Proceedings of the Third International Symposium on Air Quality Management at Urban, Regional and Global Scales. pp. 786-798, 26-30 September 2005, Istanbul – Turkey

DETERMINATION OF ELEMENTAL COMPOSITION OF PM_{10} SAMPLES AROUND HEAVY INDUSTRIAL REGION OF ALIAĞA, IZMIR; TURKEY

Sinan Yatkin, Abdurrahman Bayram*, Yetkin Sonmez Dumanoglu, Hasan Altıok and Banu Cetin

Dokuz Eylul University, Faculty of Engineering, Department of Environmental Engineering, Kaynaklar Campus, 35160 Buca, Izmir, Turkey
* Corresponding author. Tel.: 90-232-4127113; fax: 90-232-4530922
e-mail: abdurrahman.bayram@deu.edu.tr

ABSTRACT

Particulate matter samples with aerodynamic diameter less than 10 µm (PM_{10}) were collected at two stations simultaneously around industrial region of Aliağa, Izmir. One station was located in the center of Aliağa town where is surrounded by several industries mainly consist of petrochemical industry and refinery. The other was located at the nearest residential area to Horozgediği heavy industrial region, contains many iron-steel smelters that are significant source in terms of particulate matter and toxic heavy metals. In order to quantify the contribution amounts of sources to ambient concentrations by the future works, elemental composition of PM_{10} samples were determined. The measured elements were Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn. The meteorological data were obtained from stations that are located at the sampling points. The variety of PM_{10} concentrations and elemental compositions has evaluated taking the meteorological parameters that have a significant role on transportation of pollutants into consideration.

Key words: PM_{10}, elemental composition, Aliağa

1. INTRODUCTION

Since presence of particulate matters (PMs) in the atmosphere causes several environmental effects, it should be monitored and controlled. The sources PMs are nature (i.e., crust, sea, swamps) and anthropogenic ones (i.e., fuel burning, industry) (Röösli, et al., 2001). The PMs in the atmosphere have very different impacts on the environment such as effecting the solar radiation balance and visibility (Polissar et al., 2001), reducing agricultural crop yields due to reduced sunlight (He, et al., 2001), effecting coastal ecosystem due to enrichment by air-water transfer (Gao, et al., 2002), effecting the open marine atmosphere by long range transfer (Gao, et al., 2002), causing increased hospital admission records in high concentrations (He, et al., 2001), contribution to metal toxicity by toxic heavy metal associated with soluble particles (PM_{10}, with aerodynamic diameters less than 10 µm) and fine particles ($PM_{2.5}$, d≤2.5 µm) (Gao, et al., 2002). Also, presence of particulate matter in atmosphere causes several serious health effects like aggravating asthma, increasing the respiratory symptoms like coughing and difficult or painful breathing, causing chronic bronchitis, decreasing lung function, causing premature death etc. (Web page of United State Environmental Protection Agency; www.epa.gov).

The toxic metals content of inhalable PMs contributes to the total metal toxicity that human exposed. Especially, workers and inhabitants around heavy industrial regions may expose to the inhalable metal toxicity more that the other people. Metal industry, especially furnaces, may cause significant contribution to the ambient elemental concentrations. Aliağa is a town that is surrounded by heavy industries. Especially, Horozgediği region that has many iron-steel furnaces caused serious PMs and metal toxicity problems for many years.

The objective of this study was to measure the PM_{10} concentrations and their elemental composition at 2 stations which one was located in Aliağa town and the other was in Horozgediği village.

2. MATERIALS AND METHOD

2.1 Sampling Site

The sampling site, Aliağa, is located at north of Izmir city (Appr. 50 km far), Turkey. Aliağa has many industrial plants like petrochemical complex, refinery, LPG storage plants etc. These industries are located close to the Aliağa town. Additionally, there are many iron-steel manufacturers at Horozgediği Industrial Area where is at south of Aliağa (Appr. 5 km far from the town). Also, there is a natural gas burning power plant (1500 MW), a fertilizer factory, and some small plants in this industrial area.

The sampling stations were located in Aliağa town and Horozgediği village. Horozgediği village is the nearest residential to the industrial area. The sampling point was the monitoring station of the power plant and equipped with a weather station. The meteorological data were taken from this station. The sampling point in Aliağa was the garden of sports hall where is in the center of the town. The sampling area is illustrated in Figure 1.

2.2 Sampling and analysis

The sampling was performed in winter and summer period at two stations, concurrently. The winter period was between 28 March-07 April 2005 and the summer one was 13-19 June 2005. The average sampling duration was 24±2 hours. The PM_{10} samplers (Model PF 20630, Zambelli Inc., Italy) were used for sampling. The cellulose acetate (Sartorious)filters were used.

The extraction of the filters was performed by hot acid digestion. The cellulose acetate filters were placed into polypropylene bottles and 5 ml of acid solution (1:3 HNO_3:HCl, Merck Suprapure) was added. After shaking overnight at room temperature at 250 rpm, 5 ml of diluted acid mixture (1:5) was added and the digests were heated at nearly 100 ^{0}C, at least 4 hours. Then the volume of the extract was adjusted to 20 ml by the same diluted acid mixture.

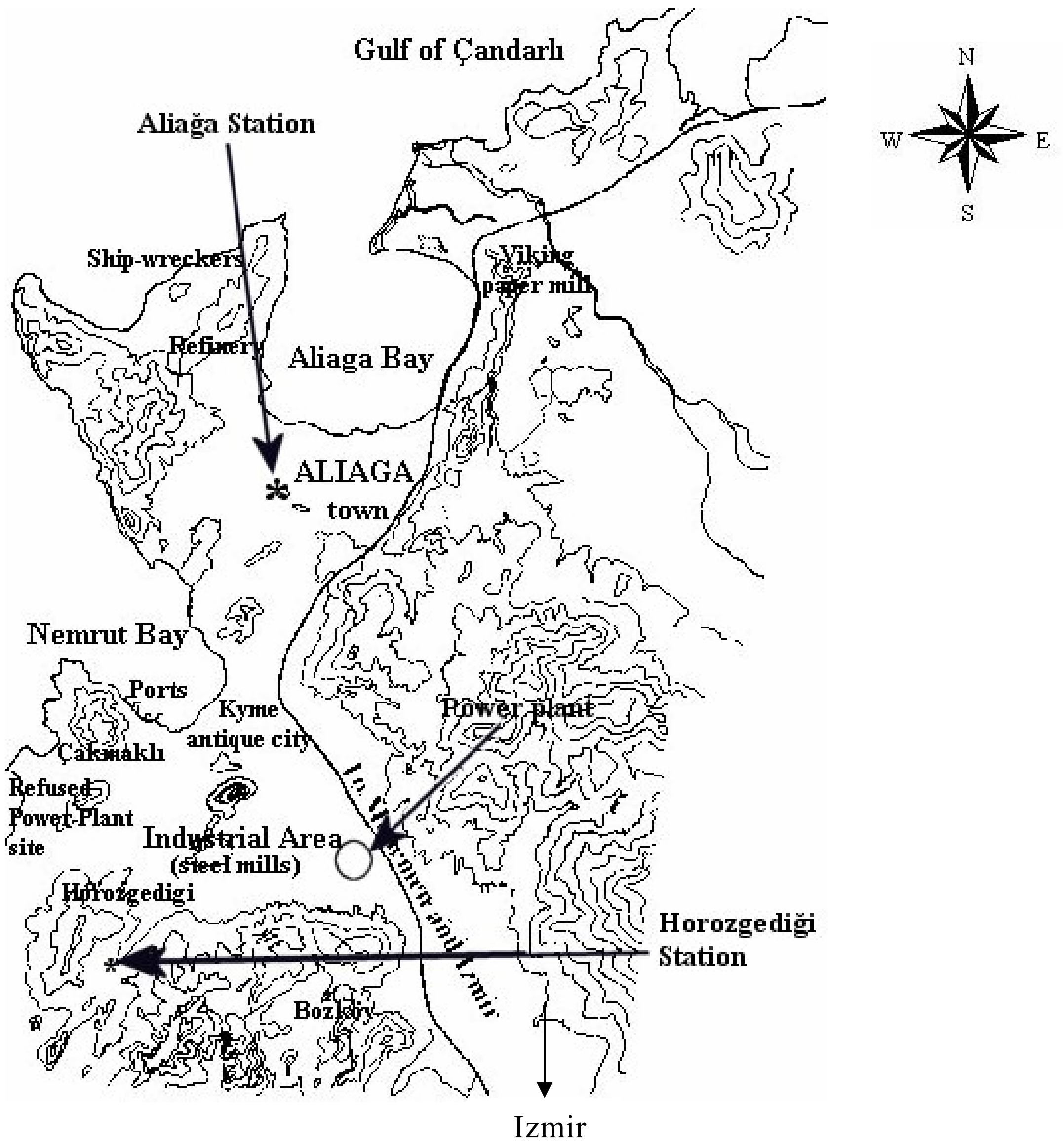

Figure 1. The sampling area.

All the bottles and plastic petri dishes that were used for digestion and transportation of the filters were initially kept in acid solution (HNO_3, 10%) at least 24 h and then rinsed with Type I de-ionized water.

The elemental analysis of all samples was performed using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) (Perkin Elmer Inc., Optima 2100 DV). The ICP-OES was calibrated daily by using certified solution. The analysis of samples was performed only if the r^2 of calibration curve was greater than 0.99. A calibration check solution was prepared by another certificated solution and the calibration curves were checked just after the initial calibration and for every 15 samples. If the deviation was more than ±10 %, the instrument was re-calibrated. To determine the recovery efficiencies of the extraction procedure, 3 aliquots of Urban Particulate Matter (SRM 1648) from NIST (National Institute of Standard Technology) were extracted and analyzed. The percent recovery efficiencies were between 70-110% except Al, K and Cr. The average recoveries of these elements were 42% for Al, 52% for K and 30% for Cr. The low recoveries of Al and Cr were probably due to their presence in silicate matrices that is difficult to extract. The recovery efficiency of Ca could not been determined since no certified value is available for this element. 10 blank samples for cellulose acetate filters were prepared and analyzed. The method detection limits (MDLs) were determined by adding 3 standard deviations to average blank values. All the values were higher than MDLs.

3. RESULTS AND DISCUSSION

3.1 PM_{10}

The PM_{10} concentrations were measured at two stations for winter and summer period. The results and the meteorological parameters are given in Table 1.

The predominant wind directions at the sampling site were NW and WNW. There was no significant difference between concentration values depending on the wind directions. On the other hand, there were clear relationships between wind speed and concentrations at two stations. These relations are illustrated in Figure 3. The concentrations at Horozgediği increased with increasing velocities in winter (r^2=0.64) and also in summer (r^2=0.70). Oppositely, the variation at Aliağa was as decreasing of concentrations with increasing wind speed. The r^2 values were 0.68 and 0.51 for winter and summer; respectively.

The significant PM sources like refinery and petrochemical complex were closer to the sampling point in Aliağa (1-2 km). The result of decreasing concentrations with increasing velocities may be because of the dilution effect that is significant at high velocities. Since there are no PM control devices at refinery and petrochemical complex, it was expected to measure higher concentrations at Aliağa station. However, the station was closer to these sources; so the PMs could probably not reached to sampling point that was located at ground level. The decreased concentrations in summer strongly show that fossil fuel burning for residential heating was effective in Aliağa in winter.

On the other hand, the profile at Horozgediği was completely opposite. Similarly, the concentrations were higher at winter. However, the concentrations increased with increasing wind speed. Although, nearly all iron-steel manufacturers equipped with bag filters, the fugitive emissions were significant. There are many slag storage areas that exposed to wind and they were another significant PM sources. As the results of these sources, the concentrations increased with increasing wind velocities. This may be also the answer of why the concentrations were lower in summer; because the velocities in summer period were lower than winter (Nearly all the velocities were lower than 5 m s^{-1}).

Table 1. PM_{10} concentrations at two stations, µg m^{-3}

Date	Horozgediği	Aliağa	Wind Direction, (%)	Wind Speed, m s^{-1}
3/28/05	62.3	NA	SE (70), SSE(30)	6.1
3/29/05	40.1	NA	W (22), WNW (19)	2.5
3/30/05	72.3	58.9	NW (35), WNW (24)	2.7
4/01/05	148.8	45.4	NW (71), WNW (29)	9.4
4/02/05	125.5	65.2	WNW (93)	8.2
4/03/05	117.2	46.3	WNW (63), NW(26)	5.6
4/04/05	116.7	49.5	WNW (49), NNW (29)	4.7
4/05/05	57.1	54.9	WNW (39), NW (37)	1.6
4/06/05	63	57.7	WSW (23), WNW (22)	1.5
4/07/05	66.7	52.1	W (44), WSW(26)	1.7
6/14/05	62.5	21.5	NW (49), WNW (43)	4.5
6/14/05	78.5	28.3	NW (52), WNW (48)	5.1
6/15/05	70.1	NA	NW (58), WNW (42)	4.0
6/16/05	55.8	38.8	WNW (39), NW (35)	2.5
6/17/05	68.5	21.1	NW (47), WNW (44)	3.2
6/18/05	40	47.3	WNW (32), W (18)	2.0
6/19/05	47.6	33.7	NW (53), WNW (38)	3.1

NA: Not available

3.2 Elemental Composition

The elemental compositions of PM_{10} samples were determined. The measured elements were Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, Pb, Sr, V and Zn. The mean elemental composition of PM_{10} samples in ng m^{-3} and µg g^{-1} were given in Table 2. The results show that the PMs of Horozgediği were dominated by elements were emitted by the iron-steel manufacturers. These were Fe, Zn and Pb. The elemental content of PM emitted by an iron steel manufacturer located in Turkey is given in Table 3 (Orhan, G., 2005). The elemental composition was dominated by Zn, Fe and Pb. The Fe/Zn, Fe/Pb and Zn/Pb ratios of this PM are 0.8, 8.5 and 10.8; respectively. The related ratios of PM_{10} collected at two stations were summarized in Table 4. The low Fe/Zn ratios clearly show that the PM_{10} concentrations were dominated by iron-steel manufacturers at Horozgediği station. The scatter plots of Zn-Fe, Fe-Pb and Zn-Pb are illustrated in Figure 4. The high correlation coefficients that were more than 0.90 clearly show that the origin of these elements was the same. On the other hand, there were no correlations between the related elements at Aliağa station.

The terrestrial elemental concentrations at Horozgediği were also high which were Ca, Mg, Al and K. However, it is difficult to claim that these elements arisen from the re-suspension of the soil by wind effect, since the content of these elements are significant in PM emitted from the iron-steel manufacturers. The Ca/Al ratio was 4.8 in PM of steel manufacturers, while the average ratio was 6.7 for Horozgediği. These values may show that these terrestrial elements were mainly arisen from the iron-steel industries. The average Ca/Al ratio was 2.6 at Aliağa. It may also show that the main source of these elements was soil. Another result that supports this inference was insignificant difference of the related ratio up to the seasons (2.4 for winter and 2.9 for summer).

The relation between PM_{10} concentrations and wind velocities was clear at both Aliağa and Horozgediği stations which were illustrated in Figure 3, previously. The Zn-Fe, Fe-Pb and Zn-Pb scatter plots of Horozgediği according to the wind velocity are illustrated in Figure 5. The correlation coefficients were higher in case of windy conditions at Horozgediği station.

4. CONCLUSION

It is very clear that the iron-steel manufacturers are the main contributor to the PM concentrations around Horozgediği region. Especially, the concentration of Pb which is one of the toxic elements reached to 3 μg m^{-3} at Horozgediği station that was located near the village. Besides, the prevalent wind direction was NW that this wind effects the village partially. In case of north-easter direction, the transportation of PM towards the village increases. Nevertheless, there was no day that wind blew from this direction within sampling period. PM_{10} concentrations and elemental content were been affected by wind velocity, significantly. High velocities caused higher concentrations both in winter and summer.

The contribution amount of sources on the PM concentrations could not been calculated because of the lack of data on sources in terms of elemental content of emitted PMs. In order to calculate them, sources characterization study has been conducted. As soon as the data obtained, they will be used in Chemical Mass Balance (CMB) model and contribution amounts will be determined.

On the other hand, the PM_{10} concentrations in Aliağa station were much lower both in winter and summer. It was expected to measure much higher, due the refinery and petrochemical complex are near to the town. However, the station was close to these sources and the PMs might have not reached the ground level. It was also expected to measure lower concentrations in case of lower wind velocities due to unable to dilution of PM; and the results realized this expectation.

Although, the distance between Horozgediği and Aliağa is around 5 km, it was observed that there were significant meteorological differences between two stations in terms of wind direction and velocity. It may be not true to use the meteorological data obtained from Horozgediği for Aliağa. There is an online meteorology station located very close to the sampling station and owning to Meteorology Directorate. The measured concentrations will be re-evaluated as soon as the receipt of the data from the Directorate.

Also, after the obtaining the data on sources, the CMB model will be used to calculate the contribution amounts.

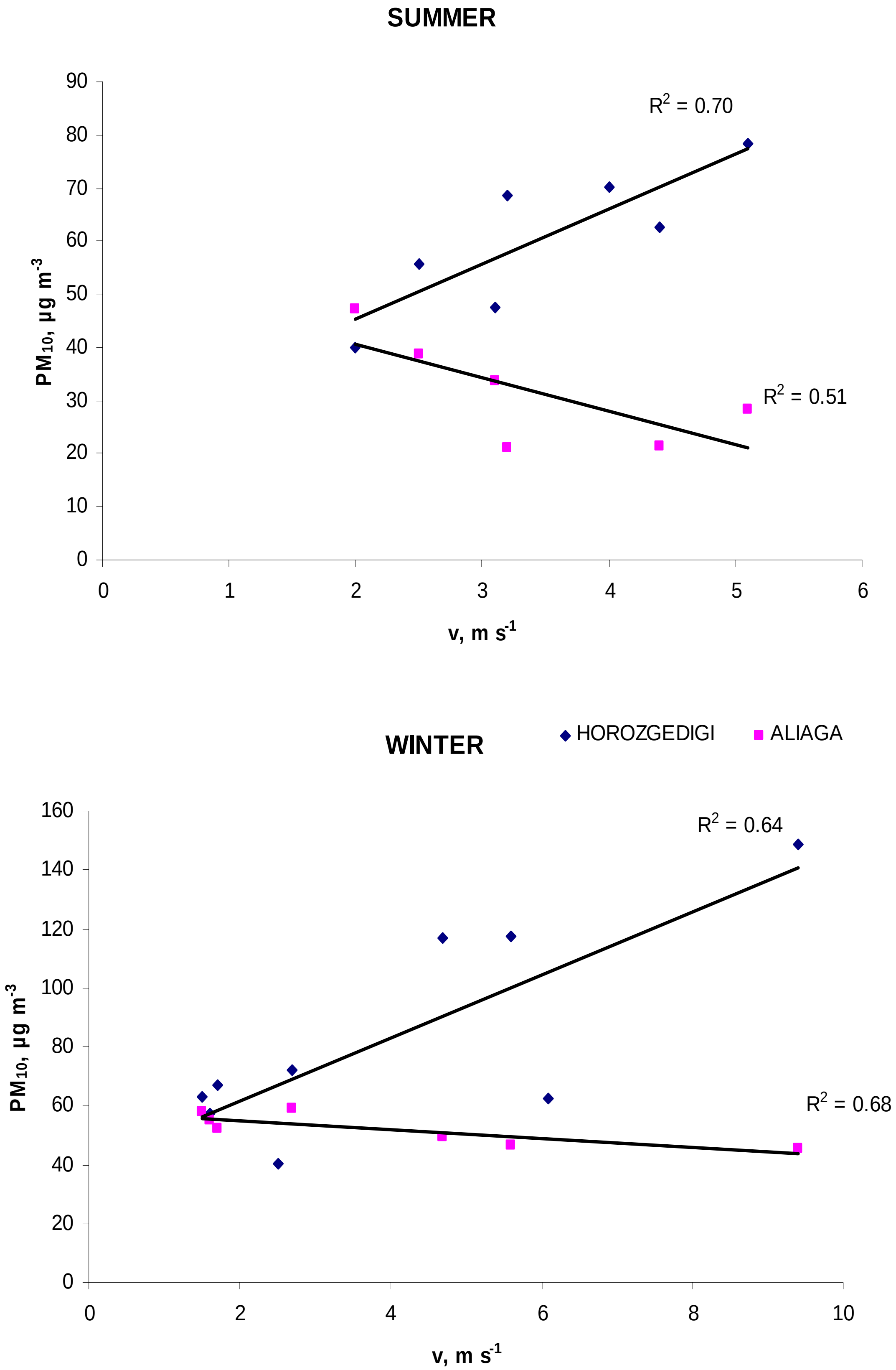

Figure 2. The relationship between PM_{10} and wind direction at two stations

Table 2. Elemental mean concentration, in ng m^{-3} and µg g^{-1}, in PM_{10} simultaneous sampling performed during winter and summer

	Horozgediği ($ng\ m^{-3}$)		Aliağa ($ng\ m^{-3}$)		Horozgediği ($\mu g\ g^{-1}$)		Aliağa ($\mu g\ g^{-1}$)	
	Winter	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**	**Winter**	**Summer**
PM_{10}	87000±35500	60400±13500	52100±5300	31800±10300				
Al	1209 ± 607	584 ± 184	762 ± 381	461 ± 221	15511 ± 9905	9660 ± 2500	15049 ± 5930	15842 ± 10542
Ba	22 ± 14	22 ± 8	9 ± 4	10 ± 4	235 ± 61	348 ± 67	184 ± 69	368 ± 240
Ca	4990 ± 2861	4828 ± 1378	1771 ± 900	1238 ± 488	54473 ± 14084	82044 ± 25886	34332 ± 15601	42083 ± 18707
Cd	11 ± 11	9 ± 9	2 ± 1	2 ± 1	104 ± 71	141 ± 119	49 ± 21	73 ± 48
Co	3 ± 2	1 ± 1	2 ± 1	2 ± 1	29 ± 18	19 ± 19	30 ± 27	63 ± 62
Cr	102 ± 57	109 ± 51	59 ± 52	51 ± 53	1267 ± 850	1759 ± 708	1273 ± 1123	2158 ± 2333
Cu	93 ± 61	61 ± 33	35 ± 17	9 ± 5	981 ± 324	1009 ± 482	603 ± 350	285 ± 114
Fe	3967 ± 3726	2674 ± 1270	549 ± 259	523 ± 207	37666 ± 22502	43203 ± 13963	10836 ± 4524	17727 ± 9518
K	787 ± 533	386 ± 145	394 ± 152	152 ± 50	8345 ± 3515	6297 ± 1472	7846 ± 2618	5168 ± 2439
Mg	503 ± 295	344 ± 96	160 ± 58	182 ± 64	5682 ± 1873	5651 ± 777	3168 ± 967	5838 ± 1582
Mn	336 ± 379	138 ± 92	16 ± 7	14 ± 6	2934 ± 2723	2147 ± 1114	285 ± 162	477 ± 250
Na	1262 ± 860	484 ± 525	562 ± 362	362 ± 340	14239 ± 8100	7601 ± 7152	11553 ± 7864	9033 ± 7142
Ni	15 ± 4	12 ± 2	11 ± 8	17 ± 13	193 ± 91	208 ± 80	195 ± 193	497 ± 231
Pb	1027 ± 1208	555 ± 515	37 ± 12	16 ± 7	8714 ± 8698	8754 ± 7222	652 ± 308	569 ± 291
Sr	14 ± 8	9 ± 4	9 ± 6	8 ± 5	158 ± 53	144 ± 57	167 ± 99	283 ± 241
V	20 ± 11	15 ± 5	9 ± 7	43 ± 36	299 ± 228	255 ± 121	143 ± 135	1193 ± 715
Zn	4457 ± 5260	3206 ± 2567	103 ± 45	93 ± 29	37733 ± 39218	43011 ± 33993	2042 ± 794	2466 ± 1557

Table 3. The components of PM emitted from electric arc furnace

Component	Wt, %
Zn	33
Fe	26
Pb	3.05
SiO_2	3.15
Cu	0.24
Cd	0.049
Cr	0.024
Al	0.6
Mn	1.83
Ca	2.9
Na	1.03
K	0.95
Sn	0.024
Sb	0.06
Cl	0.011
F	0.073
As, Ti, Ni, Mg, S	Trace

Table 4. The ratios of elemental concentrations at Horozgediği station

	HOROZGEDIĞI			**ALIAĞA**		
	Min.	**Max.**	**Ave.±Std.Dev.**	**Min.**	**Max.**	**Ave.±Std.Dev.**
Fe/Zn	0.6	12	2.8 ± 3.5	3.3	11.5	5.9 ± 2.3
Fe/Pb	3.1	53.8	12.2 ± 13.6	3	26.5	23.3 ± 15.8
Zn/Pb	2.5	9.3	4.7 ± 1.9	1.8	14.2	4.5 ± 4.3

A study has been conducted for about two years including elemental composition of all kind of PM sources and PM_{10} and $PM_{2.5}$ samples at two urban and suburban stations in Izmir. The elemental composition data from this work will be used to determine the contributions of all sources.

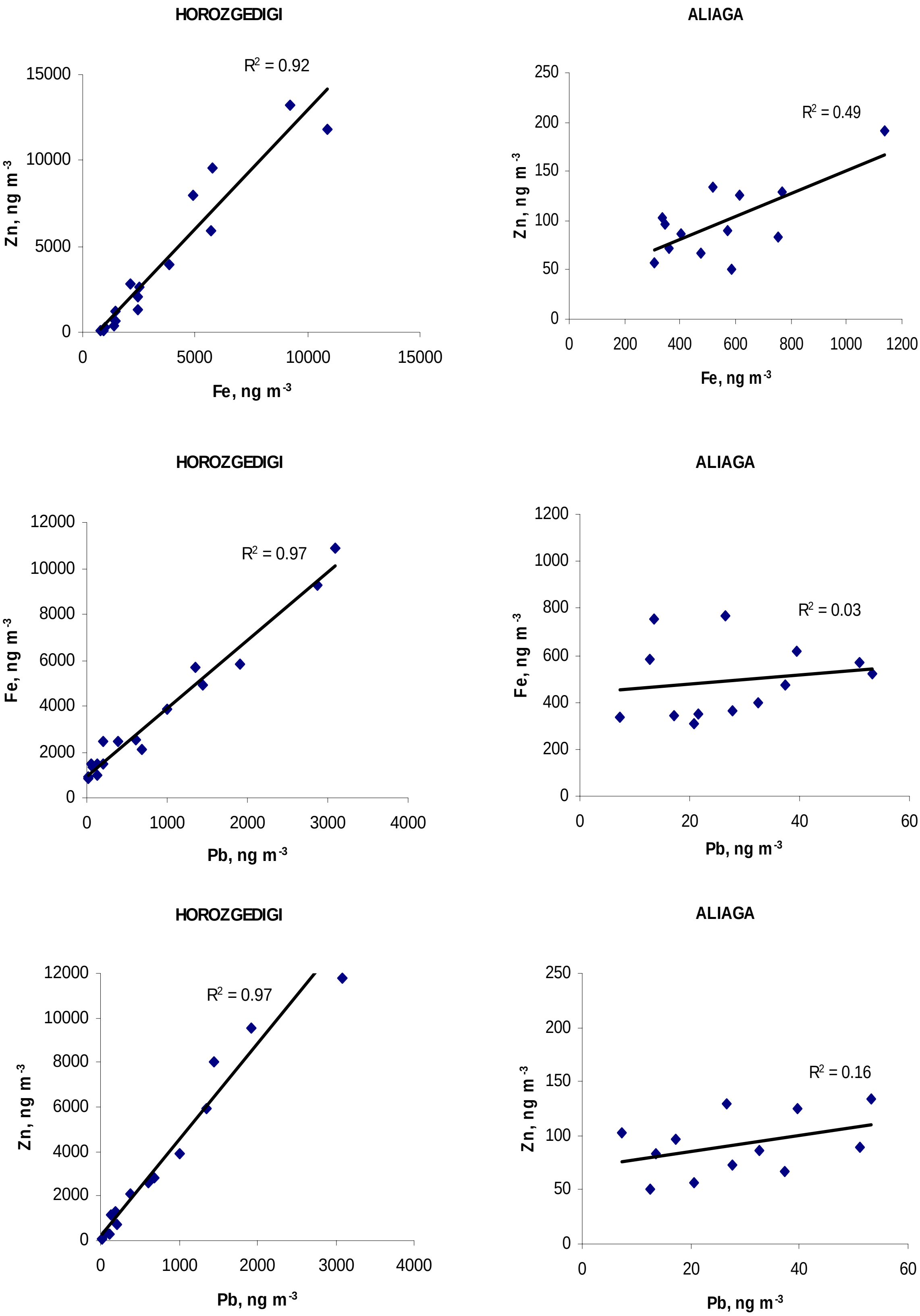

Figure 4. The scatter plots of Zn-Fe, Fe-Pb and Zn-Pb at two stations

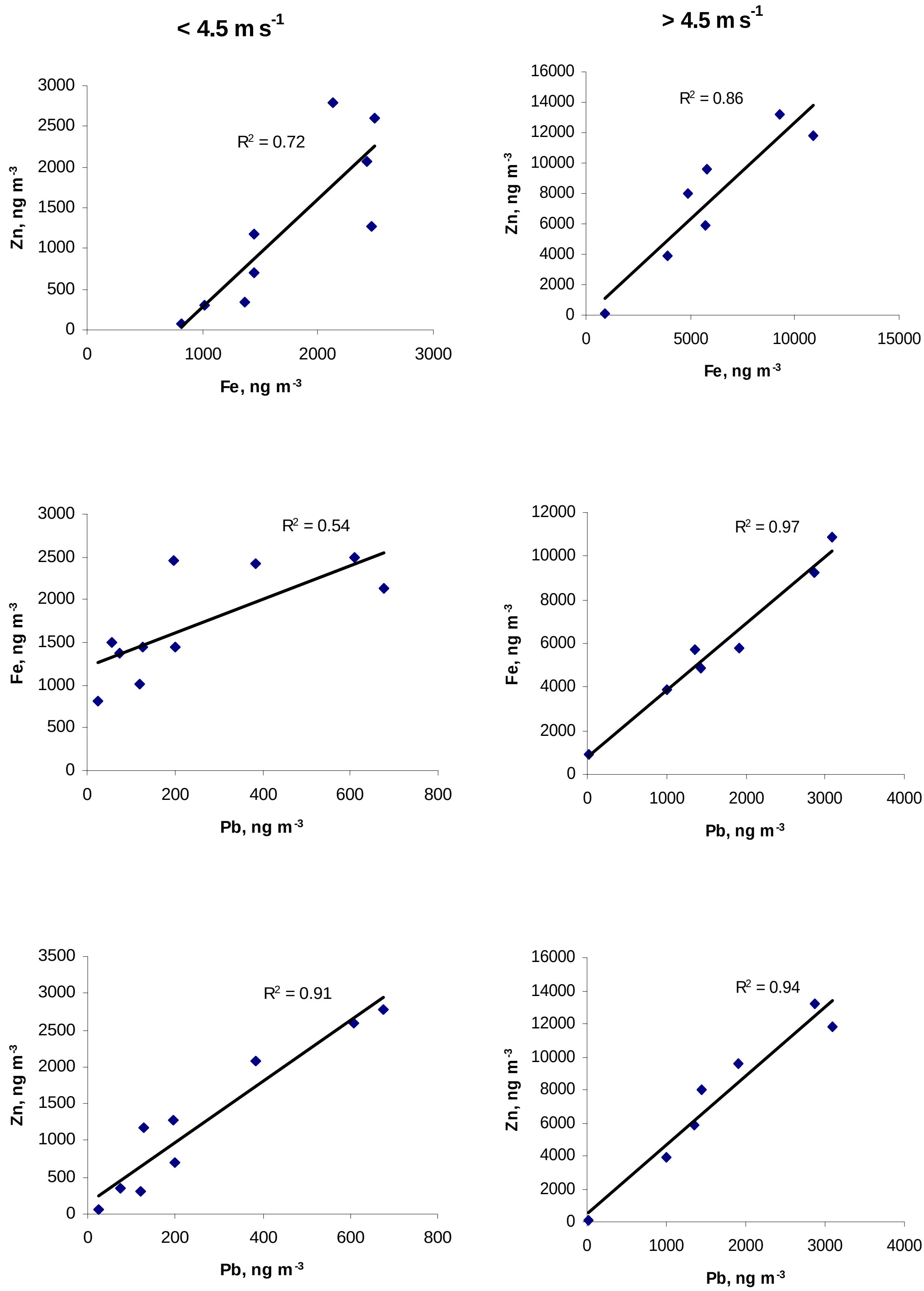

Figure 5. The scatter plots of Zn-Fe, Fe-Pb and Zn-Pb according to the wind speed at Horozgediği station.

REFERENCES

Gao, Y.; Nelson, E.D.; Field, M.P.; Ding, Q.; Li, H.; Sherrell, R.M.; Gigliotti, C.L.; Van Ry, D.A.; Glenn, T.R.; Eisenreich, S.J., 2002. Characterization of atmospheric trace elements on $PM_{2.5}$ particulate matter over the New York-New Jersey harbor estuary. Atmospheric Environment 36, 1077-1086

He, K., Yang F.; Ma, Y.; Zhang, Q.; Yao, X., Chan, C.K.; Cadle, S.; Chan, T.; Mulawa, P., 2001. The characteristics of $PM_{2.5}$ in Beijing, China. Atmospheric Environment 35, 4959-4970

Home page of US Environmental Protection Agency (www.epa.gov).

Polissar, A.V.; Hopke, P.K.; Poirot R.L.,2001. Atmospheric aerosol over Vermont: Chemical composition and sources. Environmental Science and Technology.

Röösli, M.; Theis G.; Künzli, N.; Staehelin, J.; Mathys, P.; Oglesby, L.; Camanzind, M.; Braun-Fahrlander Ch., 2001. Temporal and spatial variation of the chemical composition of PM_{10} at urban and rural sites in the Basel area, Switzerland. Atmospheric Environment 35, 3701-3713

Orhan, G., 2005. Leaching and cementation of heavy metals from electric arc furnace dust in alkaline medium. Hydrometallurgy 78, 236– 245