

# Groundwater Chemistry and Quality in Coastal Aquifers

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## 1. Introduction

Groundwater is the most abundant freshwater resource available on earth, and it accounts for more than 95% of all liquid freshwater [1,2]. This freshwater resource is important for coastal areas where it is commonly regarded as the center of social and economic development because the availability of water resources constrains socio-economic development in these areas [3]. It is reported that coastal aquifers are a nexus of the ocean, and terrestrial hydrologic ecosystems provide groundwater resources for about one billion people worldwide as well as social and economic development in coastal areas [4]. There is a direct connection between the stores of available freshwater provided by groundwater and their status in terms of quality because the good quality provided by groundwater is critical for sustaining agriculture, industries, and drinking water services [5,6]. We need to improve our knowledge of groundwater quality if we are to use groundwater sustainably and not further burden future generations by limiting resources and/or increasing treatment costs [7]. Therefore, understanding the status and challenges of groundwater quality to support sustainable water supply is fundamental to reaching key Sustainable Development Goals (SDGs) in coastal areas.

Two groups of chemical components threaten groundwater quality. One includes geogenic contaminants, such as arsenic, fluoride, and iodide [8,9]. Another is human-induced pollutants, such as nitrate and organic pollutants [10,11]. Both of them influence groundwater quality and are often complicated because of complex geological settings and anthropogenic factors. In recent decades, land use transformation from agricultural and natural ecosystems to urbanization accompanied by various human activities has intensified the complexity of groundwater chemistry and quality in global coastal areas [12,13]. For instance, large-scale urban agglomerations, such as the Yangtze River Delta (YRD) and Pearl River Delta (PRD) megalopolises of China and the Boston–Washington megalopolis of the United States, are distributed in coastal areas adjacent to the Pacific and Atlantic oceans, respectively. As a result, in order to reflect recent research advances on groundwater chemistry and quality in coastal areas, this Special Issue for the journal *Water*, entitled *Groundwater Chemistry and Quality in Coastal Aquifers*, was developed.

## 2. Advances on Groundwater Chemistry and Quality in Coastal Areas

In order to understand the advances in groundwater chemistry and quality in coastal areas worldwide, we searched related publications in the Web of Science database using the following three keywords: groundwater quality, coastal area, and groundwater chemistry in the coastal area. As shown in Figure 1A, more than two thousand papers related to groundwater chemistry and quality in coastal areas were published in the last twenty years, and the annual number of papers has increased rapidly, from around 20 papers in one year in the early twenty-first century up to nearly 200 papers per year in recent times. All countries with a high number of papers are adjacent to oceans (Figure 1B). For example, the



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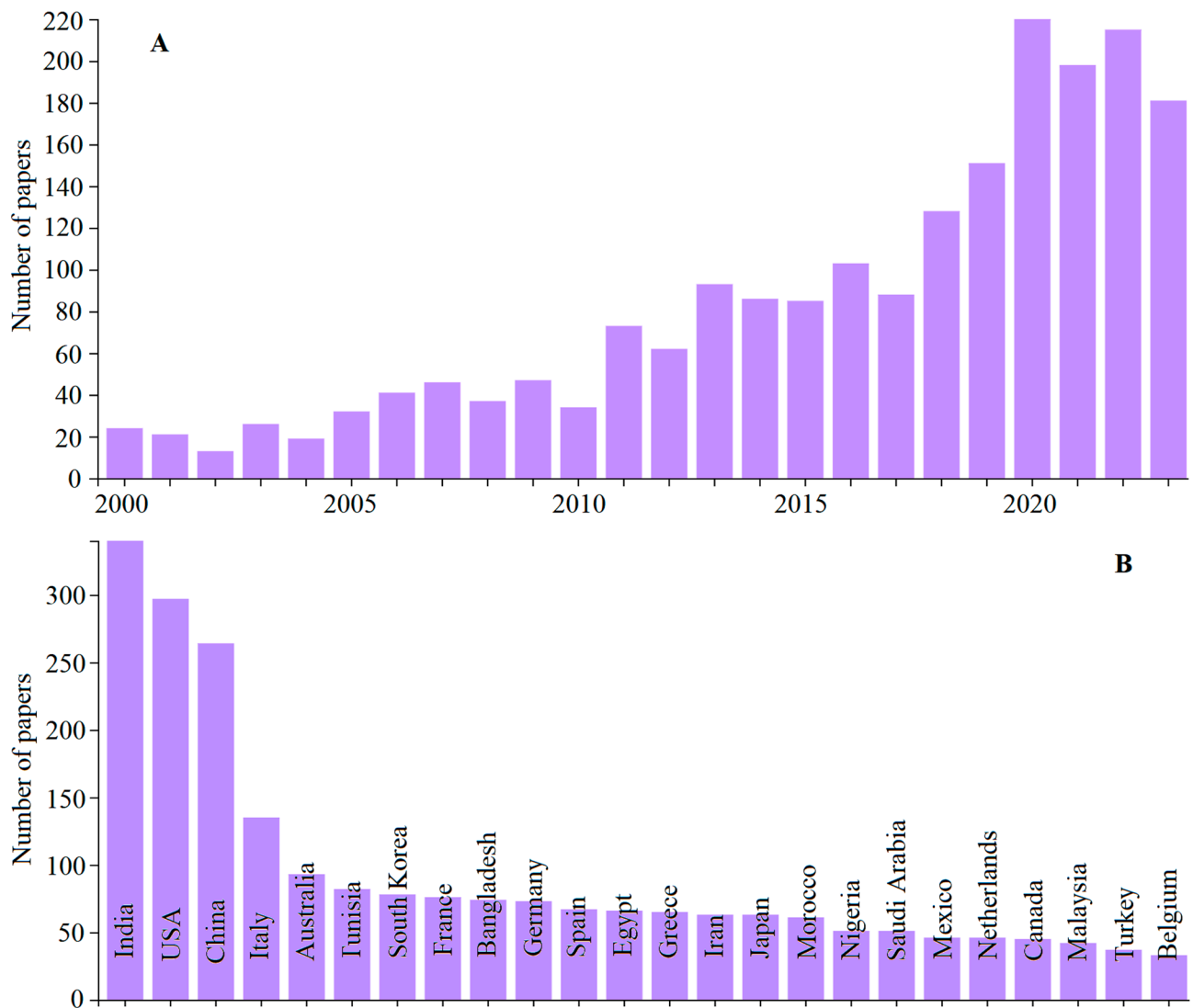
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three countries with the highest number of papers are India, the USA, and China, which are adjacent to the Indian Ocean and Pacific Ocean, respectively, and their numbers of papers have nearly doubled compared to other countries (Figure 1B). This indicates that India, the USA, and China pay much more attention to groundwater chemistry and quality in coastal areas than other ocean countries. Correspondingly, this Special Issue mainly focuses on groundwater chemistry and quality in coastal areas in one of the above countries (China). In addition, groundwater chemistry and quality in coastal areas of two other ocean countries, including Pakistan and Egypt, are also mentioned in this Special Issue.



**Figure 1.** Statistics of number of papers related to groundwater quality, coastal areas, and groundwater chemistry for different years (A) and countries (B) in the Web of Science database.

### 2.1. Groundwater Chemistry and Quality in Coastal Areas of China

This Special Issue includes 10 papers related to groundwater chemistry and quality in the coastal areas of China from the south to the northeast. Hainan Island, located at the most southern point of China and adjacent to the South China Sea, is a well-known center for tropical agricultural production, but its groundwater quality has received little attention for a long time. In this Special Issue, Liu et al. (contribution 1) paid attention to groundwater quality in a typical coastal area dominated by agriculture on Hainan Island. In order to investigate the occurrence of fluoride in the western coastal area of Hainan Island and discuss factors affecting groundwater  $F^-$  contamination in various aquifers and areas with different land-use types, the authors collected a total of 100 groundwater

samples in porous and fissured aquifers from this coastal area of Hainan Island in 2022 and analyzed 20 parameters including pH, dissolved oxygen (DO), oxidation-reduction potential (ORP), total dissolved solids (TDSs), bicarbonate, chloride, sulfate, nitrate, nitrite, fluoride, potassium, sodium, calcium, magnesium, arsenic, selenium, aluminum, barium, manganese, and strontium in water samples. Specifically, they depicted the spatial distribution of groundwater fluoride concentrations in this coastal area of Hainan Island using the inverse distance weighting method. They revealed that high levels of fluoride in porous groundwater are mainly attributed to the leaching of fluoride/aluminum-containing minerals such as phlogopite and calcite in the vadose zone using principal component analysis (PCA) and hierarchical cluster analysis (HCA). As a result, the authors recommend that the use of fluoride-containing fertilizers in the study area should be limited to prevent an increase in high-fluoride groundwater. This study is the first time to reveal the co-impacts of anthropogenic and geogenic factors on the occurrence of high-fluoride groundwater in coastal areas dominated by agriculture on Hainan Island. In addition, a recent publication pointed out that nitrate was another major groundwater contaminant in coastal areas dominated by agriculture on Hainan Island [14]. Therefore, in coastal areas of Hainan Island, preventing groundwater contamination of fluoride and nitrate is a major groundwater quality issue.

The PRD is a large-scale urbanized area, also adjacent to the South China Sea and located in the Guangdong Province of South China. Unlike Hainan Island, groundwater chemistry and quality in the PRD has received a lot of attention. During the past two decades, we investigated the characteristics of groundwater chemistry in granular, fissured, and karst aquifers of the PRD at a regional scale [13]. We also put forward contamination patterns of heavy metal(loid)s and organic contaminants in the shallow groundwater of the PRD [10], revealed the origins and driving mechanisms of iodide-rich, iron-rich, and aluminum-rich groundwater in the PRD [8,15,16], and investigated the distribution and origins of groundwater phosphate contamination in the PRD [17]. In addition, Hou et al. reported the origins and driving mechanisms of elevated manganese concentrations in shallow groundwater in the PRD [18]. Zhang et al. investigated the distributions and origins of nitrate, nitrite, and ammonium in various aquifers in the PRD [19]. Zhang et al. evaluated the shallow groundwater quality in granular, fissured, and karst aquifers of the PRD using a fuzzy synthetic evaluation method and discussed the driving forces controlling groundwater quality in these aquifers [5]. However, knowledge of the influence of large-scale land use conversion on groundwater chemistry and quality in this coastal alluvial aquifer is still limited, though shallow groundwater in the coastal alluvial aquifer is an important source of water supply in the PRD. Considering this, in this Special Issue, Liu et al. (contribution 2) investigated the impact of land use on hydrogeochemical characteristics and groundwater quality in a coastal alluvial aquifer of the PRD. They collected a total of 149 groundwater samples at once and analyzed 19 physicochemical parameters. Specifically, 75 samples, 46 samples, 25 samples, and 3 samples were collected from urban areas, peri-urban areas, agricultural areas, as well as the remaining area, respectively. They found that groundwater chemistry in this coastal alluvial aquifer was dominated by Ca-HCO<sub>3</sub> and Ca·Na-HCO<sub>3</sub> facies. They also used the fuzzy synthetic evaluation method with the groundwater quality standards of China to assess groundwater quality in this coastal alluvial aquifer and reported that the occurrence of poor-quality groundwater in urban and agricultural areas was more regular than that in peri-urban areas. In addition, they revealed that groundwater chemistry and quality in this coastal alluvial aquifer of the PRD were mainly controlled by five factors via the PCA. Therefore, they recommend many useful suggestions according to these factors to protect groundwater quality in this coastal alluvial aquifer of the PRD.

On the other hand, we assessed the natural background levels (NBLs) of many contaminants such as arsenic, manganese, nitrate, and chloride in the shallow groundwater of the PRD in recent studies via developing a new preselection method, which consists of the chloride/bromide mass ratio versus chloride concentration, the oxidation capacity,

and Grubbs' test [9,11]. However, knowledge of the NBLs of two other important contaminants (e.g., iodide and ammonium) in the groundwater of the PRD is still limited, though the contamination of these two contaminants was widely distributed in the shallow groundwater of the PRD. Therefore, in this Special Issue, Pei et al. (contribution 3) evaluated the NBLs of these two contaminants in shallow groundwater of the PRD via the method established by us and discussed the main factors controlling the NBLs of these two contaminants in groundwater to enhance the knowledge on groundwater NBLs in the PRD. The authors compared the variation in groundwater iodide and ammonium concentrations in areas with different land-use types in original and residual datasets to verify the effectiveness of the used method for assessing the groundwater NBLs of iodide and ammonium in the PRD. They found that NBLs of iodide and ammonium in shallow groundwater of the coastal alluvial aquifer were more than twice those in the other three groundwater units. They revealed the driving forces for controlling higher NBLs of iodide and ammonium in groundwater of the coastal alluvial aquifer compared with other groundwater units via the combination of hydrogeological data, land use data, and the PCA with hydrochemical data.

Fujian Province is located in the southeast of China and is adjacent to the East China Sea. Similar to Hainan Island, groundwater chemistry and quality in Fujian Province has received little attention because of its sufficient surface water resources in comparison with poorer groundwater resources. In this Special Issue, Li et al. (contribution 4) investigated the hydrochemical characteristics of groundwater in a coastal city (Xiamen) of Fujian Province and analyzed its anthropogenic impacts via statistical analysis methods, such as the Mahalanobis distance. Moreover, they compared the current status of hydrochemical characteristics in groundwater in Xiamen City to the historic hydrochemical characteristics of 1993 and found that six new groundwater contaminants, including nitrate, lead, ammonium, aluminum, nitrite, and copper, had increased during the past two decades, and the number of hydrochemical facies in groundwater rose from 19 to 28, such as the occurrence of  $\text{NO}_3$  facies and the increase in Cl and  $\text{SO}_4$  facies. In addition, the authors highlighted that the Mahalanobis distance method is useful for identifying hydrogeochemical anomalies and determining the intensity of anthropogenic influences on groundwater at regional scales.

The Yangtze River Delta (YRD) is also a large-scale urbanized area and is adjacent to the East China Sea. Unlike the PRD, many concerns over groundwater chemistry and quality in the YRD still remain unclear. In this Special Issue, Chen et al. (contribution 5) investigated the hydrochemical characteristics of groundwater in a pilot promoter region of the YRD (southeast of the Taihu Lake) and used the absolute principal component score-multiple linear regression (APCS-MLR) model to evaluate the groundwater quality in this area. Briefly, the authors collected groundwater samples from 84 sampling sites in June 2020/2021 and analyzed 16 hydrochemical parameters, including pH, DO, TDS, chloride, sulfate, nitrate, nitrite, ammonium, potassium, sodium, calcium, magnesium, manganese, total phosphorus, iodine, and antimony, in these samples. They used the PCA to identify the potential natural and anthropogenic factors impacting groundwater quality. In addition, they used the APCS-MLR model to quantify the contribution of factors for groundwater quality in the pilot promoter region of the YRD. They highlighted that groundwater quality in this region is mainly contaminated by industrial effluent and agricultural activities rather than domestic sewage.

Hebei Province is located in the east of China and is adjacent to the Bohai Sea. Similar to the PRD, groundwater chemistry and quality in Hebei Province has received a lot of attention because of the importance of groundwater resources for water supply in this area. Meanwhile, this Special Issue has four papers related to groundwater chemistry and quality in Hebei Province. For example, Qian et al. (contribution 6) investigated the current status of hydrogeochemical characteristics and groundwater quality in the Hebei Plain because of the strong impact of human activities on groundwater in this area. They collected a total of 54 groundwater samples, including 35 shallow and 19 deep samples,

from the Piedmont Plain to the littoral plain and analyzed 31 hydrochemical parameters in these water samples. They found that the quality of deep groundwater was better than the shallow samples according to the fuzzy synthetic evaluation method and suggested that deep groundwater is more suitable for drinking purposes in comparison with shallow groundwater in the Hebei Plain. They revealed the factors controlling groundwater quality using PCA and pointed out that shallow groundwater quality is mainly controlled by five factors, including the water–rock interaction, marine geogenic sources, agricultural pollution, acidification, and the reductive environment, while deep groundwater quality is mainly controlled by three factors, including the water–rock interaction and redox processes, agricultural pollution, and the input of external water. Furthermore, Qian et al. (contribution 7) also investigated the distribution and origins of groundwater total hardness (TH) in various sub-plains and different land-use areas of the Hebei Plain on the basis of analyzing 445 groundwater samples because the current status of TH-rich groundwater in the Hebei Plain is still unclear. They found that TH-rich shallow groundwater is mainly distributed in central and littoral plains rather than the Piedmont Plain, while TH-rich deep groundwater mainly occurs in the central plain. They also found that TH-rich groundwater in agricultural areas in the central plain is higher than that in rural areas, but this is the opposite case in the littoral plain. In addition, the authors revealed the driving factors controlling TH-rich groundwater in both central and littoral plains using the PCA and Gibbs diagram. According to these driving factors, the authors recommended restricting the use of nitrogenous fertilizers to limit groundwater hardness concentrations in the Hebei Plain. Unlike the above two papers, which focus on groundwater chemistry and quality in Hebei Plain at regional scales, Yuan et al. (contribution 8) investigated the distribution of groundwater chemistry and quality in a drinking water area (Hutuo River) of the Piedmont Plain in the Hebei Plain at a site scale with a sampling density of more than 60 groundwater samples/100 km<sup>2</sup> because knowledge on groundwater chemistry and quality at different scales is often distinct. The authors reported that groundwater chemistry in the Hutuo River drinking water area is mainly controlled by the water–rock interaction. They assessed groundwater quality using the entropy-weighted water quality index and pointed out that approximately 99.4% of groundwater samples in the Hutuo River drinking water area are suitable for drinking purposes. This indicates that groundwater quality in the Hutuo River drinking water area is better than that in the entire Hebei Plain. In addition, unlike the above three papers, which focus on groundwater chemistry and quality in the Hebei Plain, Gao et al. (contribution 9) focused on groundwater chemistry and quality in the hilly area of Hebei Province. They investigated the hydrochemical characteristics of groundwater (dominated by karst aquifers) in the Heilongdong Spring Basin in the Taihang Mountain of Hebei Province using two batches of samples (2013 and 2019). They revealed that groundwater nitrate and chloride contamination occurred in runoff and discharge areas in the Heilongdong Spring Basin because of domestic sewage leakage and agricultural activities.

Heilongjiang Province is located in the northeast of China and is near the Japan Sea. Similar to Hebei Province, groundwater chemistry and quality in Heilongjiang Province has also received a lot of attention because it includes many large-scale plains (e.g., Songnen Plain, Muling–Xingkai Plain) with abundant groundwater resources. In this Special Issue, Su et al. (contribution 10) focused on groundwater chemistry in the Muling–Xingkai Plain of Heilongjiang Province. They investigated the characteristics and evolution of groundwater chemistry in the Muling–Xingkai Plain by analyzing 164 groundwater samples collected in 2016–2018. They found that groundwater chemistry in this area is mainly controlled by the dissolution of silicate and carbonate minerals and the infiltration of domestic sewage, and the latter is mainly responsible for the elevated nitrate, chloride, and sulfate concentrations found in shallow groundwater. Thus, they recommended that deep groundwater below 80 m in this area is suitable for water supply.

## 2.2. Groundwater Chemistry and Quality in Coastal Areas of Pakistan

Sindh is located in the south of Pakistan and is adjacent to the Arabian Sea. In this Special Issue, Landar et al. (contribution 11) focused on groundwater quality in Sindh and evaluated the groundwater quality in the Sanghar district of Sindh by collecting 74 groundwater samples and analyzing 26 chemical parameters in these samples. The authors found that six contaminants, including chromium, lead, nickel, cadmium, arsenic, and fluoride, in groundwater samples in the Sanghar district exceeded the allowable limits recommended by the World Health Organization (WHO). They used the water quality index to assess groundwater quality and found that approximately 77% of groundwater samples had excellent-to-good water quality. They also reported that about 89% of groundwater samples with a low contamination index (<3) of cadmium were suitable for drinking purposes. Moreover, the authors assessed the human health risk of groundwater by calculating chronic daily intake indices (CDIs) and hazard quotient indices (HQIs) and found that only CDI values of lead in a few groundwater samples were above one, and HQ values of lead and cadmium in some groundwater samples were unsafe for human health, while others were safe. In addition, they also used other methods, such as the sodium adsorption ratio (SAR), to assess groundwater quality for irrigation purposes.

## 2.3. Groundwater Chemistry and Quality in Coastal Areas of Egypt

The West Nile Delta (WND) is located in the northwest of Egypt and is adjacent to the Mediterranean Sea. In this Special Issue, Hasan et al. (contribution 12) focused on groundwater chemistry and quality in the WND using integrated statistical and graphical techniques. They collected 75 groundwater samples from quaternary aquifers in the WND in 2018 and analyzed 16 chemical parameters in water samples. They used the HCA to divide groundwater samples into four groups and revealed that groundwater chemistry in two groups located to the north of the study area near the Mediterranean Sea was mainly controlled by the evaporation process, seawater intrusion, and ion exchange. They also pointed out that groundwater chemistry in the other two groups, relatively far from the Mediterranean Sea, was mainly affected by the weathering of silicate minerals and the dissolution of carbonate minerals. In addition, they highlighted saltwater intrusion in this coastal aquifer.

## 3. Conclusions

This editorial introduces the foundation of the current Special Issue, *Groundwater Chemistry and Quality in Coastal Aquifers*, which briefly reviewed recent research advances in groundwater chemistry and quality in coastal areas and summarizes the main contribution of published papers in this Special Issue. Specifically, this Special Issue reported the status and factors controlling regional groundwater chemistry and quality in eight coastal areas related to three countries, including China, Pakistan, and Egypt. Most papers in this Special Issue used some multivariate statistical techniques, such as PCA and HCA, to enhance their understanding of the factors controlling groundwater chemistry and quality, and only a few papers used some relatively new methods such as the APCS-MLR model. Most of them revealed that agricultural contamination is a main anthropogenic factor influencing groundwater chemistry and quality in coastal areas, especially in areas dominated by agriculture. The infiltration of domestic sewage and industrial wastewater is another major anthropogenic factor affecting groundwater chemistry and quality in coastal urbanized areas, such as the PRD and YRD. Nitrate contamination and seawater intrusion are also two widespread issues regarding groundwater quality in coastal areas regardless of organic contamination. Therefore, in the future, we should focus on the treatment of nitrate contamination and seawater intrusion in the groundwater of coastal areas. New statistical techniques should be adopted and used to enhance the knowledge of groundwater chemistry and quality in coastal aquifers. Organic contaminants in groundwater in coastal areas, especially in coastal urbanized areas, should not be ignored.



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