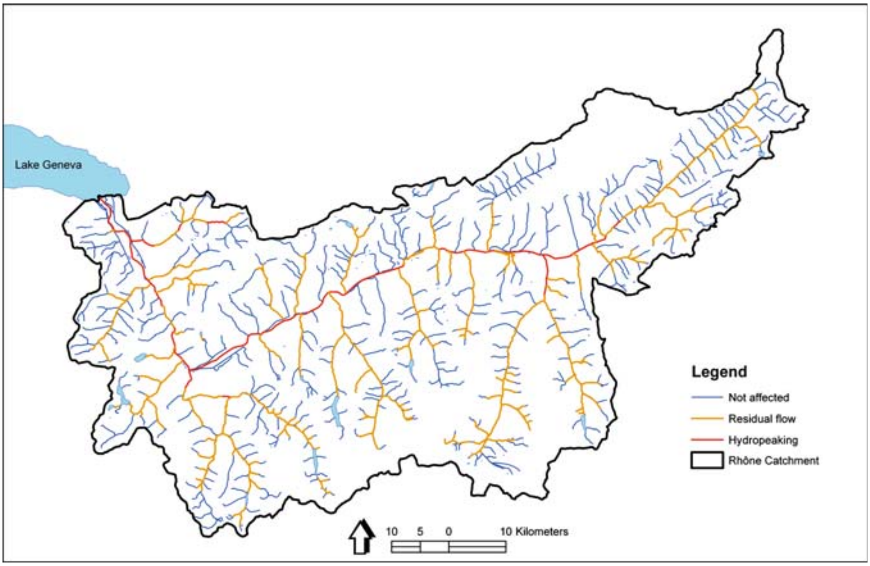

Fig. 3 The hydrological alteration of the river network of the Upper Rhone catchment in Switzerland that drains into Lake Geneva (data: Swiss Federal Hydrological Office)

water abstraction and a decrease in groundwater input. The transformation of permanent waters to temporary waters can be seen as an ultimate threshold for the diversity and the functioning of river ecosystems.

In Alpine countries such as Switzerland, water abstraction for hydropower production creates a network of residual flow channels. Almost all the main rivers in Switzerland and in the Alps are hydrologically altered. For example, the Upper Rhone catchment in Switzerland is extensively exploited for hydropower generation (Fig. 3). Hydropeaking is predominant along the main stem, water abstraction and residual flow conditions are typical for most tributaries, while hydrologically unaffected river segments are fragmented in nature and restricted to the low order sections. As a consequence of flow alteration, biodiversity decreased dramatically along the Rhone River corridor [33].

2.2 *Relevance in Mediterranean Ecosystems*

Though extremes are part of the normal hydrologic behaviour in Mediterranean-type rivers, a consistent trend of water flow decrease has been described in many of these systems. The Ebro is the largest Iberian river flowing into the Mediterranean Sea. The flow records at its mouth (mean annual runoff 13,408 Mm^3) show a decrease of nearly 40% in mean annual flow in the last 50 years. The forces behind these flow decreases are multiple. Higher water withdrawal, climate change and land use changes have all had an effect [34]. For example, illegal groundwater pumping can be excessive in many areas of the dry Mediterranean (estimated as one million wells in Spain). These practices obviously affect the hydrological behaviour of river systems, and may add an unexpected element for model previsions.

Under these circumstances it is essential to determine the causes of water flow decrease. The *naturalized flow* can be defined as the flow expected under non-direct human influence (e.g. abstraction). This is a useful parameter to be applied in areas subject to strong water withdrawal. One tool to estimate the deficiency of water flow due to human effects is the sacramento soil moisture accounting (SAC–SMA) model, which is based on a rainfall–runoff interaction. Using this model Benejam et al. [35] determined that the Mediterranean river Tordera (NE Spain) dried out for more days (76 per year) than those corresponding to the rainfall–runoff relationship (2 per year). This contrast to the long-term rainfall records in the Tordera watershed, do not show any pattern of decrease that could be causative of the enhanced temporality. The cause of the decrease may be found in the large number of industries and human settlements, which have increased enormously in the basin. More than 30% of the runoff of the Tordera is used by humans (irrigation, urban settlements, industry).

It might be derived from previous suggestions that the river sections below dams can experience even higher stress than those upstream. In the case of the Ter River (NE Spain) during the unusually dry 2007–2008 period, differences were not high

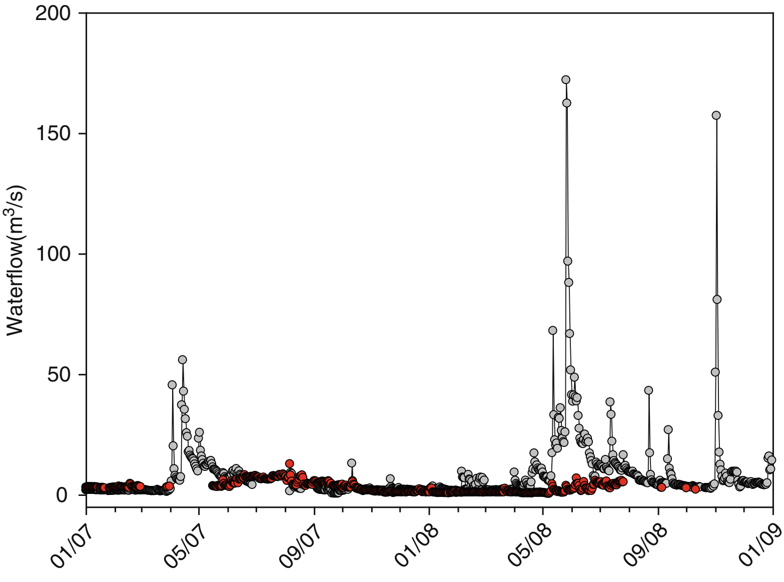

Fig. 4 River Ter (NE Spain) during the dry period 2007–2008. *Grey dots*: River Ter at Ripoll, upstream from the reservoirs of Sau and Susqueda. *Black dots*: River Ter at Girona, downstream from the reservoirs

between the sections upstream and downstream in a series of three reservoirs; however, as soon as rains began, differences rose sharply. The rains in the higher basin (Fig. 4) caused the return of water flow to the river. These waters were stopped by the reservoirs that transferred them to thirsty cities. The river section below the reservoirs was almost not flowing (Fig. 4).

3 Effects of Temporality on In-Stream Biogeochemical Processes and the Structure of Freshwater Communities

Alterations of water flow, independent of the cause, impact the structure and function of aquatic ecosystems. Extended drought produces the loss of hydrologic connectivity between stream compartments, and affects the biota. Therefore, flow cessation triggers a chain of cascading effects, eventually affecting community structure and ecosystem functioning.

The residence time of surface water increases when the discharge decreases, thereby leading to an average "ageing" of water [19]. Alteration of natural hydrological conditions includes reducing the strength and frequency of flooding and of meander migration, abnormally extending the periods of hydrological stability, and lowering the incidence of post-disturbance succession [36], and the opportunities for colonist species to re-establish from elsewhere. Water scarcity may therefore lead to the transformation of the habitat character of rivers in the direction from lotic (moving waters) to lentic (standing waters). This process is known as *lentification* [37], and may promote higher water temperature, with greater evaporative losses, that may be particularly relevant in arid and semi-arid areas [38]. Overall, this produces changes in the biogeochemical processes, as well as in the biological community inhabiting the river.

3.1 Changes in Biogeochemical Processes

The first change produced by decreased flow is the enhanced in-stream retention of particulate organic matter. In forested Mediterranean streams, for example, the falling leaves accumulate on the streambed for 1–3 months until first flooding. During the first flush events, a mass downstream transport of dissolved and particulate material (mainly organic) occurs. In the rehydration of a temporary stream after summer leaf fall deposition, nitrate did not remarkably increase, but the DOC concentration increased two to fourfold [39]. The influence of the pulse of dissolved organic matter extended to baseflow conditions during late summer and autumn. In these pulses after the restart of the flow, the proportion of readily available DOC (BDOC) can be very high (mostly attributed to carbohydrates and peptides; [40]).

Table 2 Summary of effects caused by water scarcity

Water quality descriptor	Effect of low flow	Effect on biota	Affected process
Temperature	Lower oxygen content Higher metabolic rates Combined effects with toxicants and nutrients	Invertebrates Fish All groups All groups	Decrease in oxygen availability Higher primary production Higher respiration rates General effects on structure and metabolism
Conductivity	Enhanced water salinity	All groups	Physiological regulation Changes in community composition
Organic matter	Accumulation of organic matter	Bacteria Primary producers	Slowed down decomposition? High oxygen consumption High mineralization
Sediments	Siltation	Primary producers Invertebrates Fish	Reduced production Changes in community composition Difficulties in gas diffusion
Nutrient	Higher concentration; eutrophication	Primary producers Potential bottom up-effects	Higher gross primary production Lower efficiency on materials processing
Pollutants	Increase of pollutant concentration and enhanced effects on the biota	All groups Complex food web effects	Diversity decrease? Effects on metabolism Effects on material processing

This high availability of materials can also be related to the high enzymatic activities in the water as well as relevant organic carbon uptake by the benthic microorganisms [40, 41].

A subsequent consequence of altered hydrological conditions is the export of solutes, as well as changes of the biogeochemical processes (Table 2) that derive from drought and rewetting. It has been observed that antecedent droughts in wetlands contribute to the oxidation of sulphides stored in the sediment to sulphates, which are mobilized after rewetting [42]. Pinay et al. [43] indicated that the surface area of the water-substratum interface (water-sediment or water-soil interface) is positively correlated with nitrogen retention and uptake rates. This applies both for the sediments in the stream channel as well as for the soils in the floodplain and riparian zones. The stream sediments incorporate the hyporheos, i.e. the zone immediately beneath the stream surface; Fig. 3). This compartment is highly reactive for nutrient cycling [44] because of the hydrated, porous medium that provides exchange and reaction surfaces for the microbes involved in C, N and P cycling. The active riparian area is larger during high flows, but it contracts during the drying periods [45].

The oxic and anoxic phases occurring in the riparian soil and in the hyporheos are therefore related to the variations of flow [43]. Regarding the nitrogen cycle, ammonification can occur during aerobic and anaerobic conditions, while nitrification requires aerobic conditions, and denitrification is favoured by alternating aerobic and anaerobic cycles. Water table fluctuations associated with these processes do not occur during permanently dry conditions; hence the biogeochemical cycle of nitrogen can be expected to be altered with respect to steady flow conditions. Nitrogen processing is limited during the transport from upland to riparian zones in arid areas [46]. Nitrogen processing shifts from the soil (denitrification) to the riparian vegetation (plant uptake) [47], but even this shift can be interrupted under water stress.

Aerobic penetration increases in previously dry sediments, because of better oxygen diffusion compared to saturated conditions; hence, when sediments are exposed to the air, anaerobic zones become aerobic [48]. The oxidation and desiccation affect the microbial assemblages in previously reduced sediments. Drying of sediments will result in an increased sediment affinity for P with reduced availability to biota. The return of the water to a previous dry stream bed is a "hot biogeochemical moment" [49]. Biogeochemical reactions and biological processes; (see Sect. 3.2) restart or accelerate after long quiescent periods. Re-wetted sediments liberate phosphorus and nitrogen, as a consequence of dying-induced microbial cell lysis, that again may enhance in-stream primary productivity. However, opportunistic organisms may be favoured by repeated drying–wetting cycles, which again affect nutrient cycling. In particular, the combined nitrification–denitrification may be severely limited by repeated wetting–drying [48].

Water scarcity increases the concentration of nutrients and pollutants which therefore exert a stronger effect on organisms [50]. Shallow water columns, and higher nutrient concentrations, together with higher temperatures and light availability (these conditions occurring in disturbed watercourses), trigger eutrophic conditions in rivers and coastal zones. An example of these complex relationships was seen in the Oria River (N Spain), where nutrient rich sites with poor riparian cover exhibited high water temperature, high algal biomass, and large dissolved oxygen oscillations [51]. Dissolved oxygen concentrations varied during a diel cycle from 0 to 13 mg O_2 L^{-1}, compared to 8–9 mg O_2 L^{-1} in an adjacent forested site with lower nutrient concentration. The impacted site had a fish community, dominated by cyprinids, more tolerant to hypoxia, while in the forested section salmonids occurred. Occasional fish killings occurred in the eutrophic site because of oxygen fluctuations.

Higher salt concentrations (enhanced water conductivity) from urban and industrial waste waters result in lower dilution. Salinity limits the distribution of sensitive plant and animal taxa, and triggers the abundance of others. The presence of the shrub *Tamarix canariensis* has increased in the saline soils of the low flow affected Tablas de Daimiel (Spain), while the once dominant *Populus alba* retreated.

3.2 Changes in Biological Community Structure

Abnormal hydrological stability homogenizes river habitats, and this obviously affects the performance and distribution of organisms. In some semi-arid and arid-zone streams and rivers, water extraction for human activities may lead to complete and extended dewatering during low flow years, dramatically impairing the freshwater biota [38]. However, many organisms inhabiting naturally temporary rivers have adaptive mechanisms that allow them to survive droughts and to quickly recover after water returns [52]. Microorganisms exhibit physiological adjustments during the gradual drying from permanent to temporal waters. Algal taxa, for example, synthesize energy-storage or osmotically active molecules [53]. Other algae are able to produce resistant structures such as akinetes, cysts, or zygotes, which can reactivate and grow upon rewetting [54]. The physiological plasticity of many of these taxa is remarkable. For example, desiccated cyanobacterial mats, collected from an intermittent Mediterranean stream, started to photosynthesize in the laboratory within 2 h after rewetting [55]. The extracellular enzymes associated to the cell wall allow an immediate use of dissolved organic matter [40]. The excretion of extracellular muccopolysaccharides by algae and cyanobacteria facilitates cellular water retention and therefore results in quicker rehydration. However, human-caused rapid or unpredicted drying does not provide sufficient time for the production of desiccation-resistant structures or physiological adjustments [56]. The ability to recover after drought also depends on the existence of reservoirs of propagules, stored in areas that did not dry out, or in the sediments, which facilitates recolonization processes [57].

When rivers begin to dry out, and consequently to fragment, the biota concentrates in the remaining pools leading to very high densities of invertebrates and fish [58]. Life in these pools is harsh because the accumulation of detritus increases nutrient concentrations that lead, together with the concurrent reduction of reaeration from the atmosphere, to decreased oxygen concentration. Leachates from decomposing leaves, which can be toxic to some organisms, accumulate in these ponds [59]. Fragmentation affects the entire trophic web. Algae growing on riffles disappear during the drying up process; grazers therefore decrease in numbers, while other feeding groups may benefit. Filter density may also be reduced because of the decrease of transported material [60], while collector-gatherers may increase in numbers in these pools. Predation pressure increases in pools. Acuña et al. [61] showed that the drying up of a Mediterranean stream caused an increase in macroinvertebrate density in isolated pools soon after flow ceased. Afterwards, when the pools shrank further, the invertebrate density rapidly decreased. In this Mediterranean stream, there was a difference in the macroinvertebrate community at the end of the summer dry phase (when flow resumed) compared to that present before drying began. High availability of food (detritus) for invertebrates during flow reduction in pools led to a considerable increase in invertebrate density and biomass. The taxa that increased significantly as flow decreased had low dissolved oxygen requirements (e.g. Lumbriculidae, Chironomideae), or were adults that

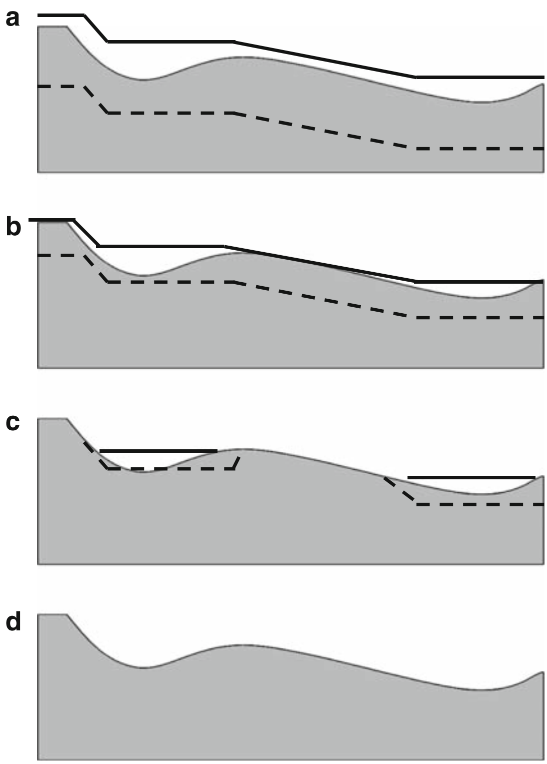

Fig. 5 Decrease of surface water and the effects on the longitudinal distribution of riverine habitats. During high flow (**a**) surface habitats, i.e. riffle (fast flowing sections) and pools (slow flowing sections), are available. Drying first affects the surface waters (**b**), causing fragmentation and the formation of remaining pools (**c**). During this phase the hyporheic compartment is also restricted to the pool habitats. Finally, both the superficial and hyporheic compartments dry completely up, and potential refuge for the aquatic biota disappear

breathe atmospheric oxygen directly (e.g. beetles). At the same time, taxa with high DO requirements (e.g. snails) were absent during this phase.

Droughts and floods have similar consequences on biota survival. Although floods may cause a complete resetting of the physical habitat, as well as the downstream drift of many individuals, the effects may be less persistent than those produced by droughts. As drying proceeds (Fig. 5), shallow surface habitats such as riffles disappear first, and a series of fragmented pools remain, together with a low water flow in the hyporheos [52]. This is called *superficial drought*. During a *subsurface drought* even the hyporheic zone can dry out [62], affecting the potential refuge of many organisms (see below). In an even more advanced step, *deep drought* implies that the phreatic layer can descend, which may cause early leaf abscission of riparian woody plants [63]. This extended decrease of the water table in the riparian zone may even impair riparian vegetation, trees being replaced by shrubs and later by herbs, with lower leaf litter input and allowing higher light penetration. In some areas of the Mediterranean where the phreatic level has decreased, riparian vegetation has disappeared, and with it has gone the function the riparian exerts as a nutrient buffer, as the refuge of species and a biological corridor [64]. This may have definite effects on moisture retention in the soil, as vegetation controls permeability near the surface. The riparian strips of headwaters and the main river sections play an essential role in the regulation of greenhouse gases (CO_2, N_2O) [65]. Riparian areas may protect against flood events and help in establishing biological corridors between polluted and unpolluted sections. In many areas of the Rivers Ter and Llobregat (NE Spain) the riparian area has been seriously damaged by overexploitation, groundwater extraction and subsequent phreatic decrease.

The fauna of seasonally intermittent streams have acquired, through evolution, a range of adaptations, such as specific life-history strategies, physiological mechanisms, and specific behaviours to search for refugia [66]. There are two major classes of refugium use strategies [67]. The most common type is refugium use within a given generation. It consists mostly of actively changing the habitat when the drought proceeds. Invertebrates may shelter below cobbles, among debris or macrophytes [66], and the most mobile seek refuge in the hyporheic (subsurface) sediment, as well as in the remaining pools [52]. This variability emphasizes the value of a well-preserved river habitat, which offers a greater variety of shelter [62] than physically disturbed reaches. A more specialized type of refugium-seeking occurs between generations, as happens when there are complex life cycles or changes in habitat use. This can be seen in some caddisflies, which lay terrestrial eggs [68], thus protecting their offspring from floods. Similarly, during droughts, some fish retreat to safe places like backwaters, or to permanent tributaries, and recolonize the stream with juveniles after the drought [56, 69].

However, other taxa do not show these adaptations, and may suffer from changing conditions. This may be seen in groups that are intolerant to desiccation or are relatively immobile (e.g. Unionid mussels; [70]). More difficulties in dispersal are faced by many groups of organisms [71], as they cannot circulate along intermittent watercourses. Water abstraction has been identified as one of the most detrimental factors for fish assemblages in Mediterranean watercourses. Fish can respond by changing their community composition, as well as their abundance, and condition [72]. The least exigent species survive these unstable conditions [73]. Droughts reduce the survival and reproduction rate of fish, and promote emigration towards other areas [58]. Some fish populations can even disappear when the frequency of drought is higher than in natural conditions.

Other consequences of decreasing water flow on biota are related to indirect effects on physical and chemical parameters (Table 2). Temperature may increase as a result of slow-moving, thinner water layers. Warmer waters and other stresses increase the possibility of fungal, viral and bacterial infections on fish. Certain invasive species can also take advantage of higher average temperatures and/or stabilized hydrological conditions. As an example, in the lower River Ebro (N Spain), reduced flow has favoured the proliferation of the mussel *Dreissena polymorpha*, the trematode *Phyllodistomum folium* that infects zebra mussels, and the Asian bivalve, *Corbicula fluminea*. Higher temperature reduces the solubility of gases in water, as in the case of oxygen. Lower oxygen may limit fish and invertebrate distribution. Temperature change and water flow changes can promote changes in the regional distribution of some taxa. Several insects [74] are sensitive to differences of only 3°C of mean summer temperature. Key life-history parameters of many species, such as egg dormancy and life cycle plasticity, may be affected by these temperature changes. Hence, increasing temperatures may support eurythermic species and generalists, resulting in less specialized communities. It is also true that the impacts of climate change might be reduced by catchment and floodplain land use; at least regionally, riparian forests may contribute to buffer future water temperature increases.

The extension of the dry period is also a critical factor. Dry periods longer than the generation times of the biota reduce the efficacy of potential adaptations. Larned et al. [75] observed that the total invertebrate richness decreased linearly while the invertebrate density decreased exponentially with increasing duration of the dry period. This is most possibly caused by dying or dispersal of the invertebrates, while few pre-adapted species remain. Drought may cause long-term effects. Although species are able to persist during droughts during their early stages, they may not recruit successfully during the next year. This lag effect in response to a drought [62] is most obviously for long-living biota (invertebrate and fish). Analogously, repeated episodes of drought can have cumulative effects on fish populations, which are not obvious at the reach scale but detectable at the watershed scale [76]. The amount and quality of fish refugia in a given summer would be dependent on the rain falling in the preceding years. Measurable changes in abundance are only apparent after several dry years with unusually high mortality or reduced recruitment [76].

4 Relevance of Water Interruption on Aquatic–Terrestrial Linkages

Rivers and their terrestrial realms are tightly linked by reciprocal flows of matter, energy and organisms [77]. The flow of material and energy is generally from the more productive to the less productive habitat. For example, a drought-induced decrease in in-stream productivity may reduce the energy flow from emerging aquatic insects into the adjacent riparian ecosystem, thereby affecting the composition and density of riparian predators. On the other hand, water stress may cause early leaf litter abscission, alter leaf litter quality (e.g. through photo degradation), and may lead to an accumulation of coarse particulate organic matter (CPOM; e.g. leaves) at the dry stream surface [78, 101]. Results from decomposition experiments along the Tagliamento River demonstrated that alterations of the inundation regime directly influenced decomposition processes [79]. After 30 days of exposure, the mean percentage of the remaining leaf litter (as AFDM) ranged between 51% (permanent wet) and 88% (permanent dry). Decomposition was significantly affected by the duration of inundation whereas frequency played a subordinate role in controlling leaf breakdown. Unexpectedly, leaf-shredding macro invertebrates played a lesser role for leaf breakdown except in the permanent wet treatment.

More generally, changing flow alters the relative proportion of input, storage, transfer, and transformation processes for organic matter and nutrients. Hence, the relative extent and the dynamics of the temporary channels within a catchment may control the capacity of a river network to produce, transform, and store nutrients and organic matter.

Dry river beds are considered temporal ecotones that shift between an aquatic and a terrestrial phase. While we are well aware of the aquatic life during the wet phase, there is a general lack of information on biodiversity patterns and ecosystem processes during the dry period and how wet and dry phases are linked to each other. We may expect that dry channels provide important habitats for terrestrial organisms [80]. However, they remain open if dry channels contain a unique fauna or just a subset of upstream communities. Further, do rivers that naturally fall dry contain a terrestrial fauna that differs from artificially dry channels? Finally, we may expect a strong functional linkage between aquatic and terrestrial organisms. Terrestrial organisms are expected to quickly react to available resources and exploit stranded aquatic organisms [81]. On the other hand, allochthonous detritus, despite a relatively high C:N ratio, provides a basal resource for intermittent stream food webs [82]. In Cooper Creek, Central Australia, fishes appeared to feed on potentially lower value resources such as detritus during the dry period, but were able to exploit the booming aquatic production during episodic flooding [83]. These boom and bust cycles are characteristic of arid and semi-arid river systems, whereas busts for the aquatic assemblages may be booms for the terrestrial assemblages. However, water management plans in many Mediterranean and dryland river systems may alter this sensitive balance between boom and bust periods, leading to the observed decline in ecosystem health.

5 Functional Alterations in River Ecosystems Associated with Water Scarcity and Temporality

Ecosystem functioning includes a variety of processes that involve the transference of matter and energy throughout the different compartments. Among these processes, the most relevant are nutrient turnover, decomposition and respiration of decaying organic matter, primary production, secondary production and respiration, and the resistance and resilience after disturbance. These processes are translated into visible entities for human societies [37], understood as goods and services. Among those, there is flood protection, improved water quality, food and timber production, maintenance of biodiversity, etc [84]. As structure and function within an ecosystem are tightly linked, it might be expected that a shift in the former implies a change in the latter.

River functioning (globally expressed as metabolism) does not often show unidirectional responses to stress, and therefore makes difficult the prediction of changes. Gross Primary Production (GPP) may be first enhanced because the decrease of water flow may result in shallower water depths and lead to more underwater light

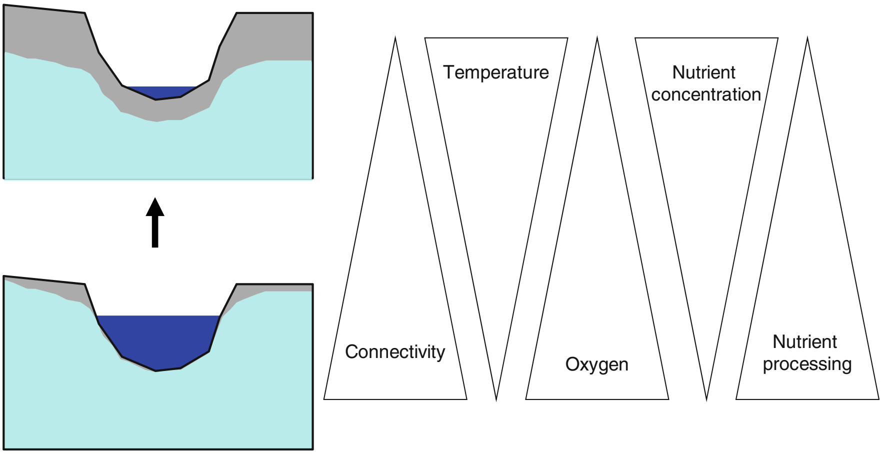

Fig. 6 Processes occurring along with drought in a river channel. Connectivity is lost, while water temperature and nutrient concentration increase in the remaining water. The efficiency of nutrient processing decreases, as well as it does the dissolved oxygen in the water and in the sediments

penetrating to the bottom. Altogether, higher nutrient concentrations and hydrological alteration may favour a shift towards autotrophy in aquatic ecosystems [85]. However there is a threshold of increase, as complete flow reduction may cause GPP to sharply decrease and finally stop during the drying phase [61].

The efficiency in many processes is expected to decrease, leading to undesired consequences (Fig. 6). The high nutrient content as well as the hydrological stability in the Llobregat River [86] favoured the massive growth of cyanobacteria during winter and early spring. These growths were associated with odours in the river caused by geosmin production. Respiration is also affected by lower flow and drought. Pinna and Basset [87] observed that the highest effects of summer drought on organic matter decomposition occurred in the headwater streams. The lesser effect detected in larger sections was mostly because the drought conditions were less intense there. Larned et al. [75] observed that the respiration rates in sediments declined rapidly with the onset of the dry period. Lower microbial biomass and sediment organic matter are found in ephemeral river sediments; there is therefore lower respiration than in wetter conditions. Claret and Boulton [88] suggested that there is threshold moisture for the sediment microbial activities, below which it might sharply decrease. In a forested Mediterranean stream, Acuña et al. [89] determined that the high accumulation of BOM during low flow caused extremely high ecosystem respiration (ER), though this depended on the intensity of the drought period in the stream which varied interannually.

Water fluctuations in Mediterranean rivers seriously affect fish production and droughts put important selective forces on fish communities [73] by reducing population density and species richness [58]. Fish also suffer from chemical and organic pollution affecting their physiological abilities [90].

Drought can increase the effect of other stressors such as pollutants, UV-impact, and thermal stress [27]. In the Llobregat River, for example, a wide range of human pharmaceuticals of high biological activity are present in low but ecologically relevant concentrations [91]. Their occurrence often coincides with low flow conditions and intensive water use, which increases their environmental risk. Multivariate analyses revealed a potential causal association between the concentration of some anti-inflammatories and β-blockers and the abundance and biomass of several benthic invertebrates (*Chironomus spp*. and *Tubifex tubifex*). Determining the relevance of the altered hydrological conditions on the multistress being suffered by organisms and ecosystems in polluted areas is an ultimate challenge.

Flooding is the predominant variable along large alluvial rivers, and as such triggers multiple functional processes. Floods not only increase the aquatic surface area but also reshape aquatic and terrestrial habitats, maintain its complexity, facilitate the dispersal of aquatic and terrestrial organisms, and provide key resources, thereby stimulating productivity and biodiversity. Recently, Bertoldi et al. [92] analysed oblique air-photos, sequentially taken at different water levels in a floodplain segment along the Tagliamento River (NE Italy). On the basis of these photos, various hydrological thresholds were identified, with lower water level thresholds nested within higher water levels. For example, an elimination of annual flood events may lead to an increase in vegetated areas, therefore altering the flow-inundation regime of the entire river-floodplain complex.

The predictions of the area-richness relationship indicate that a reduction in inundation area and duration will lead to a decrease in biodiversity, as well as in productivity [93–95]. A trait-based assessment might help to predict the species that will disappear as a consequence of flow alteration. We may speculate that the biota in Mediterranean rivers, adapted to naturally high seasonal and interannual flow variability, are less sensitive to flow reduction than biota in more temperate rivers. Evanno et al. [96] studied the effect of a severe drought on the genetics and species diversity of gastropods along the Ain River (France). They found that a natural disturbance leads to a decline in local (α) diversity and to an increase in regional (β) diversity, indicating that disturbances can lead to similar changes in genetics and community structure through the combined effects of selective and neutral processes. Thomaz et al. [97] observed that flooding increased species similarity among floodplain habitats.

There is a great need to identify and to quantify the multiple effects of duration, intensity, time, and frequency of surface flowing and drying, single and in concert, on both biodiversity and ecosystem processes. For example, the effect of inundation duration, following a rainfall pulse, controls process diversity in dry floodplains. Very short pulses, as typical for low order stream segments (or human altered ecosystems) release nutrients, which again increases in-stream productivity in adjacent permanent water bodies. Hence, the relative extent and the dynamics of the temporary channel network, as well as its spatial distribution within a catchment, may therefore influence the capacity of an entire river network to produce, transform, and store nutrients and organic matter as well as maintain its biodiversity.

6 Conclusions

Disturbances that increase water scarcity promote the physical uniformity of river systems and the decrease of biological diversity in streams and rivers. The structure and functioning of heavily impacted river systems become mutually and strikingly similar, irrespective of the river's origin and the climate. The more intense and persistent the disturbance, the greater is the resemblance. On the other hand, river organisms use resources most efficiently in spatially heterogeneous channels, and under moderate disturbance frequencies, rather than in steady conditions, to which they are not adapted.

Disturbances (both natural and anthropogenic) that increase nutrient concentration may cause the river biological components and metabolism to shift from natural heterotrophy toautotrophy, even in relatively pristine rivers. Enforced hydrological stability or increased nutrient loading, among many other disturbances, may cause pronounced changes in system metabolism.

Rising human pressure on water resources and the likely effects of climate change will probably affect the hydrological and geomorphological state of river systems in many areas of the globe. Hydrological variations will lead to a chain of effects in the structure and functioning of river systems and will make the estimation of the ecosystem services that they can sustain difficult. This will be especially relevant in arid and semi-arid areas and in those systems where water use is very intense. Decreasing flow leads to an increased exposure to UV, higher water temperature variation, further concentrations of nutrients and pollutants, and spreading of nonnative species, with cascading effects on aquatic and terrestrial biodiversity and ecosystem functioning. Further, we may anticipate a future global increase in pulsed events due to climate and land use changes; at the same time, major attempts are underway to reduce pulses by river regulation and impounding [27, 98]. Hence, a major challenge is to separate trend from event effects (e.g. gradual change in flow and temperature compared to pulsed events), and the timing and sequence of individual pulsed stressors (e.g. flood pulses, heat waves, disease outbreaks) that may shape ecosystem processes.

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Metal Ecotoxicology in Fluvial Biofilms: Potential Influence of Water Scarcity

Helena Guasch, Alexandra Serra, Natàlia Corcoll, Berta Bonet, and Manel Leira

Abstract Human activity is responsible for the entrance of toxic substances into aquatic ecosystems. These substances entail a risk for the components of the ecosystem (toxicological stress). As a result of global change, aquatic ecosystems are under strong environmental stress due to changes in water flow or nutrient concentration among others. This chapter presents a review of experimental and field studies addressing metal effects on fluvial biofilms and their implications for understanding the potential influence of water scarcity on the fate and effects of metals in fluvial systems. Water scarcity might increase metal exposure (due to low dilution), uptake (due to higher retention under low flow), toxicity and/or accumulation (depending on the dose and time of exposure) but may also cause opposite effects depending on the source of pollution. In addition, the influence that water scarcity might have on nutrient loads will also modulate the fate and effects of metals. Future studies addressing the role of environmental stress on the effects of toxicants at a community scale will be fundamental to predict the impact of toxicants in the aquatic ecosystems.

Keywords Community ecotoxicology, Fluvial biofilm, Metal pollution, Nutrients, Water scarcity

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Contents

1 Introduction

Aquatic systems are affected by many disturbances driven by local and global changes giving rise to dramatic variations in flow, light regime, water temperature or nutrient concentration [1]. For instance, water scarcity might be very critical in terms of water pollution due to the lowered dilution capacity of chemicals ([2,3]. This situation is of special concern in the Mediterranean region where scenarios of water scarcity are predicted for areas where human pressure is also high and is responsible for the entrance of many substances to the aquatic environment. In fluvial systems, these substances could be transported and/or retained in the sediment, affecting other components of the ecosystem [4].

In aquatic ecosystems, the elevated concentrations of metals are cause for environmental concern because of their potential toxicity and trophic transfer. Metal concentration is variable in time and space depending on the source of pollution (diffuse or point-source), the hydrological regime and the processes affecting their transfer from the water phase to other compartments. Based on this framework, it might be expected that water scarcity, understood as the period when surface water flow is well below average flow conditions, will also cause remarkable changes on the fate and effects of heavy metals at the ecosystem scale. Furthermore, the duration and frequency of water scarcity episodes is also important since metal bioaccumulation and toxicity are strongly influenced by the time of exposure.

In this chapter we present a review of experimental and field studies addressing metal effects on fluvial biofilms in relation to the potential influence of water scarcity on the fate and effects of metals in fluvial systems. Four aspects are specifically addressed: (1) the influence of discharge on metal pollution, (2) the use of biofilms to investigate the fate and effects of metals on fluvial systems, (3) the environmental factors influencing metal toxicity, and (4) the prediction of metal fate and toxicological effects under different heavy metal exposure scenarios differing in their origin, magnitude and duration.

2 Linkage Between Hydrology and Metals in Rivers

Metal concentration can vary due to several chemical, biological and hydrological processes. Based on recent modeling of metal fate and transport in streams [5], higher metal concentration is predicted during low flow (mostly for Zn). This tendency is common in mining areas where metal concentration is in general lowest at highest discharges due to dilution. The river Nent in UK [2], the riou Mort in France [6], streams draining the Cu-Zn belt of Sierra Nevada in California [7] and the North Fork Clear Creek in Colorado [8] fit into this category. Differences in metal concentration between the dry and rainy season in other stream types (such as those influenced by urban and agricultural activities, [9]) have also been attributed to dilution, although other studies report no linkage between discharge and metal pollution (i.e. [10]).

Sediments have a key role in metal transport and deposition. In the study of suspended sediment yield and metal contamination in a catchment affected by gold mining activities (Puyango river, Ecuador), Tarras-Wahlberg and Lane [11] provided evidence that environmental impacts of mining-related discharges are more likely to be severe during dry years compared to wet years, since metal-contaminated sediments are stored in the river bed during low flow periods. Besser et al. [12] indicated sediment transport as the main reason why lead bioaccumulation was highest in drought years in streams from the New Lead Belt in Missouri.

Metal fate and transport models [5] predict maximum concentration peaks in the early high flow period of a storm event and also predict that large metal loads might be transported during extreme events (floods). The first prediction is usually observed in urban areas in the so-called urban runoff [13]. In the Santa Monica Bay, California, storm water inputs are a large source of pollutants (also metals) discharged to receiving waters around the country [14, 15]. Meylan et al. [16] reported a marked increase in dissolved metal concentration (Zn, Cu) after rain events in the Furtbach stream in Switzerland. This increase was attributed to the release of historically contaminated sediments.

The second prediction reported above has been described in a study of metal contamination in sediments of the river Odra in Germany [17], where the highest metal levels were measured in the flood year (1997). In this case the flood had mobilized heavily contaminated sediments in upstream reaches, and transported them downstream where parts were settled. Butler et al. [8] observed that storm events may cause either decreases in dissolved metal concentration due to dilution, or increases due to flushing of acid mine drainage. Conversely, the particulate fraction usually increased after storm events due to scouring and resuspension of bed sediments and/or washing of bank materials. The same study reported that the relevance of a flow increase on metal transport was much higher after a drought. These predictions and the related results suggest that the expected effects of rising global change on fluvial hydrology will also cause remarkable changes on the fate and effects of heavy metals at the ecosystem scale.

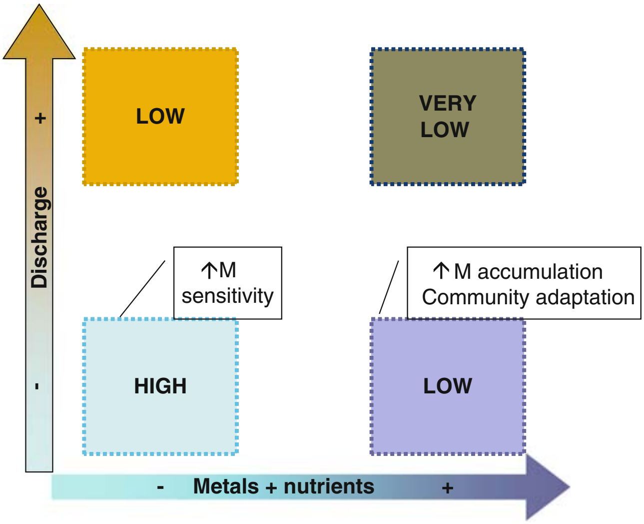

Fig. 1 Scheme illustrating the influence of water discharge (*y* axis) and solute concentration (metals and nutrients on the *x* axis) on in-stream retention efficiency measured on the basis of the nutrient spiraling concept. The most remarkable Metal (M) effects on biofilms are indicated in the boxes

The linkage between hydrology and metal retention in fluvial systems has been poorly addressed. Some studies have indicated that water velocity may influence Cu toxicity [18]. Cu retention was investigated by Serra et al. [19] applying the concepts and methodologies of nutrient dynamics in rivers based on the nutrient spiraling theory. Cu retention at subtoxic concentrations (to avoid negative/lethal effects on biota) was compared with phosphate dynamics. Higher retention efficiency was observed for PO_4^{3-} than for Cu. The biota played a key role in retaining both solutes, but, its influence was more pronounced for PO_4^{3-}. Finally, the retention efficiency for both solutes was influenced by the hydrology of the system, lower retention efficiencies occurring under higher flow conditions (Fig. 1). These results highlight that metal dynamics in fluvial systems may be strongly influenced by the prevailing environmental conditions, especially water hydrology, which modulate significantly their transport and biotic retention.

3 Biofilms and Metals: A Community Level Ecotoxicology Approach

Fluvial biofilms (also known as phytobenthos or periphyton) are attached communities consisting of bacteria, algae and fungi embedded within a polysaccharide matrix [20]. In rivers, these communities are the first to interact with dissolved substances such as nutrients, organic matter, and toxicants. Biofilms can actively influence the sorption, desorption and decomposition of pollutants [21]. Fluvial biofilms, despite being relatively simple and easy to investigate compared to other communities (i.e. macroinvertebrate or fish communities), provide a perspective of community ecotoxicology [22, 23]. In contrast to single-species tests, ecotoxicological studies with fluvial biofilms involve a higher degree of ecological realism, allowing the simultaneous exposure of many species [24]. It is possible to investigate acute effects [21, 25]; and also the response after chronic exposure [26, 27], including the evaluation of direct and indirect toxic effects [28]. Exposure might be done under controlled experimental conditions in micro/mesocosms [29] or in the field where the response can be evaluated under real exposure conditions [30, 31].

Fluvial biofilms have a high capacity to accumulate heavy metals from the surrounding environment [32, 33]. In general, the kinetics of metal accumulation involves two main processes: a rapid adsorption of the metal ions to the polysaccharide matrix and the surface of cells, which is a metabolism-independent step, and slower intracellular uptake, which depends on the metabolism of the organism [34, 35]. Once entering the cell, the heavy metal ions may either be detoxified or adversely affect cell processes such as photosynthesis and cell division [36]. Control of metal uptake, excretion of accumulated metals and intracellular or extra cellular immobilization of accumulated metals are the main mechanisms that may operate alone or in concert to protect algae from toxic effects [37]. Metals, once inside the cells, may be detoxified by accumulation in polyphosphate bodies and in intracellular metal-binding proteins [38], and within the vacuoles of some eukaryotic algae [32]. Moreover, not only can heavy metal accumulation exert numerous toxic effects on the individual organism itself, but it may also give rise to effects community-wide or in populations . Through the accumulation of metals in fluvial biofilms, metals may be transferred to higher trophic levels of the fluvial food webs [39].

4 Environmental Factors Influencing Metal Retention, Availability and Toxicity

4.1 Metal Bioavailability

Several factors can influence metal uptake by stream autotrophic biofilms in fluvial systems. These include chemical factors (pH, salinity, phosphate concentration) which affect metal bioavailability by either altering the speciation of the metal or by complexing it at the biofilm's matrix and cell surfaces [18, 40], and also other biological and physical factors.

The chemical speciation of the metal is defined as its distribution among different phases and different dissolved forms. When heavy metals enter aquatic systems, they can stay in several phases; in solution as free ions, as soluble salt, be associated with dissolved inorganic or organic ligands, or can be bound to particulate matter. All these metal species are following chemical equilibria that regulate the concentration of the free metal ion as well as all the metal complexes [16]. Metal speciation determines bioavailability and toxicity of trace metals to aquatic microorganisms [41].

Among the physical factors, current velocity has a special significance for benthic biofilms because it can modulate the diffusion of metals through the biofilm and their effects [18, 40]. pH and organic complexation are particularly significant for metal bioavailability [42]. Therefore, metal toxicity will also depend on the influence that environmental variability has on its bioavailability.

4.2 Metal Toxicity

Sensitivity of biofilms to metals will vary in a wide range depending on many environmental conditions and biotic factors. The thickness and nature of the biofilms (biomass accumulation, polysaccharide abundance in the matrix) is of considerable significance ([43, 44]) for metal toxicity. Furthermore, the duration and frequency of high metal concentration episodes is of great relevance since metal bioaccumulation and toxicity are strongly influenced by the time of exposure. Acute metal toxicity on biofilms is usually found at concentrations higher than those described in free-living organisms (Table 1). This difference relies on the structure of biofilms, that reduces the penetration of solutes into the cells [45, 46]. On the other hand, longer metal exposures will allow the metals to reach the different types of organisms embedded in the biofilm, increasing metal toxicity [47]. Since the different species of algae and bacteria found in a biofilm may differ in their metal sensitivity, it is also expected that chronic exposure to low metal concentrations may lead to changes in their competitive interactions producing community changes (Table 1).

The influence of the exposure time on Cu accumulation kinetics and toxicity in fluvial biofilms was experimentally investigated [35]. Biofilms differing in their Cu-exposure history (unexposed, acute exposure and chronic exposure) were investigated. Marked differences between the effects of pulsed and chronic exposure were observed. Biofilms that had been continuously exposed to Cu (ca. 30 μg L^{-1} Cu), differed from those being unexposed and those receiving pulses in their species composition (due to the replacement of sensitive algal classes by tolerant ones) and also on their metal content, which was several orders of magnitude higher after chronic exposure. The nonexposed and the acutely exposed communities were more sensitive to Cu than the chronically exposed community. It was concluded that acute exposure may lead to transitory inhibitory effects if the community had not been previously adapted. On the other hand, chronic exposure may lead to high metal bioaccumulation and community adaptation.

Table 1 Summary of metal concentrations (in μg L^{-1} of total metal concentration) causing toxicity on fluvial biofilms (in terms of effective concentrations: EC_{50}) after acute exposure (of few hours of exposure) and chronic exposure (of several weeks of exposure)

Metal	Test	Effects	Source
Cu	Acute toxicity on biofilms	EC_{50} (^{14}C): 20–50 (spring) 100–350 (summer)	Field samples Ter river[a]
		EC_{50} (Y): 230 (low P) 718 (high P)	Fluvial microcosms[b]
		EC_{50} (Fo) 56–92 (low P) 196–206 (high P)	Field samples[c]
	Chronic effects on biofilms	EC_{50} (Fo): 57–90 EC_{50} (Y): 290–390	Fluvial microcosms (high P)[d]
		EC_{50} (biovolume): 16 EC_{50} (chl-a): 9.7	Fluvial microcosms (low P)[e]
		63.5 change spp. Cu, Zn, Ni, Ag tolerance	Outdoor fluvial mesocosms, (low P)[f]
	Algal cultures	21–207	Toxicity standards[g]
Zn	Acute toxicity on biofilms	Effect >65 × 10^3 Bacteria more sensitive than algae	Field samples Dommel, metal polluted river[h]
		EC_{50} (^{14}C): 19–195 × 10^3 EC_{50} (thym): 7–17 × 10^3	Field samples[i, j]
	Chronic effects on biofilms	EC_{50}: 6–25 indirect effects EC_{50}: 50–2500 direct effects	Fluvial microcosms (low P)[k]
		Changed algal species >50	Experimental stream[l]
	Algal cultures	15	Toxicity standards[g]
Cd	Acute toxicity on biofilms	EC_{50} (Y): 3.4 × 10^3 high UVR 9 × 10^3 low UVR	Fluvial microcosms[l]
	Chronic effects on biofilms	10 effects on settlement 100 biomass, change spp.	Fluvial microcosms (high P)[n, o]
	Algal cultures	13–341	Toxicity standards[g]

[a][31]
[b][51]
[c][48]
[d][52]
[e][53]
[f][54]
[g][55]
[h][44]
[i][47]
[j][25]
[k][28]
[l][56]
[m][57]
[n][26]
[o][34]
*Measured end points are photosynthesis as the incorporation of radiolabelled $H^{14}CO3$ (^{14}C) and bacterial activity as the incorporation of radiolabelled thymidine (thym); fluorometric measurements: basal fluorescence (Fo) and photon yield (Y); chlorophyll-a concentration (chl-a); species composition (spp) and the biovolume of algae obtained after algal counting (biovolume)

4.3 Influence of Nutrients on Metal Availability and Toxicity

Since metal pollution is often associated with eutrophic conditions in the aquatic ecosystems, it is relevant to understand the interaction between nutrients and metal toxicity. Differences in sensitivity to metals obtained in different field and experimental studies highlight the significance of phosphate (P) on metal toxicity on fluvial biofilms (Table 1). The interaction between nutrients and copper (Cu) toxicity was investigated in field and laboratory experiments [48]. It was shown that the sensitivity of fluvial biofilms to Cu followed the gradient of eutrophy (basically driven by phosphate). Communities from oligotrophic sites were more sensitive to Cu than communities developed under more eutrophic conditions. Furthermore, P supply increased the tolerance of the communities developed under low P conditions, but did not enhance the tolerance of those developed under higher P conditions. Additional experiments performed with algal cultures showed that high P conditions during growth, as well as the presence of P in the media during the toxicity tests led to an increase in copper tolerance of the algae of the same magnitude as the previously studied field communities. These results indicated that P is one of the main factors determining Cu toxicity on fluvial biofilms. It is expected that accidental or point-source metal pollution in fluvial systems will have greater negative impact in pristine rivers, since Cu toxicity is expected to be maximum due to P-limitation.

4.4 Metal Retention

In addition to water discharge, pre-exposure conditions are also expected to modulate solute biotic retention (Fig. 1). The results obtained using constant-rate additions [49], showed that in-stream metal retention was reduced after chronic Cu exposure of the community and this was explained by the possible saturation of metal binding sites produced by the Cu pre-exposure. Similar results have been described for phosphate. Nutrient dynamics studies [50] concluded that phosphate was retained more efficiently in oligotrophic than eutrophic systems. If metals are entering the fluvial systems together with nutrients (as is the case of urban and industrial watersheds) Cu toxicity is expected to be counterbalanced by phosphate contributing to metal adaptation and high bioaccumulation. On the other hand, sensitivity to metals and retention efficiency are expected to be maximum in unpolluted areas under low flow conditions (Fig. 1).

5 Metal Fate and Effects in Different Metal Exposure Scenarios

The relationship between discharge and metal pollution may differ depending on the type of pollution, whether it originates from point sources or whether it is diffuse. Two hypothetical cases addressing the influence of hydrology on the fate

Table 2 Fate and effects of metals in a stream receiving a point-source of metals (upper part of the table) or diffuse input via urban runoff (lower part of the table). Summary of the expected influence of four different hydrological situations: base-flow in a rainy period; a flood after a rainy period; low-flow after a long period of low rainfall (water scarcity) and a flood produced after this drought. Metal concentration (M); metal retention efficiency (measured on the basis of the nutrient spiraling concept); exposure (dose and duration); bioaccumulation (in fluvial biofilms) and metal sensitivity (of biofilms)

		After high rainfall		After low rainfall	
		Base-flow	Flood	Low-flow	Flood
Point-source: stream receiving a metal polluted tributary	Metals (M)	↑↑	↓↓	↑↑↑ *	↓↓
	Metal retention	↑	↓↓↓	↑	↓↓↓
	Exposure	Chronic Low dose	Short Very low dose	Chronic Higher dose	Short Very low dose
	Bioaccumulation	High	No	Very high*	No
	Metal sensitivity	Low (adaptation)	Low (adaptation)	Very low (adaptation)	Very low (adaptation)
Diffuse source: stream receiving urban runoff	Metals (M)	Variable	↑	↓↓	↑↑ *
	Metal retention	↑	↓	↑↑	↓
	Exposure	Variable	Short High dose	No-exposure	Short Very high dose
	Bioaccumulation	High	Medium	No	Medium
	Metal sensitivity	Low (adaptation)	Low (adaptation)	High	High*

*Highlights the worst scenario in terms of metal pollution effects on fluvial biofilms

and effects of metals in fluvial systems are presented in Table 2. In each case, four different scenarios are theoretically explored: base-flow in a rainy period; a flood after a rainy period; low-flow after a long period of low rainfall (water scarcity) and a flood produced after this drought.

The first case is based on a hypothetical stream receiving a metal-polluted source (for instance the outlet of a metal factory). In this case, metal concentration is expected to be driven by dilution, being higher under low-flow than under base-flow conditions and minimum during floods. Metal accumulation is expected to be maximum under low-flow conditions and proportional to the duration of this water scarcity situation. Chronic exposure will lead to community adaptation, which is often related to changes in species composition. Metals will therefore be bioaccumulated in fluvial biofilms and transferred to higher trophic levels in the fluvial food web.

The second case (Table 2) illustrates a hypothetic urban stream receiving both metals and nutrients mainly via urban runoff. Since urban runoff is directly linked with rainfall episodes, metal inputs and exposure will be variable under base-flow during a rainy period and very low under a situation of water scarcity (low rain and low-flow). In this case, a sudden flow increase after strong rains may cause contrasting effects on water metal transport depending on the previous situation. If previous rains have already washed the metals retained in land and sediments, the subsequent discharge increase will transport only low amounts of suspended and dissolved metals. After a long drought, a flood will mobilize the accumulated metals and dissolved metal concentration in water may also increase. In this specific scenario, metal toxicity can be very high since periphyton growth in the previous water scarcity period was under low metal exposure (no adaptation) and low nutrient availability (no nutrient-metal interaction).

6 Conclusions and Perspectives

Human activity is responsible for the entrance of toxic substances into the aquatic ecosystems. These substances entail a risk for the components of the ecosystem (toxicological stress). As a result of the global change, aquatic ecosystems are under strong environmental stress due to changes, among others, in water flow or nutrient concentration. This makes new assessment methods to balance these stresses necessary. At present, the environmental risk assessment of these toxic compounds is based mostly on results obtained from standardized toxicity tests, having low ecological relevance. Development of in situ community-level bioindication (as for example, based on biofilms) is a relevant and complementary way for risk assessment.

Overall the results reported in this review indicate that water scarcity might increase metal exposure (due to low dilution), metal uptake (due to higher retention under low flow), and metal toxicity and/or accumulation (depending on the dose and time of exposure), but also might cause opposite effects depending on the source of pollution. In addition, water scarcity will influence nutrient loads and will also modulate the fate and effects of metals. Thus, future studies addressing the role of environmental stress on the effects of toxicants at community scale are key to predict the impact of toxicants in the aquatic ecosystems.

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Consequences of Climate Variability and Human Water Demand on Freshwater Ecosystems: A Mediterranean Perspective from the United States

Clifford N. Dahm

Abstract Climate variability, climate change, climate risk, and climate adaptation are topics of great interest worldwide. Mediterranean climates are particularly vulnerable to these climate-related issues because of the strong seasonality of precipitation, high human demand for water, and predicted increasingly variable worldwide climate. I will address some of these issues in Mediterranean climates from research on the Sacramento River, the San Joaquin River, and the California Bay-Delta in the western USA. The Sacramento River and San Joaquin River converge to form the California Delta. Waters from these catchments, which drain 40% of the landmass of California and discharge about 47% of the available water from California, are extensively dammed, diverted, and exported. Exports from the Delta provide a portion of the drinking water for ~25 million people and sustain more than a million hectares of irrigated agriculture. Interannual variability in river discharge is linked to Pacific climate forcing in the late fall, winter, and early spring with peak discharge from rainstorms and snowmelt in the winter and spring. Warming coupled with drought has caused substantive change in the timing of runoff and in the composition of upland vegetation in large areas of the catchment. Human adaptation to water supply risks involves shifts to groundwater supplies, increased conservation, and water reuse or desalinization. Many of the indicator variables used to assess the ecological condition of aquatic ecosystems are highly sensitive to drought and climate change. Factoring variability and climate change into integrated ecological assessments is an ongoing challenge and effort. Finally, some of the insights from managing and researching these river ecosystems and the Delta in California, USA are discussed in the context of water resource challenges in Mediterranean climates in general.

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Contents

Abbreviations

BDCP	Bay Delta Conservation Plan
CALSIM	California Water Resources Simulation Model
CALVIN	California Value Integration Network
CDEC	California Data Exchange Center
CVP	Central Valley Project
DDT	Dichlorodiphenyltrichloroethane
DOC	Dissolved organic carbon
Hg	Mercury
IEP	Interagency Ecological Program
kW h m^{-3}	Kilowatt hours per cubic meter
MW-h	Megawatt hour
RO	Reverse osmosis
Se	Selenium
SWP	State Water Project
TDS	Total dissolved solids
USGS	United States Geological Survey

1 Introduction

Mediterranean climates are found around the world in addition to the region bordering the Mediterranean Sea. More than half of the Mediterranean-climate regions do occur around the Mediterranean Sea. Other regions with Mediterranean climates include southern and southwestern Australia, central Chile, the Western Cape of South America, and coastal California in the USA. Major cities outside of the Mediterranean area with a Mediterranean climate include Perth and Adelaide in Australia, Cape Town in South Africa, Santiago in Chile, Tijuana in Mexico, and San Diego, Los Angeles, San Francisco, and Sacramento in California, USA.

The climate of Mediterranean regions is characterized by warm-to-hot dry summers and cool wet winters. Mediterranean-climate regions are found, generally speaking, between about 31 and 40 degrees latitude north and south of the equator usually on the western side of continents. Mediterranean climate zones are linked to large subtropical high pressure cells that shift poleward in the summer and equatorward in the winter. Typical of Mediterranean climates is to receive the vast majority of yearly rainfall during the winter season with prolonged (from 4 to 6 months) summer periods without significant precipitation. Climatic changes within the year are pronounced, and winter rainfall can vary considerably from year-to-year. Biotic communities found in Mediterranean climates have many adaptations to survive long, hot summer droughts and prolonged wet periods in winter.

The area of California influenced by a Mediterranean climate is home to over 30 million people. Climate variability and human water demand make freshwater a very precious resource. Allocations of water to cities, agriculture, and the environment create continual tension as demands for this vital and over-allocated resource grow. This paper presents a brief overview of water resource science and policy in a Mediterranean climate with substantial challenges from climate variability, climate change, and increasing human need.

2 Site Description

Two major rivers in California influenced by a Mediterranean climate are the Sacramento River and the San Joaquin River. The Sacramento River drains 72,132 km^2 with a relief of 4,317 m. Mean discharge is ~650 m^3/s with peak flows in the winter and early spring and with minimum flows in the late summer and early fall. The San Joaquin River drains 83,409 km^2 with a relief of 4,418 m. Mean discharge is ~130 m^3/s with peak flows in spring and low flows in late summer and fall. Population density is ~24 people/km^2 in the Sacramento River basin and ~29 people/km^2 in the San Joaquin basin. Agriculture in the Central Valley of California that encompasses parts of both basins is the primary user of water in both basins [1].

The two rivers meet in the area between the cities of Sacramento and Stockton to form the Sacramento-San Joaquin Delta, hereafter referred to as the Delta (Fig. 1). The Delta is a complex network of interconnected canals, river channels, sloughs, marshes, and subsided islands. The area of the Delta is ~2,880 km^2. Approximately half-million people live in the Delta and agriculture is the primary economic activity with annual gross value at about two billion US dollars. Tourism is the second largest economic activity with ~12 million visitors annually. The Delta also

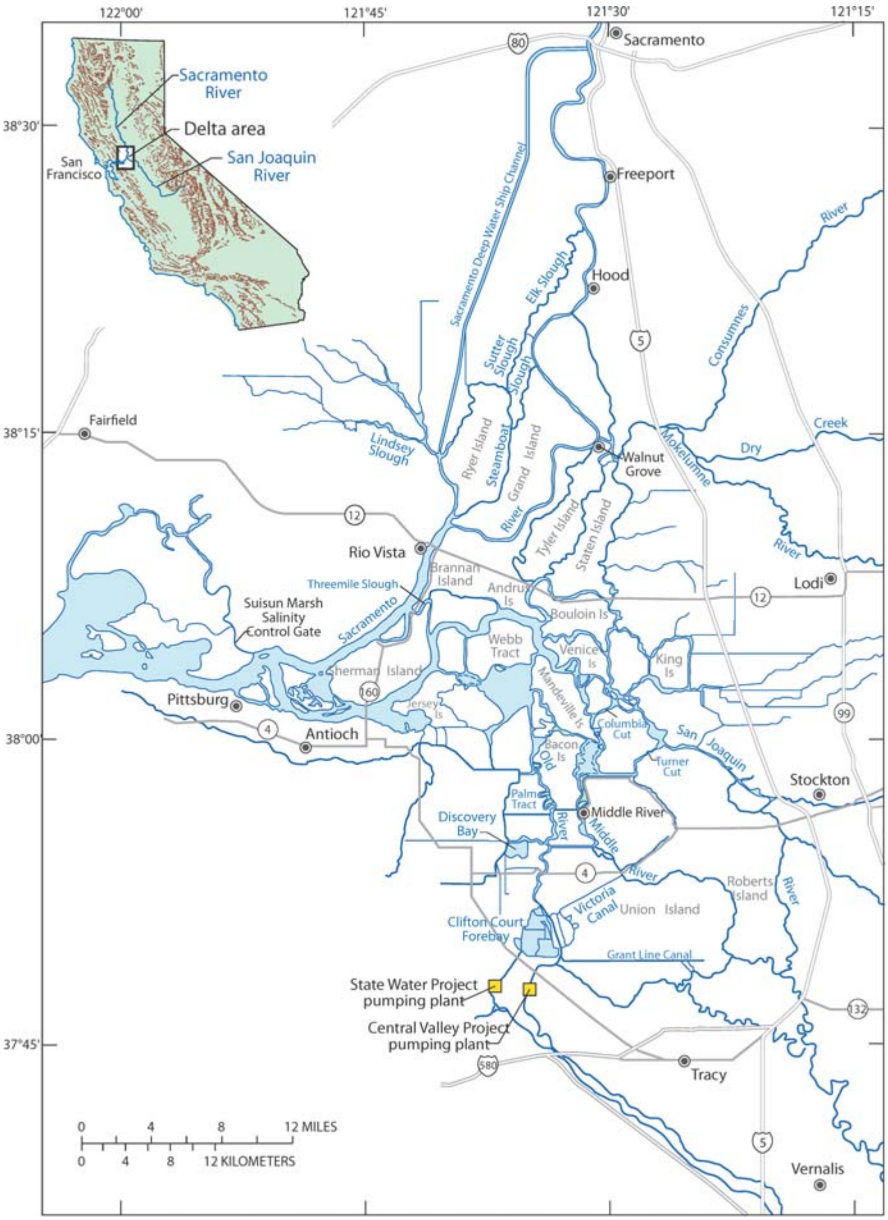

Fig. 1 Map of the Delta in central California, USA with the California state map inset to show location within the state. The Delta is formed at the confluence of the Sacramento River and the San Joaquin River. Export of water from the Delta occurs mainly from the State Water Project pumping plant and the Central Valley Project pumping plant in the south Delta

is the heart of the water supply system for the State of California. Water exported from the Delta provides part of the water needs for 25 million people and irrigates 45% of the fruits and vegetables grown in the US on approximately 1.2 million ha of irrigated farmland [2]. The focus of this paper will be on the two rivers as they enter the Delta and on the Delta.

3 Water Supply

The water supply to the Delta comes predominantly from the Sacramento River (~80%) with lesser amounts from the San Joaquin River (~15%) and rivers on the east side of the Delta (~5%). Year-to-year variability in water supply is large. Combined average annual unimpaired runoff (an estimate of flows without upstream dams or diversions) for the Sacramento and San Joaquin rivers for the past century ranges from 6.2 km^3 in 1977 to 68 km^3 in 1983 [2]. The percentage of freshwater flows that go to San Francisco Bay are estimated to be 87% in wet years, 69% in average years, and 51% in dry years. Climate variability associated with the Mediterranean climate of the region is an essential component of the Delta ecosystem.

Total storage in the major reservoirs of the Sacramento and San Joaquin basins is about 35 km^3. This is comparable to average annual freshwater flows [3]. Freshwater withdrawals in recent decades have averaged about 6 km^3 annually. Reservoir operations within the catchments have altered the timing of freshwater flows into the Delta. Flows are attenuated from historical conditions from January through June, and flows are enhanced from July through October.

California has an advanced water supply system to move water from the Delta to southern California cities and central California farmlands. The heart of this water transfer system is located at the southern end of the Delta (Fig. 1). Two major projects, the California State Water Project (SWP) and the Central Valley Project (CVP), transfer water from the Delta to the agricultural region of California's Central Valley and to the cities of southern California. The SWP is the largest publicly built and operated water conveyance system in the world. The project also is the largest single consumer of power in the State of California with net usage ~5.1 million MW-h. The initial transfer of water from the Delta starts at the Banks Pumping Station where up to ~300 m^3/s of water is lifted about 73 m to begin traveling through the 710 km of canals, tunnels, and pipelines that make up the California aqueduct (Fig. 2).

Water supply measurement and forecasting is a critical component for operations of this system. The California Data Exchange Center (CDEC) provides a wide variety of hydrological and meteorological data on precipitation, snow conditions, and riverflow, and the United States Geological Survey (USGS) maintains real-time and historical streamflow data including flow for many of the diversions facilities and canals. Water supply forecasting and water allocation decisions are based on these forecasts with particular interest in the April-to-June water supplies each year. This involves an extensive network of gauges to determine

Fig. 2 The Harvey O. Banks pumping plant, which pumps Delta water into the California aqueduct, is shown. The plant can pump up to ~300 m^3/s and lifts the water about 73 m to begin the transit southward through the 710 km of canals, tunnels, and pipelines that constitute the California aqueduct

snow-water equivalents in the Sierra Nevada Mountains, streamflow gauges on the major mountain rivers, and computer modeling to predict spring and summer flows.

Managing distribution and allocation of water for various beneficial uses (e.g., agriculture, urban uses, and the environment) is done using computer models. Two models, CALSIM and CALVIN, are widely applied to water operations in California. CALSIM is a generalized water resource planning model that evaluates water supply and is critical to planning for future conditions that reflect interannual supply variability, shifting water demands, environmental regulations, and climate change. CALVIN is an integrated economic-engineering optimization model that explicitly represents waters of the entire Central Valley including imports into the system. Science through monitoring, research, planning, and computer modeling plays a crucial role in water supply decisions under an expanding population, evolving economy, and changing climate [4].

4 Water Quality

Water quality issues for the lower Sacramento and San Joaquin rivers and for the Delta include salinity, dissolved organic carbon (DOC), suspended sediment, mercury (Hg), selenium (Se), pesticides, and nutrients. Some of the pollutants are legacy pollutants from mining in the nineteenth century (e.g., mercury), while others are byproducts of land use changes, altered hydrodynamics, and increased human population in the region. Poor water quality is recognized as a problem both for water supply issues and as important stressors of the ecological problems that exist in the Delta [5, 6].

Salinity or total dissolved solids (TDS) is generally thought to have the greatest influence on drinking water, agricultural water, and environmental conditions in the Delta [7]. Sources of salinity include San Francisco Bay and salinization of return flow waters from agriculture, particularly in the western San Joaquin Valley. Impacts on drinking water include increased costs of treatment and the formation of disinfection byproducts, especially from interactions between bromide, DOC, and disinfection processes. The USGS has made considerable recent progress on identifying the sources, transport, and fate for DOC in the Delta. The Delta is a source of DOC that stimulates microbial production within the Delta and San Francisco Bay but adds drinking water disinfection and treatment costs for water used for human consumption.

Suspended sediment is a changing variable within the waters of the Delta. The gold rush of the nineteenth century led to substantive increases in suspended sediment delivered to the Delta and the lower reaches of the Sacramento River and San Joaquin River. The dam building period in the twentieth century has brought declining suspended sediment concentrations [8]. Declining suspended sediment concentrations are thought to contribute to (1) reduced sediment supply for wetland restoration, (2) erosion and exposure of contaminated sediments deposited in the estuary in the past, (3) accelerated growth of aquatic plants and nuisance algal blooms, and (4) greater predation and less suitable habitat for native fish species [7]. Sediment supply will be an important issue as ecosystem restoration moves forward in the Delta.

Mercury contamination occurs throughout much of northern California [9]. Water quality concerns with regards to Hg include the high toxicity of methyl Hg to foodwebs, biomagnification of Hg into long-lived fishes of the Delta that are consumed by humans, bird reproduction, and the possibility that wetland restoration might enhance methyl Hg production and foodweb biomagnifications. The degree of Hg contamination varies among different habitat types, and the spatial pattern of Hg contamination will be a factor in planning and implementing future restoration projects within the Delta.

Another contaminant of concern for the Delta is Se. Selenium occurs in high concentrations in the soils of the western San Joaquin Valley associated with salts that have accumulated in this region [10]. Selenium is recycled through agricultural return flows to the river and transported to the Delta and San Francisco Bay. The Se is transformed into a more bioavailable form by microbial communities and aquatic plants. The Se is passed through the foodweb with particular concern for bottom-feeding migratory waterfowl and predatory fishes. The hydrodynamics of water from the San Joaquin River is an important consideration in the intensity and distribution of Se contamination within the Delta.

California has one of the largest agricultural economies in the world. Pesticides are a byproduct of the large agricultural economy with the focus of pesticide application being in the Central Valley. Impacts result both from legacy pesticides that are recalcitrant to degradation (e.g., DDT) and commonly stored in the sediments as well as modern pesticides that enter waterways in runoff from rainfall events. Recent research is pointing to the potential role of pyrethroids in aquatic foodwebs of the Delta and major rivers of the region [11–15]. Pyrethroids are exceeding concentrations acutely toxic to sensitive benthic organisms in areas affected by agriculture and in urban areas. Toxicities were particularly high in streams and rivers in residential areas particularly associated with stormflow events [14]. Implications of pesticide mixtures for populations of native species in the Delta is an important research need [7].

Nutrient loading to the Delta is another emerging area of water quality concern. Jassby [16] has shown increased loading of ammonium-nitrogen (N) into the Delta from wastewater treatment plants in the region with load linked to increasing human population. The impact of ammonium-N on phytoplankton production and harmful algal blooms is an active area of research. Recent research in San Francisco Bay has shown an inhibition in diatom primary production, an important source of food for zooplankton in this ecosystem, when ammonium-N levels are elevated [17, 18]. In addition, potential links between ammonium-N loading and harmful algal blooms (e.g., *Microcystis aeruginosa*) are presently being explored [19, 20]. Nutrient enrichment may be playing a more important role in ecosystem structure and productivity than has been previously recognized.

5 Aquatic Ecosystems

The aquatic ecosystems within the Delta are changing rapidly and are certainly going to change substantively in the next few decades. There also is broad agreement that the ecosystem is in poor condition [21–23]. Stressors on the aquatic ecosystems of the Delta include (1) habitat changes due to wetland reduction and river channelization, (2) nutrient and contaminant loading, (3) altered aquatic foodwebs due to nonnative species and changes in primary producers, and (4) modified hydrodynamics and physical/chemical conditions due to export pumping and human engineering. The precipitous decline of several open-water fishes (Delta smelt – *Hypomesus transpacificus*, longfin smelt – *Spirinchus thaleichthys*, juvenile striped bass – *Morone saxtilis*, and threadfin shad – *Dorosoma pretense*) plus ongoing declines of Chinook salmon (*Oncorhynchus tshawytscha*), Central Valley steelhead (*Oncorhynchus mykiss*), and green sturgeon (*Acipenser medirostris*) are indicative of the decline in overall ecosystem conditions [24].

Foodwebs of the Delta have been altered in many ways through the multiple changes that have occurred within the Delta in recent decades. For example, the turbidity and organic matter supply to the Delta have been generally decreasing due to land use changes and upstream reservoirs. Phytoplankton populations also have been changing in recent decades with decreased productivity from 1975–1995 [25] and the emergence of a colonial cyanobacteria, *M. aeruginosa*, forming strong blooms during summer months in the past decade. The zooplankton population also has undergone major changes in the past few decades. Rotifers and larger zooplankton have declined in parallel with the phytoplankton and introduced new species from Asia such as the tiny copepod, *Limnoithona tetraspina*, have become abundant. Benthic communities also have shifted markedly with the Asian clam, *Corbicula fluminea*, dominant in freshwaters and the overbite clam, *Corbula amurensis*, dominant in the brackish waters of the Delta. Nonnative species of fish also are now prevalent in the Delta [26, 27]. Half of the 32 commonly captured species in the Delta are presently nonnative with nonnative largemouth bass (*Micropterus salmoides*), bluegill (*Lepomis macrochirus*), redear sunfish (*Lepomis microlophus*), common carp (*Cyprinus carpio*), and inland silverside (*Menidea beryllina*) particularly abundant. All components of the present aquatic foodwebs are highly altered compared to historical conditions.

Mediterranean climates produce a significant mismatch between times of peak human demand and peak riverflow. Key challenges facing managers of the Delta include meeting water demands and sustaining desired ecological services. Altered flows that result from meeting human demands enhance the invasion and success of nonnative species and modified foodwebs [28]. The aquatic ecosystems of the Delta show this strongly modified structure, and considerable effort is ongoing on planning for the future Delta with the mix of native and nonnative species and altered foodwebs that presently dominate much of the aquatic habitat.

6 Integrated Assessments/Monitoring

The Interagency Ecological Program (IEP) is a long-term effort to provide necessary scientific information concerning the Delta (http://www.water.ca.gov/iep/). The IEP has provided cooperative ecological investigations of the San Francisco estuary, including the Delta, since 1970. The IEP involves nine agencies working cooperatively from the United States Federal Government and the State of California. The IEP provides a wide variety of biological, hydrodynamic, and water quality data for the Delta. Many of these data sets now exceed three decades in duration and provide an invaluable database for evaluating the status and trends of the Delta. The vision of the IEP is to help manage and protect the San Francisco estuary with good science. Monitoring, integrated assessments, and research are critical elements of effective overall evaluation efforts to track the status and condition of aquatic ecosystems in Mediterranean climates.

The IEP provides the monitoring framework to characterize the status and trends of Delta aquatic ecosystems. The IEP strives to provide information on the many factors that affect ecological resources in the Delta. Key near-term goals for the IEP include (1) collecting and analyzing data needed to understand factors controlling the distribution and abundance of selected fish and wildlife resources, (2) complying with permit terms requiring ecological monitoring in the Delta, (3) identifying human impacts on fish and wildlife, (4) interpreting information on adverse effects of human activities within the Delta, (5) assessing interannual and long-term trends on aquatic species, and (6) providing an organizational structure to assist in planning, integration, and cooperation across agencies. The long-term data sets provided by IEP monitoring have more recently been combined with problem-focused research and analysis. The combination of monitoring and research has greatly increased our understanding of the Delta [29].

Mediterranean climates are known for their variability both at interannual and at longer time scales. Extended periods of drought and extended periods of above-normal precipitation have occurred multiple times during the thirty-plus years of monitoring in the Delta. Biological communities that evolved under these climatic conditions are adapted to the natural flow regimes associated with the Mediterranean climate [28]. Sustained long-term monitoring with a robust research program are keys to understanding and managing aquatic ecosystems in Mediterranean climates where human population pressure and climate change are major stressors.

7 Adaptive Management

The concept of adaptive management has become a focal point for current and future management of the Delta. There are various definitions of adaptive management that have been promulgated and applied over the past two decades. One widely accepted definition is that adaptive management is decision making that is flexible in the face of uncertainties both from management actions and scientific understanding of the ecosystem. Careful monitoring of management actions is critical to the success of the application of adaptive management. Recognizing the importance of natural variability in aquatic ecosystems argues that monitoring and research must be both long-term and interdisciplinary. Ongoing real-time learning and knowledge creation are crucial to successful application of adaptive management.

The BDCP is an ongoing collaborative approach to restore the Sacramento-San Joaquin Delta's ecosystem and provide reliable water supplies (http://baydeltaconservationplan.com/default.aspx). A key component of BDCP is to restore about 9% of the Delta (~26,000 ha) from farmland and hunting preserves to freshwater tidal marsh, salt marsh, and riparian woodland (Fig. 3). The steering committee for BDCP recently convened an expert advisory panel to prepare an independent science report on adaptive management needs for the Delta. The advisory panel provided guidance for a robust adaptive management program for the Delta. Key elements of the adaptive management program are (1) formal setting of goals, (2) establishment of objectives, (3) use of conceptual and simulation models to synthesize the knowledge base, (4) clearly and formally designed monitoring to measure criteria to evaluate effectiveness, (5) analyses, syntheses, and evaluation protocols to provide necessary feedback for management decisions, and (6) ongoing

Fig. 3 The upper panel (**a**) shows a segment of a waterway in the California Delta that is bounded by levees and channelized. Farmland is the primary land-use in the Delta. The BDCP is calling for a conversion (restoration) back to freshwater tidal marsh (panel **b**), salt marsh, and riparian woodland of approximately 9% of the land in the Delta (~26,000 ha) over the next few decades

refinement of the knowledge base, models, objectives, and problems. The report strongly recommended institutionalizing an entity specifically tasked with assimilating the knowledge base and recommending adaptive changes to goals, objectives, models, monitoring, and conservation measures to a governing body that could implement these recommendations. Such an adaptive management strategy requires substantial investment in time, people, and resources (http://www.baydeltaconservation plan.com/bdcppages/BDCPInfoBackgroundDocs.aspx).

8 Water Conservation

Water conservation has become an increasing area of emphasis in the Mediterranean climate of California. A firmly established goal of 20% reduction in urban water use by 2020 has become the policy of the present administration. Cities and suburbs in California used approximately 10.7 km^3 of water in 2000. The goal is to reduce urban water use by 2.1 km^3 by the year 2020 through an aggressive plan developed by numerous state agencies. Recent legislation also has established penalties that restrict water resource development grants to those municipalities who fail to achieve the targeted savings in urban water use. The State of California sees urban water conservation as a key component in achieving a sustainable water supply in the twenty-first century.

The largest user of water in California is agriculture. California irrigated an estimated 3.9 million ha of cropland with 42.2 km^3 of applied water in 2000. This is equivalent to the application of about 1.1 m of water to crops growing with irrigated agriculture. Agricultural use efficiency has increased from 1980 to 2000 with inflation-adjusted gross crop revenue per unit of applied water increasing by 11% from 1980 to 2000. Agriculture remains a major focus for water conservation with the 20% reduction by 2020 a goal for the agricultural sector as well. Recent legislation, however, did not mandate the 20% reduction by 2020 as required for urban users, but incentives for agricultural water savings were included in the legislation. Increased water use efficiency in agriculture is a crucial component in achieving long-term sustainable water use in the Mediterranean climate in California.

9 Alternative Water Sources

Problems with lack of available and dependable supplies of freshwater in the Mediterranean climate of much of California have generated great interest in alternative water sources. The focus has been both on wastewater reuse and reclamation and on desalination. Research has focused on new methods of purifying water at lower costs and with less energy [30]. Alternative water supplies for California are being put online for certain urban areas of California with much additional investment in these technologies being planned for the coming decades.

The goal of wastewater reuse and reclamation is to capture water from nontraditional sources such as municipal or industrial wastewaters and treat the water to potable quality. Much of the water used in agriculture, industry, power generation, and urban uses is returned to the environment. One example of water reuse is the application of low-pressure reverse osmosis (RO) membranes for desalination of agricultural drainage water in the San Joaquin Valley [31]. RO membrane fouling and fluctuating composition of the agricultural feedwaters are two major challenges to the use of this technology for agricultural drainage water. A second example of water reuse is groundwater recharge with reclaimed municipal wastewater [32]. The State of California has taken a cautious approach for the criteria for groundwater recharge with reclaimed wastewater, but this technology offers assistance in recharging depleted groundwater aquifers in the region.

Desalination seeks to increase the fresh water supply through generating potable water from saline aquifers and seawater. Desalination is a capital-intensive and energy-intensive process. Major desalination technologies currently in use are based on membrane separation via RO or thermal distillation. Reduction in energy consumption used for RO desalination has lowered energy costs from >10 kW h m^{-3} to <4 kW h m^{-3} in the past two decades, and further reductions in energy consumption to <1.5 kW h m^{-3} is theoretically possible [30]. Desalination is likely to become an increasing alternative water source in Mediterranean regions worldwide, especially for urban water use.

10 Climate Variability, Climate Change, and Climate Adaptation

Mediterranean climates are characterized by their strong interannual variability in the strength of winter precipitation and for their hot, dry summers. Climate variability and the low flow conditions during predictably hot and dry summers, when human water demand is high, has led to human development of advanced water supply systems. This involves the construction of storage reservoirs and utilization of groundwater reservoirs. This also involves conveyance conduits (canals, aqueducts, and pipes) to carry water supplies from areas with greater available water to regions with insufficient local water supplies to meet local demands. The State of California has invested considerable sums of money into this type of distribution system so that ~25 million people and more than a million hectares of farmland now depend to some extent on water from the Delta.

Climate change is already having discernable impacts on the Delta. Sea level has risen 20 cm in the past century at the Golden Gate Bridge in San Francisco [35]. This rise in sea level leads to increased salinity in the western Delta, especially during times of low river flows and strong high tides (Fig. 4). The specter of sea level rise will loom large in the Delta for the rest of this century. Planning efforts currently acknowledge future sea level rise by 2100 of between 55 and 145 cm. The deeply subsided Delta, with most of the Delta below sea level and much of the

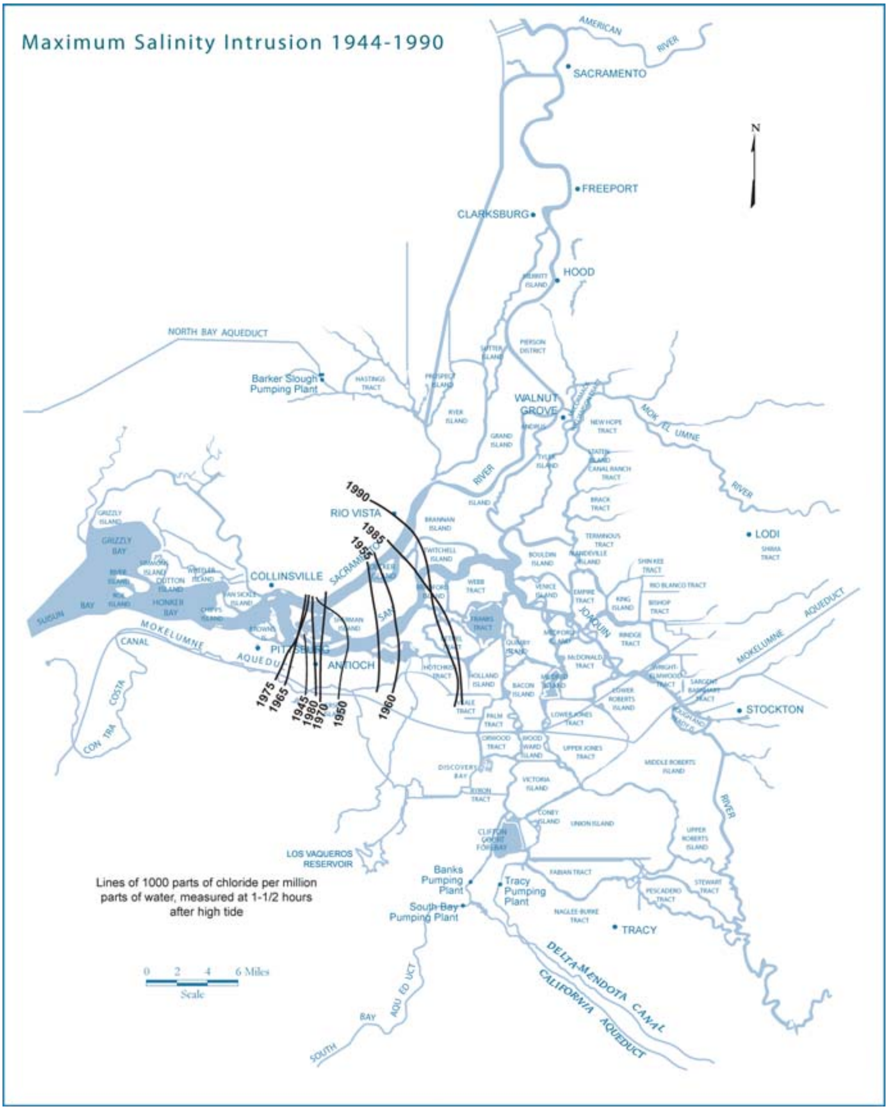

Fig. 4 Maximum salinity intrusions into the Delta at five year time intervals from 1945 to 1990 are shown. Drought conditions and rising sea level from climate change are predicted to increase salinity intrusions eastward into the Delta in the future

central Delta more than 6 m below sea level, is particularly vulnerable to future sea level rise.

Another manifestation of climate warming can be seen in the timing and volume of spring runoff from the Sacramento River [4, 33]. River flows are peaking earlier in the year compared to the early twentieth century (about 3 weeks earlier on average) and the percent of water runoff for the April-to-July time period has dropped from about 45% to below 35% [4, 33]. More precipitation also is falling as rain in the mountains of California and projections for inflows to the Delta predict an ongoing shift in runoff timing toward winter with an increase in intensity and frequency of winter runoff events and an extended period of dry summer low-flow periods [34]. Conservative estimates of snowpack loss by 2050 predict a one-third loss of snow at the beginning of April when spring runoff is normally estimated. These effects will be particularly strong in the middle montane elevations where winter temperatures are near 0°C.

A climate adaptation strategy for California has recently been issued (http://www.climatechange.ca.gov/adaptation/). Strategies for adapting to future climate change are actively being considered in the Mediterranean regions of California. Key recommendations that involve the Delta include (1) a statewide 20% reduction in per capita water use by 2020, (2) expanded surface and groundwater storage, (3) enhanced agricultural water use efficiency, (4) improved water quality, and (5) improved Delta ecosystem conditions and water supplies exported from the Delta as developed by BDCP. The adaptation strategy also calls for identifying key aquatic habitats sensitive to climate change and expanding protected areas and altering land and water management practices. Strategies for climate adaptation in Mediterranean regions of the world are undergoing accelerated development and information sharing across the various regions with Mediterranean climates that may prove very valuable and useful.

11 Summary and Conclusions

Mediterranean climates are magnets for human population but present considerable challenges for sustaining aquatic ecosystems and meeting human demands for freshwater. The Delta of California is a prime example where conflicting demands of water for the environment, water for agriculture, and water for urban uses play out in a Mediterranean climate. The confluence of two large rivers, the Sacramento and the San Joaquin, in the Delta has become the nexus for competing demands for freshwater in California. Critical issues include water supplies for competing interests, water quality for human users and the environment, and revitalizing degraded aquatic ecosystems.

Long-term monitoring, integrated assessments of Delta ecosystems, and restoration design have become central tenets in management and planning for the Delta of the future. Multiple stressors such as subsidence, seismicity, nonnative species, sea-level rise, global warming, altered water movement, habitat alteration, toxicants, and nutrient loading ensure that the Delta of the future will not be the Delta of the past. Adaptive management is viewed as the tool that will assist in planning and management for the Delta of the future.

Planning for the future in Mediterranean climates requires serious investments in water conservation and consideration of alternative freshwater sources. Alternative freshwater sources include desalination and wastewater reuse. These technologies come with a high energy cost but will inevitably become an important part of the overall freshwater portfolio in Mediterranean climates throughout the world. Those living in Mediterranean climates also must cope with the pressures of climate variability and the strong likelihood of significant climate change in this century. This will require that adaptive strategies be put in place to deal with water shortages, altered timing of water supply inputs, and more intense floods during the wet seasons and droughts during the dry season. The future of freshwater ecosystems in Mediterranean climates of the world will depend upon resolving these complex issues of supply and allocation in a variable and changing climate.

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Water Quality in Reservoirs Under a Changing Climate

Rafael Marcé and Joan Armengol

Abstract The importance of water resources stored in reservoirs on a global scale is not matched with a sound knowledge of the possible impacts of climate change on reservoir water quality. This is especially relevant in the Mediterranean regions, where most countries rely on reservoirs to fulfill their water supply needs, and virtually all climate models predict increasing water shortage in the next 20 years. In this chapter, we summarize recent findings that will help to fill this gap in knowledge. Recently, a close coupling between streamflow entering reservoirs and its hypolimnetic oxygen content has been empirically established for a wide range of systems. In brief, high streamflow maintains anoxia at comparatively low levels. Therefore, we can expect a reduction in water quality following future reductions in runoff. To illustrate these effects, we analyzed a 44 year data set of oxygen measurements from Sau Reservoir in Spain to detect possible effects of climate variability on the extent of deep-water anoxia. In addition, we show that a trend of decreasing streamflow, related to climate change, has increased the risk of anoxia in the reservoir during the last decade. From these results, we propose a framework for climate change impact studies on reservoir water quality using streamflow and labile organic matter as master drivers. Finally, we identify the research required to improve our understanding of how reservoirs will behave in a changing climate, and give some guidelines on how to manage Mediterranean reservoirs under future "scarcity" conditions.

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Contents

1 Some Remarks on Reservoir Limnology

> The reservoir is a hybrid between river and lake, and its study must be founded on a complete picture of limnology.
>
> On the other hand, reservoirs are ecosystems strongly linked with the surrounding terrestrial ecosystems, and it is hardly useful to model them independently.
>
> Ramón Margalef [1]

The above statements come from the chapter devoted to reservoirs in Margalef's [1] *Limnología*, and summarize two important topics in reservoir limnology. Firstly, they reflect the long recognized influence of river inflows on reservoir dynamics [2] that fueled the interest of limnologists in the gradients associated with advection. This reached its maximum with the seminal work by Kimmel et al. [3], who defined three theoretical zones in reservoirs (i.e., riverine, transitional, and lacustrine) depending on the expected interaction between the river inflow and some commonalities in the geomorphologic traits of reservoirs. The merit of Kimmel's characterization was to include in a common framework many observations concerning a variety of processes, including hydrology, light ambient, chemical longitudinal gradients, metabolic balances, and water quality issues. Although not exactly equivalent, this characterization could be compared with the River Continuum Concept [4]. In particular, it offered to reservoir limnologists a useful and convenient explanatory framework within which new observations and test hypotheses can be placed. Like any generalization, Kimmel's zonation has its drawbacks (e.g., only canyon-shaped, single inflow reservoirs are prone to follow expectations). It has, however, motivated much of the subsequent research on biological heterogeneity in reservoirs, in conjunction with the theoretical ideas advanced by Straškraba et al. [5]. Secondly, these quotations emphasize the fact that the same river input that fuels longitudinal heterogeneity in reservoirs also forms a strong link between the reservoir and its watershed (e.g., [6]). This link has been conceptualized mostly in the form of load-response empirical models [7, 8], or mass-balance approaches [9]. Curiously, empirical modelers usually consider reservoirs as stirred reactors, ignoring the longitudinal spatial heterogeneity present in most situations and processes.

Thus, whereas longitudinal heterogeneity in reservoirs has been considered as a new standard in limnology (i.e., as suggested in Kimmel's theoretical framework), the relationship between reservoirs and their surroundings has usually been quantified using models based on natural lakes [10, 11]. In our opinion, this promotes a structural bias in the way limnologists approach reservoirs. For some reason, the mystic of heterogeneity focuses the attention of researchers, and key limnological features like residence time or the river inflow [12] are often invoked only as generators of heterogeneity (e.g., [13]). In this way, and despite warnings by Margalef [1], Uhlmann [8], Straškraba [14], Straškraba and Tundisi [15], Tundisi et al. [16], and Kennedy [17], researchers tend to take lakes as models for reservoirs. However, this is a misconception because the comparison with a river is equally justified and pertinent. A reservoir is a river undergoing very profound changes in its geomorphologic settings. When we consider material and energy flows, it is often difficult to decide whether a reservoir is working as a slow moving river or a short residence time lake. Is the reservoir a subsidized ecosystem like a river, or are the energy flows dominated by autochthonous production of organic matter? These kinds of questions have received much less attention than heterogeneity related issues, and, to our knowledge, they remain mostly unanswered. We agree with the view of Kennedy et al. [18] and Kennedy [17], who pleaded that one of the most important research needs in reservoir limnology is a catchment or system-level understanding of the role of reservoirs on the dynamics of landscapes. So yes, reservoirs are hybrid systems, but not in the Manichaean sense that they are rivers "becoming" lakes. Reservoirs are hybrid systems in a much more profound sense, probably also reflected in its functioning as a whole ecosystem. This is at the core of Kennedy's plea: we need a theoretical framework to push reservoir limnology beyond the heterogeneity issue and to define reservoirs as a unique, idiosyncratic trait of hydrological landscapes.

2 The Importance of Reservoirs in a Global Context

Nowadays, we have more than 500,000 reservoirs in the world covering at least 0.1 km^2 [19], and an indeterminate number of smaller agricultural ponds. This is a huge number of aquatic systems, especially considering the water volume they store [19]. Although this is far from figures corresponding to lakes, reservoirs have an enormous social and financial interest since man-made lakes are usually located near human settlements. Moreover, distribution of reservoirs is highly heterogeneous and often concentrated where lakes are scarce [20]. In some semi-arid areas, like Mediterranean Spain and Italy, virtually all lowland still water systems are reservoirs: lakes are exceptional landscape features, and reservoirs and rivers replace them as the basic emotional link between people and freshwater.

Compared with the second half of the twentieth century [21], the rate of dam construction in developed countries has slowed in recent years [22]. This could be the result of an enhanced social perception of the ecological and social impacts of large dams, but we also must consider that available floodable land in these countries is now scarce [19]. However, there may now be resurgence in dam construction due to future dependences on water supply and economic growth in developing countries [23]. The spectacular rate of dam construction in China and the World Bank's decision to fund more dams are good indicators of such resurgence.

Thus, reservoir limnology and management is a promising research field. In this respect, Kennedy et al. [18] made an observation that summarizes the main weaknesses and opportunities of reservoir limnology today. On one side, developing regions have the greatest potential for hydropower development, while semiarid regions between 30° and 40° latitudes include a high proportion of the dams already built [20]. On the other hand, this is at odds with the fact that our understanding of reservoir limnology and ecology is mainly based on data collected on lakes from the North temperate region. That is, we are using data from the wrong systems to explain the ecological dynamics of reservoirs situated in very different climatic areas. Considering the wide differences between the limnological behavior of reservoirs and lakes [24], this is a far-from-optimum situation for the correct management of water resources in the present and in the future.

However, not only future dam construction and the structural deficiencies of reservoir science will place reservoir limnologists in a very demanding situation, we also lack studies of climate change impacts based on instrumental data collected in reservoirs. To date, the effect of climate change on reservoirs have been tested almost exclusively with modeling exercises [25–27] but these studies have yet to demonstrate that recent changes in the climate have already had an effect on ecological behavior of reservoirs. This could encourage researchers to take results coming from lakes as the starting point again for climate impact prospecting. Without doubt, any prediction of climate change impact on reservoir limnology, based on processes described for lakes, would be unreliable (see the example presented later for temperature trends). Thus, reservoir limnologists should try to move away from too close a comparison with lakes to find their own way in the climate change science.

One of the most important conclusions of the last IPCC report [28], was the very marked reductions in the run-off projected for the Mediterranean regions by the end of the twenty-first century (see estimates presented elsewhere in this book). Reductions of at least 20% are projected in all Mediterranean region and most current models converge on these predictions. If we then compare the global distribution of reservoirs with the predicted changes in runoff the answer is clear: the main challenge related to climate change that will face reservoir limnologists in the future is water scarcity in reservoirs located in the Mediterranean areas.

The future runoff scarcity has two conflicting implications: water supply systems that rely on reservoirs will increase their dependence on dams, but reservoirs will have less water volume available. Thus, an increasing pressure on water resources

Fig. 1 The tower of the eleventh century Romanesque church breaking the surface of Sau Reservoir (Spain). In 1963 the old town of Sant Romà de Sau and its church were flooded by the construction of the Sau Dam. However, water level never suffices to completely submerge the prominent tower, which became an unofficial monitor of the water supply available for the city of Barcelona. When the doors of the church emerge, drought is there . . . Photo by Joan Armengol

stored in reservoirs, and a growing social perception of problems related to water quantity and quality in reservoirs is expected. Just as an example, the recurrent drought episodes suffered by the Barcelona metropolitan area (Spain) in recent years placed reservoirs at the center-stage : since then people are regularly informed about water resources stored in nearby reservoirs in newspapers and TV, and an iconic view from a reservoir has become a nonofficial monitor of the water supply volume available for the city (Fig. 1).

In future, reservoir limnologists working in the Mediterranean region will be asked a number of searching questions. How much water will we have? What quality can be expected? Will treatment costs increase? However, our ability to correctly answer these questions in a changing climate is dubious. There is clearly an urgent need for a theoretical framework for reservoir limnology, grounded in observations recorded at reservoirs, analyzed in ways that are not unduly influenced by the lake-view of the problem [18].

3 Profiling Reservoirs: Key Ecological Processes Concerning Climate Change

In lakes, several studies based on field data have demonstrated climate effects on water quality variables, including modifications in stratification [29, 30], oxygen content [29, 31], primary production and algal biomass [31, 32], water transparency [30, 32], phenological patterns [33, 34], and occurrence of harmful algal blooms [35]. Williamson et al. [36] suggested that the metabolic balance in freshwater systems provides the best integrator of global change impacts, but in fact there is little consensus about the best variables to monitor in order to built a network of "sentinel" systems. In any case, climate change studies in reservoirs using instrumental data are still very rare, and it is frequently assumed that results obtained in natural lakes will be directly applicable to reservoirs.

Here we revisit two important topics in limnology just to show that climate change studies that only include data from lakes are not applicable to reservoirs. Firstly, we show that temperature trends in reservoirs and lakes cannot be interpreted in the same way. Secondly, we show that drivers of the deep-water oxygen content in reservoirs and lakes can be very different. This last analysis will be used in the following section as the starting point for a new framework for climate change impact studies in reservoirs.

In lakes, climate change impact studies have primarily been focused on increasing water temperatures and associated hydraulic and ecological consequences. The rationale is obvious: the continuous and direct heat exchange between atmosphere and the water surface make lakes ideal integrators of climate trends. Usually, mean water temperatures or the degree of stratification are the variables used as a measure of the climate-ecosystem coupling. Then, cascade effects of increasing temperatures and gradients have both direct and indirect effects on the chemistry and biology.

What about reservoirs? *A priori* reservoirs are a lot like lakes: a mass of still water with a surface in direct contact with atmosphere. The logical expectation is that both their temperature and intensity of stratification will increase in a warmer climate [29, 30]. However, the situation in reservoirs is complicated by human interventions in their water balance which greatly alters both the heat flux and the hydraulic properties of the water mass. Here, we use data collated for Sau Reservoir (Spain) to illustrate this point (Fig. 2). The records show that mean water temperature in the reservoir underwent a steady increase during the period 1964–1990 (with intriguing oscillations with period around 6 years). This coincided with an increase in the mean air temperature in the watershed upstream Sau Reservoir. However, after 1990, the mean water temperature dramatically dropped to attain values similar to those measured in the 1960s. Paradoxically, mean air temperatures continued to increase during this period. Thus, it is evident a decoupling between climate and the reservoir dynamics related to temperature. If we try interpreting this picture with the lake tool-kit the answer is not straightforward.

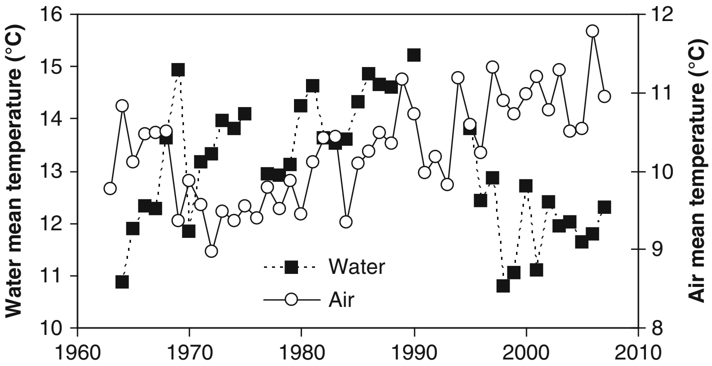

Fig. 2 Time-series of annual mean water temperature in the Sau Reservoir (Spain) and air temperature in the Ter River watershed. The series start in 1964, after the first filling of the reservoir. Annual means are based on monthly measures of the volume weighted mean temperature. Only years with at least 10 temperature profiles were included in the figure. The air temperatures are annual means for the whole Ter River watershed, calculated from data collected in several meteorological stations in the basin, and weighted according to their area of influence

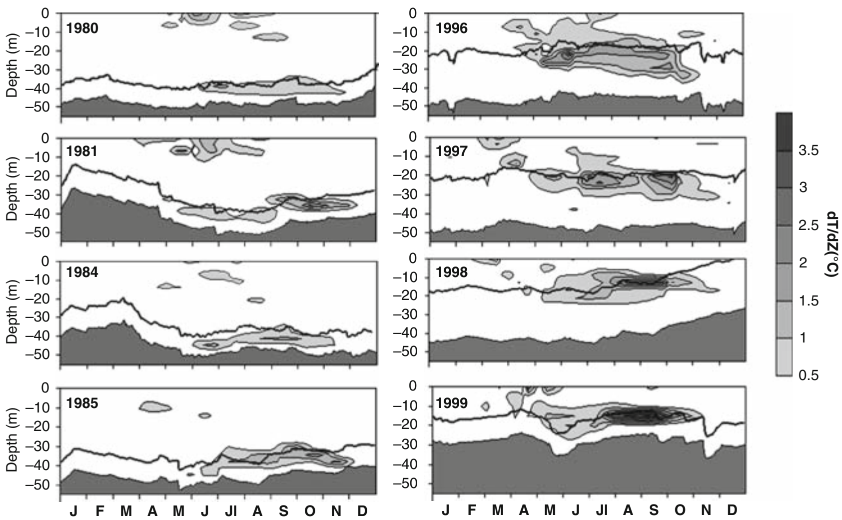

Fig. 3 The annual development of the seasonal thermocline (expressed as temperature gradients) (**a**) for a selected set of years when hypolimnetic withdrawal resulted in a deep thermocline and an extensive metalimnion, and (**b**) for a selected set of years when epilimnetic water flowed through the intermediate outlet inducing the development of a shallower thermocline. The *solid black line* shows the daily development of the withdrawal depth and the *gray areas* the bottom of the reservoir. Modified from Moreno-Ostos et al. [37]

The reason for this decoupling between climate and water temperature in the reservoir is explained in Fig. 3. Moreno-Ostos et al. [37] demonstrated that the degree of stratification and the location of the thermocline both depended on the depth of water withdrawal. Sau Reservoir, like most reservoirs devoted to water supply, has several water outlets located at different depths. The consequence is that water managers (consciously or unintentionally) modify the physical characteristics of the reservoir, introducing severe noise in the relationships between heat exchanges, hydrodynamics, and climate. In this case, water withdrawals were switched from deep to surface outlets during the early 1990s (Fig. 3). Since water extraction promotes a strong hydraulic stratification [38] that counters the stratification pattern driven by meteorology, the depth of the water extraction becomes the principal driver defining the position of the thermocline and the depth of the mixing layer. This, in turn, has a major effect on the heat balance of the system and hence water temperature: when water leaves the reservoir from surface layers a considerable amount of heat is also lost. Thus, the switch between deep and surface withdrawal caused a sharp relative cooling of the reservoir (Fig. 2).

The corollary is that we cannot blindly apply to reservoirs conclusions obtained for lakes. In the case of temperature variability, the "signal" that appears in a reservoir often owes just as much to the inner functioning of the system as to external drivers. Lakes are widely regarded as good "sentinels" of climate change but the temperature trends observed in data recorded in reservoirs must be handled with extreme care. Also important, reservoir limnologists should be skeptical about studies extrapolating lake results to explain or forecast reservoir behavior in the presence of atmospheric temperature changes.

The second process we review is the empirical modeling of the anoxic conditions that develop in the bottom layers of lentic systems. Although both lake morphometry and hydrology are represented in the equations predicting oxygen content or oxygen deficit, the key factor is the biomass of phytoplankton, which consumes the oxygen when it sinks into deep water and decays. The epilimnetic productivity can be incorporated in the equations using different proxies, including photosynthetic pigments concentration [39] in-lake phosphorus content [40, 41], phosphorus retention [42, 43], or the phosphorus content of the inflows [44, 45]. In consequence, hypolimnetic oxygen content in lakes has traditionally been modeled as a function of variables that are either measured in the epilimnion or are known to drive epilimnetic processes. However, customary empirical equations, developed mainly in North temperate natural lakes, usually fail when applied to reservoirs [46, 47].

Recently, Marcé et al. [48] demonstrated that the development of deep-water anoxia in reservoirs depends on the load of labile organic materials from the river input and the water load. With the exception of brownwater lakes [49, 50], and lakes receiving significant humic and fulvic acids inputs [44], no significant role on the hypolimnetic oxygen consumption has typically been assigned to the input of allochthonous oxidable substances. The key difference is that while runoff penetration into the hypolimnion is small and dispersive in lakes [24], in man-made reservoirs the river inflow can plunge into deep layers, directly linking the hypolimnion with the surrounding watershed. In these circumstances, organic matter carried by the river can influence the hypolimnetic oxygen content without the intervention of epilimnetic processes. Another significant difference between lakes

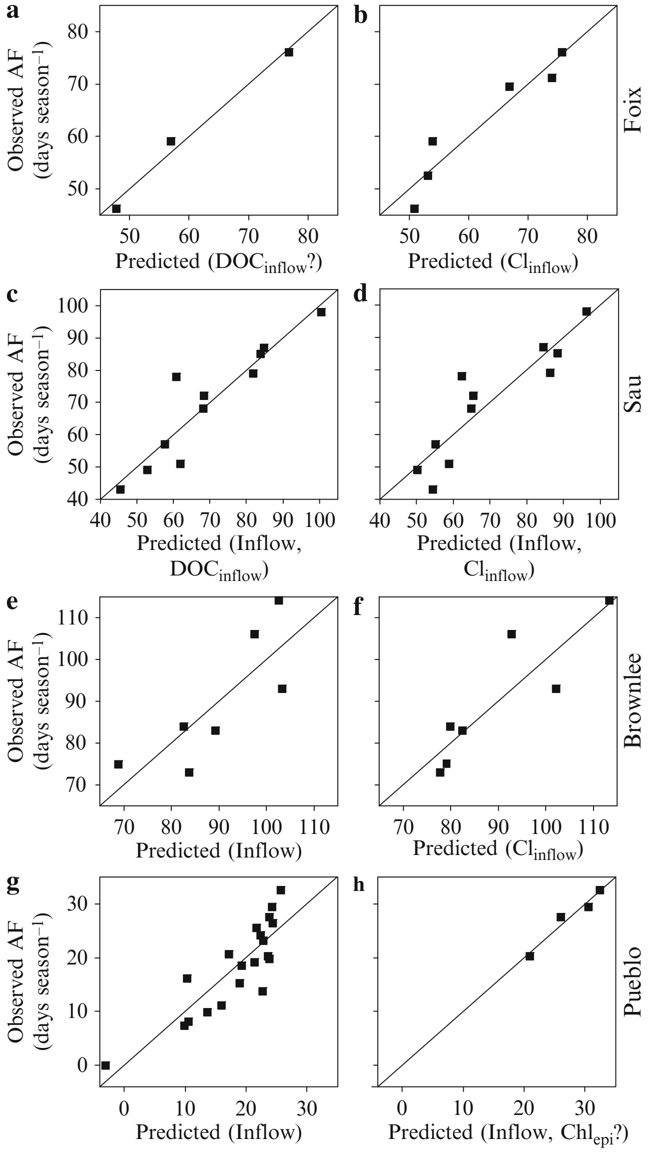

Fig. 4 Predicted versus observed summer Anoxic Factor (AF) in (**a**, **b**) Foix Reservoir (Spain), (**c**, **d**) Sau Reservoir (Spain), (**e**, **f**) Brownlee Reservoir (USA), and (**g**, **h**) Pueblo Reservoir (USA). The results have been arranged to place the systems along a gradient of relative human impact (Foix Reservoir at the *top*, Pueblo Reservoir at the *bottom*). Predictions are based on linear models using different independent variables (in *brackets*): Inflow = streamflow entering the reservoir during the period; DOC_{inflow} = mean summer river DOC concentration measured upstream the reservoir; Cl_{inflow} = mean summer river Cl^- concentration measured upstream the reservoir; and Chl_{epi} = mean summer chlorophyll-a concentration measured in the epilimnion of the reservoir. The symbol ? after a variable denotes a nonsignificant effect at the 95% level. *Solid lines* represent the perfect fit, and were added for reference. Modified from Marcé et al. [48]

and reservoirs is the mean water residence time [51]. Reservoirs tend to show relatively short water residence time (weeks to months) compared to lakes (years), and only dissolved materials that decay in a time scale equal to or shorter than that of the retention time will be relevant for carbon and oxygen cycling. Therefore, the lability of the incoming organic material plays a key role in regulating the oxygen content of reservoirs.

In their analysis, Marcé et al. [48] showed that streamflow is always a significant predictor of anoxia, except in hypereutrophic and small systems like Foix Reservoir (Fig. 4). The river DOC concentration (or the Cl^{-} concentration as a proxy of labile DOC, see Marcé et al. [48]) was a significant variable in all the selected systems except the pristine Pueblo Reservoir (Fig. 4), where the epilimnetic chlorophyll-a concentration was a significant variable. That is, in reservoirs receiving DOC load mainly from human origin (i.e., labile) its effect on the oxygen content is significant. Systems receiving DOC load from terrestrial ecosystems (i.e., refractory) do not show dependence on the allochthonous sources, and the autochthonous production of organic matter becomes increasingly important. Therefore, although autochthonous production of plankton biomass must play a role on oxygen deficit, especially in pristine reservoirs located in remote areas, this study clearly showed that the assumptions made by classical models regarding the oxygen content in the hypolimnion do not necessarily hold in reservoirs. Again, reservoirs prove to be reluctant to follow the lake pattern.

From results presented so far we can draw two important lessons: first, reservoir dynamics can be dramatically different from that showed by lakes even in processes that are classical topics in limnological research. Thus, a link between climate and a process observed in lakes cannot be supposed to be applicable to reservoirs. Simply, we need ad-hoc studies using data from reservoirs to test effects of climate change on these systems. The second lesson is less obvious. In lakes, climate change impact studies are typically focused on increasing water temperatures and the associated hydraulic and community-level consequences. In reservoirs, where climate-driven water temperature trends are difficult to detect, the focus should be on streamflow and the associated human interventions in the hydraulics. Changing runoff patterns and magnitude is an expected outcome of global warming and, in our opinion, successful climate change impact studies in reservoirs should be focused on this. We acknowledge that increasing temperatures have impacted and will have an impact on reservoir processes, but for detection of recent effects of climate change, researchers must avoid processes mainly governed by temperature.

4 Detecting and Predicting Climate Change Effects in Reservoirs Using Instrumental Data

The dependence of the oxygen content in reservoirs on the hydrological input to the system opens the interesting possibility of using long-term hydrological data to quantify the impact of recent climate change. Since precipitation and river runoff

Table 1 Spectral analysis for Niño 3.4 index, streamflow, and AF using the Maximum Entropy Method. Only results for the low frequency band are showed

Series	Main oscillation peaks (cycles $month^{-1}$)
Niño 3.4 index	0.021, 0.035
Streamflow	0.016, 0.031
Anoxic Factor	0.016, 0.031

are directly linked to climate oscillations like the El Niño Southern Oscillation (ENSO) [52] it is highly probable that a link could exist between such climate modes and the oxygen content in reservoirs. Moreover, the decline in river runoff detected in many rivers worldwide could impose a clear trend in the oxygen content of bottom layers in reservoirs, producing an additional climate change effect on freshwater ecosystems [53–55]. We used a long-term database from Sau Reservoir (Spain) to demonstrate all these oxygen content effects. The data consisted of 44 years of monthly measurements of oxygen profiles, water load to the reservoir and we used the Niño 3.4 index as a time-series of ENSO. We expressed the monthly oxygen content of the reservoir using the Anoxic Factor (AF), which is a volume-standardized measure of the anoxia extent in a water body [44].

We started by analyzing the dominant modes of oscillation showed by oxygen content, streamflow, and ENSO using the Maximum Entropy Method (MEM) (Table 1). It is remarkable that both the streamflow to the reservoir and the AF showed common oscillations with ENSO at frequencies between 0.016 and 0.035 cycles $month^{-1}$. These frequencies are very close to the two main periods of ENSO (the quasi-biennial and quasi-quadrennial periods) [56]. Although we do not have a mechanistic explanation for this teleconnection (in fact the extratropical influence of ENSO is a hot topic in climate research, Merkel and Latif [57]), it is certainly difficult to propose an alternative explanation for the oscillations in AF and streamflow observed at these frequencies.

The common oscillations were consistent during the whole 45 years period, as revealed by cross-wavelet analysis (Fig. 5). Analysis for streamflow, ENSO index, and AF indicates a persistent common power for oscillations with period between ~30 and 65 months, which appears to vary according to the intensification and weakening of the quasibiennial and quasiquadrennial band of ENSO.

In addition to the teleconnection between ENSO and the AF in Sau Reservoir, we investigated the effect of a decreasing streamflow trend on the development of the AF. This was assessed by fitting an empirical model to the time series for the annual AF, using the streamflow and a proxy of the load of labile organic matter as independent variables [48]. The model explained 85% of AF variance, and both independent variables were highly significant ($n = 29$, $p < 0.0001$). Once this model was fitted, we recalculated the output of the model using a synthetic streamflow series that did not show any trend. The difference between results obtained with the original model and the model solved with the synthetic streamflow series can be considered as the effect of the decreasing streamflow trend on the AF.

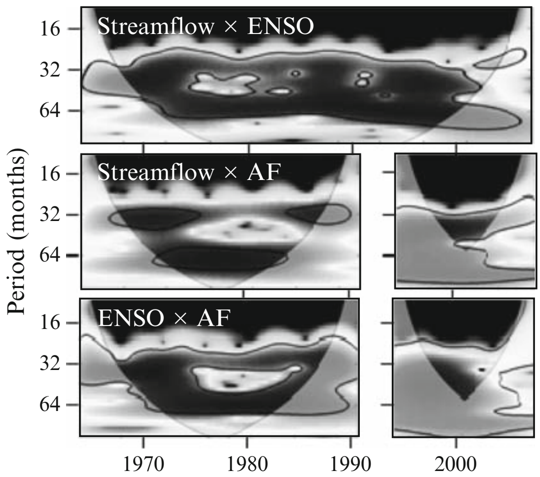

Fig. 5 Cross-wavelet analysis for Streamflow vs. ENSO (*upper panel*), Streamflow vs. AF (*middle panel*), and ENSO vs. AF (*bottom panel*). The thick black contour designates the 95% significance level against red noise. Shaded areas represent the cone of influence, where interpretations should be cautious

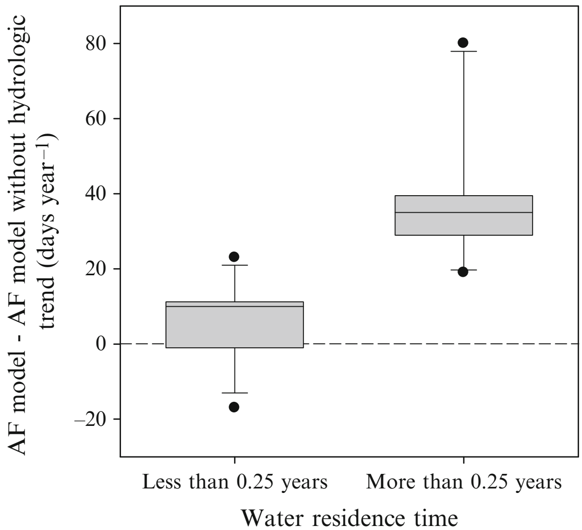

Fig. 6 Comparison of results of the AF model solved with and without streamflow trend for wet and dry years, expressed as years above and below the mean water residence time in the reservoir (0.25 years)

Results showed that in Sau Reservoir, the effects of decreasing streamflow are already measurable and especially conspicuous during dry years (Fig. 6). Note that during the dry years of the last decade the effect of the trend on the AF was an increase by 35%.

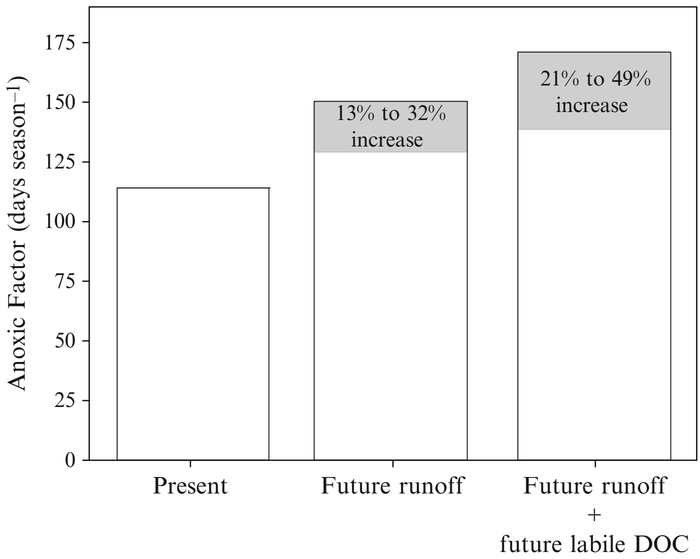

Fig. 7 Comparison of observed present AF in the Sau Reservoir and results of the AF model solved assuming a decrease in surface runoff by 20–40% during the present century, and an additional effect of lack of dilution of labile DOC in the tributary. Shaded areas represent uncertainty of predictions

We can take the analysis of the effects of decreasing streamflow trends a step further. Solving the empirical model fitted above using a mean streamflow decreased by 20–40% (that is, the prediction of the IPCC for the Mediterranean regions), produces mean annual AF increases of between 13 and 32%. This is a first approximation of future effects of climate change on the oxygen content of Sau Reservoir. However, this figure must be considered a conservative prediction, because no changes in the labile organic matter load were considered. Increasing the labile organic matter by a modest 15% (to account for the dilution effect) increases the AF by as much as 41% (Fig. 7).

Obviously, this is a crude approximation and should only be considered a rough estimate of climate change effects on future water quality. However, in view of the simplicity of the empirical equations and its robustness (due to the high interannual variability of the Mediterranean climate any modeling forecast uses independent variables beyond ranges of the calibration data), our procedure offers a new framework for testing impacts of future climate scenarios on water quality in reservoirs. In any case, our results emphasize that streamflow should be considered a climate signal that is just as important as temperature in climate change impact studies in freshwater.

Such results constitute a warning for the management of water supply systems based on reservoirs. Considering the major role of streamflow on controlling oxygen levels, water scarcity should be viewed as a threat not only for the quantity of resource, but also for its quality and the cost of treatment. All these considerations are especially relevant in Mediterranean areas, where many water supply systems rely on reservoirs, and where most climatic models predict a marked decrease in streamflow within the next 20 years. This is even more important if drought episodes become more frequent, because it is in these periods when the reduction of the oxygen content in reservoirs can be more pronounced.

5 Best Management Practices in Mediterranean Reservoirs Under Scarcity Conditions

Water managers in charge of water supply systems that include reservoirs are well aware of the relationship that exists between water scarcity and the deterioration in the quality of the water stored in reservoirs. The above considerations regarding the drivers of anoxia in reservoirs could thus prove very useful both for planning remediation measures at broad temporal and spatial scales and for predicting the impact of projected changes in the climate on the quality of water. However, once the drought is there, managers need specific solutions to avoid supplying water that pose a threat to water treatments and plumbing. In this section, we exemplify how wise limnological monitoring can help managers using real cases from Catalan reservoirs devoted to water supply.

In the Iberian Peninsula, the number of reservoirs devoted to water supply has increased steeply during the last decades. This is especially true for main urban settlements, where the fluctuating river flows and overexploited groundwater aquifers do not suffice to provide the required volume. The paradigmatic case is the Barcelona Metropolitan Area, which needs around 500 hm^3 a year, 65% coming from five reservoirs located in the Llobregat River (La Baells, La Llosa del Cavall, and Sant Pons) and the Ter River (Sau and Susqueda). Water from these reservoirs arrives in the treatment plant through a complex network of pipes, where water is treated and delivered to the end-users distribution network.

Water supply is a complex process, but for the sake of simplicity we can divide it in two main steps: storing and treatment. These two steps can be entirely independent, and in fact the treatment process was totally independent of storage in Spanish reservoirs until a few decades ago. The water was treated at the plant regardless of the quality of the incoming resource. Nowadays, the trend is to integrate the management of the resource from the origin to the treatment plant i.e., by promoting in the reservoir chemical, physical, and biological processes that improve water quality, so as to minimize the costs of any subsequent treatment.

Within this framework, the role of reservoir managers is not just to periodically check the water level, but also to understand the physical and ecological processes that drive water quality and manage the resource using this information. Although each reservoir is idiosyncratic, and hence needs managing in a particular way, it still is possible to provide some general rules. From the perspective of water quality, all situations must be faced assuming the same criteria: we must facilitate all processes that maximize the self-purifying capacity of the reservoir. In short, we want better quality in the outflow than in the inflow. Catalan water supply reservoirs are managed following this rule. In the next section, we describe some of the management strategies implemented during the last few years, when the area also experienced a number of severe droughts.

Reservoirs in the Ter River are eutrophic, and water management has been based on three processes: (1) wastewater treatment plants upstream of the first reservoir in the chain (Sau), (2) increasing water column stability in order to enhance epilimnetic self-purifying processes [37, 58], and (3) selection of the appropriate spillway in Sau (out of three) and Susqueda (out of four) [59]. During average years with respect to the volume of water stored in reservoirs, water has typically been withdrawn through the surface spillways, to avoid anoxic and metal and ammonia rich hypolimnetic waters reaching the treatment plant. However, during dry years a different approach has to be adopted since most spillways are then above the water surface. This was the case during extreme droughts in 2005 and 2007–2008, when huge amounts of sediments were carried from the riverine and littoral zones of the reservoirs, increasing nutrients, organic matter, and dissolved metals in water. Such problems are usually at their worst when the water level drops, so the best option in a chain of reservoirs is to keep the level of the last reservoir in the chain as high as possible (assuming the last reservoir is the final step before supplying water to the treatment plant). In our case, we tried to maintain high water levels in Susqueda, which is the downstream reservoir. This implied an acute deterioration of Sau Reservoir water quality, but water quality for supply was maintained at reasonable levels. One factor that helped this strategy was the fact that Sau Reservoir water enters Susqueda Reservoir at an intermediate level during stratification months and remains in a narrowly delimited layer on account of its density. Figure 8 shows an example of this interflow, recorded during October 2005, when 30 hm^3 of water were withdrawn from the only spillway available in Sau to Susqueda. As a result, one more spillway was available in Susqueda due to the improvement in water level, and the well oxygenated layer in Susqueda reached 35 m, 5 m more than at the beginning of the water transfer. During the drought of 2007–2008 a similar strategy was implemented, with a very conspicuous intermediate circulation of Sau Reservoir water in Susqueda (Fig. 9).

In the Llobregat River the situation is quite different. There, reservoirs are located in headwaters, where human impacts are lower and their trophic state is oligo-mesotrophic. In these reservoirs the favorable trophic state suffices to maintain a reasonable water quality throughout the year, and a spillway-based management is not worthwhile. In these reservoirs, the management strategy is the reverse of that already described with water being withdrawn from the deepest outlet available, thus considerably decreasing hypolimnetic water residence time. This effectively limits the development of anoxic layers during the stratification period (which last for 8–9 months in the Mediterranean area). Figure 10 shows profiles of temperature, conductivity, and dissolved oxygen measured in the three reservoirs located in the Llobregat basin. These profiles were recorded at the most acute period of the worst drought during the last decades (September 2005), but the

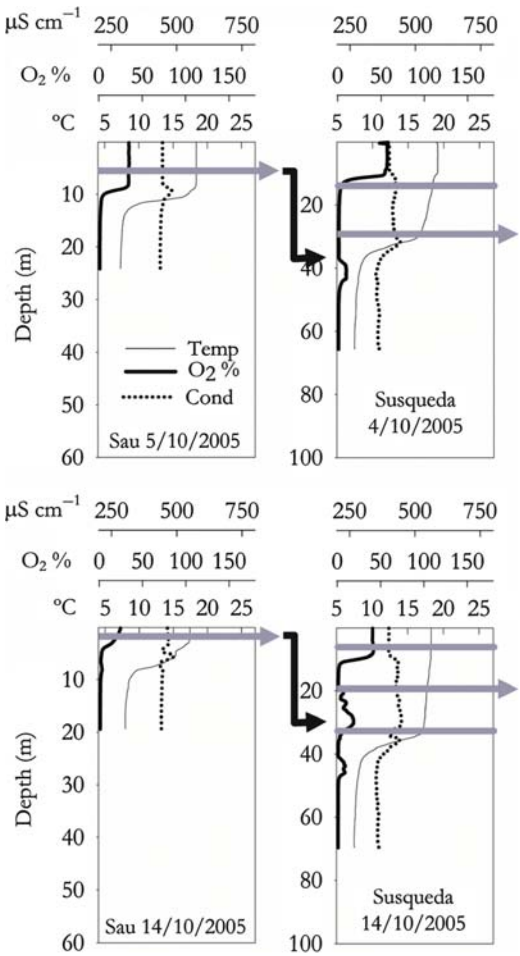

Fig. 8 Temperature, dissolved oxygen saturation, and conductivity profiles in the Sau and Susqueda reservoirs during a water transfer in 2005. *Gray* banners indicate the depth of the spillways (actual withdrawal depth indicated as an *arrow*). The path of the Sau Reservoir water inside Susqueda is indicated as a *black thick arrow*

only reservoir with even moderate deep-water hypoxia was La Baells. This is very different from the situation that developed in the Ter River reservoirs for the same period (Fig. 8). In short, in oligotrophic and mesotrophic Mediterranean reservoirs, deep water withdrawal is effective at maintaining water quality for supply during both wet and dry years.

Obviously, these examples do not cover all possible management options, but they highlight the fact that a sound knowledge of the hydrodynamics is of paramount importance for a proper water quality oriented management. Reservoirs are very dynamic systems that often stratify in a multilayered fashion to produce layers of water with huge differences in their residence time [60]. In impaired reservoirs, the best option is to increase residence time of anoxic layers, and reduce it for surface water. The presence of outlets at different depths is essential in reservoirs devoted to water supply.

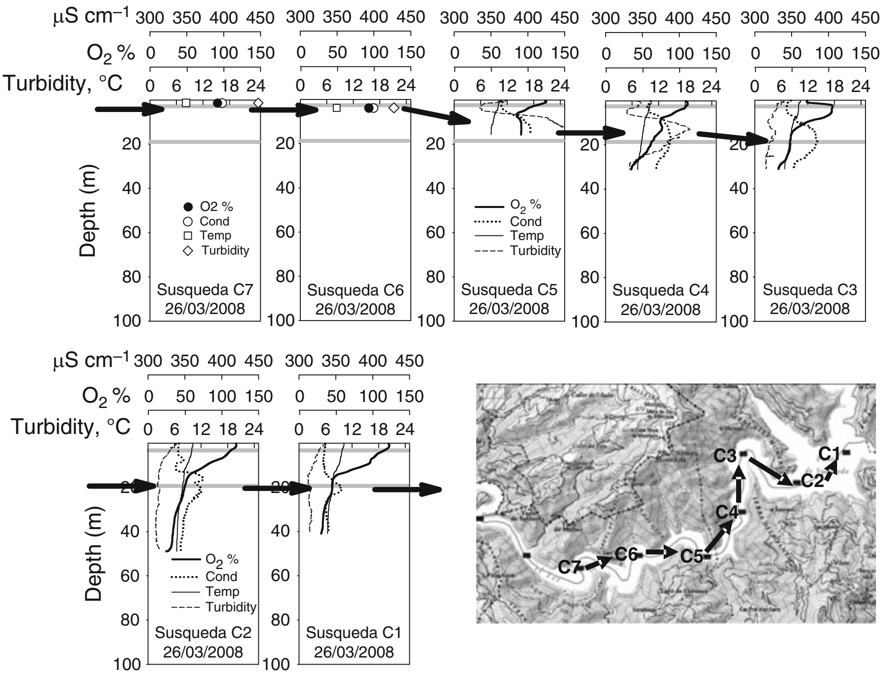

Fig. 9 Temperature, dissolved oxygen saturation, turbidity, and conductivity profiles in the Susqueda water in Spring 2008. The path of the Sau Reservoir water inside Susqueda is shown by the thick arrows. The *thin gray lines* indicate the depth of the available spillways

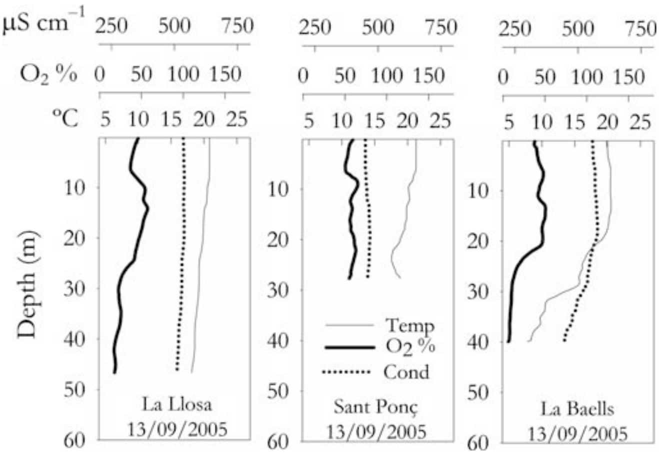

Fig. 10 Temperature, dissolved oxygen saturation, and conductivity profiles recorded in reservoirs from the Llobregat basin during the summer of 2005. Despite 6 months of stratification, oxygen saturation still showed high values except in La Baells. Compare these profiles with those from the Ter River reservoirs in Fig. 8

6 Potential Risks and Management Opportunities: A Research Agenda

All the above considerations have important implications for the management of reservoirs in the Mediterranean region, bearing in mind the decreasing runoff scenarios. Since human spills (sensu lato, including point and nonpoint sources) are usually loaded with labile organic matter (e.g., effluents from WWTP), decreasing streamflows would also diminish the dilution capacity of running waters, implying higher labile organic matter concentrations. Thus, both hydrology and organic matter changes in rivers would impact water quality in reservoirs located in Mediterranean areas.

Thus, we can expect a cascade effect driven by rainfall reduction and increased evapotranspiration (Fig. 11). However, the ways climate change will modify these processes are difficult to predict and involve high degree of uncertainty. Although climate models predict less runoff in Mediterranean countries during the present century, much more research is needed on the local and regional impacts of warming and precipitation changes. Reservoirs are very dynamical systems with very short water residence time, so we need more than uncertain annual forecasts to predict the likely outcome. The effect of increasing temperatures on the intensification and extension of the stratification period may also be less important in reservoirs than in lakes, since these may be countered by human intervention in their hydraulics. We also need to understand the causal mechanism explaining the empirical link observed between streamflow and the oxygen content of reservoirs.

Another fundamental question to be addressed by limnologists is the effect of climate change on labile DOC, because most of this organic matter comes from human activity in human populated watersheds. In particular, the relationships with streamflow and their effect on the metabolic balance of reservoirs should be established using methods that go beyond empirical analyses. In general, we lack a deep characterization of DOC quality in rivers, and its fate and potential degradability in receiving lentic ecosystems. This information is of vital importance to

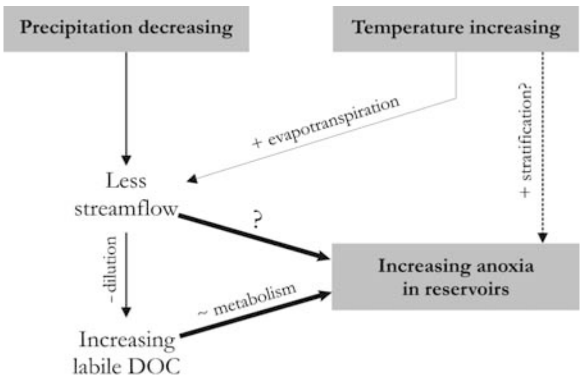

Fig. 11 Schematic representation of cascade effects of climate change on reservoir water quality (expressed as anoxia extent)

understand the role of these substances on water quality stored in reservoirs. Moreover, we need to allocate sources of labile DOC and describe the main pathways to river systems. This is crucial to implement remediation measures, which, in the case of reservoirs, must be applied at a watershed scale.

Nevertheless, we should not ignore the possibility of some temperature effects, such as those associated with the increase in evaporation and the timing and intensity of thermal stratification. It is also important to establish how these factors might interact so that we can offer managers the right knowledge to apply the right remediation measures. However, in our opinion, this is best approached within a dynamical modeling framework, since most processes involved in hydrodynamics are already well represented in many established models. In any case, we first need to solve the dependence of reservoir metabolism on streamflow and allochthonous organic matter. Until then, we can obtain preliminary guesses using empirical relationships similar to those presented in this chapter, and then use the dynamic models to test some of the hypothesis described.

Finally, a relevant question is whether there is some room for management to prevent future water quality deterioration in reservoirs. The preceding section is a good example of how ad hoc solutions based on the hydraulic management of the system can help prevent the deterioration of water quality during extreme climatic events. Of course, these remedial measures should be based on a deep knowledge of the system, and here reservoir limnologists should play a prominent role. Research efforts in this area must place more emphasis on developing expert systems for short term management [59]. This will require the simultaneous development of on line, reliable automatic data collection systems working at sub-daily time steps. However, considering the dynamic nature of reservoirs, only extensive monitoring programs can guarantee that limnologists will be there before the system crashes. Thus, managers should valuate such field programs if they want to take advantage of the answers reservoir limnology can give them.

However, in a broader context and avoiding site-specific solutions, the control of labile DOC loadings seems the only realistic option. Human intervention on streamflow can only be an alternative in specific cases. By contrast, most labile DOC in rivers comes from human activities: it is in our hands to decrease those loads through a more efficient industrial processes and wastewater treatments. This would not only improve water quality in reservoirs, but also in stream ecosystems receiving human spills. In our opinion, control of labile DOC loadings from human origin (maybe also rethinking present regulation on contaminants in rivers) should be prioritized in the present and in the future.

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Technologies for Water Regeneration and Integrated Management of Water Resources

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Abstract The contribution of water reuse to water resource management is still greatly undeveloped in the Mediterranean. The reasons for this gap are not only technological. They can be found in the long lasting absence of common regulations, in the slow acceptation to shift from agricultural irrigation to other more economically efficient applications such as urban and industrial uses, as well as in the real or assumed public reluctance and in the socio-economic hurdles that must be overcome to integrate water reuse in global water resources management.

Keywords Integrated water management, Public acceptance, Reclamation technology, Regulations, Water reuse applications

Contents

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1 Introduction

Chronic water scarcity has urged looking for new and alternative sources of water in many Mediterranean regions. Long distance transfers are very expensive and face increasing opposition from the populations threatened to be deprived of what they consider their inalienable inheritance. Consumption restrictions are not easily enforced except during extreme drought periods. Attempts are being made to develop water saving and pricing policies but, until now, they seem to have limited impacts. Therefore, the use of marginal water resources, including brackish water, sea water and reclaimed wastewater, appears as the most effective means to satisfy the water needs of many Mediterranean areas, particularly in coastal regions. This has resulted in a growing interest for water reuse. However, though it offers a lower cost of recovered water, water reuse often expands more slowly than seawater desalination in Euro-Mediterranean countries and important amounts of water resources are dumped to the sea and jeopardized.

Several reasons may explain why water reuse expansion lags far behind the needs. Though water reuse provides an alternative water supply that is consistently available even in drought periods, it faces unique hurdles. In the Mediterranean, the most important are the relative lack of experience of these countries in water reuse, regulations' uncertainties, the difficult choice of efficient and cost-effective water reuse applications, the choice of technological options, real or assumed public reluctance and the hard task of involving water reuse within integrated water management frameworks.

2 Regulations

In many Mediterranean countries, water reuse regulations to be applied have long been uncertain. Several countries have not yet set up their own water reuse regulations. This raises doubts about the credibility of water reuse criteria and thus about the treatment technologies to be used and the reliability and appropriateness of those already implemented. The result is that in several countries, a number of planned water reuse projects are getting postponed.

In the early nineties, three Spanish autonomous governments enacted their own standards in order to allow water reuse to develop. The government of Balearic Islands issued water reuse regulations in 1992, while governments of Andalusia and Catalonia set up guidelines in 1994 [1]. It was not before December 2007 that a Spanish national regulation was issued [2]. In the meantime, the volume of treated reused wastewater in Europe has increased enormously to more than 600 Mm^3 $year^{-1}$. The recent national regulation is expected to comfort the spreading of projects that should save thousands of Mm^3 of tertiary treated wastewater per year in the near future. The set of microbial parameters to be monitored include *Legionella*. The number of the parameters to be checked and the required frequency of the analysis will not preclude the economy of big reuse projects. Some amendments will be necessary in order not to undermine the feasibility of useful water reuse projects planned by small and middle-size communities.

In France, guidelines were issued in 1991 [3]. Surprisingly, enacting recommendations in an international controversial environment resulted in a dramatic slowing down of water reuse development. Since then, several national committees have been commissioned to review and update these recommendations. Reports and drafts have been issued, but the decree expected to be published since more than 15 years is not yet ready. Italian regulations were issued on June 12th, 2003, (Ministry Decree, D.M. n. 185/03). Microbiological targets are stringent, with an *E. coli* content of less than 10 UFC/100 mL. These specificities are to be implemented whatever the plants irrigated or the irrigation system used; *Salmonella* should not be found in the water used for irrigation. Moreover, a long series of physical and chemical parameters should be monitored, the criteria for many of them being surprisingly similar to the requirements for potable water. Indeed, water reuse regulations and guidelines around the world, and particularly in the Mediterranean, suffer from severe discrepancies that do not give them high credibility [4]. Regulations and guidelines are rooted in two benchmark standards, the WHO guidelines (1989), [5] and the California regulation known as Title 22 [6]. Impressive differences in the respective microbial criteria have been, for years, a matter of international controversy. These two standards have their supporters, which led, taking Spain as an example, to regional regulations on line with the WHO guidelines and projects closer to the California standards.

The effects of the recently revised WHO guidelines for the safe use of wastewater in agriculture [7] are not yet foreseeable. The revision process of these guidelines has been characterized by an innovative scientifically-based approach for setting health-related guidelines partly based on the methodology developed for the elaboration of Australian guidelines ([8] and by important steps towards a harmonization of guidelines related to different water uses. The methodology that has been used to revise these guidelines should help the Mediterranean countries, still devoid of regulations, to elaborate national guidelines more rational and close to each other [9].

3 Water Reuse Applications

Traditionally, the most popular application of water reuse has been agricultural irrigation. This application is often the continuation of long time unplanned urban wastewater reuse, but with major improvement of the quality of the irrigation water. In the Mediterranean, it accounts for a large majority of the reuse projects. As reported by [10], the selection of reuse applications has not always been made on a rational basis. Enough consideration has not always been given to cost recovery and the economic efficiency of reuse projects aimed at agricultural irrigation. This may be related to the status of agriculture in Mediterranean societies and to subsidy policies. Considering the construction, operation and maintenance costs of the additional wastewater treatment and of the storage and distribution facilities versus the income of the cultivated crops, the economic efficiency of water reuse is doubtful, especially as farmers are not prone to pay for reclaimed water. It most often remains doubtful even if the environmental benefit resulting from the reduction of wastewater discharge to the environment is taken into account. The irrigation of high income crops, such as vegetables or fruit trees, cultivated in the vicinity of the wastewater treatment plant, constitute an economically sound exception, provided that farmers are ready to pay for the water.

Therefore, sound policies should be reluctant to invest in agricultural water reuse schemes. Other options, such as urban or industrial uses as well as indirect potable reuse are much more likely to be economically justified.

Reclaimed water is a valuable but limited water resource. With respect to the limited reclaimed water volumes, transportation costs must be reduced as much as possible and reuse sites located close to the places where wastewater is produced, treated and stored. More projects to come should be devoted to town or not-far-from-town applications. The reclaimed water applications that should be preferred are (a) urban uses such as irrigation of public parks and lawns, landscape and golf courses, street cleaning, which often means offsetting potable water for non-potable purposes and maximizing the efficiency of reuse projects, (b) industrial uses, mainly cooling systems and (c), as mentioned above, vegetable crops and orchards, often located in the vicinity of towns [11]. Though these applications require high quality reclaimed water, particularly as regards microbiology, they are likely to be competitive when considering the marginal cost of the supply of conventional water resource. Otherwise, reclaiming wastewater, even to a very high quality, is cheaper than desalination; therefore, cost considerations should not hinder the development of urban and industrial water reuse.

Figure 1 shows that in the developed countries (USA, Europe, Australia, Japan), the number of urban reuse schemes is as high or much higher than the number of agricultural irrigation schemes while in the least developed regions (North Africa, Middle East, South America), agricultural irrigation is the favored reuse application. Though local situations are diverse, integrating economic considerations should contribute to revise reuse policies and turn them to applications more profitable for the communities. Moreover, the review made by the Aquarec European program shows that indirect potable reuse, mainly through ground water recharge, is developing in the USA and Europe [12, 13]. Indirect potable reuse schemes include at least one environmental barrier, such as aquifer or reservoir providing at least 1 year retention time, that serves to isolate and protect consumers of potable water.

4 Technological Options

A wide range of technologies for the reclamation of wastewater for reuse is available (Fig. 2). The choice of the appropriate technology for a given project

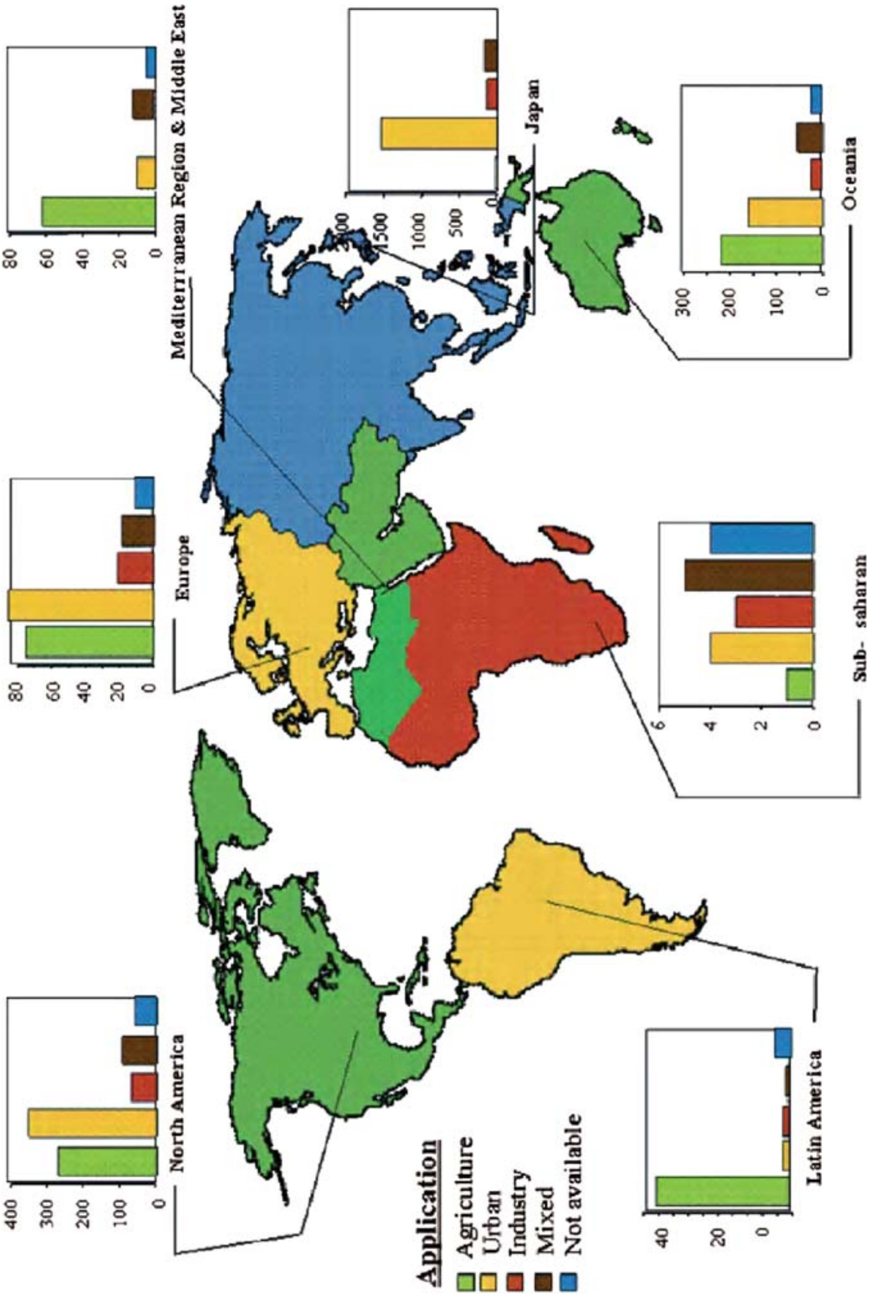

Fig. 1 Water reuse schemes identified within the Aquarec European programme [12]

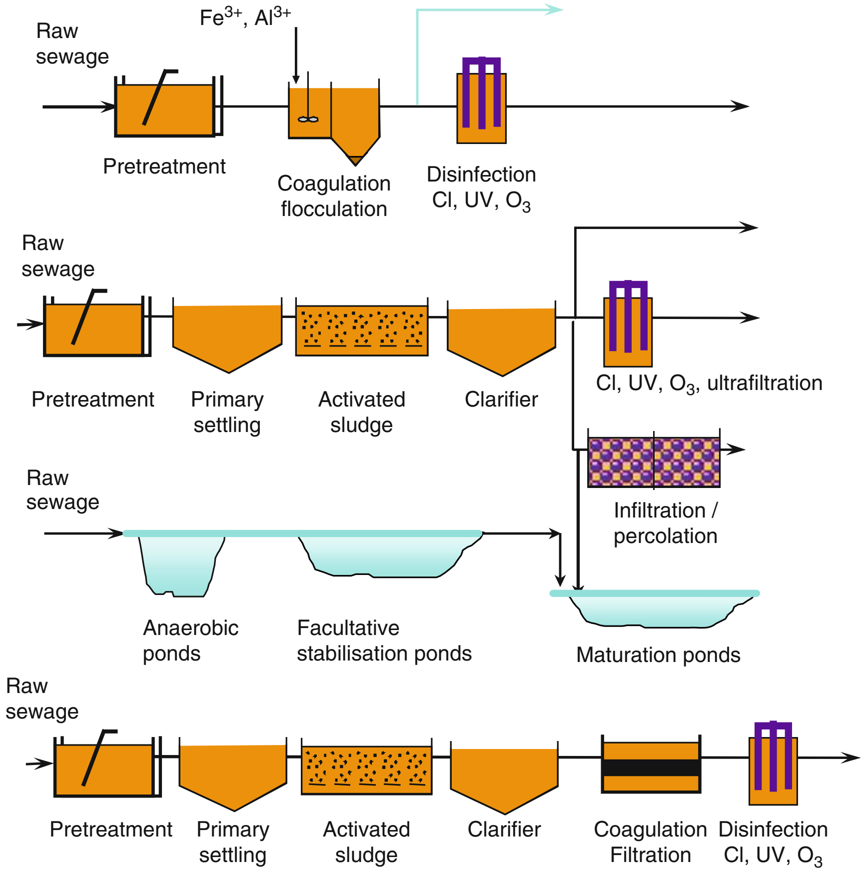

Fig. 2 Examples of treatment trains including disinfection through intensive or extensive processes for water reuse in agriculture and other applications implemented in different countries [16]

depends on the reuse application and enforced regulations. In most cases, a tertiary stage must be added to the existing wastewater reuse treatment facility, the main aim of it being the removal of pathogenic micro-organisms. Two main types of techniques can be considered: conventional or intensive technologies and natural or extensive systems.

Intensive technologies are derived from the processes used for the treatment of potable water. Chemical methods include chlorination, peracetic acid, ozonation. Ultra-violet irradiation is becoming a popular photo-biochemical process. Membrane filtration processes, particularly the combination microfiltration/ultrafiltration are rapidly developing (Fig. 3). Membrane bioreactors, a relatively new technology, look very promising as they combine the oxidation of the organic matter with microbial decontamination. Each intensive technique is used alone or in combination with another intensive technique or an extensive one. Extensive

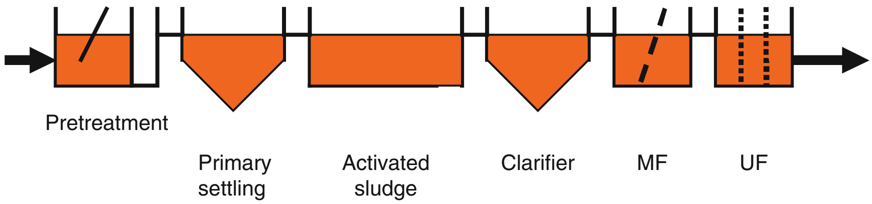

Fig. 3 Treatment train including membrane filtration for microbial decontamination

technologies, such as waste stabilization ponds, constructed wetlands or infiltration percolation are adaptations of processes occurring in the nature. They can be used either as the main treatment or as a tertiary one and, if required by the disinfection criteria, in combination with an intensive disinfection technique.

The choice among these techniques depends not only on the water reuse application and the microbial quality that must be achieved but also on several other factors such as the land availability, the respective investment, operation and maintenance costs, the process reliability, the skills required from the operation staff and the options taken to reduce health-related risks. The experience is that subjective factors also play a part in the decision process. As they originate from the treatment of potable water, intensive disinfection techniques have an image of high reliability while the potential of extensive techniques is often underestimated. However, adapting techniques originally designed for the treatment of potable water to the treatment of secondary effluent means that a number of difficulties must have been overcome. Low turbidity is a prerequisite to reach high microbial quality; therefore filtration before disinfection is a key component of intensive treatments. On the other hand, technological innovation and transfer of recent research findings to engineering practice have enhanced the potential performances of extensive techniques [4].

Extensive technologies are likely to be preferred to intensive processes for those facilities that are to serve small and medium-sized communities. Investment costs of extensive wastewater treatment techniques are not much lower than those related to intensive technologies. Most low technology systems require large areas of available land and cannot be applied in areas that are too densely populated. However, extensive techniques do offer decisive advantages: very low costs, easy operation and maintenance and high microbial decontamination potential. When the need for imposing very restrictive water quality criteria is demonstrated, combining low technology and conventional systems can be an option, particularly when a high microbial decontamination is required. As an example, combining infiltration percolation and ultra-violet irradiation is very effective and at a relatively low cost [14].

Intensive methods are preferred for big size water reuse schemes, not only for their reduced footprint but also because high technology systems, when implemented by skilled staffs, are assumed to allow higher microbial performance predictability. Moreover, designers and engineers are confident in techniques that allow calculations certified by the manufacturers and the assurance they provide. They are more reluctant to deal with natural systems, the performance of which may depend on climate and meteorological conditions.

5 Public Acceptance

Using wastewater for the irrigation of food crops has been a long tradition in the Mediterranean. Fortunately, thanks to the Directive 91/271 EEC and the health-related standards recommended or enforced in the countries of the region, this practice has dramatically improved. In the Euro-Mediterranean countries, it is now planned and implemented in a safe way. So far, populations have not expressed any noticeable opposition against water reuse, because either the projects meet the needs of the farmers or they are considered as a sound management of the water resources. For instance, using reclaimed water for golf course irrigation saves potable water, involves low degree of potential contact with the reclaimed water and is already widespread in Spain and also in France, where 45 golf courses use recycled water. An agreement encouraging this practice has been passed in 2006 between the Ministry of Environment and the French golf federation. Irrigation with reclaimed water has become mandatory in the Balearic islands and Catalonia wherever feasible. More than 2000 golf courses are irrigated with reclaimed water in the Unites States, where this application was approved by a large majority of respondents to public surveys [20]. Very few investigations of the public acceptance have been undertaken in the Mediterranean. A poll conducted in 2006 by the SOFRES Company on a 1000 people sample representative of the French population older than 17 years showed that 82% of the population considers reusing treated wastewater for non-potable applications as a priority.

Water reuse appears to meet the approval of most of the public as far as non-potable applications, such as agricultural and landscape irrigation, industrial cooling and even toilet flushing in large commercial buildings, are considered (Asano et al. 2007). Indirect potable reuse raises more concerns, mainly related to subjective perceptions of recycling treated wastewater for such purpose, to the safety and the reliability of the recycling scheme. However, public acceptance may be greatly influenced by recurrent droughts and water supply failures. Gaining the endorsement of a project by local communities may require many years of planning with great emphasis on public involvement [15].

Administrative representatives are often shy about developing water reuse projects. Evaluations of the risks related to water reuse have been twisted so as to be employed in political arguments during election campaigns, which may explain the reluctance of politicians. Examples of failure and success of indirect potable reuse projects in the United States are provided by [13]. Such experiences point out the importance of public education as regards the human interaction with the water cycle and the management of water resources. The population should be aware that the very common situation of discharge of a wastewater treatment plant in a river, and the subsequent downstream pumping from the river itself or from a connected aquifer (even after an appropriate treatment for potable water supply), results in direct/indirect water reuse. This common situation, which is increasing by population growth, has not raised much public concern until now. Instead, it seems to be well received because of its long-standing nature [13]. Droughts are appropriate periods to launch educational programmes.

6 Integrated Water Management

The water supply of Palma de Mallorca (Balearic Islands, Spain) is an example of how integrating water reuse within a water management global scheme can help saving water resources and water supply costs. Mallorca suffers from serious water scarcity. There are no permanent surface water bodies, except two runoff collection reservoirs in the mountain range in the N of the island. At least 95% of potable water supply is obtained from groundwater. Annual potable water demand in Palma area is about 44 Mm^3, which is met by exploiting 17 sources from 7 hydrologic units. Most of these aquifers are over-exploited and water quality is deteriorated by seawater intrusion. The water pumped from two main aquifers (Llano de Palma and Na Burguesa) must be desalinated in a 30,000 m^3 day^{-1} reverse osmosis treatment plant (Son Tugores) operating since 1995. Thus new resources were needed. A seawater desalination plant, named Bahia de Palma, was put into operation in 1999 with a daily capacity of 42,000 m^3 day^{-1} and enlarged to 60,000 m^3 day^{-1} afterwards. In peak period demand, about 50% potable water demand is met through seawater desalination.

Farmers in Mallorca based in the Llano de Palma, a traditional agricultural area, used to pump water for irrigation from the coastal aquifer. As the population of the island soared, this resulted in seawater encroachment and agricultural land loss. From 1975, secondary effluents were used to irrigate at first 250, 500 later on, then up to 1100 ha. This allowed growing alfalfa and cereals and recharging the aquifer with low salt content water; thus the salinity of the aquifer water decreased gradually. The quality of the wastewater reclaimed for irrigation has been recently upgraded to a tertiary treatment of the Title 22 type, including coagulation, flocculation, dual media filtration and hypochlorite disinfection. About 15 Mm^3 $year^{-1}$ effluents are used this way for agricultural over-irrigation and subsequent aquifer recharge [17].

The total capacity of the two wastewater treatment plants serving the urban area of Palma is now about 40 Mm^3 $year^{-1}$, i.e. much more than actually used for irrigation. At the same time, farmers of the Llano de Palma are continuing pumping into the aquifer up to 30 Mm^3 $year^{-1}$ of good quality water. Thanks to the installation of a network of distribution pipes, they could use high quality reclaimed water, thus preserving the aquifer that could be extracted for potable supply [18, 19]. This would allow a significant reduction in desalination needs and cost of potable water supply to the Great Palma. However, the local authority will have to persuade the farmers to give up with groundwater irrigation and shift to reclaimed water. At present, most farmers still use their private wells for irrigation. Groundwater is a free and convenient water supply in Llano de Palma, although, due to over pumping by farmers, the salinity may rise and may eventually have an adverse effect on yields of irrigated crops. The farmers have obtained high quality reclaimed water, but it is difficult to convince them to abandon their rights to pump groundwater. This example shows how integrating water reuse in a rational water management scheme could benefit the population, improving the security and decreasing the cost of water supply in a water scarce island. However, it also demonstrates that sound technical policies may encounter strong reluctance among a fraction of the population, leading to investments in underutilized wastewater reclamation facilities and costly desalination.

On the other hand, Palma de Mallorca is also a successful example of urban water reuse within an integrated water management framework. Since the end of the nineties, tertiary treated (coagulation, flocculation, sand filtration and gaseous chloride disinfection) water is used for public parks, landscape and golf courses irrigation. About 7 Mm^3 $year^{-1}$ are currently used, thus saving equal amounts of potable water. This is the most efficient water reuse application in Palma.

7 Conclusion

The potential contribution of water reuse to the integrated management of water resources still remains considerably undeveloped, though a wide range of reliable, efficient and cost effective technical solutions are available for each type of reuse application.

Economic considerations will inevitably lead the decision makers to opt for economically efficient reuse applications, i.e. urban and industrial water reuse in the short term and indirect potable reuse in the long term. Tourist resorts offer excellent opportunities for urban reuse, which should have a bright future in Spain and many other Mediterranean countries where tourism is a major component of the gross national product. Comparing the treatment costs of seawater desalination with wastewater reclamation using the same technology (reverse osmosis) to produce potable water shows that potable water reuse will eventually be considered as a wise option even if, for public acceptance considerations, this reuse will be indirect, through aquifer recharge or reservoir replenishment.

As for any project which has or might have an environmental impact, a number of socio-economic hurdles are in the way. Environmental issues are often put forward to hide private economic interests, often jeopardizing excellent reuse projects. The only way to cope with this kind of an obstacle is public education. Landscape and agricultural irrigation are likely to be well accepted, when indirect potable reuse requires sophisticated approaches. Literature stresses the importance of involving all stake holders from the very beginning of project design. However, there is little evidence that this approach is always successful. Well planned water reuse integrated in a global water management scheme is economically sound and results in significant water savings but may be difficult to implement for socio-economic reasons. The result is that desalination, a much more costly method, develops more rapidly than water reuse in the Mediterranean.

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Reuse of Regenerated Waters Under Water Scarcity

I. Ortiz, R. Ibáñez, A.M. Urtiaga, and P. Gómez

Abstract Mediterranean countries face water supply challenges due to water scarcity. Water regeneration, recycling and reuse address these challenges by resolving water resource issues and creating new sources of high-quality water supplies. Among others, industrial activities worldwide account for about a quarter of all water consumption and there is hardly any industry that does not use large amounts of water. Water standards related to industrial activities may vary in a large range of parameters and limit values. In this context the future potential for regenerated treated water is enormous. This contribution reflects the potential of advanced technologies to produce regenerated water offering specific solutions to industrial reuse needs. A general example is illustrated by a case study representative of the ability of using WWTP effluents as regenerated water sources. Appropriate combination of advanced technologies allows the production of customized regenerated water according to the standards of the potential reuse industrial activities.

Keywords Disinfection, Industry, Membrane technology, Regenerated water, Water reuse

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Abbreviations

COD	Chemical oxygen demand (mg l^{-1})
LSI	Langelier saturation index
NTU	Nephelometic turbidity units
SDI	Silt density index
TDS	Total dissolved solids (mg l^{-1})
TMP	Transmembrane pressure (bar)
TOC	Total organic carbon (mg l^{-1})
TSS	Total suspended solids (mg l^{-1})
WWTP	Wastewater treatment plant

1 Water Scarcity, an Increasing Global Problem

Water scarcity corresponds to the mismatch between demand and supply of water resources. The risks of water shortage in the Mediterranean countries are generally associated to the high water demand despite the limited renewable water resources and the irregular and unequal qualities [1].

The demand of water resource all over the world has increased considerably. This demand increased 600% in Europe during second half of the twentieth century and reached 660 km^3 yr^{-1} at the end of the century [2]. On the other hand the renewable water resources have changed worldwide. Abstracted water rates must be sustainable in order to ensure the management and protection of water resources and related ecosystems. The sustainable use of water resources implies that the annually abstracted water should not exceed a certain ratio of the annual renewable water resources. The warning threshold for water exploitation index (WEI) being around 20%; this distinguishes a non stressed region from a stressed one. Severe water stress can occur for WEI $>$ 40%, which indicates strong competition for water. In the major part of the European continent the amount of available water largely exceeds its demand. Mediterranean countries are among those with higher WEI indexes. Four countries in southern Europe, representing 18% of the population, are water stressed (Cyprus, Italy, Malta, and Spain). Other Mediterranean countries, like Romania, Turkey, Bulgaria or even Portugal are moderately water stressed [3]. WEI has decreased in countries like France, Malta and Spain, mostly due to the implementation of sustainable water use programs. Other Mediterranean countries like Turkey, Portugal or Greece have however increased on their WEI.

2 Water Reuse as an Efficient Tool Against Water Scarcity

Water reuse is a solution for water scarcity and the issues concerning the same are amongst the biggest drivers in the *water framework directive* (WFD) [4]. The water reuse benefits have been summarized by the *Mediterranean Water Scarcity and Drought Working Group* [1]. Nowadays treated wastewater in Europe is reused for agricultural irrigation, landscape irrigation, industrial recycling and reuse, groundwater recharge, non-potable urban uses and indirect potable use. Spain is at this moment perhaps the most important water reuser among the western European countries [5] with a total volume of 368 $Hm^3\ yr^{-1}$ of reuse of regenerated water in 2006 [6]. Of this amount, 71% was dedicated to agricultural irrigation, 17% for environmental purposes, 7% for recreation including golf, 4% for municipal uses, and only 0.3% was employed by industry. However, industrial reuse potential is actually growing in the most industrialized regions located in N Spain, where 73% of the total water demand is assigned for industrial supply and this use accounts for 50% of the total water consumption [7].

In this context, the *European Legal Framework* promotes the use of regenerated wastewater "*whenever appropriate*" by means of the EU water framework directive [4] and other related regulations as the EU *urban wastewater treatment directive* [8]. However, there is a lack of quality standards for regenerated wastewater that are actually being solved by regional initiatives in Spain, France, Belgium, Italy, Greece, Portugal and the UK [9]. Recent efforts were carried out in 2007 by the Spanish authorities with the new regulation of regenerated wastewater [10] that introduced specific standards for industrial reuse of regenerated wastewaters.

3 Reuse of Regenerated Water in Industrial Activities

Industry accounts for about a quarter of all water consumption and there is hardly any industry that does not use large amounts of water. Much of the water used in industry is taken from public water supplies and has therefore been treated to potable standards. This means that it is often of a better quality with respect to microbiological levels but still needs further treatment to reduce the mineral and organic contents according to the different specifications of use [11]. Different quality standards, from natural to ultrapure are required for specific duties in industrial activities as summarized in Table 1.

This high water consumption demands the use of new water sources apart from the natural and potable ones. The implementation of water reuse concepts is becoming an important operational and environmental issue in the industrial sector [12]. Industrial use of water encompasses quantity and quality requirements that range from the use of large volume of low-quality water for cleaning applications to the use of high-quality process water for manufacturing or boiler feed water, e.g., utility power plants are ideal facilities for reuse due to their large water requirements for cooling, ash sluicing, red-waste dilution, etc. Petroleum refineries, chemical plants and metal working facilities are among other industrial facilities benefiting from regenerated water not only for cooling, but for process needs as well, e.g., the viability of utilizing regenerated water in the electronics industry which requires water of almost ultrapure quality for washing circuit boards and other electronic components (Gagliardo et al. 2002). On the other hand, the tanning industry can use relatively low-quality water. Requirements for textiles, pulp and paper and metal manufacturing are intermediate, e.g., the textile industry, of great importance in the Mediterranean region, uses 60–100 $m^3\ t^{-1}$ finished textile [13]. Thus, the study of feasibility of industrial reuse of regenerated water must include an early stage on the definition of the needs of the potential users in order to determine the specific utilization.

Table 1 Generalized industrial water quality standards

Parameter	Softened	Dealkalized	Dionized	Purified	Apyrogenic	High purity	Ultrapure
Conductivity (μs cm^{-1})			20	5	5	0.1	0.06
Resistivity (MΩ cm)			0.05	0.2	0.2	10	18
TDS (mg l^{-1})			<10	<1	<1	0.5	0.005
Hardness (mg l^{-1} $CaCO_3$)	<20		0.1	<0.1	<0.1		0.001
Alkalinity		<30					0.001
Turbidity (NTU)			<0.5				
SDI			<5	<3	<3	<1	<0.5
Micro organisms (CFU ml^{-1})				<10	<1	<1	<1
COD (mg l^{-1})				<0.1	<0.1		
Silica (mg l^{-1})			0.5	0.1	0.1	<0.01	0.002
TSS (mg l^{-1})			<0.1	<0.1	<0.1	<0.1	ND
LSI	−1 to +1	−1 to +1					
Particle amount (n.q. ml^{-1})				1.0	1.0	1.0	0.1

4 New Trends in the Production of Regenerated Waters for Reuse

Potential contribution of regenerated water for the alleviation of stress on fresh water resources under water scarcity has been described in previous sections. Case studies considering the use of regenerated water contributing to the ecological flow in rivers, irrigation of farm areas or ameliorating salt intrusion problems in some delta aquifers can be found in the literature [3, 14–16]. However, industrial reuse potential is actually growing as these activities are increasing the water demand in Mediterranean countries, like Italy, Spain, France or others.

Multiple technologies are used to regenerate wastewater. The technologies are selected depending on the initial pollutant type and concentration, and treated water quality to be achieved. Stringent control of water quality and operational reliability are the main requirements which drive the technological choices.

4.1 Reuse of Secondary Treatment Wastewaters

One third of the water reclamation schemes rely on secondary treatment of municipal sewage. Municipal wastewaters are commonly treated by activated sludge systems that use suspended microorganisms to remove organics and nutrients, and large sedimentation tanks to separate the solid and liquid fractions. This level of treatment [17, 18], produces wastewater effluent that usually fulfils the requirement of cooling water in the industry, or irrigation water where the food crops are consumed after cooking [19]. The conventional activated sludge technology is being substituted by the so-called membrane bioreactors (MBRs), based on the combination of a suspended biomass reactor and separation step on porous membrane filtration. MBRs can produce high-quality effluent that is suitable for unrestricted irrigation and other industrial applications [20]. A MBR can also operate successfully where there are significant seasonal variations in load, for example tourist resorts, and can also be used to relieve overloading of existing sewage works [21]. In countries with limited water resources, the market for MBR technology is increasing considerably [15, 22].

4.2 Reuse of Regenerated Waters

Tertiary treatment is required often to meet the industry or irrigation standards, especially when disinfection is needed. This step is known as water regeneration. Typical tertiary treatment proposed in the literature [23] is composed of the following stages: low pressure membrane filtration (e.g., MF) followed by disinfection stage and finally high pressure membrane filtration (e.g., RO). Industrial quality standards and regulations for regenerated water reuse limit the presence of pathogens. Disinfection may be achieved by means of (1) chemical agents, e.g., chlorine and its compounds, ozone, hydrogen peroxide, and various alkalies, (2) physical agents, e.g., heat or sound waves and (3) radiation, e.g., ultraviolet irradiation [9, 24] and more recently advanced oxidation processes (AOP) such as electrochemical disinfection [25].

Chlorination, or the use of chlorine in various forms, is the most commonly practiced wastewater disinfection technology and is fully described in the open literature [24, 26]. Chlorination and chloramination are well-established technologies with well-known inactivation mechanisms and are relatively easy to apply and often less expensive than other alternatives, regardless of the size of the system. They provide a residual, which is useful for operational monitoring and control, as well as preventing growth in the distribution systems during reuse. Free chlorine is an effective biocide and virucide that may remove some emerging compounds of concern. Monochloramines are more stable and longer lasting than free chlorine, and have much less potential to form THMs, HAAs, cyanide and cyanogen chloride than free chlorine [27]. Considering water reuse processes, oxidizing disinfectants like chlorine may help to remove pharmaceutical and endocrine disrupting compounds (EDCs) which are of growing concern for the wastewater treatment industry [28].

Ozone can provide smaller footprint than chlorine in the treated water due to its rapid decomposition. Other advantages lie in the ability to inactivate parasites not previously inactivated by chlorination, and the absence of THMs and HAAs formation. This technology presents some disadvantages, like being more energy intensive and high capital costs and the risk of generation of disinfection by-products, some of which (e.g., bromate and aldehydes) are potentially harmful to human health. Due to these disadvantages ozone disinfection is less implemented than chlorination in conventional wastewater treatment plant (WWTP), but applications in industrial wastewater regeneration can be found in literature [29, 30].

Ultraviolet light (UV) is a valuable alternative for disinfection of treated wastewater because it forms no or very low levels of disinfection by-products. UV inactivation of microorganisms is considered to be a physical or biophysical process. The germicidal wavelength lies between 220 and 320 nm in the region of UV-B and UV-C [24]. The use of UV light in regenerated water disinfection either alone or combined with other disinfection technologies is increasing [31]. Pretreatment is needed in order to reduce turbidity, SS and some other industrial discharges that reduce UV transmittance causing ineffectiveness when UV disinfection is applied to wastewater [32].

AOPs are valuable tertiary treatments allowing not only inactivation of a wide spectrum of pathogens but also the removal of a great number of the so-called emerging pollutants (pharmaceutical, personal care products). These are not totally removed during conventional treatment, but remain in the wastewater effluents [33]. Among different alternatives electrochemical oxidation with born doped diamond electrodes (BDD) has been reported to be effective on eliminating a wide spectrum of microorganisms, although disinfection mechanisms have not been yet clearly identified [25, 34].

4.3 Membrane Separation Processes in Water Regeneration

Low pressure membrane processes of microfiltration (MF) and ultrafiltration (UF) are used for the removal of turbidity, pathogenic microorganisms and organic matter. MF refers to filtration processes that use porous membranes to separate suspended particles with diameters between 0.1 and 10 μm. UF uses a finely porous membrane to separate water and microsolutes from macromolecules and colloids. The average pore diameter of the membrane is 10–1000 A range [35]. MF and UF are mostly employed as pretreatments for wastewater desalination using reverse osmosis (RO) [36]. MF/UF systems for pretreatment comprise 35–40% of all pretreatment installations and they are expected to replace over 80% of the existing conventional/other pretreatment systems by 2012. These treatments are also the favorite technologies on sewage for the removal of suspended solids, particles, bacteria and parasites.

MF presents high efficiency eliminating turbidity and suspended solids but the MF effluent does not present standard characteristics for reuse in most industrial applications. So MF is usually used as UF pretreatment.

UF is increasingly used as a complete or intermediate water purification technique. Compared to conventional treatments UF offers several advantages such as: superior quality of treated water, a much more compact system, easier control for operation maintenance, fewer chemicals and less production of sludge [37]. UF membranes are attractive as a pretreatment prior to RO for regeneration of secondary treated sewage effluent, because permeate qualities are high and constant despite widely changing raw water quality [38]. UF is very efficient for removing different parameters, e.g., a noticeable elimination of suspended solids and turbidity is achieved; metals like Fe, Zn, Al, Cr, Cu and Mn are significantly eliminated; microbial pollution is totally eliminated; Fecal coliforms, total coliforms, fecal streptococcus, protozoan cysts (Giardia and Cryptosporidium), and even viruses are totally removed by UF [39–41]; reduction in the concentration of organic matter occurs when the organic fraction is mostly in the suspended form. No clear effect is produced on inorganic salts abatement, and consequently conductivity values are not affected by UF.

Avoiding and mitigating fouling related problems is one of the most important targets whenever membrane processes is considered in water regeneration research and development. A commonly used approach to mitigate fouling is feed pretreatment to remove/modify the components with high fouling potential [42]. The most usual pretreatment method in order to improve low pressure membrane performance includes prefiltration (MF) or others like chemical coagulation and anion exchange resins [43]. Chemical coagulation is widely used as a simple and effective means for the removal of particulates, colloids and high molecular weight organic

Table 2 Application of advanced technologies for water reuse in industrial activities, examples of R&D in countries facing water scarcity

Reference	Wastewater source	Proposed industrial reuse	Country	Technologies considered	Highlights
[29]	Poultry process	Poultry process	Greece	MBR/UF	Demonstrates the potential for the use of UF for recycling process wastewater and recovery of value added products
[59]	Digital textile printing (DTP)	DTP Direct discharge	Korea	Ozone/MF/RO	The proposed hybrid system met criteria of direct discharge or reuse
[60]	Secondary effluent from mechanical factory treatment plant	Plating wastewater reutilization	China	(MF/UF)/ED/(RO/NF)	New results of multiple membrane separation are presented, which showed a possible feasibility for industrial application in the near future
[61]	Wastewater from a cotton thread factory	Textile industry activities	Spain	UF/NF	The NF permeate obtained (membrane NF90) could meet specifications for water reuse in the textile industry
[62]	Effluent for a denim textile mill	Denim textile wastewater reuse	Turkey	Activated sludge/MF/NF	Demonstrates that NF after biological treatment can be applied to meet reuse criteria in denim textile wastewaters
[63]	Secondary effluent of a textile industry	Textile industry reuses	Spain	UF + NF UF + RO	The combined hybrid systems met criteria for reuse in the textile industry. Differences in performance are discussed
[12]	Industrial laundries wastewater	Rinsing and washing water in industrial laundries	Germany	MBR/RO	The high-quality of the reverse osmosis permeate meets the demands of the rinsing processes for industrial laundries
[64]	Car-washing wastewater	Carwash water	Kuwait	Separation tank/oil: water separator/filters	75% of the water can be recycled and reused for further local usages such as performing new carwashes
[65]	Print dying wastewater	Carpet manufacturing processes	Turkey	Different pretreatments/NF	A two stage process, optimum dose CP/NF successfully treated the print dying wastewaters of carpet manufacturing industry for the purpose of reuse
[66]	Olive mill wastewater	Water for irrigation and/or as herbicides	Greece	UF/NF/RO	More than 97% of colloidal particles were remove Fouling reduction found to be coagulant dependent

[67]	Food processing	Low and high pressure boilers	Egypt	Coagulation/UF/NF/RO	Reclamation objectives reached at laboratory scale. Preliminary techno-economic evaluation for 1,200 m^3 per day treatment plant concluded that the cost of the treatment of 1 m^3 wastewater was 0.22
[68]	Industrial park WWTP	Cooling and low pressure boiler applications	Taiwan	UF/RO	Process was suitable for the reuse of water in the desired industrial applications
[69]	Textile industry wastewater	Textile wastewater reclamation	Korea	Coagulation/UF	The final permeate is a clear transparent wastewater which may be disposed in landfills or used for irrigation without environmental risks
[70]	Pulp and paper wastewater	Paper production	Finland	Activated sludge/NF/RO	The reuse objectives were reached with the obtained regenerated water

materials from water and wastewater [44]. However three are some cases where coagulation has had negative effects on membrane performance [45, 46] Anion exchange resin has been used as a means of improving membrane performance by removing a significant faction of organic matter from drinking water sources [47] but few applications have been reported where anion exchange resins are used in wastewater treatment [43].

Several cleaning methods are used to remove the densified gel layer of retained material from the membrane surface. Alkaline solutions followed by hot detergent solutions are indicated for organic polymer colloids and gelatinous materials fouling. Ferrous deposits, typical in water treatments, are usually removed with a citric or hydrochloric wash. [35].

Backflushing is another way of cleaning heavily fouled membranes. During back flushing a slight overpressure is applied to the permeate side of the membrane forcing solution from the permeate side to the feed side of the membrane. The flow of solution lifts deposited materials from the surface. Typical back flushing pressures are 5–15 psi [48].

When high-quality water is required, an additional step apart from MF/UF treatment is necessary. High pressure membrane technologies, nanofiltration (NF), membrane pore size 0.001 μm, and RO, membrane pore size 0.0001 μm, appear as potential treatments which allow the obtention of high-quality water. RO results demonstrate the capacity of this technology for reducing and eliminating several parameters such as TDS, alkalinity, hardness, TOC, BOD_5, anions like chloride, nitrate, and phosphate, and different metals, like calcium, magnesium, chromium and iron in order to achieve ultrapure water quality for specific industrial applications [38].

Considering the high variability in the wastewater sources, the specific standards of the different industrial activities, and the broad possibilities that are technically available according to the state of the art, a combination of different centralized or decentralized technical solutions can be applied to reach the specific objectives when considering the local water cycle. The issue is not the availability of technology but the vision, experience and institutional infrastructure needed to recognize and implement reuse solutions. Table 2 compiles some representative examples of the R&D in reclamation strategies with industrial reuse purposes being developed in countries suffering some grade of water scarcity.

5 Industrial Reuse of Regenerated Waters. A Case Study

The viability of producing regenerated water for industrial reuse purposes by means of tertiary treatment of WWTP effluents is illustrated in this section, through examples in N Spain. The demonstration has been performed in Spain. The industrial activities in the selected region showed that the potential industrial demand of regenerated wastewater accounted for 5.2 $Hm^3\ yr^{-1}$ which could be obtained from WWTP facilities located 5 km away of the industrial consumers, after appropriate treatments. The uses of this water demand are cooling water (47%), process water (26%), cleaning water (26%) and vapor production (1%).

This case study defines the sustainable processes through the optimum combination of innovative and efficient technologies that after application to WWTPs effluents allow producing enough regenerated water that could be reused to satisfy the industrial needs. Suspended solids, turbidity, *E. coli*, intestinal nematodes, and *Legionella* are the main regulated standards, and the limits are defined as a function of the final industrial use of water, e.g., *E. coli* in Process and Cleaning Water (10,000 CFU per 100 ml); Process and Cleaning Water for Food Industry (1,000 CFU per 100 ml); Cooling Towers and Evaporative Condensers (0 CFU per 100 ml) [10].

5.1 Evaluation of WWTP Water Source

The WWTP *Vuelta Ostrera,* located within 5 km distance from potential industrial water reusers and designed on the basis of an equivalent population of 310,000 equivalent inhabitants (EI) that treats an average flow rate of inlet water of 109,382 m^3 per day has been selected for this demonstration. Table 3 shows average values of the physico-chemical parameters of the effluent from the secondary treatment. The data are average values from four mixed samples (collected during 24 h); in different seasons (spring, summer, autumn, winter) along 1 year. Data (Table 3) lie within the average range reported in the literature for similar characteristics WWTP in the Mediterranean Region [49–51].

As expected for a WWTP effluent, turbidity and *E. coli* are higher than the specific standards for industrial wastewater reuse included in the new Spanish Regulation of Regenerated Wastewater (RD 1620/2007). Other parameters, such as conductivity or TDS may result in too much high level considering some specific industrial uses of water [11]. Therefore further treatment of the WWTP effluent is needed before reuse.

Table 3 *Vuelta Ostrera* WWTP effluent characterisation

Parameter	Value Min.–Max.	Units	Parameter	Value Min.–Max.	Units
pH	6.6–7.6		TDS	268–738	mg l^{-1}
Temperature	12.0–20.0	°C	Salinity	0.3–0.6	$^0/_{00}$
Conductivity	495–1,485	μS cm^{-1}	Bicarbonates	61–262	mg l^{-1}
Turbidity	5.5–30.0	NTU	K	4.5–20.5	mg l^{-1}
TSS	1.0–42.0	mg l^{-1}	Ca	65–105	mg l^{-1}
COD	1.8–16.2	mg l^{-1}	Mg	12–14	mg l^{-1}
Chloride	33.1–114.0	mg l^{-1}	Silica	6.8–8.0	mg l^{-1}
Sulfate	52.1–140.4	mg l^{-1}	Alkalinity	125–225	mg $CaCO_3$ l^{-1}
Phosphate	0.7–8.6	mg l^{-1}	*Escherichia Coli*	1.3×10^4–6.9×10^5	CFU per 100 ml
Nitrate	0.5–1.1	mg l^{-1}	*Legionella*	<1.0	CFU l^{-1}

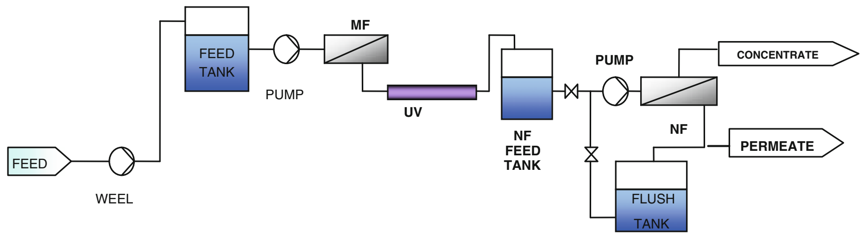

Fig. 1 Integral hybrid process flow diagram MF/UV/NF for regeneration of WWTP effluents

5.2 *Microfiltration, UV Disinfection, Nanofiltration*

Typical tertiary treatment proposed in the literature [23] is composed of MF, disinfection and high pressure membrane filtration (NF/RO). Figure 1 summarizes the flow diagram of a hybrid tertiary treatment combining the former technologies that can be used to obtain regenerated water from a WWTP effluent. The treatment includes removal of macro-pollutants by means of MF, followed by inactivation of *E. coli* in order to reach regenerated water standards (RD 1620/2007), and a final treatment by means of an advanced membrane technology in order to reach reuse standards for specific industrial uses like cooling and boiler feedwater [11].

5.2.1 Microfiltration Removal of Macro-Pollutants

Removal of macro-pollutants is a necessary pretreatment whatsoever disinfection is used. Suspended solids and turbidity reduce the efficiency of disinfection technologies like UV by reducing the light transmission through the solution [52]. Different technologies, like coagulation, sedimentation or filtration [53], can be used as pretreatment technologies. The performance of filtration though a 5 μm membrane module (Polygard, Millipore) is evaluated by the reduction of suspended solids concentration and turbidity.

Table 4 summarizes the efficiency of membrane filtration as preliminary treatment in the hybrid process to obtain regenerated water for industrial reuse. Working with the adequate cleaning cycle to avoid fouling and to keep a constant flux (10 l min^{-1}) important reduction in suspended solids (90%) and turbidity (60%) of the wastewaters is achieved but there is no significant reduction of other chemical or physical parameters, e.g., conductivity, alkalinity or TDS, or inactivation of *E. coli*.

5.2.2 UV Disinfection

Disinfection is a necessary step not only to reduce the *E. coli* concentration according to the regulation requirements but also to remove other pathogens non

Table 4 Efficiency of the hybrid system MF/UV/NF in the reclamation process of WWTP wastewater for industrial reuse

Parameter	WWTP effluent average value	MF effluent	UV effluent	Regenerated water average value	Average reduction (%)
Turbidity (NTU)	5.5–30.0	2.0–2.5	2.0–2.5	1.20–1.22	70–80
TSS (mg l^{-1})	1.0–42.0	<0.01		–	100
E. coli (CFU per 100 ml)	1.3×10^4–5.2×10^5	1.3×10^4–5.2×10^5	<100.0		99
TDS (mg l^{-1})	268–738	268–738	268–738	90–110	75
Conductivity (μS cm^{-1})	495–1,485	495–1,485	495–1,485	213–230	74
Salinity (‰)	0.4–0.6	0.4–0.6	0.4–0.6	0.1	75
Alkalinity TAC (mg l^{-1})	125–225	125–225	125–225	45–46	74.5

desirable in specific industrial uses and to avoid bio-fouling in membrane steps such as RO or NF, e.g., *Legionella* [54].

The use of UV light has been selected as disinfection agent in this case study. The advantages of this technique have been explained previously [27]. Total inactivation of the *E. coli* present in the WWTP effluent was achieved, as can be seen in Table 4 and pressure drop in the water line was increased in 0.1 bar.

5.2.3 Nanofiltration as Final Treatment Before Specific Industrial Reuse

The effluent obtained after solids removal and microbiological disinfection could be reused as cooling water, cleaning water or industrial process water in many industrial uses. A final polishing step may be necessary if higher quality requirements are needed in some specific industrial uses, e.g., cooling and boiler feedwater. Membrane processes such as NF or RO eliminate inorganic ions and reduce parameters like conductivity, alkalinity or salinity, etc.

The effluent from the disinfection step was flowed through a polysulfone spiral wound NF Pilot Plant with 0.7 m^2 of membrane (DSS TEST UNIT M20-0, 72-PSO, ALFA-LAVAL) working at room temperature and at 20 bar operation pressure.

Table 4 summarizes the efficiency of this hybrid MF/UV/NF process. Reduction of conductivity, turbidity, suspended solids and TDS was close to 100%. Conductivity values were reduced down to average values of 200 μS cm^{-1} while turbidity and TDS reached 1.2 NTU and 102 mg l^{-1} respectively. Thus, regenerated water could meet the standards for cooling and boiler feedwater [11].

Although certain variability in the quality of the WWTP effluent was found, regenerated wastewater by the selected process resulted of a good constant composition in the measured parameters, with important reduction of all the measured pollutants. Disinfection by UV achieved almost 100% of effectiveness in the destruction of microorganisms (*E. coli*). Conductivity, turbidity or TDS parameters

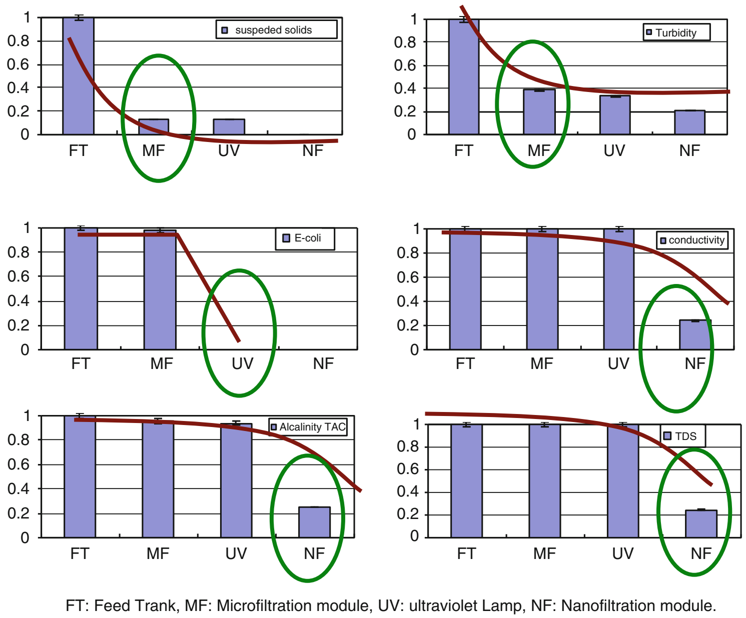

Fig. 2 Individual effect on the normalized concentration of selected parameters in the effluents for the technologies used in this study. *Red line* indicates the decreasing concentration evolution. *Circles* remark the most efficient technology in each target

were reduced up to 70% after NF treatment meeting the quality standards for different industrial uses even for cooling or boiling feedwater.

Figure 2 summarizes the individual steps in the proposed hybrid system showing the obtained reduction in normalized concentration (MF, UV, and NF) effluent. Figure 2 illustrates the concept of customized regeneration process according to the reuser needs.

5.3 Ultrafiltration and Reverse Osmosis

According to Lesli et al.[55]) and Lubello et al. [56], a combined membrane process using either MF or UF hollow fiber membranes followed by RO spiral wound membranes is recognized as a low cost alternative for municipal wastewater reuse plants. UF/MF ensures that significantly higher fluxes are obtained from the RO unit, with much less fouling, reduced chemical usage, and better on-stream time [36]. Regeneration of the effluent from a WWTP, *Vuelta Ostrera*, by means of a hybrid process UF/RO is illustrated in this section. Figure 3 represents a schematic diagram of the proposed regeneration system.

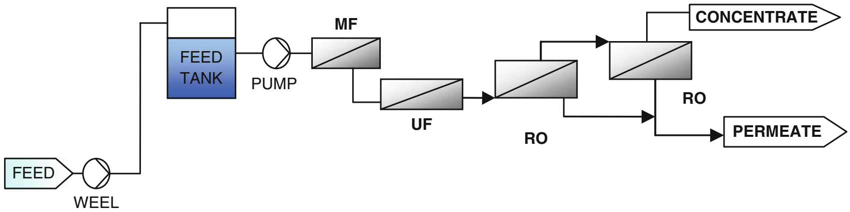

Fig. 3 Integral hybrid process flow diagram MF/UF/RO for regeneration of WWTP effluents

5.3.1 Ultrafiltration Pretreatment

Effluent pretreatment is necessary when RO is used as tertiary treatment in order to prevent membranes filters form being blocked or abraded. UF offers a powerful tool for the reduction of fouling potential of RO/NF membranes [57]. A typical pretreatment consist of a MF allowing the removal of the large suspended solids form the WWTP effluent followed by UF unit which removes thoroughly suspended solids, colloidal material, bacteria, viruses and organic compounds from the filtrated water. The UF product is sent to the RO unit where dissolved salts are removed.

A typical UF pilot plant has been used in this study. Examples of application for these membranes can be found in the literature [40, 58]. The UF unit woks in dead-end mode (2.5 $m^3\ h^{-1}$) and it can be operated in filtration, backwash and chemically enhanced backwash (CEB) modes as described in the literature for similar UF systems [40]. The specifications of the hollow fiber UF modules and the operating conditions are summarized in Table 5.

A 99% permeate recovery is obtained working under filtration mode although global recovery decreases down to 90–80% as permeate is used in backwash operation. The permeate quality of UF membrane and the efficiency of this stage are reported in Table 6. High-quality water ready to be used in many industrial applications and below regulation standards for regenerated water reuse (RD 1620/2007) is provided; e.g., turbidity and pathogens are fully eliminated. The former indicated the membrane had excellent performance for removal of pathogens and colloidal substances causing turbidity. The UF permeate was also suitable for feeding the RO unit.

5.3.2 Reverse Osmosis as Final Treatment for Industrial Reuse

A RO stage can be used to reduce salinity and related parameters for high standard industrial reuse using the former UF effluent as feed stream. A pilot plant with 0.4 $m^3\ h^{-1}$ constant permeate flux capacity has been used in this demonstration. Table 7 summarizes the main technical characteristics of this plant. In order to increase the overall system recovery ratio while maintaining an acceptable

Table 5 Membrane specifications and operation conditions for UF stage in WWTP hybrid process for industrial reuse water reclamation

Hollow fiber UF membrane specifications		UF pilot plant operation conditions		
Module	SLX-225 FSFC PVC	Parameter	Units	Value
Membrane	HDG 4000XF	Feed flow rate	$m^3\ h^{-1}$	2.5
Manufacturer	X-flow (Norit)	Backwash flow rate	$m^3\ h^{-1}$	25
Membrane material	PES/PVC	Backwash duration		
Pore size (μm)	0.02–0.0025	Forward flush	s	60
Fiber inner diameter (mm)	0.8	Air flush	s	10
MWCO (kDa)	150	Back flush	s	70
Membrane surface (m^2)	40 (per element)	Backwash frequency	m	45–60
Module length (mm)	1,537	CEB duration		
Module diameter (mm)	200	Flush	s	60
Capacity ($m^2\ h^{-1}$)	2–5	Chemical dosing	s	120
Membrane thickness (mm)	0.25	Soak period	m	15
		Chemical flush	n	2
		CEB interval	h	24
		TMP	mbar	0–400

Table 6 Efficiency of the hybrid system UF/RO in the reclamation of WWTP wastewater for industrial reuse

Parameter	Average concentration			UF efficiency	RO efficiency
	WWTP effluent	UF permeate	RO permeate		
Turbidity (NTU)	4–10	0	0	√	
TDS ($mg\ l^{-1}$)	30–500	30–500	3–7		√
TSS ($mg\ l^{-1}$)	5–15	0	0	√	
Bicarbonate ($mg\ l^{-1}$)	200	200	10–20		√
Conductivity ($\mu S\ cm^{-1}$)	600–800	600–800	5–30		√
Salinity (‰)	0.4–0.5	0.4–0.5	0		√
Total coliforms (CFU per 100 ml)	$0–10^6$	0	0	√	
E. coli (CFU per 100 ml)	$0–5 \times 10^5$	0	0	√	
Nematodes		<1		√	
Chlorine ($mg\ l^{-1}$)	0–1	0–1	0		√
SiO_2 ($mg\ l^{-1}$)	7–9	7–9	0		√
TOC ($mg\ l^{-1}$)	10–20	10–20	2		√

concentrate flow, a part of the concentrate stream is returned to the suction of the high pressure pump. Due to blending of the feed with concentrate stream, the average feed salinity is increased. Therefore, both the feed pressure and the permeate salinity are higher as well.

Table 6 shows the efficiency of the RO unit. 99.9% salt retention is reached; additionally reduction efficiencies of 99% for TDS, silica and conductivity, 95% for

Table 7 LFC1-4040 RO pilot plant characterization and working parameters

			Series configuration working parameters		
Type	Configuration	Spiral wound	Stream	Flow ($m^3\ h^{-1}$)	Pressure (bar)
	Material	Composite polyamide neutrally charged	1	0.80	0.0
	Membrane surface	7.905 m^2	2	1.20	0.0
	Nominal pore size		3	1.20	10.8
Performance	Permeate flow	8.7 m^3 per day	4	0.86	10.5
	Salt rejection (minimum)	99%	5	0.40	0.0
Application data	Maximum applied pressure	41.6 bar	6	0.46	0.0
	Maximum operating temperature	45°C	7	0.34	0.0
	Feed water pH range	3–10			
	Maximum feed water turbidity	1 NTU			

Details from Nitto Denko Hydranautics data sheet

bicarbonates, 81% for COT are achieved. Considering the former average removal efficiencies of 100% for turbidity, TDS, total coliforms and *E. coli* obtained with the UF unit, it is concluded that the hybrid UF/RO process can provide a reliable tool for the use of WWTP as regenerated water source for industrial reuse.

6 Conclusions

The capability of advanced technologies in the production of regenerated water for industrial reuse has been illustrated in this chapter. The reuse of regenerated water in industrial activities has been demonstrated as an effective tool for sustainable industrial development under water scarcity conditions as it can provide a big deal of the large amounts of water needed in those activities and moreover it can customize the regenerated water characteristics to the water standards required in different industrial activities by means of adequate combination of available advanced technologies.

The opportunities offered by the state of the art in the development and application of advanced technologies for water reclamation have been presented and illustrated by means of a general example representative of the ability of using WWTP effluents as regenerated water source by means of combination of advanced technologies.

Although certain variability in the quality of the WWTP effluent was found, regenerated wastewater by the selected process resulted of a good constant composition in the measured parameters, with important reduction of all the pollutants considered. Selection of the most suitable combination of advanced technologies should be addressed taking into account the final reuse needs.

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Decision Support Systems for Integrated Water Resources Management Under Water Scarcity

Joaquim Comas and Manel Poch

Abstract Environmental decision support systems (EDSS) can be defined as intelligent information systems that are able to integrate numerical models (linear or nonlinear) with artificial intelligence (AI) techniques, together with geographical information and environmental ontologies. EDSS emulate the expert's reasoning processes in decision making, integrating geographical information and environmental ontologies, reducing the time in which decisions are made, as well as improving the consistency and quality of those decisions. EDSS can be useful to cope with the complexity and multidisciplinary nature of Integrated Water Resource Management (IWRM). Besides, the Drought Management Plan Report written by the Water Scarcity and Droughts Expert Network (November 2007) states the "Development of decision support systems for the best exploitation of all information available, including drought forecasts, in order to optimize drought management and mitigation measures" as one of the main needs for advances in drought research. The necessity to confront complexity when dealing with IWRM is first stated in the paper. Then an EDSS as a promising tool to cope with this complexity is introduced, putting special emphasis in a proposal for EDSS development. Next the paper reviews the more relevant decision support systems (DSS) published for IWRM under water scarcity. Classical DSS to model environmental systems as well as those DSS including knowledge-based or AI techniques (i.e., EDSS) are reviewed. Open questions related to the EDSS development and

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application include improvement of data and knowledge acquisition and knowledge implementation methods, better integration of numerical models and AI techniques (both in simulation and real applications), evaluation of EDSS (lack of benchmarks), protocols to facilitate sharing and reuse of knowledge, involvement of end-users, and probably others.

Keywords Decision support systems, Integrated water resources management, Water scarcity

Contents

1 Complexity in Water Management

> “(regarding water management)... today a linear approach is not useful anymore. It is not helpful to look for a solution for each problem.”
> F. Baltasar. Ministry of Environment, Catalan Government.

Water scarcity is defined as a situation where insufficient water resources are available to satisfy long-term average requirements. It refers to long-term water imbalances, where the availability is low compared to the demand for water, and means that water demand exceeds the water resources exploitable under sustainable conditions.

Like any other environmental problems, dealing with integrated water resources management (IWRM) under water scarcity is not simple. There are at least five important factors for this complexity:

- *Temporal dynamics*. Processes take place in different time scale and dynamics:

  - Minutes/hours: for example, storms affecting sewer systems, punctual discharges, river flow rate variations due to hydroelectric plants, residence time in a WWTP, etc.
  - Days/weeks: for example, algal growth, variations of water demand, news on newspapers, residence time in a river flow, etc.
  - Months/years: elicitation of works, percolation of spills into the soil, WWTP building/upgrading, annual rainfall regime, etc.
  - Several years: large infrastructures, aquifer recharges, settlement of new water cultures, climate change, etc.

  While some of these dynamics are natural, others are due to technological systems, or to cultural/social behavior or changes. While some of them can be described with high precision (e.g., fluid dynamics in a pipe or WWTP efficiencies), others can be approached (e.g., prevision of water demand) or estimated with low precision (e.g., rainfall regime of next years).
- *Spatial scale variability.* According to the "Water scarcity and droughts expert" network (1), the development of a drought plan (linked to the River Basin Management Plan) should be done at different levels. At national level, the focus should be on policy, legal, and institutional aspects. National level measures should determine drought onset conditions through a network of global basin indices and indicators at the national or regional level. Plans at the river basin scale are mainly intended to identify and schedule onset activation measures to delay and mitigate the impacts. At the local scale, tactical and response measures to meet and guarantee essential public water supply as well as awareness measures are the main issues. It is important to notice that interactions between these scales are becoming increasingly clear. Therefore, advocating a single perspective that encompasses everything in a system is becoming increasingly difficult as well as ineffective. Moreover, each River Basin is a unit (according to the Water Framework Directive, WFD) and has its own pluviometric, hydrologic, and water demand behavior and the interrelation among River Basins has to be considered: definition of limits for each management unit, analysis of its problems (pressures and impacts) and where they take place, identifying the programme of measures and where to apply them and considering the interrelation among River Basins.
- *Uncertainty, or approximate knowledge.* Decisions in this field imply high uncertainty. Water scarcity (especially in a Mediterranean climate) is characterized by a variable natural dynamics, and on top of this uncertainty, interactions between bio-geophysical and social phenomena need to be integrated. Ecological theory has been mostly developed in pristine or undisturbed systems, while the intricate ways in which humans interact with ecological systems have been seldom considered. Some of the sources of this uncertainty can be corrected with additional data or further investigation. Such is the case of uncertainty arising from random processes or from deficiencies in knowledge (lack of data, unsuitable datasets, etc.). However, in other cases uncertainty is insurmountable. This is the case of socio-ecological systems like the one being considered, where numerous agents are involved, each with their own goals.

- *Involvement of different agents/stakeholders.* Integrated water resources management requires the participation of several agents, from the water administration at different levels (which not always are in agreement), the civil society (with different type of organizations, ecologists, farmers, scientists, etc. as can be stated in the Council for Sustainable Water Use, CUSA in Catalonia), the mass media and, according to the WFD, a new one, “the receiving media”, which can have quite different interests than all the others. The coordinating agent in Catalonia is the Catalan Water Agency (ACA), responsible for collecting information and knowledge, digesting and processing it, proposing the River Basin management plans (including the programme of measures), reasoning and reaching agreements on them, and finally applying them.
- *Need of sustainable management (ecological, economical, and social).* There is a need for sustainable water resources management, but this can also be the most difficult to recognize. Management should be respectful with the environment, but not at any economical and social prize; economically affordable, but not at any environmental and social cost; and finally, must seek for social equity (personal and territorial), but not at any environmental and economical cost. Besides there is an interrelation among the different problems related to IWRM, each problem can have different causes and each solution may affect to different problems.

To include these factors in the proper management of water scarcity, it must be considered in terms of complex systems. However, not all environmental systems present the same level of complexity in terms of the degree of uncertainty and the risk associated with decisions.

- The *first level* of complexity corresponds to simple, low uncertainty systems, where the issue to be solved has limited scope. Single perspective and simple models would be sufficient to warrant with satisfactory descriptions of the system. Regarding water scarcity, this level corresponds, for example, to the description of precipitation using a time-series analysis or a numerical mathematical model to analyze water consumption evolution. In these cases, the information arising from the analysis may be used for more wide-reaching purposes beyond the scope of the particular researcher.
- The *second level* involves systems with uncertainty, where simplified models no longer provide satisfactory descriptions. Acquired experience then becomes more and more important, and the need to involve experts in problem solving is advisable. In the case of water scarcity, this level would correspond to a general model of water infrastructures management (reservoirs, water reuse...), where the need to establish which factors are the most important arises. In this case, the goals for the quality of the output are well established, but these can be reached through different schemes, and it is the responsibility of the decision maker to choose the most appropriate configuration.
- The *third level* corresponds to truly complex systems, where much epistemological or ethical uncertainty exists and where uncertainty is not necessarily associated with a higher number of elements or relationships within the system. Moreover, the issues at stake reflect conflicting goals. For this reason it is crucial to consider

the need to account for a plurality of views or perspectives. Here, a variety of factors (economical, technical, ecological, etc.) are involved, and associated with each factor is a different set of criteria. Thus, different kinds of expertise need to be taken into account. In addition to the role of the experts, it becomes increasingly important to consider the role of widespread public participation in the decision-making processes. Policy makers, the media, and the public consult experts at large explain and advise on numerous issues. Nonetheless, many recent cases have shown, paradoxically, that while expertise is increasingly sought after, it is also increasingly contested.

Nowadays, a consensus exists that problems belonging to the second and third level cannot be tackled with traditional management tools. Required solutions should be able to face the complexity, describe the interrelationships and the side effects. To confront this complexity, a new paradigm is needed and its adoption will require that we deal with new intellectual challenges. We need tools allowing integrating data and experience to include results from different fields, different experts, different levels of description; to retrieve all the information and knowledge collected in an easy way, as different alternatives will be evaluated; and to justify the proposals, indicating what and who is supporting each one and what are the environmental effects. The environmental decision support systems (EDSS) are examples of the tools required by this new paradigm.

2 EDSS: A Promising Tool

EDSSs have generated high expectations as a tool to tackle problems belonging to the second and third levels of complexity. From the seminal work done by Guariso [1], Rizzoli [2], and Soncini-Sessa [3], there has been an impressive increase of relevant literature in the topic. The range of environmental problems to which EDSSs have been applied is wide and varied, with water management at the top (25% of references), followed by aspects of risk assessment (11.5%), and forest management (11.0%). Equally varied are the tasks to which EDSSs have been applied, ranging from monitoring and data storage to prediction, decision analysis, control planning, remediation, management, and communication with society.

Like any new methodology, there is a wide range of opinions about what constitutes an EDSS. As this approach is relatively recent and integrates multiple tools means, there is not a single, consensual definition of EDSS. However, even though one may argue that a database management system could be used as a decision support system (DSS), today's consensus is that EDSSs must adopt a knowledge-based approach, which includes the steps of knowledge acquisition, representation, and management. Furthermore, the fact that different tools can be integrated under different architectures makes EDSSs difficult to define. It also means that different approaches to design and implementation coexist.

According to Fox and Das [4], a DSS is a computer system that assists decision makers in choosing between alternative beliefs or actions by applying knowledge about the decision domain to arrive at recommendations for the various options. It incorporates an explicit decision procedure based on a set of theoretical principles that justify the *rationality* of this procedure.

Thus, an EDSS is an intelligent information system that reduces the time in which decisions are made in an environmental domain and improves the consistency and quality of those decisions. Decisions are made when a deviation from an expected, desired state of a system is observed or predicted. This implies a problem awareness that in turn must be based on information, experience, and knowledge about the process. Those systems are built by integrating several numerical models (linear or nonlinear, including or not differential equations) with artificial intelligence (AI) techniques, which emulate the reasoning processes of experts, geographical information system components, and environmental ontologies [5].

2.1 A Procedure for EDSS Development

How a particular EDSS is constructed depends on the type of environmental problem and the type of information and knowledge that can be acquired. Keeping these constraints in mind and after an analysis of the available information, a set of tools can be selected. This applies not only to numerical models, but also to AI methodologies, such as knowledge management tools. The use of AI tools and models provides direct access to expertise, and their flexibility makes them capable of supporting learning and decision-making processes. Their integration with numerical and/or statistical models in a single system provides higher accuracy, reliability, and utility. This confers EDSSs the ability to confront complex problems, in which the experience of experts provides valuable help for finding a solution to the problem. It also provides ways to automatically accelerate identification of the problem and to focus the attention of decision-makers on its evaluation. Once implemented an EDSS (like any knowledge-based system), it has to be evaluated for what it knows, for how it uses what it knows, for how fast it can learn something new, and finally, for its overall performance. Figure 1 shows schematically the methodology proposed by our research group, which has been successfully applied to different water management problems (see, e.g., [6–12]).

The methodology illustrated in Fig. 1 involves five phases: (1) environmental problem analysis, (2) data collection and knowledge acquisition, where different sources are consulted and a plurality of views are integrated, (3) model selection, among different mathematical, statistical, and AI techniques, (4) model implementation and integration, including the knowledge representation and knowledge codification steps, and (5) validation process, an iterative process carried out along all the development phases to verify robustness, accuracy, usefulness, and usability of the EDSS.

The existing tools to carry out an IWRM may include hydraulic and hydrological models, water quality models as well as knowledge bases containing the necessary knowledge for the optimal management of water resources. Besides, these tools

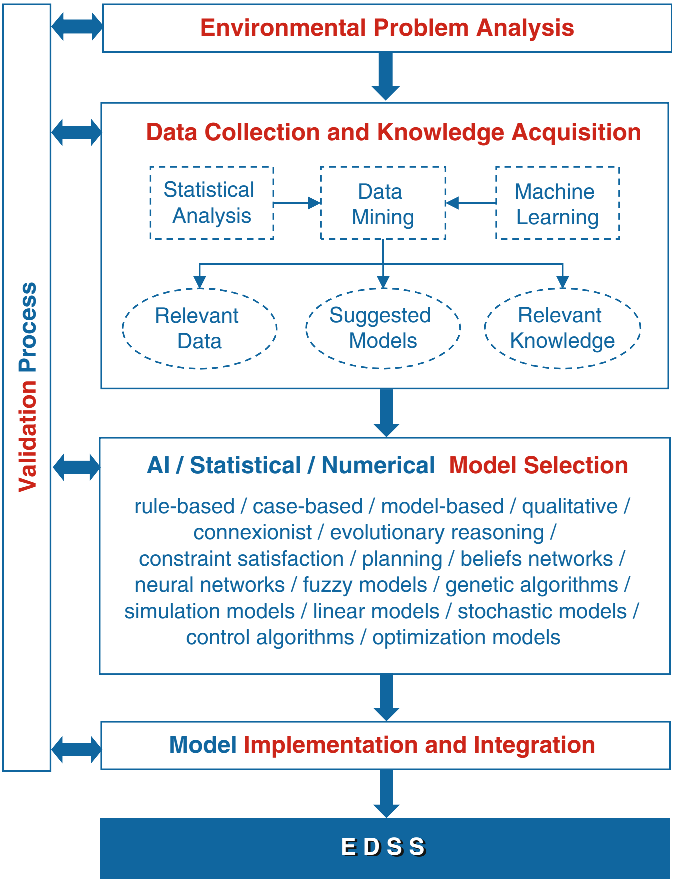

Fig. 1 Flow diagram for the development of an EDSS

have usually GIS functionalities, connectivity with databases, supervisory control and data acquisition (SCADA) systems, monitoring and forecasting systems, etc. Those tools including only mathematical models or GIS information have been classified as "classical DSS" and explained in Sect. 3, while others including at least a combination of mathematical models, GIS data, and AI techniques will be called EDSS and summarized in Sect. 4.

3 Classical DSS for IWRM

Classical DSS to carry out IWRM are based on numerical or mathematical models and GIS functionalities.

3.1 DSS for the WRM Based on Quantity Criteria

Koutsoyannis et al. [13] describe a tool composed of a hydrologic model and an optimization module for the WRM in Athens. Schlüter et al. [14] developed a mathematical model that provides the optimal distribution of water resources among users with different interests. It is based on the EPIC (from Environmental Policy and Institutions of Central Asia) modeling system. Kunstman et al. [15] demonstrates that a DSS integrating atmospheric and hydrologic models supports the decision making in catchments where meteorological data is scarce. Their tool provides spatial and temporal information of the water fluxes at quasi real time at the Volta River Basin.

3.2 DSS for the WRM Based on Quality Criteria

Maia and Silva [16] developed and applied to the Algarve region (Portugal) a DSS tool having as major purpose the sustainable management of the water resources existing in the whole region. Different strategies (combinations of water management options) were defined and evaluated using the DSS tool, aiming at minimizing the existing and foreseen water deficits in the region, having in mind the requirements specified by the Water Framework Directive. A performance assessment of strategies and an economic analysis embracing direct and environmental costs computed by the tool do enable selection of strategies. Six main modules form the main core of the program: the water availability module (based on time series of aquifers and reservoirs inflows), the water demand module (which generate hypothetical demand scenarios), the allocation module, the water quality module, the economic analysis module, and the evaluation module to facilitate the comparison of the different strategies simulated.

CatchMODS integrates different sub-models to estimate hydrological parameters, nutrient transport, and algal blooms together with spatial data [17]. Minciardi et al. [18] proposes a decision support model based on mathematical and optimization techniques for the integrated water resources management, specifically for the planning and management of groundwater.

The Elbe-DSS enables to perform an integrated management of the Elbe River Basin with different tools to carry out water policy at different temporal and spatial scales. The specific objectives of this tool are to get a good chemical, hydro morphological, and ecological status of the water surface and evaluate the flooding risks. The Elbe-DSS integrates existing mathematical models such as MONERIS for nutrient diffuse and point source pollution and GREAT-ER for more problematic compounds [19].

A DSS tool for the dissolved oxygen real time monitoring integrating the HIDRO (for hydrodynamics) and QUAL (for the description of conservative and nonconservative parameters) has been developed for the river San Joaquín in

California [20]. It is used to improve the coordination among the different institutions that are directly benefited from the water resources of the fluvial system. Vandenberghe et al. [21] presents a tool based on complex models for the description of river water quality.

Other generic tools for the efficient management of water resources, some of them commercial, include MIKE BASIN (from DHI), Infoworks WS (Walllingford Software), WASP (EPA), Aquatool (from the Technical University of Valencia), or MODFLOW for 3D modeling of groundwater. Devesa et al. [9] present an integrated model for the management of sanitation infrastructures based on Infoworks WS, GPS-X (software simulator for WWTPs), and Infoworks RS.

The work of Matthies et al. [22] collects the current issues, methods, and tools for DSS, and that of Argent et al. [23] describes a DSS generator within which users are able to select and link models, data, analysis tools, and reporting tools to create specific DSS for particular problems, and for which new models and tools can be created and, through software reflection (introspection), discovered to provide expanded capability where required. This system offers a new approach within which environmental systems can be described in the form of specific DSS at a scale and level of complexity suited to the problems and needs of decision makers.

4 Existing or Proposed EDSS for IWRM

Chen et al. [24] provide a good review of AI techniques used for modeling environmental systems. Pongracz et al. [25] presents the application of a fuzzy-rule based modeling technique to predict regional drought. Artificial neural networks model have been applied for mountainous water-resources management in Cyprus [26] and to forecast raw-water quality parameters for the North Saskatchewan River [27].

Genetic algorithms have been applied for optimization and calibration, for example, optimization to explore water management options in irrigated agriculture [28] and in a framework for modeling water quality in streams and rivers using QUAL2Kw [29].

A multiagent system (MAS) comprises a network of agents interacting to achieve goals. In the last years they are becoming more popular, for example, Pahl-Wostl [30] proposes a MAS for information, public empowerment, and management of urban watersheds, and Becu et al. [31] introduce an agent-based simulation of a small catchment water management in northern Thailand (the CATCHSCAPE model).

Any colony optimization (ACO) and swarm intelligence are forms of agent-based modeling inspired by colonies of social animals such as ants and bees [32]. ACO has become popular in engineering for optimal routing in water distribution systems [33, 34]. Particle swarm optimization has been successfully used to train ANNs, for instance, ANNs to predict river water levels [35], for parameter estimation, for example, in hydrology [36].

Rizzoli et al. [37] propose the application of neuro-dynamic programming for the integrated water resources management. This approach, although faster than stochastic models, is still under study for real applications.

Bayesian networks can be very useful to reproduce reasoning under uncertainty conditions in a consistent and efficient way. These networks provide a graphical representation of the relationship among variables and quantify these relationships by means of probabilities. Castelleti and Soncini-Sessa [38] provide an example of integrated and participative management of water resources by means of Bayesian networks. Aiming at facilitating public participation and discussion among participants, Giordano et al. [39] also propose the development of an *Integrated Decision Support System for Consensus*. Besides mathematical models, they use cognitive maps, fuzzy logic, and other natural language-based knowledge representation techniques.

Regarding specific applications, the MULINO (Multisectorial, integrated, and operational DSS for the sustainable use of water resources at catchment scale) is a DSS that integrates hydrological models and algorithms for decision support within the DPSIR (driving forces-pressure-state-impact-response) framework, enabling the cause–effect relationship among the different components of the environmental, economical, and social systems to be evaluated, and supports in organizing the information flows [40]. The model RIBASIM is the central part of the tool developed to manage water resources and water demand at the Heihe river basin (China). The model includes information from water infrastructures, users, hydrological models, and optimization rule-based models for water resources assignment [41].

There are some examples of EDSS tools combining two AI techniques, for example, genetic algorithms and neural networks for water-quality management [42], rainfall–runoff modeling [43], fuzzy systems and neural networks for predicting groundwater vulnerability [44]. Others describe optimizing water allocation [45], case-based reasoning systems and rule-based systems for wastewater management of conventional systems [6, 8, 10, 11, 46–50], and natural systems [12, 51] or fuzzy systems and genetic algorithms for modeling rainfall [52] and calibrating a rainfall–runoff model [53]. Different AI techniques such as neural networks, genetic algorithms, and intelligent control are also used recently for the modeling and management of rain water reservoirs in real time [54].

4.1 EDSS for IWRM in Catalonia

The management water plan of the Catalan Water Agency and previous works [7, 55, 56] have been used to develop an EDSS for integrated water resources management (EDSS-4IWRM). Its objective is to integrate a set of measures of the different specific plans to show that all the proposed measures are able to achieve the water quality objectives. The general scheme of this EDSS is showed in Fig. 2.

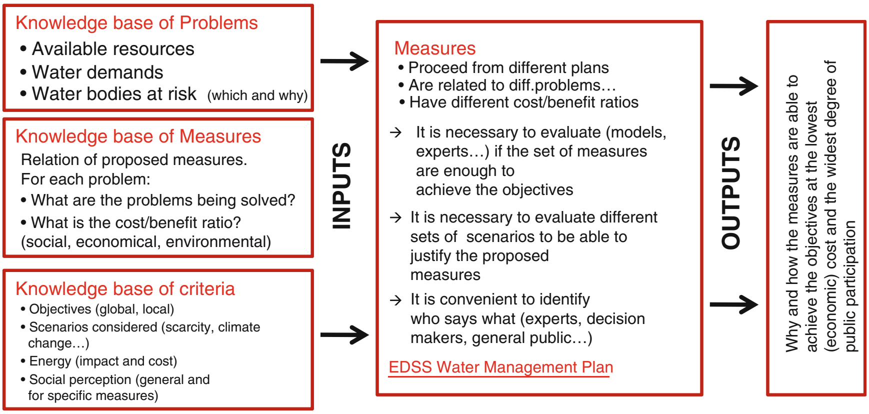

Fig. 2 General scheme of the EDSS under construction for water resources management

Problem analysis step has enabled to identify three levels for the building process of the EDSS-4IWRM:

- Level 1: For each River Basin, identification of the existing problems and their possible causes (the same problem can be originated for more than one cause). For example, the problem "*No demand satisfaction*" can be caused by water transfers, surface water and groundwater extraction, agricultural and farm activities (water pollution), a lack of urban and industrial wastewater treatment, Combined Sewer Overflows (CSOs), etc.
  - Base documents/Studies: DPSIR document (for general problems) and participatory processes (for very local problems).
- Level 2: Identification of the programme of measures to solve each problem or to regulate the responsible activities. It should be looked for the broad relationships among problems–causes–measures. A justification of how each measure can solve a problem should be provided.
  - Base documents/Studies: Guide document to write the water management plan, other plans and programmes being executed/under revision and planned/pending by the Catalan Water Agency (e.g., urban and industrial WWT programmes, drought management plan, water reuse plan, water distribution plan, surface and groundwater quality control programme, etc.), and related regulations.
- Level 3: Quantification of the improvements experienced by each of the water bodies, after the application of the planned measures within the programme and plans.
  - Planned tools/methodologies: Computer programs to simulate the evolution of the water resources and the water quality and interviews with experts to represent/quantify relationships.

5 Discussion

Water scarcity management is one of the critical domains where wrong management decisions may have important social, economic, and ecological consequences. What an EDSS contributes is not only an efficient mechanism to find an optimal or suboptimal solution, given any set of whimsical preferences, but also a mechanism to make the entire process more open and transparent. In this context, EDSSs can play a key role in water scarcity management, as they are tools designed to cope with the multidisciplinary nature and high complexity of environmental problems. EDSS can be useful to cope with the complexity and multidisciplinary nature of Integrated Water Resource Management because of the following:

- Reduce the time in which decisions are made
- Improve the consistency and quality of the decisions
- Allow integration of different modeling techniques and different type of knowledge
- Provide direct access to experience, expertise, and human-kind reasoning
- Capability of supporting learning capabilities and decision making processes in complex situations
- Allow the evaluation of different management strategies

As has been illustrated previously, the number of DSS references has increased considerably during the last years (154 references found in Scopus). Among those only a limited but increasing number of references include AI techniques, that is, can be considered EDSS. Besides, the number of DSS references related to IWRM under water scarcity situations is even lower, thus, indicating that there is still a clear need for decision support tool under water shortage periods. Figure 3 illustrates the number of references appearing related to DSS and EDSS during the last years.

Another significant point raised in Fig. 3 is that the number of references related to the development of DSS to carry out an *integrated* water resources management is very scarce before 2000s, that is, when the WFD, which emphasizes integrated management as one of the key concerns in river basin management, was launched.

In recent years, the needs for integrated approaches to water resources management and linking of water management to land uses have been stressed in many international and national fora. As water sustains life, effective management of water resources demands a holistic approach, linking to social and economic development focusing on the protection of natural ecosystems and the environment in general. An integrated water management is necessary to consider all the aspects related to water resources in their full complexity and mutual interaction, including activities such as economic development, flood control, water conservation, pollution control, conservation and restoration of ecosystems. A special issue of *Desalination* on water resources management [57] contains a number of selected papers that cover a wide range of applications including risk assessment, economics, management, and modeling.

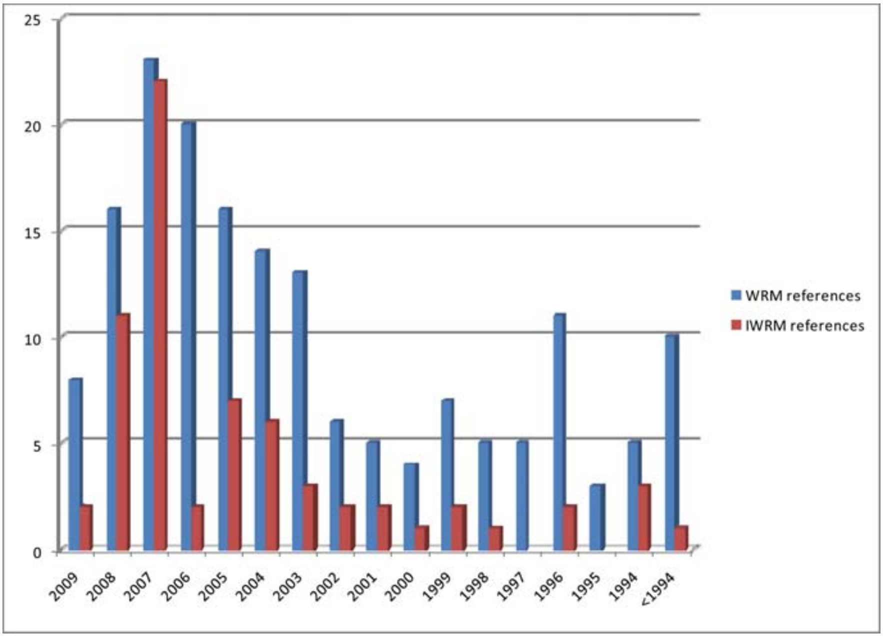

Fig. 3 References related to DSS and EDSS for water resources management

It is also important to emphasize that the risk for the development of DSS unsuccessful to solve problems of the real word is quite high. Some aspects that have to be considered when looking for DSS successful include the following [58]:

- The involvement of the final users in the conceptual design phase and during the whole development phase is crucial [40]. Users are often not able to specify all their expectations and requirements during the first stages of the system development, but periodic and continuous revisions of evolved prototypes allow them to evaluate and contribute to the improvement
- The easiness of the DSS to explore the problem at hand, to derive possible solutions, and discover and analyse the cause–effect relationships
- A user-friendly interface
- Other aspects such as the quality of the data, the model precision, and the number of possible alternatives presented to the user as possible solutions of the problem or the degree of confidence of the final user on the DSS

6 Further Research in EDSS for Integrated Water Resources Management

The *Drought Management Plan Report* written by the Water Scarcity and Droughts Expert Network (November 2007) recommends “Development of DSS for the best exploitation of all information available, including drought forecasts, to optimize drought management and mitigation measures" and "Improvement of the monitoring, modeling, and prediction capacities" as two of the most important needs for advances in drought research.

Despite the fact that EDSS have been successfully used to solve complex environmental problems, it seems clear that more research is needed in this area. From our experience during last years, we have identified the still open questions in the development and application of EDSS. It can be foreseen that the research bottlenecks for EDSS for water scarcity and integrated water resources management should be focused on the following issues:

6.1 Integration of Several Sources of Data and Knowledge (Numerical Models and AI Techniques, Both in Simulation and Real Applications)

Integration of various sources of knowledge, intelligent techniques, and numerical tools is the key step to develop successful EDSS for environmental problems. Intelligent decision-making requires, either implicitly or explicitly, a model of the world that embodies both prior knowledge and measured data. At the level of data and background-information, numerous and often incompatible bits of information from disparate sources have to be brought together. At the level of tools, there are several levels of integration, ranging from simple file transfer between different methods and programs to fully integrated systems. Typical examples of different methods that lend themselves to integration include geographical information systems and models as well as rule-based systems, models, and databases, algorithmic models and intelligent reasoning systems, simulation and optimization models.

6.2 Improvement of Data and Knowledge Acquisition and Knowledge Implementation Methods

EDSSs use different knowledge sources and this usually implies different ways of representing, extracting, and combining information. The nature of the problems that EDSSs try to solve makes the knowledge acquisition step a crucial one. For most of the problems there exist huge quantities of data coming from the process, but the information about the causal or dependence relations among variables is not well known. In many cases, AI tools are used to discover those relationships.

A possible solution to integrate and share information about knowledge structures is to build and use ontologies. This task is only starting to be generally recognized as a key issue in environmental fields. Ontologies could be used to assess and evaluate the knowledge about a certain topic or situation with the goal of informing decision-makers. Ontologies can give answers to some of the following questions: What is known and with what degree of certainty? What is not known?

What is the relevance of that knowledge to decision-makers? Construction of specific ontologies or equivalent paradigms could represent better the *know-how* and *know-what* in environmental systems.

6.3 Elaborate Protocols to Facilitate Sharing and Reuse of Knowledge

Once an EDSS has acquired information about a complex environmental process, which are the available ways to share that information with other systems? If EDSSs are designed to be cooperative, under which conditions does this cooperation occur? What happens if cooperation fails? Who will assess the quality of the exchanged information? Who will harmonize indicators and exchange protocols?

Solutions for sharing knowledge in environmental processes are far from being fully developed, but one has to consider the great variety of data and the strong dependencies of environmental processes to local constraints, such as weather conditions, climatic aspects, geographical positions, environmental or health law regulations, etc. If specific models are to be developed for environmental problems, greater generality, precision (when possible), and realism will be required.

6.4 Involvement of End-Users in EDSS Development

In general, the role of the user in EDSS development is still poorly defined. These systems are developed to support users' decision-making activities in highly complex problems.

The following questions are still to be answered: to what extent can an EDSS be modified directly by *any* user? Who should decide that an EDSS has to start a learning process? Who has to validate the results of such process? Why should an EDSS start a learning process? Who is legally responsible for the decisions made by an EDSS?

We propose, as a first approach, the creation of user profiles with different privileges and responsibilities in the interaction with the EDSS. This will lead to the definition of different levels of interaction between the user and the EDSS.

On the other hand, users must be involved in the whole process of EDSS design and development to ensure the usability of the final system. The degree to which users become involved in EDSS development will determine their level of confidence in the final system. In the worst case, the system might remain unused.

6.5 Development of Benchmarks for the Validation of EDSS

One of the most promising research lines in EDSS development is the definition of benchmarks to assess and evaluate the performance of EDSSs in a set of well-defined circumstances and their capacity to react to new situations. This will also allow the creation of a better framework for comparison between EDSSs. This validation of an EDSS in the appropriate context may simplify the tuning tasks and help to enhance the system's performance.

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Water-Borne Infectious Disease Outbreaks Associated with Water Scarcity and Rainfall Events

Juan Jofre, Anicet R. Blanch, and Francisco Lucena

Abstract An important number of major infectious diseases are related to water. The greatest consequences for the human population are the faecal-oral water-borne infectious diseases, which are transmitted by ingestion of the causal agents that are released into water through faeces. The occurrence of outbreaks of water-borne infectious diseases could be affected by water scarcity at different degrees depending on the level of water scarcity, density of population, degree of economical development, presence in the area of wild and farmed animals, etc. Still, at least in developed countries the laws and regulatory programmes regarding water quality cope with most of the problems and generally protect the population, even when scarcity obliges use of non-conventional water resources. Weather conditions influence the fate of pathogens in the water environment. Indeed rainfall favours their dissemination, and natural stressors – such as temperature and solar irradiation among others – determine their persistence. At present, heavy rain events rather than water scarcity are the main cause of failure of protective measures in developed countries. This situation is likely due to an increased dissemination of the pathogens that have survived the deleterious effects of natural stressors. Higher frequency of drought followed by heavy rains, as forecasted in Mediterranean climate areas, will likely increase deficiencies in watershed protection, infrastructure and storm drainage. Consequently, the risk of contamination events of the water resources will be greater than before. This combination of factors might also increase the failures in the drinking water treatments, and subsequently the occurrence of water-borne infectious disease outbreaks. A better knowledge about the origin, survival and transport of water-borne pathogens in the water environment is a key factor for predicting risks and taking measures to minimize them. Unfortunately in many developing countries, the quality of water for consumption is still very poor independently of whether there is scarcity or abundance of water.

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Measures to improve the present situation are urgently needed. These measures could be optimized by considering the influence of weather conditions on survival and transport of the microorganisms of faecal origin.

Keywords Indicators, Infectious diseases, Pathogens, Rain, Water scarcity

Contents

1 Introduction

The available water resources are linked to human health in several ways: water for drinking, hygiene, recreational activities and food production. As water resources decrease as a consequence of droughts or increased demand, the need to use water sources of poor quality appears, and consequently the risk of an increase in the occurrence of outbreaks of infectious diseases related to water can be higher.

However, the laws and regulatory programmes regarding water quality cope with most of the problems and legislation generally protects the population in developed countries, even when scarcity forces the use of non-conventional water resources. Outbreaks of water-borne diseases in these countries are more linked to intense rainfall events, mostly to those that follow drought periods, rather than to drought itself [1–4].

In contrast, the situation is potentially different in developing countries [5–8] including those of the Southern and Eastern Mediterranean Regions [9–12] where water scarcity leads to a clear effect on the occurrence of water-associated infectious diseases. Intermittent and insufficient water supplies, which are common conditions in most developing areas with water shortages, result in decreased household water security and compromised drinking water quality that have serious effects on health including water-related infectious diseases. Insufficient water supply for domestic use will compromise not only the quality of drinking water (water-borne diseases), but also hygiene (water-washed diseases). Also, because of water scarcity, wastewater is widely used for agricultural production, often without proper management and health controls. In the absence of proper treatment and monitoring, wastewater reuse exposes farmers, their families, communities and consumers of food to water-borne pathogens.

This review mostly summarizes the scientific information available in developed countries, where the prevalence of diseases associated with water use is kept under very acceptable levels. However, there are reasons to think that the situation might worsen as a consequence of the effects of the climatic change, the increase of population in certain areas and the deterioration of sanitation infrastructures. It may be necessary to take new measures to maintain the present situation. Better knowledge of the water-borne pathogens, where they originate, how they persist or replicate in the environment, how they survive water treatments, and how they are transported in water and soil, will allow us to take the necessary measures to prevent the effects of water scarcity as well as the effects of extreme climatic events foreseen for the future by the experts in climatic change [13].

2 Water-Related Diseases

The water-related or water-associated infectious diseases are typically arranged in four classes from the environmental engineering point of view, although more complex categorizations have also been proposed [14]. These categories are: faecal-oral water-borne diseases, water-washed diseases, water-based diseases and diseases transmitted by water-associated insect vectors. Each type has different causes and potential solutions. Too often the term water-borne disease is erroneously used to name all of them without distinction.

The *faecal-oral water-borne* diseases are those caused by the ingestion of pathogens released through faeces from infected individuals. Their transmission is through ingestion of contaminated water (drinking or recreational activities) and food, as well as through person to person contact. The *water-washed* infections are caused by sharing and reusing for washing hands and face water contaminated with pathogens specific of skin and eyes. The best known example is trachoma, an eye infection causing blindness, which is clearly related to water scarcity. The *water-based* diseases are mostly caused by parasites multiplying in intermediate organisms living in contaminated water. The best known example of this group is schistosomiasis. Finally, there is the group of diseases *transmitted by water-related-insects*, mostly mosquitoes breeding in water, including malaria, dengue and yellow fever among others. Table 1 shows a summarized outlook of the contribution of the different groups of diseases to the burden of diseases in the world and in the two verges of the Mediterranean Sea.

The faecal-oral water-borne diseases, though with very different intensity, affect both developed and developing countries. These are the most important by number of affected people worldwide (Table 1). The other three categories affect basically developing countries. The water-washed affects those with water scarcity, whereas

Table 1 Estimated burden of water-related infectious diseases in the world and the Mediterranean region according to the WHO 2004 update [8]. It includes the most prevalent of each of the four groups of water-related diseases

Water–related (associated) infectious diseases	World		Northern Mediterranean European countries		Eastern and Southern Mediterranean countries	
	Mortality (%)	Prevalence	Mortality (%)	Prevalence	Mortality (%)	Prevalence
Water-borne						
Diarrhoea	2,163,000 (3.7)	4,000,000,000[a]	<1,000 (<0.1)	≅50,000,000[a]	75,000 (4.6)	–
Intestinal helmints infections	–	150,000,000	–	LP[b]	–	≅240,000
Water-washed						
Trachoma	–	6,000,000	–	0	–	≅250,000
Water-based						
Schistosomiasis	41,000 (0.1)	260,000,000	–	0[c]	<1,000 (<0.1)	≅10,000[a]
Transmitted by water-borne vectors						
Malaria	900,000 (1.5)	300,000,000	–	0[c]	≅10,000 (0.6)[a]	

[a]Estimated
[b]Estimated low prevalence
[c]Values approaching 0, some imported cases

Table 2 Most important faecal-oral water-borne infectious diseases with their causal agents

Disease	Causal agent (pathogen)
Acute arthritis	*Giardia*, *Salmonella*, *Campylobacter*
Aseptic meningitis	Echovirus, Coxsakievirus
Cancer, gastric ulcer	*Helicobacter pylori*
Cholera	*Vibrio cholerae*
Acute gastroenteritis (diarrhoea and vomiting)	Norovirus and Sapovirus, Rotavirus, Astrovirus some enteroviruses, Adenovirus 40, 41, *Giardia*, *Cryptosporidium* *Salmonella*, *Shigella*, *Campylobacter*, Enteropathogenic *E. coli*, *Aeromonas*
Heart problems (myocarditis)	Coxsakievirus B
Insulin-dependent diabetes	Coxsakievirus B
Kidney problems	*E. coli* O157:H7 *Cyclospora*
Viral hepatitis	Hepatitis A virus Hepatitis E virus
Poliomyelitis (being eradicated)	Poliovirus

the other two groups affect those countries with abundant water resources. This review concentrates on the faecal-oral water-borne diseases.

The most important pathogens causing faecal-oral water-borne diseases, with the exception of helmints (*Ascaris*, *Trichurus*, *Taenia*, etc.) are compiled in Table 2. These, virtually absent in the developed countries, are still highly prevalent in developing countries, though without causing serious illness [8].

Acute gastroenteritis, whose main manifestations are diarrhoea and vomiting are by far the faecal-oral diseases affecting the greater number of people. The World Health Organization (WHO) estimates that about 4,000,000,000 episodes of diarrhoea occur yearly in the world, yet unevenly distributed. Thus, whereas the citizens of the United States and Europe [15] have an average of about 0.5 episodes per year, some infants in developing countries have more than 3.0 episodes per year [6]. Whereas mortality in developed countries approaches 0, still 2,163,000 persons, mostly infants, were estimated to die of diarrhoea in 2004 in developing countries (Table 1). Diarrhoea accounts for 3.7% of all mortality in the globe and 4.7% of all disability adjusted life years (DALLYs), which is a procedure used by the WHO to estimate the contribution of a disease or groups of diseases to the total burden of diseases. DALLYs besides mortality include the age of dead persons and the disability caused by the disease [8].

Some of the pathogens in Table 2, infect only humans (e.g., *Vibrio cholerae*, *Salmonella typhi*, *Shigella dysenteriae*, poliovirus, hepatitis A virus), whereas others, known as zoonotic, infect both humans and animals (*Salmonella* no *thypi*, *Shigella* no *dysenteriae*, *Campylobacter*, enteropathogenic *Escherichia coli* such as for example the biotype O157:H7, *Cryptosporidium*, etc.). The control of those that only infect humans is easier than the control of the zoonotic ones. Thus, some of them (*S. typhi*, *S. dysenteriae*, poliovirus, etc.) have practically been eradicated in many developed countries, whereas the eradication, and even the control below certain levels, of the zoonotic ones is a very difficult task.

3 Origin of the Water-Borne Pathogens and Faecal Indicators Present in Water Resources

What is the origin of water-borne pathogens found in water? Perhaps with the exception of *V. cholerae*, none of the most important pathogens causing water-borne infectious diseases grow in extra-intestinal environments (water, soil, sediments, sludges, etc.). Very few of them, such as for example *Salmonella* spp., can also grow in foods. The great majority only grow in infected hosts, some only in the gut, and others in the gut and other organs or tissues. They survive more or less successfully once outside the gut. They reach the extra-intestinal environments through faeces, where they go along with a usually much greater number of commensal microorganisms. As the pathogens, the great majority of gut commensals are not able to grow outside the gut. So, they are only found in environments contaminated with faecal wastes and this is the reason why they are considered as faecal contaminants. Certain of these commensal microorganisms are used as indicator organisms of faecal contamination (coliform bacteria, *E. coli*, enterococci, spores of clostridium, coliphages, etc.). Since they are more abundant and also are easier, faster and more cost effective to detect and count than the pathogens, they are used to assess the microbiological quality of water and to evaluate the functioning of water-treatment processes. The enormous progress made in water quality in developed countries has followed quality regulations based on levels of indicator microorganisms in waters for different uses.

The faecal contaminants, either of human or animal origin, reach the surface or ground water bodies through point or diffuse pollution. The point faecal contamination reaches the water through sewer outfalls that contribute raw or depurated wastewater. Mostly, these are either municipal (mostly domestic) or arriving from food industries (abattoirs and meat-processing industries). The diffuse pollution usually reaches the water through the soil by sewer leakage, septic tank overflow, small sewers, residues of agro-food activity (dispersion of slurries, faecal residues from farmed animals, etc.) and wild fauna. Those microorganisms contributed to the soil may reach the groundwater by horizontal and vertical transport and superficial water bodies by surface runoff and soil leakage. Generally speaking, it is easier to restrain point pollution than to bring under control diffuse pollution.

Only a small fraction of faecal contaminants contributed to the environment through human and animal faeces reach new hosts to infect them. Many of the defecated microorganisms never reach the soil and/or water bodies, since faecal wastes are submitted to purification (water) and hygienization (solids) processes, which remove a fraction of the pathogens and indicators. An important fraction of those that reach either the soil or water are removed (adsorption to soil particles and suspended solids, followed by sedimentation) and/or inactivated by natural stressors (physical, chemical and biological) in soil and water bodies.

And even a fraction, ideally all, of those that survive are removed and/or inactivated in the drinking water treatment facilities or by cooking the contaminated food.

In theory, during droughts, if there is less water and similar numbers of faecal microorganisms reach the environment, their concentrations in water bodies should increase. But, this is not exactly what occurs. The lack of rain enlarges the zones of unsaturated porous soils that lie between the surface, which is the zone reached by faecal pollution, and the saturated porous zones. Therefore, there is no transport to the aquifers used as water sources for human consumption. On the other hand, low river flows increase sedimentation of particles and adsorbed microorganisms. And those still in the water and/or soil surface are exposed to major inactivation, since droughts are associated with natural stressors like high temperatures, irradiation, etc. Thus, droughts are typically periods of great immobilization and inactivation of microorganisms of faecal origin.

In contrast, during the rainy periods many factors contribute to an increase in the numbers of faecal pathogens and indicators in the water bodies. These factors are: (1) many communities still have combined sewer systems designed to carry both storm water and sanitary water to the sewage treatment plants; when excess water reaches the plant the systems are designed to discharge the excess wastewater into surface water; (2) additionally heavy rain resuspends sediments in sewers where faecal microorganisms accumulate; (3) increase in the leaking of sewers and septic tanks; (4) surface runoff and leaching of faecally contaminated soils to both surface water bodies (rivers and lakes) and karst aquifers; (5) resuspension of sediments in water courses; (6) saturation of porous soils favours rapid vertical and horizontal transport of microorganisms; (7) rain water, with low concentration of divalent ions, favours elution of microorganisms from sediment particles and also from soil particles.

All these facts can lead to increases in the amounts of faecal pathogens and faecal indicator microorganisms such as *E. coli* and enterococci reaching: (1) surface and subterranean water bodies used as drinking water sources; (2) fresh and sea water bathing areas; (3) shellfish growing areas; and (4) water used to irrigate vegetables consumed raw. These increases in faecal contaminant loads, which are of short duration, may escape the routine water quality controls included in the regulations available for water quality of drinking, bathing and shellfish growing areas and reclaimed water used for agricultural purposes. In addition, these boosts in the densities of microorganisms are associated with increases in water turbidity. This is known to impair drinking water treatment. Recently, an association between increases in turbidity in drinking water and infectious illness has been shown [16, 17].

Abundant literature on the increase of the densities of faecal pathogens and indicators in water sources during dry and rainy periods and the significant effect of rain in water-borne infectious disease outbreaks exist and prove all these assertions.

4 Rain and Densities of Faecal Pathogens and Indicators in Water Sources

First evidences of the impact of heavy rainfall on the epidemiology of enteric pathogens were obtained from studies on the presence of various faecal organisms, both pathogens and indicators in water. Increased numbers of pathogens and indicators in different water bodies, including drinking water, had been reported after heavy rains.

Increased amounts of faecal-oral water-borne pathogens (virus, bacteria and protozoa) and microbial indicators (bacterial and viral) have been reported in groundwater bodies [18], karst springs [19, 20], surface freshwater [21–26], marine waters used for bathing [27–29] and shellfish growing [30] as well as tap water [31].

In contrast, in developing countries published information on this topic is scarce, though existing information indicates that rain levels above background values also increase the amounts of indicators in fresh water bodies. Blum et al. [32] described in Nigeria a peak period of faecal pollution of water sources in the transition between the dry and the wet seasons. Gasana et al. [33] described boosts of faecal contaminants in water supplies in Rwanda after heavy rain episodes.

5 Rain and Water-Borne Infectious Disease Outbreaks

Very little evidence associating water scarcity and an increase in outbreaks of faecal-oral water-borne infectious diseases exists in developed countries. A recent retrospective study performed in England provides some evidence that both low rainfall and heavy rain precede many drinking water outbreaks [3]. Yet, as stated earlier in this review, the situation is potentially different in developing countries [5–7, 9–12], where water scarcity, including droughts, leads to different circumstances that have a clear incidence in the occurrence of both water-borne and water-washed infectious diseases.

On the contrary, there are numerous reports of outbreaks of faecal-oral water-borne infectious diseases following heavy rain episodes.

There are some descriptions of water-borne outbreaks, or even small epidemics of acute gastroenteritis (diarrhoea), cholera and hepatitis E associated with catastrophic floods that occurred in developing countries, such as Sudan [34, 35], Nicaragua [36], Mozambique [37] and West Bengal [37]. On the contrary, no changes in the base-line outbreak incidence have been reported in developed countries after major floods [37, 38]. When infrastructures and water management are adequate, outbreaks of faecal-oral water-borne infectious diseases do not follow flood events, even in the case where water flooding has compromised the security of water facilities [37].

In developed countries heavy rain events not followed by floods have frequently been associated with outbreaks linked to drinking water supplies derived from either surface water [39–42] or groundwater [43–48], non-treated well water [49], bathing waters [50] and shellfish consumption [51]. Viruses [41, 47, 51], bacteria [39, 49] and protozoa [40, 42, 44, 45, 48] were the causal agent of these outbreaks. Outbreaks associated with heavy rains have also been described in countries of the Northern Mediterranean [39, 47, 51]. A significant percentage of these outbreaks worldwide were linked to rainfall events that followed periods of dry weather.

Three of these outbreaks deserve further discussion as they are very informative about the topic reviewed here. Firstly, the largest reported water-borne disease outbreak ever documented occurred in Milwaukee (USA) in 1993, with an estimated 403,000 cases of intestinal disease (cryptosporidiosis). The outbreak was preceded by a period of heavy rainfall and surface runoff with a subsequent turbidity boost in the surface source water that compromised the efficiency of the drinking water treatment plant [40]. Secondly, a water-borne outbreak with a high morbidity and mortality following heavy rainfall was the Walkerton outbreak of *E. coli* O157:H7 in Canada. This outbreak affected over 1,000 people of whom 60 were admitted to hospital and six died [43]. This outbreak was preceded by an extreme rainfall episode with a prevalence of once in 60 years [52]; this rainfall episode caused a contamination of the well used to provide water to the town, but no extra treatment was given to the water. Somehow this outbreak and the increase in extreme water events foreseen by experts in Climatic Change set off renewed interest in retrospective studies on the association of weather events and water-borne infectious disease. Worth noting is that this was the first water-borne outbreak that had a website to inform the public. Finally, the report of Laursen et al. [46] describes a correlation between precipitation and the onset of gastrointestinal symptoms (no agent was identified) in Denmark. The intrusion of sewage into a well was associated with rain and was followed within a few days by an increase in cases of diarrhoea. The same sequence of events repeated itself three times from December 1991 to February 1992.

In addition to these and other case-reports, some retrospective studies using data from water-borne disease and precipitation databases have been carried out in the United States, Canada, and England and Wales, where complete databases allow these studies. In a study with data from 1948 to 1994 corresponding to the United States, Curriero et al. [1] found a statistically significant association between rainfall and faecal-oral infectious water-borne diseases. Indeed, 51% of the water-borne outbreaks were preceded by precipitation events above the 90th percentile and 69% by events over the 80th percentile. The study performed in Canada also shows a significant association between heavy rainfall events and warm temperatures during the snow melting period with outbreaks of water-borne infectious diseases. For rainfall events greater than the 93% percentile, the relative odds of an outbreak increased by a factor greater than 2,200 [4]. A study of drinking water related outbreaks in England and Wales during almost the whole twentieth century found a significant association between excess rainfall over the previous week and low rainfall in the 3 weeks before the week of the outbreak [3].

6 Conclusions and Future Prospects

Water scarcity does not seem to have evident effects on the prevalence of waterborne infectious diseases in developed countries, including those in the Northern Mediterranean. In contrast, heavy rain episodes and particularly those following dry periods are associated with outbreaks of those diseases. In spite of the occurrence of a base-line of cases of diarrhoea as well as the occurrence of a certain number of outbreaks yearly the situation regarding these diseases is quite satisfactory. However, the water stress in many developed countries, including those in the Northern Mediterranean, is foreseen to intensify as a consequence of increasing demand, rainfall decrease and increase of extreme weather events, including droughts followed by heavy rains. This will lead to a deterioration of existing water sources and to the need to use non-conventional water sources. Ensuring water microbiological safety is essential during the adaptation to these changing circumstances. Mitigation measures could include:

Establishing disease surveillance and outbreak detection.
Regulating the use of non-conventional water resources and speeding up modifications according to changing knowledge and circumstances.
Establishing predictive models of water quality and early warning systems.
Reinforce safety in water treatment and supply by implementing Water Safety Plans.
Improving education programmes for water professionals in potential climate change impacts and the effect of extreme rain events.

Regarding developing countries, including those of the Eastern and Southern Mediterranean, the situation at present is far from satisfactory and circumstances reported in the previous paragraphs regarding climatic change will not help to reach the Millennium Development Goals set by the United Nations [53]. Forecasts far less optimistic than those of the United Nations and the WHO [8, 12] already exist [54]. Unfortunately, the new difficulties arising from the recent global economic/financial crisis make the worst-case scenario thinkable. A greater technical, economical and political commitment by the developed countries will be needed to avoid a catastrophic situation.

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Implications of Water Quality on Irrigation Practices Under Water Scarcity

Faycel Chenini

Abstract Extensive regions of the Mediterranean Region are currently facing serious problems regarding the supply of sufficient water resources to cover their increasing water supply demands. In the year 2025, several countries will have less than 200 cubic meters per capita per year. This problem of water scarcity in the region is continuously aggravating: while the renewable water resources decrease, the demand for potable water is increasing due to population growth and increasing economic activities. One of the most important future options for a sustainable management of water resources in affected countries is the use of poor quality water. Irrigation and water resources management under water scarcity is one of the challenges all these countries will have to deal with in the coming decades. Therefore, these countries need irrigation management for water quality control. The importance of water quality for irrigation is of particular importance in arid climates where water is scarce. On the other hand, as water resources become more limited, increased use is being made of marginal/inferior irrigation water, with high sodium or total salt content, or both. Without sound management based on knowledge of the possible harmful effects and environmental impacts, prolonged application of such resource of water may become impossible.

Keywords Irrigation, Management, Quality, Resources, Scarcity, Water

Contents

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Abbreviations

CM	Cubic meter
EC	Electrical conductivity
ESP	Exchangeable sodium percentage
FAO	Food and agriculture organization
MENA	Middle East and North Africa
ppm	Parts per million
SAR	Sodium adsorption ratio
TDS	Total dissolved solids

1 Introduction

The Mediterranean region is one of the most water-scarce regions of the world, where good water management matters even more than it does elsewhere. Several countries have already reached or even gone beyond water scarcity levels (Cyprus, Egypt, Israel, Morocco, Tunisia…). Increase in water demand, as a result of population growth and development plans, are putting serious burdens and pressure on the existing conventional water resources, including stressed water supply and deterioration of water quality. Water management problems are already apparent in these countries [1]. Indeed, water management has been a concern throughout history in countries of the region, and societies have grown in ways that adapt to water scarcity and variability [2]. For millennia, societies developed elaborate institutions and conventions governing individual behavior, and developed technologies to manage their water effectively. In the process, the region spawned some of the world's oldest and most accomplished civilizations, based on both farming and trade [1]. These communities reduced the risks of scarcity and irregular rainfall through water diversion, flood protection, exploitation of aquifers, and elaborate conveyance systems. Some of the ancient water management systems remain, still governed by traditional structures. In many cases, these systems are well operating [2].

Many publications use an absolute measure that denotes “water security,” frequently referring to an index that identifies a threshold of 1,700 CM per capita per year of renewable water, based on estimates of water requirements in the household, agricultural, industrial, and energy sectors as well as the needs of the environment. Countries whose renewable water supplies cannot sustain this figure experience *water stress*. When supply falls below 1,000 m^3 per capita per year, a country is said to experience *water scarcity*, and below 500 m^3 per capita per year, *absolute scarcity*. However, these terms are easy to misinterpret, because they do not take into account possibilities for trade in agricultural products, efficiency of water use in agriculture, and other variables, and thus obscure the primacy of economic demand rather than physical need in determining water use [3–5].

The ratio of total water use to water availability under water stress can be defined as *Water scarcity* (in % = total water use/water availability). It will generally range between 0 and 100%, but can in exceptional cases (e.g. groundwater mining) be above a 100%. For example, this ratio is in Algeria 39.8%, in Egypt 105.8%, in Jordan 114.5%, in Lebanon 33.4%, in Morocco 42.2%, in Syria 75.3%, and in Tunisia 56.6 [6].

With a growing scarcity of freshwater available for irrigation, other sources of lower quality like brackish water, saline water, and treated wastewater become more important as additional or substituting inputs for the agricultural sector. At the same time, it is clear that a sophisticated treatment like desalination or nano-filtration under current conditions is still far too expensive to be a major solution to future irrigation water needs. Hence adaptation of farming and irrigation practices to the particular water qualities constitutes a more viable approach.

As a result of the experience drawn from several countries of the region, special emphasis has to be given to the practical approaches that have been successful in the past [17]. Success, viability and acceptance of marginal water use in agriculture depends on locally adapted water and soil management practices, with appropriate selection of cropping pattern and farming practices.

2 Evaluation of Chemical Characteristics of Irrigation Water Under Water Scarcity

Irrigation has been practiced from the ancient time; it is only in the twentieth century that the importance of the irrigation water quality was recognized [7]. The use of saline water may result in the reduction of crop yields. A high sodicity of water for irrigation may cause the deterioration in the physical properties of soils with consequent reduction in crop yield. Presently, considerable attention is being given to environmental and human health aspects of irrigation water quality, including the probable presence of potentially harmful elements [8].

Water quality for irrigation is of particular importance in a water scarcity condition and especially in arid climates. Salts formed by deposition from irrigation tend to accumulate in the soil profile. Irrigation water may contain up to 1000 g of salt per cubic meter (the general case in Mediterranean region [9]. The application of 100 mm irrigation of high saline waters will introduce one ton of salt to a hectare of irrigated area. Consequently, it is necessary to include leaching and drainage as an integral part of the irrigation program. Unfortunately, this practice is not well applied in several countries in the Mediterranean region. On the other hand, mixing different water resources to decrease salinity is becoming a common practice in different countries such as Morocco, Egypt, Tunisia, Jordan and Israel. Interconnection of reservoirs and dams is also applied to improve water quality and facing local drought periods.

The following chemical characteristics determine the quality of irrigation water under scarcity of water.

2.1 Salinity/Total Concentration of Soluble Salts

The effect of water salinity on crop growth is largely of osmotic nature. Osmotic pressure is related to the total salt concentration rather than the concentration of individual ionic elements. Salinity is commonly expressed as the electric conductivity of the irrigation water. Salt concentration can be determined by Total Dissolved Solids (TDS) or by Electrical Conductivity (EC). Under a water scarcity condition, salt tolerance of agricultural crops will be the primordial parameter when the quality of irrigation water is implicated for the integrated water resources management [10].

Table 1 shows the relative salt tolerances of agricultural crops. These data serve as a guide to the relative tolerance among crops to adapt the quality of water to crops patterns under water scarcity. It is important to highlight that absolute tolerances vary with climate, soil conditions, and cultural practices.

2.2 Sodicity

This is defined as the relative concentration of sodium to calcium plus magnesium, and is represented by a parameter known as the sodium adsorption ratio (SAR). The absolute concentration values of the different cations in irrigation water are not adequate for estimating probable hazards. An important consideration is the extent to which the exchangeable sodium percentage (ESP) of the soil will increase as a result of adsorption of sodium from the irrigation water. The higher the ratio, the

Table 1 Relative salt tolerance of agricultural crops [12]

Tolerant
Barley, cotton, jojoba, sugarbeet
Alkali grass, alkali sacaton, bermuda grass, kallar grass, salt grass, weatgrass, wildrye
Asparagus, date palm
Moderately tolerant
Cowpea, oats, rye, safflower, sorghum, soybean, triticale, wheat
Barley (farage), brome (mountain), canary grass (reed), clover (hubam), clover (sweet), fescue (meadow), fescue (tall), harding grass, panic grass (blue), rape, rescue grass, rhodes grass, ryegrass (Italian), ryegrass (perennial), sudan grass, trefoil (narrowleaf, birdfoot), wheat (forage), wheatgrass (standard crested), wheatgrass (intermediate), wheatgrass (slender), wheatgrass (western), wild rye (beardless), wild rye (Canadian), artichoke, red beet, squash (zucchini), fig, jujube, olive, papaya, pineapple, pomegranate
Moderately sensitive
Broadbean, castorbean, maize, flax, millet, peanut, rice, sugarcane, sunflower
Alfalfa, bent grass, bluestem, brome (smooth), bumet, clover (alsike), clover (strawberry), clover (white dutch), corn (forage, maize), cowpea (forage), dahlia grass, foxtail (meadow), grama (blue), love grass, milkvetech (cicer), oat grass (tall), oats (forage), orchard grass, reye (forage), sesbania, siratro, sphaerphasa, timothy, trefoil (big), vetch (common), broccoli, brussels sprouts, cabbage, cauliflower, celery, corn (sweet), cucumber, eggplant, kale, kohlrabi, lettuce, muskmelon, pepper, potato, pumpkin, radish, spinach, squash (scallop), sweet potato, tomato, turnip, watermelon, grape
Sensitive
Bean, guayule, sesame,
Bean (VC), carrot, okra, onion, parsnip
Almond, apple, apricot, avocado, blackberry, boysenberry, cherimoya, cherry (sweet), cherry (sand), currant, gooseberry, grapefruit, lemon, lime, loquat, mango, orange, passion fruit, peach, pear, persimmon, plum (prune), pommel, raspberry, rose apple, sapote (white), strawberry, tangerine

Table 2 Relative tolerance of selected crops to exchangeable sodium [12]

Sensitive (ESP<15)
Avocado, deciduous fruits, nuts, bean (green), cotton (at germination), maize, peas, grapefruit, orange, peach, tangerine, mung, mash, lentil, groundnut (peanut), gram, cowpeas
Semi-tolerant (15 < ESP < 40)
Carrot, clover (ladino), dallisgrass, fescue (tall), lettuce, bajara, sugarcane, berseem, benji, raya, oat, onion, radish, rice, rye, ryegrass (italian), sorghum, spinach, tomato, vetch, wheat
Tolerant (ESP > 40)
Alfalfa, barley, beet (garden), beet (sugar), bermuda grass, cotton, para grass, rhodes grass, wheatgrass (crested), wheatgrass (fairway), wheatgrass (tall)

higher the sodicity hazard. When bicarbonate ions are present, the sodicity hazard increases.

Relative tolerance of selected crops to exchangeable sodium is presented in the following Table 2.

Under water scarcity, the two factors, salinity and sodicity of the irrigation water must be considered together for a proper evaluation of the ultimate effect of the water on the infiltration rate that generally increases with increasing salinity of the irrigation water and decreases with either decreasing salinity or increasing sodicity.

The infiltration problem caused by water quality is also related to the structural stability of the surface soil (see below).

2.3 Anionic Composition

The principal cations and anions in irrigation water are calcium, magnesium, sodium, bicarbonate, sulfate, chloride, and nitrate. The total cation and anion concentrations must be equal. If the pH exceeds 8.3, carbonate concentrations can become significant. Potassium concentrations are usually less than 1 meq liter^{-1}. On the other hand, the pH of irrigation water is not an accepted criterion of water quality because it tends to be buffered by the soil and most crops can tolerate a wide range of pH. Calcium carbonates are sparingly soluble. The calcium concentration is very low in water of high pH, and is never high in the presence of a high concentration of bicarbonate [11].

2.4 Concentration of Boron

For all natural waters, boron is one of their constituents with varying concentrations from minute traces to several ppm (parts per million). It is essential for plant growth but is exceedingly toxic at concentration slightly above optimum. Boron tolerances vary depending upon climate, and crop varieties. Relative boron tolerances of agricultural crops are presented in Table 3 [12].

Table 3 Relative boron tolerances of agricultural crops [12]

Very sensitive (<0.5 ppm)
Lemon, blackberry
Sensitive (0.5–0.75 ppm)
Avocado, grapefruit, orange, apricot, peach, cherry, plum, persimmon, grape, walnut, pecan, cowpea, onion
Sensitive (0.75–1.0 ppm)
Garlic, sweet potato, wheat, barley, sunflower, bean (mung), sesame, lupine, strawberry, artichke (jerusalem), bean (kidney), bean (lima), groundnut/peanut
Moderately sensitive (1.0–2.0 ppm)
Pepper (red), pea, carrot, radish, potato, cucumber
Moderately tolerant (2.0–4.0 ppm)
Lettuce, cabbage, celery, turnip, bluegrass (kentucky), oats, maize, artichoke, tobacco, mustard, clover (sweet), squash, muskmelon
Tolerant (4.0–6.0 ppm)
Sorghum, tomato, alfalfa, vetch (purple), parsley, beet (red), beet (sugar)
Very tolerant (6.0–15.0 ppm)
Cotton, asparagus

Above indicated concentrations are maximum tolerated values in soil-water without yield or vegetative growth reduction

Maximum concentrations in the irrigation water are approximately equal to above listed values or slightly less

Boron tolerances vary depending upon climate, and crop varieties

2.5 Turbidity

Turbidity, due to solid particles in suspension, is a parameter generally neglected. However, under water scarcity, it is very important to be controlled because it may restrict the use of water for irrigation. Solid particles may clog the water distribution systems as drippers or sprinklers. They may also affect the soil permeability. This is why in different countries in the Mediterranean region special devices for the removal of sediments especially are used when marginal waters are only available for irrigation.

3 Repercussions of Soil Properties and Irrigation Water Quality on Crop Growth Under Water Scarcity

In arid regions and under water scarcity, calcium and magnesium are the most prevalent cations in soil solutions and in exchange complexes of irrigated soils. Applying irrigation, sodium becomes the main cation in the soil solution. The salt concentration and the SAR tend to increase, and a part of the exchangeable calcium and magnesium is replaced by sodium.

Soils properties are very sensitive to the type of exchangeable ions. Calcium imparts favorable physical properties to the soil, while adsorbed sodium causes clay dispersion and swelling. It is generally recognized that an exchangeable sodium percentage of 10 is sufficient to cause soil dispersion, reduction of soil permeability and impaired growth of some crop plants. On the other hand, excess salt concentration prevents the dispersive effect of adsorbed sodium.

Applying irrigation water can be tolerated under water scarcity though it produces swelling, since swelling is a reversible process. Indeed reduction in permeability can be reversed by adding electrolytes to the system. On the other hand, dispersion is an irreversible process and must be seriously controlled because of the formation of impermeable clay pans. When high sodium water is used for irrigation, difficulties may not appear during the irrigation season. When winter rains leach the salts from the upper soil layers, the soil disperses, the surface crusts, and the permeability is significantly reduced [10].

4 Irrigation Management: Implication of Irrigation Methods in Relation to Water Quality

Under water scarcity conditions, the usability of poor water quality for irrigation is conditioned by the irrigation method employed.

With surface irrigation, water quality control procedures include careful land leveling and controlled water application to ensure adequate and rapid watering of border strip, basin or furrow with a minimum of runoff. Inadequate water quality control (salinity) is mostly due to inherent variability of intake rates and unsatisfactory land leveling. The application of additional water to assure adequate watering everywhere can result in an excessively high water table. Artificial drainage is often required to control this situation. The water table should be sufficiently low to prevent the rise of ground water into the root zone. Hence, the desirable water table level is dependent on the unsaturated conductivity of the soils. A relatively high water table of about 100 cm can be tolerated in coarse textured soils. A water table depth of about 180 cm is generally recommended for soils of medium texture. A lower table is required for perennial crops than for annuals [13]. Inadequate watering and soil salinization may occur on fine textured soils because of insufficient infiltration rates. This is particularly true of crops with high water requirements, such as alfalfa. If soil permeability is insufficient to meet the leaching requirement, a crop with a lower water requirement or higher salt tolerance should be grown.

With sprinkler irrigation, efficiencies are easier to obtain than with surface irrigation. Land leveling is not necessary and the need of artificial drainage is reduced. Therefore, in countries under water scarcity, sprinkler irrigation will save water and provides an effective means of reducing the salt concentration at the soil surface; it is therefore increasingly used for salt-sensitive row crops. Surface irrigation can then be used for the remainder of the growing season.

With micro irrigation, special management practices such as high irrigation frequency or humid strips are required to maintain soil salinity in the root zone within the tolerance range of the crop. Zones of high concentration are developed at the wetting front during the growing season and may have to be leached before a new plantation.

5 Specific Examples of Implication of Irrigation Water Quality Under Water Scarcity

5.1 Syria

To promote the use of poor quality water for irrigation, a field research study was conducted in three semi-arid regions with water scarceness in Syria in order to define, under field conditions, the wheat yield response function to irrigation water salinity, the effect of soil texture and structural characteristics on the irrigation water salinity threshold, and to compare this value with the conventional threshold value.

There was a discrepancy between water salinity limits for the three locations, which may be attributed to factors related to difference in soil texture and structure. This affects soil infiltration capacity and water retention. These soil hydrologic characteristics influence salt development in the soil profile, which affects plant growth and yield. Analysis of the obtained soil salinity profiles indicate that these differences in soil properties influence:

– Salt accumulation in the soil profile.
– The level of seedbed salinity present at sowing time.
– The extent of “natural leaching” of the soil profile.

The results of this research study indicate that wheat tolerance for irrigation with saline water is affected by various real “in-field” conditions, including soil texture and structure, climate, irrigation water management and agricultural practices.

These results underline the necessity of establishing regional water quality criteria when planning the use of saline water sources for irrigation. These criteria are of primary importance for establishing suitable strategies for the safe use of saline aquifers in Syria and other arid and semi-arid regions.

5.2 Tunisia

Despite the scarcity of water resources, Tunisia has adopted a water demand management program based on water quality monitoring. This has permitted the development of the reuse of nonconventional water resources in irrigated agriculture as treated wastewater and brackish water. This reuse is one of the main assizes of the national strategy of water resources mobilization. Tunisia has adopted an intermediate way where wastewater is mainly processed up to a secondary treatment stage and it is used for restrictive irrigation. The strategy of reusing treated wastewater has suggested some suitable answers to the national context of water resources and notably to the local specificities. The main objective is to increase the rate of reuse. The actual rate stands at about 20% and with the above mentioned national strategy, the rate is expected to reach 40–60% in 2015.

Treated wastewater salinity and the high cost of hydraulic facilities are other constraints in the development of the sector and limit project profitability. Improving quality of treated wastewater is still one important challenge for the government that could improve the reuse rate. While any quality of treated wastewater can be produced, the degree of treatment must be addressed: what constituents have to be removed and what quality will be acceptable? [14].

5.3 Egypt

According to the NRI study [15], the Nile is the main source of drinking water in Egypt. Over 85% of the country’s water is consumed annually by irrigation. Hence, safe water will provide pollutant-free agricultural products and production will increase as well. The concentration of organic material decreased 15–69% in the main course, dissolved salts decreased 1.5–2.0%, while phosphate concentration decreased 14%. The total water quality was improved by an average of 14%. The water was tested just after the excess discharge period, which took place in October and November. Surplus water was discharged from Aswan High Dam into the river in a process called “Washing the Nile”. This helps decrease the concentration of pollutants like organic material, excessive salts and bacteria. The main industrial pollutants in the Nile are pesticides [15], organic material, heavy metals, ammonia, nitrate, and phosphate, but these pollutants are concentrated in limited areas where factories and industrial workshops discharge their liquid waste.

Treated wastewater also finds its way into the Nile. The government is managing this arrival by deriving a large quantity of treated sewage water to tree plantations instead of diverting it into water channels. Over 4,620 ha of land were planted with trees in 24 areas across 16 provinces for this purpose and 2.4 billion cubic meters are being used for irrigation.Water quality awareness is still the new challenge for the Egyptian government, which is more important in solving environmental problems. This should begin with the people’s recognition that a problem of water quality exists [15].

5.4 Morocco

In Morocco, the chronic water scarcity is thus becoming a permanent situation that can no longer be ignored to draw on the strategies and policies concerning the management of water resources. The quality of these resources has undergone a considerable degradation during the last decades due to the different sources of pollution (domestic, industrial, agricultural wastewaters). On the basis of the climatic and geographic context, the resort to nonconventional waters constitutes an alternative, especially in areas suffering from droughts. The treated wastewater constitutes a national development factor through extending irrigated areas, exploiting arid lands, improving public health, controlling environment pollution and managing the quality of water resources at the level of hydrographic basins.

A total of 7000 ha is directly irrigated with raw wastewater discharged by towns, i.e., about 70 million m^3 of wastewater is used every year in agriculture with no application of health control (according to WHO standards). Many crops are irrigated in this manner (fodder, market gardening, major crops, arboriculture…). The irrigation of market garden crops with raw wastewaters is forbidden in Morocco, but this ban is not respected. This makes the consumer of agricultural products and the farmer face risks of bacteria or parasite disease. The promotion of treated wastewater reuse cannot materialize without taking quality as the mean parameter for saving human health and agriculture production [5].

5.5 Cyprus

The island of Cyprus suffers from a chronic water shortage. Droughts and insufficient rainfall are commonplace. The growing demand for sweet water and the decline of Cyprus's nonpolluted water sources place an additional heavy burden on the island's already inadequate water supplies.

The severe drought in Cyprus has led both the Greek and Turkish sides toward alternative projects to meet the growing freshwater demands. The reuse of total treated wastewater for irrigated agriculture that is continuously increasing was adopted in the water management strategy. Nowadays, about 6 Mm^3 is treated and used mainly for irrigation purposes. With the completion of the central collection and treatment plants in the cities and villages, it is expected that 30 Mm^3 of treated wastewater will be available and reused [16].

6 Conclusion

In arid and semi arid areas, due to conventional water scarcity and growing water demands, water of poor quality is increasingly used, including treated wastewater, saline aquifers and reused drainage water. Different strategies have been developed for the safe use of treated wastewater, or even saline waters. These are mainly mixing saline and nonsaline water after plant establishment, using saline and nonsaline water sequentially over the growing season. Another strategy is introducing supplemental irrigation with saline water in areas of high seasonal rainfall, and applying agricultural rotations with crops of different water quality tolerances, or managing irrigation (by operating the irrigation frequency and amount), as well as by managing soil (including tillage and fertilizer application). The application of one or more of these strategies necessitates accurate definition of crop water quality tolerance parameters.

Available reports from a variety of agro-climatic regions in the world indicate that crop water quality response is greatly influenced by prevailing local factors, including field practices and conditions. These factors differ widely among agricultural regions. Therefore, it is of primary importance to establish locally specific criteria when defining suitable strategies for quality of irrigation water use. These criteria have to take into consideration local irrigation and agricultural practices (including irrigation method and timing, practical leaching fraction values and fertilizer use), and in-situ field conditions, including soil texture and structure, as well as the local climatic conditions.

What is needed for the region's permanent water scarcity is a simple approach which takes into account the needs of both, water users (using irrigation water) and water consumers (using potable water). Properly treated wastewater and slightly saline water can provide a major share of the irrigation water demand on the farms. It is obvious that handling these water qualities requires some preparation of the farmers and eventually also assistance in developing appropriate irrigation management practices [1].

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Effects of Wastewater Treatment Plants on Stream Nutrient Dynamics Under Water Scarcity Conditions

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Abstract Despite an array of significant technological advances, effluents from wastewater treatment plants (WWTPs) generate abrupt physical and chemical discontinuities along the fluvial continuum. These discontinuities not only alter the water quality, but also significantly affect fluvial ecosystem structure and function. In particular, WWTP effluents increase nutrient concentrations and introduce toxic substances, including emergent pollutants, to the fluvial ecosystems. There is abundant evidence that these changes affect stream communities. Fewer studies, however, have examined the influence of WWTP inputs on the hydrologic and nutrient availability regimes. Yet, shifts in these regimes can have clear implications for the stream ecosystem function. This knowledge is of critical relevance for stream management as it provides insights on integrative properties of trophic state, energy transfer, and material cycling at the ecosystem level. WWTP effects on fluvial ecosystems are expected to become more exacerbated under water scarcity conditions, which are characteristic of arid and semiarid regions such as the Mediterranean region. Under these conditions, streams receiving point source inputs may turn into islands of permanent flow within a highly intermittent fluvial network. This has implications not only locally at the reach scale but also at the catchment scale. Within this context, both plant operation and fluvial management may be critical to preserve the ecological integrity of these aquatic ecosystems at the same time that a balance is met with societal demand for high quality water resources. This chapter aims to review current knowledge on this topic, with major emphasis on nutrient loads and in-stream nutrient retention, and to discuss its implications within the context of actual and future scenarios of water scarcity conditions.

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Contents

1 Introduction

Eutrophication of freshwater ecosystems is one of the major environmental problems worldwide [1, 2]. This problem is caused by an excessive enrichment of inland and marine waters with nutrients (i.e., nitrogen and phosphorus) mostly derived from human activities [3–5]. Eutrophication alters the ecological integrity of freshwater ecosystems and causes severe reductions in water quality. While nutrients at low concentrations can limit ecosystem production, in excess they enhance the growth of primary producers (algae, cyanobacteria, macrophytes) and eventual decay of organic matter, altering the trophic state of the ecosystems and modifying both community composition and ecosystem functioning. Eutrophication also has negative impacts on the human society, compromising the quality of water resources for human consumption and other uses and reducing the recreational and aesthetical services provided by aquatic ecosystems. In addition, health-related problems, associated with both high nutrient (nitrate) concentrations and excess algal growth causing taste, odor, and toxicity problems, can occur where eutrophic conditions interfere with drinking water treatment.

This chapter aims to review current knowledge on the effects of wastewater treatment plant (WWTP) inputs (as major nutrient point sources) on stream nutrient dynamics, with major emphasis on nutrient loads and in-stream nutrient retention, and to discuss its implications within the context of actual and future scenarios of water scarcity conditions. Following this introduction, the second section of this chapter describes water quality problems associated with wastewater inputs from urban areas and how they are faced within the context of increasing urbanization across the world and its higher impact on water availability. In the third section, we review existing knowledge on the effects of WWTP inputs on stream nutrient dynamics at the local scale, and hypothesize potential directions that these effects may take under water scarcity conditions. The fourth section scales up these local effects to the catchment scale within a water scarcity context and offers a perspective on sound management aimed at balancing the demand for high water quality resources and the maintenance of fluvial ecosystem integrity. Finally, the last section points at gaps in our knowledge and indicates future prospects for research and management.

2 Nutrient Inputs from Urban Wastewaters and Global Change in Semiarid Regions

Wastewaters are one of the major sources of nitrogen (N) and phosphorus (P) to freshwater ecosystems, especially in urban areas ([6, 7] and references therein). These inputs together with urban stormwater runoff caused by impervious surfaces [8] are among the major stressors of streams and rivers draining urban landscapes and the cause of their degradation. Collectively, this is referred to as the "urban stream syndrome" [9, 10]. During the last century, distribution of human population has increasingly concentrated in cities and urban areas. In 2008, for the first time in human history, half of the human population lived in urban areas [11]. This percentage, however, is not homogenously distributed among the different countries. Forecasts of population growth indicate that the urbanization trend will continue to increase up to 60% by 2030 [12]. As more people concentrate in cities, the load of urban wastewater will increase as well. In addition, in developing countries, urbanization has increasingly moved towards a metropolitan-area sprawl configuration [13]. This has resulted in an increase in the proportion of streams and rivers within the catchments being subjected to the urban stream syndrome [13, 14]. There is no doubt that current urbanization trends pose a real challenge for environmental managers and policy-makers who are trying to develop and implement sustainable wastewater collection and treatment strategies. They also constitute a scientific challenge to develop most efficient and cost-effective technologies and to increase our ecological understanding of urban freshwater ecosystems as well as the effects that urbanization causes on them [15].

In developed countries, implementation of environmental directives together with significant technological advances in wastewater treatment over the past ca. 40 years has clearly reduced the impact of urban activities on stream nutrient loads and contributed to improve water quality. For instance, in European countries there has been a significant increase in the proportion of population connected to WWTP since the implementation of the Urban Waste Water Treatment directive (Council Directive 91/27/EEC). The current percentage of population connected to WWTP ranges from 35% to over 80% depending on the country [16]. In addition, there has been an increasing trend to include tertiary treatment (i.e., chemical and biological removal of nutrients) in WWTPs in most European countries. Nowadays, tertiary treatment accounts for 20–80% of wastewater treatment in these countries [16]. As a result of this technological effort, nutrient inputs from point sources (e.g., WWTP effluents) have decreased significantly in Europe over the past 30 years, especially for P [17], contributing to a general decrease in stream and river concentrations of both P and N [18]. Similar trends have been observed in the United States of America after the implementation of the Clean Water Act (Public law 92–500 and further amendments of it), with >70% of population connected to WWTP and an increasing proportion of wastewater tertiary treatment [7]. It is also notable that improved effects of wastewater treatments have been more effective for P than for N, because agriculture and atmospheric deposition are major additional anthropogenic sources of N reaching fluvial ecosystems through diffuse pathways [17, 19]. For instance, an evaluation of source apportionment of N and P inputs to European freshwater ecosystems indicated that while point sources can still account for >60% of P loads in highly populated regions, inputs from agriculture and other diffuse sources account for >60% of N loads [17]. As a consequence, N/P ratios as well as nitrate/ammonium ratios in streams vary according to the proportion of different land uses within the catchment (Fig. 1). Therefore, the implementation of management strategies targeting particular sources may cause shifts in the relative availability of N and P, which may result in stoichiometric imbalances in stream and river ecosystems. Unfortunately, the ecological implications of these imbalances are still poorly understood.

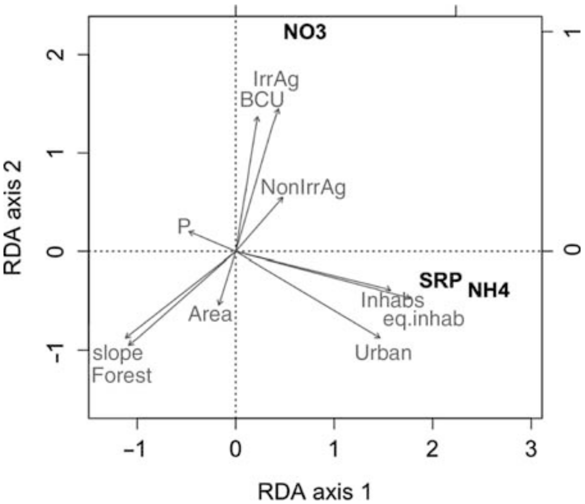

Fig. 1 Results from a redundancy analysis of stream nutrient concentrations vs. catchment characteristics in 31 headwater catchments in Catalonia (Spain). Note how phosphorus (SRP) and ammonium (NH_4) appear associated with urban point and diffuse sources (Urban: percent urban land use, Inhabs: number of inhabitants, eq. inhab: inhabitant equivalents), whereas nitrate (NO_3) concentration is positively associated with irrigated agriculture (IrrAg) and bovine cattle units (BCU), and negatively with mean catchment slope (slope) and percent forest land (Forest). The other variables are Area: log area, P: precipitation, NonIrrAg: non irrigated agriculture. Data are from the Catalan water agency (http://ww.gencat.cat/ac)

The improvements in water quality described earlier clearly contrast with the current status in developing countries. Two thirds of the urban wastewater in the world still receives no treatment before being dumped to streams and rivers. Indicators of the degree of treatment of wastewaters, such as the percentage of population connected to WWTP and level of water treatment, are far from being optimal in these countries. For instance, less than 15% of the population in China (which constitutes 20% of world population) was connected to WWTP in 2007 [20]. In South America, despite the fact that 51% of the population has access to sewers, only 15% of the collected waters are delivered to WWTP [21]; however, these numbers vary depending on the South American country under consideration. Lack of information or very low percentages are also reported for other developing countries [22]. Despite the urgent sanitary need to reduce delivery of wastewater loads into the streams and rivers in these countries, implementation of conventional treatment systems and technologies is constrained by its high economic cost. Water management in these countries should seek alternative, less-costly, and more sustainable strategies that may rely on the natural services that ecosystems potentially provide [23, 24]. Among these services, removal of nutrients and organic matter by fluvial stream communities is paramount. Nevertheless, N and P retention efficiency decreases as the proportion or the pressure of urban land use in the catchment increases [14, 25, 26]. For this reason, management strategies for these urban-stressed streams should also include restoration tasks addressed to maximize this ecosystem service [25, 27].

It is expected that the ecological effects of urban growth on stream ecosystems will be exacerbated under water scarcity conditions [9]. Under these conditions, while wastewater loads (either treated or not) are maintained or even increased, the natural base flow of recipient streams is reduced. It is obvious that the effluent release criteria developed in humid regions should be revised to account for the low dilution effect in regions under water scarcity [28, 29]. The prevalence of conditions imposed by wastewater inputs is already common in urban areas of semiarid or arid climate regions, including the Mediterranean region [28, 30] and the southwestern of USA [13, 31]. This is favored by the hydrology of streams and rivers of these regions, which are often characterized by high seasonal variability with periods of low or intermittent flow disrupted by acute floods [28, 32, 33]. The influence of wastewater inputs on river nutrient loads may be aggravated in densely populated areas of these regions due to a higher water demand for consumption or irrigation, compounded by the longer drought periods expected under climate change scenarios in semiarid areas [34]. Currently, 44% of the world population already lives in catchments with high water stress, mostly due to the arid and semiarid climate of these regions, and it is expected that by 2050 there will be nine billion people in the world, of which 2.3 billion will live under water stress. The combination of shifts in hydrologic regime due to climate change and increased water demand in expanding urban areas may also spread the problems associated with low flows to regions with temperate climates, which are not currently subjected to water scarcity conditions [11, 13, 35]. As a result of current or anticipated escalation in water demand, water reclamation and reuse programs are increasingly being implemented [7, 36].

3 Nutrient Dynamics in WWTP-Dominated Streams

3.1 Effects of WWTP Inputs on Water and Nutrient Loads

Despite continued technological advances [37–39], effluents from WWTP still account for >50% of stream and river N and P loads regardless of the climatic region where streams are located [7, 30, 40–43]. Commonly, these inputs reach the recipient streams at discrete locations, generating abrupt physical and chemical discontinuities along the fluvial continuum. The magnitude of these discontinuities depends on the water and solute load of the WWTP effluents relative to the loads of the recipient streams. Small size streams (e.g., headwater streams) or streams with highly intermittent flow regimes, such as those in arid and semiarid regions, are the most vulnerable to these inputs because of their lower capacity to dilute the effluents. For instance, Martí et al. [30] showed that WWTP effluent inputs to 15 Mediterranean streams of the NE of Spain could account for up to 100% of the stream flow, especially during summer. Similarly, contributions of WWTP to stream flow greater than 50% have been reported for other intermittent streams during low flows and severe drought conditions [7, 44]. The WWTP effect is also subjected to the existence of other anthropogenic nutrient sources in the catchment upstream of the effluent input [45]. It is worth noting that during drought conditions, the influence of WWTP inputs on stream chemistry may increase while that of diffuse nutrient sources (e.g., from agricultural activities) may decrease. While the inputs of WWTP loads are relatively constant regardless of hydrologic conditions [42], inputs from diffuse sources increase with precipitation and runoff.

Inputs from WWTP effluents can also affect the hydrologic and nutrient concentration regimes of recipient streams at different temporal scales. Daily variations of these parameters may be exacerbated in streams below the WWTP input by the diel patterns of the effluent discharge associated with plant operation [46]. In contrast, at the annual scale, seasonal variations of physical and chemical parameters upstream of the WWTP may be dampened by the constant input of additional water and nutrients from the WWTP. At its extreme, naturally intermittent or ephemeral streams may turn into permanent streams downstream of WWTPs [28, 30]. In these effluent-dominated streams, the relative contribution of WWTP inputs may vary widely on an annual basis, as shown by the 3–100% range measured in a Mediterranean stream [47]. Finally, WWTP inputs also cause shifts in the relative availability of N and P as well as in the relative importance of reduced and oxidized forms of N in the stream [30, 47]. The magnitude of these shifts depends on the level of wastewater treatment (i.e., primary, secondary, or tertiary treatment), the type of WWTP infrastructure (e.g., activated sludge reactor, membrane bioreactors, rotating biological contactors), and its degree of optimal operation.

3.2 *Effects of WWTP Inputs on In-Stream Nutrient Retention*

Many studies over the past 30 years have shown that streams under relatively pristine conditions have a high capacity to transform and retain nutrients [48]. These studies also demonstrate that water discharge and nutrient concentration are key factors controlling this in-stream capacity. In general, nutrient retention efficiency (i.e., nutrient uptake relative to nutrient flux) decreases as discharge or nutrient concentration increases [49–53]. The most plausible explanations for these controls are that high discharge reduces the contact between biologically reactive benthic zones and the nutrients in the water column. In addition, high nutrient concentrations may exceed or saturate the nutrient demand of benthic microbial communities. Within this context, alteration in the magnitude and regime of physical and chemical parameters caused by the WWTP inputs should have profound ecological effects, including changes in nutrient uptake and transformation of WWTP-dominated streams (see for instance [54]).

Despite the fact that inputs from WWTP into streams and rivers are widely spread, relatively few studies [45, 54, 55] have directly examined the effect of WWTP inputs on stream nutrient retention. These studies had a common experimental setting in which they compared nutrient retention between reaches located upstream and downstream of WWTPs, and they were all conducted within the European project STREAMES (see more details in www.streames.org). Nutrient retention metrics from the nutrient spiraling theory [56, 57] were measured using the short-term nutrient addition technique [58]. Collectively, results from these studies showed either no significant effect or a decrease in nutrient retention efficiency (i.e., longer nutrient uptake lengths) downstream of the WWTP, except for one stream where nitrate retention efficiency increased downstream of the WWTP (Table 1). Among the study streams, a negative effect of WWTPs on retention efficiency of P was the most common result. Lack of significant differences between upstream and downstream reaches were attributed to high temporal variation in nutrient retention within each reach. Alternatively, it can be attributed to the fact that average nutrient uptake lengths (which is the average distance traveled downstream by a nutrient molecule before it is removed from the water column, Table 1) at all streams and for all nutrients were in the order of kilometers at the upstream reaches, which indicates that retention efficiency was already low above the WWTP inputs. Four out of the five streams studied drained catchments dominated by agricultural land use; thus, nutrient concentrations, especially nitrate, were relatively high upstream of the WWTP inputs. These additional nutrient sources may have confounded the effect of the WWTP. Despite the fact that these studies found relatively high areal nutrient uptake rates, especially at downstream reaches, they were not high enough to counterbalance the high nutrient

Table 1 Discharge, nutrient concentrations, and nutrient uptake lengths for ammonium, nitrate, and phosphate measured at reaches located upstream (UP) and downstream (DW) of WWTP effluent inputs in five European streams

	Tordera (n = 8) Spain		Gurri (n = 9) Spain		Fosso Bagnatore (n = 6) Italy		Demnitzer Mill Brook (n = 5) Germany		Erpe (n = 5) Germany	
	UP	DW	UP	DW	UP	DW	UP	DW	UP	DW
Discharge (L/s)	2–406	15–505	0–117	9–395	3–27	NA	13–40	12–42	130–195	468–607
NH_4-N (mg N/L)	0.01–0.08	0.15–2.21	0.01–0.15	0.01–0.21	0.01–0.26	5.8–17.6	0.08–0.24	0.08–0.30	0.03–0.14	0.08–0.20
NO_3-N (mg N/L)	0.7–2.2	1.6–6.4	2.7–13.4	4.5–10.9	2.3–5.4	0.1–17.1	3.8–16.4	5.4–15.7	0.8–6.5	5.7–11.0
SRP (mg P/L)	0.01–0.04	0.05–3.78	0.02–0.38	0.12–0.69	0.25–0.53	0.14–1.59	0.03–0.14	0.05–0.18	0.01–0.05	0.10–0.27
Sw-NH_4 (km)	**0.7 ± 0.3**	**2.6 ± 0.5**	1.7 ± 0.4	2.0 ± 0.6	0.9 ± 0.3	2.1 ± 0.4	3.4 ± 1.3	3.7 ± 0.7	**2.9 ± 0.8**	**9.6 ± 5.4**
Sw-NO_3 (km)	3.0 ± 1.1	4.1 ± 1.2	**1.9 ± 0.3**	**7.5 ± 4.2**	6.1 ± 4.1	7.1 ± 0.4	49.6 ± 29.7	47.5 ± 19.3	**20.5 ± 5.3**	**11.9 ± 3.8**
Sw-PO_4 (km)	**1.0 ± 0.4**	**4.6 ± 1.2**	**1.8 ± 0.5**	**4.3 ± 1.2**	6.4 ± 3.6	3.5 ± 1.2	4.2 ± 1.6	4.1 ± 1.2	**2.2 ± 0.7**	**5.5 ± 1.0**

Data for la Tordera and Gurri are from [45], for Fosso Bagnatore are from [55], and for Demnitzer Mill Brook and Erpe are from [54, 88]. Nutrient uptake length (S_w) is the average distance traveled downstream by a nutrient molecule before it is removed from the water column and is an indicator of nutrient retention efficiency. Shorter S_w values indicate higher nutrient retention efficiencies. Note that all S_w values are in the range of kilometer, regardless of the stream and nutrient considered. The table provides the range of variation for discharge and nutrient concentrations and the average (±1SEM) for S_w from measurements done on several sampling dates. Number of sampling dates for each stream is shown in brackets next to its name. Numbers highlighted in bold indicate significant differences in S_w between the two reaches. *SRP* soluble reactive phosphorus, *NA* not available data loads; thus, nutrients were exported over much longer distances than they would have been in less human-stressed environments. No clear seasonal trends in nutrient retention were found in any of these studies. However, Merseburger [45] showed that the upstream–downstream difference in the retention efficiency of ammonium increased as the point source contribution to dissolved inorganic N (DIN) and dissolved organic carbon (DOC) load increased. This suggests higher vulnerability of recipient streams in terms of nutrient retention under drought conditions. Nevertheless, more studies are needed to draw general conclusions about this hypothesis.

A larger number of studies have evaluated nutrient retention in WWTP-dominated streams by examining longitudinal patterns in ambient nutrient concentrations along reaches below effluent inputs (see Table 2). These longitudinal changes reflect the net result of physical, chemical, and biological uptake and release processes occurring within the stream. Nutrient concentration changes are usually weighted by those of a conservative tracer (e.g., chloride concentration) to correct for dilution and effluent mixing along the reach [59]. Declines in corrected nutrient concentrations along the reach indicate that streams are acting as net sinks for nutrients. Longitudinal increases indicate that streams are acting as sources or transformers (see later discussion about nitrification). Finally, lack of a significant change indicates that uptake and release processes may be balanced or that uptake is extremely small relative to load, and so it is not detectable. Some of these studies have quantified the longitudinal changes in nutrient concentration using a similar approach as that used in the short-term nutrient addition technique [58]. This allows estimating net nutrient uptake length (i.e., from net decline of nutrients at ambient concentrations), which can then be used for comparison among streams or within streams over time or even to compare this type of streams with less polluted ones (for instance, see [30]). Unfortunately, not all the studies examining longitudinal changes downstream of WWTP consistently calculate the net nutrient uptake length. This reduces the number of comparable data that can be used to draw more general conclusions.

Considering results from all the studies together, we observe that WWTP-dominated streams show high variability both in time and space in terms of nutrient uptake, acting either as net sinks or net sources, or having no effect on nutrient concentrations exported to downstream ecosystems (Table 2). The longitudinal patterns range from being highly variable and sporadic over time, such as in the case of a large river in the Atlanta (GA, USA) metropolitan area for nitrate [60], to being relatively consistent over the study period (Fig. 2). Different responses among nutrients are also observed when P and N (either as nitrate, ammonium or both) were simultaneously studied within the same study (Table 2, Fig. 2). This suggests that the WWTP inputs exert differential pressures on the processing of these elements, and thus, mechanisms controlling them may not be the same. One remarkable finding that all studies share is a significant longitudinal decline in nutrient concentrations. However, most resulting net uptake length values are in the order of kilometer, although few values are <1 km. These values are in the same range of those observed in the experimental studies indicated earlier (Table 1) and are much longer than in pristine rivers of similar size [30]. This suggests that as

Table 2 Compilation of studies aimed to examine longitudinal trends in nutrient concentration downstream of WWTP effluent inputs

Study stream	Extent of the study	NH_4-N	NO_3-N	PO_4-P	Reference
15 streams Catalonia, Spain	2 sampling dates, spring and summer	ns 11% ↑ 27% ↓ 62% Net S_w: 0.08–26.9 km	ns 22% ↑ 35% ↓ 43% Net S_w: 0.14–31.9 km	ns 4% ↑ 29% ↓ 67% Net S_w: 0.14–14.3 km	[30]*
La Tordera Catalonia, Spain	12 sampling dates, monthly over a year	ns ↑ ↓ 100% Net S_w: 0.2–2.9 km	ns 33% ↑ 67% ↓ Net S_w: ∞ km	ns 92% ↑ ↓ 8% Net S_w: 0.5 km	[47]
Gurri Catalonia, Spain	6 sampling dates over a year	ns 66% ↑ 17% ↓ 17% Net S_w:0.5 km	ns 33% ↑ 67% ↓ Net S_w: ∞ km	ns 33% ↑ 50% ↓ 17% Net S_w: 1.4 km	[47]
River Wey UK	4 sampling dates over a year	NA	ns 75% ↑ ↓ 25% Net S_w: 10.6 km	ns 50% ↑ ↓ 50% Net S_w: 12.8–14.8 km	[67]*
Columbia Hollow Arkansas, USA	8 sampling dates over a year	ns ↑ ↓ 100% Net S_w: 0.4–1.4 km	ns ↑ 100% ↓ Net S_w: ∞ km	ns ↑ 25% ↓ 75% Net S_w: 7.5–13.4 km	[61]*
Spavinaw Creek Arkansas, USA	6 sampling dates in summer of 2 years	NA	ns ↑ ↓ 100% Net S_w: 3.1–12 km	ns ↑ ↓ 100% Net S_w: 9–31 km	[66]*

Otter Creek Florida, USA	Several dates over a year	NA	NA	ns ↑ ↓ 100% Net S_w: 3.4–11.1 km	[89]*
Sand and Caddo Creeks Oklahoma, USA	Sampling on 3 time frames	ns ↑ ↓ 100% Net S_w: 3–29 km	ns 100% ↑ ↓ Net S_w: ∞ km	ns 33% ↑ ↓ 67% Net S_w: 46–51 km	[90]*§
Chattahoochee River Georgia, USA	10 sampling dates from summer to fall, in two reaches	ns 31% ↑ 44% ↓ 25% Net S_w: 7–20 km	ns 65% ↑ ↓ 35% Net S_w: 13–60 km	ns 12% ↑ 29% ↓ 59% Net S_w: 11–85 km	[60]
Reedy River South Carolina, USA	4 sampling dates in spring of four consecutive years	NA	ns ↑ 50% ↓ 50% Net S_w: NA	NA	[44]
Bow River Alberta, Canada	2 sampling dates	ns ↑ ↓ 100% Net S_w: NA, but bdl concentration was measured at 4–7 km	ns ↑ ↓ 100% Net S_w: 20–52 km	ns ↑ ↓ 100% Net S_w: NA, but bdl concentration was measured at 4–7 km	[59]
Mankyung River Korea	2 sampling dates	NA	ns 50% ↑ ↓ 50% Net S_w: NA	NA	[91]

Table shows the number of data available (i.e., sampling dates) and the percentage of cases that nutrient (i.e., ammonium, nitrate, and phosphate) concentration showed no significant trend (ns), a significant increase (↑), or a significant decrease (↓). All trends are examined after correcting nutrient concentrations for concentrations of a conservative tracer (exceptions to this are indicated with §). When available, the range of net nutrient uptake length (Net S_w) values obtained only from significant declines in concentrations is included. NA indicates that data is not available. This table is modified and expanded from that in [61]; *indicates that the study was already included in the original table

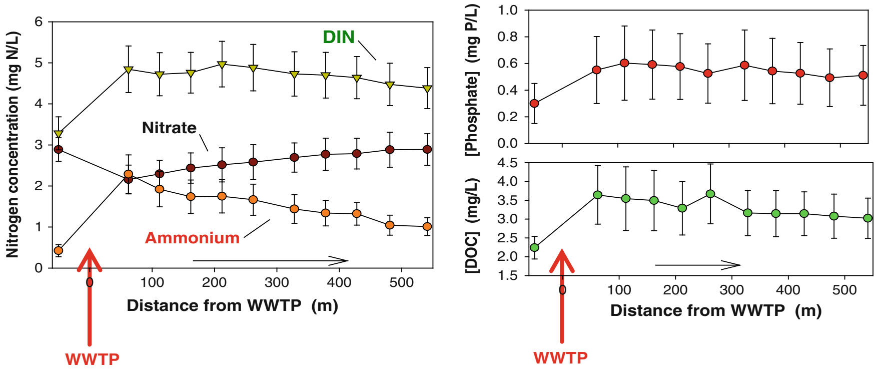

Fig. 2 Longitudinal changes in nutrient concentrations below the effluent input of a WWTP without tertiary treatment in La Tordera Stream. Values are the average (±SEM) of monthly measurements done over a year (see more details in [47]). In the left panel, note the net decline of ammonium concentration with concomitant net increases in nitrate concentration, suggesting a potential hot spot for nitrification. However, in the latest meters downstream, dissolved inorganic nitrogen (DIN) tends to decrease, which indicates net lost of DIN possibly due to denitrification. The right panel shows net changes in phosphate and dissolved organic carbon (DOC) concentrations. While phosphate does not exhibit any clear trend on an annual basis, DOC seems to decline similarly to DIN, which supports the relative dominance of denitrification

nutrient loading is elevated by the effluent inputs, nutrient removal efficiency is greatly reduced. The limited in-stream retention emphasizes that WWTP inputs may have long-term and large-scale effects on water quality. This result illustrates the strong effect that WWTP inputs exert on the streams and provides additional support to one of the symptoms considered within the urban stream syndrome [10].

Declines observed for P are generally attributed to the buffer capacity of stream sediments to adsorb this element [61]. This mechanism also helps explain the net increases in P observed when P input from the WWTP decreases [61]. Complementary measurements of sediment equilibrium P concentrations and sediment exchangeable P show a positive effect of WWTP inputs on these parameters and corroborate the sediment sorption control on P below WWTP inputs [41]. Another common finding among the studies is that net declines of ammonium concentration are usually coupled with concomitant net increases in nitrate concentrations in streams receiving ammonium-rich effluents [30, 47, 61], (Fig. 2). This suggests that these sites are acting as hot spots for nitrification. Under these conditions, DIN is basically being transformed rather than retained. However, this biogeochemical process plays an important role as it reduces ammonium below potentially lethal concentrations for stream biota and also generates nitrate that can potentially be eliminated from the stream through denitrification, provided the necessary conditions are met. WWTP effluents can represent a significant source of nitrifying bacteria from the biological sludge to recipient streams [62], and thus, could account for the observed nitrification patterns. It is worth noting that, in cases where the effluent is ammonium-rich, concentration of nitrite (an intermediate product of nitrification and denitrification) in the stream can be high if dissolved oxygen concentration is low. Similar to ammonium concentration, elevated concentration of nitrite can be very toxic to stream biota [63].

In contrast to these patterns, some studies show declines in nitrate (see Table 2) or DIN concentrations [47], which indicate that the streams are net sinks, especially in the case of loss of DIN, for this N form. This pattern, however, is less evident and consistent both among and within streams. Explanatory mechanisms for this trend point at N being either stored through biotic assimilation, or lost through denitrification, or adsorbed onto sediments (in the case of ammonium) as dominant processes in front of release processes or additional sources. As denitrification represents a loss of N from the ecosystem, approaches to estimating the relevance of this process at the whole-reach scale are valuable for understanding the fate of N below point sources. Longitudinal changes in natural abundance of stable isotopes (^{15}N) have been used for such estimates because denitrification causes considerable isotope fractionation [64]. For instance, results from Lofton et al. [64] showed that, despite the observed declines in nitrate concentration, denitrification did not play a major role on N transport along a WWTP-influenced reach, but some spots of the reach were particularly active on this process. This approach provides a promising springboard toward a mechanistic understanding of the fate of N added to streams from WWTPs. Together, all these results seem to be quite conclusive about the fact that WWTP-dominated streams can be active biogeochemical sites able to transform, store, and even remove a fraction of the nutrient load delivered by the effluent, even if the overall relevance of these processes compared to the stream loads may not be high. In addition, these results demonstrate that the biogeochemical relevance of WWTP-dominated streams varies according to the nutrient under consideration both within a single stream and among streams and that this variability can be influenced by the chemical composition of the WWTP effluent. For instance, in the case of N, the nitrate/ammonium ratio of the effluent, which ultimately depends on the type and effectiveness of the wastewater treatment, may play an important role in determining longitudinal patterns of both N forms. This is supported by contrasting results found by Merseburger et al. [47] between two streams differing in this ratio.

3.3 Effects of Water Scarcity on In-Stream Nutrient Retention in WWTP-Dominated Streams

The effect of water scarcity on nutrient retention in WWTP-dominated streams has hardly been explicitly addressed in studies of WWTP impacts (but see [44, 65]). It is also worth noting that a large number of studies have been done in relatively temperate zones (Table 2), although they may not be exempt from water scarcity conditions. Trends observed from the compilation of results provide controversial insights on the potential directions of the influence of water scarcity. For instance, the longitudinal patterns in nutrient concentration are less consistent over time and net uptake lengths tend to be longest in the stream with the highest discharge (i.e., in the order of m^3/s, [60]). In addition, studies done in two Ozark rivers (Arkansas, USA) showed relatively longer net uptake lengths in the stream with higher discharge [61, 66]. In general, studies that have included variability over time on these measurements do not reveal any clear seasonal pattern, but it should be noted that none of the studies extended for more than a year. Nevertheless, House and Denison [67] indicated net storage of P during spring and summer and net release in autumn and winter. Similarly, Demars et al. [40] showed that most of the P retention in their study stream occurred during the dry season. Merseburger et al. [47] also found that, in one of the streams (La Tordera), larger retention and transformation of N forms coincided with summer low flow (and thus, higher influence of the WWTP). Finally, Andersen et al. [65] found that higher declines in P and N were associated with very low flow conditions. Together, these results point towards an increase of in-stream nutrient retention control on nutrient fluxes under low flows, which would be enhanced under water scarcity conditions. However, other studies provide basis to draw the opposite conclusions. For instance, Martí et al. [30] showed no relationship between net nutrient uptake lengths and stream discharge among several WWTP-dominated streams, which were mostly fully driven by the point source. In addition, Hur et al. [44] reported that the stream acted as a source of nitrate during the spring of years with drought, while it acted as a net sink during the spring of years subjected to normal or above normal precipitation. Haggard et al. [66] also reported that efficiency to retain nitrate decreased as discharge decreased. In these cases, the positive effect on nutrient uptake of reduced flows may be counterbalanced by the negative effect of increased nutrient concentrations due to saturation or toxicity.

4 Point Sources Under Water Scarcity: Managing the Stream Network

In addition to their local impacts on receiving streams, WWTP effluents arguably affect stream networks, as they modify the configuration and the temporal and spatial dynamics of water discharge and materials transport. We can expect that global change (both climate and land use change) will aggravate the WWTP effects on stream networks in semiarid regions and extend them to catchments that are currently more humid and sustain permanent flows. What these effects will be in the future will depend strongly on how we decide to manage catchments under escalating water demands.

Stream networks are increasingly being viewed as spatially heterogeneous and temporally variable landscapes [68, 69]. In semiarid regions, streams compose fluvial landscapes whose configuration and dynamics are driven by the gradual process of flow reduction and drying and the opposing process of rewetting, which can be sudden or slow. The balance between these processes, which depends on the climate regime, results in river network contraction and fragmentation, followed by expansion and reconnection [70]. During low flow conditions, low order streams often stop flowing, but also other reaches along the network may dry, depending on the channel hydrogeology and water demand by riparian vegetation (e.g., [71]), leaving a patchwork of dry reaches interspersed with islands of flowing surface water or standing pools. The hydrologic longitudinal connectivity that dominates stream network dynamics during high flows is reduced during low flow to subsurface flowpaths, or severed altogether. At the network scale, stream functioning, and in particular organic matter processing and nutrient dynamics, including retention, may be enhanced during low flows at the same time that the transport of matter and nutrients downstream becomes severely limited [65, 70, 72].

Water demand and wastewater disposal by land uses in the catchment strongly modify these patterns and dynamics [31]. On the one hand, water scarcity is exacerbated due to water interception, abstraction, and diversion for forestry, agricultural, industrial, and urban uses, reducing base flow and generating intermittent reaches where flow used to be permanent or dried only occasionally. On the other hand, industrial and urban wastewater effluents sustain permanent flow in stream reaches that would otherwise stop flowing during the dry season. Altogether, the result is a strongly modified hydrologic temporal regime that is also spatially altered, exacerbating the discontinuum in the fluvial landscape that is natural to stream networks in semiarid regions, or generating discontinuities in previously permanent stream networks.

While it is generally true that characteristics of a stream reflect land uses in its catchment, in semiarid regions, and especially in WWTP-dominated streams, water flow and chemical characteristics actually depend directly on effluent characteristics. In particular, nutrient concentrations and stoichiometric ratios will depend on waste provenance and treatment at WWTP. In catchments with mixed land uses, nutrient flow will be strongly heterogeneous both spatially and temporally, reflecting distinct inputs from agricultural and urban diffuse sources during high flows and industrial and urban point sources during low flows. Stream biogeochemistry will vary accordingly. As the stream dries, urban influences on stream biogeochemistry rise to prominence, often with relative increases in ammonia, soluble phosphorus, and particulate organic matter [26], while rain events wash through soils and dry channels and produce peaks in nitrate, particulate phosphorus, and inorganic suspended solids. Based on existing evidences, stream nutrient retention may be enhanced under low flows, perhaps even below effluent outfalls, with climate variability accounting for interannual and annual variability in nutrient retention at the catchment scale (Fig. 3).

Inputs of organic matter and nutrients, benthic metabolism, and nutrient retention at each stream section depend on diffuse and point sources. Yet, under low flow conditions, water and matter transport downstream becomes impeded or discontinued due to stream contraction and fragmentation during dry periods. Therefore, nutrient export from rivers in semiarid regions will depend, more so than in more humid regions, on the interplay between the spatial configuration of organic matter

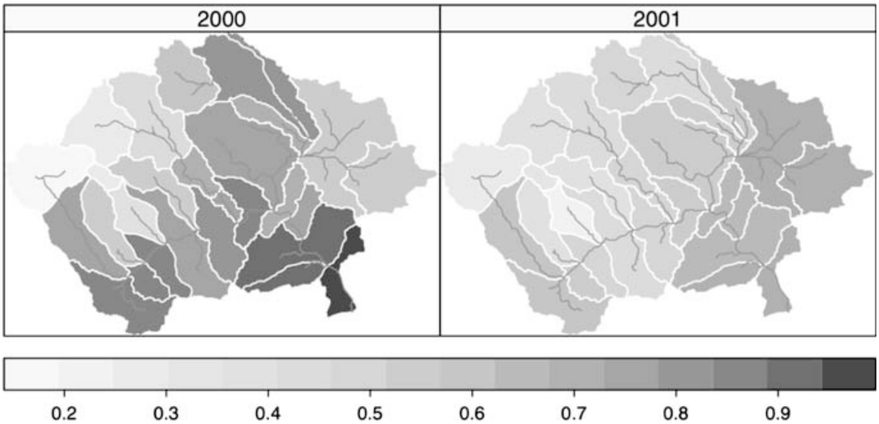

Fig. 3 Nitrogen retention (as a fraction of inputs per subcatchment) on a dry year (2000, 670 mm rainfall) and a wet year (2001, 727 mm rainfall) for La Tordera catchment (NE Spain). From [87]

and nutrient inputs, on the one hand, and the anthropogenically impacted patchwork of intermittent and permanent reaches, on the other hand. Under these conditions, river networks will be less "controlled by their valleys" (*sensu* [73]) and more by the valley's population.

How will all this be affected by global change? Climate change scenarios for the Mediterranean region and, in general, for semiarid regions suggest higher mean temperatures and lower precipitation during the dry season [74], aggravating the problems of water scarcity, as well as higher intra- and interannual climate variability [75]. Scenarios for stream networks under climate change are a matter of informed speculation and are naturally dependent on current land uses at each particular catchment and on expected socioeconomic drivers in the future. As an example, Caille et al. [76] used a participatory process to develop scenarios for a small catchment just north of Barcelona (La Tordera, 877 km^2). Stakeholders envisioned four futures for La Tordera that differed in the modes of governance and models of management but shared a number of trends. These included the abandonment of marginal agricultural lands, the intensification of productive agricultural lands, an increasing or stabilizing urbanization trend, improvements in urban runoff and wastewater management, changes in the industrial makeup (from primary industry to logistics and services), as well as an increased awareness of environmental issues and of the need to protect and enhance the ecosystem services provided by the river. In the end, this translates into an increase in water demand for both consumptive uses and stream protection under a scenario of reduced precipitation. In this situation, business-as-usual would exacerbate the fragmentation of the stream network during the dry season into sections with low or no flow due to water abstraction and diversion and effluent-dominated reaches. Preservation or rehabilitation of ecological flows and stream ecosystem services will require changes in watershed management, where WWTPs will play a crucial role [77].

Aside from sorely needed improvements in the water use efficiency of agricultural irrigation, industrial processes, and urban uses, the resolution of the water demand conflict will often require managers to resort to water importation (e.g., through interbasin transfers or from desalination plants) and the implementation of water reuse schemes. Water importation potentially provides stream flow through WWTP effluents, while water reuse may decrease the availability of effluents for maintaining stream flow, especially if treated wastewater is reused for irrigation and therefore largely lost through evapotranspiration [78]. Water quality in effluents will also depend on technological improvements and management decisions. Roach and Grimm [79], for example, showed that nutrient limitation of urban streams was driven as much by management decisions as by natural hydrologic variation in an artificially created chain-lake system in Arizona (USA). Under a scenario of increased vulnerability of receiving streams to pollution from WWTP effluents, there is a clear need to implement tertiary treatments. Finally, preserving ecological flows throughout the stream network (i.e., counteracting the fluvial landscape fragmentation) might require changes in how WWTP effluents are returned to the stream channel, moving from a localized to a more spatially distributed return of flows, for example, through groundwater recharge [80].

Severely impacted streams are not uncommon in small and heavily used semi-arid catchments and can only be expected to become more frequent, given current trends in population growth, urbanization, land use change, and climate change. Increasingly, these streams cannot and will not be restored to reference pristine conditions and depend on ecological engineering techniques and smart integrated catchment management to evolve towards stream systems that provide recovered, enhanced, or artificially promoted ecosystem services. These include flood control, nutrient retention, habitat for stream and riparian biota, and aesthetic and recreational services. These streams, which truly qualify as designer ecosystems [81], depend heavily on the use of treated WWTP effluents to sustain flow and fulfill those services. A case in point is the management of the Yarqon River in Israel [82, 83]. The Yarqon was a permanent stream in historical times, thanks to the groundwater springs that fed the river's base flow. But water abstraction for irrigation and for water supply to Tel Aviv lowered the groundwater table enough that in the 1980s the Yarqon could aptly be described as a free-flowing wastewater stream (*sensu* [84]). Starting in 1988, a restoration plan developed by the newly created Yarqon River Authority with stakeholder involvement led to a river with rehabilitated services, but quite different (in terms of water chemistry and hydrologic regime) from the river of yore. It is now a managed functioning ecosystem sustained by treated wastewater effluents.

5 Outlook: What Science Do We Need to Do?

The issues discussed in this chapter fall at the intersection of several disciplines, and suffer from the usual lack of interaction that plagues transdisciplinary research. The field falls at the intersection between basic natural sciences (ecology of fluvial ecosystems, hydrology, biogeochemistry), social and policy science, environmental management, and technology and engineering (wastewater treatment technology). Thus, much of the progress in facing the challenges posed by the management of point sources under water scarcity will come from enhanced interactions among theses disciplines.

In particular, more knowledge is needed on the factors controlling the biogeochemical processes within WWTP reactors and within receiving streams and rivers, and on how WWTP management interacts with the stream flow regime to determine patterns of physical and biological nutrient retention downstream of a WWTP. Management at the local scale will certainly benefit from effectively integrating models of stream functioning, urban runoff, and WWTP operation [85].

Nutrient retention is an important ecosystem service provided by streams, and there has been significant progress in our understanding of the biogeochemical processes, mechanisms, and controls responsible for the physical, chemical, and biological retention of N and P in running waters at the local and short-term (less than 2 years) scales. Yet there are still large gaps in our knowledge of within-catchment spatial and temporal variation over larger time frames in retention, which seriously hinder our capacity to effectively manage and restore streams in a way that maximizes the benefits of retention processes. The reason for these gaps have more to do with the cost (in terms of time, logistics, man-power, and money) of doing large-scale or long-term research than with our ignorance of the importance of processes acting on these scales.

These limitations are especially felt when trying to scale local effects of WWTPs up to the catchment scale. Modeling remains the primary tool to address upscaling issues, fluvial landscape dynamics, and upstream–downstream linkages in the fragmented stream networks which are becoming common in populated catchments of semiarid regions. While significant progress is being made in catchment and stream network modeling (e.g., [86]), better analytical and observational tools are still needed, including denser measurement networks and more widespread use of automatic sensors and sample collection, at least at the scale necessary for adequate model calibration and verification.

Good spatially explicit models of, at the very least, stream hydrology are needed before the evaluation of climate change scenarios can be undertaken. Unfortunately, semiarid and arid areas are among the least studied and more poorly monitored in the world, even if the ecosystem services that the streams in these regions provide are highly vulnerable to population growth, urbanization, and climate change.

Finally, research alone will not suffice to solve the challenges posed by water management under water scarcity scenarios. If technology can help us secure the water supply for a growing population, political will and societal commitment will be imperative to set and enforce environmental goals and to satisfy the water demands of our stream ecosystems. An environmentally sensitive use of WWTP management and wastewater recycling and a commitment to restore the services provided by streams can go a long way towards the preservation of flowing waters of acceptable ecological quality in the future.

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Occurrence and Fate of Pharmaceuticals and Illicit Drugs Under Water Scarcity

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Abstract Occurrence of emerging contaminants in environmental waters is directly related to their removal in wastewater treatment plants (WWTP) and the flow rate of the receiving waters. Mediterranean rivers are characterized by important fluctuations in the flow rates and heavy contamination pressures from extensive urban, industrial, and agricultural activities. This translates in contamination levels most often higher than in other European basins. This paper reviews the data regarding the levels of pharmaceuticals and illicit drugs detected in wastewaters and gives an overview of their removal by conventional treatment technologies applying activated sludge. Pharmaceutically active compounds and illicit drugs are selected as two important groups of emerging environmental contaminants that have raised an increasing interest in the scientific community. Their removal in WWTP, the influence of hydrological conditions in the receiving rivers, and dilution factors are described and examples are provided for selected WWTP and rivers in Catalonia (NE Spain).

Keywords Emerging contaminants, Illicit drugs, Occurrence, Pharmaceuticals, Wastewater treatment

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Contents

1 Introduction

Only less than 1% of the world's fresh water resources are readily available for human use, and even this resource is very unevenly distributed among and within the countries. A lack of water to meet daily needs is a reality for many people around the world, and water scarcity already affects every continent. World Health Organization (WHO) estimates that by the year 2025, nearly two billion people will be living in countries or regions with absolute water shortage, where water resources per person fall below the recommended level of 500 $m^3\ yr^{-1}$. In the underdeveloped countries water scarcity forces people to rely on unsafe sources of drinking water, which leads to diseases such as cholera, typhoid fever, salmonellosis, other gastrointestinal viruses, and dysentery. In the developed countries, this problem is much less critical, where contamination of drinking water is the adverse outcome of incomplete wastewater treatment and improper disposal of sewage. The partial or complete closing of water cycles is an essential part of sustainable water resources management. The increasing scarcity of pristine waters for drinking water supply and increasing consumption of water by industry and agriculture can be countered by the efficient and rational utilization of resources. One of the options is increasing reuse of effluents for various purposes, especially in industrial and agro/food production activities. However, due to high cost of end-of-pipe approach (drinking water treatment) the future of indirect potable reuse requires a planned protection of surface waters through efficient treatment of wastewaters prior to their discharge. Therefore, the key to future water treatment are environmentally friendly, efficient, and reliable technologies that will be a part of an integrated approach to the aggravating problem of water contamination.

Presence of emerging contaminants in environmental waters is directly related to their removal in wastewater treatment plants (WWTP) and the flow rate of the receiving waters. Mediterranean rivers are characterized by important fluctuations in the flow rates and heavy contamination pressures from extensive urban, industrial, and agricultural activities. This translates in contamination levels in these rivers most often higher than in other larger European basins. For instance, the Llobregat river basin (Catalonia, NE Spain), suffers from extreme and frequent flow (1–100 $m^3\ s^{-1}$) fluctuations and receives the effluent discharges of more than 55 WWTPs, and at some points especially in drought periods, the effluents may represent almost 100% of the total flow of the river. Thus, it is not strange to find considerably high levels of organic contaminants along the river and increasing concentrations when moving downstream due to the also increasing number of WWTPs and population pressure [1, 2].

This chapter gives a general introduction on emerging contaminants and an overview of occurrence data in WWTP effluents and receiving surface waters focusing on two classes of emerging contaminants, namely pharmaceuticals and illicit drugs. The issue of water scarcity and contamination of surface waters is discussed with respect to discharge of emerging contaminants by WWTP effluents into the surface waters, influence of hydrological conditions, and dilution factors, giving examples for selected WWTP and rivers in Catalonia (NE Spain).

2 Emerging Contaminants

Persistent organic pollutants (POP) and heavy metals were in the focus of interest until the beginning of the 1990s and intensive monitoring programs and ecotoxicological studies had been conducted. As a result, due to adoption of appropriate measures and elimination of the dominant pollution sources a drastic reduction of emission of these nonpolar hazardous compounds have been achieved and today these compounds are less relevant for the industrialized countries.

However, the emission of so-called “emerging” or “new” unregulated contaminants has emerged as an environmental problem and there is a widespread consensus that this kind of contamination may require legislative intervention.

A wide range of man-made chemicals, designed for use in industry, agriculture, and as consumer goods and chemicals unintentionally formed or produced as by-products of industrial processes or combustion, are potentially of environmental concern. Beside recognized pollutants, numerous new chemicals are synthesized each year and released into the environment with unforeseen consequences. However, 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 unrecognized 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 (eco)toxicity, potential health effects, public perception and on monitoring data regarding their occurrence in the various environmental compartments [3]. Today, there are several groups of compounds that emerged as particularly relevant:

- Algal and cyanobacterial toxins
- Brominated flame retardants
- Disinfection by-products
- Gasoline additives
- Hormones and other endocrine disrupting compounds
- Illicit drugs and their human metabolic byproducts
- Organometallics
- Organophosphate flame retardants and plasticisers
- Perfluorinated compounds
- Pharmaceuticals and personal care products
- Polar pesticides and their degradation/transformation products
- Surfactants and their metabolites

This chapter covers two groups of emerging contaminants: pharmaceutically active substances (PhACs) and illicit drugs. Their significance as trace environmental pollutants in waterways is due to several facts: (1) continuous introduction via effluents from sewage treatment facilities and from septic tanks, (2) they are developed with the intention of performing a biological effect, (3) often have the same type of physico-chemical behavior as other harmful xenobiotics (persistence in order to avoid the substance to be inactive before having a curing effect and lipophilicity in order to be able to pass membranes), (4) some pharmaceutical substances are used by man in rather large quantities (i.e., similar to those of many pesticides). Numerous studies revealed their presence in wastewaters, as well as surface, ground, and drinking water. This is mainly due to the fact that some compounds are not efficiently removed during wastewater treatment processes, being able to reach surface and groundwater and subsequently, drinking waters.

3 Sources and Occurrence of Emerging Pollutants in Wastewaters

3.1 Pharmaceutically Active Compounds

In a vast array of contaminants of anthropogenic origin reaching our water supplies, PhACs are among the ones with the most continuous input into the environment, especially the over-the-counter (OTC) drugs, which is raising scientific concerns of long-term consequences on human health. PhACs are a group of chemical substances that have medicinal properties, and they are produced worldwide on a 100,000 t scale.

Most of modern drugs are small organic compounds with a molecular weight (MW) below 500 Da, which are moderately water soluble as well as lipophilic, in order to be bioavailable and biologically active. After the oral, parenteral, and/or topical administration, PhACs are excreted via liver and/or kidneys as a mixture of parent compound and metabolites that are usually more polar and hydrophilic than the original drug. In the European Union (EU), around 3,000 different PhACs are used in human medicine (i.e., analgesics and anti-inflammatory drugs, β-blockers, lipid regulators, antibiotics, etc); thus, their main route into the aquatic environment is ingestion following excretion and disposal via wastewater. After administration, pharmaceutical can be excreted as an unchanged parent compound, in the form of metabolites or as conjugates of glucuronic and sulphuric acid, primarily via urine and feces. After their usage for the intended purpose, a large fraction of these substances will be discharged into the wastewater unchanged or in the form of degradation products that are often hardly eliminable in conventional WWTPs. Depending on the efficiency of the treatment and chemical nature of a compound, they can reach surface and ground waters. In the worst-case scenario, they are encountered in the drinking water, in spite of the expensive treatment steps. Besides WWTP discharges that are usually a consequence of the incomplete removal of PhACs, other environmental exposure pathways are manufacturing and hospital effluents, land applications (e.g., biosolids and water reuse), concentrated animal feeding operations (CAFOs), and direct disposal/introduction to environment. For example, a survey conducted in the US reported that a vast majority of people disposed expired medications via municipal garbage or domestic sewage [4].

The highest concentrations in raw wastewater are commonly reported for non-steroidal anti-inflammatory drugs (NSAIDs), which could be attributed to their wide consumption because they can be purchased without medical prescription (i.e., OTC drugs). For example, ibuprofen is usually detected at very high concentrations (in μg L^{-1}) [5–7]. Other very popular pain killers, often found at μg L^{-1}levels, are acetaminophen (paracetamol) and aspirin (acetylsalicylic acid). Besides these OTC drugs, pharmaceuticals ubiquitous in raw sewage are also prescription drugs β-blockers [8, 9]. Atenolol seems to be the most frequently found β-blocker worldwide in WWTP influents [10–12]. Atenolol, metoprolol and propranolol were detected at high influent concentrations in a study by Nikolai et al. [12] (i.e., 110–1,200, 170–520 and 20–92 ng L^{-1}, respectively).

Numerous studies confirmed ubiquity of several antibiotics (i.e., ofloxacin, trimethoprim, roxythromycin, and sulfamethoxazole) in sewage influent, though at low ng L^{-1} level [8, 13, 14]. However, even at very low concentrations they can have significant ecotoxicological effects in the aquatic and terrestrial compartment [15, 16]. Indiscriminate or excessive use of antibiotics has been widely blamed for the appearance of so-called "super-bugs" that are antibiotic-resistant. It is of crucial importance to control their emissions into the environment through more cautious utilization and monitoring outbreaks of drug-resistant infections.

Antiepileptic drug carbamazepine is one of the most prominent drugs with a long history of clinical usage, and it is frequently found in the environment [8, 17, 18].

This drug has proved to be very recalcitrant, as it by-passes sewage treatment. Common WWTP influent concentrations are in the order of magnitude of several hundreds of nanograms per liter [5, 8, 13, 19, 20].

Lipid regulators are ordinarily applied drugs in clinical practice, and they are used to lower the level of cholesterol and regulate the metabolism of lipids. Clara et al. [13] detected a lipid regulator bezafibrate at concentrations up to 7.6 μg L^{-1}, although normally they are found at lower nanograms per liter range [8, 18, 21, 22].

In all countries with developed medical care, X-ray contrast media can be expected to be present at appreciable quantities in sewage water. Clara et al [13] detected iopromide at a mean concentration of 3.84 μg L^{-1} in the influent of a WWTP receiving hospital wastewater, while in WWTPs without a hospital within their drainage area this contrast media was not present. Iodinated X-ray contrast media are proved to contribute significantly to total absorbable organic iodine in clinical wastewaters; up to 130 μg L^{-1} of iodine in the influent of municipal WWTP in Berlin and 10 mg L^{-1} in hospital sewage was detected [23].

3.2 Illicit Drugs

In recent years, drugs of abuse and their metabolites have been highlighted as a group of environmental emerging contaminants [24], becoming pseudo-persistent in the environment mainly as a result of their extended use. Although drug consumption trends now seem to be stabilized, around 208 million people (5% of the world's population) still make use of these substances [25]. Like pharmaceuticals, after their administration, drugs are metabolized to a different extent in the human body and subsequently eliminated in their original form or as metabolic by-products via urine and feces. They are flushed together with household sewage water towards municipal WWTPs, where they undergo several treatment processes to get biodegraded. However, most of them are only partly removed during sewage treatment, and thus released into the environmental systems via WWTPs effluents, which constitutes the main source of this type of compounds to the aquatic media, as direct disposal represents a minor route of entry to the environment.

Different drugs of abuse and metabolites belonging to the chemical classes of cocainics, opioids, cannabinoids, amphetamine-like compounds and drugs of design, and lysergics have been the subject of different research works regarding their environmental occurrence [2, 10, 11, 26–38]. Drugs of abuse residues commonly present in natural waters are the cocainic compounds cocaine and its main human metabolite, benzoylecgonine; the opioids morphine, methadone, and its main metabolite, 2-ethylidene-1,5-dimethyl-3,3-diphenylpyrrolidine (EDDP); the amphetamine-like compounds 3,4-methylendioxyamphetamine (MDMA or "ecstasy") and ephedrine; and the cannabinoid 11-nor-9-carboxy-THC (THC-COOH), which is one of the main human metabolites of the psycho active constituent of the cannabis, Δ9-tetrahydrocannabinol (THC).

4 Ecotoxicological Effects of Pharmaceuticals and Illicit Drugs

Numerous studies have been undertaken to evaluate the risk of other potentially harmful chemicals. Many of which have, eventually, either been banned completely, or had their use severely restricted (i.e., tributyltin, alkylphenolic surfactants, penta and octa PBDEs, etc.). However, compared to other pollutants the sources of pharmaceuticals are likely to be much more difficult to control and it is highly unlikely that they will be replaced or banned. This fact is of concern from the ecotoxicological point of view, as pharmaceuticals are designed to target specific metabolic and molecular pathways in humans and animals, and when introduced into the environment they may affect the same pathways in animals having the identical or similar target organs, tissues, cells, or biomolecules [39]. However, the potential ecological effects associated with the presence of pharmaceuticals in the environment have been largely ignored and their toxicity to organisms is still not well documented in the scientific literature. Based on the available information [39], acute toxicity to aquatic organisms is unlikely to occur at measured concentrations in surface waters, as levels reported to cause such effects are typically from 100 to 1,000 times higher than the concentrations found in the surveyed sampling sites (i.e., rivers receiving WWTP effluents). However, for some compounds the margin seems to be quite narrow. For example, diclofenac seems to be the compound having the highest acute toxicity within the class of analgesics and NSAIDs, since tests performed in phytoplankton and zooplankton showed EC_{50} (96 h) values of 14.5 mg L^{-1} and 22.43 mg L^{-1}, respectively [40], nearly two orders of magnitude higher than the levels detected in the WWTP effluents studied (low μg L^{-1} range). Among β-blockers, propranolol is the one showing higher acute toxicity with EC_{50} (48 h) values of 0.8 mg L^{-1} [40] and 1.6 mg L^{-1} [41] for *Ceriodaphnia dubia* and *Daphnia magna*, respectively, which are approximately 1,000 times higher than the levels detected. For blood lipid lowering agents, EC_{50} values reported for bezafibrate and gemfibrozil, the most ubiquitous compounds detected in the sites studied, were higher than 100 mg L^{-1} [39]. Among the neuroactive compounds, fluoxetine is the one showing higher acute toxicity, with EC_{50} (48 h, alga) of 0.024 mg L^{-1} [42] and LC_{50} (48 h) of 2 mg L^{-1} [43]. For antibiotics erythromycin, sulfamethoxazole, and ofloxacin, the EC_{50} values for *Vibrio fischeri* were higher than 100 mg L^{-1}, from 16.9 to 32.2 and 100 mg L^{-1} [44], respectively, being all these levels much higher than the ones found in surface waters (ng L^{-1} to low μg L^{-1} range).

Concerning to chronic effects, lowest observed effect concentration (LOEC) and no observed effect concentration (NOEC) values for pharmaceuticals, reported in the literature, are about one to two orders and two orders of magnitude, respectively, higher than maximal concentration detected in majority of WWTP effluents. However, in some studies [8] for diclofenac, propranolol, fluoxetine, and carbamazepine, the levels found in environmental waters were in the range of values causing chronic effects. It was reported that for diclofenac, the LOEC for fish toxicity was in the range of wastewater concentrations, showing renal lesions and alterations of the gills in rainbow trout at the LOEC of 5 μg L^{-1} [45], as well as subtle subcellular effects even at 1 μg L^{-1}. Moreover, impairment of renal and gill function is likely to occur after long-term exposure. The kidney was also found to be a target of diclofenac in vultures [46] and side effects have also been observed in human liver with degenerative and inflammatory alterations. LOEC of propranolol and fluoxetine for zooplankton and benthic organisms were near to maximal measured WWTP [8]. LOEC of propranolol affecting reproduction in *C. dubia* were 125 and 250 μg L^{-1}, and reproduction was affected after 27 days of exposure in *Hyalella azteca* at 100 μg L^{-1} [41]. For fluoxetine, stimulation was also found in *D. magna* exposed to 36 μg L^{-1} fluoxetine for 30 days, and in *C. dubia* fecundity was increased at 56 μg L^{-1} [47]. For carbamazepine, sublethal effects occurred in *D. magna* at 92 μg L^{-1} and the lethal concentration in zebra fish was 43 μg L^{-1} [48]. For the antibiotics erythromycin, sulfamethoxazole, and ofloxacin, the LC_{50} values observed showing chronic toxicity were 20, 520, and 1,440 μg L^{-1}, respectively.

The toxicological or cumulative effect of illicit drugs on the ecosystems has not been studied yet. Moreover, their fate and transport in the environment is to a big extent still unknown. Due to their physical–chemical properties (octanol–water partition coefficient, solubility, etc.) some of them, such as cannabinoids, are likely to bioaccumulate in organisms or concentrate in sediments; whereas the rest, much more polar compounds, will tend to stay in aqueous environmental matrices. However, continuous exposure of aquatic organisms to low aquatic concentrations of these substances, some of them still biologically active (e.g., cocaine (CO), morphine (MOR) and MDMA) may cause undesirable effects on the biota.

5 Elimination and Fate During Wastewater Treatment

It is well documented that WWTP are major contributors of pharmaceuticals and illicit drugs in the aquatic environment, due to their incomplete removal in conventional activated sludge (CAS) treatment, resulting in important loads discharged into river waters through effluent wastewaters (Tables 1 and 2).

5.1 Pharmaceuticals

The most important removal pathways of PhACs during wastewater treatment are biotransformation/biodegradation and abiotic removal by adsorption to the sludge. The efficiency of their removal at WWTP depends on their physico-chemical properties, especially hydrophobicity and biodegradability, and process operating parameters (i.e., HRT, SRT, and temperature). For certain NSAIDs (e.g., ibuprofen, acetaminophen), high removals (>90%) are consistently reported in literature

Table 1 Occurrence of pharmaceutical residues in WWTPs effluents

Pharmaceuticals	Concentrations (ng L^{-1})	References
Analgesics /Anti-inflammatories		
Diclofenac	900–2,200	[20]
	270–598	[73]
	194–748	[21]
	123	[34, 67]
	210.7–486.4	[74]
Ibuprofen	7,100–28,000	[20]
	50–320	[75]
	348–773	[21]
	227	[34, 67]
	17.7–219.0	[74]
Naproxen	1,840–4,200	[76]
	300–3,200	[75]
	452–1,189	[21]
	42.1–289.1	[74]
Acetaminophen	59–164	[76]
	<20–<20	[73]
	10–19	[77]
Ketoprofen	340–1,070	[7]
	125–210	[21]
	400	[34, 67]
	21.8–1,080.6	[74]
Acetylsalicylic acid	220–1,500	[78]
	23.5–51.5	[74]
Salicylic acid	5,190–13,000	[79]
(aspirin metabolite)	3,600–59,600	[54]
	209	[34, 67]
Codeine	900–8,100	[20]
	3,948	[34, 67]
Antibiotics		
trimethoprim	331–1,264	[76]
	271–322	[73]
	550–1,900	[75]
	320–660	[78]
	1,004	[34, 67]
Ciprofloxacin	923–3,353	[76]
	239–514	[80]
	170–860	[75]
Ofloxacin	4,422–13,426	[76]
	652–1,081	[80]
Erythromycin	519–973	[76]
	89–353	[80]
	130–294	[77]
	270–300	
Sulfamethoxazole	275–794	[76]
	400–2,000	[78]
Clarithromycin	140–260	[78]
	31–73	[80]
Roxithromycin	680–1,000	[78]

(*continued*)

Table 1 (continued)

Pharmaceuticals	Concentrations (ng L^{-1})	References
β-blockers		
Metoprolol	61–154	[76]
	730–2,200	[78]
	68	[34, 67]
	150–650	[81]
Propranolol	44–100	[76]
	291–373	[73]
	20–50	[75]
	388	[34, 67]
	32–64	[81]
Atenolol	1,720–4,850	[76]
	2,702	[34, 67]
	120–960	[81]
Sotalol	<LOD-1,008	[82]
Lipid regulators		
Bezafibrate	233–484	[76]
	418	[34, 67]
Gemfibrozil	2,337–5,428	[76]
	246–436	[21]
	47–1,220	[81]
	13.3–17.2	[74]
Clofíbric acid *(metabolite)*	27–81	[76]
	360–1,600	[78]
Antidepressants		
diazepam	16–87	[76]
	30–40	[78]
Fluoxetine	398–929	[76]
	40–73	[81]
Antiepileptic		
Carbamazepine	130–230	[20]
	290–550	[7]
	3,117	[34, 67]
	157.3–293.4	[74]
X-ray agents		
Iopamidol	660–15,000	[78]
Iopromide	2,630–4,030	[77]
Diatrizoate	80–8,700	[78]
Iomeprol	370–3,800	[78]
Antiulcer agents		
Ranitidine	684–2,722	[76]
	298–610	[80]
	<LOD-550	[81]
Broncodilatators		
Salbutamol	15–60	[76]
	8.5–18	[80]
	66	[34, 67]
	<LOD-60	[81]
Terbutaline	15–30	[76]
	<LOD-4.15	[74]

(*continued*)

Table 1 (continued)

Pharmaceuticals	Concentrations (ng L^{-1})	References
Diuretics		
Furosemide	1,050–2,957	[76]
	749–2,102	[80]
	1,144	[34, 67]
Hydrochlorothiazide	3,683–14,857	[76]
	598–1,253	[80]

[8, 13, 18]. Many studies have confirmed a complete biodegradation of ibuprofen to hydroxy-ibuprofen and carboxy-ibuprofen in biological wastewater treatment, whereas removals higher than 95% have been reached [17, 49, 50]. For diclofenac, contradictory results have been reported for its removal during CAS wastewater treatment. In some WWTPs, attenuation of 50–70% of diclofenac was reported [6, 10, 11, 51, 52], whereas some studies showed extremely low efficiency of conventional treatment (only 10–30% removal) [49, 53].

Lipid regulators gemfibrozil and bezafibrate frequently detected in wastewaters are reported to be eliminated in WWTPs with 46–69% [51] and 36–54% [13]. On the other side, clofibric acid was reported to be refractory pollutant for municipal WWTPs [22].

Many authors reported poor elimination of antiepileptic drug carbamazepine [6, 13, 17, 49, 54]. Pharmacokinetic data indicate that only 1–2% of carbamazepine is excreted unmetabolized. However, glucuronide conjugates of carbamazepine can presumably be cleaved in the sewage, and thus increase its environmental concentrations [51]. This is confirmed by its high ubiquity in the environment at concentration levels of several hundred nanograms per liter in different surface waters. Due to its recalcitrant nature, it can be used as anthropogenic marker for the contamination of aquatic environment.

Macrolide antibiotics are metabolized to a minor extent (10–20% for clarithromycin, 30% roxithromycin, 10–20% for spiramycin, 6–12% for azithromycin, and 5–10% for erythromycin), except for erythromycin that is converted into antibacterially inactive product (erythromycin-H_2O) [55]. Mass balance studies have demonstrated sewage sludge as the main reservoir for fluoroquinolone antibiotics, with ~80% elimination frequently reported for the CAS treatment [56, 57]. For sulfonamide antibiotics, unexplained variations of concentration over time are frequently observed, also possibly because of unknown conjugation and deconjugation processes that may occur during contact with activated sludge. The reported removals of sulfamethoxazole in CAS treatment vary from 60 to 94% [35, 58]. For example, significant amount of sulfametoxazole enters WWTP in metabolized form as N_4-acetyl-sulfamethoxazole that can be converted back to the original compound [59].

The removal of X-ray contrast media iopromide was reported to be negligible in conventional WWTP [58]. However, similar to antibiotic trimethoprim, negligible removal in CAS treatment was meliorated to 61% removal by employing nitrifying activated sludge [60].

Table 2 Effluent levels of drugs of abuse and metabolites and removal efficiencies of the WWTP

Compound	WWTP location	Effluent Conc. (ngL^{-1})	Removal (%)	References
Cocainics				
Cocaine	Castellón (Spain)	<30[a]–560	4–>99	[26]
	Ringsend (Dublin)	138(20)[b]	72	[28]
	Milan-Nosedo (Italy)	<0.9[a]	>99	[10, 11]
	Lugano (Switzerland)	11(3)[b]	95	[10, 11]
	Catalonia (Spain)	1–100	88–99	[63]
	South Wales (UK)	<1[a]	>99	[35]
	South Wales (UK)[d]	48–324	25	[35]
	Belgium	<1[a]–8	93–100	[68]
	Barcelona (Spain)	6(4)[b]	>98	[36]
	A.C. Valencia (Spain)	33–105	37–95	[36]
Cocaethylene	Castellón (Spain)	<30[a]–80	>99	[26]
	Milan-Nosedo (Italy)	<0.7[a]	>94	[10, 11]
	Lugano (Switzerland)	0.2(0.5)[b]	97	[10, 11]
	Barcelona (Spain)	2(1)[b]	>94	[36]
	A.C. Valencia (Spain)	2–7	66–93	[36]
Benzoylecgonine	Castellón (Spain)	<30[a]–6,790	35–>99	[26]
	Ringsend (Dublin)	22(4)[b]	93	[28]
	Milan-Nosedo (Italy)	<0.9[a]	>99	[10, 11]
	Lugano (Switzerland)	100(29)[b]	83	[10, 11]
	Catalonia (Spain)	1–1,500	88–98	[63]
	Germany	490	N/A	[32]
	South Wales (UK)	<1[a]–29	100	[35]
	South Wales (UK)[d]	202–3,275	NR	[35]
	Belgium	4–23	93–99	[68]
	Barcelona (Spain)	30(18)[b]	>98	[36]
	A.C. Valencia (Spain)	50–318	69–97	[36]
Norbenzoylecgonine	Castellón (Spain)	<30[a]–170	65–>99	[26]
	Milan-Nosedo (Italy)	<0.6[a]	>98	[10, 11]
	Lugano (Switzerland)	8(3)[b]	97	[10, 11]
Nor-cocaine	Castellón (Spain)	<30[a]–30	NR	[26]
	Milan-Nosedo (Italy)	<0.7[a]	>95	[10, 11]
	Lugano (Switzerland)	0.7(0.5)[b]	83	[10, 11]
Amphetamine-like compounds				
Amphetamine	Castellón (Spain)	110–210	85–>99	[26]
	Milan-Nosedo (Italy)	<3[a]	80	[10, 11]

(*continued*)

Table 2 (continued)

Compound	WWTP location	Effluent Conc. (ngL^{-1})	Removal (%)	References
	Lugano (Switzerland)	<3[a]	N/A	[10, 11]
	Catalonia (Spain)	4–210	52–>99	[63]
	South Wales (UK)	<3[a]–11	100	[35]
	South Wales (UK)[d]	19–739	95	[35]
	Catalonia (Spain)	0.5(0.1)[b]	>98	[36]
	A.C. Valencia (Spain)	1–3	49–97	[36]
3,4-methylenedioxy-amphetamine (MDA)	Castellón (Spain)	410–680	60–>99	[26]
	Milan-Nosedo (Italy)	1(2)[b]	80	[10, 11]
	Lugano (Switzerland)	1(2)[b]	89	[10, 11]
	Catalonia (Spain)	1–200	NR–>99	[63]
3,4-methylenedioxyeth-amphetamine (MDEA)	Castellón (Spain)	<100[a]	N/A	[26]
	Milan-Nosedo (Italy)	<2[a]	N/A	[10, 11]
	Lugano (Switzerland)	<2[a]	N/A	[10, 11]
3,4-methylenedioxy-methamphetamine (MDMA)	Castellón (Spain)	<100[a]–21,200	25–>99	[26]
	Milan-Nosedo (Italy)	4(4)[b]	71	[10, 11]
	Lugano (Switzerland)	5(3)[b]	64	[10, 11]
	Catalonia (Spain)	2–267	46–>99	[63]
	South Carolina (USA)	0.5	N/A	[33]
	Barcelona (Spain))	82(22)[b]	NR – 64	[36]
	A.C. Valencia (Spain)	30–376	NR – 66	[36]
Methamphetamine	Castellón (Spain)	<100[a]	NR	[26]
	Milan-Nosedo (Italy)	4(2)[b]	75	[10, 11]
	Lugano (Switzerland)	<1[a]	N/A	[10, 11]
	Catalonia (Spain)	3–90	44–>99	[63]
	Kentucky (USA)	n.d.–<10[b]	N/A	[83]
	Nevada (USA)	1.3	N/A	[33]
	Nebraska (USA)	350(78)[b]	N/A	[62]
	Barcelona (Spain)	6(0.6)[b]	26–80	[36]
	A.C. Valencia (Spain)	2–3	48–66	[36]
Ephedrine	Barcelona (Spain)	118(17)[b]	70–86	[36]
	A.C. Valencia (Spain)	138–266	33–69	[36]

(*continued*)

Table 2 (continued)

Compound	WWTP location	Effluent Conc. (ngL^{-1})	Removal (%)	References
LSD and metabolites				
Lysergic acid diethylamide (LSD)	Barcelona (Spain)	0.3(0.2)[b]	NR–>99	[36]
	A.C. Valencia (Spain)	0.2–2	67–84	[36]
2-oxo-3-hydroxy-LSD (O-H-LSD)	Barcelona (Spain)	0.7(0.3)[b]	69–97	[36]
	A.C. Valencia (Spain)	0.8	68–>99	[36]
N-desmethy-LSD (Nor-LSD)	Barcelona (Spain)	0.6(0.5)[b]	26–>99	[36]
	A.C. Valencia (Spain)	1–4	75–88	[36]
Cannabinoids 11-nor-9-carboxy-Δ^9THC (THC-COOH)	Castellón (Spain)	<800[a]	NR	[26]
	Catalonia (Spain)	15–72	NR – 71	[27]
	Milan-Nosedo (Italy)	<0.9[a]	>98	[10, 11]
	Lugano (Switzerland)	7(4)[b]	92	[10, 11]
	Barcelona (Spain)	8(4)[b]	NR – 81	[36]
	A.C. Valencia (Spain)	4–19	36–72	[36]
11-hydroxy-THC (OH-THC)	Barcelona (Spain)	5(2)[b]	NR – 83	[36]
	A.C. Valencia (Spain)	8–23	38–82	[36]
THC	Catalonia (Spain)	<8[a]	NA–>73	[27]
	A.C. Valencia (Spain)	13–21	8–67	[36]
Opioids				
Morphine	Ringsend (Dublin)	<856[b]	NR	[28]
	Catalonia (Spain)	<7[a]–81	16–>84	[27]
	Milan-Nosedo (Italy)	<3[a]	>96	[10, 11]
	Lugano (Switzerland)	55(11)[b]	73	[10, 11]
	Germany	40[c]	N/A	[32]
	Barcelona (Spain)	22(3)[b]	83–92	[36]
	A.C. Valencia (Spain)	12–30	53–82	[36]
Nor-morphine	Catalonia (Spain)	<25[a]–31	NR	[27]
Morphine 3-glucuronide	Milan-Nosedo (Italy)	<0.5[a]	>83	[10, 11]
	Lugano (Switzerland)	<0.5[a]	>97	[10, 11]
6-acetyl morphine	Catalonia (Spain)	<3[a]	N/A	[27]
	Milan-Nosedo (Italy)	<3[a]	>75	[10, 11]

(*continued*)

Table 2 (continued)

Compound	WWTP location	Effluent Conc. (ngL^{-1})	Removal (%)	References
	Lugano (Switzerland)	<3[a]	>70	[10, 11]
	Barcelona (Spain)	4(0.5)[b]	60–89	[36]
	A.C. Valencia (Spain)	2–3	59–77	[36]
Heroin	Catalonia (Spain)	<20[a]	N/A	[27]
	A.C. Valencia (Spain)	n.d.–1	48–>99	[36]
Methadone	Catalonia (Spain)	4–25	NR – 53	[27]
	Milan-Nosedo (Italy)	9(0.5)[b]	25	[10, 11]
	Lugano (Switzerland)	36(3)[b]	28	[10, 11]
2-ethylidene-1, 5-dimethyl-3, 3-diphenylpyrrolidine (EDDP)	Ringsend (Dublin)	48(1)[b]	NR	[28]
	Catalonia (Spain)	5–57	NR – 15	[27]
	Milan-Nosedo (Italy)	23(1)[b]	NR	[10, 11]
	Lugano (Switzerland)	72(9)[b]	21	[10, 11]

NR: analyte not removed or appearing at higher concentrations in effluent compared to influent waters
N/A: data not available
[a]Analyte present but below the method limit of quantitation
[b]Average concentration of several samples (standard deviation)
[c]Median concentration
[d]Trickling filter beds used as secondary treatment

5.2 *Illicit Drugs*

Since 2004, several authors have developed analytical methodologies based on liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS) to evaluate the occurrence of drugs of abuse in sewage and surface waters [10, 11, 26–34, 36–38, 61]. Removal of drugs of abuse residues in sewage water treatment processes has been studied so far mainly under biological treatments based on conventional activated sludge (CAS) processes. Only two peer-reviewed works investigate the elimination of these compounds under different secondary treatment techniques, such as trickling filters, biological nutrients and a mix system based on activated sludge and trickling filters [35, 62]. Concentrations of drugs of abuse and metabolites in effluent sewage waters reported in the literature and also the removal of these analytes in the studied WWTPs are summarized in Table 2.

Overall, elimination of cocainic compounds has been observed to be the most efficient under CAS treatment (above 90% in most cases), compared to the rest of the investigated drugs of abuse and metabolites. However, they are not or deficiently removed by means of trickling filters [35]. On the other hand, removal efficiency of CAS treatments for these compounds drastically decreases when high levels of these compounds are present in the influent sewage waters [26].

Regarding removal of amphetamine-like compounds, very different elimination values have been reported in the peer-reviewed literature. Higher loads of methamphetamine [26], 3,4-methylenedioxyamphetamine or MDA [63] and MDMA [36] have been occasionally observed in effluent waters compared to those present in raw sewage water. Huerta-Fontela et al. [63] indicated that an increase of MDA during the water treatment may be related to an *N*-demethylation of MDMA. On the other hand, high levels of amphetamine-like substances in treated waters may be the result of desorption processes during sewage water treatment. The elimination of amphetamine by means of CAS and trickling filters treatments was also evaluated by Kasprzyk-Hordern et al. [35], and similar removal efficiencies were observed with both processes, yielding 100 and 95% of amphetamine elimination, respectively; however, higher concentrations of methamphetamine were detected in WWTP effluents after treatment by means of trickling filters [62].

The elimination of all investigated cannabinoids has been observed to be very poor; finding occasionally higher concentrations of these compounds in effluent than in influent waters, which may be related to deconjugation of excreted conjugated forms not yet investigated. The same phenomenon may be attributed to the persistence of LSD in some of the investigated effluent samples.

Opioids have shown different behaviors during CAS treatment. The most persistent compounds are the opioid antagonist methadone and its metabolite EDDP, as none or a deficient elimination (up to 53% the highest one reported) of these analytes has been observed in the different studies performed [10, 11, 27, 28]. Morphine has also shown different elimination profiles, and also higher concentrations in effluent waters compared to influent waters. According to the study carried out by Castiglioni et al. that included a glucuronide conjugate of morphine (morphine 3β-D glucuronide) [10, 11], the high morphine loads in effluent samples may be attributed to the cleavage of conjugated molecules, as morphine is excreted in urine mainly as glucuronide metabolites and the presence of this compound in the investigated sewage waters was not very relevant.

6 Occurrence of Emerging Contaminants in Surface Waters

At present, numerous studies have made evident the presence of drugs in the aquatic environment identifying more than 150 PhACs in different aqueous matrices such as surface, ground, and drinking water, as well as WWTP effluents. While in case of WWTP effluents the levels detected can reach several tens of micrograms per liter [64], in river and groundwater the levels are much lower, generally in the nanograms per liter range. Within the framework of the European project KNAPPE an exhaustive bibliographical revision of 112 publications and national reports has been made regarding the presence of pharmaceuticals in the aquatic environment

[65, 66]. The results showed that the compounds studied with more frequency in the aquatic environment, and of which, logically, there is more information, are the antibiotics, analgesics and anti-inflammatories (like diclofenac, ibuprofen, naproxen, acetylsalicylic acid, and paracetamol), as well as the β-blocker atenolol. In the category of antibiotics, several families are included, like the macrolides (erythromycin), the fluoroquinolones (ofloxacin and ciprofloxacin), sulfonamides (sulfamethoxazole), penicillins (amoxicillin), the metronidazol, and trimethoprim. Other therapeutic groups also widely studied and frequently found in the environmental waters are the lipid regulators (gemfibrozil and bezafibrat), antiepileptic carbamazepine, and antidepressants (diazepam, fluoxetine, paroxetine) (see Table 3).

Although a lack of data on the residues of drugs of abuse in environmental water is still remarkable, some works have been carried out to cover this gap, especially in Europe [2, 27, 28, 30, 32, 33, 38, 61, 62, 67–69]. Cocaine and benzoylecgonine are the chemicals most thoroughly studied so far, followed by morphine, amphetamine, methamphetamine and MDMA, whereas the occurrence of other illicit drugs and metabolites constituted only the scope of a few works. Figures 1–3 summarize the levels of these compounds found in surface waters of different countries, which are in the picograms per liter to nanograms per liter range.

Although cocainic compounds are removed to a high extent in WWTPs (see Table 2), these compounds, especially cocaine and benzoylecgonine, are the most abundant and ubiquitous in surface water, presenting levels up to 115 and 520 ng L^{-1}, respectively (see Fig. 2). As it is shown in Figs. 1 and 3, morphine and amphetamine-like compounds, such as amphetamine, methamphetamine, and MDMA, also have a relevant presence in surface waters; however, concentrations have not surpassed 100 ng L^{-1} in any case. The rest of the investigated drugs of abuse and metabolites have been found at the picograms per liter level or at few nanograms per liter.

Overall, levels detected in surface waters are lower than those determined in treated effluents, which suggests dilution of these chemicals in the receiving waters. A direct impact of effluent discharges regarding an increase of drugs of abuse and metabolites in natural streams has been shown in several works [62, 70]. Drugs of abuse and metabolites levels have also been reported to decrease significantly with increasing distance from the WWTP discharge point [28].

7 Influence of Hydrological Conditions on the Occurrence of Emerging Contaminants in Surface Waters

7.1 Case Study: Occurrence of Pharmaceuticals and Illicit Drugs in the Ebro River Basin

Wastewater from seven WWTPs, located in the main cities in the Ebro river basin (Pamplona, Logroño, Miranda de Ebro, Zaragoza, Tudela, Lleida, Tortosa), as well as the receiving river waters downstream the plants were monitored for the presence

Table 3 Occurrence of pharmaceutical residues in surface waters

Pharmaceuticals	Concentrations (ng L^{-1})	References
Analgesics /Anti-inflammatories		
Diclofenac	(<LOD-195) Estuary	[84]
	2.2 (<LOD-3.3) River	[5]
	27 (<LOD-69) River	[85]
	9–28 River	[34, 67]
	1.36–33.2 River	[74]
Ibuprofen	70 River	[51]
	(<LOD-928) Estuary	[84]
	13 (<LOD-17) River	[37]
	<LOD-200 Well	[86]
	<LOD-4.5 River	[74]
Naproxen	(<LOD-380) River	[87]
	(<LOD-145) Canals	[88]
	5(<LOD-32) Rivers	[85]
	<LOD-91.5 River	[74]
Acetaminophen	110 Rivers	[64]
	20 (<LOD-110) River	[5]
	13 (<LOD-66) River	[85]
	62–388 River	[34, 67]
Ketoprofen	2–3 River	[34, 67]
	25[a] River	[89]
	<LOD-14.5 River	[74]
Salicylic acid *(aspirin metabolite)*	25–62 River	[34, 67]
Codeine	40 (<LOD-54) River	[90]
	27–224 River	[34, 67]
Antibiotics		
trimethoprim	(<LOD-569) Estuary	[84]
	4 (3–5) Lake	[77]
	<LOD-108 River	[34, 67]
Ciprofloxacin	360 River	[91]
Erythromycin	3 (<LOD-1.6) River	[92]
	3 (2–5) Lake	[77]
Sulfamethoxazole	38 (<LOD-160) River	[5]
	20 (2–36) River	[77]
	< LOD-1 River	[34, 67]
Roxithromycin	180[a] River	[64]
	50[b] River	
β-blockers		
Metoprolol	7–10 River	[34, 67]
	12 River	[81]
Propranolol	7–22 River	[34, 67]
	23	[81]
Atenolol	8 (<LOD-46) River	[5]
	17 (<LOD-41) River	[37]
	17–487 River	[34, 67]
	35 River	[81]
Bezafibrate	26 (<LOD-170) River	[5]
	2 (<LOD-3) River	[37]
	41–60 River	[34, 67]
Gemfibrozil	8 (<LOD-27) River	[85]
	7 (2–9) Lake	[77]

(*continued*)

Table 3 (continued)

Pharmaceuticals	Concentrations (ng L^{-1})	References
	78[a] River	[89]
	<LOD-2.3 River	[74]
Clofíbric acid	(<LOD-30) River	[87]
(metabolite)	<LOD-101 River	[34, 67]
Antidepressant		
Diazepam	31 (<LOD-34) River	[90]
	(<LOD-111) Estuary	[84]
Fluoxetine	12–20 River	[93]
Antiepileptic		
Carbamazepine	(10–320) River	[87]
	(30–55) Lake	[87]
	7–251 River	[34, 67]
	<LOD-56.3 River	[74]
X-ray agents		
Iopamidol	(<LOD-300) Groundwater	[94]
Iopromide	134 (20.-361) Lake	[77]
Diatrizoate	(1,600–9,600) Groundwater	[95]
Antiulcer agent		
Ranitidine	1.3 (<LOD-4) River	[37]
	<LOD-32 River	[34, 67]
Broncodilatators		
Salbutamol	<LOD-1 River	[34, 67]
Diuretics		
Furosemide	15 (<LOD-21) River	[5]
	4 (<LOD-67) River	[37]
	<LOD-117 River	[34, 67]

<LOD – below limit of detecion
[a]Max concentration detected
[b]Median

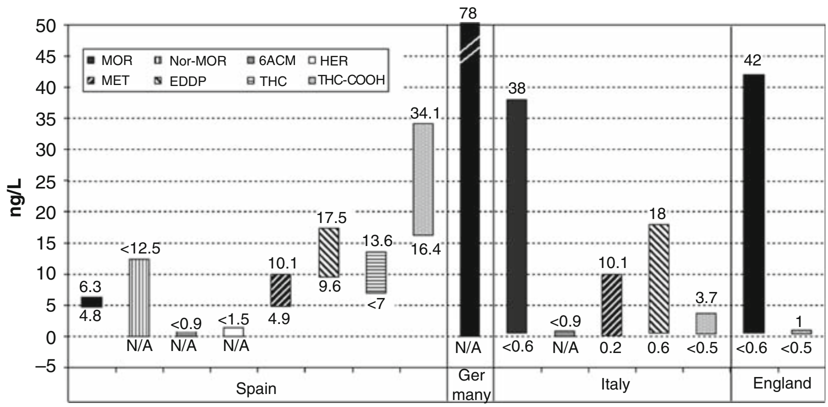


Fig. 1 Concentrations reported for opiods and cannabinoids in surface water of different European countries. *MOR* morphine; *Nor-MOR* nor-morphine; 6*ACM* 6-monoacetyl morphine; *HER* heroin; *MET* methadone; *EDDP* 2-ethylidene-1,5-dimethyl-3,3 diphenylpyrrolidine; *THC* Δ9-tetrahydro-cannabinol; *THC-COOH* 11-nor 9-carboxy-THC
N/A: Values not availabe, not measured

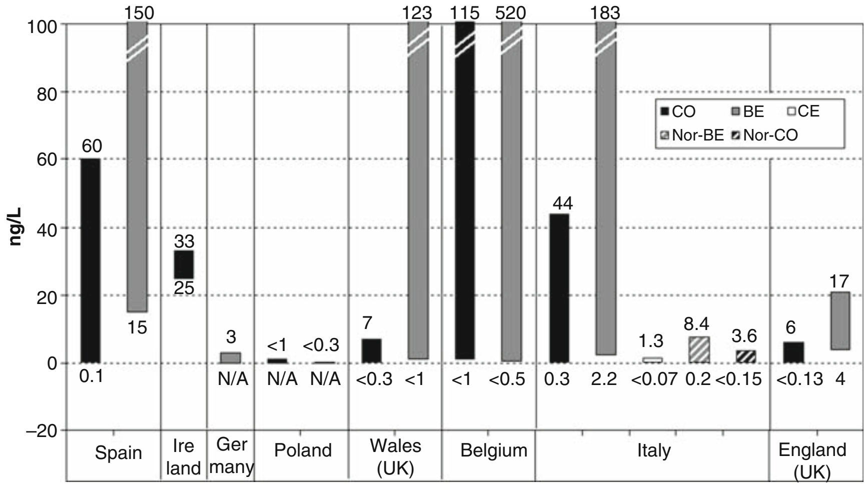


Fig. 2 Concentrations reported for cocainic compounds in surface water of different European countries. *CO* cocaine; *BE* benzoylecgonine; *CE* cocaethylene; *Nor-BE* nor-benzoylecgonine; *Nor-CO* nor-cocaine
N/A: Values not availabe, not measured

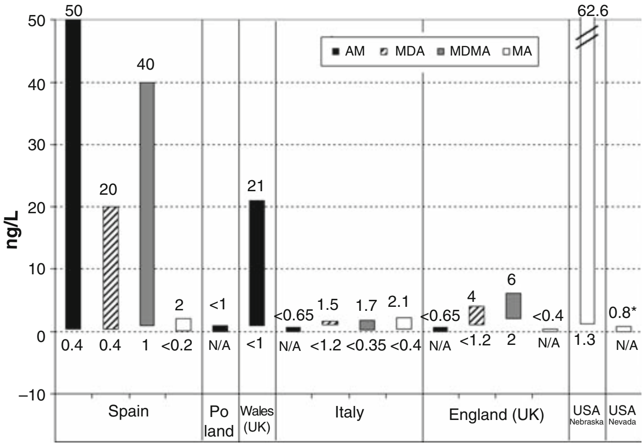


Fig. 3 Concentrations reported for amphetamine-like compounds in surface water of different European and American countries. *AM* amphetamine; *MDA* 3,4-methylenedioxy amphetamine; *MDMA* 3,4-methylenedioxy methamphetamine (ecstasy); *MA* methamphetamine
N/A: Values not availabe, not measured
* Just one value reported (Corresponding to either one sample or to the mean of various samples)

of 29 most common pharmaceuticals. Samples collected were analysed according to the analytical methodology reported in Gros et al. 2006. Table 4 summarizes the characteristics of the WWTP studied, as well as the rivers where their effluents are discharged. Effluents from WWTP2, WWTP5, and WWTP7 are discharged in the

Table 4 Characteristics of the WWTP monitored and the receiving waters where their effluents are discharged

WWTP	Population equivalent	Flow ($m^3\ h^{-1}$)	Receiving river water	Type of wastewater treated	Hydraulic retention time	Primary treatment	Secondary treatment
WWTP1 Miranda del Ebro	52,700	533	Vallas	Urban	32	–	Activated sludge
WWTP2 Tudela	90,000	833	Ebro	Urban	18	Primary settling	Biologic filters
WWTP3 Logroño	4,66,560	2,500	Iregua	Urban and industrial	8	Primary settling	Activated sludge
WWTP4 Pamplona	7,73,312	4,313	Arga	Urban and industrial	25	Primary settling	Activated sludge
WWTP5 Zaragoza	8,35,000	6,833	Ebro	Urban	10	Primary settling	Activated sludge
WWTP6 Lleida	18,000	2,917	Segre	Urban	6–10	Primary settling	Activated sludge
WWTP7 Tortosa	36,625	305	Ebro	Urban	33	–	Activated sludge

Ebro river, whereas effluents from WWTP1, WWTP6, WWTP4, and WWTP3 go to tributaries, which consist in the Vallas, Segre, Arga, and Iregua, respectively. The dilution factor in the Ebro river averages 70 in Zaragoza, the area surrounding WWTP5 (1.9 m^3 s^{-1} of WWTP effluent is mixed with 150 m^3 s^{-1} of river flow). A similar situation occurs in Lleida (WWTP6), as 0.8 m^3 s^{-1} of effluent wastewater are mixed with 50 m^3 s^{-1} of river water, showing a dilution factor of approximately 63. Nevertheless, in the Arga river, which receives the effluent from WWTP4, the dilution factor was much lower, averaging a value of 10. Such factors could not be estimated for Tudela (WWTP2), Miranda de Ebro (WWTP1), and Logroño (WWTP3), since no data referring to the river flows in these points were available. Even though pharmaceuticals present in effluent wastewaters are generally diluted when entering river waters, the same spectrum of compounds found in the first ones are also detected in the former, but generally at one order of magnitude lower than in effluent wastewaters, ranging the nanograms per liter range. This fact states that the dilution of pharmaceuticals when they enter river waters may reduce environmental risks posed by these compounds to aquatic organisms. Figure 4 shows the most ubiquitous pharmaceuticals of each therapeutic group detected in both effluent waste and river waters in relationship to the dilution factor. The highest levels of pharmaceuticals found were attributed to Pamplona and the area around Zaragoza, which are two of the most populated cities, where the most ubiquitous compounds were the analgesics and anti-inflammatories ibuprofen, diclofenac, naproxen; the lipid regulators bezafibrate and gemfibrozil; and the antibiotics erythromycin, azythromycin, sulfamethoxazole and trimethoprim.

The presence of 17 drugs of abuse and metabolites has been investigated in the same sampling points of the Ebro river basin where pharmaceuticals have been monitored. Drug monitoring was done at the beginning of the hydrological year and 3 months before its end; this is October 2007 and July 2008, respectively. Despite the removal of these compounds in the WWTPs and the dilution of effluent loads in receiving surface waters, the presence of cocainic (benzoylecgonine and cocaine) and amphetamine-like compounds (ephedrine and MDMA) in the investigated river sampling locations was noticeable in both sampling campaigns. The second part of the hydrological year 2007–2008 was the end of a drought period in Spain. As a result, total drug loads discharged to the river through effluent sewage waters were diluted up to 17 times in receiving waters in October 2007, whereas the dilution factor raised almost to 50 in July 2008. This explains how, despite the drug levels found in the WWTP effluents were in general larger in 2008 than in 2007, the concentrations in the receiving river waters were in many cases lower in 2008 than in 2007 (see Fig. 5).

7.2 Case Study: Occurrence of Pharmaceuticals in the Llobregat River (NE Spain)

The Llobregat River (NE Spain) is 156 km long and covers a catchment area of about 4,957 km^2. Its watershed is heavily populated (more than three million inhabitants).

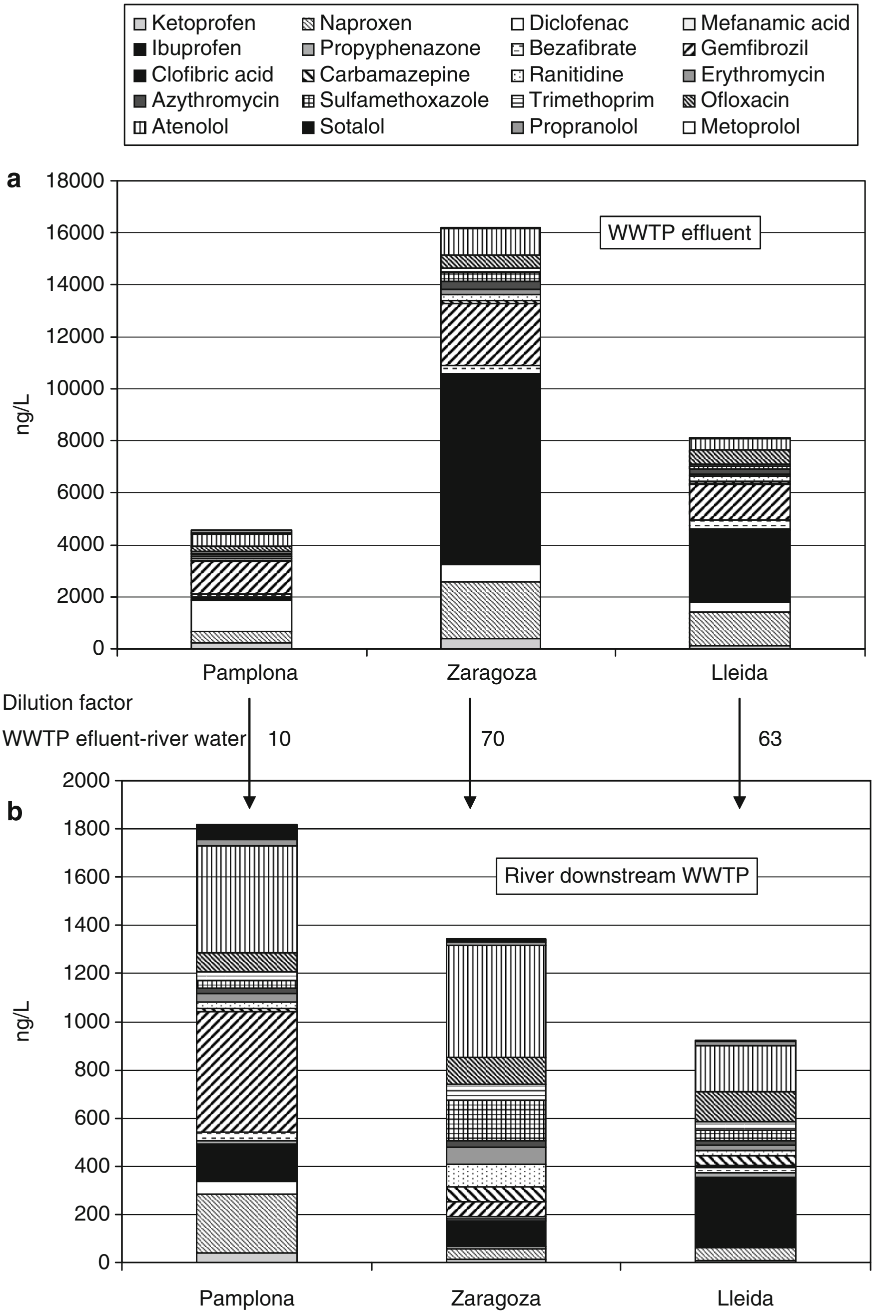


Fig. 4 Concentrations (ng L^{-1}) of the most ubiquitous analgesics and anti-inflammatories, lipid regulators, psychiatric drugs and β-blockers detected in (**a**) wastewater effluents and (**b**) river water downstream of the three WWTP in the Ebro river basin in relationship to the dilution factor

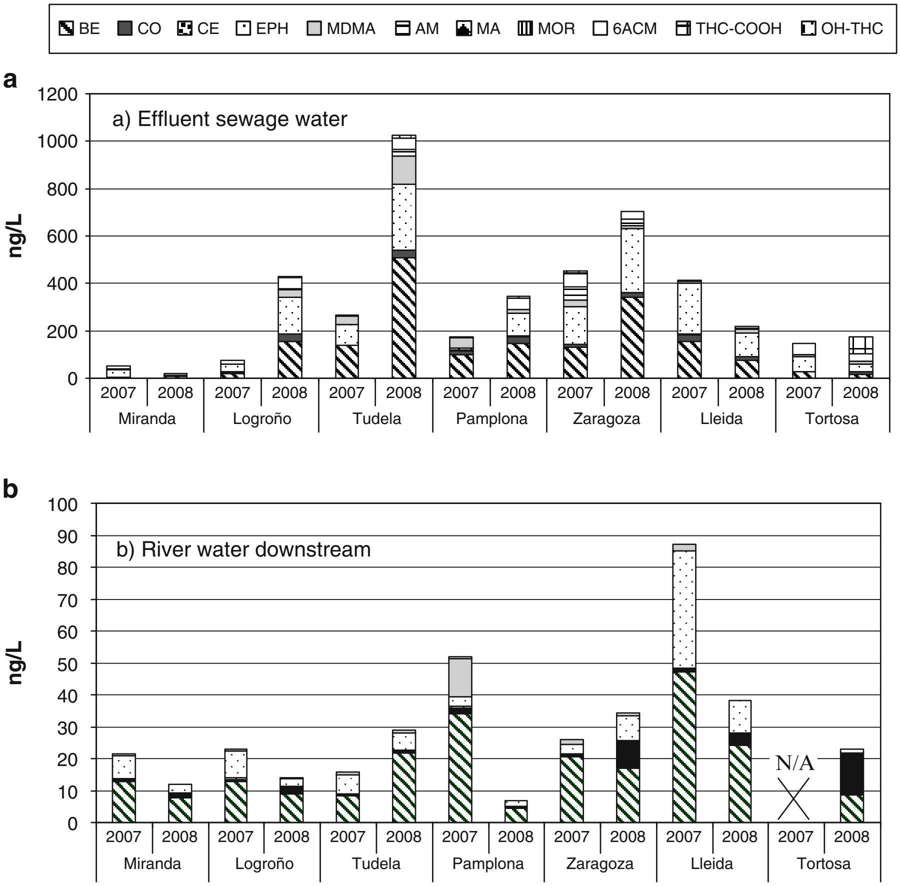


Fig. 5 Concentrations of drugs of abuse and metabolites determined in: (**a**) wastewater effluents and (**b**) river water downstream of the WWTP monitored in the Ebro river basin
N/A: Values not availabe, not measured

Together with its two main tributaries, River Cardener and River Anoia, the Llobregat is subjected to a heavy anthropogenic pressure, receiving extensive urban and industrial wastewater discharges (137 $Hm^3\ yr^{-1}$; 92% coming from the wastewater treatment plants), which constitutes a significant part of its natural flow. The Llobregat basin is thus an illustrative example of overexploited river.

Hydrologically, the Llobregat is a typical Mediterranean river, its flow being characterized by a high variability, which is controlled by seasonal rainfall. The mean annual precipitation is 3,330 Hm^3 and it has an annual average discharge of 693 Hm^3. The average monthly flow registered since year 2000, shows peaks of ca. 100 $m^3\ s^{-1}$, together with minimum values of 1 $m^3\ s^{-1}$ percent (relative standard error of 124%). These fluctuations can be considered intrinsic to the Mediterranean climatology. However, the scenarios foreseen by the IPCC [71] for this area seem to point not only to a general reduction of precipitation, but to an increase of seasonality. Therefore, rain will become more irregularly distributed along the year and a more frequent production of extreme hydrologic events, such as floods and droughts, is to be expected to take place in the near to medium future.

How these extreme events can affect the presence of pollutants in the water systems is unclear. A flow decrease may have an obvious direct effect on the dilution factor, giving rise to an increase in the concentration of pollutants and thus to a corresponding increase of risk towards the aquatic ecosystems. On the other hand, floods can give rise to sediment resuspension and transport, and thus to the subsequent remobilization of retained pollutants. While the second issue is a priori more likely to affect hydrophobic pollutants adsorbed on sediments, direct dilution by flow may be of greater relevance for the more soluble ones, such as those released from WWTPs. In the previous section (case study in the Ebro river basin), it has already been emphasized how the dilution factor varies depending on the receiving river, and how crucial it is acting as a dilution buffer in relation to emerging contaminants such as pharmaceuticals. However, the variability *within* the same river is also relevant. Due to the foregoing reasons, the Llobregat provides, in that respect, a representative case that is worth studying.

Figure 6 shows the concentration ranges of 72 pharmaceutical compounds belonging to different therapeutical classes detected in the Llobregat at Sant Joan Despí. These were analyzed along seven sampling campaigns carried out between June and August 2008, under different flow conditions. The comparison between flow and some of the most representative compounds analyzed shows that pharmaceuticals exhibit a variability (expressed as percent relative standard error) of the same order as river flow (about 100%). On the other hand, comparison of time profiles for daily flow and the sum of all pharmaceuticals again indicates a partial opposite tendency, as it would be expected if dilution is the governing factor (Fig. 7).

The correlation analysis between the 30 most representative pharmaceutical compounds and the daily measured flow (Fig. 8) shows a variable behavior and

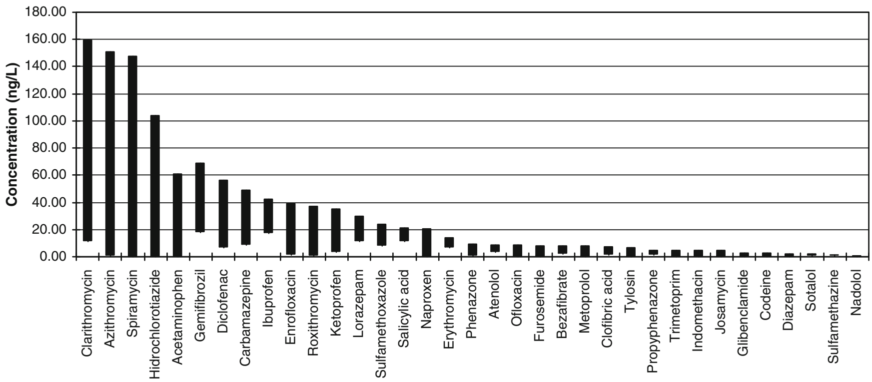
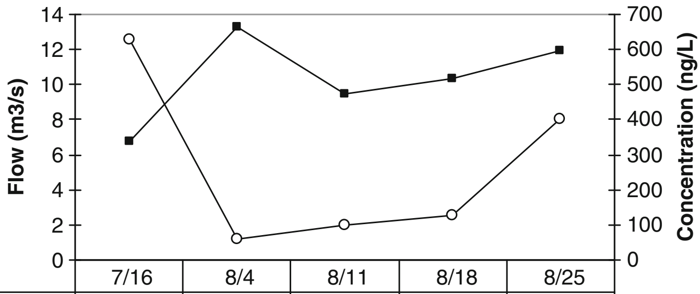


Fig. 6 Concentration range (ng L^{-1}) of some of the most representative pharmaceutical compounds measured in the Llobregat river at Sant Joan Despí (Barcelona), between June and August 2008



	7/16	8/4	8/11	8/18	8/25
Flow (m3/s)	12.55	1.19	2.01	2.58	8.01
Sum of Pharmaceuticals (ng/l)	340.0	665.7	474.4	517.2	594.9

Fig. 7 Comparison between daily flow (m^3 s^{-1}) and sum of pharmaceutical compounds (ng L^{-1}) measured in the Llobregat river at Sant Joan Despí (Barcelona), between June and August 2008

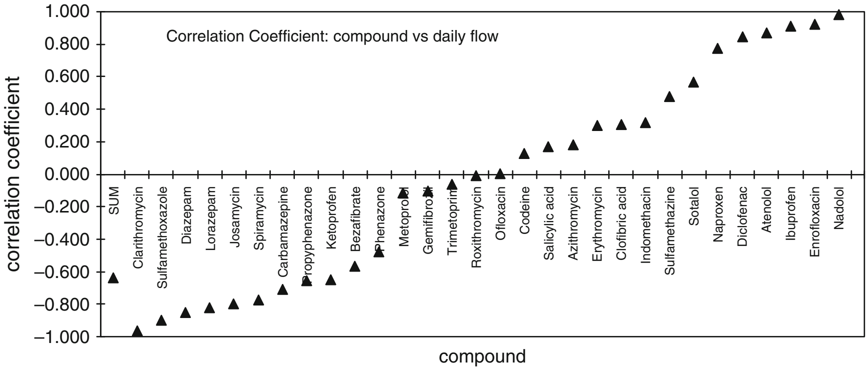


Fig. 8 Correlation between daily flow (m^3 s^{-1}) and of pharmaceutical compounds (ng L^{-1}) measured in the Llobregat river at Sant Joan Despí (Barcelona), between June and August 2008

both negative and positive correlations. Clarythromycin ($r = -0.964$) and sulfamethoxazole ($r = -0.899$) are good examples of negative correlation, easily interpretable in terms of dilution factor, while ibuprofen ($r = 0.908$), atenolol ($r = 0.869$), and enrofloxacin ($r = 0.924$) show reasonably good positive correlation. Considering the whole set of pharmaceutical products (sum of all compounds), the prevailing tendency seems to be the inverse (correlation coefficient $r = -0.639$). Therefore, we can conclude from the data presented that dilution flow is relevant but not the unique factor governing the concentration levels of pharmaceuticals in the receiving water bodies. Sources of variability are diverse [72] and dilution (flow) is only one among many others. Thus, for instance, analytical error, compound environmental variability due changes of temperature, sediment remobilization, seasonal use of certain drugs, etc., are just a few to be taken into account as contributors to the overall uncertainty.

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