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# Role of Reference Materials Used in Measurement of Oil Pollution and a Correlation Equation to Determine Oil in Seawater

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Oil pollution in seawater is determined by gravimetric, IR, HPLC, GC, GC/MS and ultraviolet fluorospectrophotometric (UVF) methods.Crude oils and chrysene were used as reference material in UVF technique in which the measurement is based on intensity of fluorescence compounds in the references, but their amounts in crude oils are not the same. Thus, the oil level determined in the samples differs depending on the reference materials used. Some authors gave the results by using both crude oil and chrysene as references (Emara and El-Deep 1988; Badawy and Al-Harty 1991; Abdullah et al. 1996) whereas some used either chrysene according to the UNEP (1986) (Yılmaz et al., 1998; Kornilios et al. 1998; Shriadah 1999) or crude oil (Ehrhardt and Petrick 1989; Emara 1990; Weber and Bicego 1990; Ehrhardt and Burns 1993, Lara et al. 1995; Güven et al.1996,1998, Shriadah 1998; Al-Saad et al. 1998; Zanardi et al. 1999a, b).

In this paper, the importance of the reference materials is examined in determining the oil pollution level in seawater and a correlation equation is proposed for unspecified pollutant oils.

## MATERIALS AND METHODS

The reference crude oils were obtained from the Izmit refinery (Sea of Marmara) (No.1-6) and Botaş (No.7) at the end of pipeline (eastern Mediterranean). They were transported by tankers through the Black Sea, Bosphorus (especially former Soviet Union) and the Sea of Marmara, Dardanelles and Mediterranean Sea. The crude oils are listed in Table 1. Chrysene (Merck).Solvent : Dichloromethane(DCM) and hexane (HPLC grade, Lab-Scan) controlled by GC/MS.

The calibration curves were plotted in concentrations of 0.25-1.5 μg/ml for crude oils and 0.05-0.3 μg/ml for chrysene in hexane. The fluorescence intensity was measured at 310/360 nm (ex/em) by UV fluorospectrometer (Shimadzu, RF-1501) and the related equations were taken from this apparatus.

The correlation equation was calculated from the equations of standard curves of crude oils examined by using least squares method via formula as :
$F_1 = a \cdot c + b$  $F_1$ = absorbance, a and b = constant, c = concentration
The seawater samples were collected the Black Sea, Bosphorus (northern entrance ) ( 22 Oct 1998 ), Dardanelles ( northern entrance ) ( 22 Aug 1998 ),

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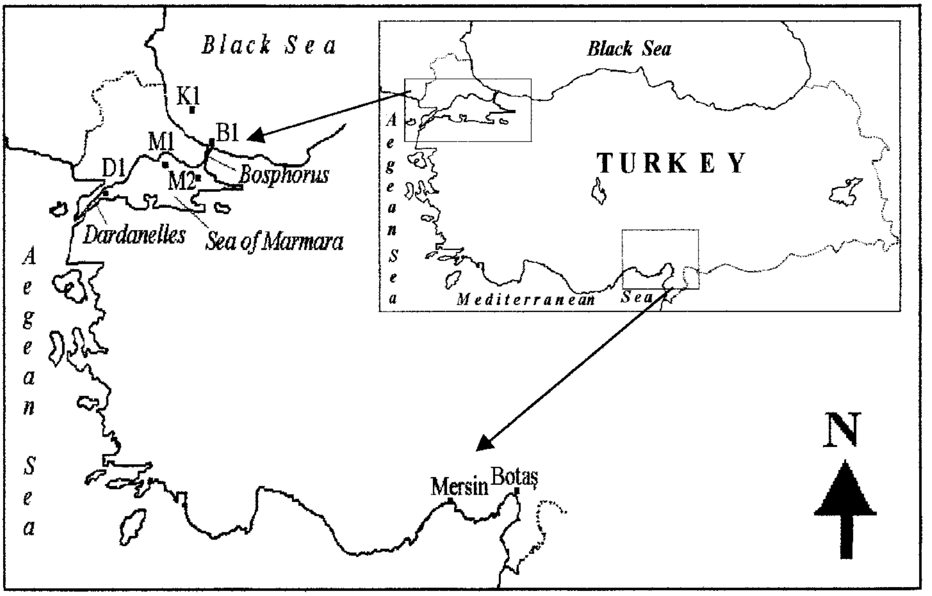


**Figure 1.** Sampling stations

**Table 1.** The equation of the standard curves of crude oils and chrysene.

| Reference materials | Equations* |
|---|---|
| Crude oil | |
| 1-Saudi Arabia | $F_1$=618.49 c + 41.867, $r^2$=0.99 |
| 2-Egypt | $F_1$=693.12 c + 30.265, $r^2$=1.00 |
| 3-Libya | $F_1$=611.11 c + 33.669, $r^2$=0.99 |
| 4-Syria | $F_1$=505.87 c + 46.145, $r^2$=0.99 |
| 5-Former Soviet Union | $F_1$=662.49 c - 0 .259, $r^2$=1.00 |
| 6-Iran | $F_1$=505.30 c + 30.631, $r^2$=0.99 |
| 7-Iraq | $F_1$=488.59 c + 49.758, $r^2$=0.99 |
| Chrysene | $F_1$=2184.7 c + 107.210, $r^2$=0.99 |

*: Each curve was plotted for six experiments.

Sea of Marmara (22 Oct 1997), and eastern Mediterranean Sea (24 Oct 1998). The sampling stations are shown in Figure 1.

All samples were taken in triplicate. The 2.8 L sea water sample was extracted with 3x50 ml DCM and organic phases were combined and dried on anhydrous sodium sulphate then distilled at 40°C. The residue was dissolved in hexane and the volume adjusted to 10 ml with hexane and its fluorescence intensity was measured at 310/360 nm (ex/em) as indicated above. The oil pollution levels in sea water were found by using the equation of standard curve of each crude oil and chrysene.

**Table 2.** Oil pollution for different crude oils (μg/L).

| Stations | Reference materials | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Chrysene | A | B | C | D | E | F | G | H |
| BLACK SEA ( K1) | 0.75±0.00 | 3.32±0.03 (4.42) | 3.78±0.03 (5.04) | 3.79±0.03 (5.05) | 3.03±0.02 (4.04) | 3.13±0.04 (4.17) | 3.60±0.02 (4.80) | 2.77±0.02 (3.69) | 3.27±0.02 (4.36) |
| NORTHERN BOSPHORUS (B1) | 0.29 ± 0.00 | 1.55 ± 0.02 (5.34) | 1.73±0.03 (5.96) | 1.81 ±0.03 (6.24) | 1.41 ± 0.02 (4.86) | 1.48 ± 0.02 (5.10) | 1.70±0.03 (5.86) | 1.32±0.02 (4.55) | 1.55±0.02 (5.34) |
| SEA OF MARMARA | | | | | | | | | |
| M1 | 0.22 ± 0.00 | 1.35 ± 0.01 (6.13) | 1.47±0.02 (4.17) | 1.55±0.02 (7.04) | 1.20 ± 0.02 (5.45) | 1.26±0.02 (5.72) | 1.44±0.02 (6.54) | 1.13±0.02 (5.13) | 1.33±0.02 (6.04) |
| M2 | 0.31 ± 0.00 | 1.62±0.07 (5.22) | 1.83±0.09 (5.90) | 1.90±0.09 (6.12) | 1.49±0.07 (7.16) | 1.55±0.07 (5.00) | 1.79±0.09 (5.77) | 1.39±0.07 (4.48) | 1.63±0.07 (5.25) |
| DARDANELLES (D1) | 0.10 ± 0.00 | 0.92±0.02 (9.20) | 0.88±0.01 (8.80) | 0.99±0.02 (9.90) | 0.75±0.01 (7.50) | 0.80±0.01 (8.00) | 0.88±0.02 (8.80) | 0.72±0.01 (7.20) | 0.84±0.01 (8.40) |
| EASTERN MEDITERRANEAN | | | | | | | | | |
| Botaş | 0.56±0.00 | 2.45±0.02 (4.37) | 2.96±0.04 (5.28) | 2.99±0.03 (5.33) | 2.38±0.02 (4.25) | 2.45±0.03 (4.37) | 2.88±0.04 (5.14) | 2.18±0.02 (3.89) | 2.57±0.03 (4.58) |
| Mersin | 0.53±0.00 | 2.34±0.03 (4.41) | 2.81±0.04 (5.30) | 2.85±0.03 (5.37) | 2.26±0.03 (4.26) | 2.34±0.03 (4.62) | 2.74±0.03 (5.16) | 2.08±0.02 (3.93) | 2.45±0.03 (4.62) |

The ratio of the oil pollution levels based on crude oil and chrysene references are given in paranthesis.
Crude oils: A: Former Soviet Union , B: Iraqi, C: Iranian, D: Saudia Arabian, E: Libyan, F: Syrian, G: Egyptian, H:Calculated from the correlation equation

## RESULTS AND DISCUSSION

The equation of the standard curves of seven different crude oils and chrysene are given in Table 1. The correlation equation calculated from seven crude oils is:

$$F_l = 583.567\ c + 33.15 \qquad r^2 = 0.99 \qquad F_l = \text{absorbance},\ c = \text{concentration}.$$

Table 2 shows the results of oil pollution at different stations calculated by each standard equation of crude oils and chrysene references and also the correlation equations. The ratios of crude oil/chrysene are given in paranthesis. The highly variable results were obtained in the oil pollution level of the same area by using crude oil and chrysene references. The oil concentration in seawater was within a range of 0.72-3.79 μg/L for crude oil and 0.10-0.75 μg/L for chrysene references. Comparing level of oil measurements in the same area, the concentration calculated from chrysene is much lower than that of crude oil references. When we considered the oil pollution results given in the literature based on chrysene and crude oil references, we found that the level of crude oils were higher than chrysene as 0.66 time (Emara et al. 1988), 2-3 times (Badawy and Al- Harty 1991) for Kuwait crude oil and 20 times for Seligi crude oil (Abdullah et al. 1996). As can be seen in the Table 2 the oil pollution levels based on crude oil are 3.9-9.9 times higher than the values found by chrysene references.

The data demonstrated that measurements of oil pollution based on solely a chrysene reference had not given true results because chrysene is one of the many fluorescent compounds in crude oil with varying amount.

The pollution level measurements in the same area changed slightly depending on the crude oil used as reference, for the fluorescent constituents vary in oils of different origins.

The difference between maximum and minimum oil concentration values calculated in Table 2 for various crude oil references varied as 1.36-2.70 μg/L. Iranian crude oil equation gave the highest pollution result while the lowest value was obtained by Egyptian crude oil. The role of reference oil in the level of pollution ranked as Iranian > Iraqi > Syrian > Libyan > former Soviet Union > Saudi Arabian > Egyptian.

Ehrhardt and Petrick (1989), suggested that the usual reference substance was a crude oil likely to be used or transported in the area under investigation. Our findings experimentally supported this opinion. Hence, the origin of crude oil must be known in determining oil pollution in seawater. In the case that the origin of pollutant oil is unknown the proposed correlation equation can be used to minimise the errors for the area indicated. The difference percent between the results of crude oil references with correlation equation was found within a range of 0.00-0.17%.

This work comprised pollution by the crude oil in the Middle East and the Black Sea. For the other seas of the world new correlation equations must be calculated based on the oils transported.

It seems necessary that a principle must be accepted on which the sea pollution measurements shall be based.

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