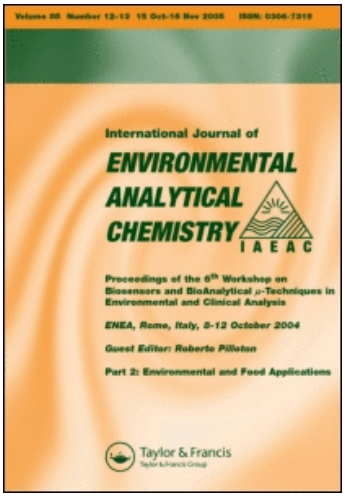

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LEAD AND NICKEL LEVELS IN BLACK SEA AEROSOLS BY ETA-AAS

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Air particulate samples were collected from the Black Sea atmosphere, using cellulose filters in the summer of 1988. Lead and nickel concentrations in aerosols collected at 10 m above sea level were determined by using electrothermal atomization atomic absorption spectrometry (ETA-AAS). Concentrations of Pb and Ni were high in the western part of the Black Sea, owing to strong influence of anthropogenic sources. Lead was highly enriched in the Black Sea aerosols due to the significant contribution of motor vehicle emissions, while Ni was moderately enriched. The Pb/Br ratio was higher than the corresponding ratio in fresh motor vehicle emissions, owing to evaporation of Br from particles. Atmospheric flux of Pb to the Black Sea was higher than riverain flux, while the opposite was observed for Ni.

KEY WORDS: Lead, nickel, electrothermal atomization atomic absorption spectrometry, atmospheric particulate matter, Black Sea.

INTRODUCTION

In the past two decades, it has been established that atmospheric pollution due to automobile emissions is one of the major sources of heavy metal contamination in urban areas. Among the heavy metals, Pb has the highest yearly emission rate due to its application as anti-knock agent in gasoline, from the use of lead arsenate as a fungicide on crops, and its emission during industrial combustion processes[1,2]. Lead levels in urban areas are well studied, but Pb measurements in rural areas are less complete[3]. Furthermore, trends in lead concentrations may be interesting because Pb is being gradually phased out from gasoline.

Nickel is a marker element for oil burning and can be used to estimate oil-fired power plant particles in the atmosphere.

Source regions for both Pb and Ni are important because they give clues on the long range pollutant transport to the Black Sea atmosphere. Recently pollution of regional seas by atmospheric transport is anticipated. Black Sea, especially the western parts, are surrounded by industrialized countries. Consequently, contribution of atmospheric transport on the pollution of the Black Sea by Pb, Ni and other metals is a worthy study.

EXPERIMENTAL

Sample collection

Atmospheric samples were collected during the Black Sea cruise of the research vessel R/V Knorr, between June 3–16, 1988, and during the summer monitoring cruise of the Turkish research vessel R/V Bilim, between August 26 and September 12, 1988. The sampling system was placed to the foredeck at approximately 10 m above sea level. Nineteen daily atmospheric particulate samples were collected during the two cruises at various points in the Black Sea, mostly along the Turkish coast. Sampling locations during the cruises are shown in Figure 1.

Air particulate samples were collected on double Whatman-41 (cellulose fiber) filters using a General Metal Works standard high-volume sampler, at a flow rate of about 45 m^3 hr^{-1}. Sampling duration was approximately 24 hours. Sampling was continuous and pumps were stopped only to change filters. A wind sector controller was used to avoid contamination of samples by the activities on the ship. Blank filters were treated similarly with sample filters, except air was pulled through for only 1 minute. After collection of each sample, filters were heat sealed in acid washed polybags. Sample and blank filters were handled under HEPA filtered air.

Reagents

Chemicals used were lead and nickel nitrate AA grade from Aldrich and analytical grade nitric acid from Merck. Solutions were prepared with double-distilled deionized water obtained from Millipore, Milli-Q Water Purication System and stored in polyethylene containers. All polyethylene material was cleaned by soaking in 10% (v/v) nitric acid solution (1 part conc. HNO_3 + 9 parts H_2O) for at least one day prior to their use.

Sample preparations and analysis

The Pb and Ni were leached from samples by slight modification of the procedure developed by Jernigan *et al.*[4] A 60–70 mg section was cut from the filter and transferred into an acid washed polyethylene beaker containing 10 ml of 0.1 M HNO_3 and treated in an ultrasonic cleaner (Branson model 2200) for approximately 15 min. The sample solution was then analyzed by electrothermal atomization AAS, using a PU9390 electrothermal atomizer coupled to a PU9200 atomic absorption spectrophotometer, which was equipped with a deuterium hollow cathode lamp for background correction and a PU9380 furnace autosampler. Electrothermal atomizer parameters used in determinations of Pb and Ni are given in Table 1. Sample preparations were carried out in a class-100 clean area and the method of standard additions were used throughout analysis.

Data quality

Lead concentrations in 5 filters collected in Dec. 12, 1989 from Ankara atmosphere were measured by XRF technique at London University, Imperial College, and by

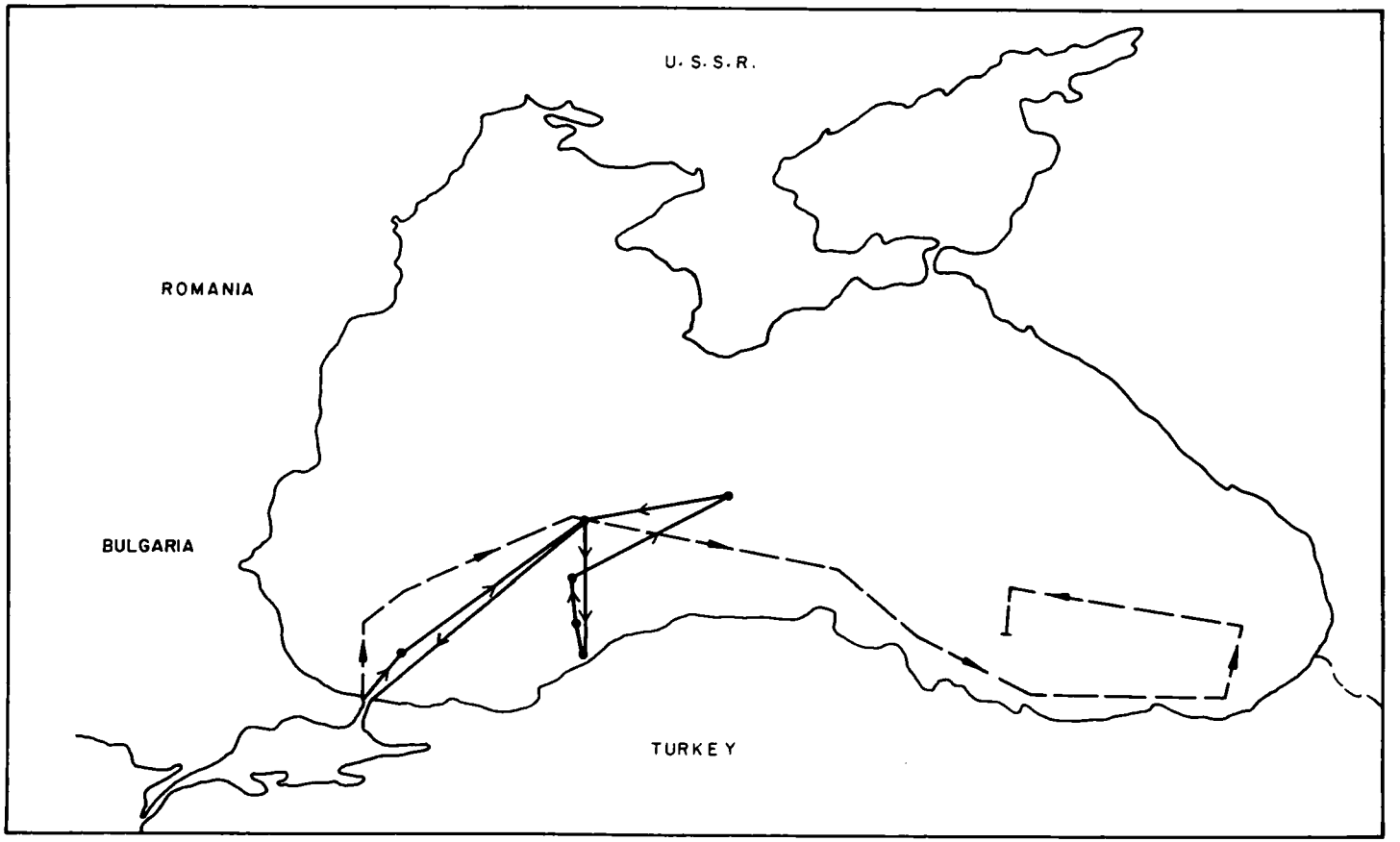

Figure 1 Cruise tracks of R/V Knorr and R/V Bilim during sampling periods. The dashed line indicates the track of R/V Bilim and solid line indicates that of R/V Knorr.

Table 1 Instrumental operating conditions

Parameter	*Pb*	*Ni*
Wavelength (nm)	283.3	232.0
Band pass (nm)	0.5	0.2
Lamp current (mA)	4.0	11.2
Temperature programme		
Drying (5°C s^{-1} ramp)	25–110°C (22 s)	25–110°C (22 s)
Drying, steady	110°C (30 s)	110°C (30 s)
Ashing (100°C s^{-1} ramp)	—	110–1000°C (9 s)
Ashing, steady	700°C (30 s)	1000°C (30 s)
Atomization[a]	1400°C (3 s)	2500°C (3 s)
Cleaning	2700°C (3 s)	2700°C (3 s)

[a] Temperature control mode and zero gas flow.

ETA-AAS technique in our laboratory. The average was 1.38 ± 0.32 $\mu g\ m^{-3}$ for XRF results and 1.51 ± 0.31 $\mu g\ m^{-3}$ for ETA-AAS results. The "*t*-test" was applied and *t* value was 0.84 which means that within 99% confidence level the two averages are similar. This indicates that the digestion procedure involved in ETA-AAS technique does not limit the accuracy.

The accuracy of the standard solutions was checked by measuring Pb concentration in NBS, SRM-1633 fly ash standard reference material. The certified value for Pb was 70 ± 4 $\mu g\ g^{-1}$ of fly ash, while the measured value was 70 ± 9 $\mu g\ g^{-1}$.

RESULTS AND DISCUSSION

Concentrations of both Pb and Ni in the Black Sea atmosphere are given in Table 2 together with similar measurements from the literature. Geometric means and standard deviations were reported, as data for both Pb and Ni were log-normally distributed.

Observed concentrations of both Pb and Ni at the Black Sea are compared with data from regional marine sites (Atlantic Ocean,[5] Western Mediterranean[6]), a remote site in the Equatorial North Pacific, Enewetak,[7] and a continental rural site in Soviet Georgia.[8] In general, elemental concentrations at the Black Sea appear to be intermediate between continental rural sites where local aerosols and long range transported particles affect observed concentrations and remote marine sites where local sources other than ocean do not exist.[9] Nickel concentration at the Black Sea atmosphere is one order of magnitude higher than that measured at the Atlantic Ocean, while Pb concentration is higher than that measured at the Atlantic Ocean, Soviet Georgia, and Enewetak, but comparable with that measured at the Western Mediterranean atmosphere.

Spatial distributions of Pb and Ni concentrations in the Black Sea atmosphere are shown in Figure 2. Concentrations of both elements are different in eastern and western sectors, with much higher concentrations observed in the western part.

Table 2 Concentrations of Pb and Ni measured in the Black Sea atmosphere and in other regions (ng m^{-3})

Sample ID	*Sampling date*	*Pb*	*Ni*
1	04/6/88	82 ± 8	3.6 ± 0.5
2	06/6/88	79 ± 8	1.7 ± 0.1
3	08/6/88	44 ± 4	1.9 ± 0.2
4	09/6/88	39 ± 4	8.8 ± 0.8
5	11/6/88	42 ± 4	2.1 ± 0.3
6	13/6/88	45 ± 4	2.2 ± 0.3
7	14/6/88	52 ± 5	3.4 ± 0.4
8	15/6/88	79 ± 7	—
9	26/8/88	79 ± 7	3.4 ± 0.3
10	27/8/88	58 ± 5	8.0 ± 0.8
11	28/8/88	63 ± 7	8.2 ± 1.1
12	30/8/88	66 ± 7	5.7 ± 0.8
13	31/8/88	54 ± 5	10.0 ± 1.6
14	01/9/88	—	—
15	03/9/88	51 ± 5	5.9 ± 1.2
16	06/9/88	45 ± 4	2.6 ± 0.6
17	09/9/88	34 ± 3	1.9 ± 0.3
18	11/9/88	23 ± 2	1.5 ± 0.3
19	12/9/88	34 ± 3	2.9 ± 0.4
Black Sea (this study)		51 (2)[a]	3.6 (1.9)[a]
Atlantic Ocean[5]		9.9	0.64
Western Mediterranean[6]		38.9 ± 31.8	—
Enewetok[7]		0.12 (0.0019)[a]	—
Soviet Georgia[8]		18	—

[a] Geometric means and standard deviations are given.

Anthropogenic sources of both Pb and Ni are stronger at regions in the west of the Black Sea. Consequently, samples collected at the Western Black Sea are under strong influence of these sources. Concentrations of Pb and Ni measured in the Eastern Black Sea correspond to longer transport of air mass during which a larger fraction of particles and elements associated with them are scavenged out. In addition to that, areas around the Eastern Black Sea are not extensively industrialized. Consequently, air masses moving from these regions to the Black Sea are not heavily loaded with Pb and Ni containing particles.

Crustal enrichment factors (EF_c) of Pb and Ni were calculated using Taylors average crustal abundance table[10] and Al was used as a reference element. The Al concentration was measured in the same samples by Hacisalihoglu *et al.*[11] and found to be 460 ± 250 ng m^{-3}. Average enrichment factors for Pb and Ni were 770 and 10, respectively. The high crustal enrichment factor of Pb indicates that motor vehicle emissions are an important component in the aerosol mass. However, Ni was not as enriched as Pb, indicating that the crustal component has contributed substantially to the observed Ni concentrations. Noncrustal or anthropogenic Ni was mostly due to oil burning in neighboring countries. Crustal and anthropogenic components of Ni were estimated to be 10 and 90%, respectively.

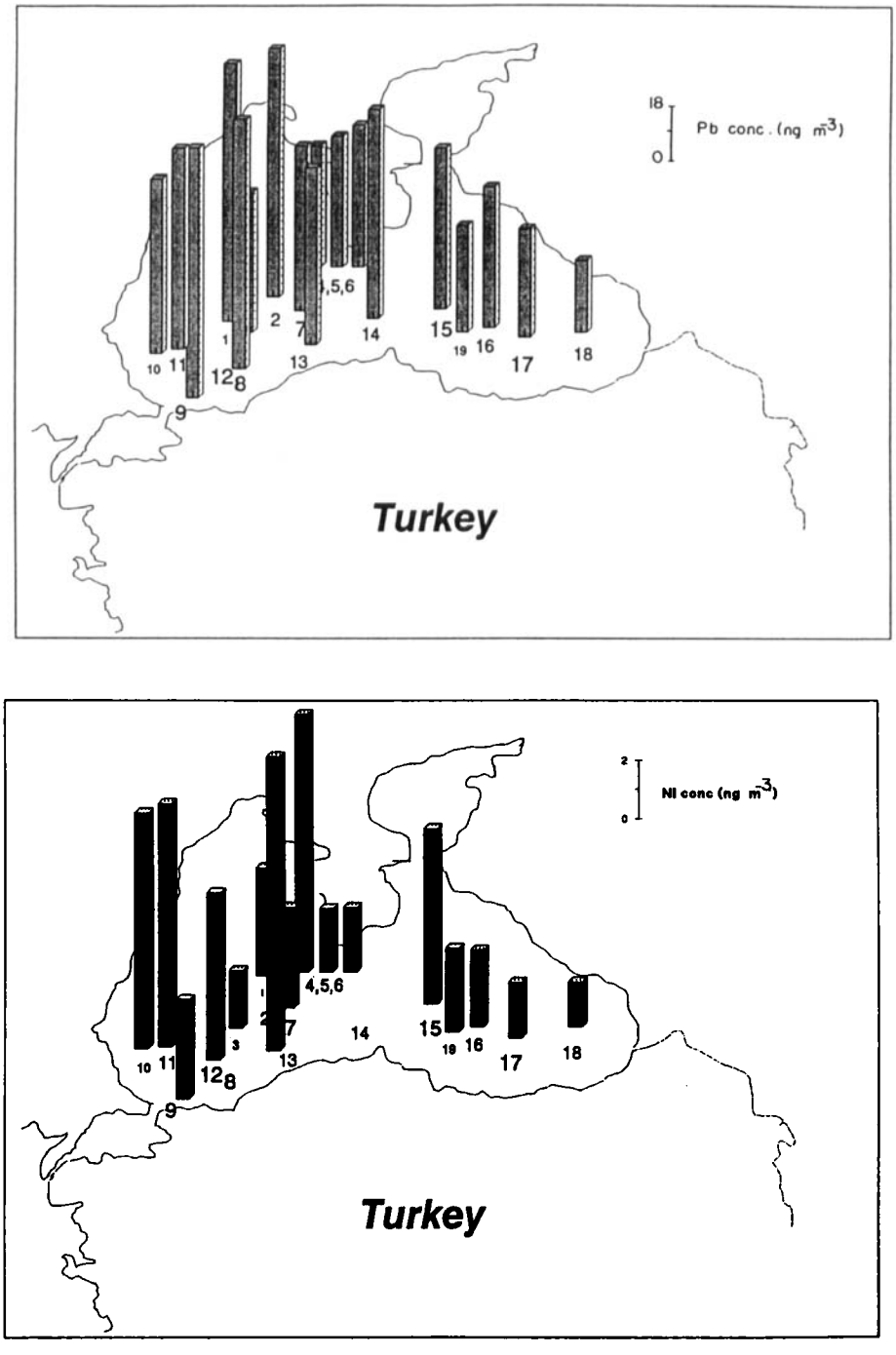

Figure 2 Spatial distribution of Pb and Ni concentrations in the Black Sea atmosphere.

Like Pb, Br in the atmosphere also originates from motor vehicles. The Br concentration was measured in the same samples by Hacisalihoglu *et al.*[11] and found to be 22 ± 20 ng m^{-3}. The relation between Pb and non-sea-salt Br (nss-Br) was studied. Lead is expected to correlate with Br, because both elements are emitted from motor vehicles. However, sea salt particles are known to contribute to atmospheric Br concentrations which must be subtracted from total Br concentration to obtain the anthropogenic Br or the so called "nss-Br"[12]. Observed Pb concentrations exhibit only marginal correlation with nss-Br ($r = 0.34$, and $P[0.34, 10] > 0.1$). The lack of correlation may be owing to (1) chemistry of Br and subsequent loss from particles,[12,13] (2) large uncertainties in the estimation of nss-Br concentrations in the Black Sea atmosphere. Marine contribution to the observed Br concentrations were as high as 50% in some of the samples,[11] subtraction of large fraction resulting in high uncertainty in the remaining anthropogenic fraction.

The Pb/Br ratio in fresh motor vehicle emissions is 2.6.[14] The Pb/nss-Br ratio in the Black Sea aerosols was 4.3 ± 1.7 which is higher than the ratio observed in fresh motor vehicle emissions. The Pb/Br ratios which are higher than fresh motor vehicle emissions have been reported in the literature and is probably due to evaporation of Br from particles.[15]

Nickel has two potential sources in the Black Sea atmosphere; (1) crustal dust, (2) residual oil burning. Consequently, non-crustal Ni (ncr-Ni) is expected to show good correlation with V which is also a marker element for residual oil burning. The ncr-V concentrations in the same samples were measured, and the average was found to be 1.6 ± 0.8 ng m^{-3} (Ref. 11). The ncr-Ni showed poor correlation with ncr-V ($r = 0.32$ and $P[0.32, 15] > 0.1$), probably owing to large crustal subtraction on both elements.

In order to assess the transport of aerosol particles from their source regions, 850 mb isobaric backward trajectories were computed for 3 days duration using synoptic weather maps obtained from Turkish Meteorological Organization. Trajectories were divided into three groups: (1) those which originated from central and Northern Europe, and crossed Europe before reaching the sampling point, (2) those which originated from the Western Mediterranean and North Africa and crossed Turkey, and (3) those which originated from the interior of Russia and moved south to the Black Sea. These 3 sectors with sample trajectories are shown in Figure 3. Thirteen out of 19 calculated trajectories were in the first group which agree with the general easterly air flow in the region.[9] Average concentrations of both Pb and Ni were calculated separately for each trajectory group to test if there were differences in the composition of particles associated with air masses originating from different source regions; the results are given in Table 3. Concentrations of Pb and Ni are comparable in the European and Mediterranean trajectory groups, and low in the third trajectory group. However, Pb and Ni concentrations in air masses originating from the Mediterranean and crossing Turkey indicate that Turkey have a significant contribution on the concentrations of these elements, but Europe is the most important source for these anthropogenic elements, because air masses originating from Europe are transported to the Black Sea region twice as frequently as air masses crossing Turkey. The central USSR which is an industrial region in Russia is expected

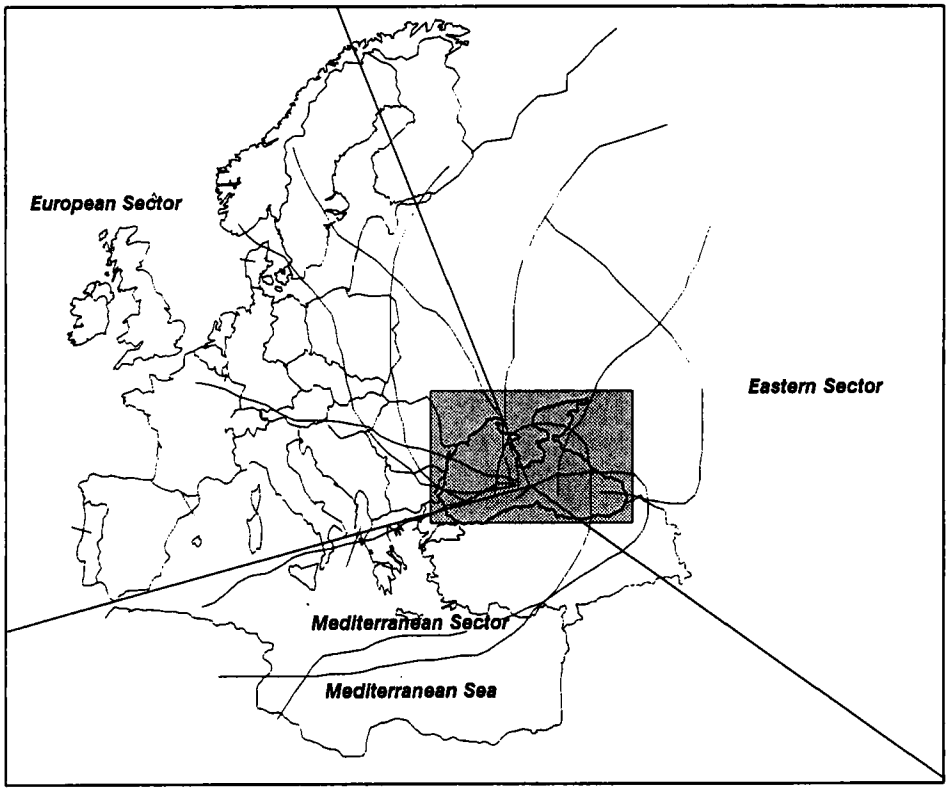

Figure 3 Trajectory sectors with sample trajectories.

to be an important source for pollution-derived elements in the Black Sea atmosphere. However, we were not able to assess the relative importance of central USSR owing to the limited number of trajectories originating from this region.

Fluxes of Pb and Ni from atmosphere to the Black Sea were calculated to understand the effect of atmospheric transport on the pollution of the Black Sea. Atmospheric transport of pollutants to the sea can be an important marine pollution source and also can play an important role in the surface oceanographic processes. For example, transport of NO_3^- from atmosphere was shown to be the main source

Table 3 Concentrations of Pb and Ni in three different trajectory groups (ng m^{-3})

Element	*I. Group Europe*	*II. Group Mediterranean*	*III. Group Western USSR*
Pb[a]	61 ± 14 (11)	48 ± 21 (4)	33 ± 11 (3)
Ni[a]	5.3 ± 2.7 (10)	3.8 ± 3.3 (4)	2.0 ± 0.6 (3)

[a] Number of samples in each group are given in parentheses.

of eutrophication in certain areas.[16] To calculate atmospheric fluxes of Pb and Ni, concentrations of these elements in rain water were estimated by using their atmospheric concentrations and scavenging ratios (SR) reported in the literature. Then, fluxes are estimated by using yearly rainfall data (0.115 kg cm^{-2} yr^{-1}) for the Black Sea.[17] The volume-weighted mean concentration of any element in rain, C_{rain} (g kg^{-1}), can be calculated from the following equation:

$$SR = \rho X(C_{rain}/C_{air})$$

where SR is the scavenging ratio, C_{air} is the arithmetic mean concentration of any element in air (g m^{-3}); and ρ is the air density (1.20 kg m^{-3} at 20°C and 76 cm Hg). Data on the scavenging ratio of elements are rare and depend on physical characteristics of particles such as their hygroscopic nature and size distribution. In a recent review on scavenging ratios, elements with anthropogenic sources are shown to have SR of 200.[18] Although size distribution of particles in the Black Sea atmosphere are not known, scavenging ratio of 200 were adopted for both Pb and Ni due to their anthropogenic nature. Atmospheric fluxes for Pb estimated by this method are, 1,150 ng cm^{-2} yr^{-1} and 700 ng cm^{-2} yr^{-1} for Western and Eastern Black Sea, respectively. Similarly, atmospheric fluxes of Ni to Western and Eastern Black Sea are 94 ng cm^{-2} yr^{-1} and 57 ng cm^{-2} yr^{-1}, respectively.

Total amounts of Pb and Ni that enter the western and eastern parts of the Black Sea from the atmosphere each year are calculated by multiplying local fluxes by half of the surface area of the Black Sea which is 2.1×10^5 Km^2 (Ref. 19). With this calculation, regional fluxes of Pb to the Black Sea were found to be 2,400 and 1,500 tons yr^{-1} for western and eastern parts, respectively. Corresponding fluxes for Ni were 196 and 120 tons yr^{-1} for Western and Eastern Black Sea, respectively.

Fluxes of Pb and Ni from all rivers flowing to the Black Sea were 1,900 tons yr^{-1} and 11,500 tons yr^{-1}, respectively. Riverain fluxes of elements are calculated by using sediment discharges of Black Sea rivers[19] and average elemental composition of soil.[10]

It can be seen from the atmospheric and riverain fluxes of Pb and Ni that rivers are the main route of Ni transport to the Black Sea, while atmospheric flux of Pb to the Black Sea is higher than riverain flux. Direct comparison of atmospheric and riverain inputs of Pb and Ni to the Black Sea is difficult because, (1) most of the particles discharged by rivers settle along the coast and only a small fraction can reach to the open sea. Consequently, the contribution of rivers to the open sea is much smaller, and (2) riverain input values are only based on sediment discharges.

Our flux estimates are prone to two main uncertainties. Atmospheric concentrations and depositions reported here represent a total of one month period. Since short term and seasonal variability of atmospheric element concentrations are known to be large in regional seas,[6] mostly owing to precipitation scavenging of particles on their way to sampling site,[20,21] our deposition values obtained from one month long data may not represent the whole year. Secondly, dry deposition of Pb and Ni were not considered in flux calculations. Exclusion of dry deposition should not cause a large error for Pb, because Pb is anthropogenic and associated with fine particles which have low dry deposition velocities. However, dry deposition of Ni may be

high, because Ni has a significant crustal component associated with large particles which have high dry deposition velocities. With all these uncertainties our flux estimates should be considered as a first approximation which can be improved by taking into account dry deposition and temporal variability.

CONCLUSION

Nineteen air particulate samples were collected from the Black Sea atmosphere in the summer of 1988. Lead and nickel concentrations in these samples have been determined using electrothermal atomization atomic absorption spectrometry (ETA-AAS).

Lead was highly enriched in the Black Sea aerosols, while Ni was moderately enriched. The high enrichment of Pb indicates that motor vehicle emissions are a significant component of the Black Sea aerosols.

The observed Pb/Br ratio was higher than the corresponding ratio in fresh motor vehicle emissions, owing to evaporation of Br from particles during transport of aerosols to the Black Sea region.

Concentrations of Pb and Ni in air masses transported from Europe to the Black Sea were higher than the corresponding concentrations in air masses transported from south. Trajectory calculations showed that air masses originate from Europe at 70% of the sampling time. Concentrations in various sectors and frequency distribution of air mass movements indicate that Europe is the main source of motor vehicle and oil combustion aerosols in the Black Sea atmosphere.

Comparison of estimated atmospheric fluxes of Pb and Ni with corresponding riverain fluxes showed that rivers are the main route of Ni transport to the sea, while atmospheric flux of Pb to the Black Sea is higher than riverain flux.

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REFERENCES

1. J. M. Pacyna, *Atmos. Environ.* **18**, 2447–2459 (1984).
2. J. O. Nariagu, *Nature* **279**, 409–411 (1979).
3. J. Völkening, H. Baumann and K. G. Heumann, *Atmos. Environ.* **22**, 1169–1174 (1988).
4. E. L. Jernigan, B. L. Ray and R. A. Duce, *Atmos. Environ.* **5**, 881–886 (1971).
5. H. Maring, *Atmos. Environ.* **23**, 285–286 (1989).
6. F. Dulac, P. Buat-Menard, M. Arnold, U. Ezat and D. Martin, *J. Geophys. Res.* **92**, 8437–8453 (1987).
7. R. A. Duce, R. Arimoto, B. J. Ray, C. K. Unni and P. J. Harder, *J. Geophys. Res.* **88**, 5321–5342 (1983).
8. T. G. Dzubay, R. K. Stevens and P. L. Haagenson, *Environ. Sci. Technol.* **18**, 873–883 (1984).

9. G. Hacisalihoglu, T. I. Balkas, S. G. Tuncel, D. H. Herman, I. Ölmez and G. Tuncel, accepted for publication in *Deep Sea Research.*
10. R. Taylor, *Geochim. Cosmochim. Acta.* **28**, 1273–1285 (1972).
11. G. Hacisalihoglu, T. I. Balkas, M. Arami, I. Ölmez and G. Tuncel, accepted for publication in *NATO Advanced Study Series.*
12. G. Tuncel, *South Pole Aerosols*, Ph.D thesis (University of Maryland, College Park, 1985).
13. J. M. Ranchard and M. A. Kritz, *J. Geophys. Res.* **85**, 5581–5587 (1980).
14. J. M. Ondov, W. H. Zoller and G. E. Gordon, *Environ. Sci. Technol.* **16**, 318–328 (1982).
15. T. L. Vossler, C. W. Lewis, R. K. Stevens, G. E. Gordon, S. G. Tuncel, G. M. Russwurm and G. J. Keeler, *Atmos. Environ.* **23**, 1535–1547 (1989).
16. GESAMP (IMO/FAO/UNESCO/WMO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution), *Atmospheric transport of contaminants into the Mediterranean region* (UNEP Regional Seas Reports and Studies No. 68, 1985).
17. M. Coleri, personal communication (1989).
18. GESAMP (IMO/FAO/UNESCO/WMO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution), *The atmospheric input of trace species to the world ocean* (UNEP Regional Seas Reports and Studies No. 38, 1989).
19. T. Balkas, G. Dechev, R. Mihnea, O. Sarbenescu and U. Ünlüata, *State of the marine environment in the Black Sea region* (UNEP Regional Seas Reports and Studies No. 124, 1990).
20. G. Bergametti, A. L. Dutot, P. Buat-Menard, R. Losno and E. Remoudaki, *Tellus* **41B**, 353–361 (1989).
21. E. Remoudaki, G. Bergametti and R. Losno, *Atmos. Environ.* **25A**, 733–744 (1991).