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The influence of drying technique on oil pollution amount in sediments

Sedimentin kurutma tekniğinin petrol kirliliği miktarı üzerine etkisi

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Abstract

In this paper was investigated the influence of drying technique on oil amount in sediments. Drying techniques used for sediments were oven at 60^0C or freeze dryer. For the comparison of the results wet and dried of sediments the highest oil pollution level was found in freeze drying technique. The comparison of the oil amount found in freeze drying sediment are 20 time fold wet weight method and two time fold oven method. The best results were obtained for freeze dryer method in tested techniques. Instead of the results showed that a seriouse lack exist for the determination of oil concentration in sediment.

Keywords: sediment, wet/dried weight, oil determination

Introduction

The origin of hydrocarbons in sediments are biogenic, bio-synthesized by living organisms and anthropogenic due to oil pollution. Exogenic hydrocarbon compounds may be released in environment during metabolism or death of the marine organism, these are calculated as 1-10 million tons per year. Anthropogenic hydrocarbons present in the sea come forest fire, industrial discharge, exhausted gases from vehicle, tanker accident and illegal discharges of water from tanker washing, etc. The

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determination of oil contamination in sediment was made wet or dried forms. Various techniques has been used for drying of sediment.

In wet weight, technique, the sediments were mixed with anhydrous sodium sulphate. For the drying of sediment oven or freeze drying methods were used. Both techniques present some problems. In the case of wet/weight, the moisture content of the simple should not be provided. In dry weight technique some volatile component of oil can be lost in the proccess of heating in oven or freeze – dry method.

In oven technique sediment was dried at 50-100 ^{0}C . Freeze dried technique was made at – 50^{0}C in vacuo.

The other problem in this determination was distillation of the extract by ordinary or rota evaporator technique. In this process some volatile components can also lost. Another problem is choice of solvents. These are important for the complete extraction. For this purpose different solvents, single/mixture were used.

For the extraction of hydrocarbons in sediments is generally methods used Soxhlet extraction (Farrington et al., 1977; Barrick et al., 1980; UNEP 1981).

The other methods used for extraction of oil in sediment were digestion in alcoholic KOH under reflux (Law and Fileman, 1985), sonification (Mc Cready et al., 2000), microwave technique (Kim et al., 1999) and distillation with steam for volatile components.

All these techniques have been some problems as loss of volatile component including naphthalene/phenanthrene, incomplete extraction of oil, influence of moisture in sediment, insufficient elution with solvent in sediments.

No report exist on the influence of drying technique of oil content amount in sediment.

In this work the oil content of sediment in wet/dried forms were discussed.

Material and Methods

The samples were taken using Van Veen Grab apparatus from Zonguldak, Turkey in the Black Sea (TRK13: 23 m depth, TRK14: 51 m depth) in the west part of the Black Sea. The sediment samples were homogenized and stored in deep freeze at – 28^{0}C until analysis.

In this study, the oil determination was based on the transported crude oil by tanker through the Black Sea originated from Russian and Caspian origin.

The oil analysis was made using the oil transported in this area. These reference oil was obtained from TUPRAS refinery, İzmit, Turkey.

The oil content of sediment was carried out using a Schimadzu ultraviolet fluorospectrometer UVF 1601. The intensity was red at 310-360 (ex/em).

The reference oil and its concentration used for plotting of calibration curve were;

1. Russian (2003)
   0.25-1.5 µg/mL
2. REB oil (26.02.2005)
   0.32-1.28 µg/mL
3. SEB (17.04.2005)
   0.4-1.2 µg/mL
4. Siberian light (24.04.2005)
   0.47-1.18 µg/mL
5. REB oil (08.06.2005)
   0.32-1.28 µg/mL
6. Siberian light (18.06.2005)
   0.36-1.44 µg/mL
7. REB oil (20.06.2005)
   0.5-1.5 µg/mL

The solvent used for dilution of reference crude oil was hexane.

All solvent used were obtained from Merck, Darmstadt, Germany. Sodium sulphate anhydrous (Le Chemia).

Extraction

Three different extraction techniques was applied to the sediments. The assay was made in each sample with two time.

1- Wet weight technique:

20 g Sample was mixed with sodium sulphate anhydrous and extracted with dichloromethane (DCM) – methanol 80:20 and then DCM in soxhlet apparatus at 8h. The extracts were collected dried over sodium sulphate anhydrous, filtered and distilled at 35 C. The residue remained of sediment is dried and weighted. The amount of oil in sediment was calculated on dry weight.

2- Dried sediment

2.1- Drying in oven: 20 g wet sediments was dried in oven at 60 C then their weight and extracted with the same procedure described above.

2.2- Freeze drying: 20 g sediment was dried in freeze dryer apparatus then weight and extracted with the same procedure described above.

Gas chromatography/Mas spectrometry (GC/MS):

The gas chromatoraphy mass spectrometer (HP6890 Series GC System; Hewlett Packard, Willmington, DE, USA) is fitted with an electronic pressure control, a mass selective detector (HP5972A); ionization energy: 70 eV; source temperature: 280^{0}C and a HP-PONA capillary column (50 m x 0,25 μm film thickness). The chromatographic conditions were: sample size 2 μl, injection port temperature 280^{0}C, configured for split injection; initial oven temperature 40^{0}C rising to 280^{0}C at 8 8 ^{0}C/min, final hold of 20 min. Helium was used as carrier gas (1 ml/min).

The oil components in sediment extract were analyzed by GC/MS. The oil component was identified by retention time data and comparison with MS data.

Results and Discussion

The oil content of sediment measured (mg/g) at TRK 13 and TRK 14 in are shown in Table 1.

Table 1. The oil amount found in sediments at different extraction techniques (mg/g)

Technique / Sample	Wet weight	Oven	Freeze dried
TRK 13	1.22	10.91	10.42
TRK 14	1.71	13.61	23.45

As seen in Table 1 the highest level of oil pollution was found at freeze dried method. The results of feeze dried method are 10 and 20 time fold wet weight and oven methods, respectively.

The amount of oil in sediment found are in excess of 10 μg/g stipulated by and hence are classified as polluted.

The comparison of the results of all methods showed that TRK14 sediment was more polluted.

It can be seen in the Table 1 freeze dried sediment contain higher amount of hydrocarbon suggesting that freeze drying is a most efficient method.

GC/MS chromatogram of wet/dried sediment are shown in Figures 1-6.

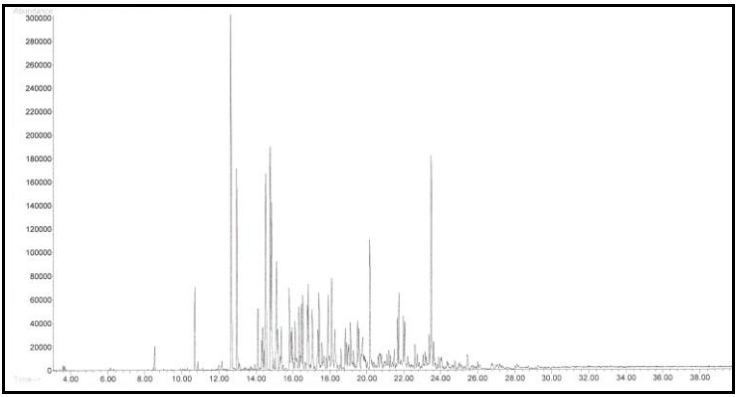

Figure 1. GC/MS chromatogram of TRK13 sediment (wet wieght)

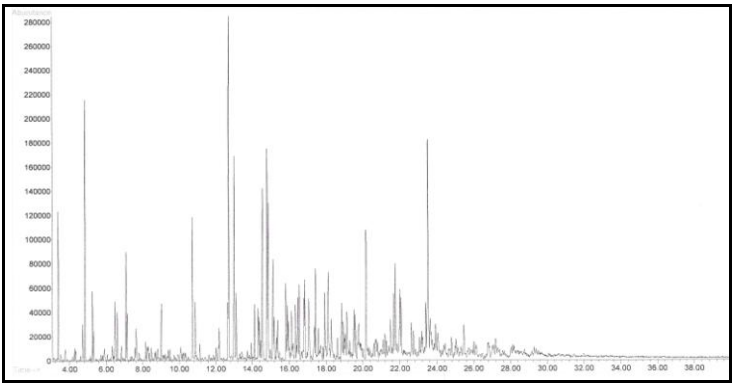

Figure 2. GC/MS chromatogram of sediment TRK13 sediment (dried in oven).

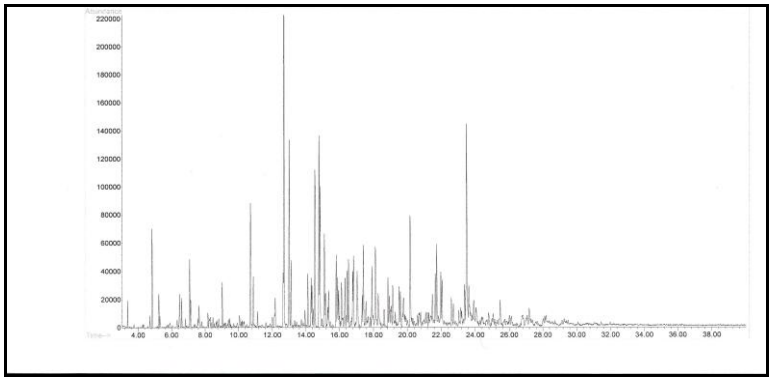

Figure 3. GC/MS chromatogram of sediment TRK13 sediment (in freze dryer).

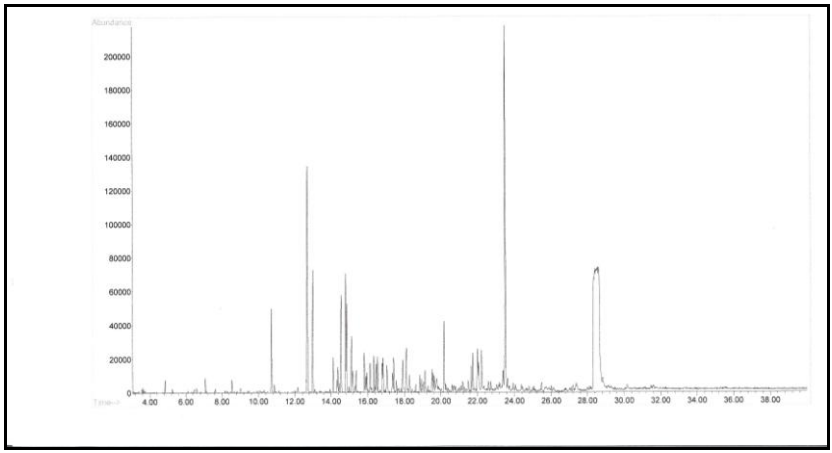

Figure 4. GC/MS chromatogram of TRK14 sediment (wet weight).

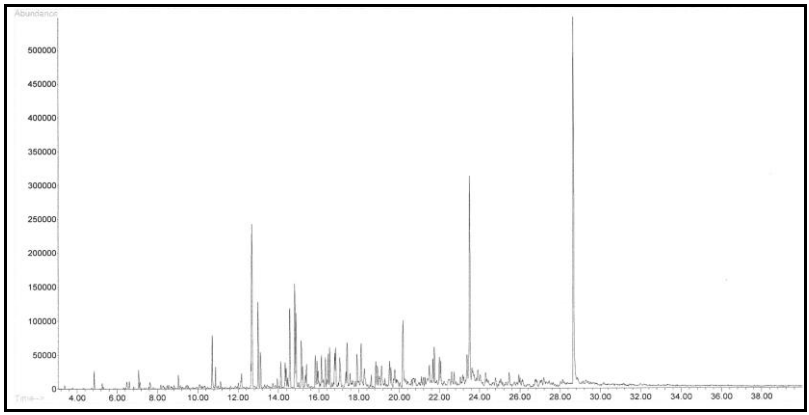

Figure 5. GC/MS chromatogram of TRK14 sediment (dried in oven).

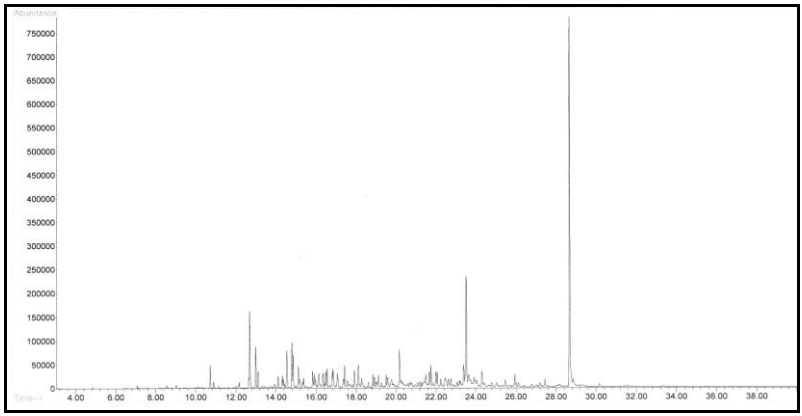

Figure 6. GC/MS chromatogram of TRK14 sediment (in freeze dryer).

The number of detected compounds using GC/MS are listed in Tables 2 and 3.

Table 2. Detected component in TRK13 sediment.

Technique / Components	Wet weight	Oven	Freze dried
Aliphatic			
Linear alkanes	6	13	11
Branched alkanes	3	5	7
Cyclic	0	8	3
Aromatic			
Mono ring	1	18	13
Two rings			
Naphtalene derivatives	15	16	18
Biphenyl derivatives	4	9	4
Three rings			
Anthracene derivatives	3	6	3
Phenanthrene derivatives	8	5	7
Benzofurane	1	2	0
Dibenzofurane	1	0	2
Fluoranthene derivatives	1	0	1
Fluorene derivatives	4	5	5

Table 2. Detected component in TRK14 sediment.

Technique / Components	Wet weight	Oven	Freze dried
Aliphatic			
Linear alkanes	3	10	9
Branched alkanes	4	4	0
Cyclic	0	0	1
Aromatic			
Mono ring	5	17	4
Two rings			
Naphtalene derivatives	11	10	12
Biphenyl derivatives	1	4	4
Three rings			
Anthracene derivatives	1	4	2
Phenanthrene derivatives	6	5	6
Dibenzofurane derivatives	2	2	2
Fluoranthene derivatives	1	1	1
Fluorene derivatives	1	1	1

The detected petroleum component numbers in TRK 14 sediment are high for aliphatic group in oven but aromatic group in freeze dried sediment sample.

Conclusion

The problems of the determination of oil pollution in sediment are: the loss of PAH components during the heating and extraction process and also applied distillation techniques. Hydrocarbons evaporate according to following sequence: low molecular weight components evaporates readily. Native PAHs were lost dramatically for the lower molecular weight PAHs, relatively volatile components such as naphthalenes.

This study shows that the process applied for the extraction of sediments significantly affect on the results. The best results are obtained with freeze drying technique.

Different laboratory were not used the same extraction technique for the determination of oil pollution in sediment.

This study show that the extraction technique dry and wet weight sediment significantly affect on the results. The best method for drying found in freze dryer technique.

In the method described in literature have a serious lack. The findings showed that the method used in this determination were not give similar results for this purpose the methods must be standardized.

Özet

Bu çalışmada sedimentte petrol kirliliği tayininde kurutma tekniğinin rolü incelenmiştir. Yaş metotta sodyum sülfat ile kurutma esnasında Soxhlet ekstraksiyonu tam olmadığı, buna karşı etüvde kurutmada uçucu petrol komponentlerinin kaybolduğu, ayrıca liyofilizasyon tekniğinde uygulanan alçak basınca bağlı olarak sedimentteki petrol miktarında kayıplar olduğu saptanmıştır. Bu kayıplar genelde 1-3 aromatik halkalı bileşiklerde görülmüştür. Literatürde bu konuda fazla bir çalışma yoktur. Bizim tespitlerimize göre en iyi teknik liyofilizasyon tekniğinin olduğu kanaatına varılmıştır fakat yine de uçucu petrol komponentlerinde kayıplar vardır. Bu sebepten dolayı bu konuda yeni bir teknik geliştirme zorunluğu vardır.

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