The Variability of Lead and Aluminium in Atmospheric particulates over the Eastern Mediterranean

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Abstract

The first long-term, land based (36° 33' 54 " N and 34° 15' 18" E) sampling of the atmosphere over the Eastern Mediterranean Sea has demonstrated the dominance of Sahara desert particles. Atmospheric samples , collected on Whatman-41 filter papers, were analyzed by AAS for Al and Pb as to represent the crustal and anthropogenic inputs respectively. Pulses of desert particles invade the region from March - May and October - November time periods. Contrary to expectations the concentrations of anthropogenic element like Pb reaches maximum levels during the dry season. Analysis of 339 samples collected during the period of August 1991 to December 1992 have also been analyzed by the use of EF diagrams backed up by 3- D air- mass back trajectory analysis. It is shown that different source regions could be identified by the use of EF diagrams enabling us to use such representation to identify different catchment regions.

key words: Mediterranean, Sahara, Enrichment Factor Diagram, Al-Pb, trajectories.

Doğu Akdeniz Atmosferindeki Parçacıklarda Kurşun ve Aluminyum dağılımı

Özet

Doğu Akdeniz atmosferinde karadan yapılan (36° 33' 54" K ve 34°15' 18" D) örnekleme, bölgenin Sahra kaynaklı çöl parçacıklarının etkisi altında olduğunu göstermiştir. Whatman-41 filtreleri üzerinde toplanan atmosferik parçacıklarda Al (karasal kaynakların indikatörü) ve Pb (antropojenik emisyonların indikatörü) analizleri atomik soğurma yöntemiyle ölçülmüştür. Çöl parçacıkları bölge atmosferini episodik olarak Mart - Mayıs ve Ekim - Kasım ayları döneminde kuşatmaktadır. beklenenin aksine antropojenik elementlerin (örn. Pb) konsantrasyonu yagış olmayan mevsimde maksimum ortalama değerine ulaşmaktadır. Ağustos 1991 ve Aralık 1992 zaman aralığında toplanan örneklerdeki (339 adet) elementlerin değişimi ZD (Zenginleşme Diyagramları) ve üç günlük geri trajektoriler yardımıyla açıklanmıştır. Ölçümü yapılan elementler için potansiyel kaynak olan bölgeleri ZD yardımıyla tanımlamak mümkün olmuştur.

anahtar sözcükler: Akdeniz, Sahra, Zenginleşme Diyagramı, Al-Pb, trajektoriler.

Introduction

The importance of assessing the inputs of trace elements from atmosphere to the Mediterranean basin attached to a continuous sampling strategy has been one of the main goals of the Co-ordinated Mediterranean Research and Monitoring Programme (MEDPOL) (UNEP,1989 and 1992). Such sampling has been undertaken by various institutions along the western basin at various land based stations. And they have shown wide variation of the trace metal concentrations in atmospheric particulates sampled daily both at a remote western Mediterranean coastal station (Bergametti et al., 1989) and on board ship (Dulac et al., 1987). Yet, apart from dust pulse episodes sampled by the Israeli scientists Yaloon and Ganor (1979) and the shipboard samples collected by Chester et al. (1981), no land based atmospheric sampling of the eastern basin has been reported.

The most comprehensive study of the atmospheric particulates in the Mediterranean Sea has been realized within the context of EROS 2000 (European River Ocean System), confined to the Western basin. The results of this study has clearly shown that the atmospheric input of material to the basin is as important as the riverine input (Martin et al., 1989). At present the Turkish rivers of Seyhan, Ceyhan and Manavgat located along southern Turkey as the only riverine sources of material to the eastern basin. These inputs, in future, will also be reduced as the fresh water requirement of the Middle East states increases. Therefore in the future the atmospheric input to the Eastern Basin will remain to be the only source that can act on the biogeochemical cycles of the elements within the basin along with the oceanographic processes. This emphasizes the importance of possessing knowledge of the long term variations of the atmospheric concentrations of those trace elements known to affect biogeochemical processes directly. The only long term study of the atmospheric particulates for the Eastern Mediterranean atmosphere has been published by Kubilay and Saydam (1995). The authors mentioned the importance of the Sahara desert input over the basin and shown that the end members of the atmospheric particulate varies in accordance with such inputs. In fact, Gilman and Garrett (1994), describing the Mediterranean heat budget, have also stressed the importance of the radiative forcing by mineral aerosols. Their work has shown that allowance for the seasonal variability of aerosols over the Mediterranean, rather than employing a constant aerosol attenuation factor, improves the calculation of the radiation budget of the Mediterranean.

Materials and Methods

The details of the atmospheric sampling station, sampling strategy and the experimental procedures have been explained in detail by Kubilay and Saydam (1995a,b). In summary, the atmospheric sampling tower constructed from the skeletons of two 20 foot commercial containers is located at the harbor jetty of the Institute in Erdemli (36° 33' 54" N and 34° 15' 18" E). To collect the total size spectrum of the particles model GMWL-2000 (General Metal Works Inc., Ohio) hi-vol, 1 m^3 min^{-1}, pump was used. Flow rates were monitored by a calibration kit (model PN G25) provided by the manufacturer. Whatman 41 (20.3x25.4 cm) filters (Whatman Int. Ltd., England) were used for collecting samples by the hi-vol pump. To minimize contamination, filters were always manipulated in a clean laminar-flow bench with the use of the teflon coated forceps and disposable nylon gloves. Blanks were obtained at regular intervals by placing the filters inside the filter holder when no air was drawn through them. Samples and blank filters were stored in polyethylene bags until analysis. One quarter of each filter was cut off and placed into a PTFE beaker, digested with HF/HNO_3 acid mixture at 120°C and subsequently made up to 25 mL volume with 0.1 N HNO_3. Milli-Q double distilled water (DDW) was used throughout the analysis. Digested samples were analyzed for their trace metal contents by a computer controlled GBC-906 model (GBC Scientific Equipment Pty Ltd, Australia) atomic absorption spectrometer (AAS) equipped with a deuterium lamp. Both flame and flameless modes of the AAS were utilized with the attachment of FS3000 and PAL3000 autosamplers, respectively.

The blank contributions from Whatman 41 filter papers for Al and Pb were less than 10% of the mean concentrations of the elements throughout the 17 months collection period. The accuracy of the analytical technique was tested by analyzing Community Bureau of Reference (BCR)--Brussels, standard reference material light sandy soil (CRM 112). The analytical precision were approximately 5% for Al and Pb

The operational trajectory model developed by the European Center for Medium-Range Weather Forecasts (ECMWF) center in Reading, England was applied to3-dimensional analyzed wind fields acquired from the MARS archive of ECMWF. Three days backward calculations were performed starting at midday (12 00 UT) and arriving at the collection point at 850 and 500 hPa barometric levels.

Results and Discussions

Table 1 summarizes the geometric mean concentrations and ranges (corrected for blanks)of Al and Pb for a total of 339 atmospheric particulate samples both for during Aug 1991 - Dec 1992 and for different seasons. Before attempting to explain the variability of Al and Pb, one compares the results summarized in Table 1 with comparable atmospheric sampling programs carried out over the Mediterranean basin in order to see the effect of geographic position on the trace metal composition of the aerosols in the coastal Mediterranean atmosphere. The major difference in the average composition of atmospheric particulates is that particulates from the eastern basin had higher mean concentrations of crustal element, Al, and lower mean concentrations of anthropogenic element, Pb.

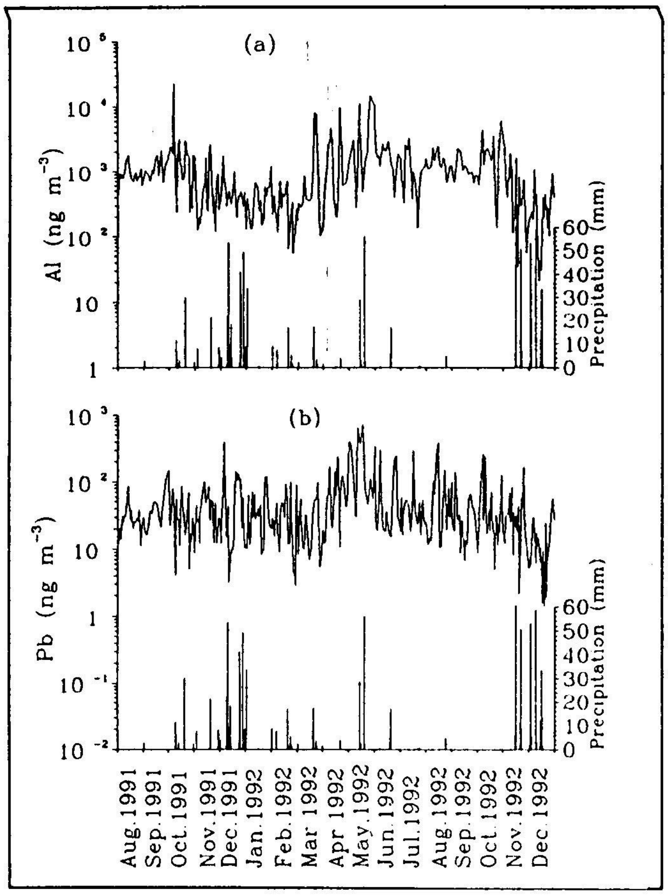
Due to local traffic emissions the land based coastal stations show much pronounced Pb concentrations than those observed at shipboard collections (Chester et al., 1993) and remote stations like Corsica (Bergametti et al., 1989). The observations of low concentrations of Pb, compared to those observed at land based stations in the western basin, show the effect of anthropogenic emissions over the eastern basin to be much less pronounced. This can be explained simply by the presence of industrialized nations which define the northern border of the western basin. In contrast the eastern basin is bounded by a desert belt to the south and east and semi-industrialized and agricultural countries to the north. Thus, the relatively low average Pb concentration compared to western coastal stations is remarkable. But as observed at the western basin during the dry season , summer, the Pb concentration increases. As will be explained in the sequel the summer time increase is entirely due to local sources, most likely increase in the traffic due to tourism industry. The increase in lead concentrations during witer is entirely due to long range transport pollutants.

Table 1. Concentrations of Al and Pb obtained in this study and from various other Mediterranean sites.

	Al	Pb
All Samples Aug91-Dec1992 n=339	685±3.05(21-22560)	30±2.8 (1.4-730)
Winter Dec-Feb n=91	270±2.34(21-1780)	20±3.1 (1.4-400)
Summer June-Sep n=103	1120±1.7(130-3435)	34±2.32(6.7-390)
Transition seasons March, Apr, May Oct- Nov n=145	850±3.4(33-22570)	36±2.82(2.1-730)
Blanes[1]	390	50
Cap Ferrat[2]	370	58
Tour du Valat[3]	380	56
Corsica[4]	168	16
Med.Sea[5]	936	10.5

concentrations are in ng m^{-3}.
1. Chester et al.,(1991).
2. Chester et al., (1990).
3. Guieu (1991).
4. Bergametti et al., (1989).
5. Chester et al., (1993).

Figures 1 (a-b) illustrates the graphical representation of the tempoal variation in the concentrations of Al and Pb in atmospheric particulates collected during Aug. 1991 to Dec.1992, representing the variations in crustal and anthropogenic components. The figures also depict local rainfall, showing scavenging of precipitation to be effective in winter, spring and autumn but not during summer, which is dry period. The most remarkable feature of the entire sampling period was the marked but sporadic variations in the concentrations of both Al and Pb during the course of the transitional months (March, April, May, October and November). Alpert et al. (1990) explained this as being due to the approach of intermonthly cyclonic routes towards the African coast during March. These become much more pronounced in April when most cyclones move along the north African coast sweeping through the sources of mineral aerosol and consequently carrying abnormal concentrations of Al over the sampling region. The variations in the composition of atmospheric particles over the eastern basin during this period were entirely governed by the approach of cyclones and their associated fronts which, most of the time were coupled to rains and followed by strong northerly, cool and dry winds (Martin et al, 1990). In this study, the sporadic pulses originating from the Sahara and Middle East deserts as a result of the synoptic scale fronts have been detected by coupling the behavior of the geochemical tracers (Al and Pb) with the air mass back trajectories throughout the March-May and October-November periods. The variation in the lead concentration can also be expressed in terms of Enrichment Factor (EF) diagrams where its possible to observe the daily variations of each sample as a function of both Al and Pb concentrations. The EF of an element has been calculated by using equation;



$$EF = \left(\frac{C_{Pb}}{C_{Al}}\right)_{sample} \Big/ \left(\frac{C_{Pb}}{C_{Al}}\right)_{crust}$$

In which the crustal ratio of C_{Pb}/C_{Al}=0.00015 was used that is given by Taylor (1964). The EF value of 10 is used to distinguish between two types of particulate trace metals in the atmosphere. The average EF value <10 is taken as an indication of crustal source and EF>10 is considered to indicate that significant proportion of an element has a significant non-crustal source. This approach together with the use of 3D air mass back trajectory analysis will be used for the comparative demonstration of the utilization of EF diagrams as opposed to daily variations in the change in the concentration of element of interest.

Fig.1.Daily variation of the atmospheric concentrations of (a) Al; (b) Pb for Aug 1991-Dec1992. The amount of the local precipitation is reported at the bottom of the figure.

The data on elemental composition of atmospheric particulate from the nineteen samples collected during April 1992 have been plotted both in terms of concentrations of Al and Pb (Fig 2) and in the form of EF diagram (Fig.3). The 3D backtrajectory analysis for each sample at 850 hPa level have also been plotted on Fig 4. The selection of the month April is based on the fact that, April is a typical month during which the maximum variations of atmospheric elemental concentrations is reached. It can be seen that from Fig.2 that there exists an inverse relation between Pb and Al. Lead concentration shows an order of magnitude variation during April within the brackets of (10.7-402 ng m^{-3}) and for aluminum within (198-9859 ng m^{-3}).

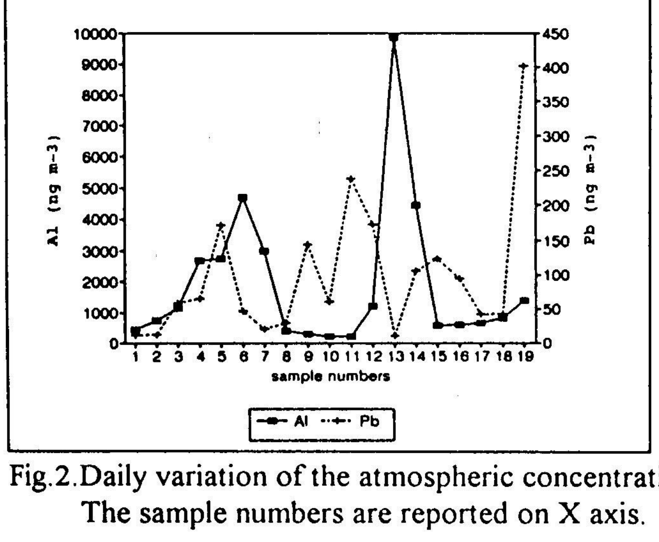
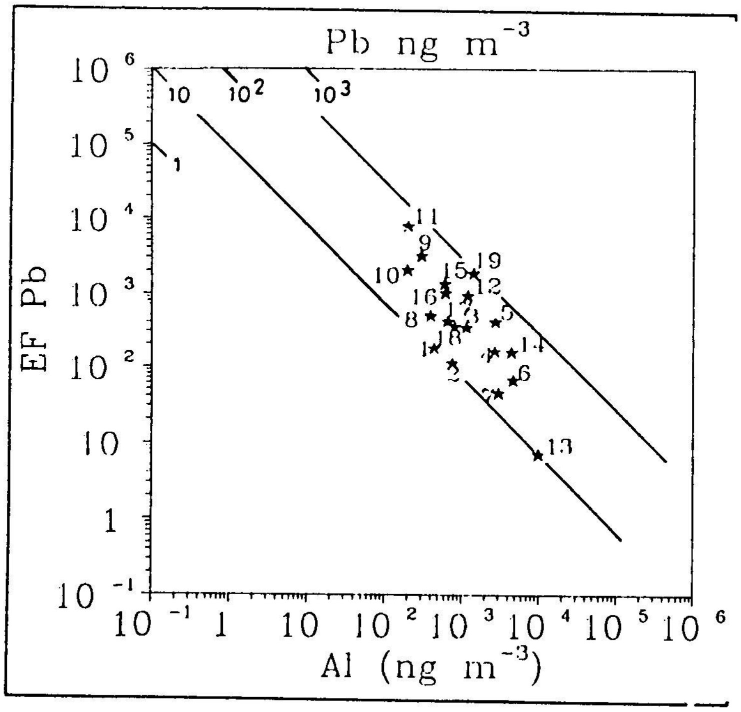


Fig.2.Daily variation of the atmospheric concentrationsof Al and Pb for April 1992. The sample numbers are reported on X axis.



The largest contrasting concentrations are reached for both elements during 20 and 29 April corresponding to sample numbers of 13 and 19 on Fig.2.

But Fig 2 can not show anything further than such large inverse correlation between Pb and Al. Thus if these two elements are to be used to define contrasting catchment areas the 3D three days air mass back trajectories for these samples should be originated from different and contrasting catchment regions.

Fig.5a illustrates the air mass back trajectories for the sample 13 collected during 20-21 April 1992. It can be seen that all trajectories transports dust from central Anatolia and from Sahara.

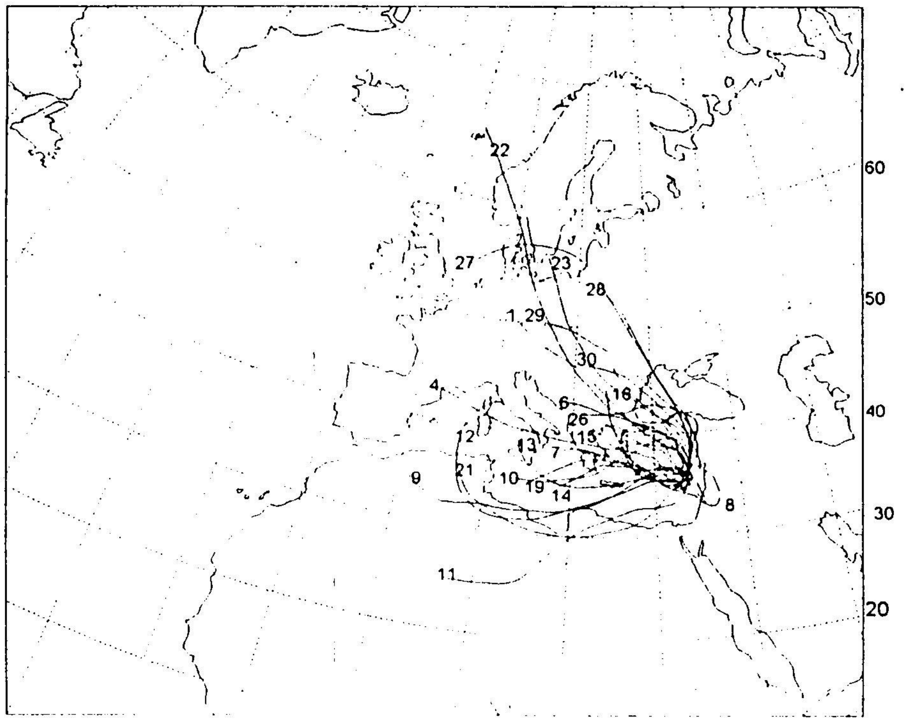
Fig.3.The EF diagram for the samples collected during April-1992.
The sample number of each point is marked on the diagram.

On 21 April 1992 as shown in Fig. 5b all trajectories are shifted towards south and originated from Sahara hence resulting with very high crustal component and very low anthropogenic input as represented on Fig.2 by the relative positions of the Al and Pb.

The other extreme has been reached for samples 18 and 19 collected during 28-29 April 1992. The air mass back trajectory analysis for this sample as shown in Fig. 6(a-b) for 28 and 29 April respectively, clearly indicates northerly catchment regions resulting with totally different concentrations than the case observed during 20-21 April.

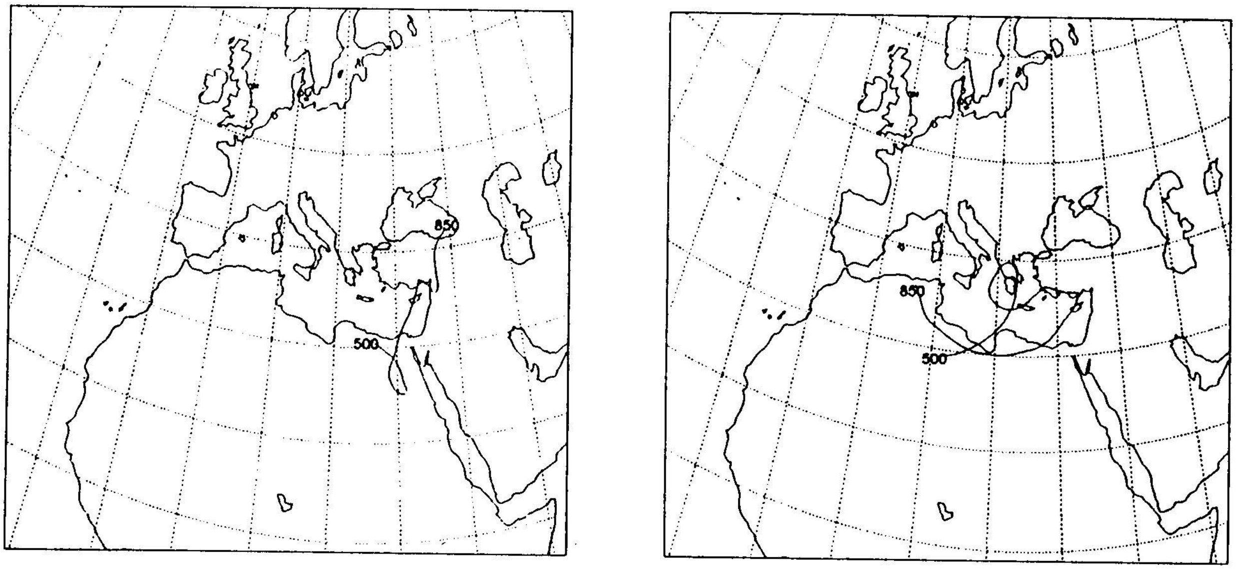
The EF diagram (see Fig.3) also puts the sample 13 to very unique position defining a region specific to desert inputs on EF diagram. The position of sample 19 defines the maximum lead concentration but its EF value is not the highest measured during April. As it can be seen from the Fig.3. points that fall on equal concentration lines could have EF values differ in two order of magnitude. For example, the concentration of Pb for the samples 1 and 13 are 12 and 10.7 ng m^{-3} and concentration of Al are 440 and 9860 ng m^{-3}, respectively whereas corresponding EF values are 176 and 7. The controlling factor on these two order of magnitude change in EF values are the concentration of Al that represents amount of crustal material in the atmosphere. The air mass trajectory for the point 1 (see Fig4) is originated from the Eastern Europe. The positions of these two points on the diagram exemplifies the dilution of anthropogenic component by the crustal component of the atmospheric particulate in the atmosphere. Such clear separation of the plot of samples on EF diagrams clearly demonstrates that such diagrams can be used to delineate specific regions for contrasting catchment regions.

Further it would be possible to delineate such regions both in terms of Al and Pb concentration as well as EF values.



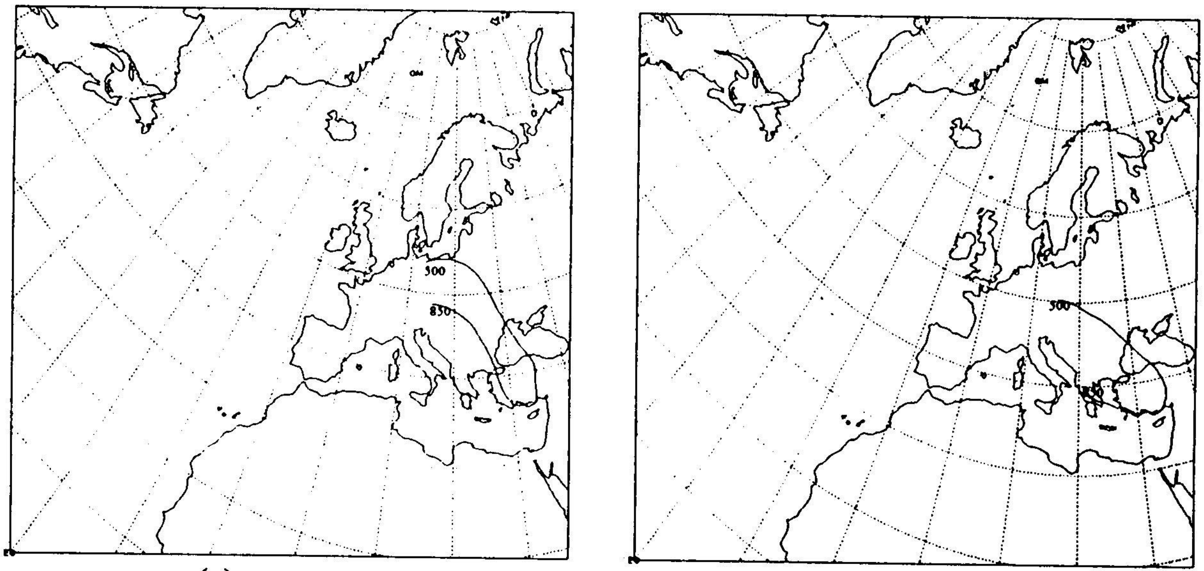
Sample no	Date
1	1/4/92
2	2/4/92
3	3/4/92
4	7/4/92
5	8/4/92
6	9/4/92
7	10-12/4/92
8	13/4/92
9	14/4/92
10	15/4/92
11	16/4/92
12	17-19/4/92
13	20/4/92
14	21/4/92
15	22-23/4/92
16	24-26/4/92
17	27/4/92
18	28/4/92
19	29/4/92

Fig.4.Three days back trajectory analysis of air mass reaching to sampling site during April 1992 at 850 hPa level. Dates corresponding to sample numbers indicated on the right.



(a) (b)

Fig.5. Air-mass back trajectories arriving at 850 and 500 hPa levels.
(a) 20 April, 1992 (b) 21 April, 1992



(a) (b)

Fig.6. Air-mass back trajectories arriving at 850 and 500 hPa levels.
(a) 28 April, 1992 (b) 29 April, 1992

The seasonal variation in concentration and EF of the Pb showed a marked difference as shown in Fig.7 (a-c). During the dry season the contribution of local sources in the absence of major inputs from desert regions and the diurnal cycle of the sea breeze tends to concentrate the points on the EF diagram within a certain cluster (Fig.7a). In other words, the composition of mineral dust during summer over the eastern basin, is very stable. The formation of thermal stratification acts as a barrier between the upper atmospheric layer in which there is occasional transport of Desert dust and the lower layer in which there are locally produced atmospheric particulates. The breakdown of the thermal stratification during diurnal cycles together with the effects of local sources, increase in the tourism activity, increases the lead concentrations in the atmospheric particulates during the dry summer months. Sporadic rains during this period can disturb the slow but steady build up of elements as shown on Fig.1b.

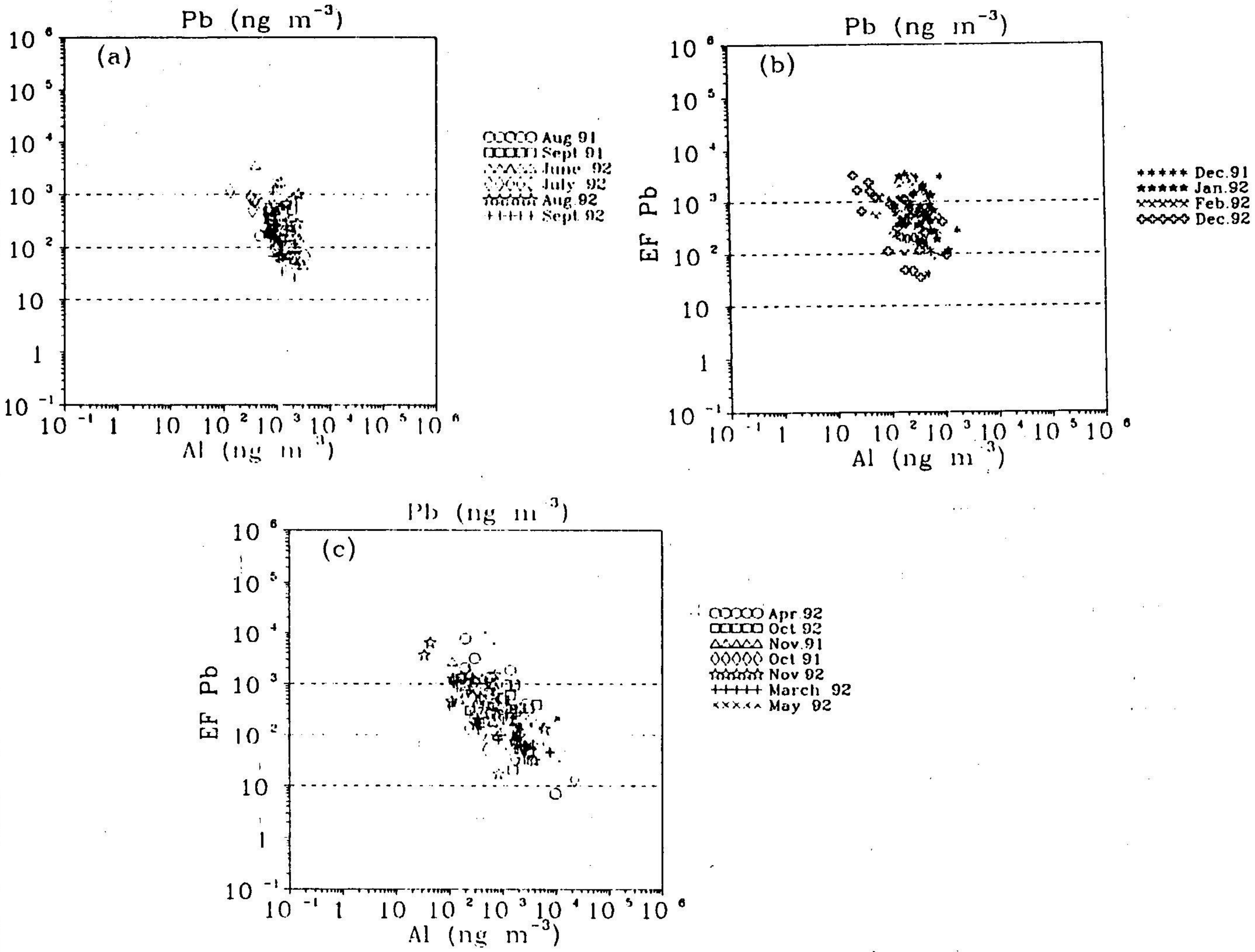


Fig.7. The EF diagram for Pb;

(a) Samples collected during summer months.

(b) Samples collected during winter months.

(c) Samples collected during transitional months

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