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ORIGINAL ARTICLE

Assessment of metal accumulation in *Otolithes ruber* and presentation of zoning map of the northern coasts of the Persian Gulf

Mehdi BIBAK*[1], Mohammad FOROUHAR VAJARGAH[2], Fatemeh ABBASI[3], Amin OUJIFARD[4]

[1]Department of Fisheries and Marine Sciences, Persian Gulf Research Institute, Persian Gulf University, Bushehr, Iran.
[2]Department of Fisheries, Faculty of Natural Resources, University of Guilan, Sowmeh Sara, Iran.
[3]Department of Fisheries, Faculty of Fisheries and Environment, Gorgan University of Agricultural Sciences and Natural Resources, Gorgan, Iran.
[4]Department of Fisheries, Faculty of Nano and Bio Science and Technology, Persian Gulf University, Bushehr, Iran.

Correspondence
mbibak@pgu.ac.ir

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Abstract
In this study, pollution zoning was mapped across all coastal areas of the Persian Gulf for three elements: seawater, sediments, and the Tigertooth croaker (*Otolithes ruber*). Four sampling regions were designated along the coast, from which 80 seawater samples, 80 sediment samples, and 40 fish samples were collected. In the present study, Inverse Distance Weighting (IDW) was used to map variations in heavy metals across different stations through spatial analysis using ArcGIS 10.7. To measure the levels of metals in the samples, Inductively Coupled Plasma Mass Spectrometry (ICP-MS) was employed. Results indicated that, in seawater, the concentrations of nickel (Ni), vanadium (V), and lead (Pb) decrease from the western to the eastern coasts. Similar results were observed for these metals in the sediments. This study is the first to produce a pollution map of the Persian Gulf coast, considering both sediment and seawater parameters. It is hoped that this method, or other modeling techniques, will replace traditional pollution detection methods in future research. This study could also pave the way for the development of other zoning models.

Keywords: Persian Gulf, Heavy metal, Tigertooth croaker, Arc GIS

INTRODUCTION

In recent years, industry has grown rapidly, and this has increased the exploitation of natural resources and environmental pollution (Gautam et al. 2016; He et al. 2005). Sewage as well as industrial and agricultural wastes are full of toxic substances such as acids, pesticides, plastics, petrochemicals, dyes, etc., which cause severe pollution and this has caused the death of various aquatic animals (Ke et al. 2016; Bibak et al. 2018; Bibak et al. 2020).

Heavy metals that are introduced into the marine environment by industries and other pollutant sources often flow into marine food chain and ultimate destination is human consumption (Tchounwou et al. 2012; Ural et al. 2012; Norouzi 2020). Some metals are necessary for human biological processes at a limit amount more than this amount would be very dangerous for human health. According to a study by Kim et al. (2019), heavy metals are among the main causes of occurring cancer in humans. The soluble forms of these metals in seawater can enter the food chain. According to the international research reports on cancer, the metals chromium, cadmium, and arsenic are the main causes of cancer (Leung et al. 2014; Kim et al. 2019).

Heavy metal pollution in the Persian Gulf is a major environmental issue. Studies indicate significant levels of metals such as nickel, lead, copper, zinc, and cadmium in the regions sediments and waters. Main sources of this contamination include industrial activities, oil extraction, and the discharge of agricultural and industrial wastewater. Additionally, desalination plants in certain areas contribute to elevated heavy metal concentrations, posing a serious threat to marine ecosystems. (Bibak et al. 2018). The use of pesticides, insecticides, and chemical fertilizers in agricultural lands can also be a secondary source of metal pollution in nature. On the other hand, natural factors such as volcanoes, floods, weathering, etc. increase the entry of metals (Herawati et al. 2000; Tchounwou et al. 2012; Masindi Muedi 2019). Heavy metals enter the human body through various ways such as: consuming contaminated food, contact with human skin, and drinking contaminated water (Walker et al. 2012; Peng et al. 2015). When heavy metals enter the human body in any way, they accumulate in the body as dangerous substances. As expected, bioaccumulation in the body causes biological and physiological effects. Various factors are involved in the level of toxicity of metals, which can be referred to the nature of the metal, the biological role of the metal, and how long the organisms are exposed to this metal. On the other hand, the level of toxicity may be different in different organisms (Zhan et al. 2019; Zhang et al. 2020).

In general, pollution deposited within sediments is more serious and dangerous for humans and the ecosystem. Therefore, it can be said that the management of contaminated sediment is a very serious issure (Sharifinia et al. 2018).

Sediment deposits all materials from land inputs as well as autogenic materials from oceans and seas and can record any environmental changes. This characteristic of sediments has made it possible to use it as an indicator to determine the evolution of metal pollution (Ziyaadini et al. 2017; Sattari et al. 2020; Bibak et al. 2021; Bibak et al. 2023).

Some studies have come to the conclusion that the interaction of natural and human forces has a great impact on the entire environment (Sattari et al. 2020; Bibak et al. 2021). A large part of the pollution that enters the coastal environment is transferred to the lower sediments. On the other hand, sediments can be considered as an archive of the marine environment and it can easily report what metals have entered the coastal environment. The concentration of elements and metals in sediments is higher compared to adjoining and interstitial waters (Ke et al. 2015; Keshavarzi et al. 2018). Very useful information, such as identifying areas with different pollution, can be obtained from sediment analysis. The introduction of pollution into sediments by humans is done in two ways: direct and indirect: Direct entry is usually through the entry of sewage, petroleum, transportation, and chemical industries, and indirect entry is usually done through the atmosphere and runoff as a carrier to the marine environment (Łuczyńska et al. 2018; Sattari et al. 2020). Sediments are assumed to be important reservoirs for various pollutants such as metals. Many researchers use sediments and seawater as important and sensitive geographic indicators for environmental pollution (Mirza et al. 2019; Ranjbar et al. 2020).

In addition to water and sediments as a fixed indicator of pollution, fish was also used as an indicator of mobile pollution (Damir et al. 2024). Fish is one of the indicators of pollution, especially for heavy metals. This issue becomes more important because? is widely used as human food. *Otolithes ruber* was used in this study. *O. ruber* is one of the fishes with commercial value in Iranian fisheries. This fish plays an important role in the fishing economy in southern Iran and is usually caught by trawl nets, gill nets, and hooks (Sepahi et al. 2023).

Geographic information is essential in studying pollution because it provides spatial context that helps identify the sources, spread, and concentration of contaminants in different areas. By mapping pollutants, researchers can track patterns over time, analyze the impact on nearby communities and ecosystems, and identify high-risk areas needing remediation. Geographic information systems (GIS) enable detailed analysis of environmental factors, making it possible to develop targeted strategies for pollution control, policy-making, and public health initiatives (Markus 2011). In addition to being a tool in environmental modeling, geographic information system is also used as a tool to support sustainable development goals. Environmental analyzes of coastal areas include a wide variety of techniques, the purpose of which is to determine pollution and qualitative assessment of the coast, and environmental modeling. A large amount of environmental data from each region is collected in environmental modeling as well as estimation and diagnosis of different sources of pollution in marine environments (Masindi & Muedi 2018). One of the spatial planning tools is zoning. This tool is taken from the concepts developed in land use planning. This tool can separate land with different uses or it can be used to protect sensitive and environmentally valuable areas.

Classification of areas in terms of suitability for

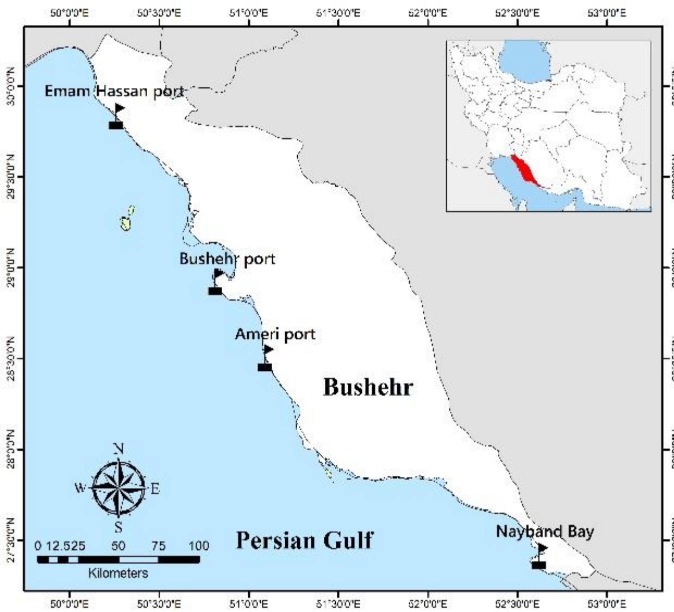


Fig.1. Sampling areas.

each use is another application of zoning. In recent years, marine or ocean zoning has been a very important part of marine management (Kearney & Fisher 2017). Zoning becomes increasingly important as the number of large-scale marine protected areas (MPAs) increases dramatically. Nowadays, this tool is widely used in marine management and marine or ocean zoning. The aim of this study is to develop a distribution map of heavy metal pollution along the northern coast of the Persian Gulf.

MATERIALS AND METHODS

In order to classify coast in terms of heavy metal pollution, nationwide biological monitoring was conducted in the northern coasts of the Persian Gulf. 700 km of the Persian Gulf coast was monitored using four sampling areas. Emam Hassan Port (29.8373°N, 50.2643° E), Bushehr Port (28.9145°N, 50.8279°E), Ameri Port (28.5058° N, 51.0984° E) and Nayband Bay (32.48°N, 57.43°E) were the sampling stations of this study (Fig. 1).

The sampling locations in this study were in special conditions, the Emam Hassan Port in the west of the coast, despite the presence of oil refineries and the passage of ships throughout the year, was expected to have more pollution than other sampling areas. The zoning of pollution in sediments and seawater showed that this theory was correct to a large extent. The sampling area of Bushehr Port, due to the large fishing and commercial ports, the proximity to residential and industrial towns, and the entry of domestic and industrial sewage were inevitable in this place. This area was located almost in the middle part of the west coast.

There were more agricultural lands and fishing ports in the Ameri Port than in other regions, and this region was located in the middle part of the coasts. Nayband Bay, which was located in the eastern part of the coast, was one of the protected areas on the coast of the Persian Gulf, which also showed less pollution.

Sampling was done seasonally in all stations under investigation. 80 seawater samples and 80 sediment samples (20 samples per station) were collected. The samples were transferred to the laboratory of the Persian Gulf University in Bushehr for testing. To dry the samples, 50g of sediments were poured into a Petri dish and placed in an oven at 105°C for 24h. To reduce the temperature of the samples taken out of the oven after 24h, they were placed in a dryer.

Due to the fact that metals are associated with fine sediment grains and these grains increase metal absorption due to their larger area and greater ion exchange capacity, fine sediment grains were also used to measure metals in this study. For this purpose, a 63 micron sieve was used to size sediment grains (Adam et al. 2022).

1g of sieved sediments was weighed and transferred to a test tube. 65% nitric acid (8 ml) and perchloric acid (2ml) were added to each sample. Then the samples were placed at 40°C for 24 h and then digested at 140°C. From Whatman 42 filter paper, the samples were filtered and poured into a 25mm Falcon tube and the volume was reached with double distilled water. Sampling of seawater was done from a distance of about 100 meters from the coast. The water depth at the sampling site was 2.5 meters and the samples were taken from 40 cm of the water surface. The sampling containers used in water sampling were polyethylene. To digest water samples, 65% nitric acid (5mm) and 30% hydrogen peroxide (2mm) were added to 20mm of seawater.

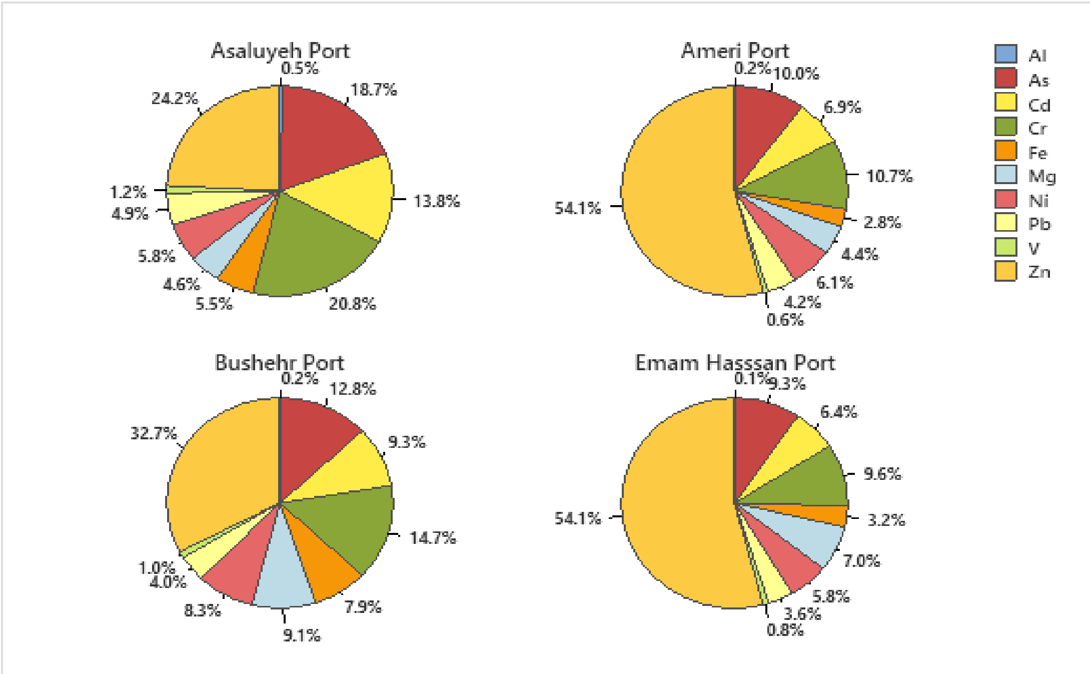


Fig.2. Investigation of the pollution of each area based on the studied metals in the liver of *O. ruber* (In this study, Asaluyeh port was used instead of Nayband Bay for fishing).

The *O. ruber* was caught from all sampling areas except Nayband Bay. Asalouyeh Port replaced Nayband Bay for fishing. 10 fish were harvested in each region and 40 fish were caught. The fish were transferred to the laboratory in a cool box at a temperature of 4°C. After transporting the fish to the laboratory, they were washed with double distilled water. Liver tissue was used to analyze the amount of heavy metals in this fish. After separating the liver tissue, the fish were kept at 80°C for 18 hours to dry completely. Then, 0.5g of tissue was separated and digested with 10ml of 65% nitric acid. Then it was passed through Whatman filter paper 40 and the desired volume was reached with double distilled water. Inductively coupled plasma mass spectrometry (ICP-MS, Agilent series 4500, HP) was used to check the amount of metals in the samples collected in this study. The detection limit of this device is as follows: Al (0.01mg/l), As (0.1µg/l), Cd (0.1µg/l), Cr (1µg/l), Fe (0.1mg/l), Mg (0.01mg/l), Ni (0.1µg/l), Pb (0.1µg/l), V (1µg/l) and Zn (0.01µg/l).

The measurement of each metal is repeated three times for quality assurance (QA). CRM-OREAS was used for quality control (QC) of results and equipment calibration. In the present study, Inverse Distance Weighting (IDW) was done for zoning the changes of heavy metals investigated in different stations in spatial analysis with the help of Arc GIS 10.7. Also, Minitab 21 software was used to draw graphs, and SPSS 24 was used for data analysis. Due to the movement and migration of fish along the Persian Gulf, it was not possible to draw a pollution map for them. For these maps, seawater and sediment pollution indicators were used.

RESULTS

Investigation of pollution in *O. ruber*: The amount of metals in the liver tissue in each region can be seen in Figure 2.

The evaluation of the most important heavy metals in this study showed that the amount of V and Pb in liver tissue was higher in Emam Hassan Port than in other areas, and the highest amount of nickel was also determined in Bushehr Port. Of course, it should be noted that there was no significant difference regarding nickel metal between the three regions (Emam Hassan, Bushehr, and Ameri). Due to the presence of oil resources and the presence of large fishing and commercial ports, it showed more contamination in the liver tissue of Emam Hassan and

Bushehr ports than in other areas.

Coastal heavy metal pollution zoning: The zoning of the northern coasts of the Persian Gulf was also done in terms of the amount of metal pollution in samples of both seawater and sediments.

Coastal zoning based on the seawater: Figure 3 shows that the amount of Al metal in seawater increases from the west side of the coast to the east side of the coast . According to the zoning of seawater in Nayband Bay, the amount of As was lower than other areas. Other areas showed different pollution .The highest amount of Cd contamination was located on the western coast of the Persian Gulf, and the contamination was usually much lower on the eastern coast. The amount of Cr increased in the eastern part in the summer and autumn seasons and decreased in the winter and spring seasons. In general, the western part of the coast was less polluted than the eastern part. During the year, the highest amount of Fe was observed in the western part of the coast, and the eastern part had the lowest amount of accumulation. Examination of all seasons showed that Mg metal was always present in the western coasts, although it was observed in some seasons in the middle part, in the eastern part of the coasts, it was observed at a minimal level throughout the year.Ni metal showed a different presentation, although it was uniformly present in all sampling areas in spring and summer, with an average amount, in two seasons and autumn and winter, it was observed more in the western part. The distribution of Pb metal along the coasts throughout the year showed a behavior similar to that of Ni metal. The amount of V was decreasing from the west to the east coast of the Persian Gulf. Dispersion of Zn metal on the coast was recorded as well as V dispersal.

Coast zoning based on the sediment: The amount of Al in the sediments was higher in the western part than in the eastern part of the coast. The amount of As was much higher in the western part of the coast than in the eastern part of the coast. Cd also registered an increase and accumulation trend from the western to the eastern part of the coast (Fig. 4). The highest accumulation of Cr was in the western part of the coast, from the western part towards the middle part, the amount of accumulation decreases and it reaches the minimum in the eastern part. The amount of Fe was different in different seasons in the western and middle coasts, but it was at a minimum in the eastern part throughout the year. The amount of Mg varied from high to moderate throughout the year in the western and middle areas of the coast, but it was at its minimum level in the eastern part of the coast in all seasons (Fig. 4).

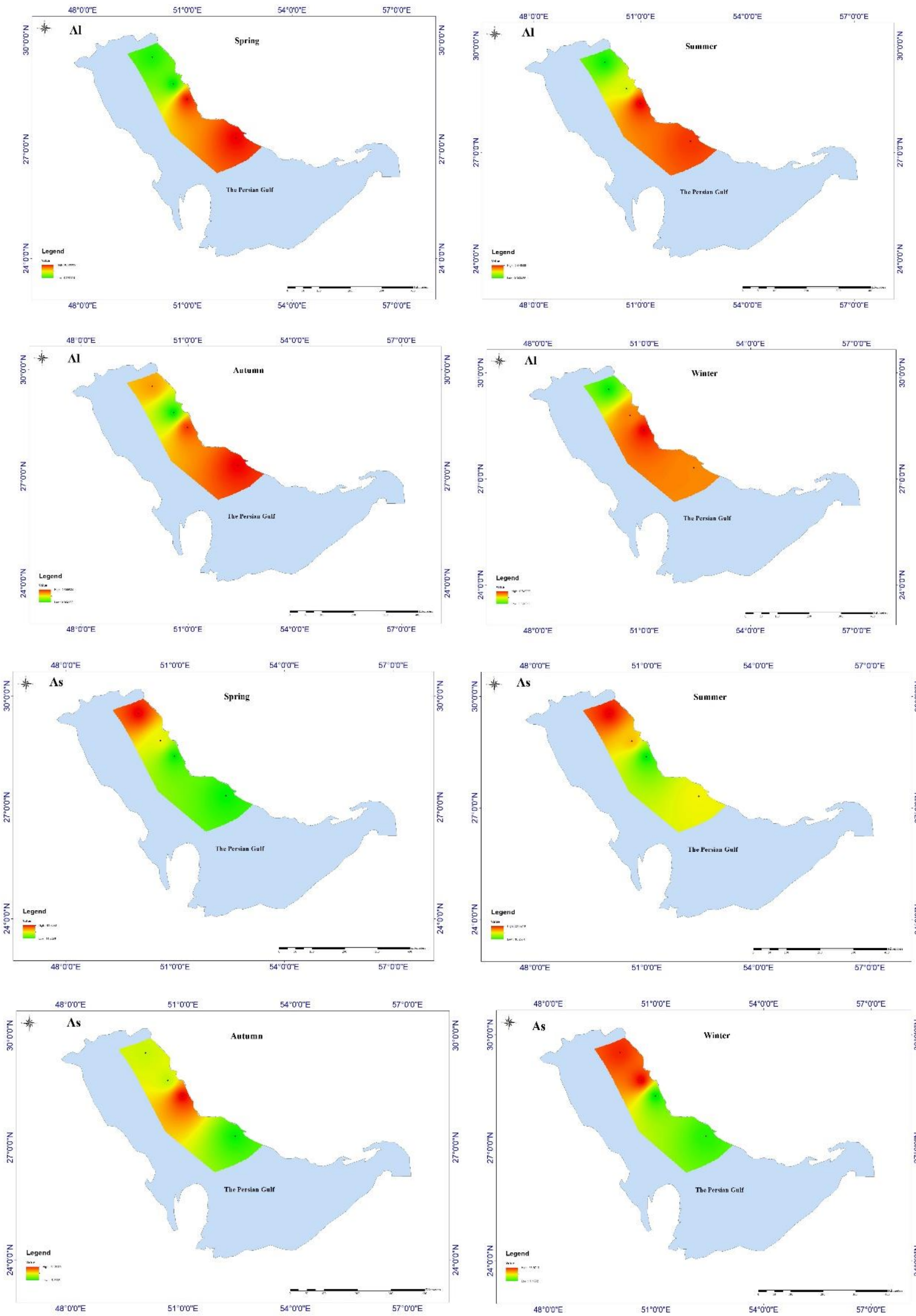
The amount of Ni in the spring and summer seasons was reported to be the highest in the western parts compared to the middle part of the coasts and especially the east coasts. The highest amount of Pb was recorded in the middle part of the coasts, and in the western part, this amount decreased to a moderate level, and in the eastern part, this amount decreased to a minimum. The amount of V in the sediments also showed a higher concentration in the western part of the coast than in the middle and eastern parts of the coast. The distribution of Zn metal in the coasts was also similar to the accumulation of V metal (Fig. 4).

DISCUSSION

Assessment of environmental health, especially in the coastal sector, has been one of the most important concerns of researchers in these years. They have been always seeking to find an index to evaluate these areas as best as possible. The use of marine organisms as indicators to determine the amount of metal accumulation can vary based on the type of organism, their age, and the specific organ being investigated. Therefore, in recent years, the use of sediments as biological indicators has increased.

Heavy metals have the ability of bioaccumulation with high stability in nature and high toxicity which cause it a destructive pollutant in environment (Li et al. 2017; Wang et al., 2018; Li et al. 2020). Their occurrence in seawater causes the accumulation of these metals in the food web, and threat to human health (Mirza et al. 2019; Fdez-Ortiz et al. 2019).

Usually, bays, as a place where land and sea interact, are greatly affected by human activities (Huang et al. 2015). As examined in this study, the Persian Gulf has also been greatly affected by human activities.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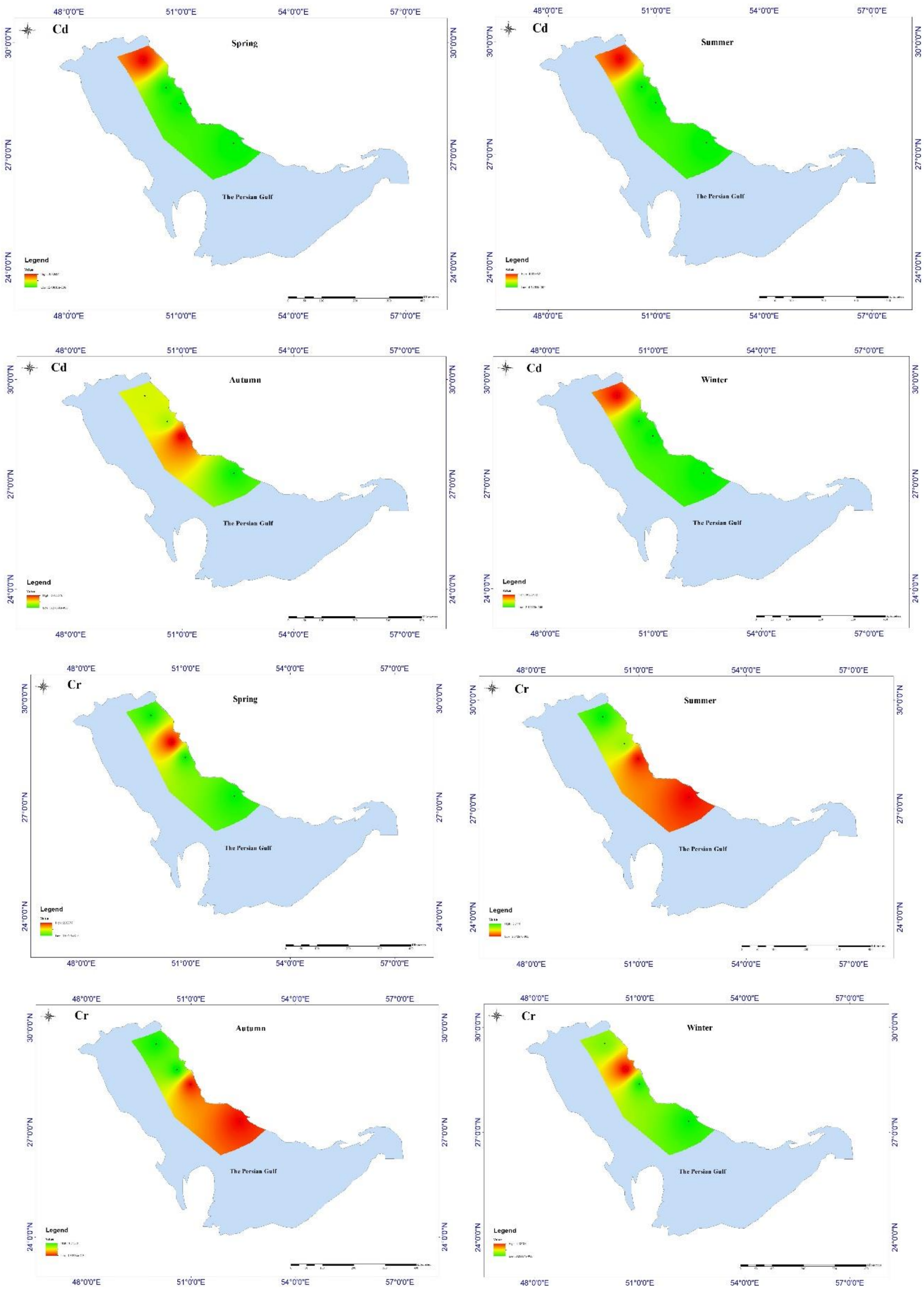
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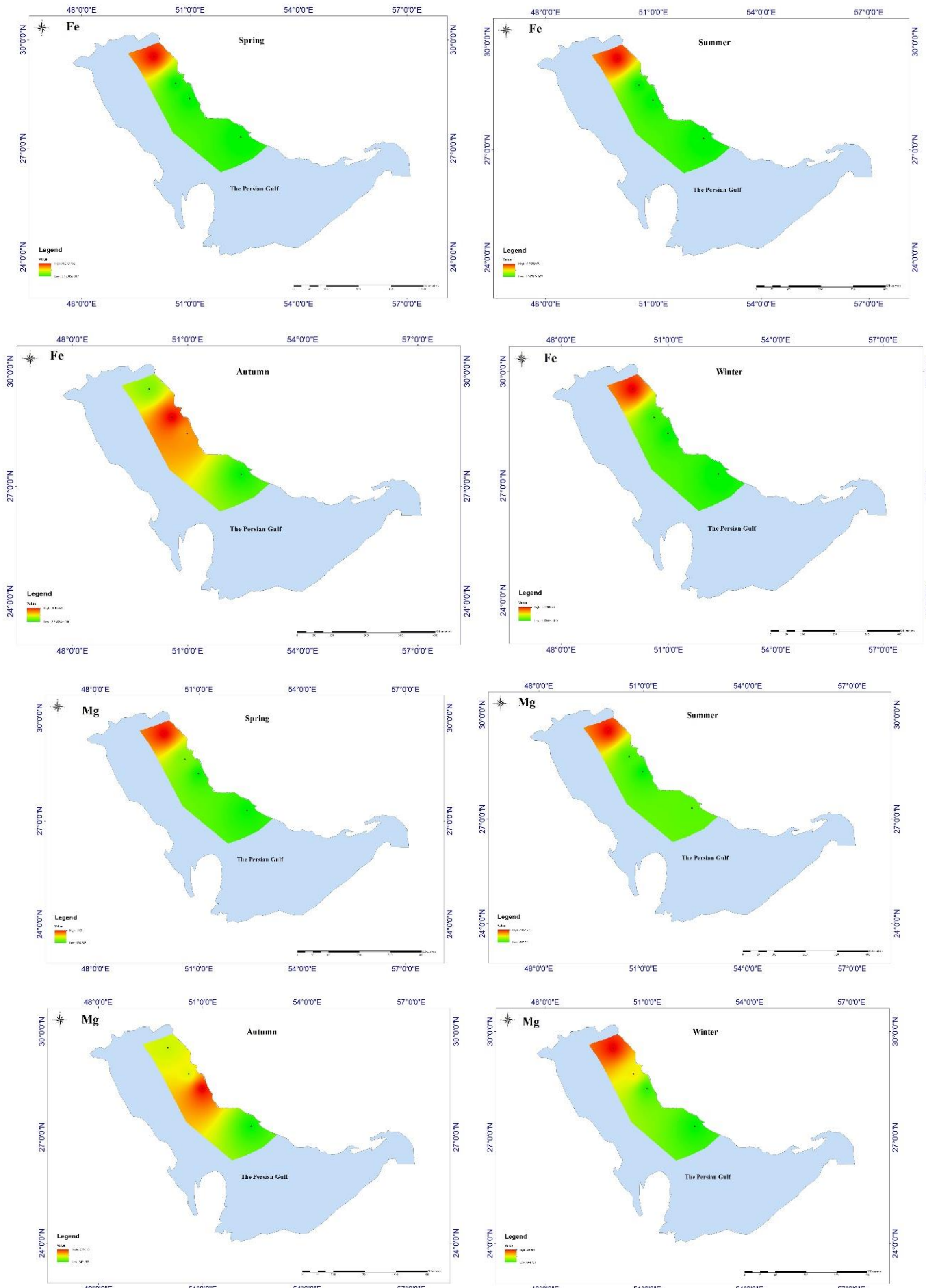
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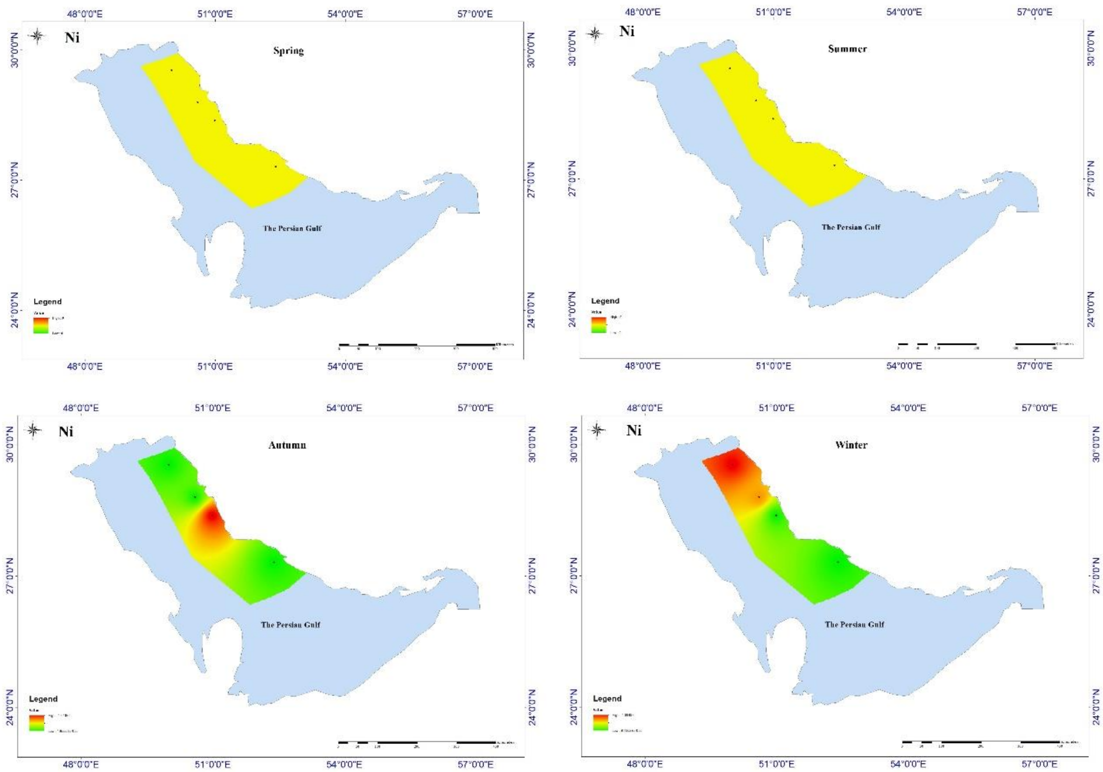
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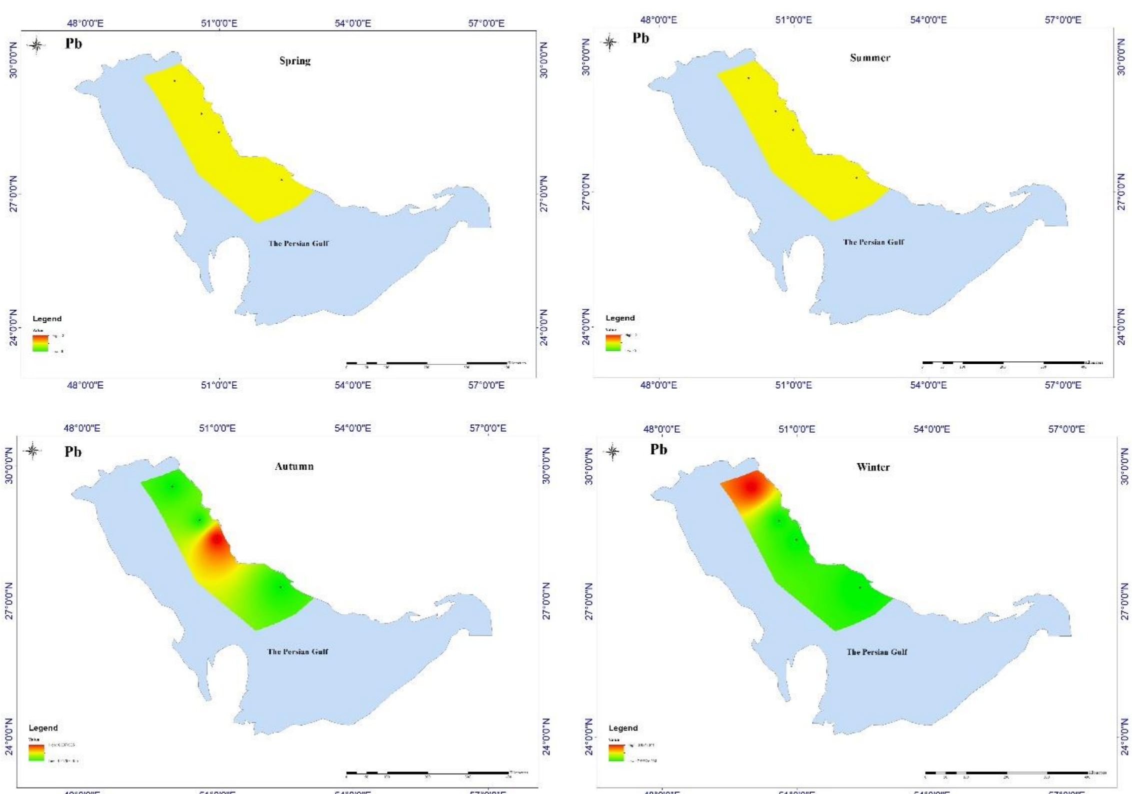
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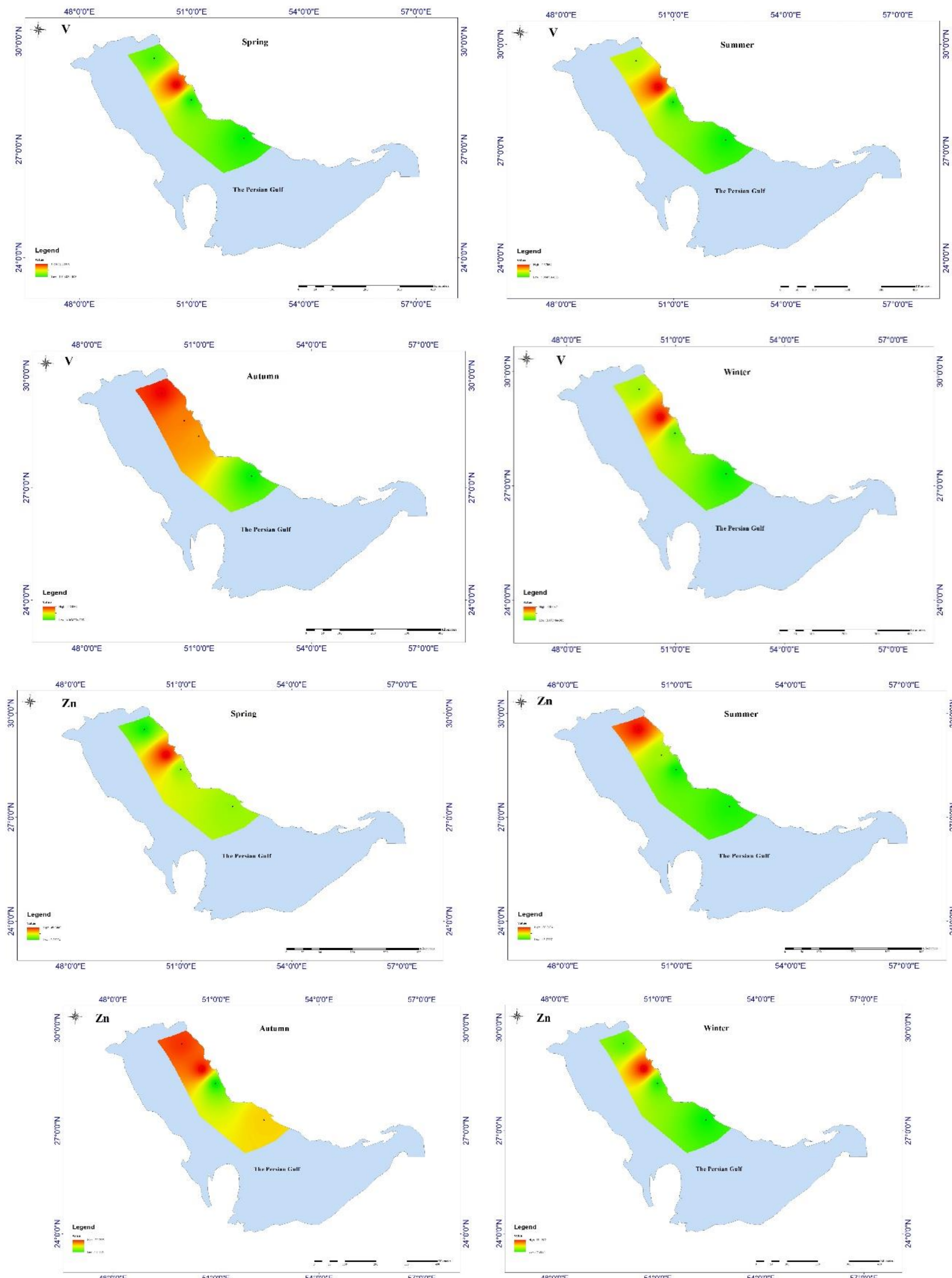
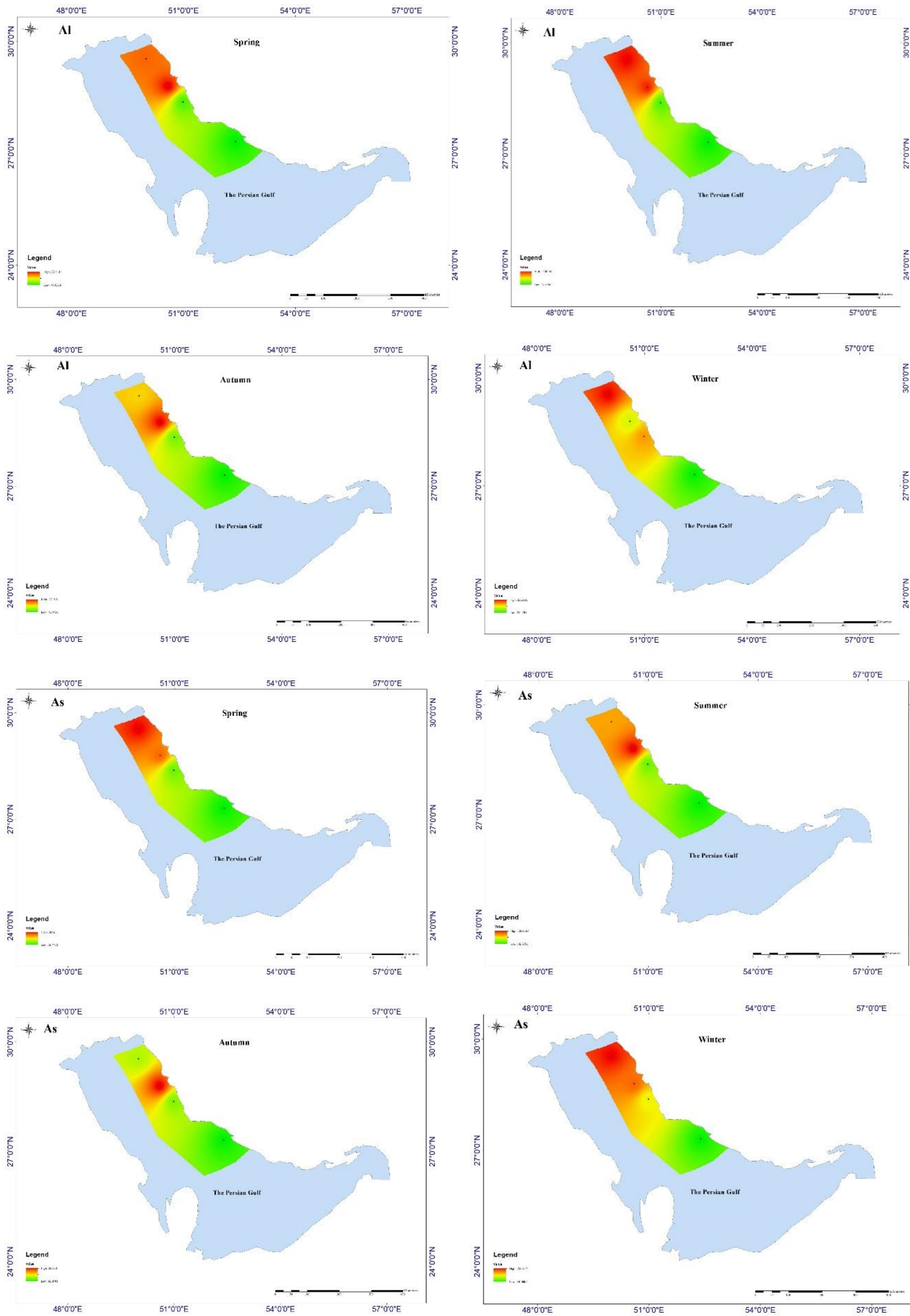


Fig.3. Pollution zoning based on the amount of metals in seawater.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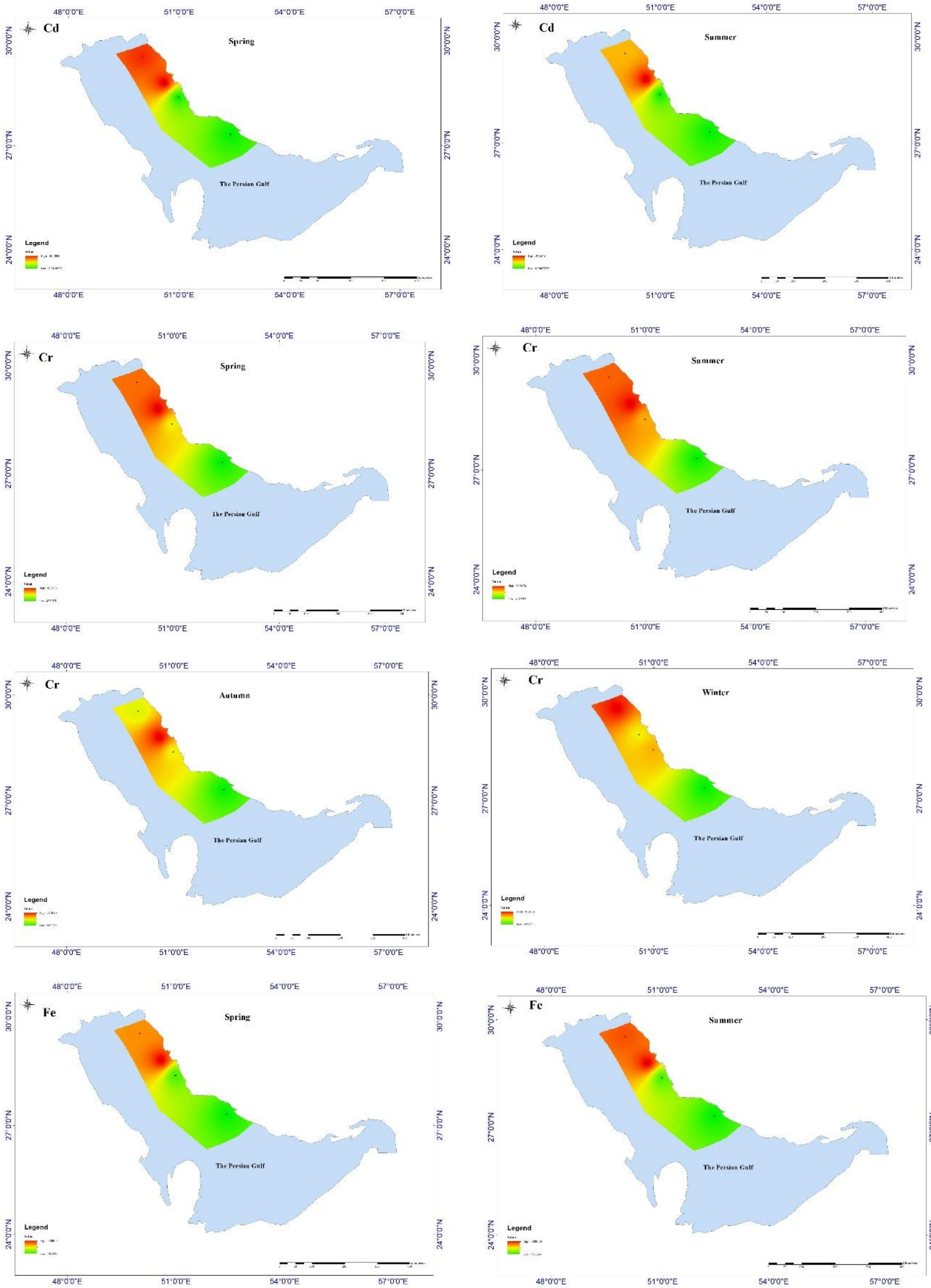
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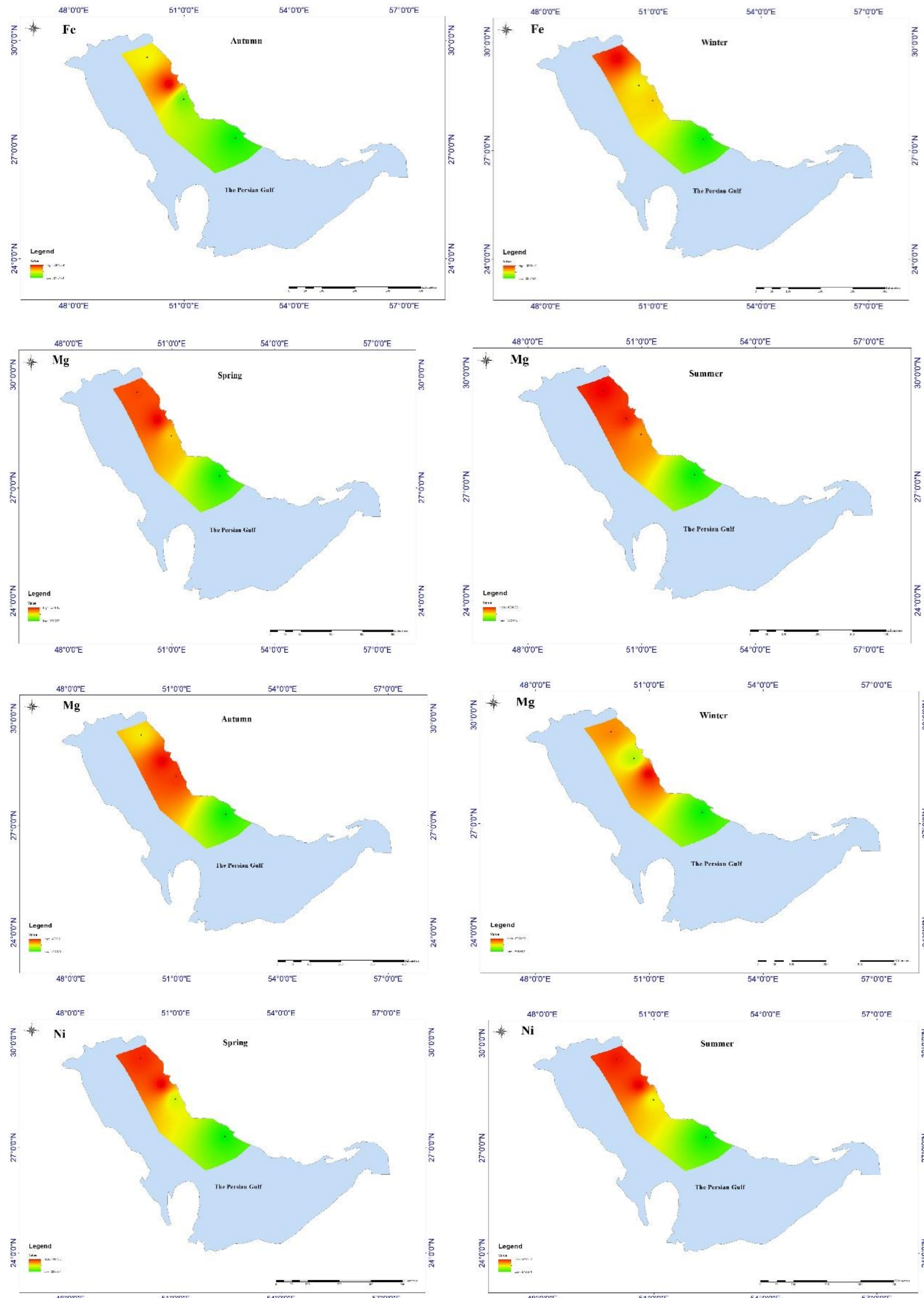

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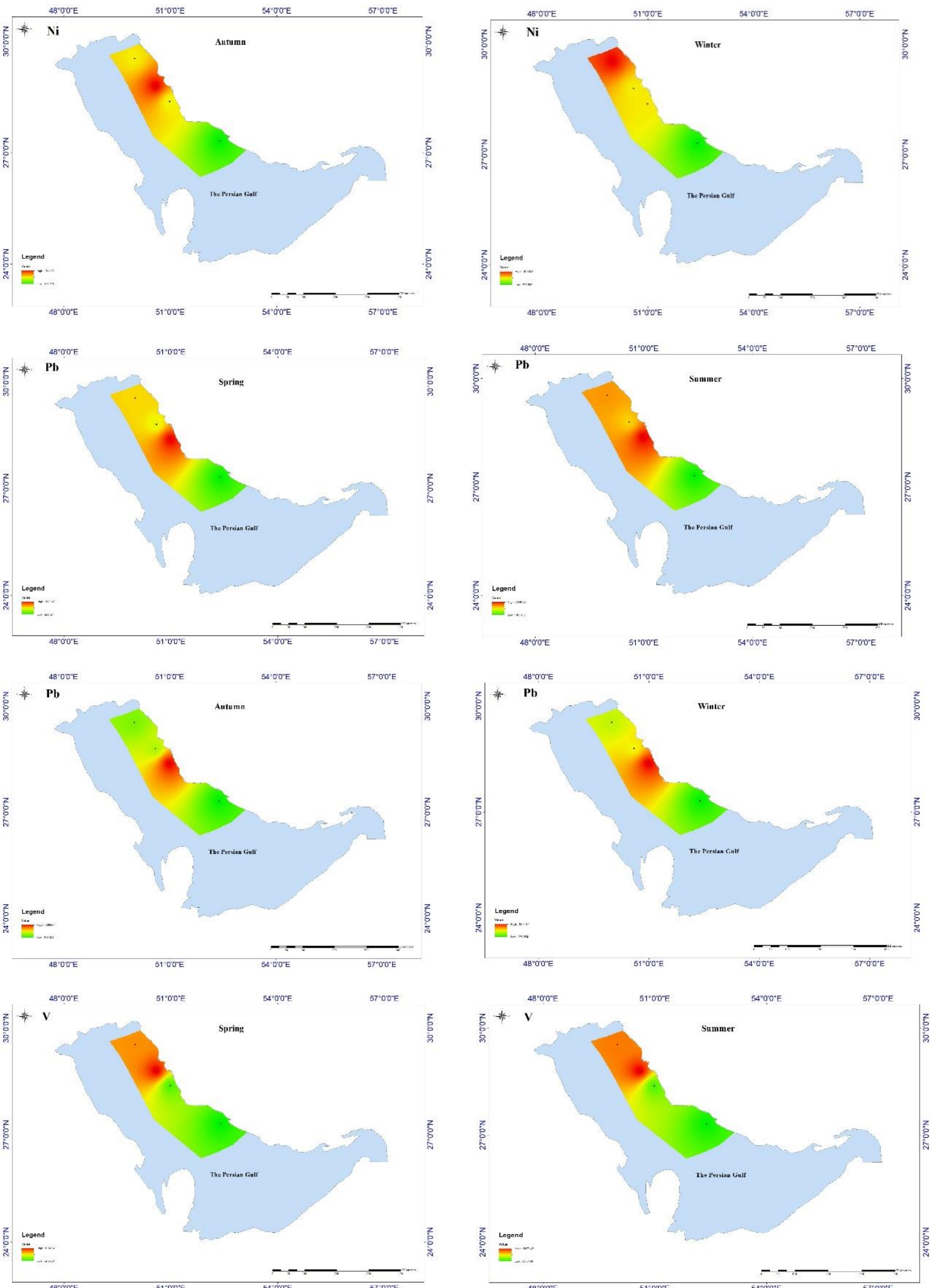
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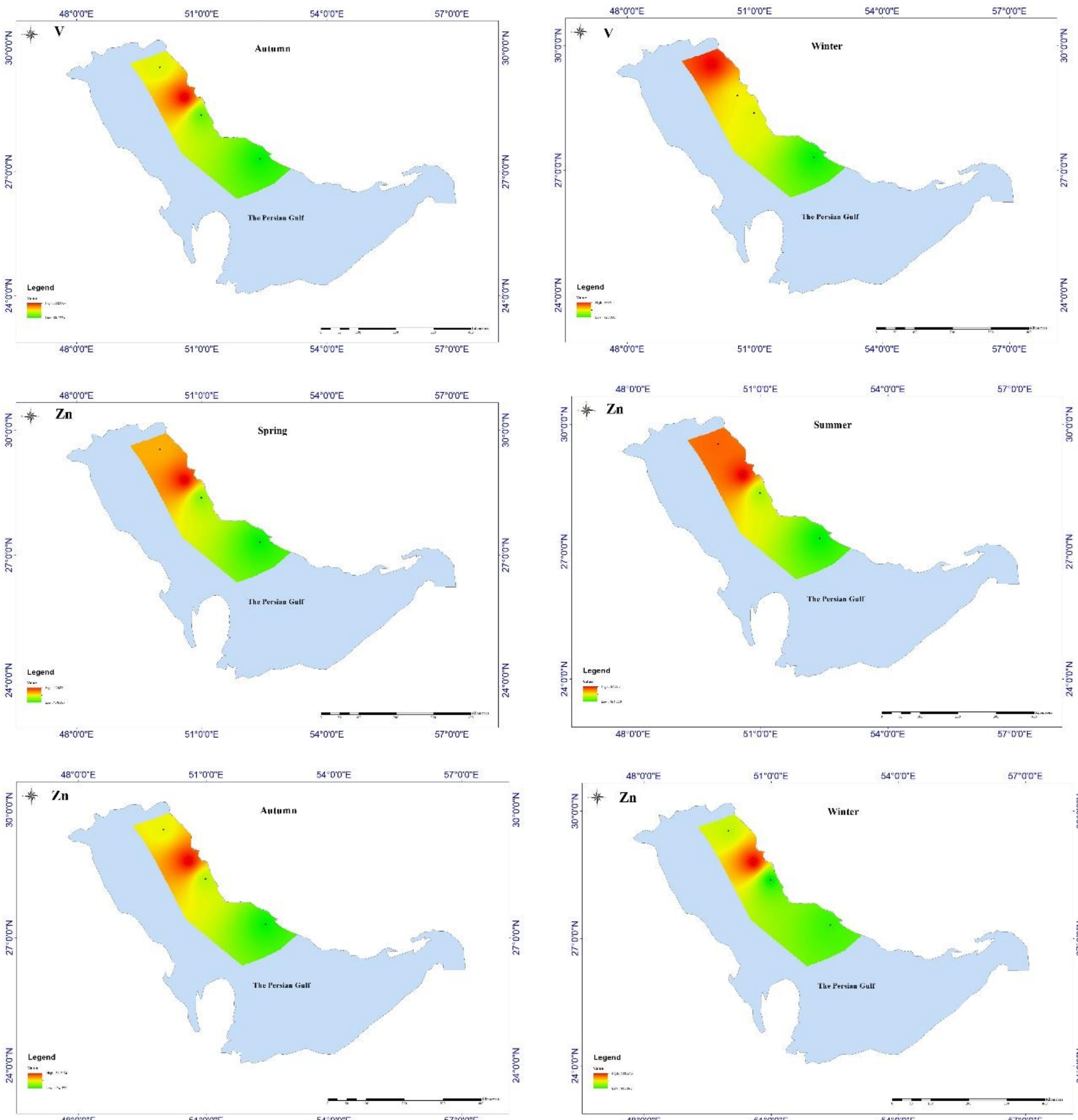

Fig.4. Pollution zoning based on the amount of metals in sediments.

The constant exchange of energy and matter in the seawater column as well as the inevitable changes in the physical and chemical conditions of seawater affect the concentration of metals (Chen et al. 2019).

Coastal zoning plays an important role in pollution management because it allows for better control and management of pollution sources by classifying coastal areas based on different characteristics (such as pollution levels, sediment types, and various coastal uses). Coastal zoning helps manage human activities, monitor water quality, and protect sensitive ecosystems more effectively. With appropriate zoning, environmental managers can identify critical points and implement measures to reduce environmental impacts, such as imposing restrictions on industrial and agricultural activities in sensitive areas or creating protected zones. These measures help minimize pollution from sources like oil, chemicals, and heavy metals, and support the restoration of the coastal environment. Another benefit of zoning is the ability to monitor and track pollution sources. By properly dividing coastal areas, potential sources of pollution can be identified within each zone, and the spread of pollution can be prevented through preventive measures (UNEP 2023).

This integration of environmental events over time makes sediments useful for obtaining spatial and temporal information (Birch 2007; Birch et al. 2008a; Birch et al. 2008b). Sediments can be considered as a wide habitat for storing pollutants, therefore it has a wide impact on the living organisms of coastal areas. Sediments can affect the quality of the water column in different ways. Ways such as resuspension, diffusion from the floor, reabsorption, etc. Most of the metals are absorbed by the fine grains of sediments, so sediments play a large role in transporting pollutants in the water column.

Therefore, it can be stated that sediments are very effective on the feeding of aquatic animals in the deep sea and pelagic areas, as well as on their habitats. The quality and pollution of sediments greatly affect the biodiversity of the coast, the quality of the surrounding water, and the survival of aquatic life (Forstner & Calmano,1998). Elements and metals are greatly affected by the water environment. The constant exchange of energy and materials in the seawater column as well as the inevitable changes in the physical and chemical conditions of seawater affect the concentration of metals.

The zoning of coast was done in two parts of seawater and sediments in this study. The analysis of the obtained data showed that there is a correlation between the elements between seawater and sediment in the three metals Al and Cd. This correlation was negative in Al metal (-0.899) and this correlation was positive in Cd metal (0.709). Other elements also did not show a correlation between seawater and sediments.

In recent years, it is possible to refer to the study of Bibak et al. (2018) and Bibak et al. (2021), who examined and evaluated the Persian Gulf coasts in terms of environmental pollution, especially heavy metals and trace elements, three years apart to be able to depict the process of pollution changes in the coasts. Allami et al. (2020) also investigated the amount of heavy metals in the sediments of the Persian Gulf coast and investigated potential environmental risks. But so far, the zoning of Persian Gulf coasts has not been investigated in terms of metal pollution.
Drawing a pollution zoning map on the northern coasts of the Persian Gulf can depict the distribution of pollution throughout the coasts. Very few studies have been done on coast zonation, which can be mentioned: Forouhar Vajargah & Bibak (2022), who mapped the pollution zonation of the southern shores of the Caspian Sea using *Rutilus kutum* muscle tissue. And also another study such as Abdollahi et al. (2020), who investigated the level of internal river pollution using zoning.

CONCLUSION

The use of GIS software (interpolation of data (IDW)) in coastal pollution research is not usual. Therefore, this software was used for zoning the environmental contamination of Persian Gulf coasts. The obtained results were very useful. Using this software, it is possible to analyze a large amount of data obtained from sediments and seawater easily for management decisions, especially the management of coastal pollution. It can be said that no practical research has been done in the field of zoning on the coasts of the Persian Gulf. Therefore, it can be stated that the present study can pave the way for the development of other zoning models.

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مقاله کامل

ارزیابی میزان تجمع آلودگی فلزات سنگین در *Otolithes ruber* و ترسیم پهنه‌بندی آلودگی سواحل شمالی خلیج فارس

مهدی بی‌باک*[۱]، محمد فروهر واجارگاه[۲]، فاطمه عباسی[۳]، امین اوجی فرد[۴]

[۱]گروه شیلات و زیست شناسی دریا، پژوهشکده خلیج فارس، دانشگاه خلیج فارس، بوشهر، ایران.
[۲]گروه شیلات، دانشکده منابع طبیعی، دانشگاه گیلان، صومعه سرا، ایران.
[۳]گروه شیلات، دانشکده شیلات و محیط‌زیست، دانشگاه کشاورزی و منابع طبیعی گرگان، گرگان ایران.
[۴]گروه شیلات، دانشکده علوم و فناوری نانو و زیستی، دانشگاه خلیج فارس، بوشهر، ایران.

چکیده: در این تحقیق پهنه‌بندی آلودگی در تمامی سواحل خلیج فارس در ۳ بخش شامل آب دریا، رسوبات و ماهی شوریده (*Otolithes ruber*) ترسیم شد. چهار منطقه نمونه‌برداری در سراسر سواحل تعیین شد. ۸۰ نمونه آب دریا ، ۸۰ نمونه رسوب و ۴۰ نمونه ماهی جمع‌آوری شد. در مطالعه حاضر، وزن‌دهی معکوس فاصله (IDW) برای پهنه‌بندی تغییرات فلزات سنگین مورد بررسی در ایستگاه‌های مختلف در تحلیل فضایی با کمک Arc GIS 10.7 انجام شد. در این مطالعه برای سنجش میزان فلزات در آیتم‌های نمونه‌برداری از از طیف‌سنجی جرمی پلاسمای جفت القایی (ICP-MS) استفاده شد. نتایج نشان داد که در آب دریا میزان فلزات نیکل (Ni)، وانادیوم (V) و سرب (Pb) از غرب سواحل به‌سمت شرق سواحل کاهش پیدا می‌کند. نتایج مشابهی نیز در مورد همین فلزات در رسوبات مشاهده گردید. این مطالعه برای اولین بار نقشه آلودگی سواحل خلیج فارس را با دو آیتم رسوب و آب دریا ترسیم کرد و امید است در تحقیقات آتی این روش یا سایر روش‌های مدل‌سازی جایگزین روش‌های قدیمی شناسایی آلودگی شود. مطالعه حاضر می‌تواند راه را برای توسعه سایر مدل‌های پهنه‌بندی هموار کند.

کلمات‌کلیدی: خلیج فارس، فلزات سنگین، ماهی شوریده، Arc GIS