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Research Article

Determination of Ion Concentrations and Heavy Metals in the Air Particulates of an Industrial Area

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Abstract

This study deals with the determination of heavy metals, anions and cations in atmospheric aerosols at four heavily polluted sites in Samsun city, Turkey. The anions (Cl^-, Br^-, NO_3^- and NO_2^-) and cations (Na^+, K^+ and NH_4^+) in the samples were determined by ion chromatography using a potentiometric detector with ion selective electrodes. Flame and graphite-furnace Atomic Absorption Spectrometer was used for the determination of Pb, Cu, Zn and Fe. The average values of Cl^-, NO_3^-, NO_2^-, Br^-, Na^+, K^+ and NH_4^+ concentrations in the samples were 4.58±1.30, 7.42±1.32, 0.86±0.10, 0.28±0.05, 0.77±0.13, 0.72±0.06, and 1.08±0.09 µg/m³ respectively. The average values of Zn, Cu, Fe and Pb concentrations in the samples were 2.32±0.21, 1.71±0.14, 2.29±0.18, and 2.46±0.22 µg/m³ respectively.

Keywords: Heavy metals, Ions, Air particulate, Air pollution

1. Introduction

Air pollution is usually concentrated in densely populated metropolitan areas, especially in developing countries where environmental regulations are generally relatively lax or nonexistent.

The chemical composition of aerosols is known to be influenced mainly by the origin of aerosol particles. Such information is hence important for the proper apportionment of different source contributions from different sources (Mishra et al. 2004, Henning et al. 2003). It is generally understood that particles in the atmosphere are produced either from natural sources (such as wind-borne dust, sea spray, and volcanoes), anthropogenic activities (such as manufacturing products from raw material, combustion of fuel, mining and smelting activities, construction works, vehicular movements, etc.) and chemical reactions in the atmosphere.

This study aims to analyze the chemical concentration of selected pollutants in aerosol particles collected in Samsun city, Turkey. The region has not been previously investigated in detail.

Samsun is a province on the black sea cost with a population of 1 500 000. It has a major commercial port and an industrial city occupied not only by small to middle industries but also big copper and fertilizer factories. Therefore, it is recognized as one of the areas with the highest air pollution in Turkey.

Determination of the anion and cation concentrations in atmospheric particulates can provide useful information on pollution sources, probability of long-distance transportation of suspended particles and effects on human health (Adriano 1986, Cabada et al. 2004). Human health may be affected by aerosols in the environment. For instance, there is substantial evidence that a high Pb level in the environment could affect blood Pb level, intelligence, and behaviour (McMichael 1985). It has been noted that children could ingest dusts including heavy metals via their hands or mouths (Watt 1993).

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A portable high performance air sampling system was constructed for this study. Air particulate samples were collected twice a month at four different stations for 12 months (February 2004 to January 2005).

The amounts of Na^+, K^+, NH_4^+, NO_3^-, NO_2^-, Cl^-, and Br^- ions in air particulate samples were simultaneously determined by using ion chromatography with ion selective electrodes designed and produced in our laboratory was used.
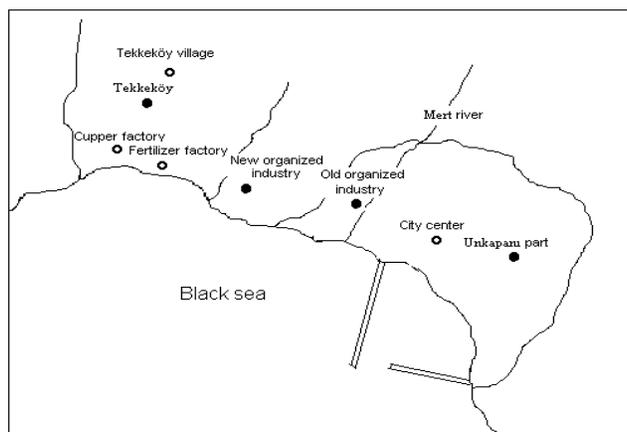
Figure 1. Sampling points in Samsun city (● sampling stations, ○ important places among the region)

The amount of Pb in the air particulates was determined using an atomic absorption spectrometer with graphite furnace; the amounts of Cu, Zn, and Fe were determined by flame atomic absorption spectroscopy.

1. Experimental

2.1 Sampling

Air particulate samples were collected from four different locations situated around Samsun (Fig. 1). The locations of copper and fertiliser factories were taken into consideration when selecting sampling points. Sampling stations had wide open surroundings. Aerosol samples were collected using a high volume air sampler developed in our laboratory. Sampling systems having flow rate of 12 L/min. can filter 17 m^3 of air in a day. All sampling at each site were performed between 9.00 am and 9.00 am the next day. The sampling was performed with the same apparatus at each station by transporting between stations. Sampling apparatus was placed to face north to be exposed by the northern winds. No sampling was made during rainy and snowy days. The system was equipped with cellulose filters. The filtering material sheets of 4.7 cm diameter were used with a plastic stamp to avoid metal contamination. The cellulose filters (Millipore SA 67120 Molshem, France, mixed cellulose acetate and nitrate filters, pore size 0.45 μm) collected an average mass of 20 mg of air particulate matter in a single experiment. Air particulate samples were sampled twice a month; in total 96 air particulate samples were collected during March 1, 2004 to February 31, 2005.

It has been reported that filter paper materials include various amounts of a variety of elements and ions (Dams 1992). For the accurate determination of trace amounts of heavy metals and common anions and cations in the air particulate matter on the filters, blank filters were also treated in the same manner with sample filters to check anion and cation and heavy metal impurities (Rizzio et al., 1993).

2.2 Sample preparation and analysis

The samples for the analysis of heavy metals were extracted in acid solution. Filter samples were placed in a Teflon container and treated initially with concentrated acid solutions (4.5 mL HNO_3 and 0.5 mL HF) (High purity) (Mishra et al. 2004). Ion chromatography with ion selective electrode detection systems were utilised for the analysis of ionic constituents. Samples were prepared by filter extraction in deionised water; for the determination of ionic constituents. Perkin Elmer series 3 instruments with a dual channel pump and Rheodyne injection valve with a 20 μl sample loop was operated. Separations were performed with Ionpac-CS5 analytical and Ionpac-CG5 guard mixed-bed columns. Ion selective electrode detector cells were placed subsequent to the end of the separation column (Isildak 1999, Isildak and Covington 1993, Isildak and Asan 1999).

2.2.1 Preparation of solid-state contact tubular membrane electrodes and flow cells

The construction of all solid-state contact tubular polyvinylchloride (PVC) matrix membrane anion and cation–selective electrodes without an inner reference solution was carried out as described by Isildak et al. (Isildak 1999, Isildak and Covington 1993, Isildak and Asan 1999).

Two identical potentiometric cells were designed for the simultaneous detection of anions and cations.

The sensing membrane was prepared by mixing 28 % PVC, 2 % tetradodecylammonium bromide (TDDA-Br) for the anion selective electrode and dibenzo-(18-crown-6) (DBC) for the cation selective electrode as the active ligands, 66 % dibutylphalate (DBP) for the anion selective electrode and dioctylsebacate (DOS) for the cation selective electrode as plasticizers in tetrahydofuran (THF). The solvent was evaporated at room temperature in 4 h.

To reduce the membrane resistivity and anionic selectivity in the case of neutral carrier electro active materials, the membrane contained 1 % potassium tetraphenylborate (KTPB). The detector cell consisted of an all solid-state tubular PVC-matrix anion-selective or cation-selective electrode and a double junction calomel reference electrode (Russell pH, Auchtermuchty, Fife, Scotland) with tetramethylammonium chloride in the outer compartment. In case of simultaneous detection, ion selective electrodes were associated with the reference electrode. Calibration plots of the electrodes for anions and cations were obtained by the constant volume dilution method (Isıldak and Covington 1993, Isildak and Asan 1999). Speed of response and selectivity were obtained by testing in a flow-injection mode.

2. Results and Discussion

3.1 Chemical composition of ions

The concentrations of ions and heavy metals in Samsun are presented in Table 1 with a statistical summary, the seasonal variation of concentrations of anions and cations are illustrated in Fig. 2 and Fig. 3. The results are discussed considering the level of anion and cation concentrations and their possible sources. The concentrations of ions as an average all four of sampling areas were in the order of $NO_3^- > Cl^- > NO_2^- > Br^-$ and $NH_4^+ > Na^+ > K^+$. Pearson correlation analysis was performed on the ion and heavy metal data using SAS 8.0 for windows. Table 2 shows the matrix of correlation coefficients among seasonal variation of ion and heavy metal concentrations in Samsun region.

Nitrate concentration was 7.42 µg/m^3; decrease in seasonal variation as shown in Fig. 2. There was a high correlation between NO_3^- and K^+ (r = 0.93), suggesting that they could have the same origin, i.e., dust particles. Chloride was the second abundant anion with an average concentration of 4.58 µg/m^3

because of sea spray. In addition, chloride emitted from the chemical plants in Samsun and surrounding area might contribute to Cl^- in air particulate. According to the previous studies in coastal location, the molar ratio of Cl^- to Na^+ increase linearly with the decrease of NO_3^- to Na^+ molar ratio (a possible replacement of Cl^- by NO_3^-) (Mishra, 2004). The relative enrichment in Cl^- (or Na^+) may be accounted for by substantial input of sea aerosols due to the coastal location. Sea salt can act as a major contributor to the total particulate matter in Samsun Atmosphere, as it is usually the most abundant aerosol component at coastal sites (Mishra, 2004; Hall and Wolf, 1998). Correlation between Na^+ and Cl^- ions is poor which can be due to the high concentration of Cl^-. The mean equivalence ratio of Na^+/Cl^- was 0.168±0.1. The high Cl^- concentration may be related to emissions from the chemical plants in the surrounding area.

Br^- and NO_2^- ions had at the lowest concentration values of 0.28±0.05 and 0.86±0.10 µg/m^3 respectively. There is a poor correlation between Br^- and NO_2^- ions and other anthropogenic species, which express with its depletion in the particulates.

NH_4^+ was the most abundant cation with a concentration of 1.08 µg/m^3. NH_4^+ containing particles in our region could be $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$ and NH_4NO_3 (Kim et al. 2002). The results of the correlation analysis indicate a strong correlation between NH_4^+ to NO_3^- which may be because of their common source.

Similar chemical compositions in air particles have also been found in many other areas around the world, such as, Brazil, Spain, Singapore, China, and Antarctic Peninsula (Avila 1996, Mello 2001, Hu et al. 2003).

3.2 Seasonal variations of chemical composition

The concentrations of chemical compositions as a function of time were investigated through the least square linear regression analysis. The Cl^- concentration in particulates had a significant decreasing trend (r= -0.674), which was assumed to result from downward trends in Cl^- emission and concentration of Cl^- in ambient air of Samsun. The high concentrations of Cl^- in air particulates at summer times are due to the evaporation of sea salt aerosols. The NO_2^- concentration showed a slightly decreasing trend (r= -0.159, Fig. 2). The concentrations of NO_3^- were lower during fall

months than its annual average values (Fig. 2 and Table 1). The ratio of NO_2^- to sum of anions in particles showed a slightly increasing trend (r= 0.054). NO_3^-

Table 1. A statistical summary of aerosol-bound ion and metal concentrations determined in 4 different region of Samsun city (4 samples from each site).

	Mean±SD	Article I. Range
(A) Ionic composition (µg / m³)		
Cl⁻	4.58±1.30	4.16 – 4.84
NO₃⁻	7.42±1.32	6.01 – 9.37
NO₂⁻	0.86±0.10	0.45 – 1.15
Br⁻	0.28±0.05	0.18 – 0.48
Section 1.01 Na⁺	0.77±0.13	0.57 – 1.06
K⁺	0.72±0.06	0.54 – 0.92
NH₄⁺	1.08±0.09	0.79 – 1.39
(B) Elemental composition (µg/ m³)		
Pb	2.32±0.21	0.99 – 3.04
Cu	1.71±0.14	0.89 – 2.42
Zn	2.29±0.18	1.46 – 3.01
Fe	2.46±0.22	1.55 – 3.28

concentration had a closely significant increasing trend (r= 0.537) (Fig. 2). The variation of NO_3^- had a significant increasing trend in winter season (Fig. 2). No trend was shown in Br⁻ (r= 0.694; Fig. 2), although values of Br⁻ in winter are slightly higher than the annual average values and values are lower during summer time.

Among cations, Na⁺ had a slightly decreasing concentration (r= -0.357, Fig. 3). There was no significant change for the other cations. K⁺ and NH_4^+ which showed a slightly increasing concentration (r= 0.403, r= 0.206 respectively). However, the trend was not statistically significant. Compared to annual average concentration, the concentration of Na⁺ was seen to decrease in winter periods, while that of K⁺ and NH_4^+ were increased (Fig. 3).
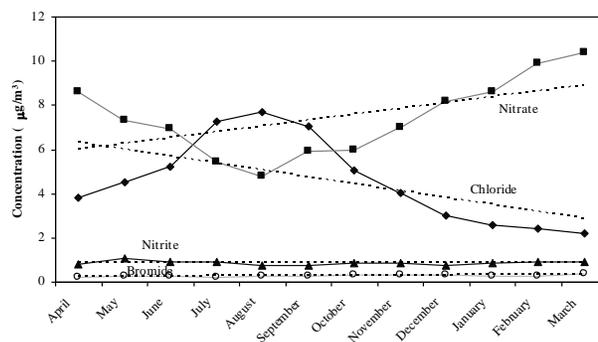
Figure 2. Seasonal variations of bromide, chloride, nitrate, and nitrite concentrations in the samples collected per month.
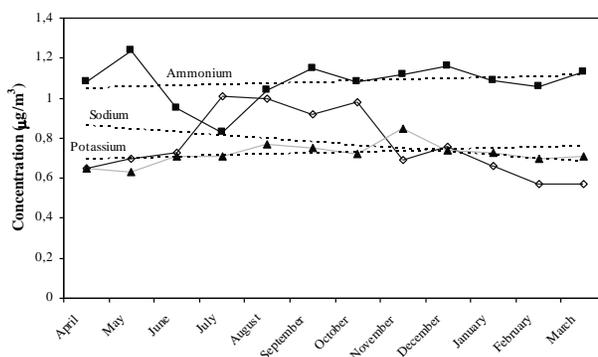
Figure 3. Seasonal variations of ammonium, sodium, and potassium concentrations in the samples collected per month.

3.3 The concentrations of heavy metals

The concentrations of heavy metals in air particulate samples are presented in Table1. Fig 4 illustrates temporal variation patterns of all heavy metals over the whole study period using the normalized concentrations of each individual metal. Concentrations of heavy metals in air particulate samples in our study area were found higher than the World Health Organization (Hu et al. 2003).

Contents of Pb, Zn, Cu and Fe in air particulate samples showed an increasing trend with r values of 0.500, 0.242, 0.337, and 0.579 respectively. These increasing concentrations for heavy metals in air particulates can be attributed to intense coal combustion and automobile emissions, and may be related to the chemical plants and industrial activities. Analysis of Cu, Pb, and Zn in an industrial area (Helwan, Egypt) suggested similar sources for these metals (Ghandour et al. 1982).

A Strong negative correlation was seen in the data between Pb to Na⁺ and NH_4^+ with r values of -0.987, and -0.910 respectively suggesting that these metals

could have the same origin, as Pb is indicating a poor correlation with other species too. There were high correlations between Cu to Zn, Fe and NO_3^- with r= 0.971, r= 0.971, r= 0.920 respectively, and Fe to NH_4^+, NO_3^- and Zn with r= 0.971, r= 0.965, r= 916 respectively.
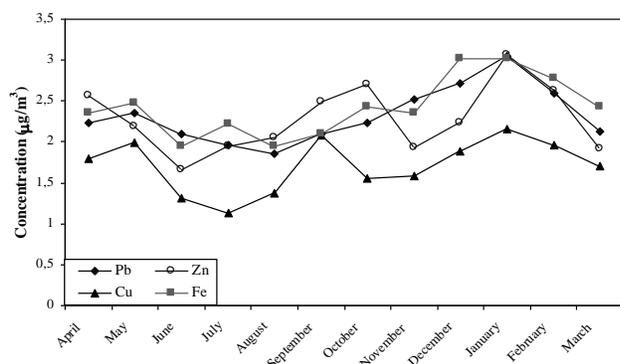
Figure 4. Seasonal variations of lead, zinc, copper, and iron concentrations in the samples collected per month.

3. Conclusion

The concentrations of ionic and heavy metal species causing air pollution in Samsun were investigated for a period of 12 months. The annual average and seasonal variation of all ion contents and heavy metals showed that the values obtained were much higher than the values recommended by the World Health Organization (WHO 1999). Anthropogenic and crustal sources were expected to make significant contributions to the air pollution in Samsun.

Cu, Zn, Fe, Na^+, K^+, NH_4^+, and NO_3^- concentrations in air particulate matter were found to be considerably high. These species play a significant role in over the atmospheric pollution. The possible source of atmospheric pollution is the large and middle sized industrial factories in this region. High concentrations of Na^+, K^+, Cl^-, Br^- and heavy metals

Table 2. Matrix of correlation coefficients (and P value) among average monthly concentrations of ions and heavy metals.***

	Na^+	K^+	NH_4^+	NO_3^-	NO_2^-	Cl^-	Br^-	PB	CU	ZN	FE
Na^+	1.00000										
K^+	0.72862*	1.00000	0.2714**								
NH_4^+	0.94004	0.80047	1.00000	0.0600	0.1995						
NO_3^-	0.83577	0.93624	0.94644	1.00000	0.1642	0.0638	0.0536				
NO_2^-	0.53652	-0.06951	0.54217	0.26517	1.00000	0.4635	0.9305	0.4578	0.7348		
Cl^-	-0.65004	-0.69161	-0.46021	-0.50871	0.21720	1.00000	0.3500	0.3084	0.5398	0.4913	0.7828
Br^-	-0.16920	-0.71993	-0.16936	-0.43297	0.72999	0.70534	1.00000	0.8308	0.2801	0.8306	0.5670	0.2700	0.2947
PB	-0.98740	-0.79029	-0.91015	-0.84228	-0.39914	0.75740	0.31238	1.00000	0.0126	0.2097	0.0899	0.1577	0.6009	0.2426	0.6876
CU	0.68171	0.75676	0.89026	0.92034	0.42954	-0.13243	-0.15779	-0.63750	1.00000	0.3183	0.2432	0.1097	0.0797	0.5705	0.8676	0.8422	0.3625
ZN	0.58535	0.58193	0.81926	0.80819	0.55856	0.08439	0.06210	-0.50824	0.97199	1.00000	0.4146	0.4181	0.1807	0.1918	0.4414	0.9156	0.9379	0.4918	0.0280
FE	0.83420 0.0280	0.81300 0.0833	0.97196	0.96558	0.48236	-0.31811	-0.18867	-0.79923	0.97198	0.91667	1.00000	0.1658	0.1870	0.0280	0.0344	0.5176	0.6819	0.8113	0.2008

*   Correlation coefficient (r)
**   P value for the corresponding r
*** The number sample is 4 for all the variables

This result indicated that air pollutants came from local natural or anthropogenic sources such as industrial activities, construction factories, as well as combustion sources. On the other hand, a large part of Pb may be related to emissions from vehicular exhausts. By analyzing aerosol samples Hong et al. reported significantly high concentrations of heavy metals (like Pb, Cu and Zn) in King George Island and ascribed it to contributions from local (or regional) pollution (Hong et al. 1999).

at all the stations in summer and autumn periods could be explained by natural processes such as sea, river and barrage by evaporation and generation of sea salt aerosols. Higher winter concentrations of heavy metals can be attributed to intense coal combustion in addition to emissions from industrial sectors in the region. The increases in the concentration of some species (especially Na^+, Cl^- and NO_3^-) were mainly attributed to oceanic input.

The concentrations of Pb and Zn were higher in air particles, which were mainly due to the traffic density and direct emission of exhaust gases into the atmosphere.

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