FINGER PRINT ANALYSIS OF PETROLEUM HYDROCARBONS AND THEIR DERIVATIVES FOR THE IDENTIFICATION OF ILLEGAL DISCHARGES: CASE STUDY TURKISH COASTS

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Abstract
An increasing traffic of over 55,000 ships a year in Turkish seas are producing an average of 12 illegal oil spills a year. Fingerprint analysis is initiated by comparison of fluorometric spectra of polluted sea water sample and suspected source sample. ‘Matching’ is confirmed or rejected by subsequent comparison of FTIR, HPLC and GC-FID. In this study, 39 clean sea waters, 41 polluted sea waters and 111 suspected samples were analysed. 76 suspected samples were spectrofluorometrically analysed and categorised as “Non-match”. Finally, 28 suspected samples were classified as a “Match”.

Keywords: Petroleum, Marmara Sea, Pollution

Introduction
Oil is the black blood that runs through the veins of the modern global energy system (Höök, 2009). Oil spills discharges could be “mystery spills” or “known-source spills” (Stout, and Wang, 2007). Normally, determination of the mysterious spill method is based on direct comparison of matching peaks among chromatograms/spectra. The aim of this paper is to identification of the spilled oil pollution source coming from illegal discharges.

Material and Method
Clean sea water, polluted sea water and suspected vessel samples were analysed according to the fingerprint procedures explained in ASTM methods (ASTM, 2011a; ASTM 2011b; ASTM 2006; ASTM, 1996). For each occasion/event, at least three samples were taken from clean water (sea/fresh) as a reference site, polluted waters from polluted site and samples from different tanks/section of suspected sources like sludge, bilge, slope, bunker tanks etc. Collecting samples were scan by using synchronous spectrofluorometer between 200-600 nm. Samples scan patterns were compared between polluted sample and suspected sample. If polluted sample and suspected samples pattern were similar than further analysis are done by using, HPLC, GC-FID and FT-IR methods.

Results and Discussion
For present study, samples were collected from 38 illegal discharges events from Turkish Coasts. 39 clean sea water, 41 polluted sea water and 111 suspected samples were analysed (Table 1). 76 samples of them were sym-spectrofluorometrically analysed and polluted samples spectral results were not similar with suspected samples. They were classified as “Non-match”, so there were no need for further analysis (Table 1). Other 35 suspected sample were classified as “Match or Probable Match”, and they were required further analysed by using other methods such as FT-IR, HPLC and GC-FID. Finally, 28 samples were classified as a “Match”.

Case 1; Non match: Samples were compared for the similarities and analysis was started with syn-spectrofluorometry. (Figure 1). Figure 1 showed that polluted samples and suspicious sample were completely different each other (Non-match) and clean sea water spectrum was also behaving differently.

Case 2; Match: In second case, since, syn-spectrofluorometric results were matched with either polluted sample or suspicious samples, finger printing analysis should be continued with other methods by using HPLC, FT-IR and GC-FID

Conclusion
Finger print analysis is a qualitative method and consists of four different methods were used for the comparison of the chromatogram/spectra. In addition to this, expert judgement is another important step for the assessment of the results. Although, achieve the highest success rate in terms of the correct result, sometimes, specific cases, the finger print method could not show one source or sometimes shows more than one sources. If the source sample and polluted sample outputs were not the same, finger print analysis were ended and legal proceedings were completed in a short time.

References