Combined scenarios of chemical and ecological quality under water scarcity in Mediterranean rivers

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Water resources are directly and indirectly affected by anthropogenic activities (e.g., changes in land use) and natural factors (e.g., climate change), that is, global change. The Mediterranean basin is one of the most vulnerable regions of the world to global change, and one of the "hot spots" for forthcoming problems of water availability. The present review provides an overview about the relationship between chemical quality (especially concerning organic microcontaminants) and water scarcity, particularly in the Mediterranean area. We include an overview of environmental contaminants and analytical methodologies and consider the fate and the behavior of organic contaminants, and the effects of pollutants on ecosystems.
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Abbreviations: ADI, Acceptable daily intake; COMMPS, Combined monitoring-based and modeling-based priority setting scheme; CRPHR, Consumption rate posing health risk; DDT, Dichlorodiphenyltrichloroethane; DEET, N,N-Diethyl-meta-toluamide; DEHP, bis(2-ethylhexyl)phthalate; DWTP, Drinking-water treatment plant; E1, Estrone; EDC, Endocrine disruptor; EE2, 17α-ethynylestradiol; EQS, Environmental quality standard; GC, Gas chromatography; IPCC, Intergovernmental panel on climate change; IT, Ion trap; LC, Liquid chromatography; LCA, Life-cycle assessment; LCIA, Life-cycle impact assessment; MAE, Microwave-assisted extraction; MS, Mass spectrometry; oaTOF, Orthogonal acceleration time of flight; PAH, Polycyclic aromatic hydrocarbon; PBDE, Polybrominated diphenyl ether; PCB, Polychlorinated biphenyl; PFOA, Perfluorooctanoic acid; PFOS, Perfluorooctanesulfonic acid; PHS, Priority hazardous substances; PLE, Pressurized liquid extraction; POP, Persistent organic pollutant; PPCPs, Pharmaceuticals and personal care products; PS, Priority Substances; Qq-LIT, Quadrupole linear ion trap; QqQ, Triple-quadrupole instrument; SCCP, Short-chain chlorinated paraffin; SFE, Supercritical fluid extraction; SPE, Solid-phase extraction; SPME, Solid-phase microextraction; UHPLC, Ultra high-performance liquid chromatography; WFD, Water framework directive; WWTP, Wastewater-treatment plant

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1. Introduction

The preservation of aquatic resources must be seen as a major concern for both ecosystem integrity and human health and well-being. Ensuring environmental sustainability, reducing biodiversity loss and reducing the proportion of people without access to safe drinking water are explicitly cited as part of the fundamental *Millennium Development Goals* established by the United Nations General Assembly in its Millennium meeting in 2000 [1]. Water resources are directly and indirectly affected by anthropogenic activities (e.g., land-use changes) and natural factors (e.g., climate change), that is, global change. Two of the most evident outcomes

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of global change are the losses of water quantity and water quality, both essential for ecosystem preservation and water safety for human use (drinking, agriculture and industry) [2].

The most distinctive feature of Mediterranean climate is its seasonality, characterized by summer drought. However, the temporal and spatial variability of rainfall in Mediterranean regions is influenced by surface relief, as high relief areas are commonly associated with higher than mean rainfall values [3]. The topography of the region as well as the intense pulses of rain and marginal growth of vegetation in Mediterranean river systems makes this region vulnerable to processes of land degradation [4]. River flows in Mediterranean regions vary from perennial to ephemeral, these differences occurring within one single basin [5]. The Intergovernmental Panel on Climate Change (IPCC) predicts that the Mediterranean will be particularly sensitive to climate change. IPCC foresees a decrease of annual precipitation and an increase of average temperature, with a higher frequency of extreme events [6], meaning that water resources will be not only less abundant but also less available.

In Mediterranean regions, water abstraction is a relevant part of global change, and it often implies an overpressure on the ecosystems, causing structural drought effects. For the Mediterranean watersheds of the Iberian Peninsula, the use of water accounts for 30–224% of the total available water [7]. Land-use changes also modify the amount of available water in Mediterranean basins. Thus, the significant reduction of the mean annual flow in the last 50 years in Spanish rivers [8] has equal contributions from climate change, rising water consumption, and the historical increase in evaporation due to progressive afforestation of headwaters. Finally, the complex hydrological responses in Mediterranean river systems are compounded by multiple stressors (e.g., dams and other barriers, which prevent biological migration across river networks), the existence of dry sections as a result of water withdrawal, reaches with heavily modified hydraulics, and chemical stressors (e.g., contaminants and nutrients). Intermittent, low flows, which are associated with water scarcity affect the biogeochemical processes, loss of dilution capacity of nutrient loads and fractionation, and also decrease the natural ability of river biota to process sewage waters.

From the European regulatory perspective, the issue addressed in the present review falls within the domain of the application of the Water Framework Directive (WFD, Directive 2000/60/EC) [9]. The WFD, as stated in its title, aims to provide a common action framework to the different member states of the European Union (EU) for the sustainable management of water, its ultimate objective being the achievement of the so-called ''good status'' of the different water bodies; that milestone must be reached not later than 2015.

For surface waters, this qualification includes the simultaneous fulfillment of the ''good ecological and chemical status''. Whereas chemical status is essentially defined by compliance with established environmental quality standards (EQSs) of a list of selected key compounds, the so-called ''Priority Substances'' (PSs) and Priority Hazardous Substances (PHSs), which have been fixed by daughter Directive 2008/105/EC [10], the ecological status is defined in terms of biological, hydromorphological and physico-chemical indices. Within the last category, besides general physico-chemical conditions (thermal, acidity, salinity, oxygenation and nutrients), all other specific pollutants identified as being discharged into the river basin or sub-basin are included, whether priority substances or any other pollutant considered relevant.

The close relationship between quality (both chemical and ecological) and quantity existing in water systems is therefore fully recognized by the WFD, in not only the aforesaid definitions of ecological quality, but also the conception of monitoring of surface-water status, which explicitly covers ''the volume and rate of flow to the extent relevant for ecological and chemical status'' (WFD, art. 8). Such an integrative view of the concept of quality of aquatic systems is essential to the WFD and is one of its cornerstones.

The aim of the present review is to provide an overview about the relationship between chemical quality (especially concerning organic microcontaminants) and water scarcity, in particular in the Mediterranean area. We also discuss the consequences for the ecological status of surface waters, and its implications for water use and ecosystem services. We first introduce the analytical techniques necessary to handle the pollutants existing under water scarcity, and later relate the dynamics of pollutants to water-flow characteristics of scarcity. Finally, we tackle the effects of pollutants on ecosystems.

2. Analysis and fate of contaminants

2.1. Overview of environmental contaminants

As mentioned above, the WFD defines the chemical status by compliance with established EQSs of a list of selected key compounds: 33 priority substances and 8 other hazardous substances covered by the daughter directives of the Dangerous Substances Directive. This group includes contaminants regulated mainly on the basis of persistence, bioaccumulation and toxicity (PBT) properties, including carcinogenicity, mutagenicity and reproduction (CMR), which have been long recognized as posing risks to human health, due to their acute toxicity, carcinogenic, or mutagenic effects and their persistence in the environment. [10].

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