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Editorial

Geochemical Equilibrium and Processes in Seawater

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Abstract: The geochemical equilibrium in seawater must be observed taking into account the chemical and geological, as well as biological, processes. The concept of equilibrium takes into account the composition of the system and the kinetics of the reactions taking place therein. In coastal waters, nutrients and trace elements can be delivered not only through rivers but also through atmospheric input and submarine groundwater discharges. In addition to natural sources, levels of different elements can also be influenced by growing and diverse human activities along coasts. Consequently, the pathways and fate of different environmental chemicals in coastal areas are governed by various factors. The multiparameter approach, combined with different statistical tools, is a well-established way of interpreting their inputs and behaviour in marine systems. Nevertheless, the data for the karst regions, as found in the Mediterranean, are particularly scarce. This Special Issue—*Geochemical Equilibrium and Processes in Seawater*—of Geosciences gathers five articles on different topics related to water and sediment geochemistry of the coastal karst areas of the Mediterranean, including Slovenia, Croatia and Egypt. The topics included in this Issue refer to (1) geochemistry of sediments in the area of intensive anthropogenic activity; (2) the geochemistry of sediment and biota in a protected area under increasing pressure due to tourist activity; (3) the influence of a thermal power plant on the geochemistry of the surrounding area; (4) the influence of underground water discharges on water quality; and (5) the possibility of monitoring natural and anthropogenic processes in karst systems by using a specific group of elements.

Keywords: marine geochemistry; geochemical modeling; interaction of sources; anthropogenic influence; Mediterranean

1. Introduction

In coastal waters, geochemistry of trace elements is determined by both natural and anthropogenic factors. Among natural sources, trace elements could be supplied by riverine inputs but also by atmospheric pathways and submarine groundwater discharges, where the latter includes the discharge of fresh and saline groundwater, as well as the advection of the sediment porewater. Recent studies have highlighted the importance of atmospheric transport and deposition modes, and have mentioned the effects of groundwater discharges on the overall nutrient and trace element fluxes in marine environments, as well as their influence on overall marine (bio)geochemistry [1]. In addition to this, the more intensive settlement of coastal areas and development of the supporting industry and infrastructure relentlessly change maritime landscapes and contribute to the overall budget of trace elements in coastal areas [2–5].

The input of nutrients and trace metals to coastal waters, however, varies both spatially and temporally, with different studies providing different angles on this topic. Given that multiple factors influence the pathways and fate of different environmental chemicals, there is a growing need for further studies, whereby the collected data could be used for validation and modeling, and can serve to enhance our understanding of nutrient and trace element inputs and their behaviour in coastal systems.

Although karst makes up around 12% of the world's surface (excluding the Antarctic, Greenland, and Iceland), karst areas are unfortunately under-represented in the literature, as well as in globally protected areas [6]. Given their formation character, defined by the dissolution of soluble carbonate bedrock, karst regions display distinctive surface features and complex underground drainages. Such landscapes create the conditions in which chemical and microbiological pollutants easily enter aquifers, spreading rapidly through the network of fractures and conduits, often without effective processes of filtration and self-purification. Consequently, such regions require specific protection and management approaches.

The topics included in this Issue refer to (1) the geochemistry of sediments in the area of intensive anthropogenic activity; (2) the geochemistry of sediments and biota in a protected area under increasing pressure due to tourist activity; (3) the influence of a thermal power plant on the geochemistry of the surrounding area; (4) the influence of underground water discharge on water quality; and (5) the possibility of monitoring natural and anthropogenic processes in karst systems by using a specific group of elements.

Each of these papers [7–11] provides an insight into the problem that is ubiquitous in populated areas, but with a unique viewpoint, i.e., taking into account the features of the karst background.

2. Overview of the Special Issue Contributions

Rogan Šmuc et al. [7] described the heavy metal signature of the sediments near the Port of Koper in the northern Adriatic Sea. Koper is a small coastal city located in Slovenia's Mediterranean region. Due to its geographic location, it is influenced by various anthropogenic contamination sources from an international port (the Port of Koper), an industrial zone with a chemical factory, agriculture, and viticulture developed in the hinterland of the city. The Port of Koper is one of the biggest and most important ports in the northern Adriatic Sea and reflects both anthropogenic and geogenic influences [12–14], thereby presenting an ideal system for heavy metal mobility determination. Despite these influences, most of the studied elements were only found to be marginally enriched in the sediments. Only nickel was present at levels higher than threshold effect concentration (TEC) and probable effect concentration (PEC) values defined by Sediment Quality Guidelines. Sequential chemical extraction, on the other hand, showed that the majority of heavy metals in the sediments near the Port of Koper are immobile due to their prevalence (more than 50%) in the residual phase, with molybdenum as an only exception.

Ilenič et al. [8] examined the eligibility of defining the Kornati National Park as a reference area for environmental studies. Kornati National Park (eastern Adriatic coast, Croatia) is considered an unpolluted reference area in environmental and ecological studies, but with an increase in tourist activities and a higher exposure to anthropogenic inputs, some parts of this park are deteriorating. The factors that contribute the most to environmental risks are the fishing industry and chemical pollution, invasions of exotic species, and global climate change, leading to eutrophication and physical changes of the ecosystem [15].

Stable isotopes of carbon (C) and nitrogen (N) are commonly used to decipher the environmental conditions and trophic relations in ecosystems [16,17]. Stable isotope compositions of organisms are used to identify the biochemical processes and sources of the pollution, as they are mainly influenced by the isotopic ratios of their diet, metabolic pathways, and fractionating processes [18,19]. With isotopic analysis, it is also possible to determine the source of sedimentary organic matter (marine, terrestrial) and assess the anthropogenic impacts on the observed area [20].

The conducted isotopic analysis revealed that even though some parts of the Kornati National Park are still preserved and intact, there are some areas where human activity has already made an evident impact and has consequently contributed to changes of the environment. The study of Ilenič et al. [8] shows that the areas closer to marinas and villages are more likely to be under the influence of anthropogenic pollution, whereas more distant ones remain anthropogenically unaltered.

Medunić et al. [9] studied the selenium, sulfur, and trace element signature of the Raša Bay environment contaminated by superhigh-organic-sulfur coal. In the Labin city area (also situated in the northern Adriatic, Croatia), in the vicinity of the Raša Bay, historic (back to the 18th century) coal mining and associated foundry industries are located. Coal mining and ash-generating processes like coal combustion and smelting, and metal foundries, are known as the predominant sources of various potentially toxic emissions [21] which pollute the atmosphere, pedosphere, hydrosphere, and biosphere [22]. They are represented by complex mixtures, which include particle matter, semi-volatile matter, and various gases [23,24].

To assess the potential contamination of soil by selenium and trace metals in the Labin area, the authors calculated the enrichment factor and the geo-accumulation index. Their study showed that historic coal mining and combustion, as well as the accompanying metal foundry industries, have considerably polluted the entire environment of the Labin city area.

Geochemical and isotopic evidence of groundwater salinization processes was studied by Eissa et al. [10]. Groundwater geochemistry in coastal aquifers reflects both the geological conditions and the current anthropogenic processes, which subsequently influence the groundwater quality [25–27]. However, the importance of these aquifers at the local and regional scales, the main hydrogeologic patterns, hydrochemical features, and the groundwater origins, still remain poorly understood [28]. By combining geochemistry and isotopic tools, the origin of karst water mineralization can be deciphered [27–30]. Ion chemical ratios can also be helpful in detecting the hydrochemical processes affecting water quality, such as leaching, mixing, or ion exchange, as well as in assessing the impact of seawater intrusion on the groundwater chemistry.

In the complex system of the El Dabaa Area, on the northwestern coast of Egypt, Eissa et al. [10] identified the origin of salinization and the hydrogeochemical processes affecting groundwater quality using dissolved major ions, conservative tracers (Br and Cl), and stable environmental isotopes ($\delta^{18}O$ and $\delta^{2}H$). Additionally, the main source(s) of groundwater mineralization in different aquifers were assessed by simulating the geochemical processes using NETPATH modeling, a geochemical groundwater reaction and mixing code [31].

According to the work of Eissa et al. [10], the main factors causing deterioration of the said groundwater quality are the water–rock interactions of carbonate rocks of marine origin mixing with seawater. Their work provided new insights into the hydrochemical features of groundwater in this area, the sources of groundwater recharge and their mixing pathways, as well as the main processes worsening its quality.

Fiket et al. [11] described the distribution of rare earth elements, including Y (REY), in sediments of the marine lake Mir (Dugi Otok, eastern Adriatic coast, Croatia). A growing number of current or emerging alternative energy technologies and types of digital equipment contain REY-bearing components, such as glass, magnets, metal alloys, catalysts, and phosphors [32,33], causing not only increasing trends in the annual demand for REYs but also leading to the increasing exploitation of rare earth minerals [32,34]. Consequently, REYs increasingly enter soil and water systems, mainly through microelement fertilizers and mine tailings, and subsequently accumulate in soils and sediments, bioaccumulate in biota [35,36], and enter the food chain, causing serious environmental problems [37].

In order to successfully identify sources that can influence the increase of REY concentration in water systems, it is necessary to know the processes and mechanisms that determine their distribution in the environment. The study of Fiket et al. [11] provides an insight into the influence of local soils on the distribution of REY in sediments of the nearby marine lake Mir and suggests the possibility of differentiation between external influence and substrate, which is the main premise when determining the external source of REY in the environment. In addition, the study provides background concentrations for the unique environment of marine lakes situated in the karst environment.

3. Final Remarks

Understanding the sources and processes that define the distribution of elements in coastal marine environments is not just important for quantifying their total budget or describing geochemical equilibrium but also for purposes of defining management strategies. Many challenges have arisen due to environmental changes, i.e., sea-level rise, flooding or erosion, inducing changes in material sources and their role in nearby water systems, as well as increasing human activity along coastlines. Karst regions are particularly sensitive to such environmental changes, as well as increasing anthropogenic pressures. Although studies encompassed by this Special Issue include small areas and issues described are of local character, each paper contributes to the knowledge of the geochemistry of karst regions and presents a step forward in their adequate protection and preservation.

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