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Escalating Trends of Hydrogen Sulphide (H_2S) and its Role in Structuring Pakistan Coastal Zones Barren

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ABSTRACT

The presence of hydrogen sulfide (H_2S) gas in the muddy ecosystems is consequence of anthropogenic interference. To understand ecosystem health present study was intended to gauge H2S concentrations involved in annihilation of meiofauna and associated aquatic life from four hotspots including Manora channel, Korangi creeks, Sonmiani, and Bhambhore along the Pakistan coastal belt. Using a handheld gas detector device, it was observed that Bhambhore exhibited lower levels of H_2S therefore embraces numerous benthic organisms whereas Manora channel (backwater) and Korangi creek area showed elevated level that does not allow macro-organisms to stay around. The diversity varied across locations, with Bhambhore collecting the most species of mudskippers and Manora creeks collecting the rarest. Overall result of this study reveals that H_2S 5~274 ppm is alarming. The data of crabs, mudskippers, fishes, mantis shrimps, shells in relation to the environmental variables of temperature, salinity, conductivity dissolved oxygen and H_2S were used to develop canonical correspondence analysis. The variability among first two components was 64.47 and 28.44%, eigenvalue (0.154, 0.068 and trace 0.239) respectively. Considering baseline findings of this study, greater efforts are required for ecosystem resilience for the sake of human health concerns.

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INTRODUCTION

Hydrogen sulfide (H_2S) is a remarkable compound with a profound impact, it originates from bacterial activity and geothermal processes, making it a common presence in aquatic environments (Beauchamp et al., 1984). It is a passive player can either boost or hinder the metabolic processes of organisms, delicately balancing their functioning (Nicholls and Kim, 1982). However, when H_2S levels rise beyond a certain point due to external sources, it turns toxic (Reiffenstein et al., 1992). Life faces a critical choice when exposed to H_2S's toxic grip - adapt or perish (Tobler et al., 2008). Organisms have evolved diverse strategies for survival. Some, like mobile fish species, have developed early warning systems, detecting elevated H_2S and swiftly moving away from danger zones (Abel et al., 1987; Rossi et al., 2019; Martin and Currie, 2020). Even at low concentrations, such as 20 µg/L, it induces extreme stress in fish populations. This emerging neuromodulator threat acts as a defense mechanism in various organisms, spanning from bacteria to mammals (Habeeb et al., 2018). In contrast, sessile organisms such as bivalves seal themselves off, relying on anaerobic metabolism to endure H_2S exposure (Vismann, 1991). Another remarkable adaptation occurs in certain invertebrates. They form partnerships with sulfur-oxidizing bacteria, which convert H_2S into less harmful

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forms (Dubilier et al., 2001). This symbiotic relationship not only mitigates H_2S toxicity but also showcases nature's intricate web of cooperation. Lastly, some organisms manage H_2S internally, detoxifying it through sulfur oxidation, transforming it into less harmful substances like sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), and thiosulfate ($S_2O_3^{2-}$), which can be safely stored or excreted (Bagarinao, 1992). Marine invertebrates have been extensively studied as H_2S-tolerant animals, shedding light on their remarkable adaptations to sulfidic environments (Tobler et al., 2018). In contrast, our understanding of H_2S tolerance in aquatic vertebrates remains somewhat limited, despite the presence of several fish species in sulfidic-rich habitats. However, there are intriguing examples of fish species around the world that offer valuable insights into their strategies for H_2S tolerance, providing compelling models for the study of adaptations to challenging environments. For instance, in Pakistan's coastal regions, mudskippers, a group of gobies (fish belonging to the family Gobiidae), exhibit unique adaptations to H_2S-rich mangrove habitats (Kachhi et al. 2020). These amphibious fish are known to navigate between aquatic and terrestrial environments, frequently encountering sulfidic substrates during their daily activities. Their ability to thrive in such condition's hints at specialized physiological and behavioral adaptations that allow them to tolerate elevated H_2S levels. Additionally, in Mexican caves, distinct populations of guppies (*Poecilia mexicana*) have independently evolved multiple strategies for H_2S tolerance, setting them apart from closely related non-sulfidic populations (Tobler et al., 2018). This example highlights the dynamic nature of H_2S adaptation in aquatic vertebrates and underscores the importance of further research to unravel the intricacies of these adaptations.

As a pressing concern of coastal zone management, some hotspots along Pakistan coast identified for monitoring H_2S to underline relevance of this issue in a global perspective. Moreover, endurance of macro-organisms inhabiting in muddy habitats and elucidate their intriguing relationship with H_2S were aims of this research.

MATERIALS AND METHODS

Location description

Four hotspots including Korangi creek (Kc), Manora channel (Mc), Sonmiani Bay (Sb), and Bhambhore (Bh) were designed to monitor H_2S gas concentration in winter and summer seasons of 2022. The location of Kc and Mc lie closed to the Karachi metropolis and are heavily polluted by multiple sources, whereas, Sb and Bh locations are somehow far from the Karachi receiving least load of pollutants. Only live macro-organisms including meiofauna and nektons were enumerated and some of them brought to the laboratory for identification.

Sensitivity and efficiency of H_2S monitor

A handy smart sensor intel instruments model Pro-4, ST8900 gas monitor was used during sunny summer days of winter and summer 2022. The muddy bottom of each location was excavated at 1-3 feet deep at three stations of 20-meter distance of each location. To test the efficacy of the gas detector instrument, a motor bike gaseous emission through silencer was tested prior using in the field because it releases carbon monoxide in large quantity. In addition, it was used in kitchen area and bathrooms/washroom to check variable quantities for further satisfaction. This handheld instrument was used for the first time in Pakistan to detect and monitoring H_2S gas in the coastal ecosystems to monitor environment degradation.

An enormous variety of chemical sensing devices has appeared for both in the fields of research as well as commercialization works. Previously there are several authors have exposed the potential of several narrative firm state equipment ranging from metal oxides to polymer composites as active sensing materials (Tobler, et al., 2018). Mostly these sensors work according to demanding operating circumstances at different types of environmental factors,

concentrations which may result in diverse troubles in terms of poor strength, low sensitivity and selectivity (Riesch, et al., 2015). Among the lots of materialistic sensors made up from copper acetate have giving most promising and accurate results in all manors, Copper acetate always reacts with H_2S both in solution as well as in solid state (Volkel and Berenbrink, 2000). Much dangerous areas of industries, including offshore oil and gas platforms, onshore refineries processing plants, pipelines, storage farms and LPG/LNG plants all produce or utilizes a wide range of these detectors.

Multivariate statistical approach

A canonical correspondence analysis (CCA) was used to test the relationship between diversity of the sampled organisms in relation to the environmental variables. It is an ordination of axes practice that determines linear combination of measured predictors in ecological systems.

Environmental variables

In situ environmental parameters of temperature, dissolved oxygen, pH and salinity were recorded with Hydrolab HL-4, USA whereas air temperature, wind direction and speed was recorded with handy wind meter.

RESULTS & DISCUSSION

Present study was conducted to appraise hydrogen sulfide (H_2S) gas presence in four hotspots including Korangi creek (Kc), Manora channel (Mc), Sonmiani Bay (Sb), and Bhambhore (Bh along the costal belt of Pakistan. Significant variation in H_2S intensity, environmental parameters and organism assemblage was noticed in winter and summer season from highly and least polluted zones (Fig. 1). From each location only live macro-organism including mudskippers,

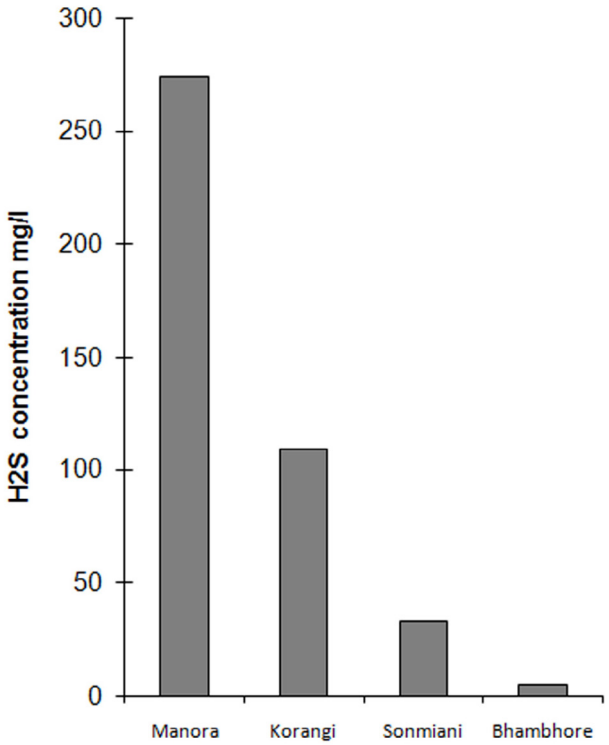

Fig. 1. Concentration of H_2S at most polluted areas due to rampant dischargement of untreated industrials, domestic solid waste, prolonged anchored cargo ships, oil wastes and areas of least polluted along Pakistan coastal belt.

crabs, mantis shrimps, fishes and presence of mangroves were observed (Fig. 2). *In situ* water quality parameters, which were instable (Fig. 3).

The swampy area with scattered mangroves Manora channel area found to be the most polluted site among all surveyed locations. It has been noted that an increase in hydrogen sulfide gas results in a corresponding decrease in dissolved oxygen, implying that H_2S levels are inversely proportional to dissolved oxygen levels. Poor water quality is primarily caused by the discharge of untreated municipal liquid waste, leaking sewage lines, and industrial wastewater directly into the sea.

Environmental variables display tremendous impact on the associates communities abundance and distribution. *In situ* water quality parameters such as dissolved oxygen, salinity, pH, temperature and O_2 were recorded with Hydrolab, HL-4 instruments. The results highlight significant impact on benthic community, as different organisms such as fishes, gastropods, mudskippers, shrimps, and bivalves are dependent on these parameters. In instances where these parameters are negatively impacted, some species, such as crabs, may have to migrate to more favorable environments, while mangrove species can utilize through pneumatophores to balance the intrinsic condition (Fig. 3).

The data of crabs, mudskippers, fishes, mantis shrimps, shells in relation to the environmental variables of temperature, salinity, conductivity and dissolved oxygen were used to develop canonical correspondence analysis. The variability among first two components was 64.47% and 28.44%, eigenvalue (0.154, 0.068 and trace 0.239) respectively. Moreover, crab lie on the

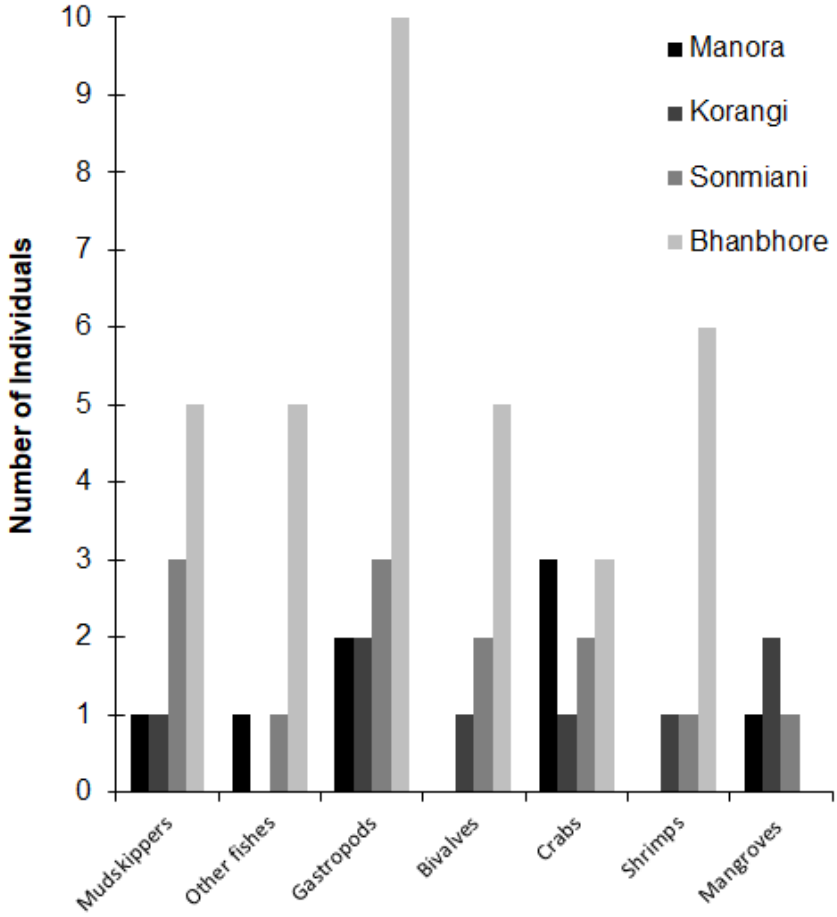

Fig. 2. Number of individuals belonging to animal and plant groups encountered in this study from four hotspots along the coastal belt of Pakistan.

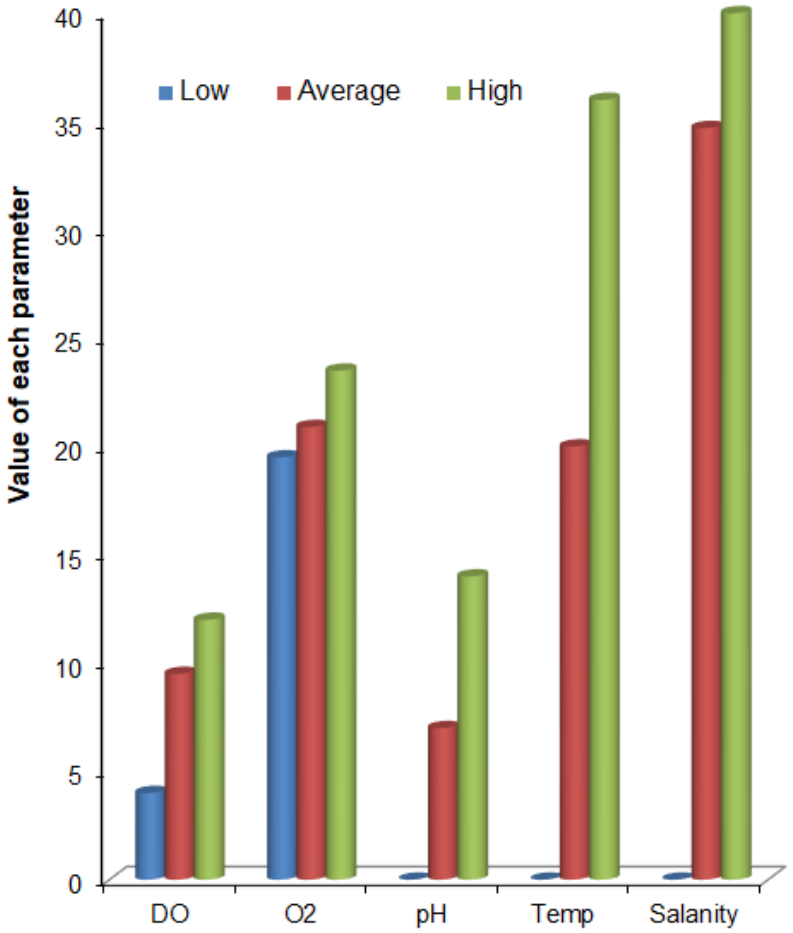

Fig. 3. Summary of environmental and water quality parameters recorded at each sampling locations were categorized as low, high, average and *in situ* using Hydrolab, HL-4, oxygen ~ %, temperature ~ ºC, salinity ~ psu, and dissolved oxygen ~mg/L

right side of the axis I reflects that extreme environmental situation showed minimum harm on the survival while pH showed positive relationship with mangrove plants this may be due to their wider range of tolerance. Nevertheless, dissolved oxygen, salinity, temperature remined trigger in the distribution of shrimps, mudskippers, bivalves, gastropods and fish is interpretable from the bi-plot (Fig. 4).

Keeping in mind coastal zone management, present data not merely highlight growing issue of H_2s that is involved in harming prominent coastal zones but would also help to understand tolerance level of numerous organisms. Mudskippers a kind of amphibious fish, navigates between aquatic and terrestrial environments is of great ecosystem concerns. Their adaptations to this challenging environment are an integral part of our exploration, shedding light on how organisms thrive in the face of adversity. These adaptations to H_2S, akin to chapters in a captivating story, manifest in diverse forms, often shaped by the unique environmental challenges organisms face (Tobler et al., 2008). Frequently, H_2S-tolerant organisms employ multiple adaptations at various levels, from the whole organism down to cellular mechanisms, each contributing to their overall survival (Vismann, 1991). In essence, H_2S is not just an agent of change; it's a catalyst for adaptation, illustrating the interconnectedness of life and how organisms navigate their environments. Its influence extends far beyond scientific fields,

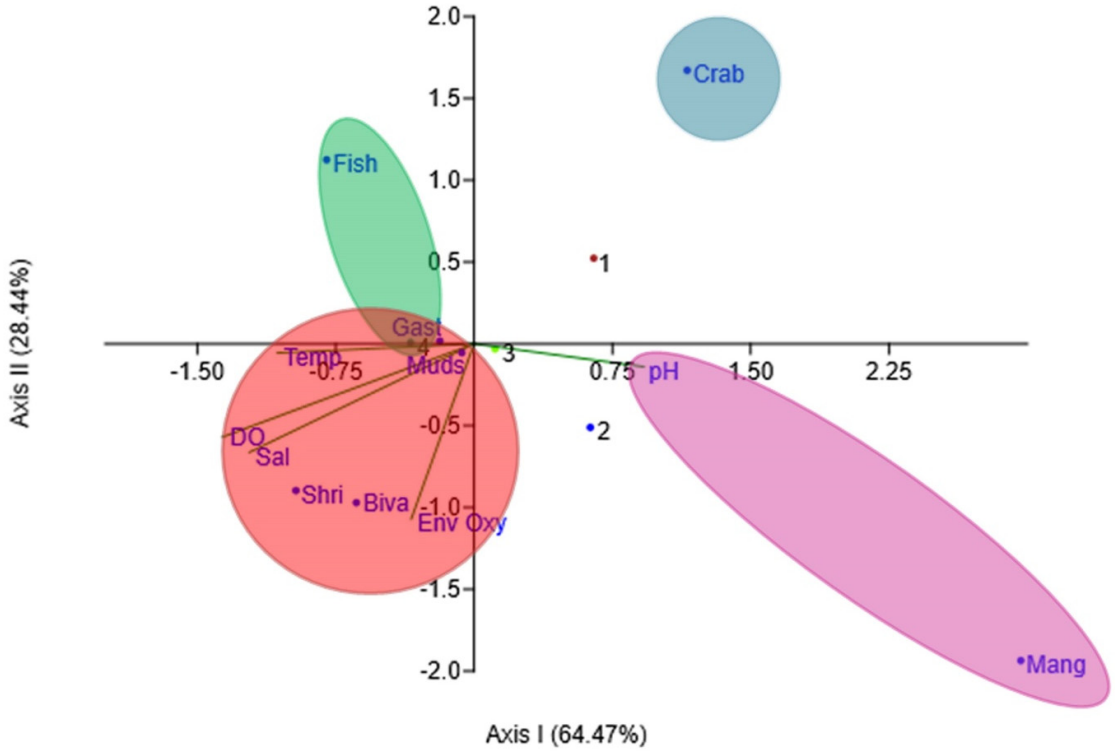

Fig. 4. Canonical corresponding analysis (CCA) performed using environmental variable of temperature, dissolved oxygen (DO), pH and salinity in relation to the species sampled from respective locations.

affecting ecosystems, human health, and industrial processes alike.

The efficiency of gas detectors (sensors) in detecting hydrogen sulfide (H_2S) pollution was validated by testing various locations, including pollution hotspots, less polluted coastal beaches, and mangrove footprints. The study found that areas with high H_2S concentrations had little aquatic life, while areas with low or undetectable H_2S concentrations had numerous aquatic organisms such as mudskippers, crabs, shrimps, bivalve, gastropods, and benthic communities. Hence, the study emphasizes the importance of considering the sources of H_2S pollution, such as drainage water, industrial waste, and ship emissions, in controlling pollution levels and protecting human and environmental health.

The study also examined the efficiency and capabilities of gas detectors in detecting H_2S concentrations in different environments. International public safety organizations have established exposure limits ranging from 1 ppm to 100 ppm to limit the olfactory disturbance caused by natural and industrial production of H_2S and to protect workers from acute and chronic exposure (Colby and Smith, 1967). Humans can smell H_2S at low concentrations (0.5 to 300 ppb), and exposure to high concentrations can cause severe health effects such as nausea (at around 2 ppm), loss of smell (at around 20 ppm), severe lung/nose/throat irritation (at around 100 ppm), and death (at concentrations greater than 250 ppm) (Harbison et al., 2015; Virjim et al. 2006; Sarfraz et al., 2014).

Hydrogen sulfide (H_2S) is a naturally occurring in moist areas, are highly toxic gas that can formed from the rotting of sulfur compounds. H_2S is a common source of existing and metal decomposition that results in huge economic losses in wastewater compilation and treatment plants (Sherief and Hassan, 2022). Pollution and manmade activities have continuously increased H_2S in the wetland and coastal areas have severely threatened benthic communities which are fundamentals key point of an ecosystem. In this study we have determined the rate of H_2S

and status of benthic communities. Moreover, the fluctuation of five water quality parameters have been measured through hydro Lab and categorized in low, average, high and resulted. Hydrogen sulfide occurs obviously in several marine aquatic environments, together with hydrothermal vents, cold seeps, mudflats, and marshes. In each of these environments, diverse communities of animals adapted to the occurrence of H_2S. These physiochemical parameters such as, temperature, dissolved oxygen, salinity, pH, and oxygen were used to establish (CCA) Canonical Correspondence Analysis. Overall, the negative effects of H_2S on human health, plant growth, and marine ecosystems highlight the need for continued research and monitoring of H_2S pollution levels. By understanding the sources and effects of H_2S pollution, we can work towards implementing effective strategies for controlling pollution and protecting the environment and human health.

Moreover, different organism's communities of fishes, gastropods, mudskippers, shrimps, and bivalve are depending on these physiochemical parameters, if these parameters increase or decreases then some of the changing may occurs in benthic community, crabs may frequently migrate from negative to favorable environments, and mangroves species use their pneumatophores to balance these physiochemical parameters. In particular, the presence of H_2S in marine environments has been shown to negatively impact benthic communities. Research has found that areas with high levels of H_2S pollution often have lower levels of species richness and diversity, as well as reduced numbers of key species such as crabs and gastropods. Through continued research and innovation, it may be possible to develop more effective solutions for detecting and mitigating the negative effects of H_2S pollution on marine environments.

CONCLUSIONS

It is concluded that to gauge H_2S levels in least and massive polluted hotspots along Pakistan coastal belt to understand their impact on aquatic life is of great concerns of coastal zone management. The use of handheld gas detector gave in situ data of H2S. The study, provides a comprehensive understanding of the complex relationships between environmental variables and organisms using multivariate approach of CCA. Presence of H_2S gas in considerable amount is an indication deteriorate state of coastal degradation, therefore, management priorities must be set to refrain further damages to the coastal belt. Habitat characteristics and tolerance level of organism against H_2S determined across the locations. Among nektons mudskippers demonstrating higher tolerance level of H_2S gas that is exciting opportunities for further research on the topic. The elevated H_2S levels in Manora creek and its impact on aquatic animals spark concern.

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LIFE SCIENCE REPORTING / COMPLIANCE WITH ETHICAL STANDARDS

No life science threat\ was practiced in this research. This article does not contain any studies with human participants performed by any of the authors.

AVAILABILITY OF DATA AND MATERIAL

The data supporting the findings of this study are available within the article [and/or] its supplementary materials.

AUTHOR CONTRIBUTION

Kishwar Kumar Kachhi performed field and laboratory handling, Najeeb Akhter drafted manuscript, Sher Khan Panhwar designed and supervised research, Imtiaz Kashani participated in laboratory handling and gathered literature.

CONFLICT OF INTEREST

The authors declare that they have NO conflicts of interest.

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