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Editorial

Special Issue: Advancement in Biomonitoring and Remediation Treatments of Pollutants in Aquatic Environments

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A series of negative, attendant circumstances threaten the ecological equilibrium, the quality, and even the existence of the different aquatic ecosystems nowadays more than ever. In both fresh and marine waters, it is possible to find traces or significant amounts of contaminants produced by and for human activities, unpredictably affecting the different trophic levels. Together with the excessive drawings on freshwater reserves, driven by the rise in population and the drought crisis linked to the climate changes, the pollution of the tiny fraction of freshwater available to us urgently requires effective, sustainable, and innovative monitoring and remediation tools. In light of the above, this special issue was proposed and so far, 16 papers have been published in this Special Issue, fairly equally distributed between monitoring activities and remediation proposals.

The first paper reported the application of a polar organic chemical integrative sampler (POCIS) to the monitoring, by passive sampling, of marine water employed in aquarium tanks [1]. The passive accumulation devices provide in situ integrative sampling, pre-concentration and purification steps, allowing the determination of time-weighted average (TWA) concentrations of trace levels in the supply water of hydrocarbons, DPS, 2,4-DTBP, BPA and the UV-filters OC and EHMC. The result highlighted the usefulness of pre-concentration in the passive sampling approach, which permitted enhanced sensitivity.

In the paper [2], the performance of conventional monitoring of PCBs by water sampling followed by GC-MS/MS determination was compared with biomonitoring using the Baikal omul, *Coregonus migratorius*. Comparative statistical analyses were carried out to study both the influence of the year, season, locations, layers of the water column on water samples values and that of the age and sex of omul on the ratio and concentrations of indicator congeners in fish tissues. The determination in water was simple, obtained by measuring only two indicator congeners. The PCB accumulation in the muscle tissue depended on their hydrophobicity and on the age of individuals. Hence, the ratio of congeners in fish tissues did not reflect their ratio in the water samples.

By using a manipulative feeding experiment, possible damages to the intestinal microbial community and morphology of *Micropterus salmoides* produced by virgin polypropylene microplastics (MPs) were investigated [3]. The tested MPs were fibres, fragments, and films added into the water or to the feed. After a four-week trial, no significant differences were detected in weight gain (WG%) and specific growth rate (SGR). MP exposure had no statistically significant effect on the composition or diversity of the intestinal microbial community, although it could partly influence the intestinal morphology and the recombination process of the intestinal microbial community.

In [4], the authors carried out a numerical study, reproducing the changes in 1,4-dioxane concentrations in groundwater observed in the monitoring wells of a waste dumping site. The quasi-3D flow and transport simulation model was useful in predicting the changes in pollutant amounts in the hydrologic environment, elucidating the transport under both natural and artificially induced water flows. The simulation revealed that the pumping actions could promote pollutant transport to areas where it would otherwise be difficult

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to reach. This phenomenon was unanticipated, and it would influence the groundwater treatment efficiency.

In light of the differences that exist among pollutant mechanisms and among organism sensitivity, a careful evaluation of the suitability of three freshwater and marine microalgae and of *Vibrio fisheri* bacteria in assessing the long-term toxicity of a set of benzo-fused nitrogen heterocycles was reported in [5]. No species-specific sensitivity for any whole family of pollutants was observed and the freshwater *R. subcapitata* was the only alga affected by most of the compounds at the lowest concentrations. The *Vibrio fisheri* assay showed low detrimental effects or even growth stimulation regarding the contaminant levels in surface and drinking waters.

Heavy metal (HMs) contamination in fish from aquaculture can represent a serious health risk. The patterns of HM accumulation (Cu, Zn, Cd, Hg, Pb, As) in the muscles and livers of *Cyprinus carpio* and *Ictalurus punctatus* grown in a net cage deployed in a lake, where the sediments were rich in heavy metals, were monitored over a 16 month period [6]. The water pH values (8.6–9.5) promoted the aggregation of metals, reducing their content in water. The fish raised in aquaculture that were provided only metal-free feed and with limited access to natural food sources do not represent a health risk for their HM content. Conversely, native fish in free contact with sediments and contaminated sources of food represented a moderate-to-high risk.

The groundwater quality and the origin of threats to it can be determined by analysing the physico-chemical parameters and the metal content, as it was assessed in [7] on samples collected from different countries. Various parameters were associated with anthropogenic activities. High EC conductivity can affect shallow depth groundwater. The concentration of nitrate can be connected to high agricultural waste and sewage contamination. A high concentration of chloride indicates a high degree of organic pollution, whereas ammonium is an indicator of recent organic pollution, both of natural and artificial origin. Turbidity in groundwater depends on the exploitation activities in the area. The statistical analysis of data can reliably indicate the pollution source.

The integrated biomarker response index (IBR), the bioeffects assessment index (BAI) and the principal components analysis (PCA) were evaluated for their sensitivity in revealing stress patterns in *Phaeodactylum tricornutum* under contaminant exposure [8]. The antioxidant enzymes CAT, SOD and APX, and the TBARS oxidative stress markers revealed an overall suitability, producing statistically significant dose–response relations. IBR appears as a useful tool, as it reflects the contaminant levels at the sites, despite the variability in biomarkers used for its calculation. The BAI index revealed low sensitivity against the oxidative stress data set, confirming that its applicability is more adequate for general toxicity biomarkers and non-specific stress parameters. PCA satisfactorily delivered a significant negative correlation for the overall experiment relative to compound concentration and index scores and it was positively correlated with the BAI index.

In [9], a model for the assessment of the health risk depending on the consumption of contaminated water is proposed, depending either on the hydraulic or on water quality models. The health impact without using water quality stations was compared to that obtained in the presence of ten water quality sensors, both deployed utilizing the volume of the contamination water (VCW) and the time detection (TD), respectively. The use of water sensors has shown a large difference in reducing the number of people exposed to the risk of using contaminated water; the result was quite optimal (the health impact was reduced by up to 98.37%) in the case of sensors deployed using TD.

A remedial investigation and feasibility study was carried out on groundwater contaminated by tetrachloroethene, trichloroethene, and vinyl chloride [10]. A double tracer approach was used to reassess the hydraulic conductivity and hydrodynamic dispersity. A soybean oil-based emulsion (EVO), with and without hydrogen gas infusion, was employed and the simple EVO treatment was the most suitable in supporting the native microbial consortia and in removing the substrate from the subsurface. Microbial consortia changes

were monitored. Careful and frequent addition of substrate to the low permeability regions was key in successfully remediating them.

The work reported in [11] focused on the same topic. The chemical reduction by an organo-iron compound (liquid ferrous lactate), combined with emulsified vegetable oil, was employed to minimize the accumulation of the tetrachloroethene by-product in groundwater. Ferrous lactate (FL) forms aqueous solutions that are convenient for injection during in situ operations and that may have a longer distance of transmission than solid, zerovalent iron. The used mixture was effectively adsorbed into soil pores and continued to release electron donors; it had at least 90 days of slow-release effect and reached a minimum distance of 5 m. Moreover, the metabolites did not accumulate in a notable manner in areas where FL concentration was adequate.

The tolerance mechanisms developed by microorganisms that inhabit the impacted sites could be exploited in remediation processes, for example in [12], where it is reported that marine bacteria collected from seven Portuguese fishing ports were isolated and grown in the presence of Tributyltin (TBT). The bacteria that exhibited higher growth were evaluated for their capability to degrade this highly toxic, endocrine disrupting compound. The results were ascertained using ecotoxicological tests. Two strains were selected and identified as *Pseudomonas putida* and *Serratia marcescens*. *P. putida* showed the highest degradation potential. After 96 h of exposure to *S. marcescens*, the media was still toxic, suggesting the need for longer contact time or the production of toxic by-products.

An effective remediation of polluted water was obtained by removing the unwanted chemicals by physical absorption mechanisms on nanomaterials, thanks to the large specific surface area [13]. Multi-walled carbon nanotubes (MWCNTs) were synthesized, purified, functionalized, and used as an adsorbent for the removal of Ismate violet 2R dye from the contaminated water. The morphological structure, the physical, chemical, thermodynamic, and kinetics properties were evaluated throughout. The adsorption is a physisorption process and under optimal conditions, the percentage of removal of the MWCNTs from real wastewater reached 88%.

The in situ degradation of pesticide containing agro-wastewaters (remnant volumes from spraying activities or leftover pesticide waste) was realized by a portable photo-reactor prototype, employing UV lamps and H_2O_2 [14]. The degradation process was evaluated by the pesticides' absorbance decrease, the mineralization process by measuring the TOC values, and the toxic effects of irradiated and non-irradiated solutions by biological tests. The photo-reactor prototype was able to remove about 80% (mean value) of the active molecules in an acceptable time (8 h). The mean mineralization rate was about 44%. These results were extremely positive, since the photoproducts are more prone to inherent water remediation processes than the parent compounds.

The effectiveness of a TiO_2 photo-catalysis in removing glucocorticoids (GCs) under simulated and natural sunlight from solutions prepared in tap water or in river water at environmental concentrations has been evaluated [15]. The degradation profiles followed a pseudo-first order kinetics and the TiO_2-assisted photo-catalysis appeared to be independent of the chemical structure of the GCs. The photocatalytic process was from one to two orders of magnitude faster than the not-catalysed photolysis. The two main photo-oxidation paths, directly linked to OH radicals from the irradiated TiO_2 catalyst, were defined. The author concluded that the great stability of the titania crystals under irradiation, coupled with the good adsorption properties and catalytic activity, overcome any other depollution method.

The paper [16] reports the degradation of the highly toxic pesticide methiocarb (MC) by electrochemical oxidation in aqueous solutions, utilizing a boron-doped diamond anode and two different supporting electrolytes. The removal rate, total organic carbon (TOC), and total nitrogen (TN) were determined. The effects on the biotoxicity were assessed using the freshwater crustacean *Daphnia magna*. The hydroxyl radical-dependent degradation showed a first-order mechanism and the MC and TOC removal rates were higher for the solutions containing NaCl instead of Na_2SO_4. Moreover, in the presence of Na_2SO_4, no

nitrogen removal occurred. The electrochemical oxidation effectively degraded methiocarb, reducing drastically the acute toxicity towards *D. magna*, especially in chloride-containing solutions. In those solutions, the electric charge increase must be avoided, since this increase in the ecotoxicity is probably due to the formation of perchlorate and organochlorinated compounds, which can exert a toxic effect on *Daphnia*.

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