Distribution, characterization and weathering of tarmats along the west coast of Qatar

Faculty and PostDoc, Science and Engineering

P. Vethamony, S. Veerasingam, Jassim A. Al-Khayat, V.M. Aboobacker, Fadhil N. Sadooni, Hamad Al-Saad Al-Kuwari

UNESCO Chair in Marine Sciences, Environmental Science Center, Qatar University, P.O. Box 2713, Doha, Qatar

ABSTRACT: Oil residue in the form of tarmat (TM) deposited on the coast of Arabian Gulf countries is a major environmental concern. In this study the current TM pollution trend along the west coast of Qatar has been assessed and compared with historical deposition trend. The range of TM distribution is 0–104 g m^{-1} with an average value of 9.25 g m^{-1}. Though the current TM level is thirty-fold lesser than that was found during 1993–1997 (average 290 g m^{-1}), the distribution pattern is similar. The chemical composition and structural characterisation of TMs were studied using an ATR-FTIR spectroscopy, which indicated the presence of higher aromatic compounds in the north (N) coast TMs than those found in the northwest (NW) and southwest (SW) coasts. TM of NW coast is highly weathered compared to those found in the N and SW coasts. We found that the ATR-FTIR spectroscopic method is a rapid approach to characterize and study the weathering of TMs without any tedious sample preparation or solvent extraction.

1. INTRODUCTION

Tarmat (TM) is oil residue, originated from natural and anthropogenic marine oil spills, and deposited as mats of different sizes and forms on the inter-tidal or coastal belt after weathering processes. During the 1991 Gulf War, about 10.8 million barrels of crude oil was spilled (world's largest oil spill) along with a large amount of ash fall-out. Other sources in the Arabian Gulf are spills during offshore oil exploration, oil tanker accidents, oil well blowouts, accidental and deliberate release of bilge and ballast water from ships, river run-off and discharges through municipal sewage and industrial effluents. Two decades ago, Al-Madfa et al.[1] quantified TM deposits along the Qatar coast and reported that north and northwest coasts of Qatar were severely affected by 1991 Gulf War oil spill. In addition to previous oil spills, Qatar coast is continuously exposed to fresh oil spills, however, may not be in large quantities. The hazardous or toxic substances of oil residues may have severe short and long-term impacts on marine ecosystems and economy, depending on weather conditions, location and ecological sensitivity of the area. The level of TM contamination along the Qatar coast due to Gulf war oil spill had been assessed two decades ago, and since then the physical and chemical characteristics of stranded TM could have been changed as a result of physical, chemical and biological processes. Hence, the present study is taken up with the following objectives: i) to assess the current status of TM contamination along the west coast of Qatar, ii) to characterize the structural and chemical composition of TM using ATR-FTIR Spectroscopy and iii) to examine the weathering pattern of TM using FTIR spectral indices.

2. STUDY AREA AND SAMPLING LOCATIONS

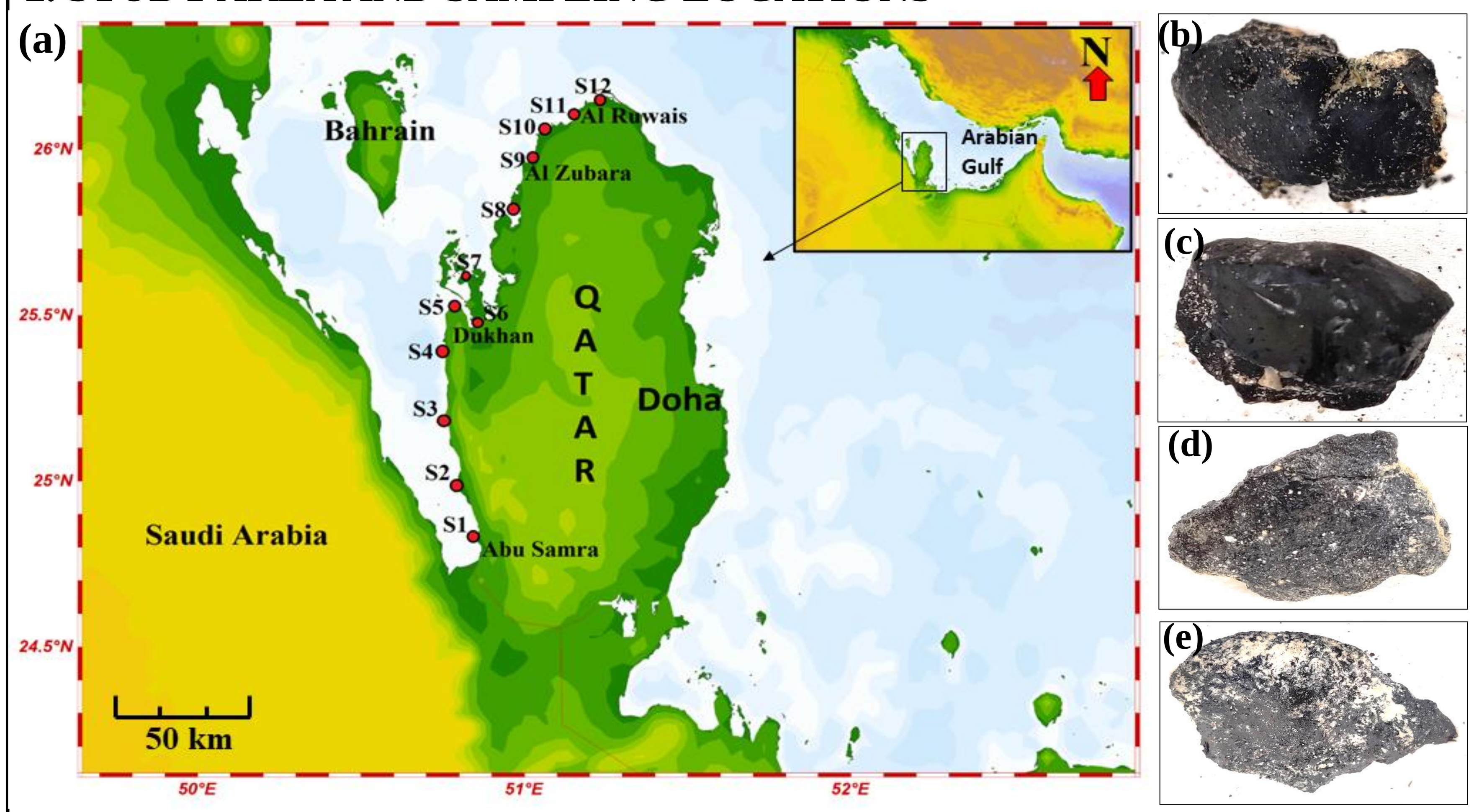

Fig. 1(a). The study area and sampling locations: S1– Abu Samra, S2 – Umm Bab, S3 – Fahahil, S4 – Dukhan, S5 – Ras Al Ghariya, S6 – Zekreet, S7 – Al Buruq, S8 – West Island, S9 – Al Zubara, S10 – Al Arish, S11 – Abu Dhalouf, S12 – Al Ruwais; (b-e). The collected TM samples.

We have conducted TM sampling survey at 12 beaches from Abu Samra to Al Ruwais along the west coast of Qatar in September-November 2019 (Fig. 1). At each beach, three randomly selected transects (1 m wide) were marked in low tide, high tide and berm line.

3. ANALYTICAL METHODS

The collected TM samples were weighed in a high precision balance (0.1 mg). TM samples were analyzed using Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy (Thermo Scientific Nicolet iS10 spectrometer with Smart iTR Diamond crystal plate). Samples were sliced into half using a solvent-rinsed razor blade and a small internal section (~1 cm diameter) was removed and placed it on the ATR crystal for analysis. Absorbance spectra were recorded in the mid-infrared region (4000 – 600 cm^{-1}) using 32 scans at 2 cm^{-1} resolution. A background atmospheric spectrum was subtracted from all TM spectra. Peaks were integrated using Omnic software. Different indices representing the structural and functional features of TM were calculated on the basis of peak areas. Peak areas were measured from valley to valley[2]. The following indices were calculated to compare the structural and chemical composition of TMs using peak areas[3]:

Aliphatic index: (A1460 + A1376) /ΣA, represents all aliphatic compounds in the sample.

Aromatic index: A1600/(A814 + A743 + A724), represents all aromatic compounds in the sample.

Carbonyl index: (A1700/ ΣA), indicates the degree of photo-oxidation

Long chain index: A724/(A1460 + A1376), represents straight chain alkanes with 4 or more carbon atoms in a sample.

In the above indices, ΣA = (A2953 + A2923 + A2862 + A1700 + A1600 + A1460 + A1376 + A1030 + A864 + A814 + A743 + A724). 'A' refers to peak area in the absorption spectrum and the subscript number represents the wavenumber.

4. RESULTS AND DISCUSSION

The field campaigns clearly showed that the TM contamination along the west coast of Qatar exhibits in several physical forms, in a wide range of sizes and with different degrees of weathering. The physical appearance of TM indicated that these were originated from relatively old spills, and none of the samples showed the indication of any fresh slicks - a good sign indicating that in spite of exploration activities of oil in the EEZ of Qatar, the waters of Qatar are healthy. The surface of TM was highly weathered and asphalt-looking material (Fig 1b-e). The spatial distribution showed considerable variability in TM quantity, ranging between ND (not detected) and 104 g m^{-1} with an average value of 9.25 g m^{-1}. The largest quantity of TM has been observed on the north and northwest coasts of Qatar. The southern beaches were less contaminated with TM. However, among the 12 beaches, no TM was found at 4 beaches on the central part of west coast of Qatar (Fig.2a). Comparison of the beached TMs with historical data[1] indicates that the present quantity (average 9.25 gm^{-1}) is thirty-fold lesser than those found during 1993-1997 (290 gm^{-1}).

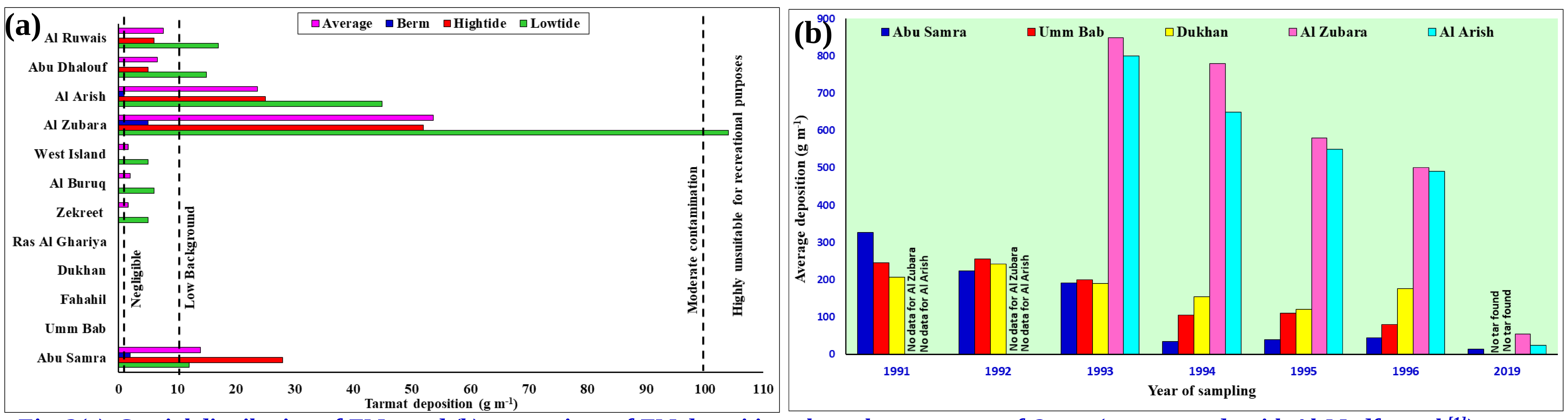

Fig. 2(a). Spatial distribution of TMs, and (b) comparison of TM deposition along the west coast of Qatar (present study with Al-Madfa et al [1])

Table 1. FTIR characteristic absorption peak assignments for TMs

Characteristic peaks (cm^{-1})	Assignment
3650–3200	O–H stretching vibration
3080–3010	=C–H stretching vibration
2953	C–H asymmetric stretching vibration in CH_3 ($\nu_{as}CH_3$) and C–H stretching in alkanes
2923	C–H asymmetric stretching vibration in CH_2 ($\nu_{as}CH_2$)
2862	C–H symmetric stretching vibration in CH_3 ($\nu_{s}CH_3$) and C–H asymmetric stretching vibration in CH_2 ($\nu_{as}CH_2$)
1700	C=H stretching vibration
1600	C=C stretching vibration aromatic compounds
1460	Methyl C–H (CH_2 and CH_3) asymmetric/symmetric bending vibrations
1376	C–H (CH_3) symmetric bending vibrations
1030	C–OH stretching vibrations
864, 814, 743	Out of plane bending vibrations of C–H in aromatic compounds
724	Out of plane bending vibrations of C–H in aromatic compounds and bending vibrations (rocking type) of C–H in CH_2

Representative FTIR spectra for TM samples are shown in Fig. 3. These spectra were evaluated using different spectral ranges with stretching, bending and rocking vibrations. The characteristic peaks for aliphatic hydrocarbons were observed at 3100–2800 cm^{-1}, 1460 cm^{-1}, 1377 cm^{-1} and 720 cm^{-1}, respectively. Peaks at 1600 cm^{-1} and 900–700 cm^{-1} indicate the presence of aromatic hydrocarbons. The peak assignments for functional groups in the variety of TMs are presented in Table 1. Carbonyl values for TMs collected from the NW coast of Qatar indicate that these TMs are highly weathered than those found in the north and SW coasts of Qatar.

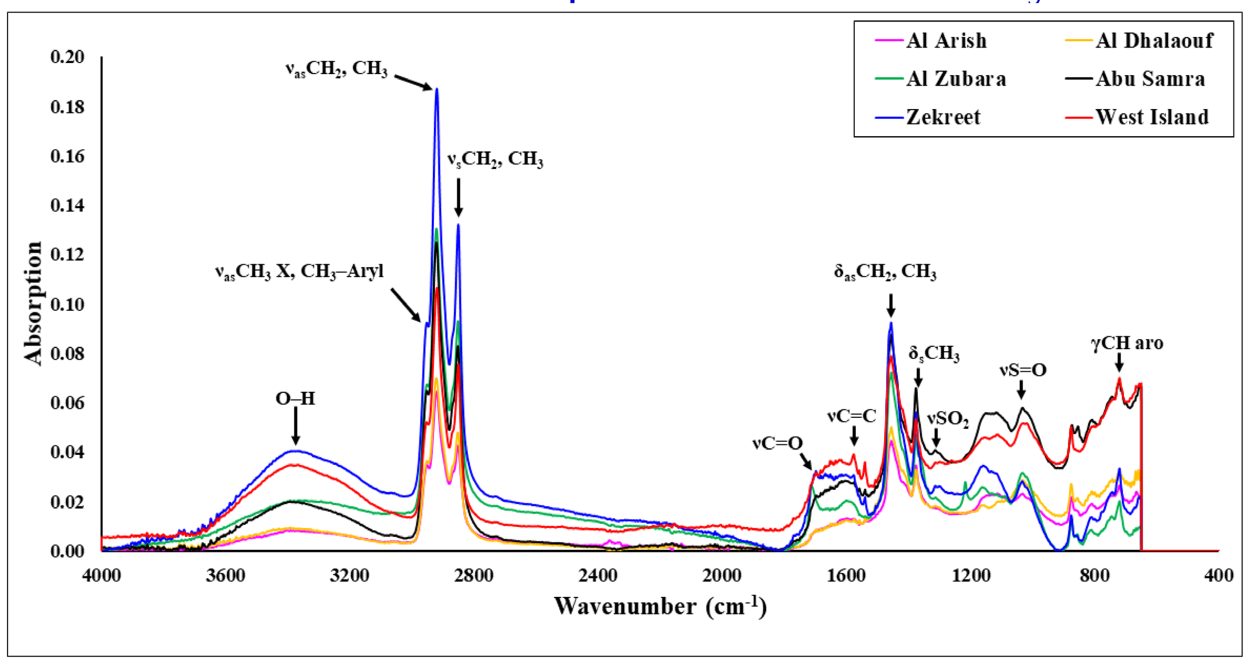

Fig. 3. Representative ATR-FTIR spectra of TMs deposited in Qatar

5. CONCLUSION

The NW coast of Qatar is highly contaminated with TMs, and the current status of contamination shows that it is thirty-fold lesser than those found during Gulf War oil spill. The prevailing winds and currents might have dominated the surface drifting of floating oil residues towards the NW coast of Qatar. Chemical and structural properties of TMs were calculated using FTIR spectral indices and some of their features are comparable to that of Iranian crude oil asphaltenes. Carbonyl Index values indicate that TM samples from the NW coast are highly weathered than those found in the north and SW coasts. The quantification of the concentration of PAHs in large number of samples using GCMS and other chemical analyses would be very expensive and time consuming, and for such analysis, ATR-FTIR method would be suitable to characterize the oil residues and study their weathering patterns.

6. ACKNOWLEDGEMENT: This work is funded by the Qatar Petroleum (QUEX-ESC-QP-TM-18/19). Part of the objectives of UNESCO Chair in Marine Sciences, namely, Marine Pollution, was implemented through this project.

7. REFERENCES: [1] Al-Madfa, H., Abdel-Moati, M.A.R., 1999. Beach tar contamination on the Qatari coastline of the Gulf. Environment International, 25, 505-513. [2] Permanyer, A., Douifi, L., Lahcini, A., Lamontagne, J., Kister, J., 2002. FTIR and SUVF spectroscopy applied to reservoir compartmentalization: a comparative study with gas chromatography fingerprints results. Fuel, 81, 861-866. [3] Asemani, M., Rabbani, A.R., 2015. Oil-oil correlation by FTIR spectroscopy of asphaltene samples. Geosciences Journal, 20, 273–283.