II. Uluslararası Ekoloji ve Cevre Sorunları Sempozyumu, 5-7 Kasım 1992, Ankara: 93-95

6 Kasım, A-Seksiyonu: 2. Oturum: 10.50-11.10

## **ENVIRONMENTAL EFFECT OF OIL FIELD FIRES IN THE GULF** "BLACK RAIN" IN TÜRKİYE Hunay EVLİYA, İlyas DEHRİ\* Alec GAİNES, Nilgün KUBİLAY, Cemal SAYDAM\*

\* Cukurova University, Research Centre for the Environment, Adana 01330, Turkey

\*\* Middle East Echnical University, Marine Sciences Institute, PK 28, Erdemli 33731 Icel, TURKEY.

ABSTRACT: "Black Rain" precipitated near Adana - 1500 km. north east of Kuwait City was collected in the vicinity of the city of Adana (37° 00'N, 35° 20' E on 25 th February 1991 It is suggested that "Black Rain" contained products from burning of fields which were trapped by an anticlockwise (cylonic) atmospheric eyre and carried westwards. It is possible that the products originated from the burning oil fields. Little low boiling organic materials was present in the rain. But alkannes above C22 were detected by GC and polynuclear aromatic hydrocarbons by their fluorescence. The content of iron was significant and the rain. Beyond our expectations. Was basic.

Precipitation of this nature has not previsously been recorded in the region and no local source can be found. Rain samples contained from 80 to 800 mg/l of suspended material and their colour varied correspondingly. The particular sample whose analysis is undertaken was ideed black: It was obviously oily with a characteristic colour. It contained 675 mg/L suspended material of which 270 mg/L was extractable and organic. Rain samples had pHs in the range 7.8 to 9.0 (whereas. at this time of the year. Normal rain samples have pHs in the range 6.5-8.2) Under the circumstances it has been assumed that the cleaginous nature of the precipitation arose from burning of Kuwait or northern Iraqı oil fields (AVHRR satellite observations, 1991).

KÖRFEZDEKİ PETROL SAHASI YANGINLARININ ÇEVRESEL ETKİLERİ TÜRKİYE'DEKİ "SİYAH CAMUR"

ÖZET: Çevre Araştırma Merkezi, Çukurova Üniversitesi tarafından 25 Şubat 1991 günü Kuwait City'den 1500 km mesafedeki Adana şehri (37°00' kuzey '53° 20' Batı) civarına yağan "Siyah Yağmurdan" numuneler toplandı. Siyah çamurun, yanmakta olan petrol sahalarından çıkan maddelerin saat yönünün tersine dönen (siklonik) bir atmosferik hava hareketine kapılarak batıya sürüklendiği düşünüldü. Yağmurun içerisinde az miktarda kaynama noktası düşük organik maddeler bulunuyordu. Ancak, GC ile C22 üzerinde hiç bir alkalın veya poli-nükleer aromatik hidrokarbon tespit edilemedi. Yağmur içerisinde belirgin oranda demir olup beklentilerin aksine yağmur büyük ölçüde olağan özelliklerdeydi.

Bu şekilde bir yağış bölgede daha önce hiç kaydedilmemişti. Ayrıca civarda buna neden olabilecek bir kaynak bulunamadı. Yağmur örnekleri 80 ile 800 mg/l asılı madde ihtiva etmekte ve bunların renkleri de konsantrasyona göre farklılık göstermekteydi. Analizi yapılan örneğin rengi siyahtı. Belirgin bir şekilde petrol ihtiva etmekte ve buna bağlı karakteristik koku vardı. İçerisinde 675 mg/l asılı madde vardı. Bunlardan 270 mg/l ayrılabilir ve organik cinstendi. Yağmur örneklerinin pH değerleri 7.8 ile 9.0 arasında değişmekteydi. (Halbuki o mevsimdeki normal yağmur örneklerinin pH değeri 6.5-8.2 arasındadır). Bu gözlemler ışığında yağmurun petrollü görünümü Kuveyt veya Kuzey İrak'ta yanan petrol kuyularından kaynaklandığı kabul edilmiştir. (AVHRR uydu gözlemleri. 1991).

#### 1. INTRODUCTION

THE PARTY OF THE P

It is suggested that "Black Rain" precipitated near Adana, -1500 kam north of Kuwait City-on 25 th February 1991 contained products from burning oil fields which were trapped by an anticlockwise (cylonic) atmospheric gyre and carried westwards. It is possible that the products originated from northern Iraq. Little low boiling organic material was present in the rain but n-alkanes above C22 were detected by gas chromatography and polynuclear aromatic hydrocarbons by their fluorescense. The content of iron was significant and the rain was basic.

Figure 1 shows the gas chromatogram obtained from a hexane extract of "Black Rain" which fell and was collected in the vicinity of the city of Adana (37° 00' 20'

E) on 25th Feruary 1991,

Rain samples contained from 80 to 800 mg/l of suspended material and their colour varied correspondingly. The particular sample whose chromatogram is shown in Figure 1 was indeed black; it was obviously oily with a characteristic colour. It

Çerkezköy bir zamanlar küçük bir ziraat kasabası iken son 10 yıl içinde bir sanayi kenti haline gelmiştir. Kasabanın hemen altında başlayan bölgede irili ufaklı 69 tekstil, otomativ, elektromekanik, plastik, kimya, metal, ayakkabi, un ve yağ fabrika ve atölyeleri atıklarını hiç bir işlem uygulamaksızın doğrudan Çorlu deresine vermektedirler (3). Derenin rengi, tekstil fabrikalarının kullandıkları boyanın rengine göre zaman zaman mavi, kırmızı v.s. değişmektedir. Kirlenmiş bir durumda kenarlarında sadece yer yer Ph. australis ve Lepidium sp. bulunarak Çorlu kasabasına kadar 39 km. aktıktan sonra Çorlu'da bulunan tekstil, deri, margarin, otomotiv, un, yağ, elektromekanik, metal makinaları ve diğerlerinden oluşan 170 irili ufaklı fabrikanın attığı ve buna ek olarak Çorlu'nun kanalizasyonu ile çok yüksek düzeyde kirlenerek Ergene nehrine ulaşmaktadır (3,4). Çerkezköy'den Çorlu'ya kadar hiçbir bentik makroomurgasız grubuna rastlanılmamıştır. Sadece az sayıda su yüzeyinde atmosferik 02 soluyan birkaç ergin Corixidae ve Collembola vardır. Çorlu'dan sonra ise suda yalnızca hayvan ve insan kaynaklı koliform bakteri bulunduğu bildirilmiştir (4). Ergene nehrine kadar 50. km. boyunca derede nötralizasyon, çökelme, absorbsiyon, oksidasyon ve seyrelme gibi nedenlerle iyileşme beklenirken ne yazık ki bu görülmemektedir.

# 1. WELCH, P.S., Lidmnological Methods, Mc Graw-Hill Book comp.

2. ZAJIC, J.E., Water Pollution, Disposal and Reuse, Margel Dekker, Inc., New Inch., New York, 381 pp, 1948

3. Anonymous, Environmental Profile of Turkey, Environmental Problems York, Vol. I, 73-87, 1971.

Foundation of Turkey, Ankara, 1989, 327 pp. 4. EMİR, B.D., F., OLGUN, T., KIRGIZ, H., GÜHER, M., TUĞRUL, C., UZUN, Çerkezköy-Çorlu Bölgesinde Çorlu deresi Çevre Kirlenmesinin Incelenmesi, Çevre Sempozyumu, Çorlu, Tekirdağ, 12. s. 1991. contained 675 mg/l of suspended material of which 270 mg/l was extractable and organic. Rain samples had pHs in the range 7.8 to 9.0 whereas, at this time of the year, normal rain samples have pHs in the range 6.8 to 8.3.

2. BLACK RAIN

Precipitation of this nature has not previously been recorded in the region and no tocal source can be found. Under the circumstances it has been assumed that the oleaginous nature of the precipitation arose from burning Kuwait or northern Iraqı oil - fields (AVHRR satellite observations, February, 1991). Comparison of the gas chromatogram of the "Black Rain" with that obtained under the same conditions from a known sample of Kuwait crude oil having a characteristically low pristane/phytane ratio shows the oil composition of the "Black Rain" to be consistent with its postulated origin as a heat-treated (pyrolysed) crude oil. Traces of n-alkanes are readily observed tough they are not significant til in C22. Thus, virtually all low boiling material has been removed. Peaks not seen in the chromatogram of the crude oil-nor seen in chromatograms of other Middle East crudes-having residence times of 68.1 mins. and 50.7 mins., for example, must presumably have been formed by samples of "Black Rain" contained up to 560 ppm of iron (Atomic Absorption Spectrometry). This should be compared with concentrations of 3 ppm and 30 ppm which have been found respectively in hexane soluble material and in asphaltenes from Kuwait, Turkish and Iraqian crudes (1). Should all the iron in the "Black Rain" have arisen from burning crude oil, its high concentration would indicate that combustion was virtually complete (2), One does not know to what extent evaporation of metal from the well head and scavenging of ironrich Saharan dust sometimes present in our atmosphere contributed to the iron content of the "Black Rain", The vanadium/nickel ratio of the material suspended in the "Black Rain", was much lower than that usually found in Kuwait crude (1,3). A previous study of tar residues from a burning oil tanker also found diminished vanadium: nickel ratios (1) and the phenomenon may be a characteristic consequence of oil fires. The "Black Rain" fluoresced. Emmission intensities, compared to those of chrysene, indicated that hexane soluble material contained 4 mg/l of polynuclear aromatic hydrocarbons. No fluorescence by substituted benzenes could be detected; like the low-boiling material, such compounds had evidently been removed by the fire. Figure 2 shows that the wavelengths of the maximum excitation, 315 nm, and of the corresponding emission maximum excitation, 315 nm, and of the corresponding emission maximum, 365 nm, were much lower than those observed in Kuwait crude- but similar to the fluorescense wavelengths of samples of Iraqian crudes previously examined (1). It is possible that the larger polynuclear aromatic hydrocarbons became strongly absorbed on particles of soot. More practically, the observed fluorescence by polynuclear aromatic hydrocarbons reminds one that the "Black Rain" is very probably carcinogenic. Normal rain samples had dissolved silicate values in the range 0.2-15.5 uM (varies seasonally) whereas the Black Rain contained 38.2 μM dissolved silicate (Auto-analyzer). This may indicate the transportation of a different type of aerosol particulate to the region during the Black Rain episode.

Perhaps the most interesting observation is the simple fact that "Black Rain" was precipitated 1500 kms north west of Kuwait City and 500 kms west of northern Iraq a few days after the oil-fields were fired. It has been estimated that smoke formation from the oil-fields extends only to a height of 3 kms and travels eastwards (2). Immediatly before the precitation of the 25 th February an anticlockwise (cyclonic) atmospheric gyre was centred over the eastern Mediterranean and extended to the Persian Gulf (personal communication, Turkish Metereological Office). Presumably combustion products from the burming oil-fields were tpapped by the gyre and transported eastwards. This would be easier to understand were the "Black Rain" from northern Iraq rather than from Kuwait. It is obviously possible that similar weather patterns could carry "Black Rain" westwards in future. In fact, rain falling in mid-April was also

### REFERENCES

- 1. SUNAY, B. M., Distribution and Source Identification of Petroleum Hydrocarbons in the Marine Environment, Ph. D. Thesis, Middle East Technical University, 1982.
- 2. SMALL, R.D., Environmental Impact of Fires in Kuwait, Nature, 350, 11-12, (1191).
- 3. BAKER, M. JENIFER, in The Ecological Effects Of Oil Pollution On Littoral Communities (ed Cowell, E.B.) 72-77 (Applied Science Pubhishers Ltd, Essex, England, 1971).
- 4. HAHN, J., Environmental Effects of the Kuwaiti oil field fives, Environ. Sci. Technol.

Vol. 25, No: 9, 1991.

Figure 1: Gas chromatogram of the Feb. 25, 1991, black rain in Turkey

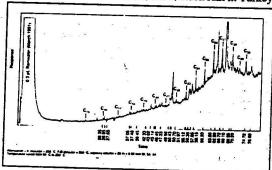


Figure 2: Gas chromatogram of the Feb. 25, 1991, black rain in Turkey

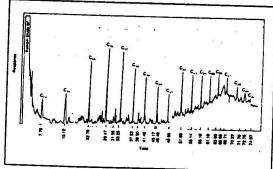
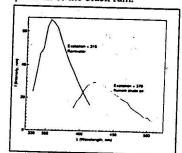


Figure 3: Fluorescence spectrum of the black rain.

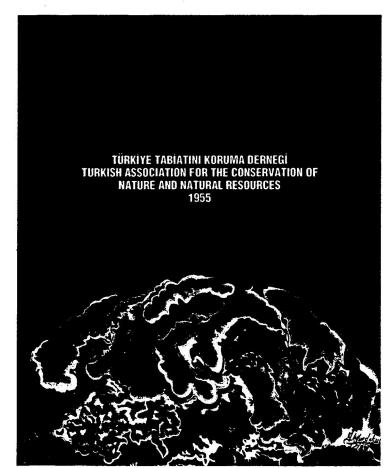


TÜRK-ALMAN KÜLTÜR İŞLERİ KURULU YAYIN DİZİSİ

1993 Nr.: 3 SCHRIFTENREIHE DES TÜRKISCH-DEUTSCHEN KULTURBEIRATES

## 2. ULUSLARARASI EKOLOJİ VE ÇEVRE SORUNLARI SEMPOZYUMU

2. INTERNATIONALES SYMPOSIUM ZUR ÖKOLOGIE UND UMWELTFRAGEN 2. INTERNATIONAL SYMPOSIUM OF ECOLOGY AND ENVIRONMENTAL PROBLEMS



EDITÖR: PROF.DR. İLHAMİ KİZİROĞLU