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Editorial

Assessment of Different Contaminants in Freshwater: Origin, Fate and Ecological Impact

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Abstract: Freshwater ecosystems cover over 15% of the world's surface and provide ecosystem services that are pivotal in sustaining human society. However, fast-growing anthropogenic activities have deleterious impacts on these ecosystems. In this Special Issue, we collect ten studies encompassing five different factors of freshwater contamination: landfill leaks, nutrients, heavy metals, emerging organic contaminants and marble slurry. Using different approaches, the studies detailed the direct and indirect effects that these contaminants have on a range of freshwater organisms, from bacteria to vertebrates. Although the papers covered here focused on specific case studies, they exemplify common issues that are expanding in groundwaters, hyporheic zones, streams, lakes and ponds around the world. All the aspects of these issues are in dire need of being continuously discussed among scientists, end-users and policy-makers. To this end, the Special Issue presents a new free software suite for the analysis of the ecological risk and conservation priority of freshwater ecosystems. The software can support local authorities in the preparation of management plans for freshwater basins pursuant to the Water Directives in Europe.

Keywords: heavy metals; EOCs; nitrate; landfill; marble slurry; neonicotinoids; microplastics; software

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1. Introduction

Freshwater sustains human society with some 93,000 km^3 of water stored in lakes and rivers and much more in groundwater or as ice [1], covering about 15% of the world's surface [2]. From nanograms of pharmaceuticals to large pieces of plastics, freshwater ecosystems are a sink for anthropogenic contamination, which is predicted to become more severe in the coming decades as a result of population growth and urbanization. Contaminants can enter freshwater directly, through countless anthropogenic activities ranging from legal and illegal discharges from factories to imperfect water treatment plants, landfill leachates, mines, quarries and agricultural runoff. Mining activities are the major contributors of heavy metals [3], while emerging organic compounds (EOCs), including pesticides, pharmaceuticals and personal care products, are mainly released by wastewater treatment plants and agricultural practices [4]. Long-lasting contamination with nitrates, nitrites, ionized ammonia and pesticides in groundwater is a common consequence of intensive agriculture [5,6]. Modern high-tech methodologies, such as nanofiltration, electrodeposition, and sequestration, can only help in stemming the tide of aquatic pollution without solving the problem completely [7]. Strict obedience to environmental laws and regulations is the only way of bringing freshwater pollution down to its barest minimum [8].

As a result of contamination, biodiversity loss continues to occur in freshwater ecosystems at a rate double that in other ecosystems [9]. Rivers and lakes sustain nearly 10% of all described animal species, including 40% of the world's fish diversity and a third of all vertebrate species [10], while groundwater hosts at least 5000 species of invertebrates, of which 70% are represented by crustaceans [11,12]. These numbers translate into a great diversity of life forms, consisting of prokaryotes and microscopic single-cell eukaryotes through to meiofauna and macrofauna and up to vertebrates. Freshwater organisms are subjected directly to the toxic actions of pollutants. Their responses to contaminants are varied, and the most drastic responses are represented by death or migration, potentially leading to local extinction. Other responses may include reductions in reproductive capacity and morphological and physiological changes. Changes at the community, population and individual levels not only constitute direct evidence of the ecological impact that a contaminant can have in freshwater ecosystems but can also serve as bioindicators to track the source and fate of contamination.

This Special Issue collects ten studies on the response of freshwater ecosystems to anthropogenic pollution. The papers detail the direct and indirect effects that pollutants have on a range of freshwater aquatic organisms, from microbes to vertebrates. The overview covers a variety of contaminants, from nutrients and heavy metals to emerging contaminants and microplastics, and from landfill leaks to marble quarry slurries. The studies involve different types of fresh water ecosystems, from groundwater to mountain karst ponds, hyporheic zones, stream waters and lakes. The papers of the Special Issue are hereafter presented with reference to the types of water bodies to which they refer. A final paragraph is dedicated to a new software tool for the assessment of the ecological risk and the conservation priority of freshwater ecosystems.

2. Overview

2.1. Groundwater

Changes in groundwater quality, such those induced by municipal solid waste disposal in landfills, can directly affect the functional properties of aquatic microbial communities. Melita et al. [13] explored the structural alterations, as well as the functional responses, of groundwater microbial communities to a gradient of geochemical alterations induced by a municipal solid waste landfill in central Italy. The microbial communities were characterized by flow cytometry and the Biolog EcoPlates^{TM} assay, with the aim of highlighting biogeochemical cycling patterns along the gradient. The microbial communities from the pristine and mildly-altered groundwaters showed a low affinity for most of the carbon sources. By contrast, the microbial community thrived in the altered groundwater conditions defined by high concentrations of organic matter and fecal bacteria. The profiles of the carbon substrate use highlighted the efficient metabolization of a large number of organic compounds, including those with complex molecular structures.

Nitrate is likely to be the most common pollutant in groundwater and is such a serious pollutant that the EU dedicated the subject of a specific directive to it. In alluvial aquifers of agricultural areas, the ion can reach concentrations up to hundreds of milligrams per liter. In aquifers that are well oxygenated and have a low organic content, denitrification processes (i.e., the reduction of nitrate) do not take place or take place at such low rates that they do not allow the recovery of the groundwater body. Nitrate contamination can, therefore, persist for years [14]. Di Lorenzo et al. [15] analyzed the effects of long-term nitrate contamination on the groundwater fauna of an alluvial aquifer in central Italy. The study revealed that structural traits of the biological assemblages, such as the ratios of juveniles to adults and of males to females, as well as the relationships between abundances and biomasses, provide indicators of the alteration of the communities in a more efficient way than classical taxonomy-based analyses, which are focused on species richness and abundances only.

Both taxonomy-based and trait-based approaches, although providing important information, are not able to identify which is the lethal concentration of a pollutant for a given species. To obtain this information, it is necessary to carry out ecotoxicological tests; that is to say, experiments in controlled laboratory conditions. Unfortunately, ecotoxicological studies with the so-called stygobiotic species (i.e., species that carry out their entire life cycles in groundwater) are extremely few due to the low abundances with which these animals are collected and the difficulty of breeding them in the laboratory [16,17]. Hose et al. [18] provided an important contribution to the field of ecotoxicology with stygofauna, through testing the effects of some heavy metals—such as As, Cr and Zn—on an undescribed species of syncarid (Malacostraca: Syncarida: Bathynellidae). The study revealed the high sensitivity, both in terms of survival rates and bioaccumulation, of syncarids to metals, with particular reference to As. Zinc was the least toxic metal for the syncarids, which showed significant metal bioaccumulation at exposure concentrations higher than 1 mg of Zn/L.

If the studies on the toxic effects of chemical pollutants on stygobiotic species are few, the analysis of the impact of non-chemical stressors, such as marble slurries, on stygobiotic communities are, to date, non-existent. This Special Issue presents the first preliminary study on this topic. Piccini et al. [19] characterized, from a sedimentological and chemical point of view, the fine marble powder that is produced at quarries during the extraction and squaring of marble blocks by means of chain and diamond-wire saws. The study was conducted on an iconic area of marble quarry activity, the Apuan Alps in central Italy, a karst area exploited for marble since the time of the ancient Romans. The results of the study showed that, during intense rain events, the marble slurry—which, in the Apuan Alps, is called *marmettola*—is washed into the karst springs, making the water temporarily unsuitable for domestic uses. A very preliminary investigation suggests that the *marmettola*, consisting of calcite granules with a diameter between 8 and 32 μm, could fill the voids of the Apuan Alps karst system, making the voids unavailable for some stygobiotic taxa. The results need to be supported by further studies; however, stygobiotic amphipods are, in fact, unable to penetrate fine-grained sediment with a diameter <60 μm, as already observed by Korbel et al. [20].

2.2. Streams and Hyporheic Zones

Insecticides, especially neonicotinoids, are among the most commonly used and detected EOCs in stream waters worldwide [21]. Hunn et al. [22] investigated the effects of the neonicotinoid imidacloprid on the mayfly *Deleatidium* spp. (Leptophlebiidae), collected from the Silver Stream, a fourth-order stream near Dunedin in New Zealand. Imidacloprid exposure had severe lethal and sublethal effects on *Deleatidium* spp., with significant impairment at concentrations as low as 1 μg/L of imidacloprid. Starvation worsened the effect of the neonicotinoid on the mayfly species, affecting their ability to swim or right themselves and leading to immobility.

The contamination of freshwaters with EOCs is predicted to become more pronounced in the coming decades [4]. The hyporheic zone (i.e., the zone where water is exchanged between the open channel and the saturated permeable streambed sediments) is particularly susceptible to EOC contamination due to the long residence times of these toxicants in the pore-spaces and, consequently, long exposure periods for organisms dwelling in the hyporheic zone. Peralta-Maraver et al. [23] reported the effect of EOC pollution on the composition and abundance–body mass (N–M) relationships of the hyporheic communities (prokaryotes, single cell eukaryotes, meiofauna and macrofauna) of thirty streams in the UK. Emerging organic compounds negatively affected the hyporheic assemblages, inducing significant changes in the N–M coefficients, with an increase in the biomasses and abundances of the organisms chiefly associated with pollutant-tolerant groups such as Asellidae and Oligochaeta.

Under a scenario of pollution and a concomitant increase in tolerant, large-sized taxa, bioaccumulation is expected to be more acute. Labuschagne et al. [24] tested the potential for the bioaccumulation of platinum group elements (PGEs) using artificial and natural bivalves. Platinum group elements are pollutants of emerging concern almost everywhere but particularly in areas where PGEs are mined. The study was undertaken along a contamination gradient in the Hex River, South Africa and compared the accumulation of metals in a passive sampling device made up of artificial mussels with the uptake by transplanted individuals of the freshwater clam *Corbicula fluminali africana*. Both bioindicators were efficient in highlighting the presence of As, Cd, Co, Cr, Ni, Pb, Pt, V and

Zn, but the uptake pattern for Pt, Cr and Ni—between the artificial mussels and natural clams—was different. The results showed that a combination of the two bioindicators, rather than the use of only one of the two, provided a more holistic assessment of PGE contamination in the Hex River.

2.3. Lakes and Karst Mountain Ponds

Morphological deformities of chironomids are known to provide information about contamination by heavy metals, pesticides and, in general, substances that act as endocrine disruptors [25]. Goretti et al. [26] examined the incidence of mentum deformities in populations of *Chironomus plumosus* (Diptera: Chironomidae) in Lake Trasimeno, central Italy. The 26-month study showed that <10% of the *C. plumous* population had a mentum deformity, with a higher incidence during spring and in the littoral populations. The most common type of deformity found was the "round/filed teeth" type. Compared to the results of the years 2000–2010, the incidence of *C. plumosus* mentum deformities has decreased significantly. This result is suggestive of a recovery of the chemical conditions of Lake Trasimeno in the last decade.

The study of Iannella et al. [27] focused on karst mountain ponds, which are high-altitude ecosystems usually exploited as watering points for livestock. The ponds may show high ammonium concentrations and the significant depletion of dissolved oxygen due to eutrophication induced by cattle excrement. The study, which examined the karst ponds of the Apennines in central Italy, showed that the enrichment of the ponds with organic nutrients due to the manure may have a significant effect on the diet of the Italian crested newt *Triturus carnifex*, a "Near Threatened" species included in the Italian IUCN red list. In particular, the study reported an impoverishment of the *T. carnifex* diet in the most nutrient-enriched ponds, probably due to a low diversity of the benthic invertebrate assemblages. Alarmingly, the study also reported the first evidence of the occurrence of microplastics in the stomach contents of *T. carnifex*.

2.4. AQUALIFE Software

Finally, Strona et al. [28] presented the AQUALIFE software, a user-friendly online interface (available at http://app.aqualifeproject.eu), that can be used to assess the ecological and hydrological-hydromorphological risks to aquatic ecosystems dependent on groundwater (e.g., springs, hyporheic zones, streams and rivers, aquifers etc.) along with their conservation priority. The Ecological Risk suite of the AQUALIFE software computes the probability (from 0 to ∞) that a toxicant may cause the impairment of a biological aquatic community at a measured environmental concentration. The Hydrological-Hydromorphological Risk suite identifies and scores the risks posed by human-induced alterations to the hydrological connectivity of springs and hyporheic zones. Finally, the Conservation Priority Index suite determines the conservation priority of aquatic ecosystems based on selected species traits such as distribution, endemicity, degree of groundwater dependence, ecological affinity to groundwater, ecological niche breadth, thermal tolerance, microhabitat preferences, trophic role, life span, frequency of occurrence, abundance, evolutionary origin and phylogenetic rarity. With its multi-metric facet, the AQUALIFE software provides a novel tool to assist policy-makers and local authorities in managing groundwater-dependent ecosystems.

3. Conclusions

In this Special Issue, we had the pleasure of collecting ten studies that each increased the level of knowledge regarding the origin, fate and ecological impact of contaminants on freshwater ecosystems. The studies covered various geographical areas, from Europe to South Africa to Australia and New Zealand, and numerous types of aquatic environments, from groundwater to karst mountain ponds, rivers, lakes and the areas of transition between surface water and groundwater. The stressors examined in these ten studies ranged from heavy metals to emerging organic pollutants, and also included non-chemical contaminants, such as the dust produced at marble quarries. The approaches used were ecotoxicological, taxonomy-based and trait-based, and touched upon many of the components of the freshwater communities, from bacteria to vertebrates. We believe that the collation of these papers may contribute to and stimulate further interest in some critical issues of vulnerability in freshwater ecosystems.

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