DETERMINATION OF GERMANIUM, SILVER, BARIUM, POTASSIUM, AND IRON IN INDOOR AND OUTDOOR AIRDUST OF SAKARYA USING ICP-OES TECHNIQUE

Mustafa S. Dündar*, Hüseyin Altundağ, N. Deryaoğlu, F. Özdemir, Z. Karaçoban#

*Sakarya University, Fen-Edebiyat Fak. Kimya Bölümü Serdivan-SAKARYA
#Sakarya Üniversitesi Fen Bilimleri Enstitüsü Serdivan-SAKARYA

*E-mail:dundar@sakarya.edu.tr, Tel:+90 264 2956044
Fax: +90 264 2955950

ABSTRACT

This paper presents Ge, Ag, Ba, K, and Fe contents of indoor and outdoor dustfall depositions collected from residences located in six different places across Sakarya city center between March and September 2002. At each indoor sampling site, duplicate samples were collected using buckets at the heights of 30 cm and 150 cm above the floor. Outdoor dust depositions were also collected using similar buckets placed on balkony of sampling houses.

The deposition rates at 30 cm height ranged from 0.38 to 1.78 μg/cm^2/day and at 150 cm height ranged from 0.27 to 1.13 μg/cm^2/day during the sampling period. The arithmetic mean deposition rate for all houses was 0.98 μg/cm^2/day at 30 cm and 0.57 μg/cm^2/day at 150 cm heights. Outdoor mass deposition rates ranged from 0.38 to 1.78 μg/cm^2/day. In general, indoor elemental loadings were observed to be highest in Yeşiltepe area whereas Kampüs area showed the lowest elemental concentrations. These results indicated that as the indoor to outdoor ratio increases the effect of outdoor dust to indoor dustfall increases.

***Keywords*: ICP-OES, trace metal, indoor, outdoor, dust, Sakarya**

1. INTRODUCTION

Indoor and outdoor dust depositions make a significant contribution to pollution with heavy metals in the urban environment [1]. Indoor air pollution may come from heavy metal sources being vehicle emissions [2]. Other sources may come from the infiltration of outdoor pollutants, e.g., dust, soil, fuel consumption products, smoking and building materials [3, 4]. Atmospheric heavy metal deposition studies of dustfall are important for human health [1, 5, 6]. It is well known that many heavy metals have toxic effects on humans [7, 8, 9]. Indoor particulate concentrations are often closely dependent upon ambient concentrations. It may be assumed that any process affecting ambient concentrations will lead to a subsequent change in indoor levels [10]. Indoor dust is composed of a very heterogeneous mixture of

fibers and irregularly shaped particles. Particle sources are varied and include soil, road dust, atmospherically-derived particulate matter, and that of smoking, cooking and other combustion processes [11].

Meteorological factors can also influence both the ambient concentration of particulate matter and the ability of particles to penetrate indoors. Therefore, it seems likely that local meteorology plays a key role in determining the relationships between indoor and outdoor particulate concentrations [11].

Outdoor dust contains particulate matter, which can be inorganic, organic, or a mixture of both types. Among the inorganic elements present in dust, heavy metals and other toxic elements, which arise from different environmental sources, are an important group to be considered. Some of these elements, e.g., As, Pb, Cd, Hg, Zn, Ni, Cu, and Cr are considered as toxic metals while others, e.g., Fe, Ca, Ba, and Mn are mainly linked to the earth's crust or resuspended soil [1]. The present study was undertaken to characterize the total concentrations of Fe, K, Ag, Ge, and Ba metals in indoor and outdoor dustfall depositions representative of Sakarya city center, Turkey. The aims of this study are to assess: (a) the influence of urban traffic on the heavy metal content in house and street dust, and (b) the relationships between heavy metals and the soluble fraction contents in indoor/outdoor dust.

2. MATERIALS AND METHODS

2.1 Sample Collection

Outdoor sampling: Atmospheric outdoor dustfall was collected in duplicate between March and September 2002 at six sites, located in various places of Sakarya. Collection periods in this study represent a standard collection time of 30 days. The non-electrostatic dust collection buckets (312 cm^2) were placed on balkonies at each site (3m above ground level) to limit problems of vandalism, rain and wind current modification by large obstacles. Collectors were covered during rainfall and for most of the sampling periods it was therefore leaved open to get a standard collection period. All analyses were conducted in duplicate and each value measured is a mean of three replicate determinations. The concentrations of each element were determined by inductively coupled plasma optic emission spectrometer.

Indoor sampling: Indoor dry dustfall from residences located in six different representative zones of Sakarya city center was collected between March and September 2002. Pre-cleaned dust sampling buckets were used to collect the dust mass deposited over a 30-day period. The non-electrostatic buckets were (400 cm^2) placed on household surfaces in the living room. Two buckets were positioned on surfaces approximately 30 cm above the floor, and two were positioned on surfaces approximately 150 cm above the floor in each house. Each sampling bucket was placed on a different surface so that no two sampling buckets were placed adjacent to each other. However, buckets were not placed next to the electrical appliances and windy positions due to the disturbtion of buckets during the collection period. The concentrations of each element were determined by inductively coupled plasma optic emission spectrometer.

Table 2. Metal concentrations in standard reference material ($\mu g\ g^{-1} \pm$ Uncertainty)

Element	Certified Value	Measured Value	Recovery %
Fe	0.56 ± 0.09	0.55 ± 0.012	98.21
K	5.20 ± 0.09	5.27 ± 0.120	101.35
Ag	0.066 ± 0.010	0.069 ± 0.001	104.55
Ge	1.70 ± 0.30	1.81 ± 0.03	106.47
Ba	185.00 ± 24	180.00 ± 8.50	97.30

Recovery = (Measured value/Certified value x 100).

2.2 Reagents and Standards

All glassware and polyethylene bottles were kept overnight by soaking in 10 % HNO_3, and cleaned by rinsing five times with destilled de-ionised Ultra High Quality (UHQ) water (Millipore, France) prior to use. The standard solutions (1000 mg L^{-1}) for Ge, Ag, Ba, K, and Fe were spectroscopic grade and obtained from Merck (Darmstadt, Germany). These solutions were prepared by serial dilution with 0.2 % (v/v) HNO_3 to the required concentrations with UHQ water (chemical resistivity:18 MΩ cm^{-1}) prior to use. All chemicals used throughout the experiments were of analytical-reagent grade (Merck, Darmstadt, Germany).

2.3 Apparatus and Chemicals

Perkin Elmer Optima 2100 DV model ICP-OES was used for the determination of elements. The operating parameters of ICP-OES were operated at 1000 W RF power and other parameters set as recommended by the manufacturer. The pH of solutions with a Hanna 213 pH-meter. ICP-OES calibration curve parameters is shown in Table 1.

Table 1. Calibration data of elements analysed by ICP-OES.

Element	Ba	Ag	Ge	K	Fe
Wavelength (nm)	455.4	328.0	265.1	769.9	238.6
Number of replication	3	3	3	3	3
R	0.9999	0.9995	0.9999	0.9999	0.9999

2.4 Quality Control and Quality Assessment

Quality of the analytical procedures was assured by using Certified Reference Material (LGC Promochem NCS-DC 73312). Each sample batch prepared for the study of recovery and analytical reproducibility were evaluated using sample duplicates, blanks and certified standard. Analysis of Certified Reference Material (CRM) was allowed an assessment of accuracy and precision over a wide range of element concentrations. Concentration data for Germanium, Silver, Barium, Potassium, and Iron determinations of CRM drawn against certified values indicate that observed values correlate well with certified values. Percentages of recoveries are in the range of 98-106 (Table 2).

2.5 Chemical analysis

Collected dust samples were digested with aqua regia according to the method described by Harrison et al. [7]. After making up the final solution to volume with UHQ water, the concentrations of each of Ba, Fe, K, Ge, and Ag were determined by ICP-OES equipped with an auto-sampler. Prior to analysis, the instrument was calibrated according to manufacturer's recommendation. Blank digestion was also carried out by completion of full analytical procedure without sample.

3. RESULTS AND DISCUSSION

The results for soluble fractions of Fe, K, Ag, Ge and Ba in indoor and outdoor dust depositions are presented in Table 3. The aims of this study are to assess: (a) the influence of urban traffic on heavy metal content in house and street dust, and (b) the relationships between heavy metals and the soluble fraction contents in indoor/outdoor dust.

Indoor elemental loadings were observed to be highest in Yeşiltepe area compared to the other areas studied. It is apparent that Yeşiltepe area is a substantial source of elemental dry fallout, from stack or entrained fugitive emissions (stock piles, road dust and material handling). These results can be linked to closeness of Yeşiltepe to industrial area, traffic, etc. The lowest levels were obtained in Serdivan and Kampus area. These results suggested that ventilation of the houses and rainy weather were affected re-

suspended particles to enter and led to the variability of the settled dust levels. Measurement of contaminant levels in house dust to estimate exposure, therefore, should take into consideration both the weather conditions and height differences in dust mass.

The results show that Fe and K are present at the highest levels in indoor dust. Germanium previously constituted a base in the production of semiductor technique but is nowadays largely replaced by Si. It is emitted in flue dust from Zn smelters. Germanium is also used to support diet as an antioxidant.

Silver (Ag) is usually minor or trace constituents of sulphide ores and great reduction of dust emission from metallurgical industry in recent decades would have contributed to their decrease. Some of these elements, e.g., Fe and Ba are mainly linked to the earth's crust or resuspended soil.

Among the inorganic elements present in particulate matters, heavy metals and other toxic elements, which arise from different environmental sources are an important group to be considered. Outdoor dust contains particulate matters, which can be inorganic, organic, or a mixture of both types.

Indoor and outdoor dust elemental concentrations at each site as $\mu g/m^2$/day are summarized in Table 3. Indoor house dust samples collected in duplicate at 30 cm and 150 cm heights above the floor. The deposition rates at 30 cm height ranged from 0.38 to 1.78 $\mu g/cm^2$/day and at 150 cm height ranged from 0.27 to 1.13 $\mu g/cm^2$/day during the sampling period. The arithmetic mean deposition rate for all houses was 0.98 $\mu g/cm^2$/day at 30 cm and 0.57 $\mu g/cm^2$/day at 150 cm heights [12]. Outdoor mass deposition rates ranged from 0.38 to 1.78 $\mu g/cm^2$/day. The mass deposition rate was calculated for each sampling bucket over the 30-days collection period [13].

In general, higher metal concentrations occur in outdoor dust which may come into the indoor environment through the open windows, doors, etc., thus settling out the fine particles. Total element concentrations in dust are likely to be influenced by the relative proportion of biogenic particles (molds, fungi and other organic matter), which have an ability to accumulate metals to high concentrations. Inadequate exchange between indoor and outdoor air can result in increased indoor fungal concentrations [10].

It is indicated that highest indoor Fe, K, Ag, and Ge levels at 30 cm height of indoor sample were measured in Yeşiltepe, Çark C., and Kampus areas, respectively. Fe, K, and Ag in Yeşiltepe area and Ge in Kampus area were observed at 150 cm height. The lowest indoor Fe, K, Ag, and Ge levels at 30 cm height were measured in Ozanlar, Serdivan, Yeşiltepe, and Ozanlar areas, respectively. At 150 cm sampling height, the only difference was observed for Ag presence in Çark C compare to the sampling at 30 cm height.

Although Ba is hardly considered among elements of environmental concern, it is widely used (in the manufacture of glass, ceramics, television picture tubes, fireworks, etc.) and some Ba-containing household and consumer products (insecticides, depilatories, etc.) are of toxicological importance [14]. The element also has many applications in the automotive industries including the rubber production, lubricating oil additives and fuel synthesis. In addition, Ba is found in samples of petrol. This agrees with available data on the elemental composition of urban street dust and of diesel and unleaded petrol-powered vehicle emissions [15, 16, 17]. Thorpe and Harrison [18] reviewed metals which are typically used in brake lining materials and road vehicle

Table 3. Metal concentrations of indoor and outdoor dust depositions (μg/m^2/day)

Sampling		Element	Fe		K		Ag		Ge		Ba	
Type	Height (cm)	Location (Earth Crust)	μg/m^2/day									
			Range	Mean±RSD%	Range	Mean±RSD%	Range	Mean±RSD%	Range	Mean±RSD%	Range	Mean±RSD%
Indoor	30	*Serdivan*	2083.33 - 6833.33	3500.00 ± 0.47	891.67 - 1916.67	1383.33 ± 1.09	ND		ND		ND	
	150		1250.00 - 5500.00	2750.00 ± 0.54	750.00 - 2083.33	1391.67 ± 1.09						
Outdoor	-		*295940.17 - 2649572.65*	*1041239.32 ± 0.66*	*49252.14 - 781730.77*	*259615.38 ± 0.40*	*0,00 - 2670.94*	*373.93 ± 0.78*	*ND*		*61965.81 - 993803.42*	*272329.06 ± 0.41*
Indoor	30	*Çark C.*	7000.00 - 21250.00	16166.67 ± 0.34	3416.67 - 11250.00	7350.00 ± 1.45	0.00 - 500.00	70.83 ± 3.49	ND		ND	
	150		5500.00 - 29083.33	16775.00 ± 0.41	3916.67 - 14583.33	6625.00 ± 0.98	0.00 - 158.33	22.50 ± 3.35				
Outdoor	-		*566239.32 - 2657051.28*	*1592094.02 ± 0.43*	*91132.48 - 692735.04*	*364957.26 ± 0.75*	*ND*		*ND*		*131410.26 - 385576.92*	*268162.39 ± 0.57*
Indoor	30	*Yeşiltepe*	5750.00 - 47916.67	22475.00 ± 0.64	2750.00 - 14750.00	8241.67 ± 1.08	0.00 - 175.00	25.00 ± 2.78	ND		ND	
	150		10000.00 - 67416.67	25866.67 ± 0.41	2916.67 - 15500.00	8141.67 ± 2.15	0.00 - 833.33	116.67 ± 3.19				
Outdoor	-		*986111.11 - 2784188.03*	*1853632.48 ± 0.43*	*108760.68 - 797863.25*	*345512.82 ± 0.69*	*ND*		*ND*		*218696.58 - 758547.01*	*454380.34 ± 0.61*
Indoor	30	*Erenler*	4666.67 - 13000.00	7391.67 ± 0.42	2000.00 - 8083.33	5341.67 ± 1.07	0.00 - 275.00	41.67 ± 3.64	ND		ND	
	150		1500.00 - 31416.67	6700.00 ± 0.34	1166.67 - 3583.33	2083.33 ± 1.05	ND					
Outdoor	-		*897435.90 - 2013888.89*	*1337606.84 ± 0.45*	*159294.87 - 649358.97*	*304166.67 ± 0.50*	*ND*		*0.00 - 10.68*	*2.14 ± 0.43*	*118589.74 - 304166.67*	*198717.95 ± 0.33*
Indoor	30	*Ozanlar*	1166.67 - 6833.33	3033.33 ± 0.58	1083.33 - 3750.00	2408.33 ± 0.94	ND		*0.00* - 41.67	14.17 ± 3.13	ND	
	150		416.67 - 3750.00	1858.33 ± 0.22	750.00 - 2333.33	1531.67 ± 0.84			0.00 - 58.33	16.67 ± 3.17		
Outdoor	-		*668803.42 - 4077991.45*	*2200854.70 ± 0.33*	*71367.52 - 1645299.15*	*632478.63 ± 0.52*			*ND*		*59188.03 - 431196.58*	*215705.13 ± 0.56*
Indoor	30	*Kampüs*	2916.67 - 14250.00	7283.33 ± 0.87	2916.67 - 11000.00	5625.00 ± 0.75	ND		0.00 - 450.00	116.67 ± 4.14	ND	
	150		1833.33 - 5250.00	3225.00 ± 0.56	1583.33 - 6166.67	3225.00 ± 1.30			0.00 - 208.33	73.33 ± 3.24		
Outdoor	-		*123931.62 - 563034.19*	*330876.07 ± 0.45*	*13995.73 - 44658.12*	*27243.59 ± 0.60*	*0.00 - 117.52*	*21.37 ± 2.10*	*ND*		*8440.17 - 70192.31*	*22649.57 ± 0,70*

brake dust. At traffic-influenced sites it seems likely that brake wear is the main source of barium, which is often used in the form of barite in the filler material of brake pads. Being contributed by only one major source is an important prerequisite for a substance to be used as a tracer for emissions, and other sources of barium are likely to be few [19].

Outdoor elemental loadings were reached to maximum levels for Fe and K in Ozanlar, for Ag in Serdivan, and for Ba in Yeşiltepe areas. Germanium was not detected. Minimum values of Fe, Ag, and Ba contents of outdoor dust samples were detected in Kampus area, Potassium in Serdivan area, and Germanium in Erenler area.

According to Table 4, the ratios of residential indoor to outdoor elemental composition were calculated highest for Potassium in Kampus area. The lowest levels were obtained in Ozanlar site. For Iron element

Table 4. The ratio of the residential indoor-to-outdoor elemental compositions.

Sampling		Element	Fe	K	Ag	Ge	Ba
Type	Height (cm)	Location	Indoor to Outdoor Ratio%				
Indoor	30	*Serdivan*	0.34	0.53	NA	NA	NA
	150		0.26	0.54			
	30	*Çark C.*	1.02	2.01			
	150		1.05	1.82			
	30	*Yeşiltepe*	1.21	2.39			
	150		1.40	2.36			
	30	*Erenler*	0.55	1.76			
	150		0.50	0.68			
	30	*Ozanlar*	0.14	0.38			
	150		0.08	0.24			
	30	*Kampüs*	2.20	20.65			
	150		0.97	11.84			

NA:Not applied.

the highest ratio at 30 cm height was measured in Kampus area, and at 150 cm height in Yeşiltepe region. Ozanlar area showed the lowest levels for Iron at both heights.

These results indicated that as the ratio increases the effect of outdoor dust to indoor dust increases. The ratios of Ag, Ge, and Ba elements were not calculated because of unavailability of outdoor data. In general, higher metal concentrations occur in outdoor dust which may come into the indoor environment through the open windows, doors, etc. thus settling out the fine particles.

4. CONCLUSIONS

It is concluded that suspended airdust collected within the house itself can contribute some elements, such as Iron, Potassium, Silver, Germanium, and Barium. In general, the elemental contents of house dust deposited on indoor surfaces at both levels were higher in Yeşiltepe area due to its closeness to the industrialised and heavy traffic, etc. environments and the lowest levels measured in Kampus area except for Germanium which is interestingly higher than expected. The elementel loadings of outdoor dust were obtained highest in Yeşiltepe area for Barium and Ozanlar area for Iron and Potassium, and lowest levels in Kampus area for all detectable elements.

REFERENCES

[1] Rashed, M.N. Total and Extractable Heavy Metals in Indoor, Outdoor and Street Dust from Aswan City, Egypt, Clean, 36 (10-11), 850-857, 2008.

[2] Sezgin, N., H. Ozcan, K., Demir, G., Nemlioglu, S., Bayat, C. Determination of heavy metal concentrations in street dusts in Istanbul E-5

highway, Environment International 29, 979-985, 2003.

[3] Ondera, S., Dursunb, S. Air borne heavy metal pollution of Cedrus libani (A. Rich.) in the city centre of Konya (Turkey), Atmos. Environ. 40, 1122-1133, 2006.

[4] Rasmussen, P.E., Subramanian, K.S., Jessiman, B.J. A multi-element profile of house dust in relation to exterior dust and soils in the city of Ottawa, Canada, Sci. Total Environ. 267, 125-140, 2001.

[5] Dundar, M.S. Vanadium Concentrations in Settled Outdoor Dust Particles**,** Environmental Monitoring and Assessment, 123**,** 345–350, 2006.

[6] Mahler, B.J., Van Metre, P.C., Wilson, J., Musgrove, M. Fipronil and its Degradates in Indoor and Outdoor Dust, Environ. Sci. Technol. 43, 5665-5670, 2009.

[7] Harrison, R.M., Laxen D.P.H., Wilson S.J. Chemical associations of lead, cadmium, copper and zinc in street dusts and roadside soils, Environ Sci Technol., 15, 1378-1383, 1981.

[8] Dermentzoglou, M., Manoli, E., Voutsa, D., Samara, C. Sources and patterns of polycyclic aromatic hydrocarbons and heavy metals in fine indoor particulate matter of Greek houses, Fresen. Environ. Bull., 12(12), 1511-1519, 2003.

[9] Hunt, A., Johnson, D.L., Watt, J.M. and Thornton, I. Characterizing the sources of particulate lead in house dust by automated scanning electron microscopy, J. Environ Sci Technol., 26, 1513-1523, 1992.

[10] Dundar, M.S., Altundag, H. Heavy Metal Determination of House Dust in Adapazari, Turkey, After Earthquake, Trace Elements and Electrolytes, 19(2), 55-58, 2002.

[11] Shilton, V., Giess, P., Mitchell, D., Williams, C. The Relationships between Indoor and Outdoor Respirable Particulate Matter: Meteorology, Chemistry and Personal Exposure**,** Indoor Built Environt, 11, 266-274, 2002.

[12] Dundar, M.S., Ozdemir, F. Heavy Metal Contents of Indoor Airdust Particulate Matter from Adapazarı, Fresenius Environmental Bulletin**,** 14(3), 189-193, 2005.

[13] Dundar, M.S., Deryaoglu, N. Heavy Metal Determinations in Outdoor Atmospheric Dust Depositions, Fresenius Environmental Bulletin, 14(3), 185-188, 2005.

[14] WHO, Barium. Environmental Health Criteria 107. WHO/UNEP, Geneva, p. 148, 1990.

[15] Lowenthal, D. H., Zielinska, B., Chow, J. C.,Watson, J. G.W.,Gautam,M., Ferguson, D. H.,Neuroth, G. R. and Stevens, K. D., Atmos. Environ., 28, 731,1994.

[16] Que Hee, S. S. Arch. Environ. Contam. Toxicol., 27, 145, 1994.

[17] Monaci, F., Bargagli, R. Barium and Other Trace Metals as Indicators of Vehicle Emissions, Water, Air, and Soil Pollution, 100, 89–98, 1997.

[18] Thorpe, A., Harrison, R.M. Sources and properties of non-exhaust particulate matter from road traffic: a review, Science of the Total Environment 400(1-3), 270-282, 2008.

[19] Gietl, J.K., Lawrence, R., Thorpe, A.J., Harrison, R.M. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road, Atmospheric Environment, 44(2), 141-146, 2010.