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# Airborne Material Collections and Their Chemical Composition Over the Black Sea

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**The chemical composition of the Black Sea aerosol was studied during the July 1992 CoMSBLACK 92 cruise on board R/V *Bilim*. It has been shown that the chemical composition of the Black Sea aerosols can change very rapidly in accordance with changes in the wind regime. The influence of the Saharan desert particles can alter the elemental concentrations of trace metals. The result has been summarized on Enrichment Factor diagrams to permit comparison with previous and future studies. The atmospheric input of oxidized nitrogen ($NO_3$+$NO_2$–N) can reach 13% of the total inorganic nitrogen input of the Danube. Lead (Pb) input reaches 39% of this riverine input. Such loads can play an important role in the present state of the sea.**

The Black Sea, the world's largest anoxic basin has a very restricted circulation through the strait of the Bosphorus and is subjected to heavy commercial use. The present state of the sea is a good example of a marine ecosystem that has been under considerable stress from the riparian states especially through their riverine inputs (Mee, 1992; Kideys, 1994). Although much effort has been spent in monitoring the hydrological properties of this anoxic basin there exist very few investigations related to the chemistry of the atmospheric particulate matter over the Black Sea (Dzubay *et al.*, 1984; Antonovskiy *et al.*, 1987; Hacisalihoglu *et al.*, 1991, 1992).

Recently, scientists have documented the ecological significance of those elements associated with atmospheric particles deposited onto the sea surface in different marine regions. Hardy and Crecelius (1981) conducted laboratory experiments in which the addition of urban aerosols to relatively unpolluted coastal waters of the Pacific inhibited primary productivity. Comparison of the riverine and atmospheric fluxes of the elements, Pb, Cd, Cu and N to the western Mediterranean has revealed the importance of the atmospheric pathway especially for the open ocean (Martin *et al.*, 1989). There is growing evidence that aeolian transported material, particularly that rich in elements of ecological concern such as Fe, could be important as a trigger of phytoplankton production in the oceans (Duce & Tindale, 1991; Donaghay *et al.*, 1991; Martin *et al.*, 1994).

This paper, based on atmospheric aerosol sampling during the course of a survey of the Turkish EEZ of the Black Sea between 3–25 July 1992 and part of HydroBlack'92, investigated variations in chemical constituents of the Black Sea aerosol. The results obtained from this study form an important contribution towards understanding Black Sea aerosols using the future participation of the riparian states in an atmospheric sampling programme.

## Materials and Methods

Eighteen particulate samples were collected on Whatman 41 (8×10 in) filters, using a standard General Metal Works® hi-vol sampler equipped with a continuous flow recorder. The response of this recorder was calibrated before the cruise with a calibration kit (Model PN G25) provided by the manufacturer. The flow rate of the pump was $1.5 \pm 0.2$ $m^3$ $min^{-1}$. The sampling system was placed at the bow section of the research vessel approximately 6 m above the sea level. During sampling no wind sector controller was used. To eliminate shipborn contamination the bridge was instructed to turn off the sampler whenever the wind direction was greater than 30° from the heading of the ship. Sampling periods of between 12 and 24 h were selected according to weather conditions. Sampling ceased 15 min before hydrographic stations were reached and commenced 30 min after sailing from each station. The samples and the blank filters were kept in polyethylene bags before and after sampling until analysis. All sample manipulations were carried out in a laminar-flow clean hood. One quarter of the filters were placed in PTFE beakers and digested with HF/$HNO_3$ acid mixture at 120°C and the resulting solutions made up to 25 ml volume with 0.1 N $HNO_3$ (Saydam, 1981). Milli-Q double distilled water (DDW) was used throughout the analysis. Digested samples were analysed for their trace metal contents by a GBC-906 model atomic absorption spectrometer (AAS) equipped with a deuterium lamp. Either flame or flameless modes of AAS were utilized when necessary. Blank corrections were made on the results before reporting.

To test the quality of the obtained data a reference sample (Community Bureau of Reference—BCR, Brussels) was analysed. Results obtained from analysis of the reference samples (BCR No. 142 which was a light sandy soil) together with certified values are shown in Table 1. The reproducibility of the digestion and analytical procedure was assessed from subsamples of seven replicate analyses of a mesh-collected atmospheric particulate sample. Analytical precision were approximately 5% for Al, 4% for Fe, 2% for Mn, 6% for Cr, 6% for Ni, 3% for Zn, 5% for Pb, 5% for Cd, 8% for V, 7% for Co, 5% for Na, 6% for Ca and 7% for Mg.

For the analysis of $NO_3+NO_2$—N and $PO_4$—P, one quarter of the filter papers were placed in beakers with 30 ml of DDW and left for 30 min in an ultrasonic shaker. Concentrations were measured using a Technicon AutoAnalyser according to the methods described by Strickland and Parsons (1972).

Air parcels back-trajectory calculations were evaluated as a basic tool to detect remote sources of the atmospheric particles over the Black Sea. The trajectory model of the European Center for Medium-Range Weather Forecasts (ECMWF) centre in Reading, England was applied to three-dimensional analysed wind fields available at the archive of ECMWF. Three days backward calculations were performed starting at noon (12 00 UT) and arriving at the collection point at 850 and 700 hPa standard pressure levels.

TABLE 1

Results of the BCR sample.

| Element | Determined | Certified |
|---|---|---|
| Cd | 0.25 ± 0.08 | 0.25 ± 0.09 |
| Co | 9.03 ± 0.1 | (7.9) |
| Cr | 77.3 ± 5.3 | (74.9) |
| Ni | 27.2 ± 1.5 | 29.2 ± 2.5 |
| Mn | 529 ± 17 | (569) |
| Pb | 35.9 ± 4.6 | 37.8 ± 1.9 |
| Zn | 99.2 ± 8.3 | 92.4 ± 4.4 |
| $Al_2O_3$ | 90.9 ± 5.9 | (94.8) |
| $Fe_2O_3$ | 29.5 ± 1.4 | (28) |
| MgO | 11.1 ± 0.5 | (10.9) |
| CaO | 47.2 ± 2.2 | (49.4) |
| $Na_2O$ | 6.3 ± 1 | (9.7) |

Values in brackets are not certified. Concentrations for Cd, Co, Cr, Ni, Mn, Pb, Zn in μg $g^{-1}$ and for $Al_2O_3$, $Fe_2O_3$, MgO, CaO and $Na_2O$ in mg $g^{-1}$. There is no certified value for V.

## Results and Discussion

The R/V *Bilim*'s track and the numbers of the samples collected BS3–BS18 (Black Sea), during the course of the cruise are illustrated in Fig. 1. Mean values of the concentrations, enrichment factors (EFs) and ranges of 13 elements for samples BS3–BS18 and the water soluble phosphorus and oxidized inorganic nitrogen are given in Table 2. When calculating the mean concentrations, the data from samples collected in Istanbul (BS1 and BS2) are not included to avoid any bias of the true marine values, instead the averages of these samples are indicated in a separate column. The samples collected at and around the city of Istanbul (BS1 and BS2) are important since any trajectory that transports air mass over the city will be affected by this local emission point.

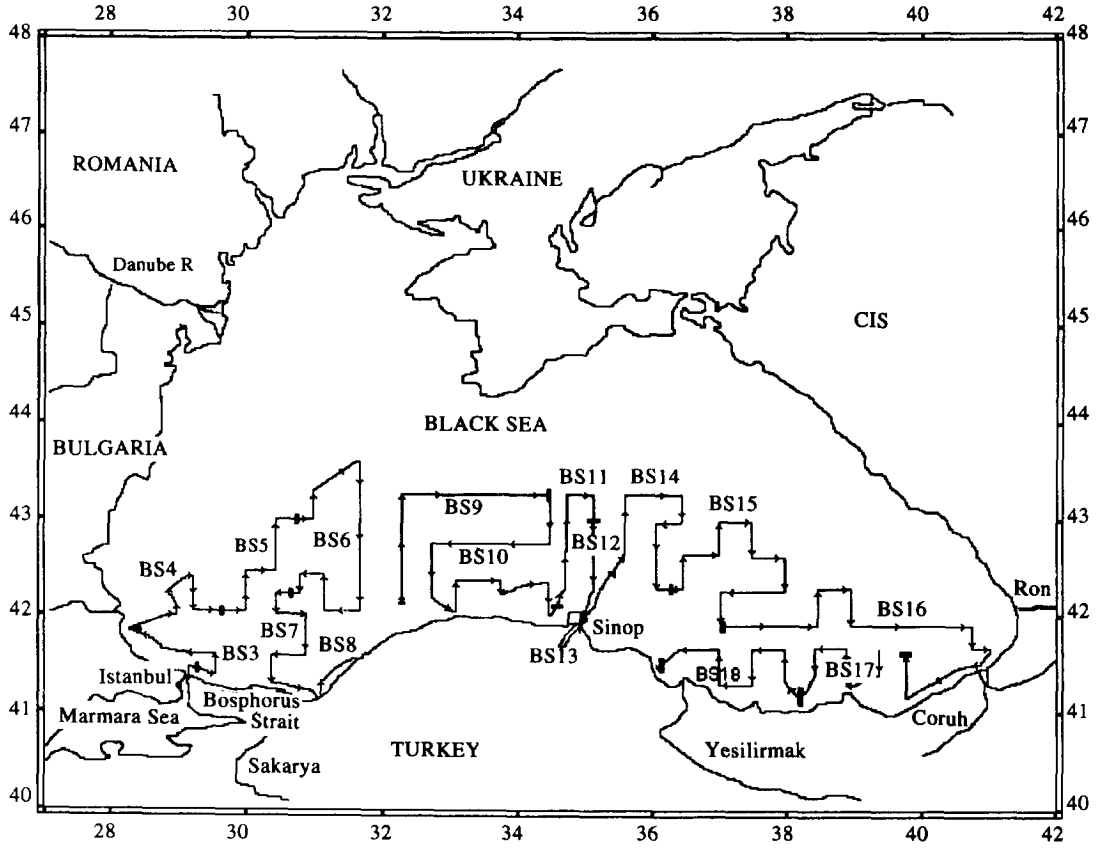



Fig. 1 The ship's track and sampling intervals.

For comparison of the trace metal levels obtained in this study with others from the Black Sea and contrasting marine regions, concentrations of the measured elements are given in Table 3. The average Pb concentration of 19 ng $m^{-3}$ found in this study is consistent with that reported by Antonovskiy *et al.* (1987), of 18 ng $m^{-3}$ measured at a rural background station in the USSR. On the other hand, Hacisalihoglu *et al.* (1992) reported Pb levels much higher than the present average, ranging from 60 to 37 ng $m^{-3}$ for the western and eastern Black Sea respectively. Hacýsalihoglu *et al.* (1992) confined their sampling to the Turkish coast whereas the present sampling region extended into the central Black Sea. Initially, collections were made around the western Black Sea under calm weather conditions when the samples had maximum concentrations of Pb and V. These two elements are associated markedly with petroleum products and such products would be expected at this specific site of the Black Sea for the following reason:

The Bosphorous acts as the neck of a funnel for the entire Black Sea shipping traffic. Any stagnant air mass tends to concentrate such elements as V and Pb over the western Black Sea. Trajectory analyses for samples BS1 and BS5 have shown that short range transport from the north-west was likely to be associated with low wind speeds. The shortness of the trajectories reveals the dominance of the effects of local emissions. The concentrations of Pb and V decreased gradually as the cruise track extended away from the immediate vicinity of the Bosphorous. An order of magnitude decrease in both Pb and V concentrations was observed in association with the storm event of 7–8 July 1992 (see Table 4). Thus, synoptic scale meteorological events can be seen to change elemental concentrations of the Black Sea atmospheric particulate. As can be seen from Table 2, the concentration ranges of the elements are wide, resulting in high standard deviations of the means. The observations of large variations from the mean values for the enclosed marine environment can only be

**TABLE 2**

Elemental concentrations and enrichment factors in the Black Sea atmospheric particulates.

| Element | Arithmetic mean ± SD (geo. mean) (BS3–BS18) | Range | Arithmetic mean. (BS1 and BS2) | EF mean | EF range |
|---|---|---|---|---|---|
| Al | 960 ± 455 (8.40) | (350–1725) | 3980 | – | – |
| Fe | 1380 ± 955 (1070) | (255–3620) | 4160 | 2 | (0.8–7) |
| Mn | 20 ± 20 (15) | (5–90) | 72 | 2 | (0.3–8) |
| Co | 0.14 ± 0.12 (0.1) | (0.01–0.53) | 1.2 | 0.7 | (0.1–3) |
| Zn | 17 ± 16 (13) | (3–70) | 290 | 29 | (3–104) |
| V | 1.15 ± 1.43 (0.27) | (0.01 ± 4.6) | 20 | 1 | (0.3–7) |
| Pb | 19 ± 13 (11) | (1.8–47) | 270 | 172 | (7–759) |
| Cd | 1.45 ± 1.28 (1) | (0.3–4.5) | 2.5 | 1800 | (215–5490) |
| Ni | 4.8 ± 2.7 (4.3) | (2.1–12) | 25 | 8 | (2–32) |
| Cr | 9.2 ± 9 (6.3) | (1.4–34) | 25 | 10 | (1–65) |
| Ca | 600 ± 690 (375) | (132–2400) | 4660 | 1 | (0.2–4) |
| Na | 470 ± 2140 (763) | (66–8790) | 640 | 5 | (0.2–18) |
| Mg | 620 ± 550 (458) | (134–2300) | 1790 | 2 | (0.4–5) |
| $NO_3+NO_2$—N | 0.22 ± 0.09 (0.2) | (0.07–0.5) | – | – | – |
| $PO_4$–P | 0.28 ± 0.31 (0.11) | (0.001–1.51) | – | – | – |

All concentrations are given in ng $m^{-3}$, except $NO_3+NO_2$—N (μg $m^{-3}$).

**TABLE 3**

Concentrations of elements in atmospheric particulates over different marine regions (in ng $m^{-3}$).

| | Western Black Sea* | Eastern Black Sea* | Eastern Mediterranean† | North Sea‡ | North Pacific§ |
|---|---|---|---|---|---|
| Al | 540 ± 240 | 330 ± 220 | 1031 | 294.5 | 21 |
| Fe | 420 ± 230 | 290 ± 190 | 711 | 353 | 18 |
| Mn | 17 ± 7 | 17 ± 11 | 11 | 14.5 | 0.29 |
| Co | 0.25 ± 0.11 | 0.16 ± 0.08 | 0.37 | 0.25 | 0.0076 |
| Zn | 46 ± 29 | 26 ± 17 | 19.2 | 41 | 0.18 |
| V | 2.8 ± 1.0 | 1.8 ± 0.8 | 6.4 | NR | 0.82 |
| Pb | 60 ± 15 | 37 ± 10 | 23.1 | 34.5 | 0.12 |
| Cd | NR | NR | 0.18 | NR | 0.0035 |
| Ni | 4.9 ± 2.9 | 3.0 ± 1.6 | 6.4 | 3.8 | NR |
| Cr | 9.0 ± 2.2 | 8.3 ± 3.5 | 11.2 | 4.7 | 0.91 |
| Ca | 70 ± 880 | ND | 3118 | NR | 240 |
| Na | 1400 ± 1200 | 3900 ± 2900 | 1021 | NR | 5200 |
| Mg | 340 | ND | 844 | NR | 650 |

*Hacisalihoglu *et al.* (1992).
†Kubilay *et al.* (1994).
‡Chester & Bradshaw (1991).
§Duce *et al.* (1983).
NR: Not reported; ND: not detected.

**TABLE 4**

The variations at the concentrations of Pb and V as a function of distance from the Bosphorous.

| Sample No. | Pb | V ($ng\ m^{-3}$) | Distance from Bosphorous (miles) |
|---|---|---|---|
| BS3 | 47 | 4.6 | 10–20 |
| BS4 | 34 | 3.9 | 40–60 |
| BS5 | 24 | 2.5 | 60–90 |
| BS6 | 23 | 1.3 | 60–120 |
| BS7 | 1.8 | 0.6 | 40–60 |

At the Black Sea exit of the Bosphorous the number of commercial vessels was not less than 10 as observed from RV *Bilim*'s 60 nautical mile radar.

explained by the presence of contracting catchment areas of the Black Sea basin. Such assessment can only be quantified by the computations of air mass back trajectories. The calculated air mass back trajectories corresponding to each sample show the variations in the concentrations to be the result of the different origins of the air masses, even during such a short time period.

The present data permit the identification of four types of air mass trajectory. Thus, Table 5 distinguishes episodes.

(a) influenced by Saharan dust,
(b) with mixing of air masses from Anatolia and local marine sources,
(c) with atmospheric input from Eastern Europe, and
(d) with atmospheric input from Russia.

Examples of each type of air mass trajectory are illustrated in Fig. 2(A–D).

*Type A aerosols: North African contributions*

The air masses whose back trajectories crossed North Africa had a unique elemental composition. The example of a Type A air mass trajectory is illustrated in Fig. 2(A). North Africa is a well-known potential source area which supplies soil-derived dust particles to the atmosphere of both the eastern and western parts of the Mediterranean Sea (Ganor & Mamane, 1982; Martin *et al.*, 1990; Dayan *et al.*, 1991). Geochemical tracers coupled with air mass trajectory analysis have verified that air masses originating from this source area also affect the aerosol composition over the Black Sea.

*Type B aerosols: Local contributions*

As shown in Fig. 2(B) the air mass trajectory at 850 hPa originated over the sea surface (local Black Sea), whereas that at 700 hPa originated over Anatolia. The concentrations of trace elements are among the lowest observed during the cruise, implying that the atmospheric contributions from the semi-arid Anatolian peninsula were much less than from the African or European sectors.

*Type C aerosols: Those that have crossed the eastern European mainland (north west)*

A Type C air mass trajectory is illustrated in Fig. 2(C). Elemental contributions from this sector are among the highest especially for such elements as Mn, Zn, V and Pb that are known to be effected by anthropogenic sources. As shown by Hacisalihoglu *et al.* (1991) this sector is an important contributor of both anthropogenic and crustal elements to the atmosphere of the Black Sea.

*Type D aerosols: Russian mainland (north east)*

As illustrated in Fig. 2(D), air masses whose trajectories originated from central Russia influence the atmosphere of the Black Sea. Considering the frequency of the northerly winds during the summer season, this sector is of great importance to elemental composition of the Black Sea. Nevertheless, the elemental analysis of the data shows the contributions of Al (indicator for crustal material) to be less than in other sectors.

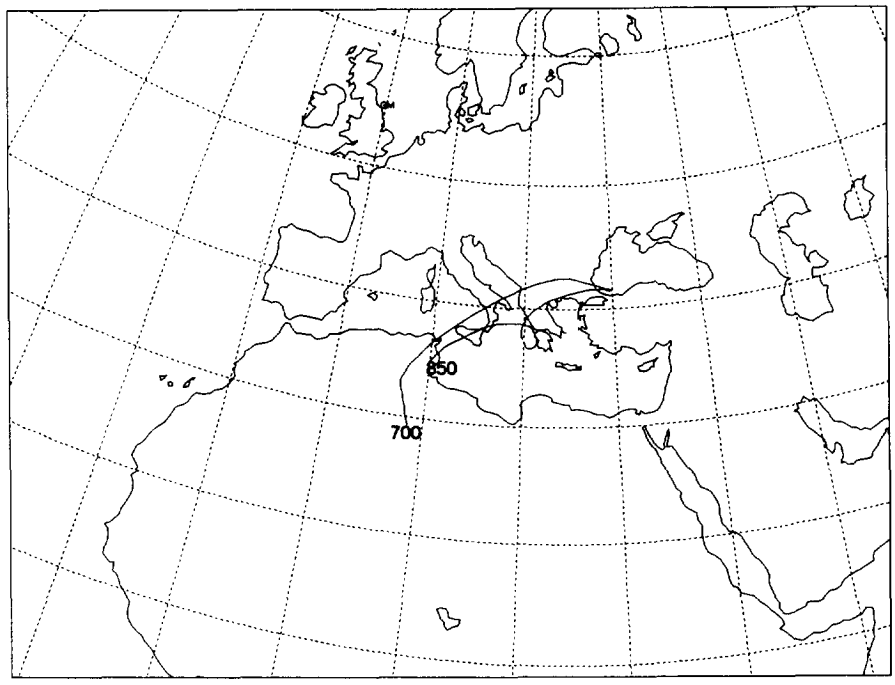
If it is assumed that aerosols over the Black Sea were mainly composed of a four component system, then we might consider our data set to be representative of the Black Sea summer time conditions. The frequencies of the trajectories corresponding to sample collection for the catchment areas of the Black Sea were calculated. The percentage were 10, 19, 38 and 33 for Type A, Type B, Type C and Type D air masses, respectively.

Inter elemental ratios of Al/Fe and Pb/Cd were utilized to differentiate between the sectors. The ratio of Al to Fe for the North Africa sector is 1.3 whereas for the other sectors it is 0.6. Taylor (1964) showed the ratio to be 1.5 for average crustal material. This result implies the existence of anthropogenic sources of Fe in all sectors except North Africa. The values for Pb/Cd were 6, 9, 13 and 22 for North Africa, Anatolia, Russia and Eastern Europe, respectively. These ratios are still lower than the mean ratio of 46 for anthropogenic European emissions (Pacyna, 1983). As a consequence of the decrease by 50% in consumption of leaded gasoline between 1988 and 1991 this ratio was found to have decreased from 35 to 24 in precipitation samples

**TABLE 5**

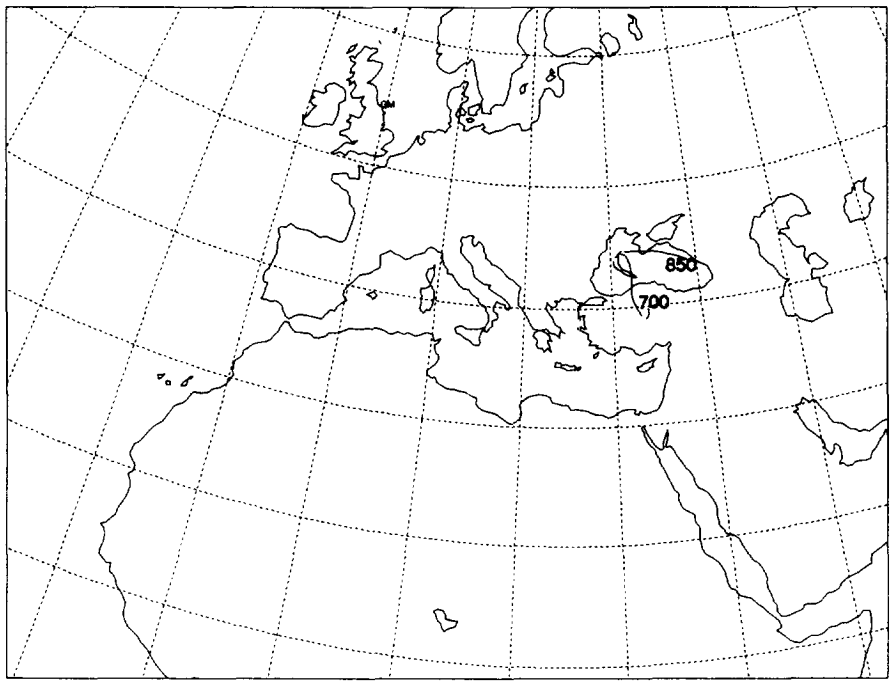
Average concentrations of the elements for different sectors.

| | Al | Fe | Mn | Co | Zn | V | Pb | Cd | Na | Mg | Ca | Ni | Cr |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| North Africa (Type A) | 1400 | 1095 | 13 | 0.10 | 13 | 1.5 | 16 | 2.8 | 3230 | 940 | 635 | 4.8 | 15 |
| Anatolia (Type B) | 920 | 1550 | 13 | 0.11 | 12 | 0.39 | 10 | 1.1 | 760 | 430 | 270 | 4.5 | 7.8 |
| Eastern Europe (Type C) | 1045 | 1780 | 30 | 0.17 | 24 | 1.9 | 29 | 1.3 | 1414 | 670 | 900 | 4.1 | 4.9 |
| Russia (Type D) | 390 | 650 | 17 | 0.17 | 15 | 0.23 | 12 | 0.9 | 780 | 460 | 410 | 6.8 | 14 |




July 8, 1992

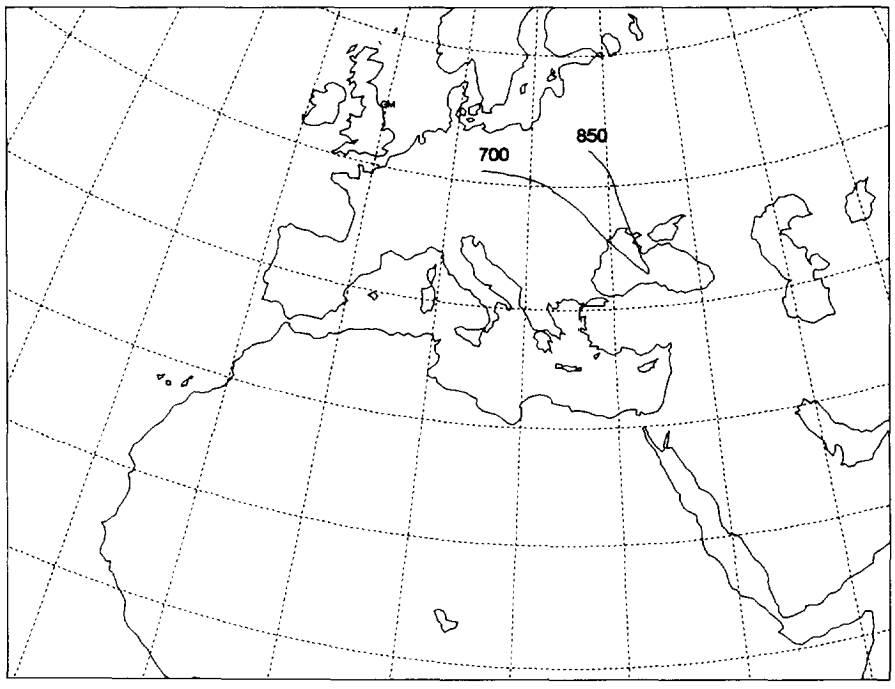
(A)




July 16, 1992

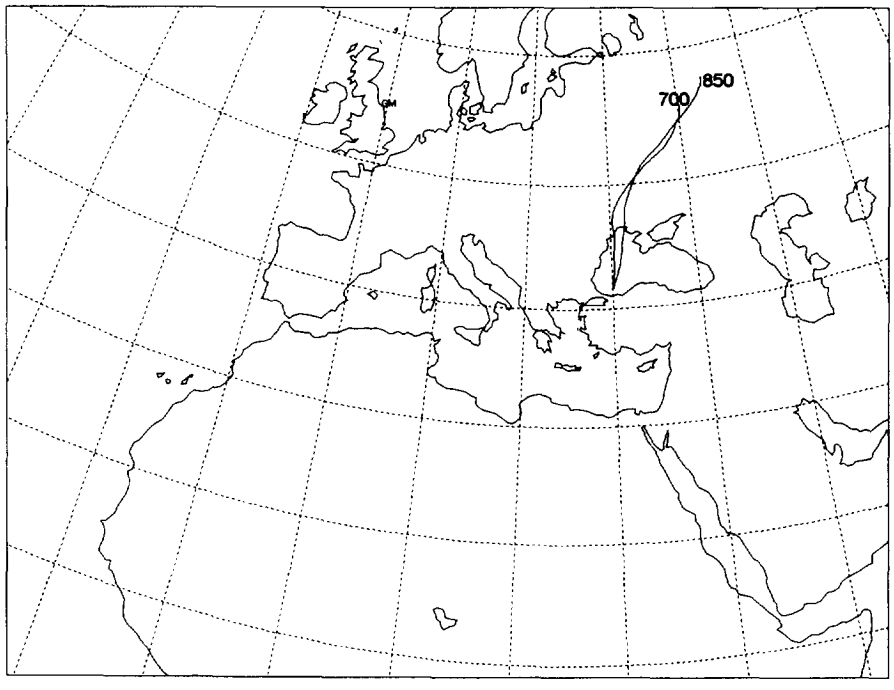
(B)

**Fig. 2** Air mass back trajectory types. (A) Type A air masses, which have originated from North Africa. (B) Type B air masses, local marine contribution at 850 hPa and continental Anatolia contribution at 700 hPa.




July 19, 1992

(C)




July 25, 1992

(D)

**Fig. 2**—*Contd.*

(C) Type C air masses, which have crossed eastern Europe. (D) Type D air masses, which have crossed the Russian mainland.

and the same decrease was postulated for aerosols over France (Nicolas *et al.*, 1992). This does not mean that the same decrease would necessarily be expected throughout Europe. Pacyna and Munch (1987) have shown also that the relative emissions of Pb and Cd from different sources are higher in the western part of Europe than in the eastern part.

Enrichment Factors (EF) and Enrichment Diagrams have been utilized by scientists for the characterization of atmospheric particulate and the nature of their sources (Rahn, 1976; Chester *et al.*, 1981, 1983, 1989, 1993; Guerzoni *et al.*, 1989). The EFs of the elements have been calculated according to the equation given below:

$$EF = (E/Al)_{air}/(E/Al)_{crust},$$

and presented in Table 1. $(E/Al)_{air}$ and $(E/Al)_{crust}$ are the concentrations of an element E and of Al in the atmospheric particulate and in crustal material (Taylor, 1964), respectively. Although there exist anthropogenic materials in the atmosphere (e.g. fly ash) having elemental composition similar to the crust and geographical variabilities in elemental composition of the crust, as a first order approximation we used the EFs of the elements to distinguish natural and anthropogenic sources. Fe, Mn, Co, V, Ca and Mg with mean EF values close to 1 are considered to be non-enriched elements. Pb, Cd and Zn with mean EF values greater by two orders of magnitude (up to 104 for Zn, 750 for Pb and 5490 for Cd) are obviously of anthropogenic origin. Although Ni, Cr and Na have mean EF values of about 10, their maximum values are greater than 10. They comprise the intermediately enriched elements in the Black Sea atmosphere.

EF values of the elements together with Al concentrations, Al being assumed to be a reference element for soil derived particulate, have been utilized for the construction of EF diagrams (see references above). Such diagrams can be used to describe the distribution of Pb in the atmospheric particulate over different seas as illustrated in Fig. 3. It can be seen that the EF of lead changes by two orders of magnitude change for an order of magnitude change in Al concentrations. The results of previous work from adjacent seas and from the North Pacific help to define the mixing–dilution field of the Black and Mediterranean seas. Samples collected over the North Pacific Ocean (Duce *et al.*, 1983) define a region isolated from the others. The remoteness of a sampling site from continents reduces the relative contributions of crustal elements. It is impossible to talk about the remoteness from major source areas of any sampling site in the Black or Mediterranean seas. Therefore, in Fig. 3, regions in which concentrations of a European urban dominated component and a Saharan crust dominated component are mixed will plot to the right of the North Pacific field. For example, the maximum EF's and the associated Al levels observed for samples BS 1, 2, 3 and 13, which are known to be affected by anthropogenic sources, together with samples collected at a land based station at the north-western Mediterranean coast, Cape Ferrat (Chester *et al.*, 1989) all plot to the right of the mixing-

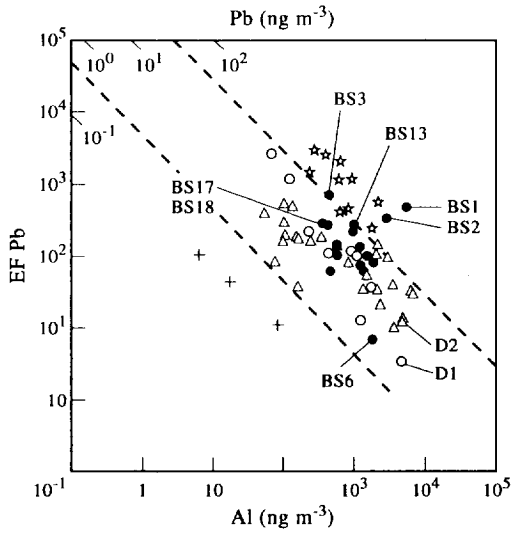



**Fig. 3** The composite EF diagram for Pb. Samples BS1 and BS2, collected while the ship was at dock in the Bosphorous in Istanbul (10 million population), have unique places on the EF diagram delineating a region which has suffered from anthropogenic inputs. BS3 collected at the coast of the western Black Sea and BS13 collected while the vessel was in dock at Sinop (200 000 population) where there is little industrial activity. The rest of the samples show a variation of two orders of magnitude in EF with variations in the Al levels. The composite EF diagram for Pb incorporates the data from the present study (solid dots) and individual populations; i.e. those from the North Pacific (Duce *et al.*, 1983) (plus signs), the eastern Mediterranean (Chester *et al.*, 1981) (empty circles), the central Mediterranean (Correggiari *et al.*, 1989) (triangles) and the western Mediterranean (Chester *et al.*, 1989) (stars). The left hand broken line that indicates the minimum concentration of Pb (0.87 ng $m^{-3}$) is drawn on the basis of the samples collected on board in the central Mediterranean. The right hand broken line that indicates the maximum concentration of Pb (47 ng $m^{-3}$) is drawn on the basis of the samples collected in the present study excluding samples BS1 and BS2. The field enclosed by 45° broken lines represents the atmosphere over the Black Sea and the Mediterranean in which the concentration of Pb was mixed and diluted with anthropogenic and crust dominated particles. Sample D1, identified as pure desert input by Chester *et al.* (1981), sample D2 defined as crust dominated aerosol by Guerzoni *et al.* (1989) and sample BS6 whose air-mass back trajectory originates from the Sahara all fall in the same region of the diagram. The highest EFs for Pb within the mixing–dilution region are seen to belong to samples BS17 and BS18 whose back trajectories originate from the Russian mainland. This sector has the lowest Al concentration, thus the dilution of the Pb concentration with crustal material is minimal and it is this that results in the high EF values.

dilution region, Thus, any sample that suffered from local inputs whose position lies outside the mixing–dilution region on the EF diagram may be identified easily. The behaviour of Pb within this region complies with the general trend of enriched elements as described by Rahn (1976), suggesting that every sub region is further controlled by internal mixing and dilution. Thus, the field enclosed by 45° broken lines represents the atmosphere over the Black Sea and the Mediterranean in which the concentration of Pb was controlled by mixing and dilution of the components of particles (whether anthropogenic, crustal or natural) of European and desert origin. With the help of the composite EF diagram for Pb it is possible to delineate three different marine regions. These regions are:

(a) remote marine areas (Pacific),
(b) regional seas (Black Sea and the Mediterranean),
(c) coastal areas influenced by local emission (coast of the Black Sea and the Mediterranean).

Recently, it has been well stated that the ecosystem of the Black Sea suffers from land-based pollution. The main consequences of the pollution of this fragile marine environment are eutrophication and the decline of biological resources. The Danube, supplying as it does 53% of the total riverine input and being the major source of pollution for the entire Black Sea basin, forms an excellent basis for comparison with the amount of material transported by atmospheric pathways. It is reported that the Danube annually introduces 340 000 t of inorganic nitrogen and 4500 t of Pb (Mee, 1992). Since it is verified that about 78% of the detrital load of fluvial input to the Black Sea is deposited near the mouth of the river (Brewer & Spencer, 1974) the effect of this addition is important only for local areas. Sur *et al.* (1994) have shown that due to the rim current the Danube effluent meanders along the coast of Bulgaria and Turkey. The major shelf–open sea interactions that take place beyond the mouth of the Sakarya river may diminish much of the pollutant properties of the riverine water. This further highlights the importance of the atmospheric input that can effect the entire basin. The material flux transported through the atmosphere of the Black Sea has yet to be quantified because of the lack of a continuous sampling strategy. The data obtained during ship-borne sampling in this study are insufficient to observe either the temporal variation of elemental concentrations or to estimate annual depositions to the sea surface. Yet, the recognition that atmospheric deposition affects a wider area than river input has forced us to make some assumptions and estimate the relative importance of the atmospheric deposition. Accordingly, we have calculated the total (wet+dry) depositions of ($NO_3$+$NO_2$—N) and of Pb. Dry deposition fluxes are estimated simply by multiplying average element concentrations given in Table 2 by deposition velocities. Since we did not have rain samples from the region, it was not possible to calculate the wet deposition directly. So, wet deposition fluxes have been estimated from particulate concentrations of the element, the annual rainfall and the scavenging ratios. During the calculation of the fluxes, the dry deposition velocities and the scavenging ratios were obtained from the literature (GESAMP, 1989) and the calculated fluxes were extrapolated to include the whole basin ($4.2 \times 10^5$ km$^2$). The estimated atmospheric deposition of $NO_3$+$NO_2$—N is 44 100 t yr$^{-1}$ (23% in dry form, 77% in wet form) which corresponds to 13% of the total inorganic input by the Danube outflow. These deposition amounts include only the oxidized form of nitrogen. It has been stated that about the same amount of water soluble form of oxidized nitrogen in aerosols and about 30% of the dissolved oxidized nitrogen concentration in precipitation in the western Mediterranean region exists as $NH_4^+$ (Alarcon & Cruzado, 1990; Loye-Pilot & Morelli, 1988). The total atmospheric deposition of Pb has been estimated as 1740 t yr$^{-1}$ (14% in dry form, 86% in wet form) which comprises 39% of the Pb input by the Danube outflow. Thus it can be seen that the atmospheric inputs of particulate matter can significantly contribute to the Black Sea ecosystem.

## Conclusions

The elemental compositions of the atmospheric particulate over the Black Sea have been shown to vary by an order of magnitude in association with the synoptic scale weather system. It has also been shown that, even during summer, samples originating from the Sahara can reach the Black Sea. An order of magnitude increase in the crustal elements and a decrease in the anthropogenic elements is characteristic of air masses originating from the Sahara.

It has been shown that any stagnant air mass over the Western Black Sea tends to increase the concentration of elements associated with heavy fuel burning due to the increase in the number of ships through the Bosphorous.

The construction of EF diagrams allows us to identify the aerosol composition of each element specific to the Black Sea. The continuation of aerosol sampling during future cruises will improve these EF diagrams and hence the background levels specific to the Black Sea region, thereby allowing us to define deposition rates for specific elements more precisely.

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