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Review Article

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An overview of persistent organic pollutants along the coastal environment of Kuwait

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Abstract: The oil discovery in the Arab Gulf, and particularly in Kuwait, has led to rapid urbanization, population development, industrialization, and, with it, many problems of oil and nonoil pollution. The rapid growth of the manufacturing sector in Kuwait occurred mainly along its coastal margins. Natural oil sequestration areas have been established and are deemed as critical point pollution sources at different locations along the coast. This has allowed the release of a variety of toxins directly into the marine ecosystem, including petroleum hydrocarbons. The ecotoxicological effects of persistent organic pollutants (POPs) in the aquatic environment have been causing a significant concern. Much work concentrated primarily on hydrocarbon emissions from petroleum/ combustion, with few papers authenticating other target POPs (PCBs, PBDEs, and dioxins). This study aims to reflect past ideas on the production and sources of POPs in the marine environment in Kuwait and their comparison with worldwide outcomes. Much of the literature reviewed reported that while Kuwait's aquatic ecosystem has been exposed to a wide variety of incidents of pollution, overall emission rates remain relatively low. Nonetheless, soil pollution hotspots are also associated with point sources of chemical waste, such as those from the Shuaiba industrial area, in a variety of areas along the coast.

Keywords: POPs, Kuwait, marine environment, Arabian Gulf, Gulf War

1 Introduction

The present scenario in the environment makes a serious attention toward the environmental pollution. Persistent organic pollutants (POPs) are a class of organic compounds, and they have detrimental problems in the environment due to their toxicity [1,2]. Twelve groups of chemicals have much concern, comprising polychlorinated biphenyls (PCBs), polychlorinated dibenzo-p-dioxins and dibenzo-furans (PCDD/Fs), and pesticides such as DDT, chlordane, and heptachloride [3]. In recent years, considerable concern has been generated by the ecotoxicological consequences of POPs in the marine ecosystem, contributing to regulation or total ban of the use of such chemicals in several nations. Thus, POPs are particularly obstinate to chemical and biological degradation and thus live for long periods in the environment [4]. Absorption and inhalation systems in humans are continuously susceptible to environmental POPs [5], and certain contaminants from this group have been detected in the tissues, the blood, the breast milk, and the adipose tissues of human [6,7]. Typically, POPs are considered as lipophilic in nature [8]. They split heavily into solids in aquatic systems and soils, particularly organic matter, thus escaping the aqueous phase. Among the major classes are a number of chlorinated (and brominated) aromatic groups, including PCBs, PCDD/Fs, polybrominated diphenyl ethers (PBDEs), and various organochlorinated pesticides (e.g., DDT and its metabolites, toxaphene, chlordane) [9]. Some are accidental by-products of combustion or other industrial synthesis of chemical compounds not purposely produced (e.g., PCDD/Fs) (e.g., PCBs, chlorinated paraffin, PBDEs) or as agrochemicals (e.g. DDT, Lindane, chlordane). Phenols (e.g., nonionic surfactants, polyethoxylated alkylphenols) and chlorinated phenols are examples of more polar POPs. The Stockholm Convention on POPs is an international environmental agreement with the intent of removing or reducing the production and usage of persistent organic contaminants, signed in 2001 and operational as of May 2004. In May 2006, the state of Kuwait ratified the Stockholm Convention. Kuwait's oil discovery has made

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huge strides in the development of agriculture, industries, and urban areas.

The oil exploration in the Arabian Gulf, and in Kuwait in particular, has resulted in rapid urbanization, population growth, industrialization, and as a result, many oil and nonoil pollution issues [10,11]. Kuwait is located in the northwest part of the Arab (Persian) Gulf and is considered to be one of the largest anthropogenic regions in the world [12]. The territorial waters are marked by small oceans, extreme summer water temperatures (>30°C), severe light sensitivity to ultra violet, and heavy salinity (average 41 ppt) [13,14]. Kuwait Bay, a semi-shallow water body of 750 km², roughly 35 km long with a mean depth of 5 m, is a vital part of its aquatic ecosystem [15]. Major factories are located along the coast in the Gulf States. This covers broad nonoil industries, including power and desalination plants, petrochemical plants, refineries, etc. It resulted in the absorption of a variety of chemical pollutants into coastal marine sediments, including heavy metals, coal and petroleum-related products, minerals, and halogenated organic compounds. To date, several studies performed in Kuwait have concentrated on oil and oil-based contaminants [16-20], in particular, the production of polycyclic aromatic hydrocarbons (PAHs) and metals [18,21,22], in marine sediments. Before now, reports on many types of chronic biologic contaminants have gained relatively little coverage [23]. However, recently, many studies on PCBs and PCDD/Fs, especially in the state of Kuwait [24,25], have been reported. Some attempts were made to rectify this balance by including some of these chemicals in the efforts of national monitoring. These findings are still not open to the broader field of research. This study aims to portray a short review about the distribution and sources of POPs in Kuwait's marine environment and their comparison with the worldwide data.

2 Sources of POPs

The two major known sources of dioxins and dibenzofurans are volcanic activity and fire deforestation. There are plenty of these volcanoes in Central Africa. Any preference can be given to sources or uses that are specific to South and South Africa. Fire, which is both natural and accidental and regulated vegetation burning, is one such trigger [26–29]. They originate from a variety of industrial sources such as power stations, heating systems, incineration plants and domestic furnaces, packing, seed

spray, water surface evaporation, and waste or landfill. [29]. Various accidental growth can be obtained through incinerations, industrial installations, numerous combustions, bushfires, and putrefaction and waste containing PCBs. Some of the POP's primary origins are lakes and rivers, where they collect water sediments, air contamination, waste disposal, and accidents. They are accumulated on the rivers, oceans, and large fields of lakes in sediments from which they can be removed after a while and then restored to the atmosphere [30]. For the past 10 years, a number of POP suppliers have been disrupted due to systemic changes in the region. In addition, a number of new wastewater treatment facilities have been constructed since this period. Occasionally referred to as persistent organic compounds, PAHs are formed by oxidation of organic compounds during burning. Their occurrence is correlated with anthropogenic processes, and in high-density urban environments, PAH pollution of river sediment is extremely significant. The most common persistent pollutants are the chemical structures shown in Figure 1.

The rapid growth of the manufacturing sector in Kuwait has mainly occurred along its coastal margins. This has contributed to the release directly into the aquatic ecosystem of a variety of contaminants [31–33]. It is well known that the Arabian Gulf holds the largest oil reserve in the world. Kuwait and other countries of the Gulf Cooperation Council (GCC) have expanded their production potential to satisfy oil production and manufacturing and transportation needs, resulting in hot spots of coastal erosion and pollution in industrial areas [29]. Incidents such as the 1991 Gulf War have traditionally exacerbated problems relating to the increased industrialization. It is recorded during this period that 9-10.8 million barrels of oil were intentionally leaked into Kuwait's coastal waters by sabotaged tankers and pipelines at the Al-Ahmadi terminal [34,35]. The atmosphere is prone to a range of toxins as a result of the war, including burning pyrolytic petroleum hydrocarbons in the oil field, battle-damaged radioactive waste (such as PCBs and metals), and bombs expended or abandoned [10,18,35,36]. Furthermore, natural oil sequestration zones have been identified and are known to be critical sources of emissions at different locations along the coast [10,18,31,37,38].

Around 20% of the overall crude oil hydrocarbons are PAHs and are the most metabolically toxic of all petroleum compounds [39]. Carbon spillage is a global problem where, as a result of more than 250 accidents, around 32.2 million gallons (1,09,400 tons) of oil are wasted in aquatic and terrestrial habitats worldwide in

1999 for example. PBDEs, like many anthropogenic substances, can penetrate the marine system from a number of sources: (i) direct atmospheric absorption, (ii) soil drainage, and (iii) directly from industrial and wastewater treatment plant discharges [40,41]. Chemicals linked to the industry can reach the atmosphere by releases from several phases of the supply chain; imports of resources; manufacturing and combustion processes; and imports and exports of products. Their potential fate depends on a range of physical, chemical, and biological interactions, including biotic absorption, abiotic degradation, volatilization, and burying of sediments [42,43]. As they are immune to physical, chemical, or biological deterioration, bioaccumulated in the food web [44-46], PCBs are of environmental importance and pose a threat of adverse effects on human health and the ecosystem [4,47,48].

3 Key findings of marine sediment contamination of POPs

3.1 Polyaromatic hydrocarbons

The proliferation of pollutants in the oil field remains comparatively limited, aside from unique events related to the Gulf War. From the years 1988 to 1995, total petroleum hydrocarbon (TPH) concentrations were found to remain relatively stable at a number of locations encompassing the entire Kuwaiti coastline. Although observed values peaked in 1991-1992 (8-22 µg/L), they remained below the background ranges [31,49]. Higher concentrations were reported by Bu-Olayan and Al-Yakoob [50], who observed PAHs (expressed as chrysene equivalents) ranging from 21 to 320 µg/L between 1993 and 1994 over a

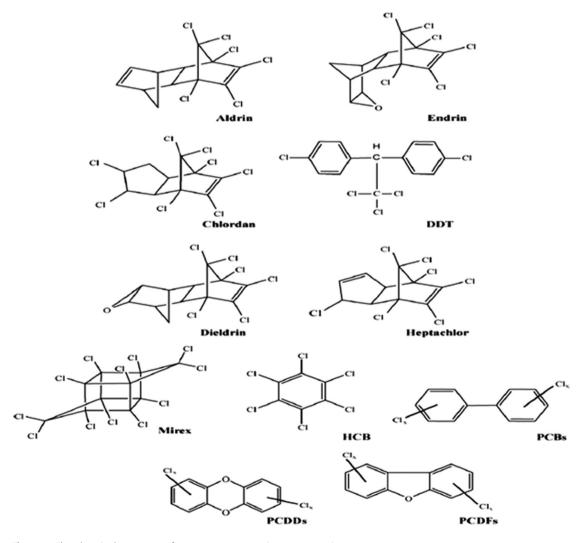


Figure 1: The chemical structure of most common persistent contaminants.

number of locations along the Kuwaiti coast. However, the direct interpretation of this study is problematic due to differences in the locations examined and the methodologies used [10]. Although the literature have predominated research on TPH and metal concentrations, only a few studies to date have concentrated on crude oil fractions including volatile liquid hydrocarbon (VLH). VLH contains hydrocarbon molecules such as benzene, xylenes, and toluene, which can compensate for up to 40% of crude oil components [51]. Information on VHL pollution of seawater is especially important to Kuwait's marine ecosystem because it is established that they co-distilled with drinking water during the desalination cycle [52]. Saeed et al. [51] registered coastal seawater concentrations of VLH within the range of 307-5,017 ng/L, with benzenoids accounting for 65% of the total VLH documented. At Doha and Ras Al-Zor, a study was conducted to analyze the contribution capacity and desalination plants to the observed values [53]. The intake and outflow levels through the Doha power/desalination plant ranged from 307 to 7,811 ng/L, while the volumes of Ras Al Zor in the further south ranged from 465 to 4,652 ng/L. Benzenoids (76-84%) dominated the structure of the VLH, followed by *n*-alkanes (12–22%) and cycloalkanes (2-4%) [53].

The analysis of the total contamination of TPH and PAH sediments across the coast of Kuwait was comprehensive, especially during periods immediately following the 1991 Gulf War [10,18,35,36,54]. Initial research carried out in 1991 found that emissions of TPH and PAH are apparent from the supply of leaking oil up to around 400 km [35]. These concentrations decreased by about 50% in successive surveys performed between 1992 and 1993, with some modest geographic adjustments due to the resumption of the economic activity following the cessation of hostilities [10,35,36,55]. TPH concentrations (range: 40-240 µg/g dw) were small compared to that at polluted sites in Europe and North America [56,57], except at heavily contaminated sites in Al-Bedaa and Az-Zor. Metwally et al. [54] reported the findings of a larger geological survey covering locations inside and around the southern coastline of Kuwait Bay. Related TPH contamination rates were observed at sites near point industrial waste sources around the Shuaiba Industrial Area (SIA) with values ranging from 7 to 15 μ g/g compared to 426–459 μ g/g sediments. In addition to the elevated rates near the SIA, several other locations were considered to contain TPH levels that matched the region's natural background values [54]. Although some information on the rates of chemical exposure has been given, limited work has been conducted to identify the environmental danger faced by these forms of pollutants. In this regard, an attempt to compare TPH concentrations with mortality using a 96 h marine amphipod toxicity test [58] analyzed the environmental threat faced by oil spill-contaminated sediments during 1991 Gulf War [10].

de Mora et al. [59] identified Sulaibikhat Bay (29 µg/g dw chrysene equivalents) as marginally polluted by the implementation of the criteria for TPH sediment pollution suggested by Massoud et al. [38] in the Gulf zone, where standard area background values are assumed to reflect concentrations of <15 µg/g dw chrysene equivalents. de Mora et al. [59] were also able to achieve a quantitative indicator of chronic, degraded oil toxicity at the examined locations by examining the aliphatics of the unresolved complex mixture (UCM). Ras Al Zour and Sulaibikhat Bay also at Doha Bay have reached a historical concentration of 10 µg/g dw. Ironically, further study of the elevated ratio of UCM/n-alkanes found in Ras Al Zour (an oil weathering index) showed a more recent supply of oil compared to other sites surveyed [59]. Complete hydrocarbon content related amounts were reported at concentrations ranging from 4 to 744 µg/g dw from the Kuwait Bay and Mina Abdulla (south of Shuaiba) coastal sites [60].

Sediment contamination levels along the SIA based on a 12.5 km section of the coast of south of Kuwait City have been reported in various studies [61-63]. The total PAHs at the SIA were in the range of 5.65–778.01 µg/kg [61]. The Σ PBDE concentration at the SIA ranged from 80 to 3,800 pg/g [61]. The correspondent Σ PCDD/Fs at the SIA ranged from 0.4 to 284.3 pg/g and 0.2 to 29.2 pg/g [63]. The SIA is estimated to contain more than 51,000 m³/day effluent, 95% of which was directly discharged into the sea [63,64]. In addition to the industrial complex, a variety of contaminants such as PAHs, polychlorinated dibenzo-p dioxins (PCDDs), and PBDEs are known to pollute the marine environment (PBDEs). Lyons et al. [60], in a systematic study of sediment PAH contamination, surveyed 21 locations covering 15 km of the SIA coastline. The collecting method used a sequence of transects at 0.5 km intervals leaving the shoreline. Especially high levels of pollutants were detected across a number of transects across Shuaiba Harbour, with average concentrations of PAH ranging from 201 to 1,333 µg/kg dw. These values are substantially higher than those found elsewhere in Kuwait [59,60,65]. The concentrations of individual PAHs, including phenanthrene (maximum reported value: 165 µg/kg), fluoranthene (maximum reported value: 293 µg/kg), and benzo[a]pyrene (maximum reported value: 95 µg/kg) at the most polluted sites near the SIA exceeded foreign sediment protection criteria [61,66].

3.2 PCBs

The coastal area across the SIA also undertook a systematic evaluation of PCB sensitivity [62]. Penta-PCBs dominated the homologue distribution, with the most various congeners 138, 101, 110, 180, 153, 132, 149, and 118. Two orders of magnitude ranged from 0.40 to 81.7 ng/g dw around the sample site and was equivalent to other comparative surveys of developed coastal sediments that the scientists examined. Port and near-water drainage areas were correlated with the highest amounts, indicating that atmospheric PCB deposition might not be a major source of pollution in Kuwait [10,11]. A number of cores from Sulaibikhat Bay have documented the history of PCB sediment contamination deposition [67]. Data showing sediment deposition over a period of 37 \pm 5 years showed a peak in some PCB concentrations around 1991, after which values fell by 15 times to the current sedimentwater interface concentrations of around 2 ng/g dw [67]. The spike in 1991 was due to the unexpected flood of PCBs following the devastation at the end of the Gulf War of a collection of PCB-charged electrical transformers [10]. The degradation of PCB sediments at many locations in coastal waters in Kuwait was studied by de Mora et al. [59] and found 0.1-5 ng/g dw concentrations that were commonly deemed poor by global standards [68]. With regard to industrial chlorinated hydrocarbons, only a few stations (based on the volume of Aroclor) have found comparatively high concentrations of PCBs, such as those around Doha (2 ng/g dw) and Sulaibikhat Port Bay, respectively (8 ng/g dw). The concentrations of PCB sediment from all other locations were not unusual and were close to those recorded elsewhere in the area [23,69].

3.3 PBDE, dioxins, and furans

The statistics available in Kuwait was largely restricted to a couple of studies based on the dioxins and furans [60,62,63,70]. Owing to their durability, strong lipophilicity, and tolerance to degradation, these compounds are of environmental significance [63,71]. As such, on joining the marine environment, they can be easily attached to suspended particles and transferred to low sediments where they can join the aquatic food chain [10] and present a toxicological hazard [62,63]. The first study regarding the distribution of PBDE and PCDD/Fs in Kuwait was performed by Gevao et al. [62]. Data from the SIA locations showed the dominance of PBDE congeners such as BDE 153, 154, and

183, which typically account for 60% of the congener blend. The values of PBDE varied between 0.1 and 4 ng/g dw. A broader geographic study, including offshore sediment samples and those in Kuwait Bay, showed a comparatively lower degree of PBDE contamination, but the composition of PBDE differed as the dominant conger with BDE 209 [60,70]. The mean concentrations ranged from 0.1 to $0.5 \,\mathrm{ng/g}$ [70] and <0.02 to $0.35 \,\mathrm{ng/g}$ dw, respectively [60], while the combination of congeners studied varied in all the tests. The core sample analysis at the Kuwait Bay entrance showed that detectable PBDE levels first appeared above natural concentrations in the mid-1950s with peak inputs associated with military fight times [70]. Globally, the recorded concentrations of PBDEs for the marine ecosystem in Kuwait are small, with values sometimes below those documented for locations in Northern Europe [71], Japan [72], and China [73].

Studies on the spatial distribution of toxins, PCDDs, and PCDFs that are anthropogenically released into the atmosphere as by-products of agricultural activities have also been carried out across the SIA [61]. Marine sediments were obtained from ten locations around the port area, along with the defined effluent discharge points. Concentrations of PCDD/Fs ranged greatly across sampling locations, varying from 0.40 to 313 pg/g dw, with the PCDD/Fs pattern being seen as symbolic rather than atmospheric point emission source aggregation. PCDF congeners contributed to most of the total TEQ (72%), with the highest values recorded near an oil loading terminal and a cement factory [63]. They were relatively small and showed the context concentrations of sites in New Zealand and Europe when the TEQs were compared with the previous values [63].

4 Conclusions

While a wide variety of emission incidents have occurred in the aquatic ecosystem in Kuwait, the real levels of emissions remain comparatively low compared to highly populated regions in a different place in the world. To date, the study has focused primarily on hydrocarbon petroleum/combustion emissions, with only a small range of studies authenticating other target POPs (PCBs, PBDEs, and dioxins). Where elevated pollution rates have been reported in studies, they tend to be located and associated with common pollution sources such as large factories centered in Doha, Sulaibikhat Bay, and the SIA. The prevalence of contaminants remains relatively high in the oil sector, aside from rare events linked to the Gulf War. Full TPH concentrations have been found to remain relatively stable at a number of locations from 1988 to 1995, covering the entire Kuwaiti coastline. Available figures in Kuwait are mainly limited to a few studies that indicate environmental concern for their longevity, high hydrophobicity, and resistance to degradation of these compounds. A comparatively lower degree of PAH, PBDE, and PCDDs/Fs emissions in Kuwait Bay was observed in research on a broader regional scale, including offshore sediment samples.

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