Assessment of Tarmat contamination and its chemical characterization along the west coast of Qatar, Arabian Gulf

Graduate Students, Science and Engineering

K.P. Haseeba, S. Veerasingam, H. Shafeeq, JassimAl-Khayat, P. Vethamony

Environmental Science Center, Qatar University, P.O. Box 2713, Doha, Qatar

ABSTRACT: Tarmat/Oil residue (hereafter 'TM') is one of the serious threats to the marine ecosystem due to their toxicity, persistence and bioaccumulation problems. To assess the level of TM contamination and to determine the primary differences in the chemical composition, a sampling campaign was conducted in 12 beaches along the west coast of Qatar. TM contamination ranged from 0 to 104 gm^{-1} with an average value of 9.25 gm^{-1}. Moreover, all the TM samples were found to be highly weathered, blackish and asphalt-like material. Though the current TM pollution level is thirty-fold lesser than those found during 1993 to 1997, the contamination pattern was similar (i.e., northwestern part was highly contaminated). The distribution of TM along the Qatar coast is as follows: Low tide> high tide> berm line. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was used to examine the bulk chemical characteristics of the TMs. These bulk chemical characteristics have revealed several features unique to different types of TM samples.

1. INTRODUCTION

TMs originate from natural and anthropogenic oil releases into the marine environment, which are formed after liquid petroleum is transformed by various processes. The hazardous or toxic substances of TM may have severe short or long-term impacts on marine ecosystems and economy, depending on weather conditions, location and the ecological sensitivity of the area of deposition. Even in the absence of acute toxicity, oil persistence in sediments can induce long-term ecological effects through complex biological interactions. The bioavailable oil fractions can cause chronic sub-acute toxicological effect (poor health, reduced growth and reproduction, low recruitment rates), which can alter population dynamics and disrupt trophic interactions and the structure of natural communities within ecosystems[1].The 1991 Gulf war oil spill was the world's largest oil spill, which released about 10.8 million barrels of crude oil and a large amount of ash fallout. Large quantities of oil were transported to southeast by northwest winds and regional circulation patterns, affecting virtually most of the beaches, particularly west coast of Qatar. Two decades ago, Al-Madfa et al[2] reported that north and northwestern coasts of Qatar were severely affected by 1991 Gulf war oil spill. GC-MS and CHEMSIC source identification method on oil residues along the northwestern coast of Qatar revealed that the oil residues were originated from two different sources such as Saudi Arabia and Kuwait crude oils[3]. Recent GC-MS-MS analysis of hopane fingerprint of the tarmat samples collected from the Ras Rakan island closely matched the Basrah and Kuwait crude oil fingerprints, confirming that these tarmats might have formed from the 1991 Gulf War oil spill[4].Qatar coast is continuously exposed to new oil spills as well in addition to earlier oil spills, making it mandatory to monitor and detect long-term fate of TMs along the Qatar coast.

2. STUDY AREA

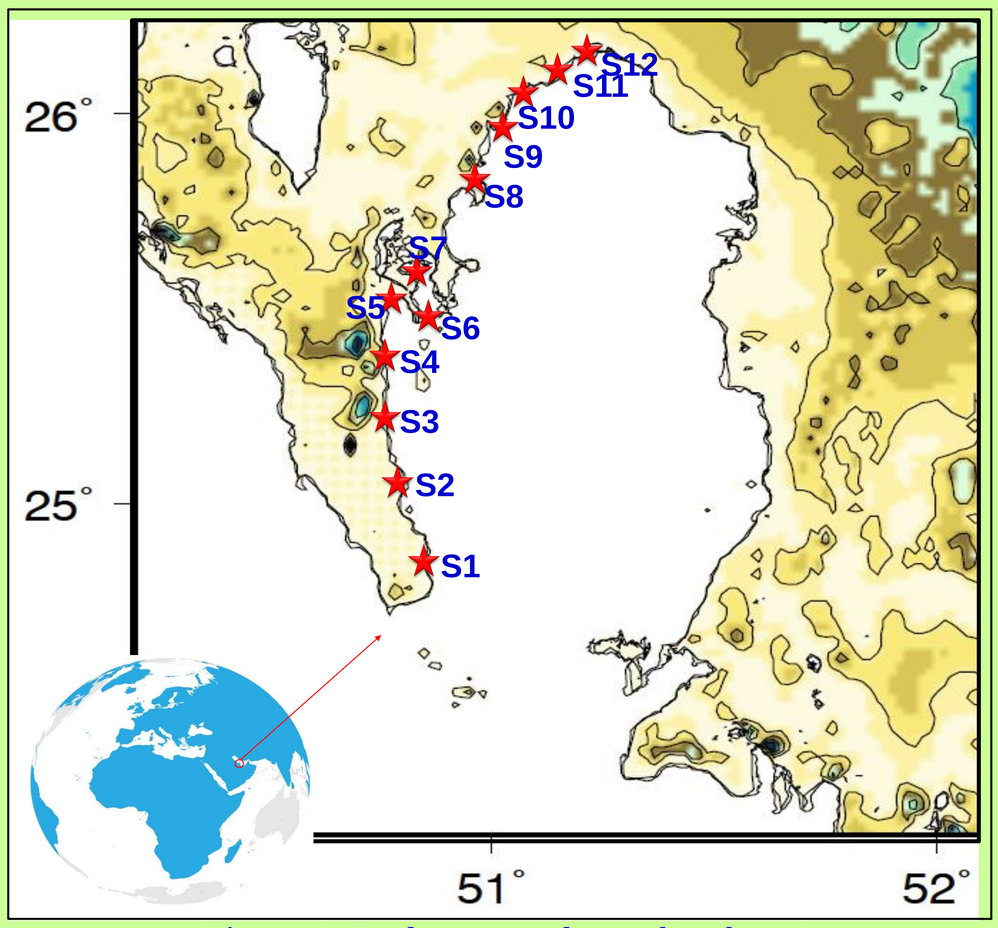

Figure 1. *Study area and sampling locations*

3. SAMPLING AND ANALYTICAL METHODS

Figure 2 (a). Sampling transect in low tide, high tide and berm line; **(b-c).** Tarmats observed at Abu Samara and Al Zubara coasts, respectively and **(d)** ATR-FTIR analysis carried out at GPC, QU.

- In the September 2019 field campaign, we have covered over 250 km of coastline from Abu Samra to Al Ruwais along the west coast of Qatar.
- At each beach, TMs were sampled from three transects (low tide, high tide and berm line) with 1m transect width based on Galgani et al[5].
- TMs (diameter larger than 5 cm) within each transect were collected by hand and weighed. The level of TM contamination for each beach were reported as weight of TM per linear meter (gm^{-1}).
- TMs were analyzed through ATR-FTIR spectroscopy using a Thermo Scientific Nicolet iS10 spectrometer with an ATR monolithic diamond crystal accessory.
- TMs were sliced in half using a solvent-rinsed razor blade and a small internal section (~5 mm dia.) was removed and placed on the ATR crystal for analysis [6].
- Absorbance spectra were collected using 32 scans at 2 cm^{-1} resolution measuring between 400 and 4000 cm^{-1}.
- A background atmospheric spectrum was subtracted from all sample spectra.
- Notable peaks include O–H stretching at approximately 3390 cm^{-1}, C=O stretching at 1712 cm^{-1}, C=C stretching at 1608 cm^{-1}, CH2 and CH3 bending at 1460 cm-1, CH3 bending at 1376 cm^{-1}, and the C–OH stretching in alcohols at 1024 cm^{-1}.
- Peaks were integrated using Omnic software and the integrated areas of the absorbance were normalized to the C–H peak at 2910 cm^{-1}.

4. RESULTS AND DISCUSSION

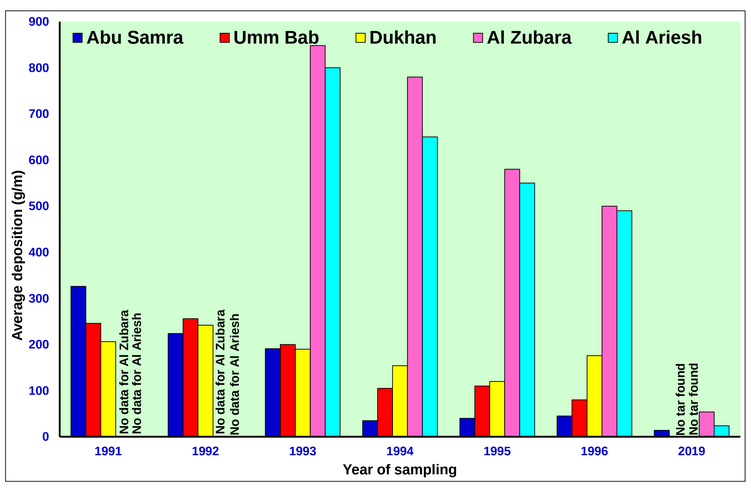

Figure 3. Historical deposition trend of Tarmat

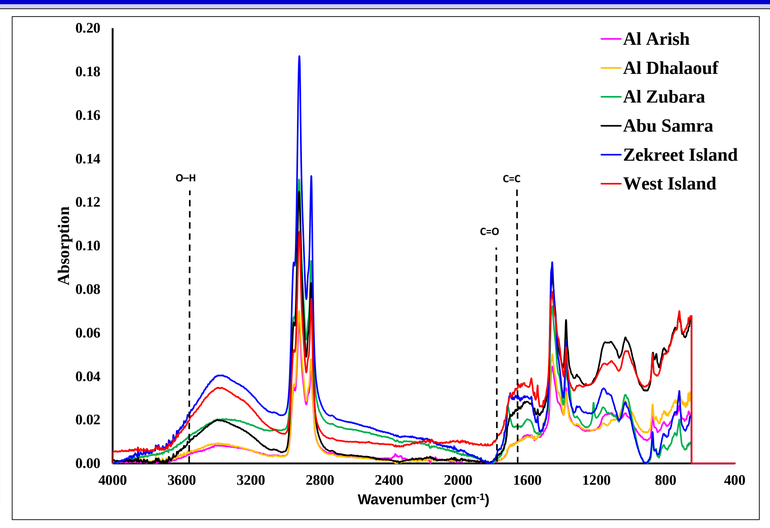

Figure 4. Representative ATR-FTIR spectra of TM samples

- TM contamination pattern along the west coast of India showed that the northern part of the study area was highly contaminated than southern and central parts.
- The distribution of TM along the Qatar coast is as follows: Low tide> high tide> berm line.
- Oxygen-containing functional groups were observed in the ATR FTIR spectra of all TM samples as evidenced by a O–H stretching band at 3390 cm^{-1}, C=O stretching at 1712 cm^{-1} and C–OH stretch at 1024 cm^{-1}.
- Closer examination of different TMs revealed difference in absorbance of functional groups between 600 and 1350 cm^{-1} that could be used to distinguish between samples.
- The Aliphatic index, Long chain index, Aromatic index, Substitution 1 index and Substitution 2 index were calculated for all the collected TMs based on their corresponding FTIR spectra. The aforementioned indices were also calculated for the Kuwait Crude oil and Iranian Crude oil, which were the sources of two large oil spills in the past, based on the FTIR spectra in literature.

5. CONCLUSION

- TM contamination trends showed that the northern part of the study area (especially, Al Zubara) was highly contaminated than the southern part.
- This study demonstrates that instead of expensive and time consuming chemical methods, we can use FTIR spectroscopic technique which is a rapid and effective method to characterize and fingerprint the TMs in marine environment.

6. ACKNOWLEDGMENT

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7. REFERENCES

[1] Warnock, A.M., Hagen, S.C., Passeri, D.L., 2015. Marine Tar Residues: a review. Water Air and Soil Pollution, 226, 68.
[2] Al-Madfa, H., Abdel-Moati, M.A.R., 1999. Beach tar contamination on the Qatari coastline of the Gulf. Environment International, 25, 505-513.
[3] Al-Kaabi, N.S., Kristensen, M., Zouari, N., Solling, T.I., Bach, S.S., Al-Ghouti, M., Christensen, J.H., 2017. Source identification of beached oil at Al Zubarah, Northwestern Qatar. Journal of Petroleum Science and Engineering, 149, 107-113.
[4] Maria A., Leigh, T., Gerald, J., Azenith Castillo, JassimAl-Khayat, Vethamony P, Clement TP. Field and laboratory investigation of Tarmat deposits found on Ras Rakan island beaches in Qatar (under review in Science of the Total Environment).
[5] Galgani, F., Hanke, G., Werner, S., De Vrees, 2013. MSFDT group 10 report marine litter, ICES/JRC/IFREMER. p57.