

## **Oil pollution in the surface water of Sakarya River**

### **Sakarya Nehri yüzey suyu petrol kirliliği**

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#### **Abstract**

In this paper the oil pollution was investigated seasonally in the mouth and 4 stations of Sakarya River water during February 2008- January 2009. The oil pollution levels were determined by UVF, using Russian crude oil and chrysene as reference materials. The maximum oil level in river water was found as 37.47 µg/L at station 2 in November-2008 and 45.38 µg/L at station 4 in April- 2008. The highest polluted area in all time is the station 2 where fishing vessels and yachts stations. The comparison of results in Sakarya River with the rivers of Turkey flowed to Black Sea as Yenice, Kızılırmak and Yeşilirmak, the oil pollution found is lower in Sakarya River.

The oil pollution level found in Sakarya River is higher than the limit value given by UNESCO.

**Keywords:** Sakarya River, oil pollution, surface water.

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#### **Introduction**

Oil pollution is one of the most serious problems for river as seawater. The sources of oil pollution of rivers are municipal sewage, oil industries, fishing vessels etc.

The effects of the oil pollution are classified as long-term and short- term effects. Long-term effects are not known certainly yet but short-term effects cause airless on the surface (Altuđ 2008). The main problem of oil pollution in rivers is toxic effect on fish.

Over 160 rivers flow from the territory of Turkey into the Black Sea.

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Their total annual run off makes up 44.44 km<sup>3</sup>.

Sakarya River is an important river starting from 3 km southeastern of Eskişehir- Çifteler. Its length and width are 810 km and 60-150 m respectively. The runoff of the Sakarya, Kızılırmak and Yeşilirmak rivers is equal to 4.54, 5.94 and 4.89 km<sup>3</sup> per year respectively. More than 55% of the rivers runoff from the Turkish territory occurs from February through May, making up to 12-15% per month; in other month this portion is only 3-7% (Reshetnikov 1984).

The investigations made on the pollution of Sakarya River are: organochlorine pesticides (Barlas 1999), phosphorus fractions, chlorophyll a concentrations (Çalimli and Pulatsü 2003), nitrogen fractions and ferro silicon concentrations (Çelik and Pulatsü 2003).

Oil pollution is main problem of the Black Sea. Besides this oil pollution of rivers flow to the Black Sea were investigated and found that the higher oil product in the Black Sea waters are to be related to the Danube River waters (Bojkova 1991). Oil pollution level in Danube offshore 160 ng/L in 1989. Pollutant flowed to Black Sea were 300.9 ton from the Dnieper River in 1987 (Fashchuk and Shaporenko 1995).

Oil pollution was investigated at river of Kızılırmak shoreline and found that the highest concentration of total PAH was found as 14.17 µg/L (Üstün-Kurnaz and Büyükgüngör 2007). Oil pollution in river flow to the Black Sea was investigated in 2003 by Güven et al. (Unpublished data).

In this paper oil pollution levels is reported in surface water of Sakarya River.

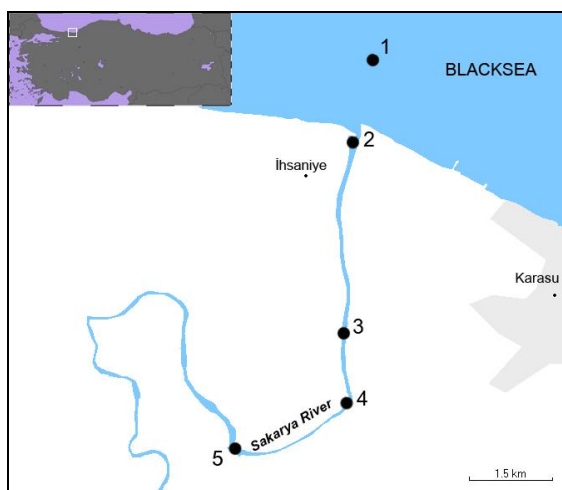
## **Materials and Methods**

2.8 L surface water samples were taken by boat during the period February 2008 and January 2009 at mouth and 4 stations in Sakarya River. The samples were collected in dark brown glass bottles and 10 ml dichloromethane (DCM) was added for preservation. The sampling stations are shown in Figure 1.

800 ml samples taken from 2.8 L sea water were extracted 3 times with 30 ml DCM. The extract was dried over anhydrous sodium sulphate and distilled at 36°C. The residue was dissolved in hexane and the volume adjusted to 10 ml and its intensity was measured at 310/360 nm (ex/em) by UVF (Shimadzu RF 5310).

The calibration curve was drawn in a concentration of 0.25 - 1 µg/ml for 7 different Russian crude oil obtained from TUPRAŞ refinery, Izmit, Turkey and 0.025- 0.25 µg/ml for chrysene (Aldrich). Their fluorescence intensity were measured at 310/360 ex/em using fluorospectrometer (UVF) (Schimadzu RF 5310). Their standard equations were taken from apparatus.

All solvent and chemicals used are (Merck products, Darmstadt, Germany).



**Figure 1.** Sampling stations

## **Results and Discussion**

The calibration curve and standard equations for Russian crude oils and chrysene are shown in Figures 2-9 and Figures 10-11 respectively. The correlation equations were calculated from the standard equations of 7 different Russian crude oil (Figure 12) and 3 chrysene assays (Figure 13).

Correlation equations are:

For Russian crude oil

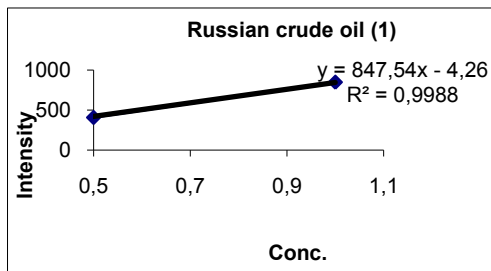
$$F_1 = 814.9052xC + 51.554$$

$$r^2 = 0.99$$

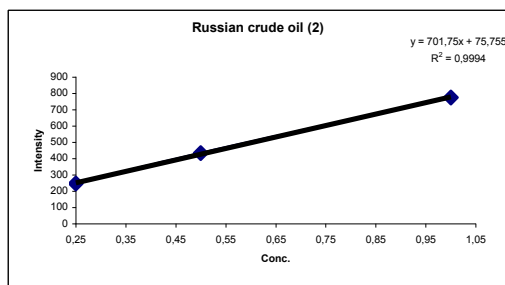
For Chrysene

$$F_1 = 2127.56xC - 1.834$$

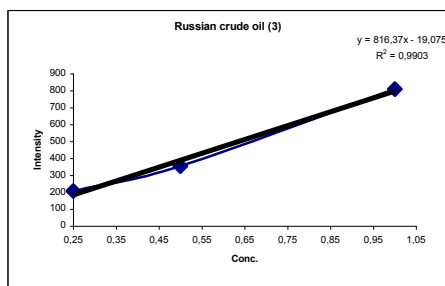
$$r^2 = 0.99$$



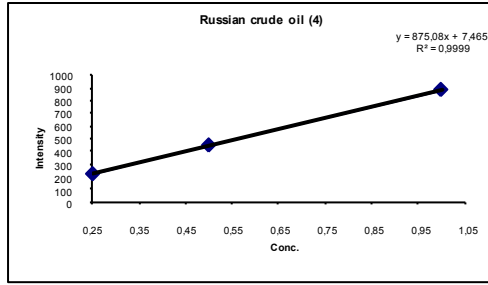
**Figure 2.** Calibration curve and standard equation of Russian crude oil No.1.



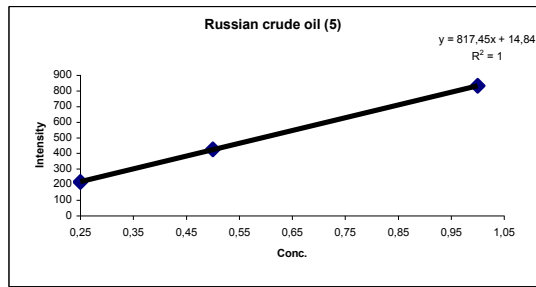
**Figure 3.** Calibration curve and standard equation of Russian crude oil No. 2.



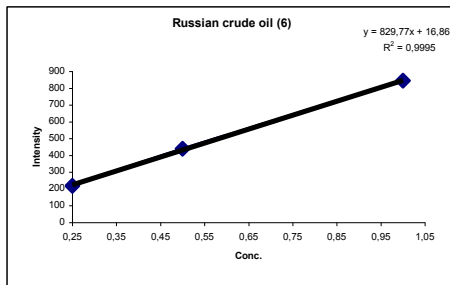
**Figure 4.** Calibration curve and standard equation of Russian crude oil No.3.



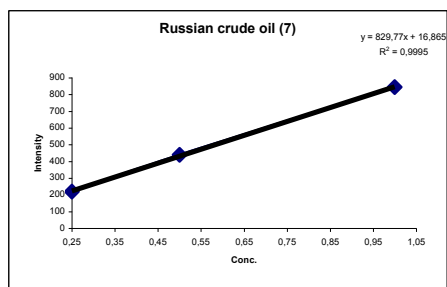
**Figure 5.** Calibration curve and standard equation of Russian crude oil No.4.



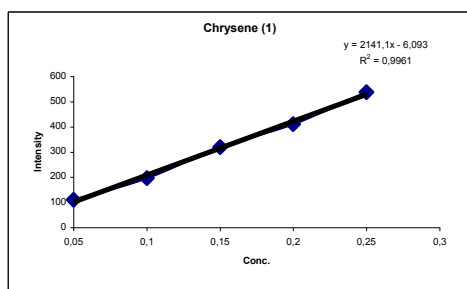
**Figure 6.** Calibration curve and standard equation of Russian crude oil No.5.



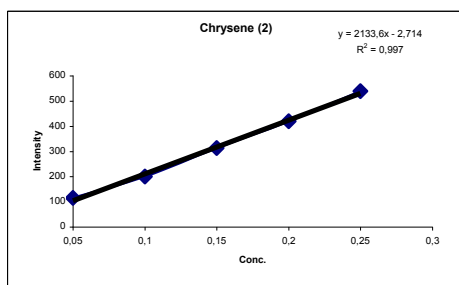
**Figure 7.** Calibration curve and standard equation of Russian crude oil No.6.



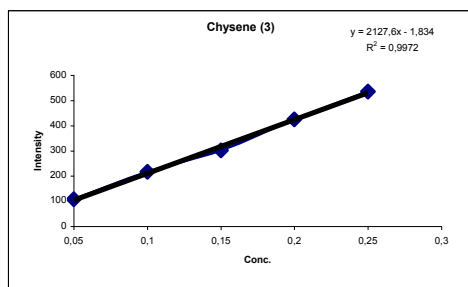
**Figure 8.** Calibration curve and standard equation of Russian crude oil No.7.



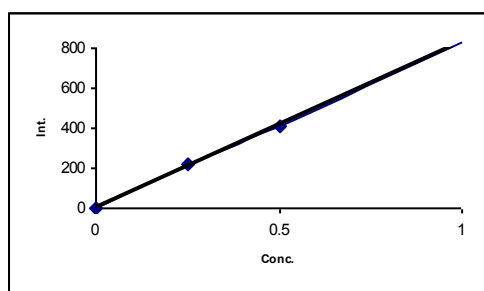
**Figure 9.** Calibration curve and standard curve for Chrysenes assay No. 1



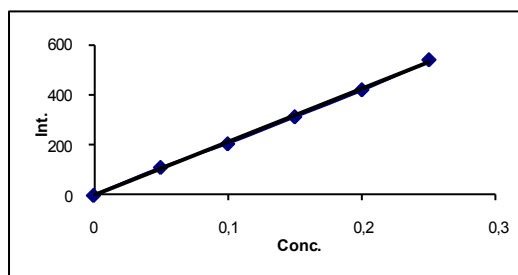
**Figure 10.** Calibration curve and standard curve for Chrysenes assay No.2



**Figure 11.** Calibration curve and standard curve for Chrysene assay No.3



**Figure 12.** Correlated calibration curve for approximate Russian crude oil equation.



**Figure 13.** Correlated calibration curve for approximate Chrysene equation.

The oil concentrations obtained for the surface water samples are given in Table 1.

**Table 1.**Oil pollution calculated from Russian crude oil and chrysene equivalent in the stations of Sakarya River ( $\mu\text{g/L}$ ).

Sampling Stations (Number)	Coordinates	Feb 2008		April 2008		July 2008		Nov 2008		Jan 2009	
		Russian	Chr.	Russian	Chr.	Russian	Chr.	Russian	Chr.	Russian	Chr.
1	41° 08.19 N 30° 39.10 E	9.36	3.98	28.63	11.75	14.26	6.26	3.13	1.28	-	-
2	41° 07.31 N 30° 38.54 E	31.28	12.35	31.31	12.77	-	-	37.47	15.12	5.46	2.17
3	41° 05.40 N 30° 38.47 E	-	-	21.07	8.86	13.03	5.38	31.46	12.83	6.15	2.43
4	41° 05.00 N 30° 38.49 E	15.15	6.20	45.38	18.14	-	-	5.54	2.20	8.43	3.30
5	41° 04.33 N 30° 38.49 E	6.24	2.55	17.64	7.55	6.95	2.74	31.61	12.89	-	-

-: No sampling



The highest oil pollution was found as 45.38 µg/L at station 4 in Nov. 2008 and the lowest value was found as 3.80 µg/L from the mouth of Sakarya River. Oil level of the samples ranged between 3.13-45.38 µg/L in 2008 and 5.46- 8.43 µg/L in 2009 calculated from Russian crude oil and 1.28- 18.14 µg/L in 2008 and 2.17- 3.30 µg/L in 2009 from chrysene equivalent. As can be seen from the Table 1 the oil pollution decreased in a year from February-2008 to January-2009.

The flow of Sakarya River was 5.60 km<sup>3</sup>/year (Jaoshvili 2007). When calculated from the maximum oil pollution in Sakarya River to river volume as 5.60 km<sup>3</sup>/year, the oil pollution was found 254.13 ton/year.

There are different critters for the limit value of oil pollution in sea water: The concentration of 1 µg/L is considered to be typical of sea water without significant petroleum pollution, while concentration of about 5 µg/L is considered low for inshore water (Law 1981). Sea water containing hydrocarbon level as less than 0.00025 mg/L (2.5 µg/L) can be classified as unpolluted. The limit value for sea water established by UNESCO (1982) was 10 µg/L.

According to our findings the oil pollution level of the examined area are much higher than the limit value given by UNESCO.

## **Özet**

Bu çalışmada Sakarya Nehri'nde motorla gidilebilen en dar noktadan Karadeniz' e döküldüğü yerden (Yenimahalle) açığına kadar olan bölgenin petrol kirliliği 2008 Şubat- 2009 Ocak tarihleri arasında mevsimsel olarak incelenmiştir.

Petrol miktarı Rus ham petrolü ve krizen referansına göre tayin edilmiştir. Bu tayinler alınan su örneklerinin DCM ile ekstraksiyonunu takiben UVF aletinde 310/360 nm'de yapılmıştır. Sakarya Nehri'nde 2008 yılında en yüksek miktar 4 numaralı istasyonda Nisan ayında 45.38 µg/L, 2009 yılında ise Ocak ayında 8.43 µg/L olarak bulunmuştur. 2008 yılı ile 2009 yılı arası mukayesesinde kirlilik miktarı 5 misli daha az bulunmuştur. Genel olarak istasyonlar arasında balıkçı teknelerinin ve yatlarının durmakta olduğu 2 numaralı istasyon incelenen bütün aylarda en kirli bölge olarak bulunmuştur. Daha önce Güven ve ark. yaptığı çalışmada Karadeniz'e akan diğer Türkiye nehirlerinden Yenice, Yeşilırmak ve Kızılırmak ile Sakarya Nehri'nin kirliliğinin mukayesesinde Sakarya Nehri'nin daha az kirli olduğu bulunmuştur.

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