TOX-TOXIC AND HAZARDOUS POLLUTANTS

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INVESTIGATION OF ATMOSPHERIC PARTICLES SOURCES IN URBAN AND INDUSTRIALIZED AREA AT DUNKERQUE, FRANCE

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ABSTRACT

A physico-chemical characterization of different atmospheric particles samples collected at Dunkerque (France) under the influence of the city centre or a heavy industrialized area has been undertaken. Analytical techniques SEM-EDX, GC-MS, XRD and EPR have been used in combination to reveal specific features following the particulate matter origin. The SEM-EDX study shows the influence of different industrial sources with the detection of Fe-rich spherules, Mn-rich and C-rich particles. The latter were associated to particle-phase PAHs. Specific information on some chemical forms of Fe and Mn present in particles were obtained by XRD and EPR techniques and correlated to the particles origin.

Key Words : Industrial emissions, Suspended Particulate Matter, chemical form, tracer

1. INTRODUCTION

A majority of atmospheric particulate matter in urban and industrial areas is a result of human activities. Many potential anthropogenic emission sources can generally be listed : vehicle and chimney exhausts, waste incineration and various industrial processes. Sometimes it can be difficult to identify the origin of particles as some elements as Fe, Ca, Al, Si, Ti,... can be found in different particulate emissions and can also be encountered in natural particles (Ebert et al., 2000). For this reason, the knowledge of the elemental chemical composition is not always sufficient to indicate the particles origin. To be able to link physicochemical characteristics of particles to their origin, an approach consists to apply in combination different analytical techniques for their specific contribution, and permitting finally to get complementary information.

The purpose of this work is to compare different atmospheric particles samples collected under the influence of a city centre and others under the influence of different industrial activities. Different techniques have been applied to evidence physico-chemical parameters that could be used to differentiate between the urban and the different industrial particles. The morphology of particles and their individual composition have been studied by SEM-EDX. The organic fraction of particles has been analysed by GC-MS. Complementary investigation of the inorganic fraction has been undertaken with the use of XRD and EPR techniques, to specify the structure and the chemical environment of some metal elements.

2. MATERIALS AND METHODS

2.1. Study Area and Sampling methodology

Sampling was performed at Dunkerque situated on the southern coast of the North Sea (51°04'N ; 2°38'E). This city counting 210 000 inhabitants has been subject to a high implantation of industries in the field of metallurgy, petrol refinery and chemistry during the last 30 years. In 2003, it was estimated that the area of Dunkerque was responsible of 65% of the total industrial emissions of particles in the Nord-Pas-de-Calais county, one of the most industrialized county in France. In the present study, we focused on especially some particulate emissaries present in this area : steel plant (steel works, coke plant, blast furnace, iron ore handling and tanker unloading), ferromanganese metallurgy plant, and particles induced by transport and human activities in the city have also been studied to make a comparison. Five samples have been collected at a distance between 300 meters and 500 meters downstream from the following sources: A: urban emissions, B: coke plant, C: iron and steel plant, D: tanker unloading and blast furnace, E: ferromanganese metallurgy plant.

Atmospheric particles have been collected using high volume samplers (100 m^3/h) onto cellulose filters (Whatman® 41) and glass fibre filters (Whatman® GF/F). In parallel, sampling was also done on polycarbonate filters at a flow rate of 5 m^3/h filter in order to perform SEM-EDX study. To reduce analytical blank, cellulose filters and glass fibre filters have been cleaned prior to the sampling using an acid washing solution and a heating treatment at 450°C respectively.

2.2. Analytical techniques.

SEM images and automated single particle analysis were performed on a LEO 438 VP microscope equipped with an Energy Dispersive X-ray spectrometer (Oxford instruments, UK) (SEM-EDX). For each sample, 1000 particles were analysed. Carbon, nitrogen and oxygen were not taken into account in this analysis. Each data set was then submitted to hierarchical cluster analysis (HCA) using IDAS, a windows based software for cluster analysis (Bondarenko et al., 1996), then similar particles are grouped according to their composition giving the different types of particles in the sample.

Polycyclic aromatic hydrocarbons (PAHs) present as particle-phase PAHs were Soxhlet extracted with dichloromethane for 18 h. The extract was then concentrated to 0.2 ml under pure N_2 gas. PAHs were subsequently analyzed by chromatographic method coupled to mass spectrometry (GC-MS Varian saturn 4D).

X-ray diffraction (XRD) analyses were performed on a Bruker D8Advance X-ray diffractometer using CuKα radiation generated at 40 kV and 40 mA. The 2Θ range was varied from 10 to 70° in steps of 0.02°. Measurements were directly performed on glass fibre filters with an integration time of 25 seconds. The EPR spectra were recorded at room temperature (T_A = 293 K) and at liquid nitrogen temperature (T_{LN} = 77 K) on a EMX Bruker spectrometer, using a cavity operating with a frequency of ~9.5 GHz (X-band). EPR parameters considered were : (a) *g factor* value, (b) *peak-to-peak signal width* ΔHpp, (c) *normalised double integration value of a signal recorded* at room temperature $Ns(T_A)$ and at liquid nitrogen $Ns(T_{LN})$. Moreover the $Ns(T_{LN}) / Ns(T_A)$ *ratio* was determined to get informations about interactions between species and their magnetic properties (Ledoux et al., 2005).

3. RESULTS

3.1 SEM-EDX

Individual particle analysis of A sample collected close to the city centre (Table 1) shows that this sample is composed with a wide variety of particles with low size (<10 µm) being dominated by gypsum (32.7%), Fe-rich (19.9%) and aluminosilicates (13.6%). SEM images of such particles indicate that gypsum (Fig. 1.f) have an angular shape whereas aluminosilicates (Fig. 1.d) and Fe-rich particles (Fig. 1.c) do not have any specific geometry. Carbon particles are not considered in the automated individual particle analysis, nevertheless, many soot particles (Fig 1.h) are observed on this sample. Soot can be typically related to the

Table 1. Types of particles identified using individual particle analysis* (SEM-EDX) and Hierarchical Cluster Analysis.

Particle type	A	B	C	D	E
Aluminosilicates	13.6	6.1	19.1	4.1	5.6
Ca-rich**	2.1	6.6	1.6	4.9	14.5
Ca-S (Gypsum)	32.7	2.3	3.7	1.3	13.8
Other Ca compounds (Ca-Cl ; Ca-S-Si ; Ca-Fe-Si ; Ca-S-K)	5.7		9.5	9.5	1.9
S-rich	1.4		0.6		
Si-rich	4.3	4.1	3.5	1.8	3.2
Other Si Compounds (Si-Al-S ; Si-Al-Mn ; Si-Al-Fe)	5.6	6.2	2.0		5.3
Cl rich	1.9	0.4	6.4		
Na-rich	1.8		11.7		
Other Na Compounds (Na-S-Ca)	3.6		2.2		
Fe-rich	19.9	68.2	33.0	71.6	8.1
Other Fe Compounds (Fe-Ca ; Fe-Ca-Si ; Fe-Ca-S ; Fe-S-K)	7.3	4.9	4.0	6.8	8.5
Mn-rich		1.1			21.8
Other Mn Compounds (Mn-Fe ; Mn-Al-Fe ; Mn-Ca ; Mn-Zn ; Mn-Cl)			1.3		17.1
Pb-rich			1.3		0.3

* carbon, nitrogen and oxygen not considered in the individual particle analysis

** rich compounds composed with more than 75 wt% of the element, other compounds containing a major concentration of the considered element

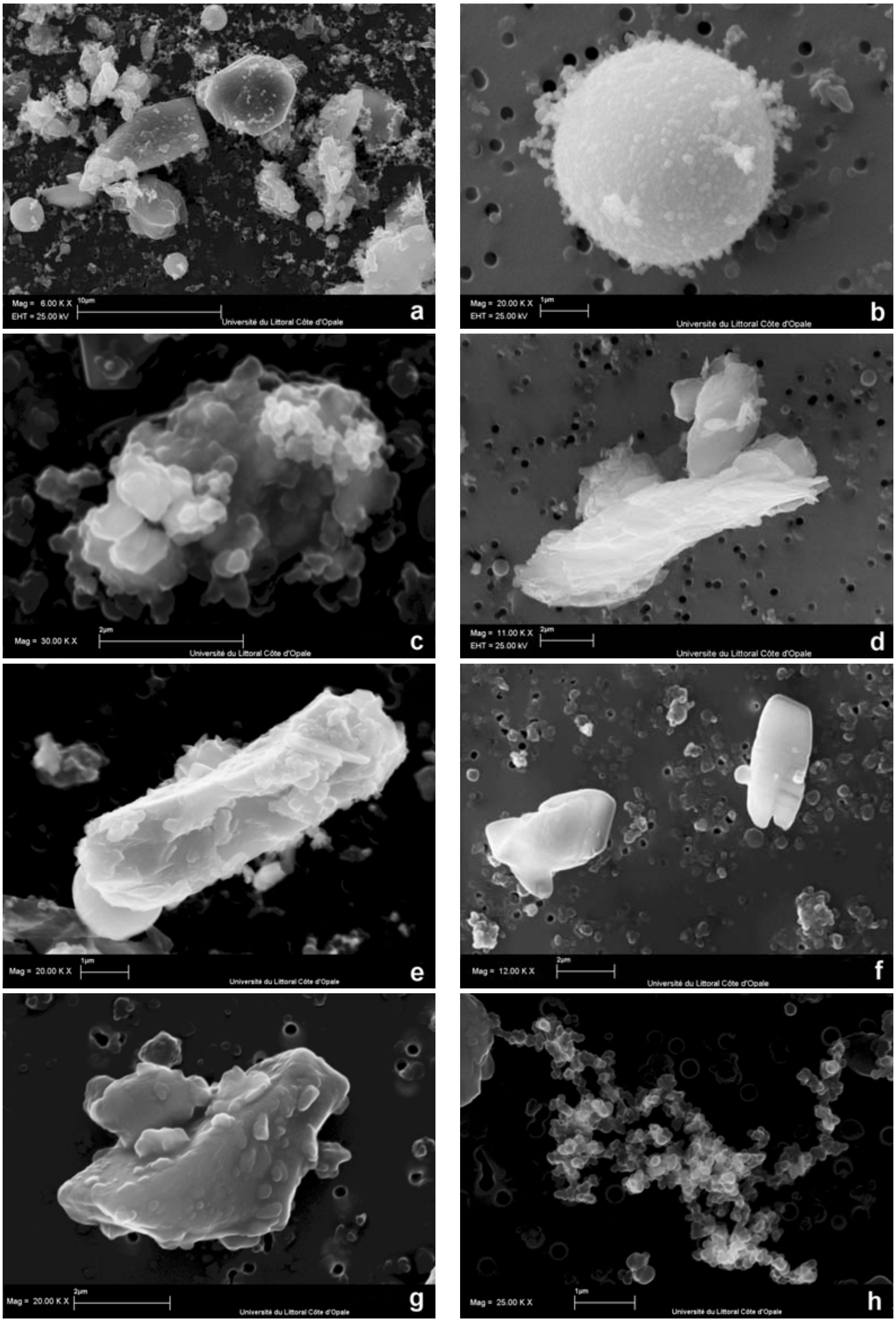

Figure 1. Secondary Electron images of some particles collected in the atmosphere of Dunkerque downwind of different sources : a) Fe ores with angular shape and spherical Fe oxide ; b) Spherical iron oxide ; c) non spherical Fe oxide ; d) Aluminosilicates ; e) Mn-rich ; f) Gypsum ; g) Carbon-rich particle ; h) soot

traffic (Ortner, 1999) with the presence of extremely busy roads inside and southwest of the city. These data for A sample were assumed to be representative of particles found in the city air, even if variations in the chemical composition of particles are typically expected (Ebert et al., 2000). In B sample collected downwind of the coke plant, other C-rich particles (Fig 1.g) appearing with irregular shape and smooth surface were identified (almost 80% of particles). Such particles can be assumed as the most representative of the coke plant activity (coke and coal particles). This influence is also recognized with the detection of Fe-containing particles, due to the presence of iron in the coal raw material. Individual particle analysis shows that C sample is mainly composed with Fe-rich particles (33.0%) and aluminosilicates (19.1%). Fe rich appears in this case as perfect spherical particles (< 5 μm) themselves composed with smaller spherical particles (Fig. 1.b). Xhoffer et al. (1991) reported that such Fe-rich spherules can be classified as purely anthropogenic. These particles are formed during high temperature processes as the coal combustion (Esbert et al., 2001) but can be most likely derived from industrial processes encountered in steel factories (Moreno et al., 2004). D sample collected under the simultaneous influence of Fe ore tanker unloading and blast furnace emissions is also dominated by Fe-rich particles. The proportion of such particles (71.6%) is very high compared to the other samples and it is important to notice that these Fe-rich particles have two different morphologies (Fig. 1.a). First ones are spherical with a smoother surface than steel factory particles and, are characteristic of the blast furnace emissions insofar as the process requires high temperatures. Second ones are mainly angular and are attributed to Fe ore particles. Mn-rich particles are only detected in E sample collected under the influence of the ferromanganese metallurgy plant (Table 1). Mn bearing compounds represent 38.9% of the particles which however do not possess any specific morphology (Fig 1.e). In parallel, only a weak proportion of Fe-rich particles is detected in this case.

3.2. Organic compounds

Due to the differences revealed by SEM on the type of carbon-rich particles found downwind of the city and the coke plant, investigation in PAHs compounds was then undertaken. The range of PAHs concentrations were generally higher under the

Table 2. Concentration ranges (ng/Nm^3) of individual PAH in particles collected under the influence of the city or industrial sources.

Compounds	Acronyms	Coke plant	City
Phenanthrene	PA	23-62	1-4
Anthracene	Ant	15-44	1-2
Fluoranthene	FL	20-67	1-12
Pyrene	Pyr	16-58	1-10
Benzo(a)anthracene	BaA	3-59	2-16
Chrysene	CHR	16-80	1-3
Benzo(b+k)fluoranthene	B(b+k)F	18-60	1-11
Benzo(a)pyrene	BaP	24-84	1-11
Indeno(123dc)pyrene	IND	16-42	1-2
Benzo(ghi)perylene	BghiP	10-26	1-2

influence of the coke plant unit (Table 2). More precisely, the proportion of PA and Ant tends to be higher in samples from the coke plant than the city ones, in agreement with observations of Khalili et al. (1995). On the contrary, constant tendencies appeared for Fl and Pyr. Hence, concentrations ratios could be proposed to differentiate the PAHs origin : (PA + Ant)/ FL ratio is at least twice higher for the coke plant influence than the city one.

3.3 XRD

Figure 2 shows the X-ray diffractograms relative to A, C, D and E samples. Only a few diffraction lines were observed on the diffractogram of particles collected under the influence of the city (A) with two low intensity lines at about 11° and 21° attributed to the presence of gypsum $CaSO_4.2H_2O$ (JCPDS 33-1311). No diffraction lines were detected for B sample but results obtained for other industrial influences are very different. For the samples collected under the influence of the steel factory (C) or the iron ores handling area and the blast furnace (D), iron oxides are detected. Hematite (α-Fe_2O_3) is mainly identified by the lines at $2\theta = 33°$ and 35.5° (JCPDS 33-0664). Moreover, a split up of the line at 35.5° is observed and indicates the simultaneous presence of hematite and magnetite, Fe_3O_4 (JCPDS 19-0629). These two iron compounds have already been observed in atmospheric particles collected near iron and steel manufacturing facilities (Machemer, 2004). The presence of quartz SiO_2 (JCPDS 46-1045) and calcite $CaCO_3$ has also been noticed in C and D samples, in agreement with SEM-EDX data evidencing Si-rich and Ca-rich particles respectively. Well crystallized calcite particles are detected in E sample but despite its high proportion of Mn containing particles, no characteristic crystalline structure associating Mn was detected by XRD. The absence of iron oxides in E sample confirms that particles were not collected under the influence of the steel manufacturing facilities.

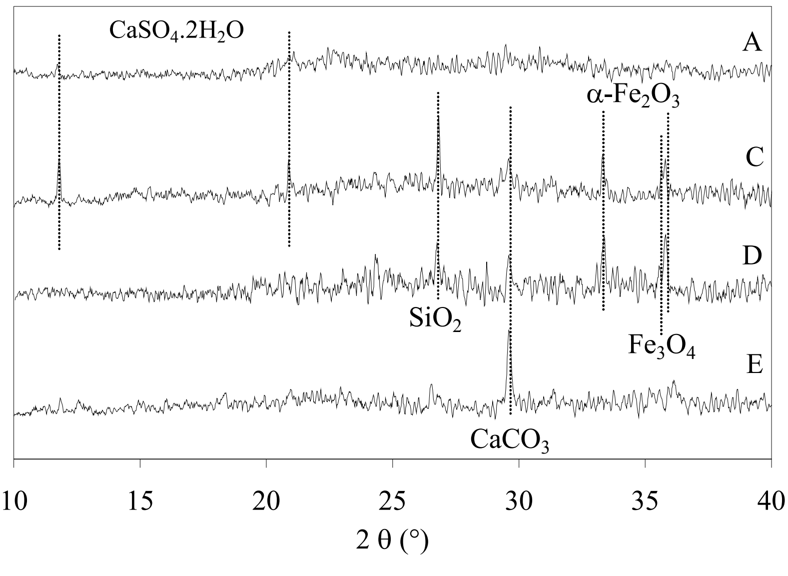

Figure 2. XRD patterns obtained for suspended particulate matter collected under the influence of the city (A) and different industrial sources (C-E).

3.4. Electron Paramagnetic Resonance

Figure 3 displays EPR spectra recorded at 293 K and 77K for the different particles samples. For winds under the influence of the town (A sample), the EPR spectra obtained are the superimposition of two elementary signals: a signal centrered at g = 2.003 with ΔHpp = 11 G relative to carbonaceous radicals (Yordanov et al., 1996) and a broad signal (T_A: g = 2.084 and ΔHpp = 564 G and T_{LN}: g= 2.161 and ΔHpp = 957 G). This latter signal was previously observed and attributed to Fe^{3+} ions in interaction, revealing the aggregation of the paramagnetic species (Ledoux et al., 2004). In the case of particles collected under the influence of the coke plant (B sample), the same EPR features were revealed with however a more intense signal of carbonaceous radicals. This observation could be related more specifically to radical stabilized in carbonaceous particles emitted from the coke plant. This observation is

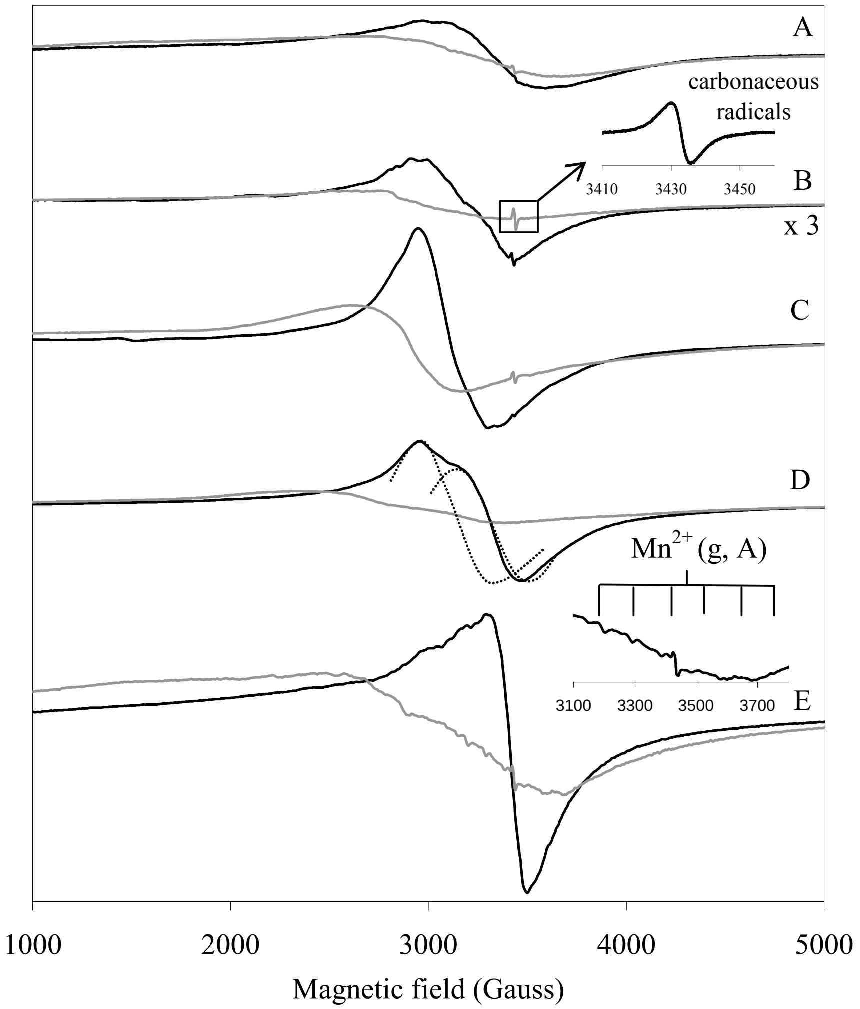

Figure 3. EPR spectra for particles from urban and industrial activities origins: spectra recorded at 293 K (black line) and 77K (grey line). Superimposition of signals (dashed line) giving the resulting experimental signal for D sample.

in agreement with the SEM and organic compounds analysis given above. As mentioned by SEM-EDX and XRD techniques, the influence of siderurgic activities has been detected in C and D samples. Particularly for winds from the steel factory, intense EPR signals were mainly obtained (T_A: g = 2.188 and ΔHpp = 390 G and T_{LN}: g = 2.380 and ΔHpp = 564 G). This signal, relative to species present in iron-rich particles, is characterized by a high g value in comparison with the EPR signal one relative to A sample. This difference can be explained considering the presence of both α-Fe_2O_3 (antiferromagnetic) and Fe_3O_4 (ferrimagnetic) phases in the Fe-rich spherules of C sample. Indeed, a shift of the EPR line toward low magnetic field is consistent with a ferrimagnetic ordered state of the species detected (Guskos et al. 2002). Consequently this EPR signal could be ascribed to Fe^{3+} species present in the iron oxide spheres resulting from the high temperature treatment encountered in the steel unit.

The EPR spectra of D sample correspond to the superimposition of two signals: the first one corresponds to the presence of Fe^{3+} species in iron oxide spheres as in the case of C sample and the second one is a new signal characterized at T_A by g = 2.110 and ΔHpp = 360 G. The intensity of this signal is drastically decreased at T_{LN} ($Ns(T_{LN}) / Ns(T_A) <0.5$) evidencing that such species possess antiferromagnetic properties, similar to that encountered in α-Fe_2O_3. Taking into account XRD and SEM-EDX, we deduced that the iron-rich particles with angular shapes correspond to α-Fe_2O_3 particles leading to the observation of the second EPR signal in D sample. The EPR technique allows to us in this case (D sample) the discrimination of at least two influences of iron-rich particles.

The E sample (containing a high proportion of Mn rich particles) gives an intense signal at T_A (g = 2.049 ; ΔHpp = 360 G), markedly broadened at T_{LN} (g = 2.230 ; ΔHpp = 360 G) and $Ns(T_{LN}) / Ns(T_A) = 2.3$. A g value around g = 2 and a high $Ns(T_{LN}) / Ns(T_A)$ ratio can both be considered to ascribe a such signal to the interaction between of few species mainly corresponding to Mn^{2+} ions with a low level of aggregation. In addition, we observed a specific signal of isolated Mn^{2+} ions (g = 2.002 and A = 96 G) proposed as a tracer of particulate emissions from manganese metallurgic plants (Ledoux et al. 2005).

4. DISCUSSION AND CONCLUSION

From these characterization data, it is possible to propose specific physico-chemical parameters related to the different emission sources. The Fe-rich particles possess different characteristics dependent on their origin. Under the influence of the city, most of Fe-rich particles do not have specific geometry. From XRD and EPR data, the latter are not crystallized and correspond to Fe^{3+} ions in interaction inside small aggregates (Ledoux et al. 2004). On the contrary, two kinds of Fe-rich particles were collected downwind of the steel manufacturing facilities. First, we detected iron ores particles with angular shape corresponding to hematite α-Fe_2O_3. Because this phase possess antiferromagnetic properties, such particles gives a specific EPR signal intensity evolution versus the recording temperature ($Ns(T_{LN}) / Ns(T_A)<1$). On the other hand, the Fe-rich spherules are the result of the condensation of iron released into the atmosphere during high temperature processes. Taking into account the high temperature and the low oxygen partial pressure, when this condensation occurs, the particules formed are not completely oxidized. Indeed, we detect even after transport in the atmosphere both Fe_3O_4 and α-Fe_2O_3 for the Fe-rich spherules. The stability of Fe_3O_4 could be explained considering spherules as magnetite Fe_3O_4 particles with their surface partly oxidized in hematite (α-Fe_2O_3).

SiO_2, $CaCO_3$ and $CaSO_4$. $2H_2O$ are frequently encountered in suspended particulate matter, assigned to natural and anthropogenic particles. Inside the industrial area and notably the steel manucfacturing facilities, we have to notice that Si and Ca containing compounds are found in ores and fluxing agents respectively, so that these elements can be included in particles re-suspended in the atmosphere. In addition, $CaSO_4$. $2H_2O$ can also be secondary particles being formed in the atmosphere by the oxidation of SO_2 with Ca-rich particles.

Under the influence of the ferromanganese factory, no specific particles shape, neither specific crystallized phase were noticed. In this case, the origin was clearly confirmed by the individual particle analysis (almost 39% of Mn bearing particles) and by specific EPR signals (Mn^{2+} isolated species and Mn^{2+} small aggregates).
Finally, the combination of the different techniques applied in this work appeared as a successful approach to evidence physico-chemical parameters to differentiate the atmospheric particles origins.

5. ACKNOWLEDGMENTS

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REFERENCES

Bondarenko, I., Treiger, B., Van Grieken, R., Van Espen, P., 1996. IDAS: a windows based software package for cluster analysis. Spectrochimica Acta Part B 51, 441-456.
Ebert, M., Weinbruch,S., Hoffmann, P., Ortner, H.M., 2000. Chemical chracterization of North Sea aerosol particles. J.Aerosol Sci. 31, 613-632.
Esbert, R.M., Diaz-Pache, F., Grossi, C.M., Alonso, F.J. and Ordaz, J., 2001. Airborne particulate matter around the Cathedral of Burgos (Castilla y León, Spain). Atmospheric Environment, 35, 441-452.
Guskos, N., Papadopoulos, G.J., Likodimos, V., Patapis, S., Yarmis, D., Przepiera, A., Przepiera, K., Majszczyk, J., Typek, J., Wabia, M., Aidinis, K., Drazek, Z. , 2002. Photoacoustic, EPR and electrical conductivity investigations of three synthetic mineral pigments : hematite, goethite and magnetite. Materials Research Bull., 37, 1051-1061.

Khalili, N.R., Scheff, P.A. and Holsen, T.M., 1995. PAH source fingerprints for coke ovens, diesel and gasoline engines, highways tunnels and wood combustion emissions. Atmospheric Environment, 29, 533-542.

Ledoux, F., Zhilinskaya, E.A., Courcot, D., Aboukaïs, A. and Puskaric, E., 2004. EPR investigation of iron in size segregated atmospheric aerosols collected at Dunkerque, Northern France. Atmospheric Environment, 38, 1201 -1210.

Ledoux, F., Laversin, H., Courcot, D., Courcot, L., Zhilinskaya, E.A., Puskaric, E. and Aboukaïs, A., 2005. Electron paramagnetic resonance study of Fe^{3+} and Mn^{2+} speces in atmospheric aerosols from anthropogenic sources. Atmospheric Research, in press.

Machemer, S.D., 2004. Characterization of airborne and bulk particulate from iron and steel manufacturing facilities. Environmental Sci. Technol. 38, 381-389

Moreno T., Jones T.P., Richards R.J., 2004. Characterization of aerosol particulate matter from urban and industrial environments : example from Cardiff and Port Talbot, South Wales, UK. Science of Total Environment 334-335, 337-346

Ortner H.M, 1999. Sampling and characterization of individual particles in occupational health studies, J. Environ. Monit., 1, pp 273-283.

Xhoffer, C., Bernard, P. And van Grieken, R., 1991. Chemical chracterization and source apportionment of individual aerosol particles over the North Sea and the English Channel using multivariate techniques. Environ. Sci. Technol. 25, 1470-1478.

Yordanov, N.D., Veleva, B. and Christov, R., 1996. EPR study of aerosols with carbonaceous products in the urban air. Appl. Magn. Reson. 10, 439-445.

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PAH MASS CONCENTRATIONS MEASURED IN PM$_{10}$ PARTICLE FRACTION

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ABSTRACT

This paper presents the analysis of PAH mass concentrations measured in PM$_{10}$ particle fraction (PM$_{10}$ particles with aerodynamic diameter less than 10 μm) collected at one measuring site in Zagreb air over four years, and of seasonal differences in PAH mass concentrations in PM$_{10}$ samples collected from 21 March 2003 to 20 March 2004. Twenty-four hour samples were taken in the northern part of Zagreb using a low-volume (50 m^3) sampler with glass fiber filters. The average mass concentrations over four-year measuring period ranged for BaP from 1.17 to 1.87 ng/m^3 and were below the limit value (2 ng/m^3) set by the Ordinance on Recommended and Limit Air Quality Values in Croatia. The highest concentrations of all PAHs measured in PM$_{10}$ samples collected from 21 March 2003 to 20 March 2004 were found in the winter and the lowest in the summer. Mass concentrations of all measured PAHs were much higher in the autumn than in the spring.

Key Words: benzo-a-pyrene, PM$_{10}$, seasonal variations, limit value

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widespread compounds generated by incomplete combustion of organic materials. They are emitted from a large variety of industrial processes, motor vehicles and residential heating. Levels of PAH concentrations in the atmosphere vary with season and meteorological conditions. They consist of two or more fused aromatic rings. Some studies showed that PAHs with two or three benzene rings were found to exist in the vapour phase, while PAHs with more than five rings were observed primarily in the particulate phase (Baek, 1992). Most of them are associated with fine airborne particles. It is generally accepted that PAHs associated with small particles (<1 μm), tend to result from combustion or other high temperature sources (Sheu, 1997). More than 500 PAHs have been identified in the air, but only 1-20 are measured (Lee, 1981). Benzo-a-pyrene (BaP) is the most commonly measured PAH since it has been always present and used as an indicator for the carcinogenic hazard in the polluted environment. The natural background level of BaP may be nearly zero, in rural areas the concentration of BaP ranges from 0.01-1 ng/m^3, in urban areas it ranges from 1-10 ng/m^3 and around some industries it goes to 40 ng/m^3 (Guidelines, 2000).

Due to the fact that some PAHs are mutagenic and some carcinogenic, they should not be present in the air, or their concentrations should be the lowest possible. The concentrations of 2 ng/m^3 for the annual average BaP concentration are the limit value set by the Ordinance on Recommended and Limit Air Quality Values in Croatia (Ordinance, 1996).

This paper presents the analysis of PAH mass concentrations measured in PM$_{10}$ particle fraction (PM$_{10}$ particles with aerodynamic diameter less than 10 µm) collected at one measuring site in Zagreb air over four years and of seasonal differences in PAH mass concentrations in PM$_{10}$ samples collected from 21 March 2003 to 20 March 2004.

2. MATERIAL AND METHODS

Samples were collected at one measuring site in the northern part of Zagreb, Croatia, continuously from 2001 to 2004. Twenty-four hour samples of PM$_{10}$ particles were collected by low volume PM$_{10}$ sampler – Ingenieurbuero Sven Leckel, on glass or quartz filters. Samples were kept in the deep freeze at -18 ˚C, wrapped in aluminium foil until analysed. Samples were extracted with cyclohexane in an ultrasonic bath for one hour, separated from undissolved parts by centrifugation and evaporated to dryness, and redissolved in acetonitrile (Šišović, 1991).

Sample analysis

The analysis was performed by Varian Pro Star high performance liquid chromatograph (HPLC) and a fluorescence detector with changeable excitation and emission wavelength, in order to optimise the selectivity and sensitivity for individual PAH species. PAH are separated on a Varian Chrompac CP-Eco Spher 4 PAH column. Mobile phase is a mixture of acetonitrile and water and flow rate is 0.4 ml/min. Samples were analysed for the following PAHs: fluoranthene (Flu), pyrene (Pir), benzo-b- fluoranthene (BbF), benzo-k-fluoranthene (BkF), benzo-a-pyrene (BaP) and benzo-ghi-perylene (BghiP).

3. RESULTS AND DISCUSSION

Figures 1-4 show monthly average PAH mass concentrations, and minimum and maximum daily concentrations measured in PM$_{10}$ particle fraction continuously from 2001. The concentrations of all measured PAHs were the lowest during warm period of the year (May, June, July, August). Slightly higher concentrations were measured during March, April, September and October and the highest concentrations were measured during winter months (January, February, November and December). Monthly average BaP mass concentrations, during the warm period of the year, varied from 0.04 to 0.24 ng/m^3, and during the cold season they varied from 2.00 to 5.21 ng/m^3. Concentrations of other PAHs show similar variations during the winter and summer period.

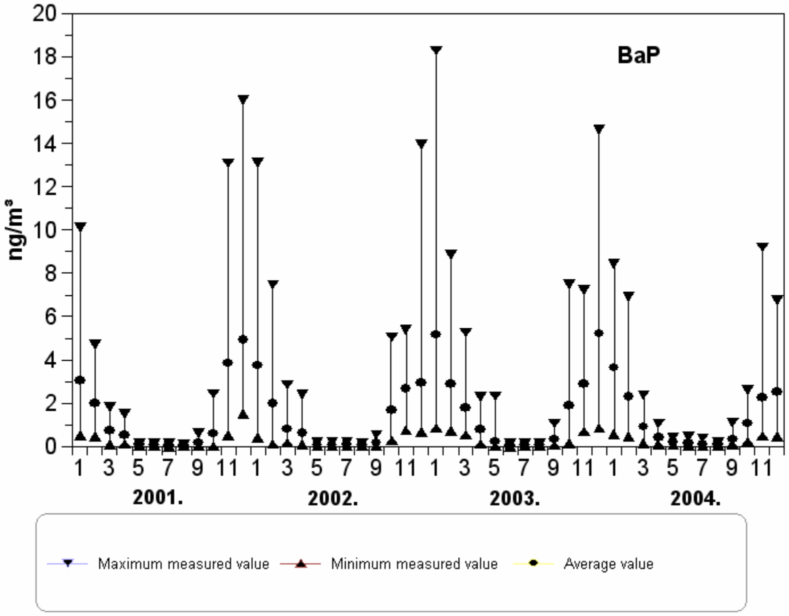

Figure 1 – Monthly average BaP mass concentrations measured during four year period

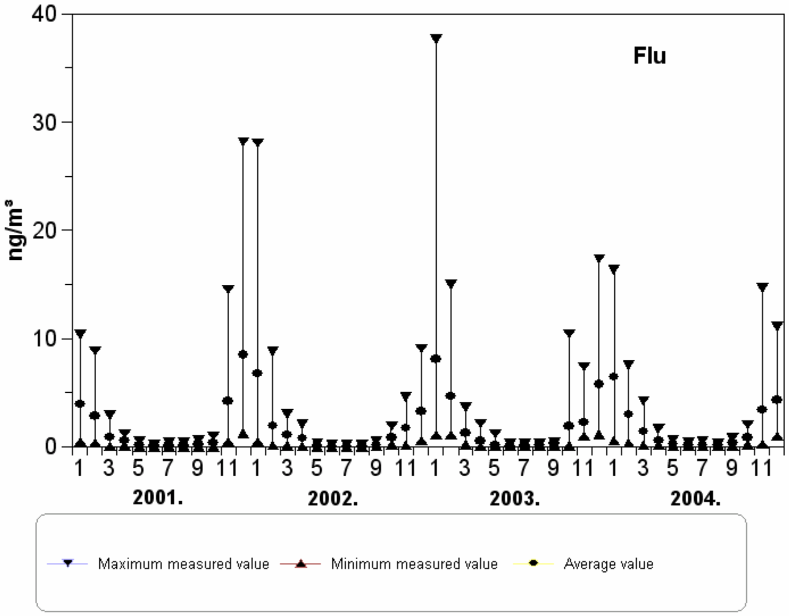

Figure 2 – Monthly average Flu mass concentrations measured during four year period

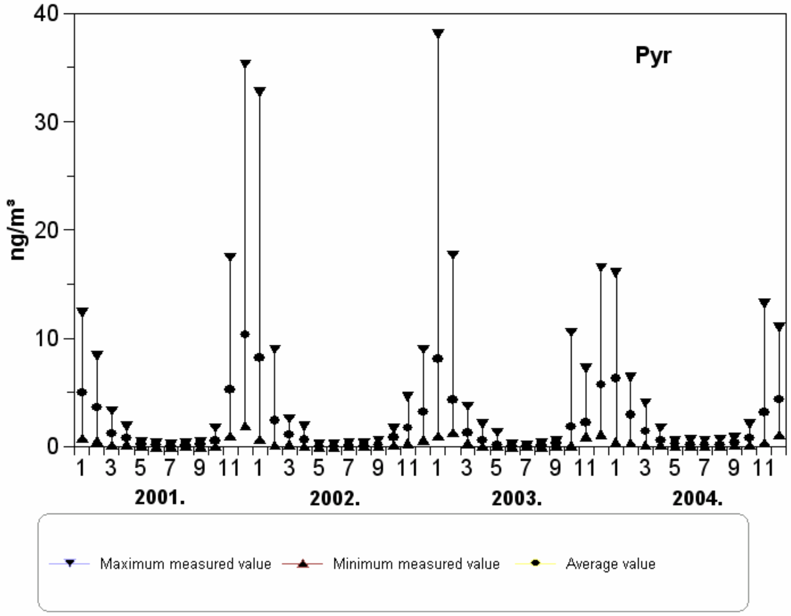

Figure 3 – Monthly average Pyr mass concentrations measured during four year period

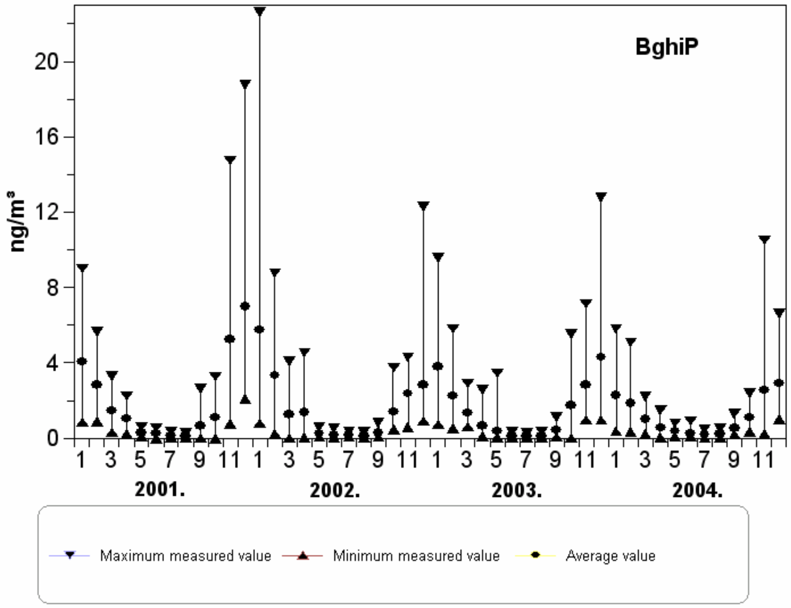

Figure 4 – Monthly average BghiP mass concentrations measured during four year period

Concentrations of Flu and Pyr were higher than those of BaP during the winter months and lower or similar during the summer months. Concentrations of BghiP were similar or higher than BaP in winter, but in summer they were two or three times higher than the concentrations of BaP. Concentrations of PAHs depend on sources and stability of PAHs during the cold and warm months (Yamasaky, 1982; Greenberg, 1989).

Figure 5 shows daily variations of BaP mass concentrations measured during 2004. Very low concentrations of BaP were found in April and it lasted till September. The highest daily concentration of BaP in 2004 was during November and it was 9.21 ng/m^3. Daily variations of BaP mass concentrations mainly depend on weather conditions (wind direction and velocity).

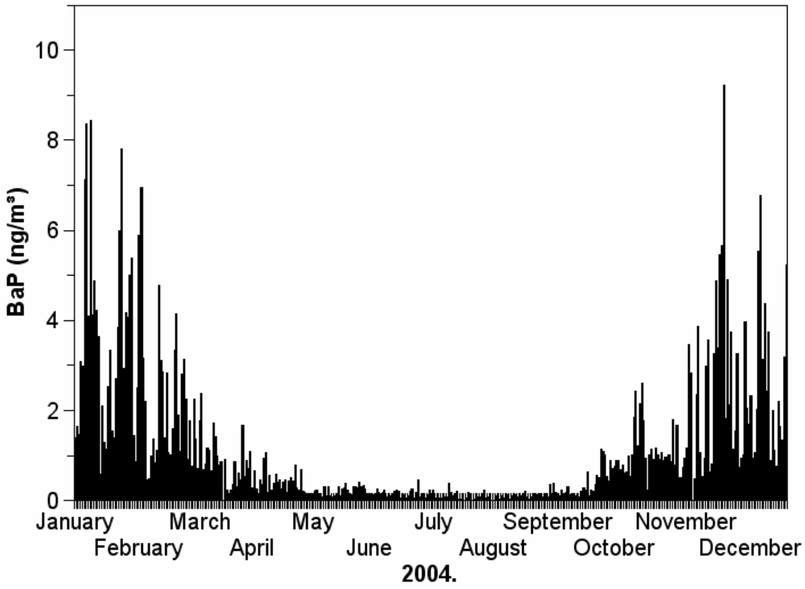

Figure 5 - Daily variations of BaP mass concentrations measured during 2004

In Table 1 are shown the annual average mass concentrations of PAHs (ng/m^3), except for BaP, measured during four-year period. Annual average mass concentrations of Flu and Pyr varied from year to year, and the lowest were in 2002. The concentrations of BbF, BkF and BghiP were the highest in 2001 and after that they went slowly down.

Table 1 - Annual average mass concentrations of PAHs (ng/m^3), except BaP measured at one measuring site during four year period

PAH	2001.			2002.			2003.			2004.		
	N	**C**	C_M	N	**C**	C_M	N	**C**	C_M	N	**C**	C_M
Flu	355	**1.9**	28.2	362	**1.4**	28.1	362	**2.1**	38.7	364	**1.8**	16.4
Pyr	355	**2.3**	35.3	362	**1.6**	32.8	362	**2.06**	38.1	364	**1.7**	16.0
BbF	355	**1.5**	11.2	362	**1.2**	13.3	362	**1.20**	9.9	364	**1.1**	8.5
BkF	355	**0.9**	6.8	362	**0.7**	7.3	362	**0.63**	5.3	364	**0.6**	4.4
BghiP	355	**2.1**	18.8	362	**1.6**	22.6	362	**1.53**	12.8	364	**1.2**	10.5

Table 2 shows annual average BaP mass concentrations measured during a four-year period. The highest annual average value was in 2003 and it was 1.79 ng/m^3 and the lowest was in 2004 and it was 1.17 ng/m^3. The obtained results show that the annual average value for BaP mass concentrations measured during four-year period were higher than the recommended value (0.2 ng/m^3) and lower than limit value (2 ng/m^3) proposed by Croatian law. It can be concluded that the air around the measuring sites regarding BaP was in the 2nd category.

Table 2 - Annual average value of BaP mass concentrations (ng/m^3) measured during four year period

Year	N	**C**	C_{98}	C_M
2001.	355	**1.37**	8.66	15.99
2002.	362	**1.24**	6.95	13.95
2003.	362	**1.79**	9.28	18.28
2004.	364	**1.17**	5.96	9.21

N – number of samples **C – arithmetic means** C_m . minimum value
C_{98} – 98 percentile C_M – maximum value

Table 3 shows seasonal variations of PAH mass concentrations in PM_{10} particles collected from 21 March 2003 to 20 March 2004. The highest concentrations of all measured PAHs were in winter and the lowest in summer. Flu and Pyr had the highest concentrations in winter and they were about 4.2 ng/m^3. Average mass concentration of BaP in winter was 2.94 ng/m^3 and it was lower than those measured earlier. Average mass concentration of BaP in summer was 0.118 ng/m^3 and it was higher than those measured earlier (Šišović, 2002).

Table 3 - Arithmetic means and ranges of PAH mass concentrations (ng/m^3) measured during four seasons

Season	Statistical parameters	PAH (ng/m^3)					
		BaP	Flu	Pyr	BbF	BkF	BghiP
Spring	N	91	91	91	91	91	91
	C	**0.58**	**0.41**	**0.41**	**0.44**	**0.22**	**0.55**
	C_m	0.01	0.03	0.02	0.02	0.02	0.02
	C_M	3.31	3.65	3.71	1.45	1.45	3.48
Summer	N	92	92	92	92	92	92
	C	**0.12**	**0.13**	**0.12**	**0.12**	**0.06**	**0.19**
	C_m	0.01	0.02	0.01	0.02	0.01	0.02
	C_M	0.71	0.49	0.53	0.64	0.31	0.99
Autumn	N	89	89	89	89	89	89
	C	**2.76**	**2.73**	**2.68**	**1.79**	**0.94**	**2.59**
	C_m	0.06	0.08	0.08	0.09	0.04	0.10
	C_M	10.45	15.30	15.10	6.71	3.43	8.18
Winter	N	90	90	90	90	90	90
	C	**2.94**	**4.22**	**4.17**	**2.34**	**1.23**	**2.16**
	C_m	0.16	0.17	0.13	0.12	0.06	0.24
	C_M	14.62	16.38	16.03	8.09	4.32	12.81

N –Number of samples
C – arithmetic means
C_m –minimum value
C_M – maximum value

The concentrations of all measured PAHs were much higher in autumn than in spring. The reason for this is that in spring there are more warm and sunny days than in autumn, and that increased reactivity of these compounds at higher temperatures result in their photochemical, thermal and chemical degradation (Butler, 1981; Greenberg, 1989).

4. CONCLUSION

The annual average BaP mass concentrations measured during four-year period were higher than the recommended value (0.2 ng/m^3) and lower than limit value (2 ng/m^3) proposed by Croatian law. It can be concluded that the air around the measuring sites regarding BaP was in the 2nd category.

Seasonal variations of PAH mass concentrations show that the highest concentrations of all measured PAHs were found in winter and the lowest in summer. Mass concentrations of all measured PAHs were much higher in autumn than in spring. Seasonal variations mainly depend on differences in temperature, but daily variations on the weather conditions (wind direction and velocity).

REFERENCES

Baek SO, Goldstone ME, Kirk PWW, Lester IN and Perry R. 1992. Concentrations of particulate and gaseous polycyclic aromatic hydrocarbons in London air following a reduction in the lead content of petrol in the United Kingdom. Sci Total Environ. Vol. 111, pp 169-199.

Butler J.D. and Crossley P. 1981. Reactivity of polycyclic aromatic hydrocarbons adsorbed on soot particles. Atmos. Environ. Vol. 15, pp. 91-94.

Greenberg, A. 1989. Phenomenological study of benzo(a)pyrene and cyclopenteno(cd)pyrene decay in ambient air using winter/summer comparison. Atmospheric Environment 23, 2797-2799.

Guidelines for Air Quality, WHO, Geneva, 2000.

Lee, M.L., Novotny, V.M., Bartle, D.K. 1981. Analytical Chemistry of Polycyclic Aromatic Compounds. Academic Press Inc. New York.

Ordinance on Recommended and Limit Air Quality Values, 1996. Official Gazzette No. 101, 4198-4200 (in Croatian).

Sheu H L. et al. 1997. Particle bound PAH content in ambient air: Environmental Pollution. Vol. 96, pp. 369-382.

Šišović A, Fugaš M. 1991. Comparative Evaluation of Procedures for the Determination of PAH in Low-volume Samples, Environ. Monitoring and Assessment. Vol. 18, pp. 235-241.

Šišović A, Škrbec A, Vadjić V. et al. 2002. PAH Levels and Profiles in the Suspended Particulate Matter in Zagreb through Four Seasons. Environmental Monitoring and Assessment. Vol. 74, pp. 217-224.

Yamasaki H, Kuwata K and Miyamoto H. 1982. Effects of ambient temperature on aspects of airborne polycyclic aromatic hydrocarbons. Environ Sci Technol. Vol. 16, pp. 189-194.

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MONITORING OF PM2.5 PARTICLE FRACTION IN ZAGREB AIR

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ABSTRACT

Investigations of PM2.5 in Zagreb ambient air started in autumn of 1998 by developing and testing sampling equipment and analytical procedures. For a period of five years samples were collected at only one sampling site. Parallel measurements of total suspended particulates (TSP), PM10 and PM2.5, as well as heavy metal and anion content in particle fractions were performed. Later step was the investigation of seasonal and space differences in PM2.5 particle fraction performed at four sampling sites, for a month period in summer and again in winter period. The results of these investigations, together with the conclusions of several recent WHO meetings resulted in PM2.5 Zagreb network implementation in year 2005.

Key Words: PM2.5 particle fraction, Concentration Distribution, Proposed Limit Values

1. INTRODUCTION

Investigation of particulate pollution in Zagreb air started in 1972 by monitoring the concentrations of total suspended particulate matter (TSP) and their heavy metal content. Because of better relation to the health outcomes (ISO 1995, WHO 1998) in 1999 parallel PM10 and PM2.5 particle fraction monitoring started at one sampling location representing northern, residential part of Zagreb. Monitoring included determination of lead, manganese and cadmium, as well as anion content (sulphates, nitrates and chlorides) (Čačković 2004) and PAHs in both particle fractions (Šišović 2004). Health outcomes based on measured concentration data were evaluated by means of AirQ computer program (Šega 2001). Concentrations of PM2.5 particle fraction were related to TSP and PM10 fraction concentration. In order to get the insight in seasonal and spatial distribution of particle concentrations in Zagreb area a pilot investigation was performed at four sampling sites located at different parts of the town, for a month period during summer and again in winter season. The results of these investigations, together with the conclusions of several recent WHO projects and WHO meetings (WHO 2000, WHO 2002, WHO 2004) resulted in PM2.5 Zagreb network implementation. Samples are collected on daily basis and additional analyses of lead, cadmium, manganese, sulphates, nitrates, chlorides are performed, as well as the determination of sample total β-activity.

Clean Air For Europe (CAFE) programme Second Position Paper on Particulate Matter (2004) states that there is strong evidence to conclude that fine particles (PM2.5) are more hazardous than larger ones (coarse particles) in terms of mortality and cardiovascular and respiratory endpoints in panel studies. Epidemiological studies on large populations have been unable to identify a threshold concentration below which ambient PM has no effect on health. WHO developed new exposure response relationship for PM2.5. Paper recommends a range of values (12 to 20 µg/m³) for the integrated assessment procedure to identify an appropriate PM2.5 annual average limit value. Recommends value for PM2.5 around 35 µg/m³ (not to be exceeded more than 10% of the days of the year) as a starting point for consideration.

In this paper, the results of PM2.5 mass concentration obtained at Zagreb monitoring network during 2000-2005 period are presented and assessed.

2. MATERIALS AND METHODS

For the 1999-2004 period monitoring was performed at one sampling site located at northern residential part of town. Daily PM2.5 particle fraction samples were collected on 47 mm diameter Whatman Quartz filters from 55 m^3 of ambient air by means of low volume samplers LVS3. Filters were preconditioned for 24 hours before and after the sampling in desiccators for low humidity. Particle mass is determined by weighing on microbalance Mettler Toledo MX-5. Concentration results are normalized to the air pressure of 1 bar and air temperature of 20 °C.

In 2005 PM2.5 monitoring started at five sampling sites. Sampling site located in the town center is characterized by dense traffic in street canyons and numerous individual heating appliances. Northern residential sampling site is characterized by medium traffic density and individual heating, western residential-industrial by dense traffic and individual heating, eastern residential-industrial, while southern sampling site is located in residential area characterized by dense traffic and district heating. For 2005 monitoring campaign filters are kept for 48 hours under ~50% relative humidity and temperature of 20 °C.

3. RESULTS AND DISCUSSION

Statistical parameters of PM2.5 concentrations for the 2000-2004 monitoring period are presented in table 1. Capture rate for 2000-2003 period was very high, though enabling good description of the results, while during the year 2004, due to the equipment failure and service, a number of concentration data for summer (5 June - 19 July) and again winter (12-31 December) are missing. No significant difference was found between measuring periods (one way ANOVA). Average concentrations ranged between 24.8 μgm^{-3} and 28.8 μgm^{-3}, while interquartile range was between 14 μgm^{-3} and 36 μgm^{-3}. Concentration distributions are skewed towards higher concentrations resulting in medians lower compared to the average concentrations.

Table 1. Statistical parameters of PM2.5 particle fraction concentrations (µgm^{-3})

Year	**2000**	**2001**	**2002**	**2003**	**2004**
N	364	364	364	364	301
C_{avg}	27.2	26.8	26.5	28.8	24.8
Median	21.3	20.0	22.7	21.4	20.2
C_{25}	14.1	14.4	15.0	13.9	14.3
C_{75}	31.9	31.4	31.7	36.0	30.9
C_{98}	80.3	82.6	79.2	96.0	69.7

To avoid the influence of accidental and/or unusual situations, 98th concentration percentiles are shown instead their maximum concentrations. As it is shown in Figures 1-5 distributions of yearly concentration sets could be best fitted to lognormal distribution (Kolmogorov-Smirnov), as is the usual case with air pollutant concentrations.

Mass ratio of PM2.5/PM10 was in the range 30-100 % and their distributions could be fitted to normal distribution. Variations are caused by weather conditions (rain, snow, wind, washout, air temperature and pressure) and show no seasonal dependence. In table 2. average values and attributable standard deviations of PM2.5 proportions in PM10 for the year periods are given.

Table 2. Average values and standard deviations of PM2.5/PM10 ratio (%)

Year	**2000**	**2001**	**2002**	**2003**	**2004**
N	364	364	364	364	301
Average	68.5	72.9	71.3	71.3	73.3
Std	15.5	12.6	14.0	14.3	11.9

Results show that approximately 70 % of PM10 mass contribute particles in PM2.5 size range. Since the correlations of PM2.5 to health endpoints are much stronger compared to PM10 and almost all PAHs, heavy metal and anion content is found in PM2.5 particle fraction, monitoring of PM2.5 will probably replace PM10 monitoring in the future.

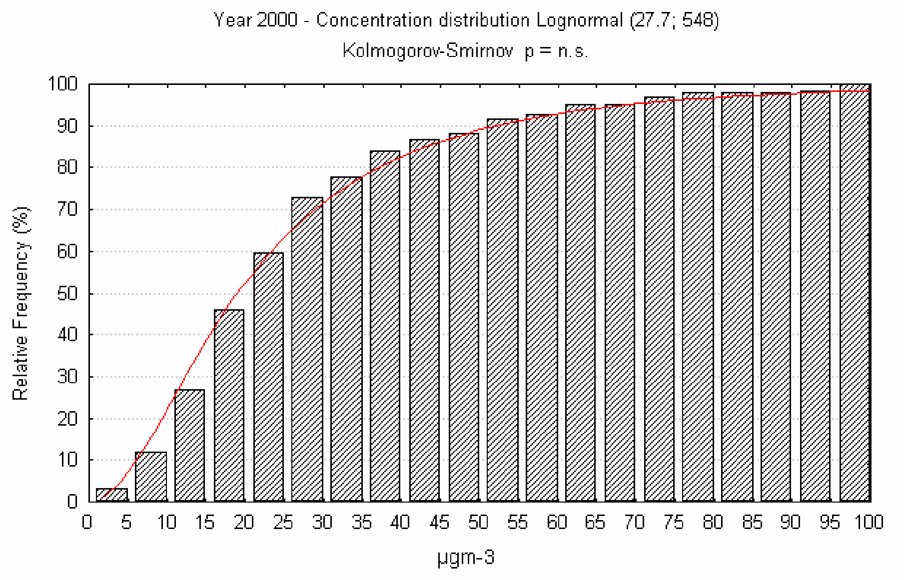

Figure 1. PM2.5 concentration distribution fitting – year 2000

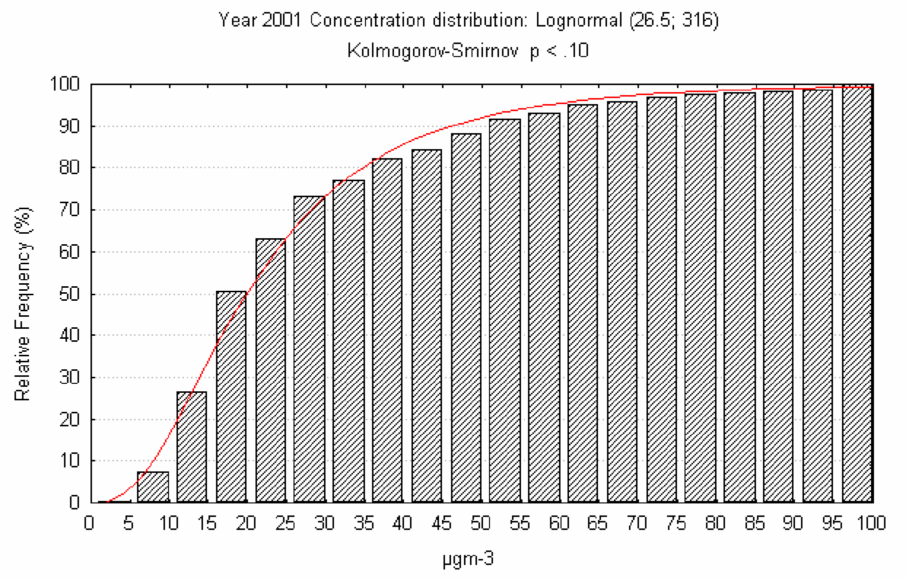

Figure 2. PM2.5 concentration distribution fitting – year 2001

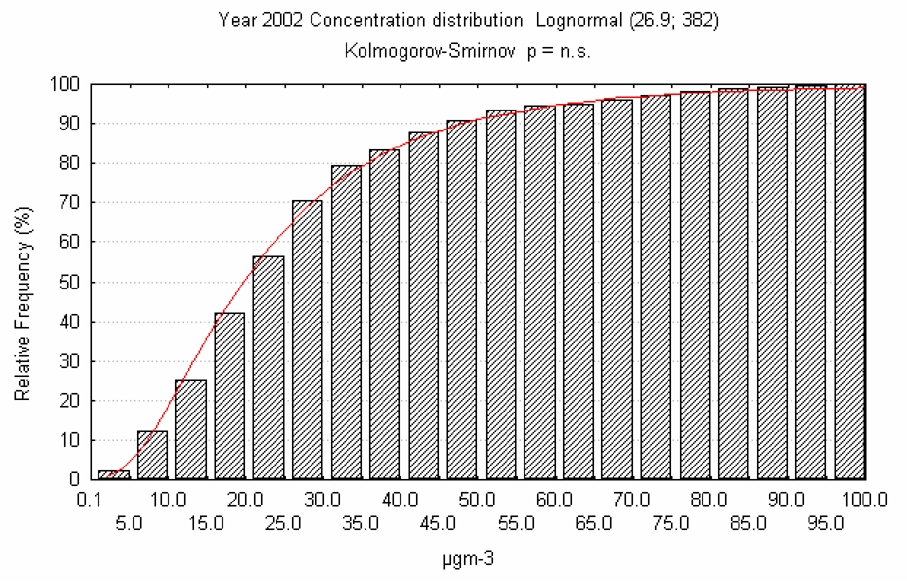

Figure 3. PM2.5 concentration distribution fitting – year 2002

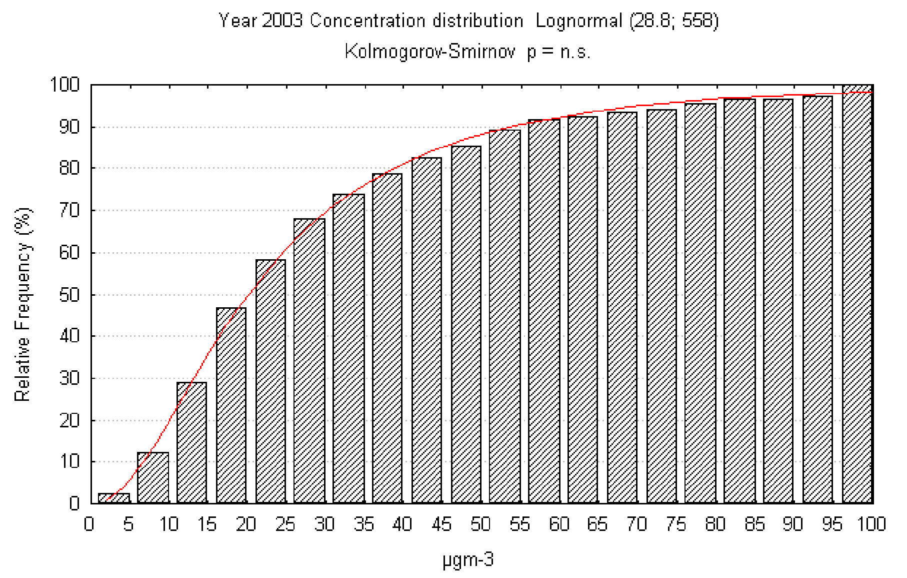

Figure 4. Concentration distribution fitting – year 2003

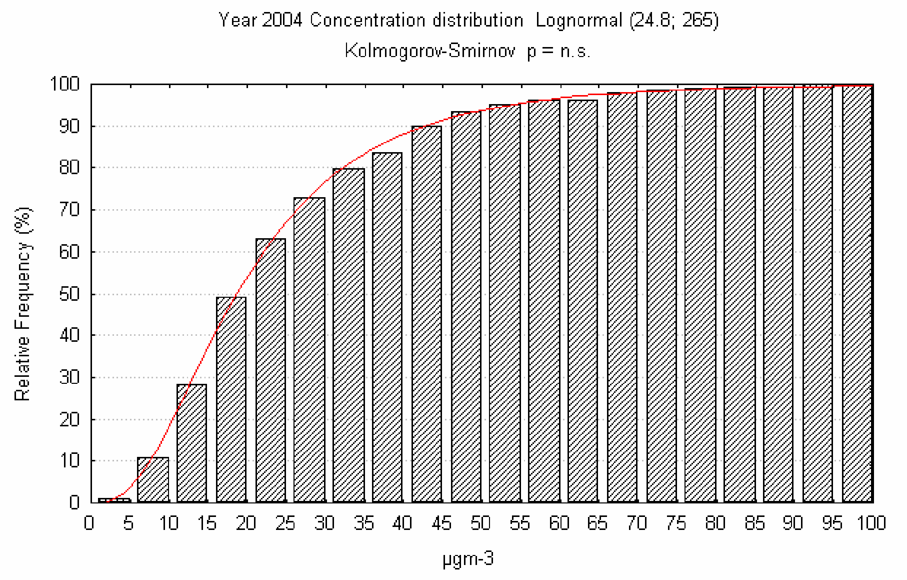

Figure 5. PM2.5 concentration distribution fitting – year 2004

Although there are no prescribed limit values, PM2.5 concentration levels measured in Zagreb could be compared to the proposed values (CAFÉ 2004). Annual averages for the whole monitoring period were much higher and out of proposed concentration range (12-20 µgm^{-3}). The percentages of measured concentrations higher than 35 µgm^{-3} are presented in table 3. Their frequencies are more than two times higher compared to the proposed one of 10 %.

Table 3. Percentage of the concentrations higher than 35 µgm^{-3} (%)

Year	2000	2001	2002	2003	2004
%	22	23	21	26	20

These comparisons allow us to conclude that PM2.5 concentration levels are elevated and the quality of Zagreb atmosphere regarding PM2.5 concentrations is not satisfactory.

Daily concentrations of PM2.5 particle fraction for the first six month period of year 2005 at all five sampling sites are presented at figure 6. Although the concentrations at all measuring sites follow the same trend, it could be noticed that somewhat higher concentrations were measured at sampling site south, and lower at the station located at the northern part of the town. It could be concluded that the fine particle fraction in Zagreb does not come primarily from the local source but that their transport over longer distances plays a significant role.

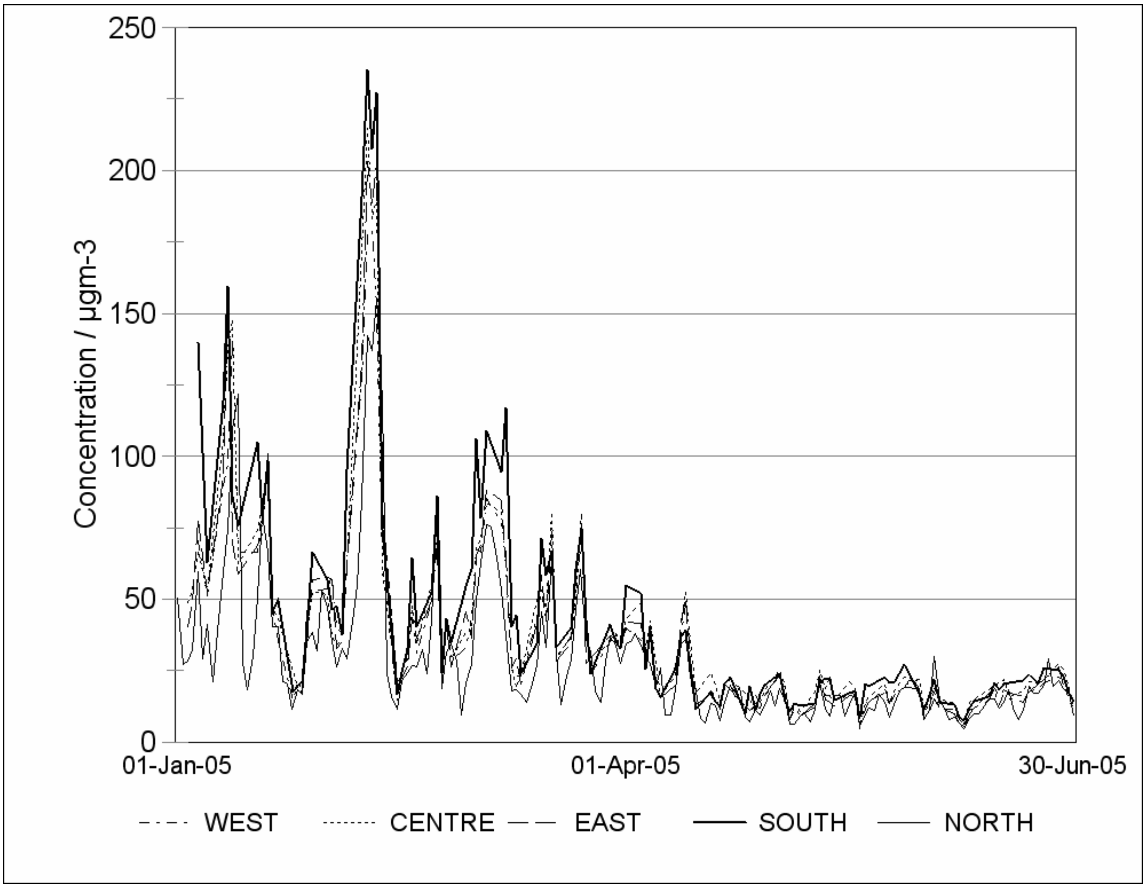

Figure 6. Trends of PM2.5 concentrations in Zagreb network (January – June 2005)

4. CONCLUSIONS

Concentration distributions and levels of PM2.5 particle fraction in Zagreb air do not differ significantly from year to year.

Air quality in Zagreb regarding PM2.5 particle fraction is unsatisfactory since the results obtained are higher compared to the proposed limit values.

Concentration levels do not depend on local pollutant sources only, and the transport of fine particles, because of their long airborne residence time, plays a considerable role, leveling the concentrations over a waste region.

In the future Zagreb monitoring network should abandon TSP monitoring and focus to PM10 and even more to PM2.5 particle fraction.

REFERENCES

Čačković, M., Vađić, V., Šega, K., 2000. Sulphates, nitrates and chlorides in particle fractions of different size. Archives of Industrial Hygiene and Toxicology 51, 193-198.

CAFÉ (Clean Air For Europe programme Second Position Paper on Particulate Matter) 2004.http://europa.eu.int/comm/environment/air/cafe/pdf/working_groups/2nd_position_paper_pm.pdf)

Šega, K., Bešlić, I., Šimić, D., 2001. Procjena i modeliranje zdravstvenih učinaka onečišćenja zraka u gradu Zagrebu (Health Impact Assessment of Air Pollution on Zagreb Population). In: Valić, F., Šega, K. (Eds.) Proceedings of the National conference Zaštita zraka 2001, Sibenik, Croatia, 35-41.

Šišović, A., Vađić, Ž., Šega, K., Bešlić, I., Vađic, V., 2004. Usporedba masenih koncentracija PAU mjerenih u različitim veličinama lebdećih čestica (Comparison of PAH mass concentrations measured in different size particle fractions). Gospodarstvo i okoliš. 12, 590-593.

WHO (2000) Evaluation and use of epidemiological evidence for environmental risk assessment, Guideline Document, Copenhagen, Denmark.

WHO (2002) Exposure assessment in studies on the chronic effects of long-term exposure to air pollution, Report on a WHO/HEI Workshop, 4-5 February 2002, Bonn, Germany.

WHO (2004) Meta-analysis of time-series studies and panel studies of Particulate Matter (PM) and Ozone (O_3)

WHO (2005) Review of Methods for Monitoring PM2.5 and PM10, WHO Workshop 11-12 October 2004, Berlin, Germany.

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AIR QUALITY STATUS OF BENZENE, TOLUENE, ETHYLBENZENE AND XYLENE IN MUMBAI CITY

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ABSTRACT

An attempt has been made to determine the levels of Benzene, Toluene, Ethyl benzene and Xylene (BTEX) in air at different locations of Mumbai city. The locations were selected so as to represent five categories viz. residential, commercial, and industrial, traffic intersections and petrol pump. Three locations in each category were selected for monitoring. Levels of BTEX have been determined by using USEPA TO 17 Compendium Method. The result shows high concentrations of benzene at all the locations exceeding the WHO guideline value of 5-20 $\mu g/m^3$.

Key Words : BTEX, air quality, Mumbai

1. INTRODUCTION

Volatile Organic Compounds(VOC's) are ubiquitous atmospheric species of both natural and anthropogenic sources (Ciccioli et. al. 1993). Some VOC's are themselves toxic having both carcinogenic and non-carcinogenic hazard e.g Benzene, Formaldehyde, while others react in air to form other harmful substances. USEPA study on Air Toxics related to vehicular emission (USEPA 1993) establishes benzene in air as a pollutant strictly related to industrial emissions and automotive emissions. Efforts to reduce lead content of the fuel gasoline and to maintain the octane number has led to increase in benzene and other aromatic hydrocarbons in gasoline.. Benzene content in petrol in different cities of India – Delhi : 1% of the total volume, Mumbai : 3% of total, Ahmedabad : 5% of total, rest of India : 5% of total volume. This paper presents a study of Benzene, Toluene, Xylene and Ethyl benzene in ambient air of Mumbai city during June 2001 to May 2002.Three location each in residential, commercial, industrial, traffic intersection and petrol pumps were selected for monitoring.

Mumbai is located on west coast of India. The population density of Greater Mumbai averages about 16,500 persons per km^2. In 2001 the population is over 12 million. Mumbai is India's main industrial city with many air polluting industries located in Chembur, in eastern Mumbai. Municipal and commercial activity is concentrated in the city's southern part. Commuting to and from populated areas to the south, places a large burden on the road system. Traffic flows in Mumbai can be divided into four cordons namely Mid-city, Mid-suburban, Island and Outer cordon. Maximum traffic flow (Annual Average Daily Traffic –AADT) at a road section was about 1,200,000 vehicles per day in 1995. Three suburban surface, electric train systems provide the main public transportation to 4 million passenger /day. Municipal Corporation owned buses caters to the need of 4.5 million people /day.

2. SELECTION OF SAMPLING LOCATIONS

The locations were in each category were selected to as to represent important areas of Mumbai city in southern, northern and central Mumbai (Figure 1). Three locations were selected for residential area one each in south, central and north Mumbai. R1 falls under residential cum commercial area. R2 is a purely residential area adjacent to Mahim Creek R3 residential cum commercial area adjacent to Malad creek. C1, C2 and C3 represent the commercial areas. C1 is a wholesale market in south of the Mumbai city. C2 is in the central part of the Mumbai city. Monitoring was carried out near railway station. C3 is a suburban region in northern Mumbai. Sampling location was selected near a shopping centre, opposite local railway station. In the industrial category, three notified industrial areas I1, I2 and I3 were chosen. I1 is in the western part of Mumbai city. The area has a large number of small scale industries. The traffic of heavy duty vehicles, passenger vehicles and buses is quite high in this area. Sampling location I2, was in front of a main gate of Petroleum refinery. I3 is an industrial area under the Maharashtra Industrial Development Corporation (MIDC). Monitoring was carried out near an industrial site. Traffic intersections, chosen for this study are T1, T2 and T3 these are junctions of multiple roads and number of vehicles that ply up and down direction during peak hours is large. Three petrol pump chosen are P1, P2 and P3. All the three petrol pumps have heavy traffic inflow. Samplings were carried out in the middle of petrol pumps, where vehicles halt for filling petrol.

3. MONITORING METHODOLOGY

Ambient air samples were collected on adsorption tubes in accordance with TO-17 compendium method using low volume samplers (USEPA 1999). A battery operated personal air sampler Staplex Model PST – 3000A was used to sample ambient air at the rate of 20 ml/min. All locations were monitored during 8 am to 12 noon and 5 pm to 9 pm once a month. VOCs were thermally desorbed and analyzed on Varian GC-MS. Quantification of VOCs was carried out using VOC Mix 15 of Dr. Erhenstrofer as standard with an accuracy of ±15%.

4. RESULTS AND DISCUSSIONS

High levels of benzene have been observed at all the locations monitored. Similar results have been reported earlier (Srivastava, et.al., June 2004). Observed annual concentrations (average of 24 values) of BTEX species at each category viz. residential, commercial, industrial, traffic intersections and petrol pumps is presented in Figure 2. Residential location R3 showed highest concentrations and these may be due to being a residential cum commercial site. Among the commercial areas higher concentrations were observed at C2 and C3 as compared to C1 and residential areas. Heavy traffic in the vicinity of commercial sites contributes to VOC levels.

Concentrations at the industrial sites were higher in terms of benzene as compared to residential and commercial areas whereas, toluene, ethyl benzene and xylene were observed to be in the comparable range. Petrol refinery, small and medium scale industries contribute to VOC concentrations in this category. At a traffic intersection T1and T3, the traffic consists of Taxi, Private Vehicles and Local Buses. At Traffic Intersection T2 along with taxis and Private vehicles, heavy duty vehicles form a major portion of the traffic. Close to traffic intersection T2, there are a large number of repair garages. Degreasing, auto repair, diesel internal combustion, vehicle exhaust and evaporative emissions contribute to ambient VOC levels. There is a truck terminal close to the intersection. Concentrations of toluene observed at traffic intersections were higher than those observed at other locations. Concentrations of BTEX observed at petrol pumps were higher in terms of benzene as compared to other categories. At petrol pumps vehicle exhaust diesel internal combustion and degreasing activities along with evaporative emissions of petrol form the major sources of VOC emissions.

Higher concentrations of benzene observed at traffic intersections and petrol pumps may be attributed to evaporative emissions from fuel tanks of vehicles and spillage at petrol pumps. (Srivastava, et.al., 2004). Table 1 gives a B/T ratio observed at different category of locations. Sweet and Vermette, 1992; Scheff and Wadden, 1993 have related B/T ratio of 0.5 to vehicular exhaust. In the present study B/T ratios have been observed to be higher than 0.5 at all locations.

Table 1. Benzene to Toluene Ratio

Category	**B/T**
Residential	2.5
Commercial	1.0
Industrial	1.6
Traffic Intersection	0.8
Petrol Pump	10.2

It indicates additional source of benzene other than vehicular emissions or long range transport. Life times of benzene, toluene and xylene in tropics have been reported to be 4.8, 0.9 and 0.4 days respectively (Singh and Zimmermon, 1992). Highly reactive species of VOCs react near the vicinity of sources while slow reacting species may be transported over large distances. Toluene has much shorter life time than benzene. So higher B/T ratio is expected to be observed in aged air due to long range transport. In an urban area most BTEX comes from vehicle exhaust, thus B/T can be used to predict whether the pollutants to remote site have influenced the local source via transport. The observed high B/T values can be attributed to both evaporative emissions and long range transport (Srivastava, 2004). Being a coastal city the land and sea winds dilute the effect of long range transport. The wind rose pattern (Figure 3) shows that the winds are predominately from north and north-west. Levels of benzene are above the WHO guideline value of 5-20 $\mu g/m^3$. Levels of toluene, ethyl benzene and xylene were observed to be within the safe levels recommended by

WHO (Toluene -260 $\mu g/m^3$ –one week average, ethyl benzene – 22,000 –one year average, xylene -870 –one year average).

5. CONCLUSIONS

Higher concentrations of benzene have been observed at all the locations. These levels can be attributed to evaporative emissions predominately and to some extent to long range transport. Observed high levels benzene necessitates the need for control of VOCs. In order to control VOC's in air the management strategy should thus focus on cost effective vapour recovery systems at refueling stations and in vehicles. Effective inspection and maintenance programs and measures against tampering and spillage can reduce evaporative and exhaust VOC emissions. Besides this fuel volatility control can be an effective measure to reduce VOC emissions from in use motor vehicle.

6. ACKNOWLEDGEMENT

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REFERENCES

Ciccioli P,Bracaleoni E, Frattoni M, Cecinato A, Brachetti A, Ubiquitous Occurrences of semi-volatile carbonyl compounds in troposphere samples and their possible sources. Atmospheric Environment, 1993 Vol. 27A(12), 1891-1901.

Srivastava A., Joseph A.E., Nair S., June 2004, Ambient Levels of Benzene in Mumbai City, International Journal of Environmental Health Research 14(3), 215-222.

Srivastava A., Joseph A.E., More A., Patil S., 2004, Emissions of VOCs at Urban Petrol Retail Distribution Centres in India (Delhi and Mumbai), Environmental Monitoring and Assessment, Accepted Proof Online –PIPS No. D000006292

Sweet C.W., Vermette, S.J., 1992, "Toxic volatile compounds in urban air in Illinios" Environ Sci & Technol., Vol. 26, 165-173

Scheff P.A. and Wadden, R.A., 1993 "Receptor Modelling of Volatile Organic Compounds: Emissions Inventory and Validation", Environ. Sci. Technol., 27, 617-625.

Singh, H.B. and Zimmermon, P.B., 1992, "Gaseous Pollutants Characterization and Cycling", Edited by O.Nriagu, Vol. 24, pp 177, Wiley Services on Advances in Environment Sc. and Technology

Srivastava A., 2004, Source Apportionment of Ambient VOCs in Mumbai City, Atmospheric Environment, 38, 6829-6843.

USEPA Motor Vehicle Related " Air Toxic Study EPA-420 (R-93-005) Ann. Arbor Michigan"

US Environmental Protection Agency Office of Mobile Sources.

USEPA, "Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air",1999,EPA 1625/R-96/010B.

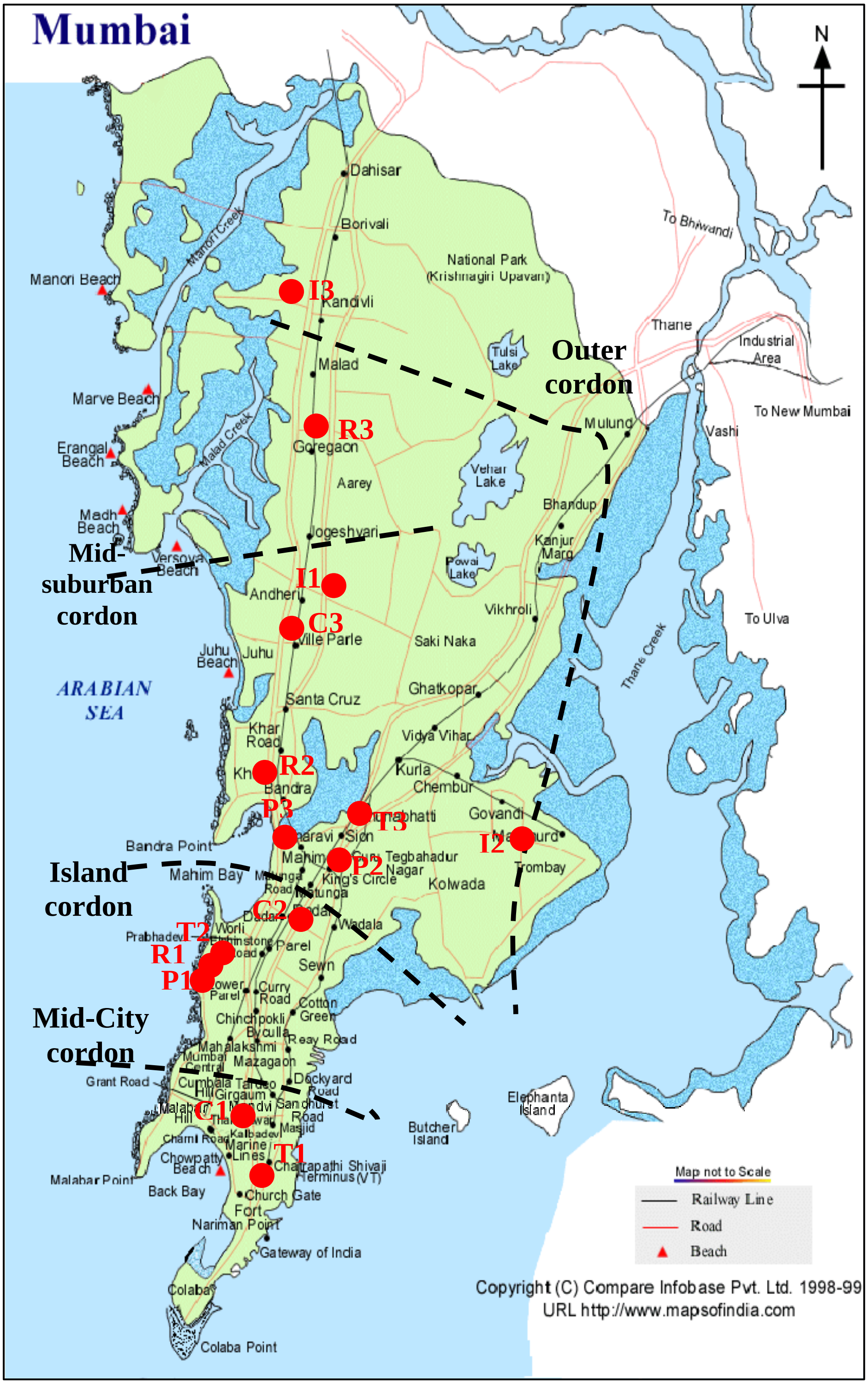


Figure 1. Sampling Locations in Mumbai Metropolitan Region

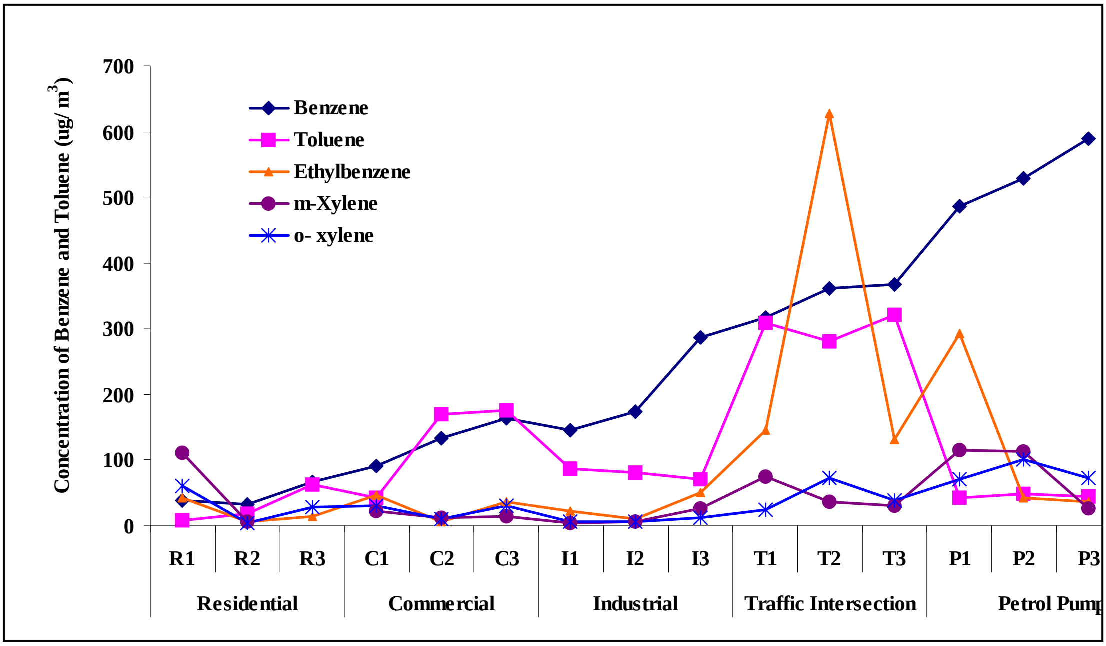
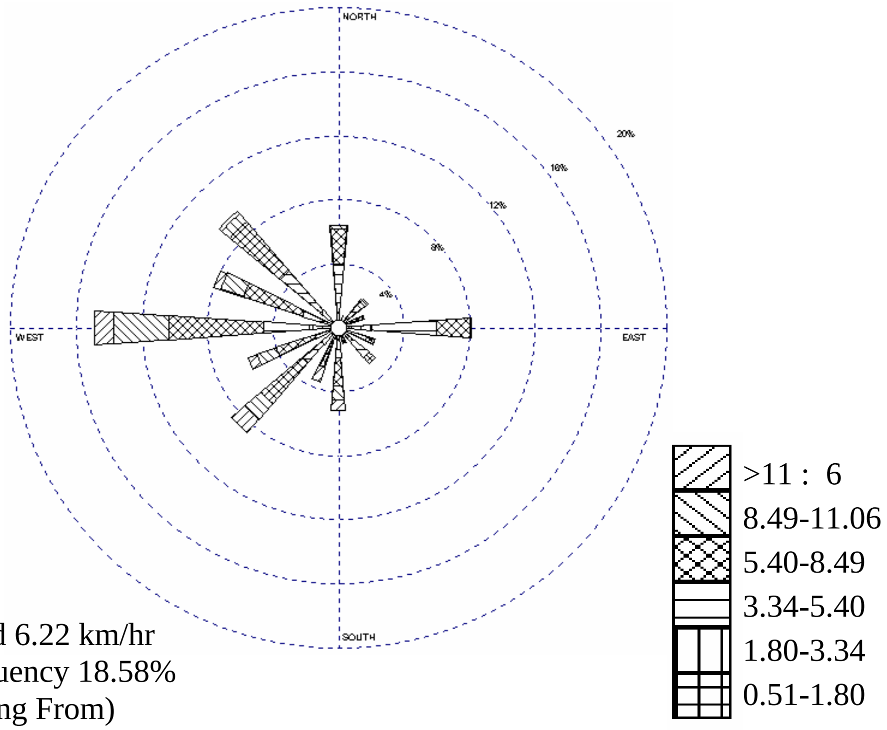


Figure 2. Ambient Concentration of Benzene, Toluene: Ethyl benzene and Xylenes (BTEX)



Avg. Wind Speed 6.22 km/hr
Calm Wind Frequency 18.58%
Direction (Blowing From)

Figure 3. Annual Windrose for Mumbai City

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OPTIMALIZATION OF RECUPERATION PROCES WITH METHYL BROMIDE FOR STATIONARY QPS-TREATMENT FOCUSED TOWARDS MINIMAL ENERGY CONSUMPTION

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ABSTRACT

Desclean Belgium together with Vito, supported by the Flemish Government (IWT-Institute for the Promotion of Innovation by Science and Technology in Flanders), enrolled a project to investigate optimalization of recuperation of MeBr with fumigation of containers in the harbor of Antwerp (Quarantine and Pre-Shipment treatments - QPS). The objective of this investigation was to provide an answer towards the question if it was feasible to recuperate MeBr on a practice and mobile way by active carbon in order to reduce the emissions of MeBr towards zero (part of Montreal protocol). Practical stands for the dimensions and weight of the total systems. With mobile the daily appliance and substitution of the current approach is meant with minimum number of persons for proper execution. It was necessary to further investigate the process of recuperation of MeBr towards energy efficiency. Besides the improvements of the recuperation process of active carbon, alternative absorbents were evaluated. Thermal management (heating of active carbon and active fan control) had a significant roll within the process control. The results shows that is possible to recuperate MeBr on a practical and mobile way by combination of one or several steps, followed by an additional step that eliminates Me Br completely. The result is a feasible and economical process that allows large-scale introduction of emission free MeBr treatments for QPS. Furthermore the developed approach shows high potential for successful introduction into other applications like agriculture.

Key Words: Quarantine and Pre-Shipment treatments – QPS, Methyl Bromide – MeBr, Integrated Pollution Prevention and Control - IPPC

1. INTRODUCTION

The project consisted of several Work Packages (WP):

In WP 1, the process of recuperation of MeBr in active carbon was evaluated applying quantum chemical methods like chemisorptions, mass spectrometry, gas chromatography, thermo spectrometry, thermo graphical metrical analyze (TGA), and Differential Scanning Calorimeter (DSC). In WP2 possible alternative materials for sorption were evaluated like zeolites, focused on minimum energy usage. In WP3 thermal management was further optimized to obtain minimum electric energy usage as well on peak power as total energy consumption to allow introduction of a battery power system.

2. PROCESS OF RECUPERATION OF MeBr

Four different types of Active Carbon (AC) were characterized towards adsorption (Table 1). Provided specifications were checked. All samples had a specific surface (BET) of 900 – 1000 m^2/g and contained 5% tot10% water. Hydrafin CC8*30 is an AC derived from coconut fiber which, according to the literature should be very efficient for sorption of MeBr. No specifications were obtained from Organosorb 10-CO, a catalytic activated AC on basis of cupper. All materials were micro porous with an average dimension < 10 Å.

Table 1. Specifications and measured values of AC samples

Type	**Specification**		**Measured**		
				48 h Vacuüm	**TGA**
	BET (m^2/g)	**Conc H_2O (Wt%)**	**BET (m^2/g)**	**Conc H_2O (Wt%)**	**Conc H_2O (Wt%)**
Hydrafin 30N	900	5%	890	5,5%	1,7%
Hydrafin CC8 * 30	1000	10%	1160	18,9%	18,7%
Desorex K47	900	5%	950	4,8%	8,5%
Organosorb 10-CO	—	—	1140	2,8%	4,4%

The specific surface (BET) was determined with N_2 adsorption / desorption. Notice the relative small differences between specified and measured.

The amount of absorbed water on the samples was determined by the diminution of the weight after 48 hours of storage in vacuum at room temperature. Significant reduction in weight with ~100°C in the thermo gravimetric analyses of the samples were noticed. (see figure 1a). The TG analyses of all monsters were executed from room temperature up to 1200 °C (temperature rises of 5 °C/min) under constant flow (70 cm^3/min) of argon. The results are given in table 1 (colon 5 and 6). Figure 2 compares the specifications. It is clear that hydrafin CC8*30 –with 20% – has the highest power to sorption for water. Given that the BET of Organosorb is almost the same as Hydrafin CC8*30, the sorption capacity for water is limited (~3 – 4 %). The reason lies within the catalytic activation. Within the DSC spectrum (figure 1b) it is clear to see that the desorption of H_2O is endothermic and –as expected– according the quantity of absorbed water. Above 600°C a possible degradation of the product is noticed.

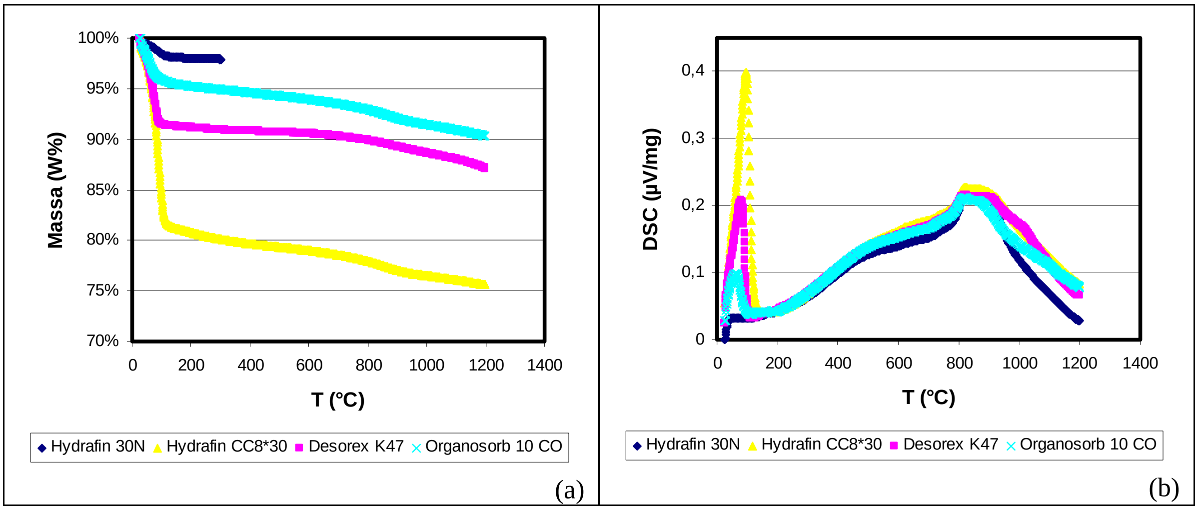

Figure 1: TGA (a) en DSC (b) measurements of different types AC under inert (Ar) atmosphere

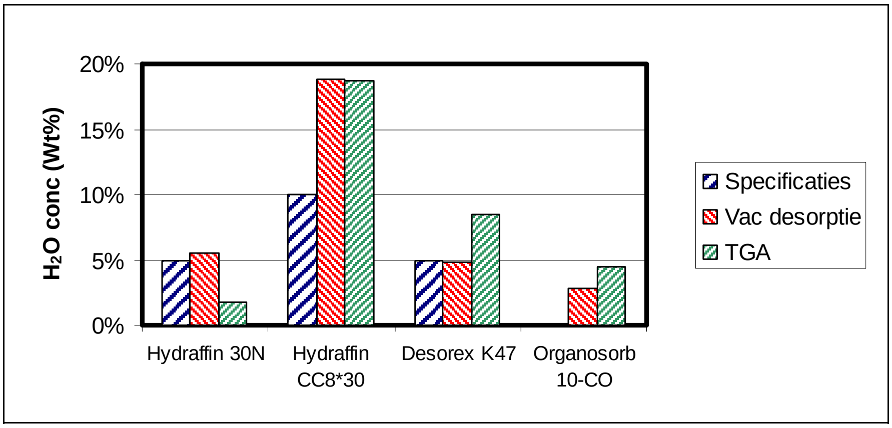

Figure 2: Concentration of H_2O for the different types of AC under vacuum desorption and TGA under inert (Ar) atmosphere compared to the provided specifications.

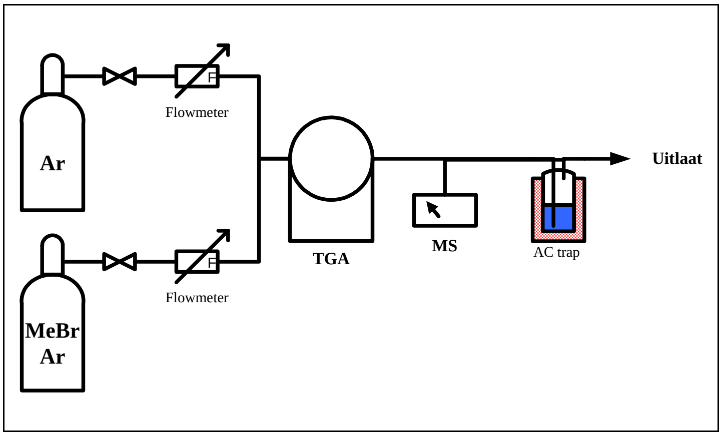

Figure 3: TGA: MeBr adsorption and desorption under inert (Ar) atmosphere

A significant difference is noticed between the ‘pure’ active carbon (Hydrafin en Desorex) and the catalytic active Organosorb (figure 5). The adsorption of MeBr on Organosorb is much faster (~14%/h) then for Hydrafin en Desorex (2 – 3.5 %/h) (table 2). Given that the adsorption time was not sufficient to achieve equilibration, a relative good estimation of the sorption capacity was obtained. The capacity of absorption of Organosorb is significant higher (> 20 %) then the other AC types. The capacity of absorption of Desorex is maximum ~10% while Hydrafin is lower.

The velocity of desorption is –with room temperature– like expected lower: about the 50%. With higher temperature the velocity increases significant. This phenomenal can also be obtained under vacuum conditions. The quantity of heath that is released with adsorption and required for desorption can normally retrieved from DSC signal. However this signal is given the materials to weak to allow any statement. A possible conclusion is that the amount of heath (per gram AC) will be limited.

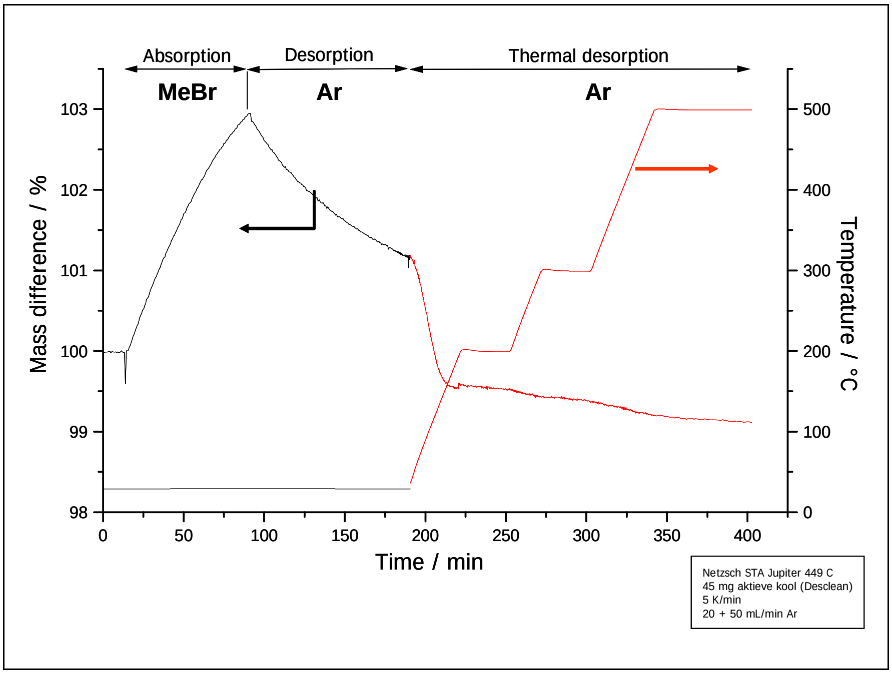

Figure 4: TGA measurement: MeBr adsorption and desorption under inert (Ar) atmosphere

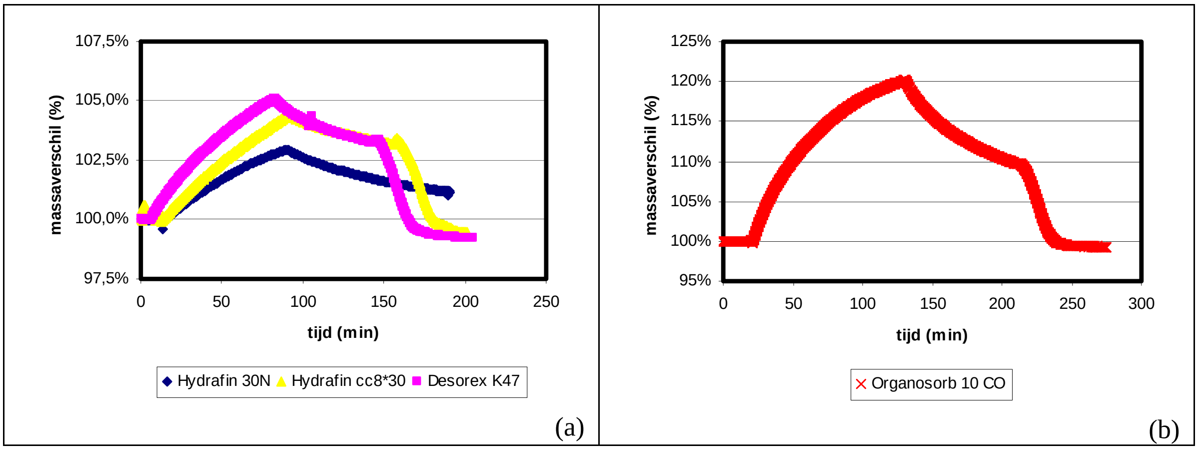

Figure 5: TGA for absorption and desorption of MeBr for the different AC samples

Table 2: Adsorption and desorption velocity of MeBr for different types of AC

Type	**MeBr Sorptiesnelheid**	
	adsorptie (Wt%/h)	**desorptie (Wt%/h)**
Hydrafin 30N	2.33	1.06
Hydrafin CC8 * 30	3.44	1.19
Desorex K47	3.65	1.84
Organosorb 10-CO	14.2	7.75

3. SIMULATION OF DE ENERGY DEMAND

Based on the article “Methyl Bromide Recovery on Activated Carbon with Repeated Adsorption and Electrothermal Regeneration” (J.D. Snyder & J.G. Leesch in Ind. Eng.Chem Res. 2001 p. 2925 ev – see References) statically and dynamical simulations related with the energy demand were executed. These simulations programmed in Engineering Equation Solver (EES).

The static simulation were based on the chemical equilibrium between the active carbon and the MeBr partly in the containers, partly absorbed by the AC. From these simulations the conclusions were made towards the distribution of mass of the MeBr in the different cartridges (sequence of cylinders used after each other to allow reduction of MeBr in multiple steps) and number of applied cartridges in function of the temperature, desorption and absorption.

The dynamic simulations were focusing on several time depending aspect of the process, like:

- the amount of required energy at each moment
- the temperature behavior of the AC during the process
- the absorption and desorption of MeBr

- the concentration of MeBr in the container

All simulations were executed for a container of a volume of 35 m³ with air temperature of 30 °C and atmospheric pressure of 1,013 bar. As assumption was take that the complete container department had to be filled from 0 to 15.000 ppm MeBr (about 2 kg MeBr). In reality less MeBr will be applied since the container will be filled when disinfection has to take place. On the other side the container will consists of material that will absorb MeBr (e.g. wood) resulting in more initial MeBr to obtain the required initial concentration of MeBr. Furthermore the effect of humidity was not taken into account.

For the obtained energy consumption the energy for the thermal management (heating/cooling) is only taken into consideration, exclusive the energy required for the ventilation. This is acceptable given the fact that the thermal energy demand is in general much larger.

4. THERMAL MANAGEMENT AND ENERGY CONSUMPTION

A test set-up (see Figure 6) was constructed to allow to understand the impact on thermal management and to capturing the energy consumption. Key question that had to be addressed was if it is possible to obtain a portable and practical system.

The following components were applied:
Cylinder: diameter 160 mm length 1 m filled with active carbon
Ventilator: VENPLAST Type P 282, 0.75 kW 3F 380V 50 Hz powered by an 3-phase inverter with frequency regulation for speed regulation
Heating: 12 m heating ribbon, (120°C, 66W/meter) with 3 D metal grid

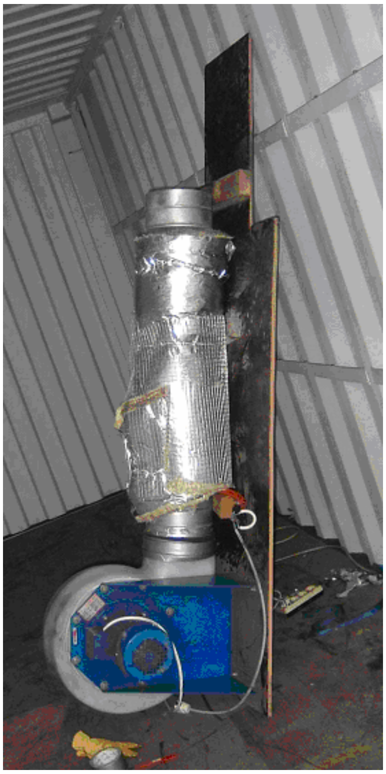

Figure 6: Test set-up

With this relatively simple construction it was easy to obtain a first step MeBr absorption of more then 60% (40000 towards 13500 ppm). With the addition of multiple steps (cartridges) almost fully absorption was obtained (40000 towards 5 ppm).

5. CONCLUSION

Major differences were found between the ‘pure’ active carbon (e.g.. Hydrafin en Desorex) and the catalytic active Organosorb. The absorption of MeBr on Organosorb is much faster (~14%/h) then for Hydrafin and Desorex (2 – 3.5 %/h). The adsorption capacity of Organosorb is significant higher (> 20 %) then the other types of AC. The adsorption capacity of Desorex is maximum (~10%) while Hydrafin is lower. The desorption velocity is –with room temperature– as expected significant lower (50%). With higher temperature this velocity increases rapidly. Similar effect can be obtained by applying vacuum. Besides the specific capacity, the size of the grain is important for the airflow and the required energy. Relevant information concerning the usage of MeBr and possible alternatives were studied.

From the simulation can be concluded that the time to achieve equilibrium is directly dependent of the airflow. A possible approach is the two step process, starting with the adsorption of MeBr with active carbon, followed by the destruction of the remaining fraction of MeBr via the chemical reaction of natriumthiosulfaat (NaS_2O_3). Although Hydrafin CC8*30-active carbon possesses relative good absorption property and thermal stability with higher temperatures (150 °C), the less efficient Desorex K47 was restrained due the more compact packing.

Partially recuperation of MeBr (up 60%) is possible on a practical and mobile way. And with the introduction of the second step MeBr is no longer released and opens the door for emission free MeBr treatments on a practical way.

REFERENCES

Gan J., Megonnell N.E., Yates Scott R., 2001, Absorption and catalytic decomposition of Methyl Bromide and Methyl Iodide on activated carbons, TEKTRAN.

Radosevich M., Jin Y., Cha D. K., 2004, The effect of Biosurfactants on the Fate and Transport of Nonpolar Organic Contaminants in Porous Media, University of Delaware.

ARS, 1997, Bromosorb Unit/Methyl Bromide Alternatives: A New Patented Process Contains, Recaptures an Methyl Bromide, www.ars.usda.gov.

Willis E., New design for Zeolite-based recapture, Knowzone Solutions, Ontario, Canada.

Talbot M., Koehler P., 1991, Pest Management Strategies for Storing Grains in Florida, University of Florida, Institute of Food and Agricultural Sciences.

2002, Stored Grain Research Laboratory, Research Report 1999-2001, Canberra.

Great Lakes Chemical Corporation, 1999, First Methyl Bromide Recapture Unit Installed, Volume 5, Issue 1, Dallas.

Ren Y., O'Brien, Desmarchelier J.M., 1997, Improved Methodology for Studying Diffustion, Sorption and Desorption in Timber Fumigation, Elsevier Science Ltd, J. stored Prod. Res.Vol. 33, No. 3, pp. 199-208, Australia.

Gan J., Yates S. C., 1998, Recapturing and decomposing methyl bromide in fumigation effluents, Elsevier Science, Journal of Hazardous Materials 57, 249-258,; Riverside.

Snyder J.D., Leesch J.G., 2001, Methyl Bromide Recovery on Activated Carbon with Repeated Adsorption and Electrothermal Regeneration, Ind. Eng. Chem. Res.,Vol. 40, No. 13, 2925-2933, Fresno, California.

Gan J., Megonnell N. E., Yates S.R., 2001, Adsorption and catalytic decomposition of methyl bromide and methyl iodide on activated carbons, Athospheric Environment 35, 941-947, Riverside, Pittsburgh.

Leesch J. G., Knapp G. F., Mackey B.E., 2000, Methyl bromide adsorption on activated carbon to control emissions from commodity fumigations, Journal of Stored Products Research, 36, 65-74, Fresno, San Clemente, Albany.

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AIR QUALITY AND NATURAL SOURCES IN AN INDUSTRIAL AREA

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ABSTRACT

The air quality data, collected through a monitoring station network in a large industrial area in Sicily (Italy), have been analysed in order to highlight the role played by natural pollution sources. The area is opened to sand storms from north Africa, marine aerosols, emissions from agricultural activities, emissions from Etna volcano and emissions from the intensive shipping along the coast.

While the concentrations measured for pollutants like SO_2, H_2S, NMHC, NO_x and benzene are strictly related to wind direction and may be charged quite completely to industrial sources, those for PM_{10}, CH_4 and O_3 show no evidence of a possible correlation either with wind or with local sources. On the contrary, there is evidence of a quite relevant contribution from natural polluting sources also through long-distance and transboundary transport phenomena. The quite simple methodology here adopted to evaluate the natural source contributions allow to look for more reasonable and efficient prevention strategies.

Key Words : air quality, natural pollution sources, ozone, PM_{10}

1. INTRODUCTION

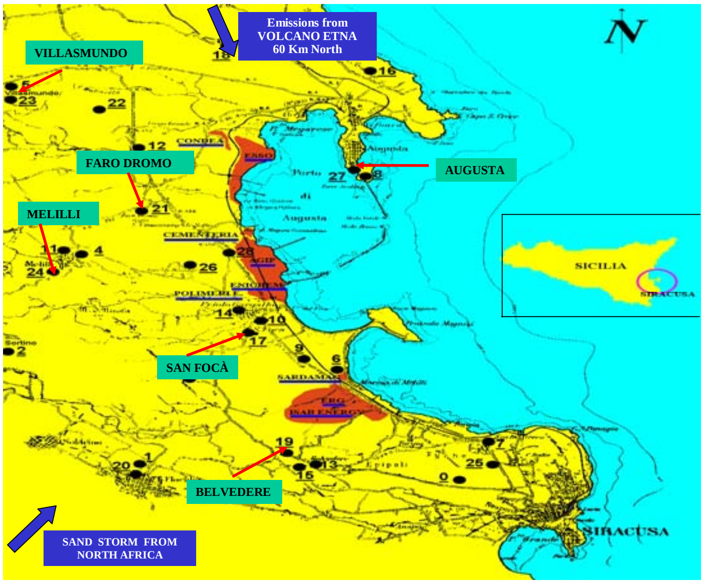
On January 1st 2005 new limit values for the protection of human health for SO_2, PM_{10} and CO came into force all over the European Union. They add to other limits already in force, for the protection of ecosystem or vegetation, for SO_2, NO_x. By January 1st 2010 limits for NO_2 , benzene and ozone shall be met and those for SO_2 will be lowered.The directives which establish those limits contains a kind of contradiction in that on one side establish that the objective is to avoid, prevent or reduce harmful effects on human health and the environment as a whole, while on the other side consider *pollutant* any substance released directly or indirectly in the ambient air by man and not by natural sources. When exceedances of limit values occur Member States may be obliged to implement action plans and in the case the exceedances are due to natural events or resuspension Member States shall provide the necessary justification.

The problem is: how to evaluate and quantify contributions other than from industrial sources and which action plans may be implemented when a significant contribution from natural sources is evident.

2. SIRACUSA INDUSTRIAL AREA

The difficult situation just mentioned in the introduction is particularly perceived in the industrial area of Siracusa, located along the east coast of Sicily (Fig. 1), which is subjected to frequent sand storms from north Africa, to normal marine aerosols, to emissions from agricultural activities all around the area itself, from time to time to emissions from Etna volcano, which is about 60 Km far, and lastly to emissions from the intensive shipping in the Sicilian canal.

Fig. 1 - INDUSTRIAL AREA IN SIRACUSA (Italy) AND SOME OF THE AIR QUALITY MONITORING STATIONS



A consortium of local industries have been monitoring air quality for 30 years through a 12-station network, analysing several pollutants as SO_2, H_2S, NO, NO_x, NO_2, O_3, CH_4, NMHC, THC, PM_{10}, benzene, toluene and some other organic compounds. The network is equipped with three meteorological stations other than with RASS and SODAR for the measurement of vertical thermal and wind (direction and velocity) profiles.

Air quality data collected in the different stations and in different years have been assembled and averaged in 16 sectors corresponding to wind directions measured at the CIPA meteorological station. Just to give an example the only data monitored at the Melilli station, for 2003 and 2004, are referred in this paper since the results do not differ conceptually from those achieved in the other measuring stations.

Looking at the circular graphs in fig. 2, it may be observed that the prevailing wind for 2003 has blown from NE to SE (sectors 3-7) for 37% and from SW to NW (sectors 11-15) for 38%, while for 2004 has blown from NNE to E (sectors 2-5) for 32% and from SW to NW (sectors 11-15) for 40%.

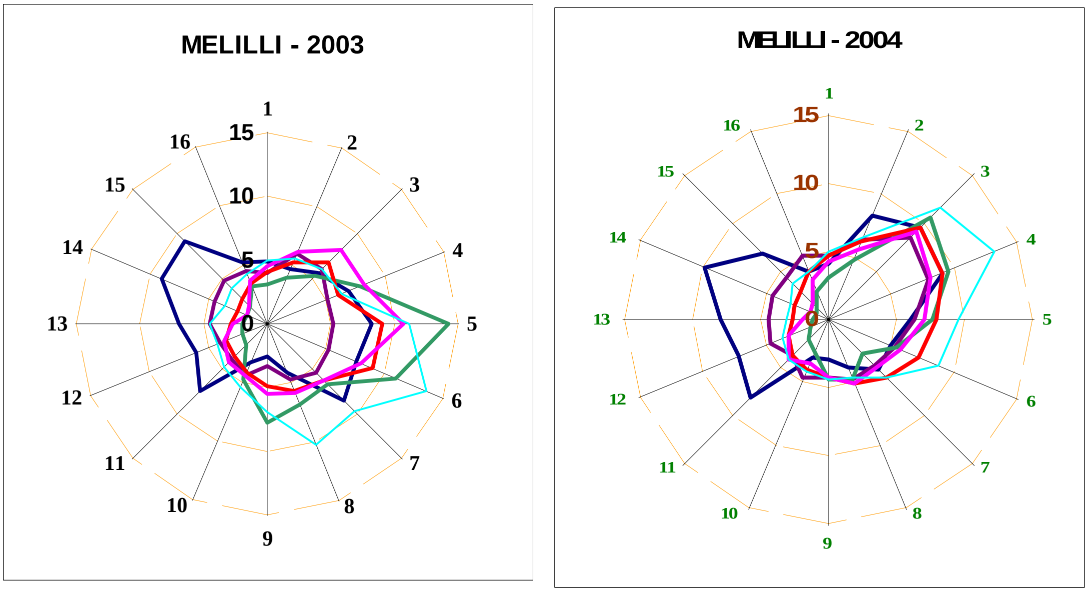
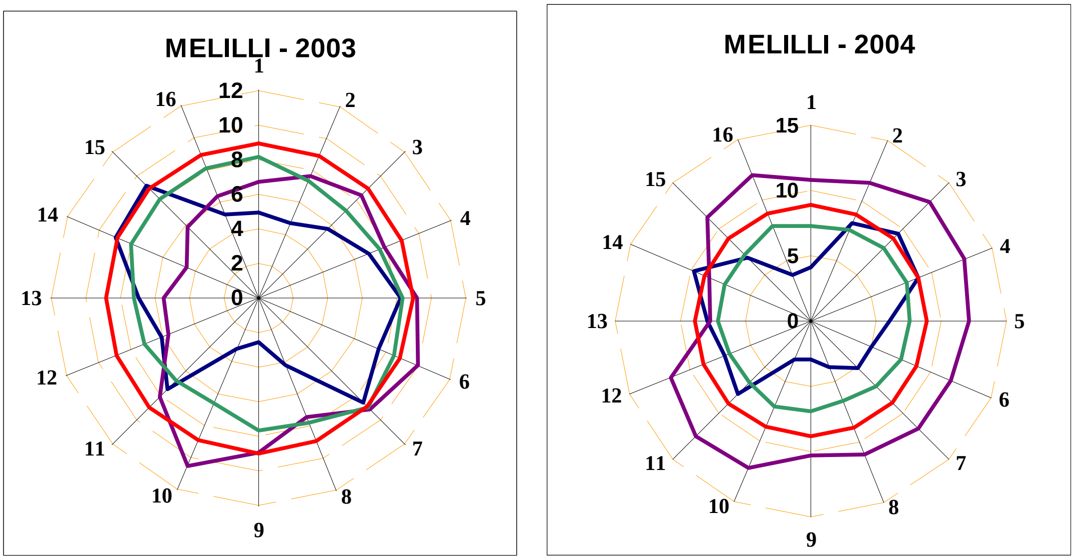


Fig. 2 - Legend: — **% wind direction,** — **H_2S (x 10),** — **SO_2 (x 0,25),**
— **NHMC (x 0,1),** — **NOx (x 0,5),** — **Benzene (x 3)**

Looking at the air quality data monitored at Melilli station, higher concentrations for SO_2, H_2S, NO_x, NMHC and benzene are clearly observed for wind blowing from the sectors 3 to 7, in a position downwind to the industrial sources. It is useful to stress that for the five pollutants the concentrations averaged over the sectors 3 to 7 are 1/3 to 1/4 of those averaged for wind blowing from the sectors 9 to 16. In any case, the hourly averaged limit value for SO_2, not to be exceeded more than 0,27% in one year, actually was exceeded 0,05% in 2003 and 0,25 % in 2004. On its turn the daily limit value not to be exceeded three times a year has been exceeded once in 2003 and twice in 2004. For NO_2 the annual average has been 16 µg/m^3 and 12 µg/m^3, respectively for 2003 and 2004, much lower than the limit for the protection of the health (40 µg/m^3) which has to be met by 2010. Furthermore the maximum hourly concentration has been 140 µg/m^3 in 2003 and 121 µg/m^3 in 2004, while the limit value, which should be met by 2010 is 200 µg/m^3 not to exceed more than 18 times. For benzene the annual average has been 2,3 µg/m^3 in 2003 and 2,4 µg/m^3 in 2004 lower than the limit of 5 µg/m^3 which has to be respected starting 2010.

Completely different is the situation for O_3, CH_4 and PM_{10} concentrations which do not display any correlation with wind directions (fig. 3). On the contrary, in case of PM_{10} the higher concentrations are measured with wind blowing from SW that is from north Africa direction.

Furthermore the European limit values for PM_{10} which have to be met by January 1st 2005, in the past years should have not be respected. In particular, the daily average limit of 50 µg/m^3, not to exceed more than 35 times per year (9,6%) in 2003 has been exceeded 13,7% and in 2004 28,6% (Fig. 4). On its turn, the annual average has been 31,5 µg/m^3 in 2003 and 47 µg/m^3 in 2004 against the limit of 40 µg/m^3.



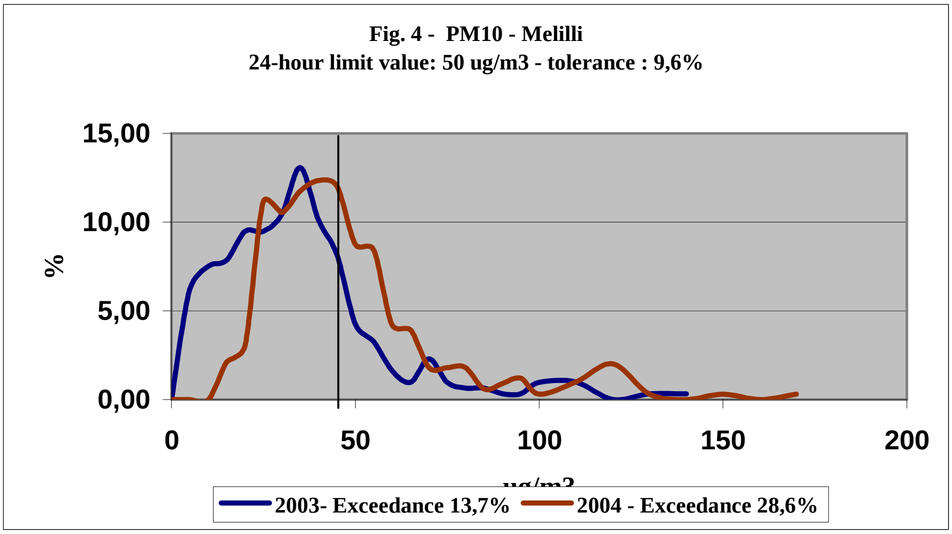


Fig. 4 - PM10 - Melilli
24-hour limit value: 50 ug/m3 - tolerance : 9,6%

Fig. 3 - Legend: ▬ **% wind direction,** ▬ **PM10 (x 0,25),** ▬ **Ozono (x 0,1),** ▬ **CH4 (x 0,01)**

Much worst is the situation for ozone. For example, the target value for the protection of vegetation (AOT40) averaged on five years, to be met by 2010, is 18.000 µg/m^3.h, while in Melilli station the averaged from 2000 to 2004 has been 32.854 µg/m^3.h, in Belvedere and Villasmundo stations, respectively 33.741 µg/m^3.h and 47.806 µg/m^3.h.

The concentrations of methane are quite stationary during the year and the annual average has been the same in 2003 and 2004 equal to 1357 ppbv at 25 °C.

3. NATURAL EVENTS

In fig. 5 the ozone concentrations measured in Melilli in 2004 have been reported together with the temperature behaviour.

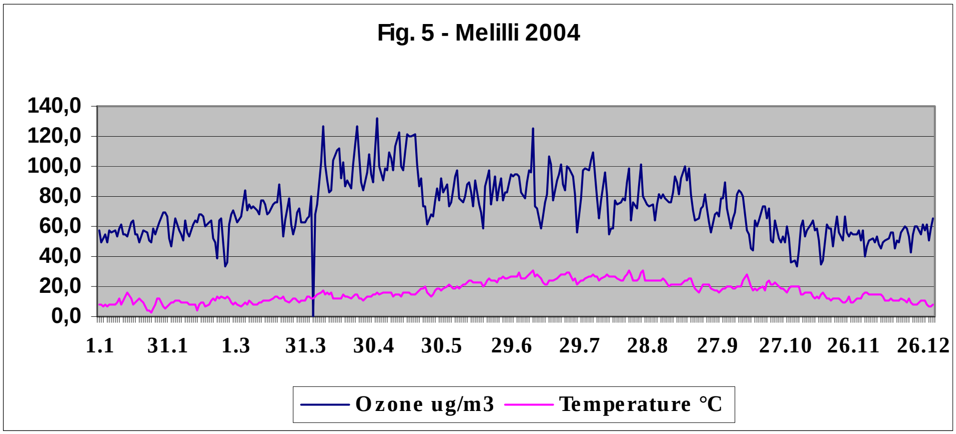


Figure 5. Melilli 2004

They show a kind of correlation in that the sunlight radiation induce the ozone formation, but from April 6 to May 16 2004 an anomalous situation has been recorded. The period average was 102 µg/m^3, 40% more than the annual average of 73 µg/m^3. In the same period the temperature was normal for the season, no episodes for other pollutants were registered, the instrumentation was no failed, the period averages for NO_x, NO, NO_2, NMHC, PM_{10} were very close to the annual average.

Many more for the whole year are the episodes for PM_{10}, normally short, with peak up to 1000 µg/m^3 and wind clearly blowing from south or south-west directions.

A significant contribution to PM_{10} come from sea spray due to rocky and indented coast as is may be observed through the concentrations measured at Augusta station for wind blowing from sectors 3 to 6.

4. CONCLUSION

In many geographical area a great contribution to air pollution comes from natural sources and/or from far away so that any prevention action plan appears critical and doubtful. This is the case of the industrial area close to Siracusa in Italy.

The industrial emissions, namely of NMHC and NO_x, certainly give a contribution to ozone formation, but the air quality data show that the phenomenon is not local and may not be strictly related to industrial sources. A similar situation is evident for PM_{10} whose level suffer of a contribution from sand storms from North Africa, marine aerosol, shipping emissions, agricultural activities and sometime Etna volcano.

Along the current system of air pollution control, based on ambient concentration limits, in order to prevent the exceedances, the local sources are obliged to reduce their emissions as the air quality approaches the limit. This plan not only does not help too much in case of a large contribution from natural sources but also cause a floating production with an uneconomic management.

An action plan based on the population exposure, through a selection of special measuring stations, could be more effective in terms of public health benefits. However it should also combined with a progressive closure of the gap between the current natural background concentration and the current exposure.

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LONG-TERM INVESTIGATIONS OF RADIOACTIVE MATTER IN THE AIR IN THE CITY OF ZAGREB

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ABSTRACT

The activity concentrations of radioactive matter in the Zagreb have been manifesting the constant exponential decrease ever since early 1960s. The Chernobyl nuclear accident caused a major increase in Zagreb air radioactivity only in 1986, which over next few years quickly decreased to pre-Chernobyl values. However, due to changing meteorological conditions at that time, resulting in very complex dispersion pattern of Chernobyl debris over Europe, major parts of Croatia have been initially unaffected by the plumes of contaminated air.

The mean residence time of ^{90}Sr and ^{137}Cs in fallout are estimated for respective pre-Chernobyl and post-Chernobyl periods.

Despite of constant presence of radioactive matter in the Zagreb air, in the observed period activity concentration values never exceeded the legal limits. Consequently, the doses incurred by ^{90}Sr and ^{137}Cs by inhaling the polluted air after the Chernobyl accident are very small.

Key words: radioactivity, ^{90}Sr, ^{137}Cs, Chernobyl accident, dose

1. INTRODUCTION

Nuclear tests conducted in the atmosphere and releases of radioactive material from nuclear facilities are the main causes of the man-made radioactive contamination of human environment. Once released to the atmosphere, long-range atmospheric transport processes can cause a widespread distribution of such radioactive matter, although it may, like in the case of Chernobyl accident, originate in a single point.

The resulting fallout, consisting of short and long-lived radionuclides, eventually affects humans, either directly or indirectly by entering the food chain through the plants and animals. In both cases it causes a health hazard to the population either through the direct irradiation or consumption of contaminated foodstuffs.

Among man - made radioactive nuclides, those of the strontium and caesium, particularly ^{90}Sr and ^{137}Cs, are regarded as a great potential hazard to living beings. Namely, these fission products have unique combinations of relatively long half-lives (29.1 and 30.14 years respectively) and chemical and metabolic properties resembling those of the potassium and calcium respectively.

Investigations of the distribution and fate of natural, nuclear weapons produced and reactor released radionuclides in the Zagreb air have been conducted as a part of an extended and still ongoing monitoring programme of radioactive contamination of human environment in Croatia. The gross beta activity in air has been measured ever since 1961, while systematic gammaspectrometric measurements started in 1983. Before that time and starting in 1965, ^{137}Cs activity concentrations were measured by NaI detector. Investigations of ^{90}Sr, involving radiochemical methods, started in 1987, i.e., one year after the Chernobyl accident. The measurements of external ambient gamma dose rates have been performed since 1985 ((Popovic 1966-1978; Bauman et al. 1979 – 1992; Kovac et al. 1993 – 1998; Marovic et al.1999 - 2005).

2. MATERIAL AND METHODS

Air samples have been collected daily 1 m above the ground by a high volume air sampler that pumps air through glass-fiber filter. Total volume of air passing through the filters is 40,000 to 50,000 m^3.

Fallout samples were collected monthly in the city of Zagreb at the location of the Institute for Medical Research and Occupational Health (45° 50' 7.3" N, 15° 58' 58.7" E). The funnels that were used for fallout collection had a 1 m^2 catchment area. Precipitation quantity was measured by Hellman pluviometer.

A gamma-ray spectrometry system based on a low-level ORTEC Ge(Li) detector (FWHM 1.87 keV at 1.33 MeV ^{60}Co and relative efficacy of 15.4% at 1.33 MeV) coupled to a computerized data acquisition system was used to determine radiocaesium and beryllium-7 levels in the samples from their gamma-ray spectra. Samples were measured in cylindrical plastic containers of appropriate volume, which were placed directly on the detector. Counting times depended on sample activities, ranging from 10,000 to 250,000 seconds, typically being 80,000 s.

The activity concentrations of ^{90}Sr were determined after the radiochemical treatment of samples, by beta counting its decay product, (^{90}Y), in a low-background, anti-coincidence shielded Geiger-Müller counter.

Quality assurance and intercalibration measurements were performed through participation in an International Atomic Energy Agency (IAEA) and World Health Organization (WHO) international intercalibration programmes.

3. RESULTS AND DISCUSSION

^{137}Cs activity concentrations in air and fallout

The radioactive fallout resulting from large-scale nuclear weapon tests in the atmosphere conducted in the 1960s, followed by similar, but smaller scale tests by the Chinese and French in the 1970s and afterwards, was the dominant route for the introduction of artificial radionuclides in the environment until the nuclear accident at Chernobyl, in former USSR, on 26 April 1986. Therefore, activity of most environmental samples could be expected to be in correlation with fallout activity (i.e. surface deposit in Bqm^{-2}).

Severe radioactive fallout from highly radioactive air plumes that originated from the damaged Chernobyl nuclear reactor was spread and transported all over Europe. Fortunately, due to the prevailing meteorological conditions at the time after the accident that influenced the formation and spreading direction of Chernobyl plumes, Croatia was only on the North-Western region partially affected by the edge of one of the plumes (UNSCEAR, 1988), as indicated on Figure 1.

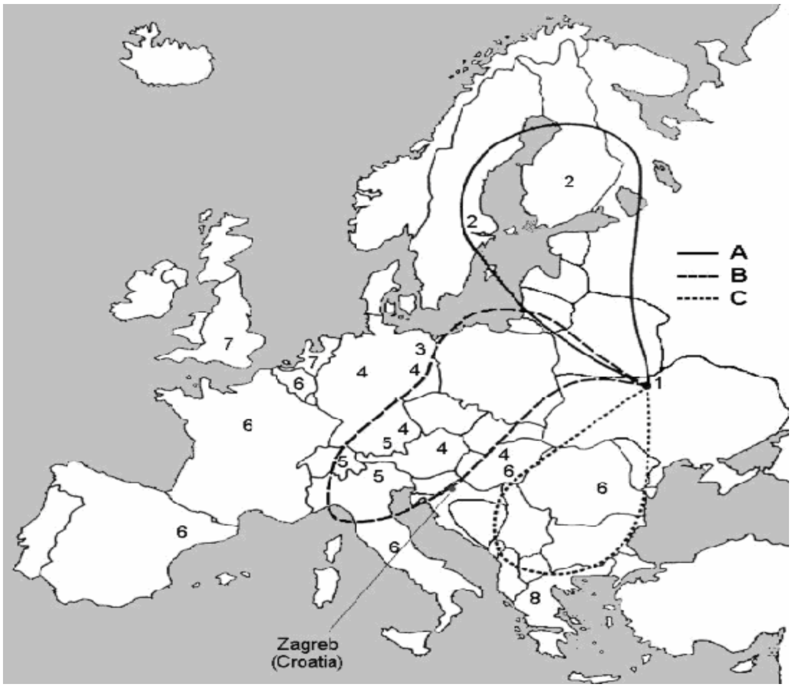

Fig. 1. Spreading of radioactive plumes over the Europe after the Chernobyl nuclear accident. Numbers 1-8 represent plume arrival times at respective areas: 1 = April 26, 2 = April 27, 3 = April 28, 4 = April 29, 5 = April 30, 6 = May 1, 7 = May 2 and 8 = May 3. The figure has been adopted from UNSCEAR report for 1988.

The highest ^{137}Cs activity concentrations in the observed period were recorded in May 1986, being 6200 Bqm^{-2} for the surface deposit by fallout and 0.85 Bqm^{-3} in air. Such high values could be attributed to the second of the three radioactive plumes originating from the Chernobyl reactor, which edge passed over Northwest Croatia (UNSCEAR 1988). The radioactive material introduced to the atmosphere by Chernobyl accident was by global dispersion processes distributed throughout the troposphere, causing the increased radiocaesium activity concentrations in the environment in years to come. However, ^{137}Cs these showed a significant exponential decrease over time because of natural removal as well as radioactive decay. Also, no new releases of ^{137}Cs occurred after the Chernobyl reactor accident either from nuclear facilities or nuclear weapons testing.

In 2004, average ^{137}Cs activity concentration in air was 0.02 Bqm^{-3}, while total ^{137}Cs surface deposit by fallout was 2.07 Bqm^{-2}. Activity concentrations of ^{137}Cs in air and fallout are shown on figure 2.

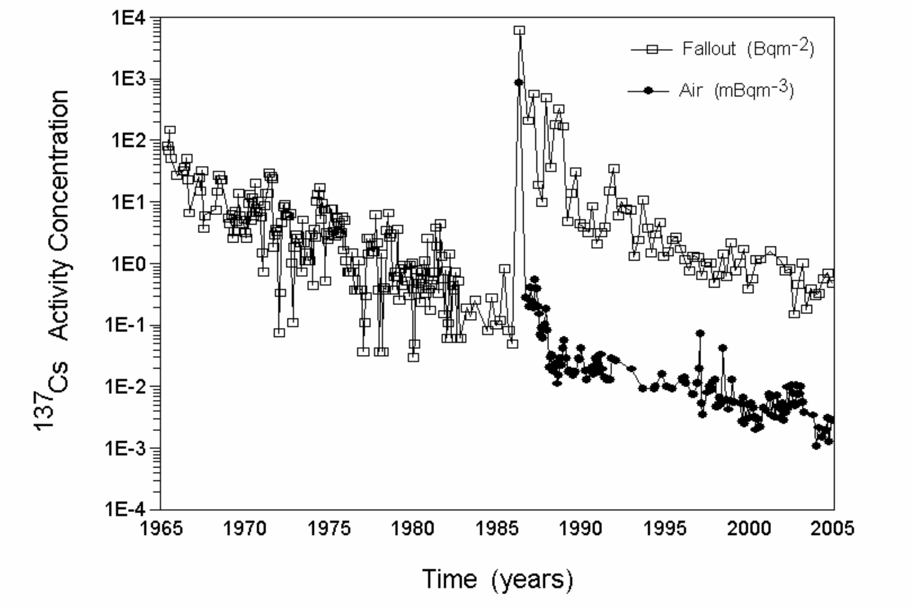

Fig 2. ^{137}Cs activity concentrations in air and fallout

The ^{137}Cs activity concentration in surface deposit in May 1965 was 81.4 Bqm^{-2}. The minimal value for the pre-Chernobyl period was recorded in December 1985, being 0.05 Bqm^{-2}, while the maximal value was 150.2 Bqm^{-2}, which was recorded in July 1965. The lower limit of total amount of ^{137}Cs surface deposit delivered by fallout for the period January 1965 – April 1986 was about 1300 Bqm^{-2}. This value is being regarded as a lower limit since some data are missing, which is especially true for the 1960s, when ^{137}Cs activity concentrations were quite large and it was no possible to include those data into the overall sum. For post-Chernobyl period, i.e. from May 1986 to December 2004, the lower limit of total amount of ^{137}Cs in surface deposit is 8450.5 Bqm^{-2}. However, if year 1986 is excluded, the total amount of ^{137}Cs in surface deposit is 2040.5 Bqm^{-2}.

^{7}Be activity concentrations in air

^{7}Be ($t_{1/2}$ = 53.3 days is naturally occurring radionuclide of cosmogenic origin, formed by spallation processes of light atmospheric nuclei such as nitrogen and oxygen when they capture protons or even neutrons from the primary component of cosmic rays. Once formed, ^{7}Be is rapidly attached to the particles in the atmosphere. Naturally produced ^{7}Be, with almost unchanged activity concentrations throughout the entire observed period, is a good quality check of the methods used.

In addition, this radionuclide has been recognized as a powerful tool in the description of environmental processes precipitation scavenging (i.e. washout), atmospheric particle deposition as well as deposition patterns of airborne contaminants. High ^{7}Be concentrations in air are related to low solar activity like in

1987, while low concentrations are related to high solar activities. The downward trend in the ^{7}Be air concentrations in 2004 can therefore be attributed to an increase in solar activity.

The mean ^{7}Be activity concentration in the air for the 1987 – 2004 period is (5.4 ± 2.8) ×10^{-3} Bqm^{-3}. ^{7}Be activity concentrations in air are shown on figure 3.

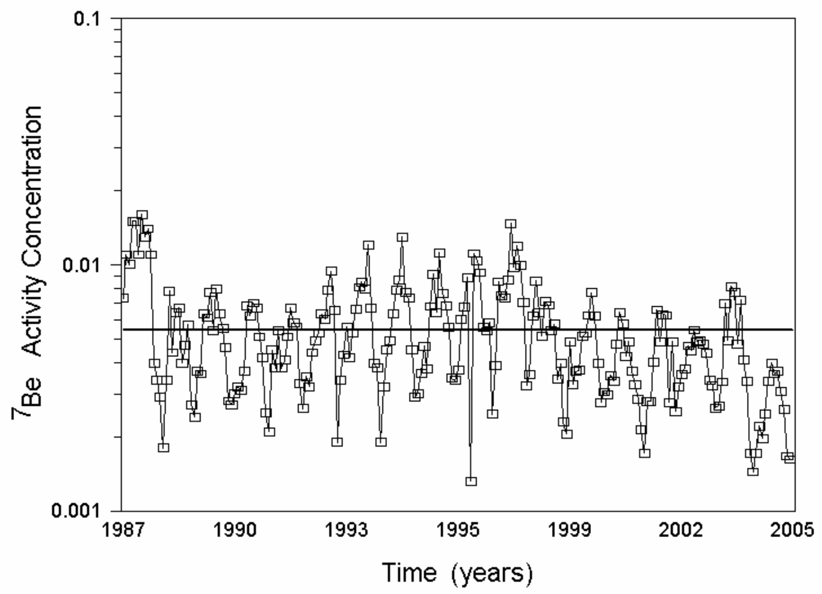

Fig 3. ^{7}Be activity concentrations in air

These values are very similar as observed elsewhere (Papastefanou et. al., 1995).

^{90}Sr activity concentrations in air and fallout

The minimal value of ^{90}Sr activity concentration in surface deposit delivered by fallout for the pre-Chernobyl period was recorded in October 1990, being 0.02 Bqm^{-2}, while the highest value was 247.9 Bqm^{-2}, which was recorded in June 1964. The total amount of ^{90}Sr surface deposit for the period January 1962 – April 1986 was 3782.8 Bqm^{-2} and 439.4 Bqm^{-2} for the post-Chernobyl period, i.e. from May 1986 to December 2004.

It should be noted that ^{90}Sr fallout peak, attributed to Chernobyl accident in Croatia decreased very rapidly, as in August 1986 was recorded only 1.81 Bqm^{-2} and 0.13 Bqm^{-2} in November.

Regarding the ^{90}Sr activity concentrations if air, the highest value for the overall observed period was recorded in the first quarter of 1987, being 44.6 mBqm^{-3}. The minimal value of 0.15 μBqm^{-3} was recorded in 2004.

It should be noted that in late 1990s and afterwards, ^{90}Sr activity concentrations approached very low values, being essentially background variations. Therefore, transient increases and decreases in activity concentrations can be partially explained by a variety of environmental physical factors that naturally fluctuate.

^{90}Sr activity concentrations in air and fallout are shown on figure 4.

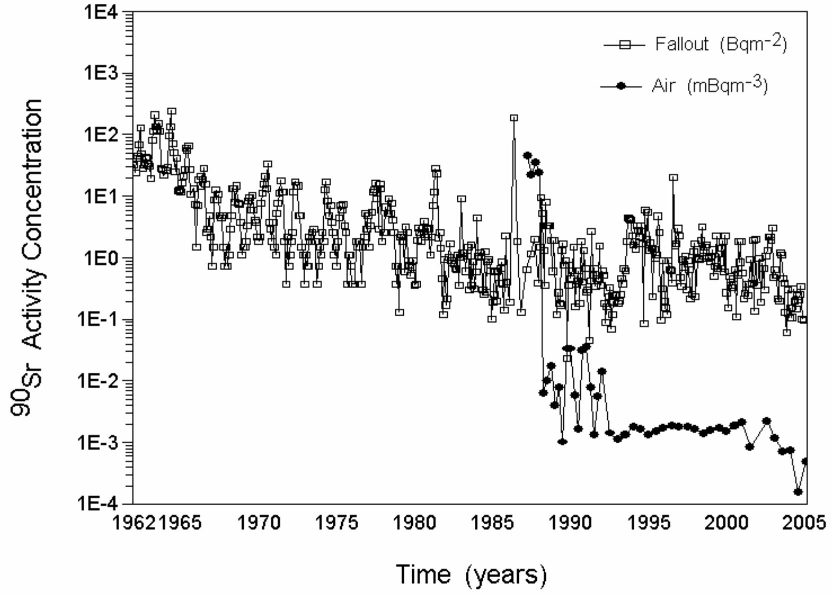

Fig 4. ^{90}Sr activity concentrations in air and fallout

Dosimetry of ^{90}Sr and ^{137}Cs

Data on activity concentrations of ^{90}Sr and ^{137}Cs in air allow for the estimate of the doses incurred by inhaling the polluted air. Dose conversion factors, i.e. effective dose per unit intake via inhalation for the member of public older than 17 years and moderate absorption, are 3.6×10^{-8} and 9.7×10^{-9} SvBq^{-1} respectively (IAEA, 1996). As the ratio of dose conversion factors for ^{90}Sr and ^{137}Cs is ≈3.7, it implies that inhaling ^{90}Sr contributes 3.7 times more to the dose, compared with inhaling the same activity concentration of ^{137}Cs.

The data on volume of breathed air have been taken from the International Commission on Radiological Protection (ICRP) publication 23 (1974). The ICRP reference man breathes 7.5 Lmin^{-1} during rest and 20 Lmin^{-1} during light activity (ICRP, 1974). As the daily activities include approximately 8 h resting and 16 h of light activities, the total daily volume of breathed air is 22,800 L.

Therefore, the annual effective dose in year 1987, incurred by inhaling ^{90}Sr from air is 1.2×10^{-5} Sv and 3.1×10^{-9} Sv in year 1988, decreasing to only 9.2×10^{-11} Sv in year 2004. Regarding ^{137}Cs, similar analysis yields to 1.7×10^{-4} Sv in 1986, 8.23×10^{-8} Sv in 1987, 1.1×10^{-8} in 1988, decreasing to only 7.4×10^{-10} Sv in 2004.

As the doses incurred by ^{90}Sr and ^{137}Cs by inhaling the polluted air after the Chernobyl accident are very small, it can be argued that air was not the critical pathway for human intake of ^{90}Sr and ^{137}Cs from the environment.

Mean residence time of ^{90}Sr and ^{137}Cs in air and fallout

Decrease of activity concentrations of radioactive matter either in air or fallout can be described by the exponential function:

$$C_A(t) = C_A(0)\, e^{-kt} \qquad (1)$$

where:

$C_A(t)$ is time-dependant activity concentration of observed radionuclide (^{137}Cs or ^{90}Sr) in fallout or air (Bqm^{-2} for fallout and Bqm^{-3} for air),

$C_A(0)$ initial activity concentration of observed radionuclide in fallout or air (Bqm^{-2} for fallout and Bqm^{-3} for air) and

$1/k=t_o$ observed mean residence time of considered radionuclide in fallout or air (years).

By fitting the experimental data to the curve (1) the observed mean residence time for ^{137}Cs in air, for the immediate post-Chernobyl period, i.e. January 1987 – December 1990 was estimated to be 1.0 years, while the observed mean residence time for ^{137}Cs in fallout was estimated to be 0.9 years. The year 1986 was excluded from the analysis due to direct influence of the plume. For comparison, the observed mean residence time of ^{137}Cs in fallout for the period January 1965 – April 1986 was 3.7 years (Franic 1992).

Regarding ^{90}Sr, the observed mean residence time in air for the period January 1962 – April 1986 was estimated to be 5.95 years (Franic 1994). For the immediate post-Chernobyl period, i.e. May 1986 – December 1990 was estimated to be 1.9 years.

^{137}Cs : ^{90}Sr activity ratio in fallout

In early 1960s radiochemical analysis of most environmental samples studied in the investigations of the consequences of nuclear fallout yielded ^{137}Cs : ^{90}Sr activity ratios generally ranging between values 1 and 3 (UNSCEAR 1964). Since both of these radionuclides have inert gaseous precursors in their fission chains, and generally similar chemical characteristics, substantial fractionation from the time of their creation in the nuclear explosion is considered to be unlikely. Therefore, in 1960s the major part of the variation in observed ^{137}Cs : ^{90}Sr activity ratios in environmental samples reflect errors in analyses.

For the pre-Chernobyl period, ^{137}Cs : ^{90}Sr activity ratio in fallout samples collected in Zagreb was 1.27 ± 1.38. Interestingly, ^{137}Cs : ^{90}Sr activity ratio in Adriatic sea water was a little bit higher and far more constant, being 1.52 ± 0.40 (Franic and Bauman, 1993).

The Chernobyl nuclear accident has altered this ratio by several orders of magnitude. In 1986 this ratio in Zagreb fallout was 32 in May and 162 in November, increasing ever since April 1987, when it started to decrease. In 1990, it again reached pre-Chernobyl values being 1.51.

4. CONCLUSIONS

The main sources of radioactive matter in the Zagreb air are still the atmospheric tests of nuclear weapons conducted in the 1960s. Activity concentrations for ^{137}Cs and ^{90}Sr in radioactive fallout are exponentially decreasing. ^{137}Cs activity concentrations in fallout are decreasing with different rates for the pre-Chernobyl and post-Chernobyl period, the observed mean residence times in fallout being 3.7 and 0.9 years for the respective periods. The observed mean residence time for ^{137}Cs in air for post-Chernobyl period is approximately 1 year.

The mean residence time of ^{90}Sr in fallout is estimated to be 5.95 years for 1962 – April 1986 period. After the Chernobyl accident, which caused major increase of ^{90}Sr activity concentration in fallout only in May 1986, its activity concentrations soon reached pre-Chernobyl values, nowadays being only background variations.

The doses incurred by ^{90}Sr and ^{137}Cs by inhaling the polluted air after the Chernobyl accident are very small, and it can be argued that air was not the critical pathway for human intake of ^{90}Sr and ^{137}Cs from the environment.

REFERENCES

Bauman, A., Cesar, D., Franic, Z., Kovac, J., Lokobauer, N., Marovic G., Maracic, M., Novakovic, M., 1979 – 1992. Results of environmental radioactivity measurements in the Republic of Croatia, Annual Reports 1978 - 1991. (In Croatian). Institute for Medical Research and Occupational Health, Zagreb, Croatia.

Franic Z., 1992. ^{137}Cs in a Radioactive Fallout in Zagreb. *Croatian Meteorological* Journal 27, 63-68.

Franic Z. and Bauman A., 1993. Radioactive contamination of the Adriatic Sea by ^{90}Sr and ^{137}Cs. Health Phys. 64(2):162-169.

Franic Z., 1994. Distribution Analysis and Mean Residence Time of ^{90}Sr in Wet Fallout in Zagreb. *Croatian Meteorological* Journal 29,25-30.

International Atomic Energy Agency (IAEA), 1996. International Basic Safety Standards for Protection against Ionizing Radiation and for Safety of Radiation Sources. Safety Series No. 115, IAEA, Vienna.

Kovac, J., Cesar, D., Franic, Z., Lokobauer, N., Marovic, G., Maracic. M., 1993 – 1998. Results of environmental radioactivity measurements in the Republic of Croatia', Annual Reports 1992 - 1997. (In Croatian). Institute for Medical Research and Occupational Health, Zagreb, Croatia.

Marovic, G., Franic, Z., Kovac, J., Lokobauer, N., Maracic, M., 1999 – 2002. Results of environmental radioactivity measurements in the Republic of Croatia, Annual Reports 1998 - 2001. (In Croatian). Institute for Medical Research and Occupational Health, Zagreb, Croatia.

Popovic, V. (ed.), 1966-1978. Environmental radioactivity in Yugoslavia, Annual Reports 1965 - 1977. (In Croatian). Federal Committee for Labour, Health and Social Welfare, Belgrade, Yugoslavia.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1964. 19th Session of General Assembly, Rep. A/5814, Annex A:24, United Nations, New York.

United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), 1982. Ionizing Radiation: Sources and Biological Effects, United Nations, New York.

Papastefanou C, Ioannidou A, Stoulos S, Manolopoulou M., 1995. Atmospheric deposition of cosmogenic ^{7}Be and ^{137}Cs from fallout of the Chernobyl accident. Sci Total Environ. 170(1-2):151-156.

International Commission on Radiological Protection (ICRP), 1974. Report of the Task Group on Reference Man. Pergamon Press, Oxford, New York, Toronto, Sydney, Braunschweig.

FLUORO-EDENITE: A NEW AMPHHIBOLE FIBER

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ABSTRACT

Protection of People's health and of environment represent a first line commitment of all Institutions and of each citizen. In Italian public health programs a particular attention has been given to sanitation of common and work environments where asbestos is present, being associated health hazard long been proven. A specific "Protection plan from asbestos" has been designed; it includes interventions aimed at knowing exactly places where such material is present, in order to promote necessary interventions for its removal or making it safe. By doing so, one could remove health hazards linked to inhaling fibres made free in the environment by asbestos when it is present in the friable form.

In a recent epidemiological study, investigating mortalities from malignant pleural neoplasm in Italy, a significant increase of mortality from pleural mesothelioma was observed in the town of Biancavilla, located at the slopes of Etna volcano, if compared with expected figures derived from Regional Sicilian rates. An environmental survey suggested the stone quarries located in "Monte Calvario", as a possible source of asbestiform fibre exposure. A detailed crystal-chemical analysis of amphiboles contained in this material allowed the discovery and the identification of a new fiber that was named fluoro-edenite.

In our Laboratories daily we analysed environmental samples looking for asbestos fibres both in solid and dispersed form, using MOCF and analytic SEM.

During some survey carried out during modernization of the railway line F.C.E. Paternò-Adrano, in Biancavilla, we found numerous fibers of this mineral in the various monitored areas.

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CHARACTERIZATION OF ORGANICS HAZARDOUS AIR POLLUTANTS IN AN INDUSTRIAL CITY IN TAIWAN

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ABSTRACT

Hazardous air pollutants (HAPs) have been evaluated for their health and environmental significance on a targeted in Taiwan until recently. Taiwan Environmental Protection Administration (TEPA) have numerous control strategies aimed at controlling HAPs emissions with the focus largely on volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and selected heavy metals, with some limited work on exposure assessment. This study selected volatile organic compounds (VOCs) as target pollutants to characterize speciation in Kaohsiung, the largest industrial city in Taiwan. Two hours-averaged concentration of airborne volatile organic compounds (VOCs) was conducted by canister during rush hour (7-9 am) and non-rush hour (2-4 pm). The samples were analyzed by GC/MS. Field sampling works were conducted at a traffic station (Chian-kin) and an industrial station (Lin-yuan) during ozone episode days (October, 2003) and non-episode days (July, 2003), respectively. The finding shows that the mean concentrations for VOC in traffic monitoring stations in the ambient air for rush hours (07:00-09:00) ranged from 173.7-403.9µg/m^3. For non-rush hour (14:00-16:00), VOC levels were found in range 32.1-97.6µg/m^3. In industrial stations, VOC concentrations in the ambient air for rush hours ranged from 37.6-360.9µg/m^3. For non-rush hour, VOC levels were found in range 10.7-189.1µg/m^3. Airborne VOCs concentration at the traffic station is higher than those at industrial station regardless of rush hour or nighttime.

The results show that mobile source is the dominant impact source of airborne volatile organics at streetside station in Kaohsiung. The speciation of airborne volatile organics result indicated that the dominant volatile organics species included benzene, toluene, ethylbenzene, m,p-xylene, styrene, and o-xylene in both stations. The species mean concentrations at a traffic station during ozone non-episode days were toluene(7.1µg/m^3), o-xylene(3.8µg/m^3), benzene (2.6µg/m^3), m,p-xylene(2.1µg/m^3), styrene(1.6µg/m^3), and ethylbenzene (0.9µg/m^3). At an industrial station, the mean concentration results were toluene(3.7µg/m^3), o-xylene(2.0µg/m^3), benzene (1.2µg/m^3), m,p-xylene(1.0µg/m^3) , and ethylbenzene(0.2µg/m^3) during ozone non-episode days. The results in ozone episode days at a traffic station were toluene(144.5μg/m^3), ethylbenzene(27.1μg/m^3), m,p-xylene(13.6μg/m^3), o-xylene(12.4μg/m^3), styrene (3.4μg/m^3), and benzene(1.6μg/m^3). The industrial station results of ozone episode days were toluene(188.3μg/m^3), ethylbenzene (15.4μg/m^3), o-xylene(6.8μg/m^3), m,p-xylene(6.6μg/m^3), styrene (6.1μg/m^3) ,and benzene (5.1μg/m^3).

Key words: hazardous air pollutants, volatile organic compounds, ozone episode/non-episode day, and industrial city

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CORRELATION BETWEEN METALLIC AND ACIDIC COMPONENTS IN DEPOSITED MATTER

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ABSTRACT

The paper presents the results of the monitoring of acidic components (fluoride, chloride, nitrate, sulphate) and heavy metals (lead, cadmium, thallium) in total deposited matter at three measuring sites in Šibenik and one site in an unpolluted area. Research was carried out during six years (1999-2004). Samples of the deposited matter were collected by the Bergerhoff method. Total deposited matter was determined gravimetrically. Acidic anions were analysed using ion chromatography. Metallic components were determined by atomic absorption spectrometry. The correlation between measured pollutants varied and it depended on the measuring site and investigated pollutants.

Key Words: Heavy metals, fluoride, chloride, nitrate, sulphate

1. INTRODUCTION

Deposited matter are solid or liquid particulates in the atmosphere in excess of 10-20 μm in diameter (Noller, 1981), which settle on the ground and contaminate soil, plants and materials, but do not affect people and animals directly. Climatic conditions are important in determining the effects of deposited particulate emissions on plants, water and animals. Light rains may cause particle deposition from the atmosphere on vegetation, whereas heavy rains may partially wash off dusts from vegetation to soil. In arid regions, the dusts may accumulate on vegetation and be ingested by grazing animals. It is very important to know the quantity of deposition, especially the content of toxic substances such as acidifying ions and heavy metals, lead, cadmium and thallium.

2. MATERIALS AND METHODS

In the period 1999 to 2004, monthly samples of atmospheric depositions were collected using the Bergerhoff-type deposit gauge (VDI, 1972) at three sampling sites in Šibenik (A,B,C) and at a site in an unpolluted area (K) of the island of Žakan in Kornati National Park (Figure 1). Measuring sites were selected at a distance from emission sources (such as aluminium plant destroyed during the war in 1991, and a plant for electrode and ferroalloy production which stopped operating under decision of the Croatian Government), population density and meteorological parameters.

Figure 1 – The position measurement sites

The total deposition was determined gravimetrically. Samples were analysed for acidifying ions (fluoride, chloride, nitrate and sulphate) using an ion chromatograph (Dionex DX-120) and for heavy metals (lead, cadmium and thallium) using a flame atomic absorption spectrometer (SOLAAR 969 AAS).

3. RESULTS AND DISCUSSION

Air quality in Croatia is currently assessed by comparing annual mean values with recommended (RV) and limit (LV) values stipulated by the Law on Air Quality Protection in Croatia and the Ordinance on Recommended and Limit Air Quality Values (Ordinance, 1996). The Law on Air Quality (Law, 1995) in Croatia should be in accordance with EU laws.

Overall monthly values of total deposited matter ranged from 8 to 511 mg/(m^2d) during the entire measuring period and at all sampling sites. Annual values are shown in Figure 2. They were below the recommended value 200 mg/(m^2d) according to the Law on Air Quality Protection in Croatia and the Ordinance on Recommended and Limit Air Quality Values.

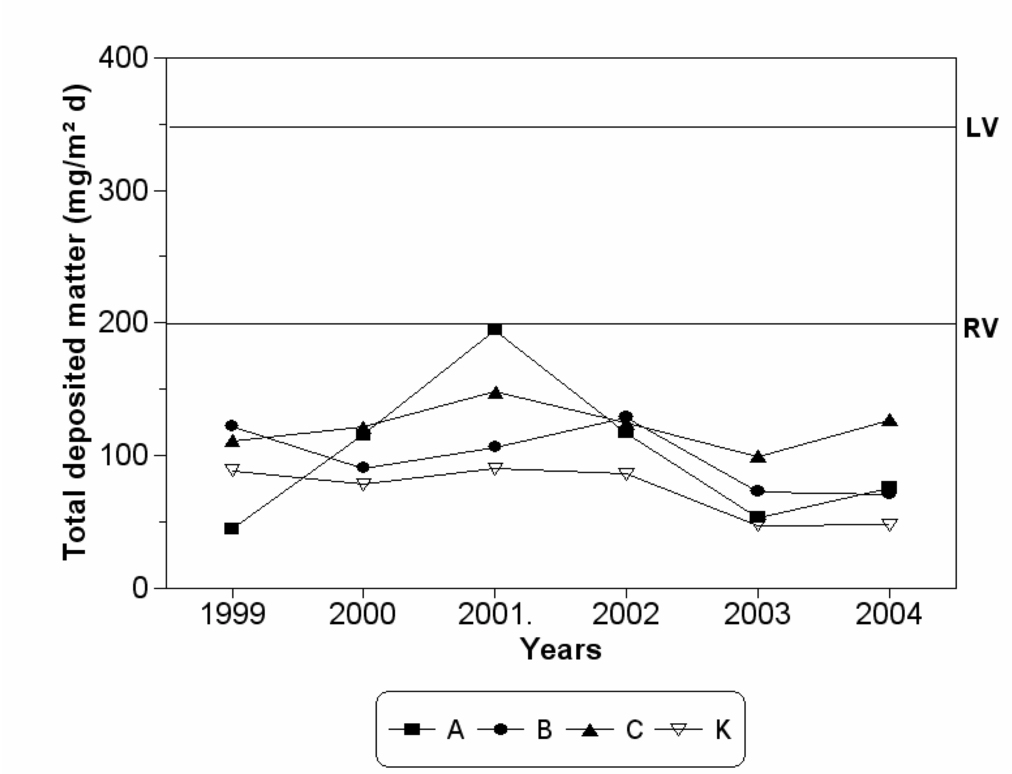

Figure 2 - Annual values of total deposited matter in Šibenik from 1999 to 2004

Monthly lead content in total deposited matter ranged from 0 to 215 μg/(m^2d). Annual values are shown in Figure 3. All results were below the recommended value 100 μg/(m^2d).

Overall monthly cadmium content in total deposited matter for the same period ranged from 0 to 2.11 μg/(m^2d). Annual values are shown in Figure 4 and they were below the recommended value 2 μg/(m^2d).

Overall monthly thallium content in total deposited matter ranged from 0 to 14.77 μg/(m^2d). Annual values are shown in Figure 5, and until 2001 they were below the recommended value 2 μg(m^2d) at three measuring sites (A, B, K). During 2001, the annual mean concentrations of thallium were above recommended value, but below limit value (10 μg/m^2d) at all measuring sites. In 1999 and 2000 at the measuring site C, and in 2002 at the measuring sites A and B the annual mean concentrations of thallium exceeded recommended value (Figure 5). Figure 5 clearly shows that concentrations of thallium decrease during 2003 and 2004.

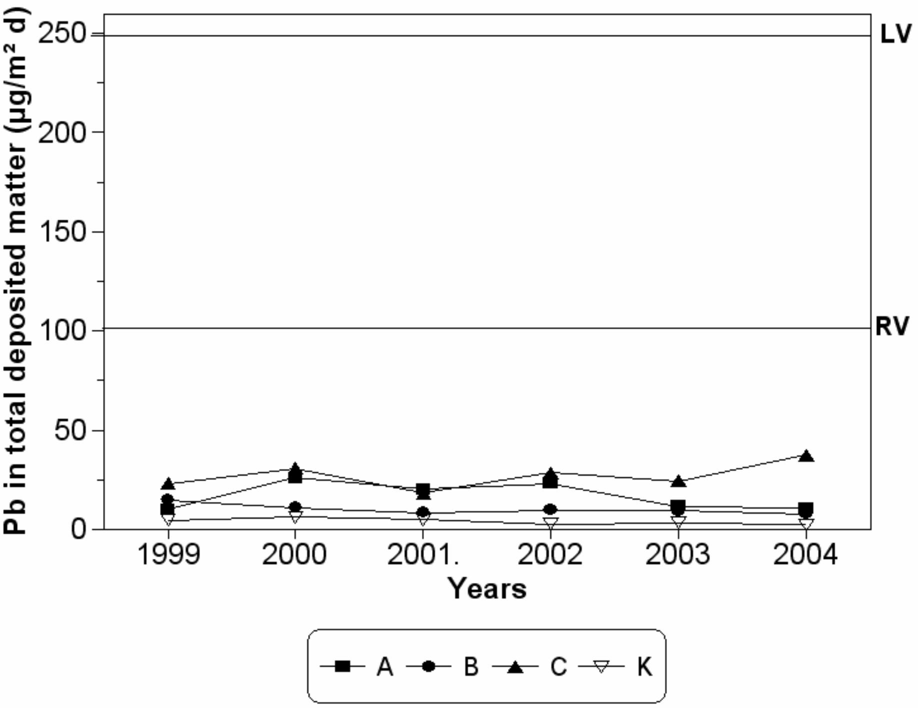

Figure 3 - Annual values of lead in total deposited matter in Šibenik from 1999 to 2004

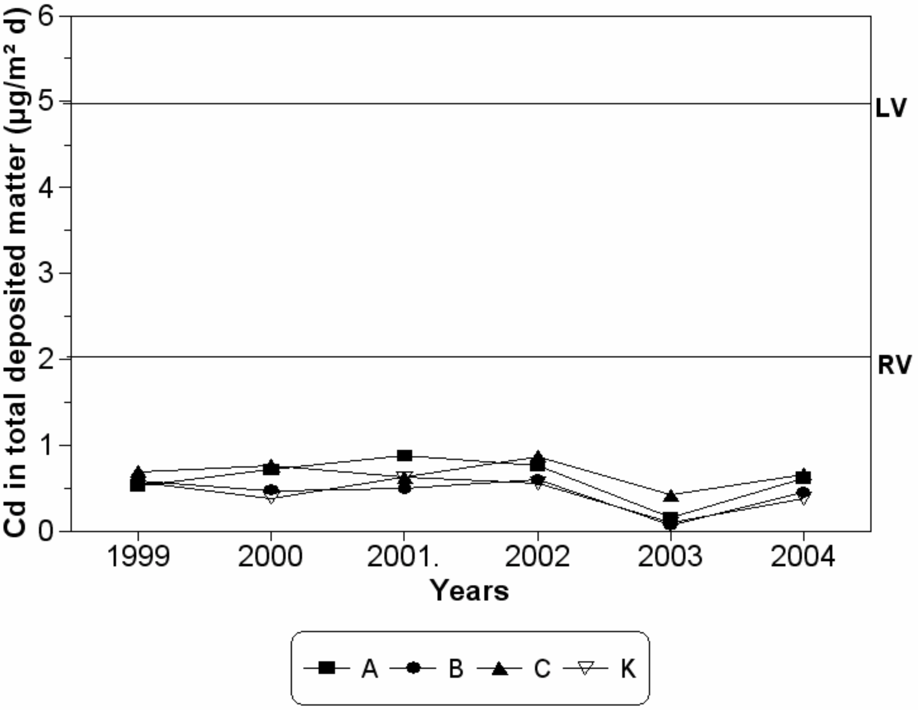

Figure 4 - Annual values of cadmium in total deposited matter in Šibenik from 1999 to 2004

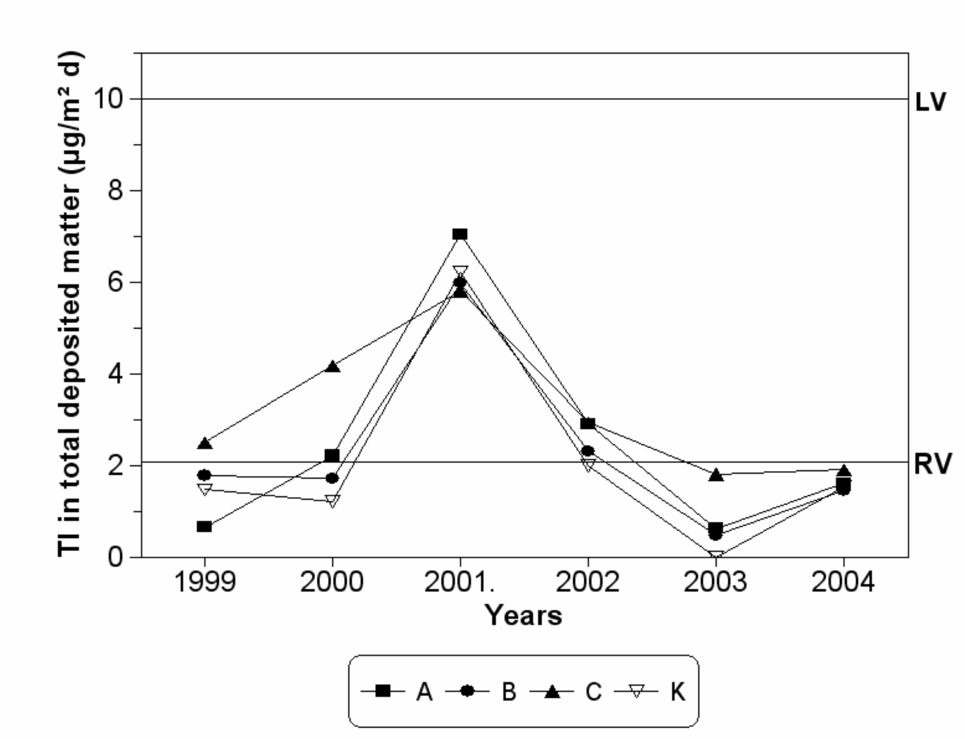

Figure 5 - Annual values of thallium in total deposited matter in Šibenik from 1999 to 2004

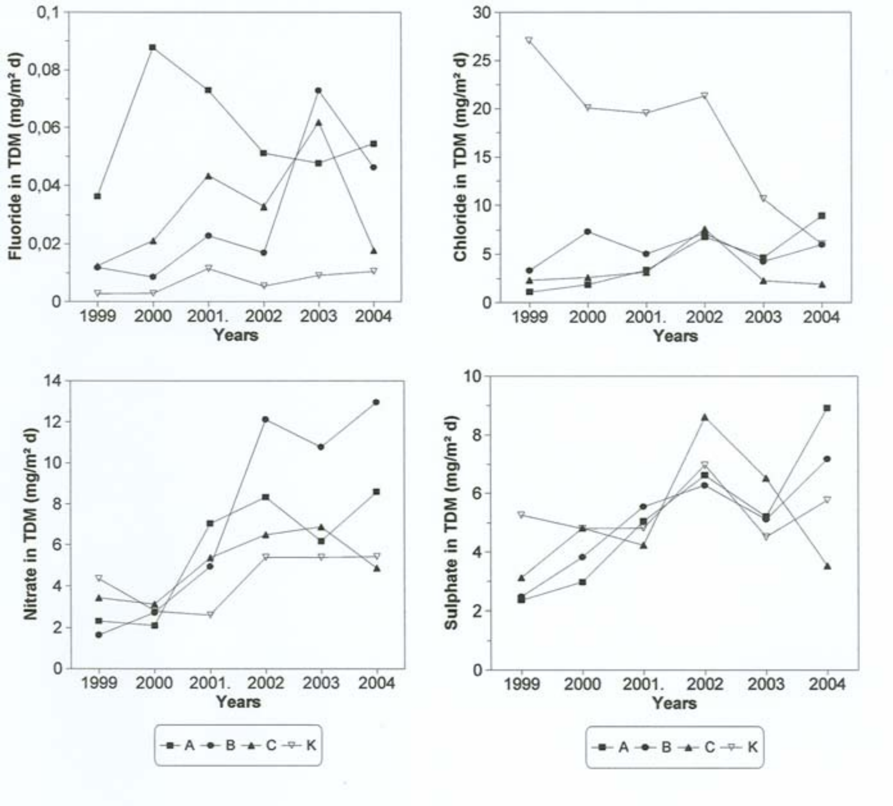

Figure 6 - Annual values of fluorides, chlorides, nitrates and sulphates in total deposited matter in Šibenik from 1999 to 2004

Overall monthly fluorides in total deposited matter ranged from 0 to 0.18 mg/(m^{2}d), chlorides from 0 to 85.56 mg/(m^{2}d), nitrates from 0 to 74.29 mg/(m^{2}d) and sulphates from 0 to 24.13 mg/(m^{2}d). Annual values for acidifying ions are shown in Figure 6. It should be noted that the Croatian Ordinance does not define recommended or limit values for acidifying ions.

The correlation coefficients between acidifying ions and heavy metals for the entire measurement period are presented in Table 1.

Table 1 – Significant correlation coefficients between acidic components and heavy metals in total deposited matter

Measuring site	Correlated components	F^-	Cl^-	NO^{3-}	SO_4^{2-}
A N=54	Pb	0.558**	0.111	0.465**	0.132
	Cd	0.297*	0.133	0.284*	0.303*
	Tl	0.338**	0.057	0.351**	0.102
B N=67	Pb	0.359**	0.374**	0.110	0.306**
	Cd	0.066	0.710**	0.121	0.424**
	Tl	0.059	0.126	0.007	0.123
C N=64	Pb	0.025	0.226	0.203	0.144
	Cd	0.114	0.132	0.234*	0.031
	Tl	0.074	0.201	0.332**	0.243*
K N=57	Pb	0.033	0.104	0.297*	0.188
	Cd	0.238*	0.155	0.018	0.032
	Tl	0.026	0.015	0.115	0.022

* - $P<0.05$ ** - $P<0.01$ N – number of samples

Before the war in Croatia in 1991, the air pollution in the Šibenik area resulted mostly from fluoride emissions from the light-metal factory and the measuring site A was chosen in this part of the town. At the same measuring site a significant correlation ($P <0.01$; $P<0.05$) was found between fluorides and lead, cadmium and thallium. Correlation between lead, cadmium and thallium with chlorides, and lead and thallium with sulphates was not significant. At the measuring site B (long distance from the light-metal factory) a significant correlation ($P<0.01$) was found between lead with fluorides, chlorides and sulphates and between cadmium with chlorides and sulphates. At the measuring site C (city centre) a significant correlation was found between cadmium and nitrates ($P<0.05$), and thallium with nitrates ($P<0.01$) and sulphates ($P<0.05$). At the measuring site K (the island of Žakan) a significant correlation was found only between lead and nitrates and cadmium and fluorides ($P<0.05$).

The correlation between measured pollutants varied and it depended on the measuring site and investigated pollutants. Significant higher correlations indicated that the pollutants might originate from the same source. No significant correlation may indicate that other components were involved in the deposition, such as sodium, potassium, calcium, ammonia etc., which can react with measured metals and acidic components.

4. CONCLUSION

During the six-year period of measurement, the total deposited matter at all measuring sites was relatively low and below the recommended value (200 mg/m^{2}d). Acidifying ions (fluorides, chlorides, nitrates, sulphates) were relatively high (Hršak, 2003), but for them no recommended or limit values are set by the Croatian Ordinance.

Over the six-year measuring period, lead and cadmium content in total deposited matter was found to be low and below the recommended value (100 µg/m^{2}d for lead and 2 µg/m^{2}d for cadmium) at all sampling sites.

Thallium content in total deposited matter was below the recommended value (2 µg/m^{2}d) until 2001 at all measuring sites, except at measuring site C where it was above the recommended value in the years 1999 and 2000. During 2001, thallium content in total deposited matter exceeded the recommended value at all measuring sites, and in 2002 it remained above the recommended value at the measuring sites A and B. Finally, during 2003 and 2004, thallium content dropped below the recommended value at all measuring sites.

The correlation between measured pollutants varied and it depended on measuring site and investigated pollutants. Significant higher correlations indicated that the pollutants might originate from the same source. No significant correlation may indicate that other components were involved in the deposition, such as sodium, potassium, calcium, ammonia etc., which can react with measured metals and acidic components.

REFERENCES

Hršak, J., Čačković, M., Kalinić, N., Balagović, I., 2003. Deposition of acidic components and heavy metals in Zagreb in 1999-2001. Proceedings of the 14th International Conference "Air Quality – Assessment and Policy at Local, Regional and Global Scales", Dubrovnik, Croatia, 361-367.
Law on Air Quality Protection in Croatia, 1995. Official Gazette No. 48, 1452 (in Croatian).
Noller BN, Bloom H, and Arnold AP.1981, Technical report No. 3: Review of Data on Heavy Metals in Ambient Air in Australia.
Ordinance on Recommended and Limit Air Quality Values, 1996. Official Gazette No. 101, 4198-4200 (in Croatian).
VDI Richtlinie 2119 Blatt 2, VDI-Handbuch Reinhaltung die Luft, 1972, 1-4.

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EMISSION CHARACTERISTICS OF PCDDs/DFs, DLPCBs AND PAHs FROM DIFFERENT FUELED VEHICLES WITH VARIABLE SPEEDS

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ABSTRACT

Emission characteristics of polychlorinated dibenzo-*para*(*p*)-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) from different fueled vehicles were studied with variable speeds. The speed of vehicle is changed from 30 km/hr, 60 km/hr and 80 km/hr at constant load rate. Concentration and phase distribution of PCDD/DFs, DLPCB and PAHs with the isokinetic sampling of exhaust gas is obtained in this study. The averages WHO-TEQ concentrations of exhaust gas from LPG, gasoline and diesel fueled vehicles are 9.89, 3.27 and 1.86 pg-TEQ/Nm3, respectively. PAHs concentrations of exhaust gas from LPG, gasoline and diesel fueled vehicles are 1.47, 669.33 and 2417.74 μg/Nm^3, respectively.

PCDD/DFs, DLPCB and PAHs among the exhaust gas emitted from automobiles are examined by the cluster analysis and the result confirms that gasoline and LPG fueled vehicles of spark ignition engine and diesel fueled vehicle of compression ignition engine form a separate cluster respectively. Also confirmed that PAHs have counter-correlations with PCDDs/DFs, DLPCBs and PAHs in their generation.

Key Words: Diesel, LPG, Gasoline, PCDD/DFs, DLPCBs, PAHs, Exhaust gas

INTRODUCTION

Persistent organic pollutants (POPs) with such characteristics as toxicity, bioaccumulation, persistency and long-range transfer are noted as critical environmental pollutants that have toxic effects on the carcinogenesis, decrease the reproduction and the growth rate, and corrupt the immunity system (UNEP, 2001; Govers et al. 1998).

Ballschmiter(1986) measured PCDD/DFs from the automobile exhaust gas and pointed out them as emission sources. Since then, for the last 10 years, not a few studies in relation to automobiles have been reported (Marklund et al., 1990; Oehme et al., 1991; Geueke et al., 1999; Miyabara et al., 1999; Takasuga et al., 1999; Ryan and Gullet, 2000). Most research related to motor vehicles has been conducted with much attention to diesel and leaded gasoline fueled vehicles and considerable data deviation is concidered due to the differences in experimental conditions such as sampling methods, etc. (Schwind et al., 1991).

Therefore, this study invented a new device, based on US EPA method 5 using a stack sampler, for the sampling of PCDD/DFs, DLPCBs and PAHs among the automobile exhaust gas and made the isokinetic sampling possible in order to take representative samples on speed changes and effects of the turbulent current of exhaust gas. Also, measures and analyses are carried out to grasp emission characteristics of gaseous and particulate phase PCDD/DFs, DLPCBs and PAHs emitted from automobiles of different fuels and velocities.

METERIAL AND METHOD

Sampling

Samples of PCDD/DFs, DLPCBs and PAHs were collected difference condition by fuels (LPG, gasoline, diesel) and speeds (30 km/hr, 60 km/hr, 80 km/hr) of vehicles. Experiments are carried out for 1997 year-type gasoline fueled vehicle (77,951 km mileage) with 1,323 cc engine displacement, 70 ps/3500 rpm maximum power and 12.0 kg·m/3,000rpm maximum torque, 2000 year-type LPG fueled car (64, 351 km mileage) with 1,997 cc engine displacement, 115 ps/5000 rpm maximum power and 18.1 kg·m/4500 rpm maximum torque, and 2002 year-type diesel fueled vehicle (52, 310 km mileage) with 2,874 cc engine displacement, 95 ps/4000 rpm maximum power and 19.6 kg·m/2800rpm maximum torque, with cars fixed to chassis dynamometers.

Sampling apparatus was divided into filter part that sampling particulate phase, absorber I that sampling gaseous phase, XAD resin and absorber II. Before taking samples, cleanup standards (EPA-1613 CSS, Wellington Laboratories, Canada; 68A-CS, Wellington Laboratories, Canada) are spiked on XAD resin. After samplings are classified into gaseous and particulate phase, extraction and analyses are performed. Sampling apparatus is shown in Figure 1.

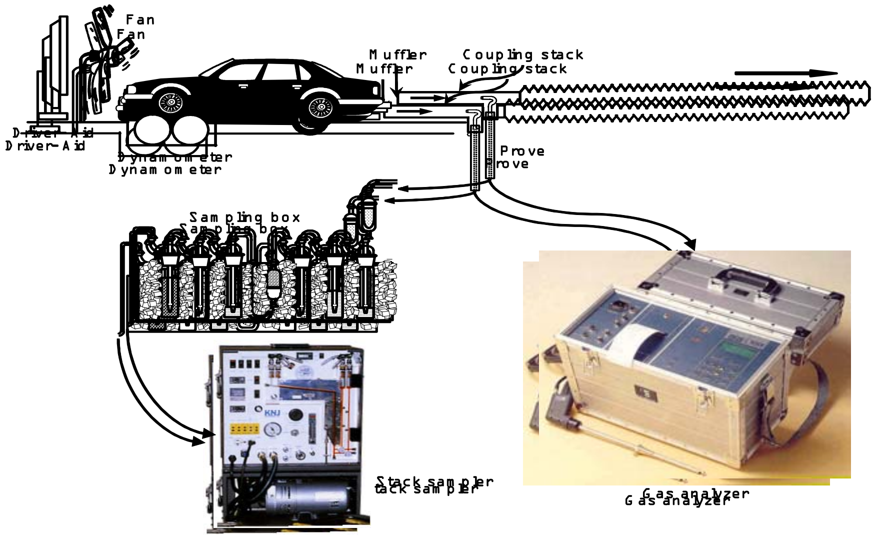

Fig. 1. Schematic diagram of sampling for differently fueled vehicle.

Extraction and analyses

Particulate and gaseous phase of exhaust gas from vehicles were extracted with 350 ml of toluene for 16 h under soxhlet. After extraction, extracts were concentrated to 10 mL in a rotary evaporator. And than, samples were divided 9 mL and 1 mL for Dioxin-like compound and PAHs, respectively.

Reduced extracts were added to 0.5 mL of n-nonane as a keeping solvent and concentrated to <0.3 mL under a gentle purging of nitrogen gas. Solutions were transferred to 10 mL of n-hexane, ensuring the complete removal of toluene, and internal standard solutions of 15 $^{13}C_{12}$-labeled PCDDs/DFs (EPA-1613LCS, Wellington Laboratories, Canada) and 27 labeled DLPCBs (68A-LCS, Wellington Laboratories, Canada) were spiked. Solutions were pre-cleaned up with a multi-layer silica gel column chromatography and cleaned up with an activated alumina column chromatography (Ok et al., 2002).

Samples analyses were carried out using an high resolution gas chromatography (HP-6890, Hewlett Packard, USA) coupled to a high resolution mass spectroscopy (JMS 700D, Jeol, Japan) at a resolution of 10,000 (10% valley) under selected ion monitoring (SIM) mode, and a SP-2331 (60 m length, 0.25 mm inner diameter, 0.25 μm film thickness, Supelco, USA) and a HP-5MS (30 m length, 0.25 mm inner diameter, 0.25 μm film thickness, J&W Scientific, USA) were used for the separation and detection of PCDDs/DFs compounds. For the separation and quantification of DLPCBs, HRGC/HRMS (HP 6890 GC/JMS 700D MS) was operated at a resolution of 10,000. The capillary column used for DLPCBs separation was HT-8 (50 m length, 0.22 mm inner diameter, 0.25 μm film thickness, SGE, Australia) (Ok et al., 2002).

1mL of divided each samples for PAH were transferred to n-hexane and an internal standard labeled standard (ES 4087, CIL, USA) were spiked. The extracted samples were purified using activated silicagel (70-230 mesh, Neutral, Merck) column(300 mm length and 15 mm inner diameter) chromatography with successive elutants of *n*-hexane and 10% methylene dichloride (Pesticide residue analysis, Cica-Merck, Japan) in *n*-hexane. The PAHs fraction was analyzed by gas chromatography (QC 2010, Simadzu, Japan) coupled to mass spectrometry (QP 2010, Simadzu, Japan) (Ok et al., 2002; Kim et al., 2001a; 2001b; 2003a; 2003b).

RESULTS AND DISCUSSION

PCDDs/DFs and DLPCBs

Concentration of gaseous and particulate phase in the automobile exhaust gas does not concider any constant distribution trait as is shown in Table 1 and Figure 2. In LPG fueled vehicle, gaseous concentration is high and in gasoline fueled car, gaseous and particulate phase are similar in concentration level. But, diesel fueled vehicle, concentration of particulate phase higher than gaseous phase.

For emission concentration based on speed, in cases of LPG and gasoline fueled vehicles of spark ignition engine, the concentration is relatively high at 60 km/hr and in diesel fueled car of compression ignition engine, concentration reaches maximum at 30 km/hr. Especially, when LPG vehicle speed at 60 km/hr, the emission concentration is 10 times higher than those at other speeds.

The examination of PCDD/DFs homologue profile pattern indicates that in all the vehicles, HpCDDs and OCDD among PCDD/DFs are high and in diesel fueled vehicle, generation concentration and ratio of PCDFs homologue groups except TCDFs are very low when emitted.

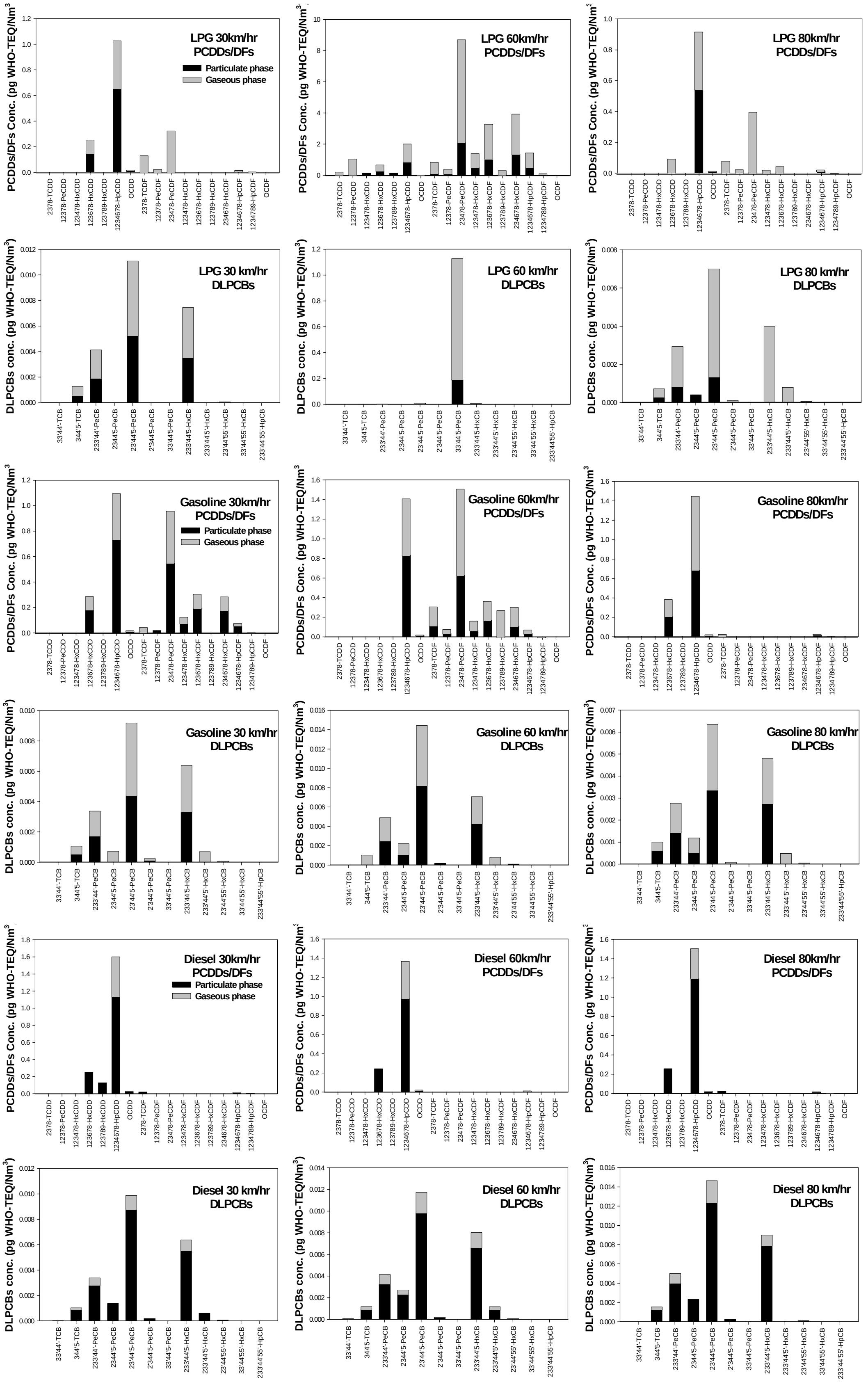

Fig. 2. Concentration of toxic 2,3,7,8 substituted PCDDs/DFs and DLPCBs from different fueled vehicles with variable speeds.

Table 1. Summary of 2,3,7,8-substituted concentration and homologue of PCDDs/DFs and DLPCBs from different fueled vehicles with variable speeds

Fuel type	Speed (km/hr)	WHO-TEQ concentration (pg WHO-TEQ/Nm^3)		PCDDs/DFs Homologue (pg/Nm^3)	
		Gaseous phase	Particulate phase	Gaseous phase	Particulate phase
LPG	30	1.009	0.832	182.605	240.458
	60	18.652	7.446	1,332.154	980.725
	80	1.092	0.575	159.006	193.584
Gasoline	30	1.250	2.019	155.084	306.643
	60	2.566	2.039	293.044	342.461
	80	1.007	0.937	279.879	253.611
Diesel	30	0.448	1.590	320.710	808.092
	60	0.412	1.271	269.431	657.692
	80	0.329	1.543	214.289	818.558

Table 2. Dioxins concentration from vehicle in other studies

Study and year	Concentration (pg I-TEQ/Nm^3)	Fuel type
This study	1.94–4.60†	gasoline(30, 60, 80 km/h)
This study	1.68–2.08†	diesel(30, 60, 80 km/h)
This study	1.66–26.10†	LPG (30, 60, 80 km/h)
CARB (1987)	218	Diesel-truck, 50 km/hr
Hagenmaier et al. (1990)	9.8	Gasoline unleaded-p. car. No cat , FTP 73 test cycle
Hagenmaier et al. (1990)	0.93	Gasoline unleaded-p. car. with cat
Hagenmaier et al. (1990)	141.5	Gasoline leaded –p.car.
Hagenmaier et al. (1990)	1.20	Diesel-p.car
Miyabara et al. (1999)	3.46–5.33 (mean: 4.18)	Gasoline
Miyabara et al. (1999)	7.13–14.0 (mean: 10.57)	Diesel
Chang et al. (2004)	6.27	Diesel, 40 km/hr
Chang et al. (2004)	41.9	Diesel, Idled

† unit: WHO-TEQ/ Nm^3

The result of this study, the average emission concentration of diesel and gasoline fueled vehicles are 1.86 and 3.27 pg WHO-TEQ/Nm^3 respectively. Compared with the emission concentration of leaded gasoline and diesel fueled vehicles from the other studies, as is shown in Table 2, the concentration level is very low.

From these results, it is judged that concentration deviation varies greatly depending on fuels type, age of vehicle and driving conditions.

PAHs

In case of the concentration of PAHs in the automobile exhaust gas, as is shown in Table 3 and Figure 5, gaseous phase concentration is detected more highly than particulate phase concentration in all kinds of vehicles except diesel at 60 km/hr. But, in carcinogenic PAHs (PAHcarc.), particulate phase concentration is higher than gaseous phase concentration. Among them, LPG fueled vehicle indicates four times higher and diesel fueled vehicle 18 times higher results. The reason is that PAHs with medium and high molecular weight take relatively higher ratio in particulate phase PAHs presence.

In gaseous phase, concentration ratio declines with PAHs of higher molecular weight and it increases with PAHs of lower molecular weight. But, in case of diesel, it rises unusually in 3 ring-PAHs. In case of PAHs, the highest concentration is concidered in diesel fueled vehicle at 60 km/hr. High concentration is detected from the relatively old gasoline vehicle.

Emission concentration of PAHs according to the vehicle speed, the concentration of LPG and gasoline vehicles turns up in order of 30 km/hr   60 km/hr   80 km/hr and that of diesel appears in order of 60 km/hr   30 km/hr   80 km/hr.

Table 3. Summary of PAHs and PAHcarc.(μg/Nm^3) concentration in this study

Fuel type	Speed (km/hr)	16PAHs concentration (μg/Nm^3)		PAHcarc. concentration (μg /Nm^3)	
		Gaseous phase	Particulate phase	Gaseous phase	Particulate phase
LPG	30	2.629	0.020	0.020	0.006
	60	0.381	0.748	0.044	0.297
	80	0.577	0.048	0.015	0.029
Gasoline	30	1,059.683	0.236	0.152	0.126
	60	898.992	0.473	0.642	0.162
	80	47.685	0.925	0.663	0.017
Diesel	30	15.369	175.468	0.015	1.284
	60	6,775.919	131.444	0.136	2.470
	80	13.751	141.271	0.171	1.994

Table 4. PAHs concentration from vehicle in other studies

Study and year	Concentration(μg/Nm^3)	Fuel type
This study	47.71–1052.92	gasoline(30, 60, 80 km/h)
This study	155.02–6907.35	diesel(30, 60, 80 km/h)
This study	0.62–2.65	LPG (30, 60, 80 km/h)
Brož et al. (2000)	150–420	leaded gasoline
Mi et al. (1996)	180.4	gasoline
Mi et al. (2000)	318–1,500	diesel(heavy duty diesel): mode 1
Mi et al. (1998)	297	gasoline (fuel additive SA)
Mi et al. (1998)	265	gasoline (fuel additive SB)
Šebor et al. (1994)	46.6	gasoline (Test ECE)
Šebor et al. (1994)	186.0	gasoline (90 km/h)

As is inferred from these results, in gasoline and LPG fueled vehicles, the higher the speed is, the lower the emission concentration becomes. These results are explained as follows. As the temperature of emission gas increases with the speed of vehicle, connecting rings of benzene nucleus involving PAHs are broken into chlorinated compounds and low molecular PAHs. Then, the emission concentration of PAHs declines abruptly (Gullet et al., 2000).

Result of this study, the concentration of PAHs from the diesel fueled vehicle as table 4 is 155.02–6,907.35 μg/Nm^3, higher than 318–1,500 μg/Nm^3 of the other studies level. In case of gasoline, the concentration is higher than the other studies concentration range (46.6–420 μg/Nm^3) (Brož et al., 2000; Mi et al., 1996, 1998, 2000; Šebor et al., 1994). PAHs in the LPG fueled vehicle are 0.62–2.65 μg/Nm^3

indicating very low range of concentration. Therefore, the different concentration levels of PAHs generation are clearly discriminated according to the fuels.

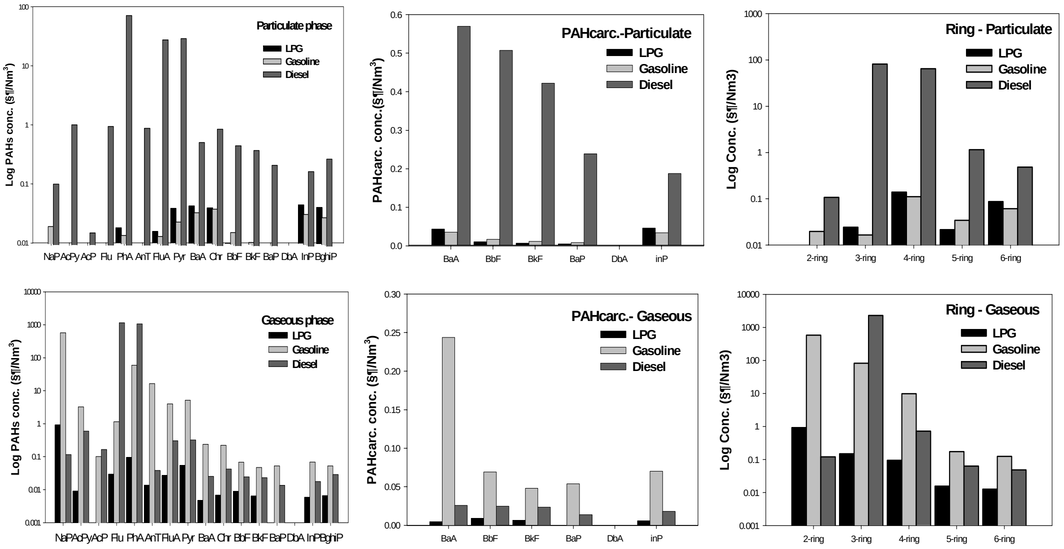

Fig. 3. Distribution of carcinogenic PAHs (upper) and ring-PAHs (under) concentration in differently fueled vehicle experiment.

Data Analyses

PCDDs/DFs, DLPCBs and PAHs among the exhaust gas emitted from automobiles are examined by the cluster analysis and the dendrogram of the analysis is shown in Figure 4. The results from the cluster analysis of PCDDs/DFs, DLPCBs and PAHs are largely grouped into the spark ignition engine of gasoline and diesel, and compression ignition engine of diesel.

But, the result from the cluster analysis of PAHs in the gasoline fueled vehicle shows that the cluster is not dense, unlike the cases of LPG and diesel fueled vehicles, and is dispersed depending on the vehicle speed. Compared to other vehicles, it is considered that the speed of gasoline fueled vehicle affects PAHs emission pattern.

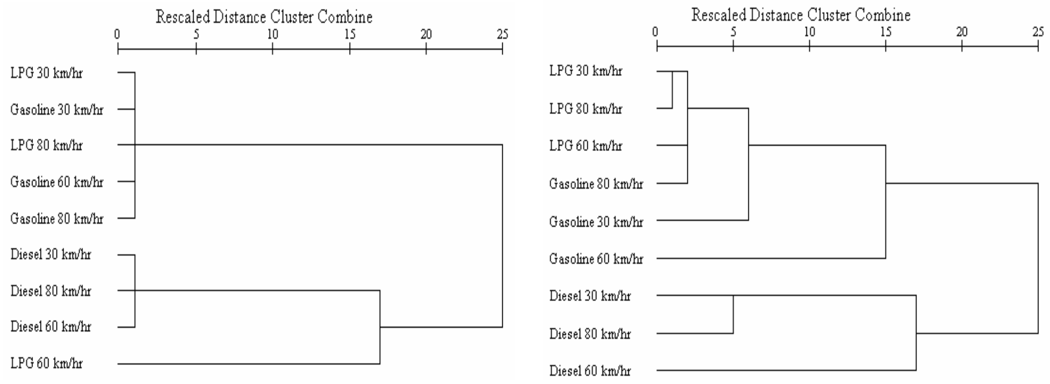

Fig. 4. Dendrogram of PCDDs/DFs, DLPCBs profile (left) and PAHs profile (right) in exhaust gas from different fueled Vehicles with variable speeds.

The correlation between UPOPs generated from the automobile experiment is investigated by the statistical analysis system and the findings show that as a whole, PAHs mostly have counter-correlations with PCDDs/DFs, DLPCBs and PAHs. As a consequence, it is explained that PAHs is affected by several factors such as combustion temperature, combustion state of fuel, excess air, etc. The basic structure of PAHs, the polycycle is separated in the middle process. This function contributes partly to the generation of PCDD/DFs and partly to the additional reaction of cyclic expansion (Gullet et al., 2000).

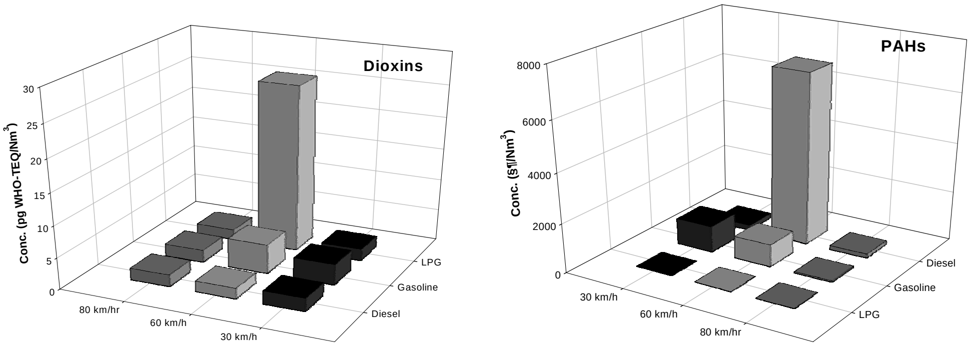

Fig. 5. Distribution of UPOPs (PCDDs/DF and DLPCBs, PAHs, PAHcarc and CBs) concentration in different fueled Vehicles with variable speeds.

CONCLUSION

The results of this study present the following points;

1. For the sampling in this study, coupling stack is air-tightly fixed to the muffler in order to maintain isokinetic sampling and then used for the measures. The ratio of isokinetic factor in the automobile driving experiment shows a range of 95.7–104.7%.
2. Automobile speeds and age of vehicles are proved to be important variables in the generation of PCDDs/DFs, DLPCBs and PAHs.
3. PCDD/DFs, DLPCB and PAHs among the exhaust gas emitted from automobiles are examined by the cluster analysis and the result confirms that gasoline and LPG fueled vehicles of spark ignition engine and diesel fueled vehicle of compression ignition engine form a separate cluster respectively.
4. It is also confirmed that PAHs have counter-correlations with PCDDs/DFs, DLPCBs and PAHs in their generation.

Therefore, in order to illuminate the mechanism of POPs generation in automobiles, experiments should be carried out in a variety of conditions like temperature distribution from the engine to the muffler as well as repeated studies in the same conditions.

REFERENCES

Ballschmiter, K., Buchert, H., Niemczyk, R., Munder, A., Swerev, M., 1986. Automobile exhausts versus municipal-waste incineration as sources of the polychloro-dibenzodioxins (PCDD) and -furans (PCDF) found in the environment. Chemosphere 15, 901-915.

Brož, J., Grabic, R., Kilián, J., Lojkásek, M., Marklund, S., Ocelka, T., Pekárek, V., Přibyl, J., Tydlitát, V., Výška. J., 2000. The effect of oils on PAH, PCDD, PCDF, and PCB emissions from a spark engine fueled with leaded gasoline. Chemosphere 41, 1905-1911.

CARB (State of California Air Resources Board), 1987. Determination of PCDD and PCDF Emissions from Motor Vehicles (Draft report).

Chang, M.B., Chang, S.H., Chen, Y.W., Hsu, H.C., 2004. Dioxin emission factors for automobiles from tunnel air sampling in Northern Taiwan. Sci. of the total environment 325. 129-138.

Geueke, K.J., Gessner, A., Quass, U., Bröker, E., Hiester, E., 1999. PCDD/F emission from heavy duty vehicle diesel engines. Chemosphere 38, 2791–2806.

Govers, H. A., Krop, H.B., 1998. Partition constants of chlorinated dibenxofurans and dibenzo-p-dioxins. Chemosphere 37, 2139-2152.

Gullet, B.K., Touati A., Lee, C.W., 2000. Formation of Chlorinated Dioxins and Furans in a Hazardous-Waste-Firing Industrial Boiler. Environ. Sci. Technol. 34, 2069-2074.

Hagenmaier, H., Dawidowsky, N., Weberru, U., Hutzinger, O., Schwind, K.H., Thoma, H., Essers, U., Biihler, U., Greiner, R., 1990. Emission of polyhalogenated dibenzodioxins and dibenzofurans from combustion engines. Organohalogen Compd. 2, 329-334.

Kim, D.H., Kim, S.J., Kim, Y.K., Kim, S.Y., Ok, S.B., Ok, G., 2001a. Distribution characteristics of PCDDs/DFs and polycyclic aromatic hydrocarbons in soil at Daegu city. J. Korea Society for Environ. Anal. 4, 23-28.

Kim, D.H., Ok, G., Kim, Y.K.,.Kim, S.J., Kim, J.H., Gong, S.H., 2001b. Survey on contamination characteristics of polycyclic aromatic hydrocarbons (PAHs) in soil in Seoul, Korea. Organohalogen compounds 51, 150-153.

Kim, D.H., Hwang, J.S., Lee, M., Ok, G., 2003a. Estimation of polycyclic aromatic hydrocarbons emission from sewage sludge of sewerage treatment plants in Korea. J. Environ. Sciences 12, 1167-1171.

Kim, D.H., Kim, Y.K., Kim, S.J., Ok, G., 2003b. Estimation of PCDDs, PCDFs and PAHs emission from crematories in Korea. Organohalogen compounds 63, 9-12.

Marklund, S., Rappe, C., Tyslind, M., et al., 1987. Identification of polychlorinated dibenzofurans and dioxins in exhaust from cars run on leaded gasoline. Chemosphere 16, 29-36.

Marklund, S., Andersson, R., Tysklind, M., Rappe, C., 1990. Emissions of PCDDs and PCDFs in gasoline and diesel fueled cars. Chemosphere 20, 553–561.

Mi, H.H., Lee, W.J., Wu, T.L., Lin, T.C., Wang, L.C., Chao, H.R., 1996. PAH emission from a gasoline-powered engine. J.Environ. Sci. Health. Part A – Environ. Sci. Eng. 31, 1981-2003.

Mi, H.H., Lee, W.J., Chen, S.J., Lin, T.C., Wu, T.L., Hu, J.C., 1998. Effect of the gasoline additives on PAH emission. Chemosphere 36, 2031-2041.

Mi, H.H., Lee, W.J., Chen, C.B., Yang, H.H., Wu, S.J., 2000. Effect of fuel aromatic content on PAH emission from a heavy-duty diesel engine. Chemosphere 41, 1783-1790.

Miyabara, Y., Hashimoto, S., Sagai, M., Morita, M., 1999. PCDDs and PCDFs in vehicle exhaust particles in Japan. Chemosphere 39, 143–150.

Miyata, H., Aozasa, O., Mase, Y., Ohta, S., Khono, S., Asada, S., 1994. Estimated annual emission of PCDDs, PCDFs and non-ortho chlorine substituted coplanar PCBs from flue gas from urban waste incinerators in Japan. Chemosphere 29, 2097-2105.

Oehme, M., Larssen, S., Brevik, E.M., 1991. Emission factors of PCDD and PCDFs for road vehicle obtained by a tunnel experiment. Chemosphere, 23, 1699-1708.

Ok, G., Ji, S.H., Kim, S.J., Kim, Y.K., Park, J.H., Kim Y.S., Han, Y.H., 2002. Monitoring of air pollution by polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans of pine needles in Korea. Chemosphere 46, 1351-1357.

Ryan, J.V., Gullet, B.K., 2000. On-road emission sampling of a heavy-duty diesel vehicle for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. Environ. Sci. Technol. 34, 4483–4489.

Schwind, K.H., Thoma, H., Hutzinger, O., Dawidowski, N., Weberuss, U., Hagenmaier, H., Buehler, U., Greiner, R., Essers, U., Bessey, E., 1991. Emission halogenierter dibenzodioxine (PXDD) und dibenzofurane (PXDF) aus verbrennungsmotoren. Z. Umweltchem. Ökotox. 3, 291–298.

Šebor, G., Pospišil, M., Maxa, D., Blažek, J., Černy, J., Vaňura, J., 1994. Emissions from combustion of gasolines. Project MŽP ČR No. 1677-94, Czech Republic (in Czech).

Takasuga, T., Baba, F., Kobayashi, T., Sato, M., Kurata, M., Kokado, M., 1999. Investigations regarding separate sampling of PCDD/F in gas and solid phase of incineration flue gas by filtration techniques. Organohalogen Compd. 40, 275.

UNEP, 2001**.** Resolutions adopted by the conference of plenipotentiaries on the stockholm convention on persistent organic pollutants.

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THE ANALYSIS AND CHARACTERIZATION OF POLYCYCLIC AROMATIC HYDROCARBONS (PAHs) IN SELECTED AREAS : KUALA TERENGGANU CASE STUDY IN A STATE OF TERENGGANU, MALAYSIA.

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ABSTRACT.

Analysis and characterization of polycyclic aromatic hydrocarbons (PAHs) were measured at two selected industrial areas and four selected school areas in Kuala Terengganu, Malaysia. Airborne particles were collected using High Volume Air Sampler (HVAS) in school areas and 24 hours in industrial areas respectively. From the analyses, the highest concentration of PAHs on air particle samples obtained in oil palm industry which represent an industrial areas. The value of the concentration is 1342.87 µg/g dry weight. On the other industry area (paddy industry), the concentration value obtained is only 50.86 µg/g dry weight. Meanwhile, the highest concentration of PAHs on air particle samples obtained in representing school areas is in Agama Khairiah school area which is 39603.5 µg/g dry weight. The lowest concentration of PAHs obtained in school areas is in Paya Bunga school area with the value of 2214.719 µg/g dry weight. The results obtained from this study shows that school areas are the most contaminated place with PAHs compounds compared to an industrial areas

Key Words: Polycyclic Aromatic Hydrocarbons (PAHs). Airborne Particles. Naphthalene.

1.0 INTRODUCTION.

In Malaysia, the major sources of air pollution are comes from mobile sources, stationery sources, and open burning sources. For the past five years, emissions from mobile sources (i.e., motor vehicles) have been the major source of air pollution, contributing to at least 70-75% of the total air pollution. Emissions from stationery sources generally have contributed to 20-25% of the air pollution, while open burning and forest fires have contributed approximately 3-5% (DOE, 1996). According to the Department of the Environment (DOE), Malaysia, in 1996, the percentages, of the air emission load by type were motor vehicles, 82%; power stations, 9%; industrial fuel burning, 5%; industrial production processes, 3%;

domestic and commercial furnaces, 0.2%; and open burning at solid waste disposal sites, 0.8% (DOE, 1996).

As a result of rapid population growth, explosive industrialization and few environmental regulations, air or atmosphere pollution play a role in the incidence of respiratory diseases and cancers because a large number of chemical compounds that damage the ambient air quality are formed during incomplete combustion of organic materials. Among the compouns formed are polycyclic aromatic compounds. Polycyclic aromatic hydrocarbons (PAHs) comprise the largest class of chemical compounds known to be cancer-causing agents (Peter, 2002). By definition, PAHs consist solely of carbon and hydrogen (Baek, 1991). PAHs, predominantly the products of incomplete combustion, are ubiquitous in the atmosphere as the result of natural events, such as forest fires, and widespread anthropogenic sources, such as biomass burning (e.g. slash-and-burn agriculture), vehicle traffic, home heating and industrial emissions (Baek *et al*., 1991; Howsam and Jones, 1998). Incomplete combustion of wood and petroleum products is responsible for a large proportion of their formation. In the development of oil palm and paddy industries in Malaysia, PAHs pollution level from this industry emissions were studied. In addition, some sample were collected which situated nearby the road since it is one of the most important sources of PAHs in urban area.

However, the concern and awareness of the sources and effects of PAHs on human health are still very low among the people in Malaysia especially in Kuala Terengganu. Therefore, the objectives of this study were to determine and compare the concentration of total PAHs, and to identify the types and characteristics of PAHs compounds in selected school and industrial areas of Kuala Terengganu. The results from this study provide a baseline reference for a global database as well as for regulatory action to improve air quality in the city of Kuala Terengganu.

2.0 LITERATURE REVIEW

Aromatic hydrocarbons are the molecule that contains one or more benzene compound, which sometimes called as unsaturated cyclic hydrocarbons. Unsaturated hydrocarbons are compounds that have less hydrogen atom attach to the carbon atom (e.g. alkenes and alkynes). Besides, aromatic hydrocarbons also referred as Arene which are derived from benzene, C_6H_6. Benzene (C_6H_6) is the most basic compound of these hydrocarbons. Although benzene is a good solvent in fractionating organic compounds in all kind of media, but the usage of its has been band due to its carcinogenic effect to human. According to Masterton and Hurley (1997), chronic exposure to benzene vapor leads to various blood disorders and, in extreme cases, aplastic anemia and leukemia.

2.1 Polycyclic Aromatic Hydrocarbons (PAHs)

Poly (or polycyclic or polynuclear) aromatic hydrocarbons more simply known as polyarenes, are one of the largest classes of organic molecules found in nature. PAHs are chemical compounds with a similar structure comprising two or more (up to seven) condensed aromatic and other cyclic rings. The simplest form of these chemicals is naphthalane which consist of two fused benzene ring. PAHs are formed naturally in the environment, during such processes as thermal geological reactions and natural fires. Human activities are more significant sources to the environment, as PAHs are formed in all processes involving incomplete combustion of carbon-based fuels, and are therefore emitted during burning of common fuels, such as coal, oil, wood and gas. PAHs concentrations in atmosphere which consist a great level where lower molecular weight forms of PAHs account are greater than 90% of total atmospheric load. The main sources that emit PAHs into the air are from stationary sources and mobile sources. Exposure to PAHs has long been identified as an environmental concern whereby the PAHs were found to exhibit a wide spectrum of acidity as mutagens and carcinogens, which range from inactive to highly potent (Harvey, 1997). Some PAHs are present at ambient temperatures in air, both as gases and associated with particles of their low vapour pressure. PAHs with four or fewer rings usually remain as gases when they are released into the air. Nevertheless, they do undergo degradation by the sequence of free radical reactions after several hours and PAHs with more than four benzene rings do not exists long in the gaseous state.

2.2 Health Effect of PAHs.

The PAHs have high molecular-mass (4 and more condensed aromatic rings) are considered to be more dangerous than two and three rings PAHs in view of their potential (Tuhackova *et al.*, 2001). For the past three decades, PAHs have been of environmental concern due to their toxicity and their ubiquitous in the environment. Men exposed occupationally to high concentrations of PAH mixtures show an increased incidence of tumors of the lung, skin and possibly bladder and other sites. Of these various tumors, lung cancer is the one most obviously linked to exposure to PAHs through inhaled air. Most carcinogenic PAHs occur almost exclusively in the long-lived particulate phase. Irrespective of their physical properties and initial routes of exposure, the tumour-inducing effects of carcinogenic PAHs depend on their conversion in the body into compounds which, unlike the parent substances, are capable of reacting with and damaging the genetic material (DNA) in the nuclei of cells which called as genotoxic carcinogens.

2.3 Mobile Source

Motor vehicle is a significant source of ambient polycyclic aromatic hydrocarbons (PAHs) in urban areas where the emission coming from gasoline and diesel vehicles, as well as from small two-stroke engines such as mopeds and lawn movers. PAHs include a large number of species representing a whole range of boiling points and volatility. Even if these compounds all have boiling points exceeding 200 ºC, they are distributed between the gas and particulate phase in emissions from an internal combustion engine, and the enrichment technique used has to be adjusted accordingly.

3.0 THE COLLECTION OF DATA.

3.1 Location of Sampling

The data were collected at annurban areas of Kuala Terengganu, capital city of Terengganu State, Malaysia. It is located in the east coast of Malaysia (about 500 km north east coast of Kuala Lumpur. Figure 1 shows the site locations of the study. Four sampling locations of school area that chose were based on the sources of PAHs from vehicle traffic which are namely ; 'Sekolah Rendah Chung Hwa Wei Sin' (S1), 'Sekolah Kebangsaan Paya Bunga' (S2), 'Sekolah Menengah Agama Khairiah' (S3) and 'Sekolah Rendah Sultan Sulaiman 1' (S4). In addition, two sampling locations which represented an industrial areas were chosen based on the sources of PAHs from combustion process and non-combustion process. The site location for these sampling are namely ; Nazra Paddy Industry Sdn. Bhd (non-combustion process) andSungai Tong Palm Oil Mill (combustion process)

Figure 1. Location of the study area.

3.2 The PAHs Data Analyses

Generally, the analytical method that been used in this study referred to the US EPA Method TO-13 (USA EPA, 1999). In this study, the airborne samples were collected by using a High-Volume Air Sampler (HVAS), which fitted with glass fiber filters. Sampling was carried out over an eight hours period for school areas while 24 hours for industrial areas. Exposed filter then were cut into small pieces, stored in a 100 ml beaker to which 10 ml of dichloromethane were added to inhibit microbial activity, wrapped with aluminum foil and kept in refrigeration until the day of analysis. Each sample was extracted three times using ultrasonic agitation (Barnson 1200 (USA) Ultrasonic Cleaner) for a 30-min period with the addition of 50ml dichloromethane for each extraction. Column chromatography (CC) technique was used for the separation of hydrocarbons fraction. In this step, the column used was alumina-silica column where the silica gel and alumina acted as the stationary phase, the sample was ready to analyze by gas chromatography-flame ionization detector (GC-FID). Quantification and identification of individual hydrocarbon component from fraction 2 (aromatic) were performed on a Shimadzu GC17A chromatography fitted with a fused silica capillary column (30m x 0.25mm SUPELCO PTE^{TM}) and a standard Flame Ionization Detector (FID). 'Hot needle' / sandwich technique (air-sample-air) was used to inject the sample in order to achieve the exact amount of sample injected in the GC-FID.

4.0 RESULTS AND DISCUSSION

4.1 PAHs of air particle samples in selected industrial areas

The concentration of individual aromatic hydrocarbons identified in air particle samples was showed in Table 1. The table clearly showed that the concentration of PAHs from air particle samples in Sungai Tong Palm Oil Mill was generally higher than the samples from Nazra Paddy Industry Sdn. Bhd. The total concentration of PAHs in air particle samples from Palm Oil Mill was in the range of 239.831 µg/g.D.W to 2214.390 µg/g.D.W, which was 26 times higher than the samples in paddy industry (152.957 µg/g.D.W).

Thus, the air quality in oil palm industry was poorer than paddy industry. This indicates that the oil palm industry has a combustion process resulted in formation of relatively stable aromatic hydrocarbons. The results shows that biomass fires are pyrolysis processes causing the formation of PAHs from the process of either high temperature thermal alteration of natural product precursors in the source organic matter or process of recombination of molecular fragment in the smoke. Besides the factor of combustion process, the second factor that result the high PAHs concentration of air particle samples in oil palm industry was the high mass combustion of waste. The total PAHs concentration between two sites is shown in Figure 2.

The results also indicates that ,there are some similarities in PAHs profile in both of industries samples. Acenaphthylene and benzo[k]fluoranthene were found to be present in both industries samples. The highest concentration of acenaphthylene was observed in oil palm industry on November, where about 116.359 µg/g is obtained, followed by paddy industry sample on November (2.881 µg/g). However, benzo[k]fluoranthene was found in oil palm industry on November with the highest concentration 261.949 µg/g. Meanwhile, 3.326 µg/g of this compound is obtained in paddy industry on January.

Table 1 : Concentration of individual aromatic hydrocarbons identified in air particle samples

Compound	Nov		Dec		Jan	
	Paddy Filter[a]	Oil Filter[b]	Paddy Filter	Oil Filter	Paddy Filter	Oil Filter
Naphthalene	41.709	1196.012	43.592	239.831	45.158	1501.305
Acenaphthylene	2.881	116.359	n.d	n.d	n.d	n.d
Acenaphthene	1.908	n.d	n.d	n.d	4.529	n.d
Pyrene	n.d	n.d	n.d	n.d	n.d	713.085
Benzo[a]anthracene	n.d	n.d	n.d	n.d	4.248	n.d
Benzo[b]fluoranthene	n.d	n.d	n.d	n.d	5.606	n.d
Benzo[k]fluoranthene	n.d	261.949	n.d	n.d	3.326	n.d
Total Concentration (µg/g.D.W)	46.498	1574.320	43.592	239.831	62.867	2214.390

[a] Air particle sample from Nazra Paddy Industry Sdn. Bhd.

[b] Air particle sample from Sungai Tong Palm Oil Mill

n.d = not detectable

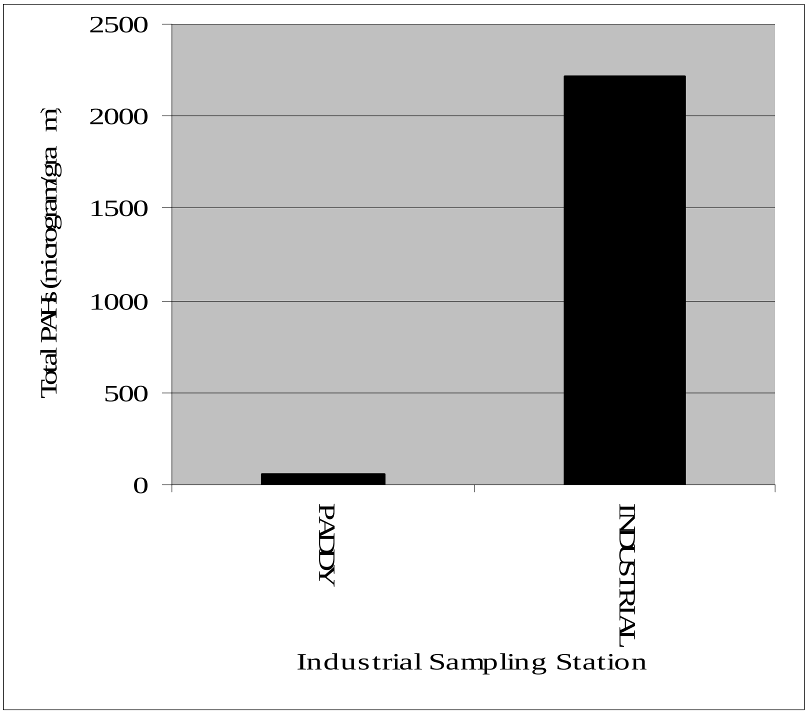

Figure 2 : Total PAHs for sampling station representing industrial area.

4.1 PAHs of atmospheric particles in school areas

The results of the 16 priority PAHs and the total PAHs representing school areas obtained from this study in is shown in Table 2. From the observation, it is clear that the concentration of S3 air samples shows the highest total PAHs with a value of 39603.50 µg/g compared to other samples. The lowest total identified concentration is found in S2 air samples where its concentration is 2214.719 µg/g. In other samples, the analyzed results show the average concentration of total identified PAHs fall in the range of 2872.812 µg/g to 7502.976 µg/g. The total PAHs according to the different sampling station are illustrated in Figure 3. The highest total PAHs value obtained in S3 air samples which located near road junctions where are most probably emitted from vehicle exhaust system. In addition, production of PAHs is greatly influenced by change of speed in which the largest production of all PAHs occurred during acceleration and deceleration. S1 sampling station which is located near the T-road junctions shows very low concentrations compared to the total PAHs concentrations in S3 sampling station. This can be concluded that the traffic flow in the S3 sampling station gives an impact on the concentration of PAHs compared to S1 sampling station. Total PAHs for sampling station representing school area is shown in Figure 4. From the analyses, only 13 PAHs compound were identified in all of the air samples which include naphthalene, acenaphthylene, acenapthene, fluorene, phenanthrene, anthracene, pyrene, benz[a]anthracene, chrysene, benzo[k]fluoranthene, benzo[b]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene. In addition, it is clear that naphthalene is the majority dominant and abundant compound detected in air samples for each sampling station.

Table 2 : Results of PAHs compounds (µg/g) obtained from different sampling.

Name of Compound [a]	Composition	Molecular Weight & Target Ion	S1	S2	S3	S4
Naphthalene	$C_{10}H_8$	128	5613.380	1545.210	21981.500	2303.090
Acenaphthylene	$C_{12}H_8$	152	111.476	N.D	817.131	N.D
Acenapthene	$C_{12}H_{10}$	154	N.D	N.D	2565.915	N.D
Fluorene	$C_{13}H_{10}$	166	N.D	N.D	810.615	N.D
Phenanthrene	$C_{14}H_{10}$	178	N.D	N.D	705.318	N.D
Anthracene	$C_{14}H_{10}$	178	586.749	226.316	1022.462	569.722
Pyrene	$C_{16}H_{10}$	202	N.D	N.D	300.414	N.D
Benz[a]anthracene	$C_{18}H_{12}$	228	142.948	271.188	4628.148	N.D
Chrysene	$C_{18}H_{12}$	228	1048.423	100.561	135.119	N.D
Benzo[k]fluoranthene	$C_{20}H_{12}$	252	N.D	N.D	1684.591	N.D
Benzo[b]fluoranthene	$C_{20}H_{12}$	252	N.D	N.D	2402.437	N.D
Benzo[a]pyrene	$C_{20}H_{12}$	252	N.D	N.D	1053.630	N.D
Indeno[1,2,3-	$C_{22}H_{12}$	276	N.D	71.444	1496.220	N.D
Total PAHs			7502.976	2214.719	39603.500	2872.812

Note :[a] Compound listed were in its elution order , N.D = Not Detected

From the analyses it's indicates that naphthalene is majority dominant and abundant compound detected in air samples. The lowest concentration of PAHs compound is pyrene in which only one sample showed the presence of this compound that is in S3 air samples with the concentration of 300.414 µg/g. Since Naphthalene and Anthracene are the low molecular weight PAHs, therefore it can be concluded that the combustion and traffic vehicle emissions are the dominant sources of total PAHs in ambient air in Kuala Terengganu.

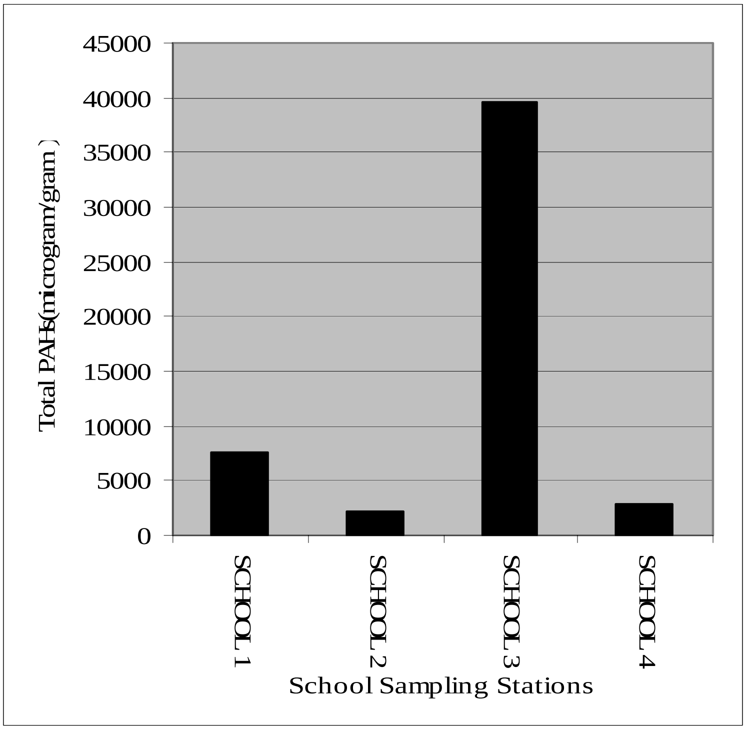

Figure 3 : Total PAHs for sampling station representing school area.

5.0 CONCLUSION AND SUGGESTIONS

As the conclusion, in comparing between two selected industry areas, the concentration of PAHs for air particle samples in oil palm industry was higher than the air particle samples from paddy industry which was 26 times higher than the air particle samples in paddy industry. It can be concluded that the air quality around the area of oil palm industry was polluted than the area around paddy industry. The highest concentration of PAHs air samples obtained is in S3 (39603.50 µg/g) sampling station compared to other sampling station can be concluded that the air particles located near the roadsides especially at road junctions are most probably emitted from vehicle exhaust system. Although the traffic volume and the speed of motor vehicles parameter are not included in this study, the results shows that that the production of higher PAHs collected especially when the areas situated nearby to the traffic junction. It's also can be concluded that the driving mode of the vehicles during acceleration and deceleration of the motor vehicle operations contributes to the emitted of higher pollutants concentrations.

However, the existence of variations could be attributed from other factors such as sites characteristics, topography of surrounding area, frequency of vehicles passing through, type of vehicles utilizing the road and history of the location of concern are not included in this study. The meteorological factors such as wind speed, relative humidity and atmospheric pressure and temperature parameter study can be included in future study.

In conclusion, the results of analyses provides as an indicator of the air pollution levels and database as well as for regulatory action references to improve the air quality particularly in the city of Kuala Terengganu and Malaysian as a general.

REFERENCES

Baek SO, Field RA, Goldstone ME, Kirk PW, Lester JN and Perry R (1991) A Review of atmospheric polycyclic aromatic hydrocarbons: sources, fate and behavior. Water, Air and Soil Pollution, 60, 279-300.

Department of the Environment, Malaysia, 1996. Malaysia Environmental Quality Report. Department of the Environment, Ministry of Science, Technology and Environment, Malaysia

Harvey, Ronald G. (1997). Introduction. In Polycyclic Aromatic Hydrocarbons, pp 1-20. USA: Wiley-VCH Inc. International Agency for Research on Cancer (IARC). (1984a/1987). Monographs in the series Evaluation of Carcinogenic Risk of Chemicals to Huamans, Vol.32, Polynuclear Aromatic Compounds, Part 1, Supplement No. 7, Overall Evaluations of Carcinogenicity: An Updating of IARC Monographs, Vols. 1-42.

Ho KF, Lee SC, Chiu GMY. Characterization of selected volatile organic compounds, polycyclic aromatic hydrocarbons and carbonyl compounds at a roadside monitoring station. Atmos Environ 2002; 36: 57-65.

Howsam M and Jones KC (1998) Sources of polycyclic aromatic hydrocarbons in the environment. In Neilson AH (ed.), The Handbook of Environmental Chemistry, vol. 3, Part I. PAHs and Related Compounds. Springer-Verlag, Berlin, pp. 137-174.

Masterton, W.L. & Hurley, C.N., ed. (1997). “Chemistry; Principles and Reaction.” Third Edition. Sounders College Publishing. Pp 621-623.

Park SS, Kim YJ, Kang CH. Atmospheric polycyclic aromatic hydrocarbons in Seoul, Korea. Atmos Environ 2002; 36: 2917-2924.

Peter.S. (2002). “Determination of polycyclic aromatic hydrocarbons in smoked meat products and smoke flavouring food additives.” *Chromatography B*. **770**. 3-18.

Strnad, M, M. Sanka, Z. Bohacek, I. Borkovcova and J. Vondra. 1993. Soil Pollution By Heavy Metals And Polycyclic Aromatic Hydrocarbons In The Town Of Bino (Czech Republic). Intern. J. Environ. Anal. Chem. 54: pp 233-248.

Tuhackova, J., Cajthaml, T., Novak, K., Novotny, C., Mertelik, J. & Sasek, V. (2001). “Hydrocarbons deposition and soil microflora as affected by highway traffic.” *Environmental Pollution*. **113**. 244-262.

US EPA, Compendium method TO-13A, Determination of polycyclic aromatic hydrocarbons (PAHs) in ambient air using gas chromatography-mass spectrometry (GC-MS), 1999. In Fang, G.C., Wu, Y.S., Chen, M.H., Ho, T.T., Huang, S.H. and

Rau, J.Y. 2004. “Polycyclic aromatic hydrocarbons study in Taichung, Taiwan, during 2002-2003.” *Atmospheric Environment*. 38. 3385-3391.

Vecchio V. Del, P. Valori, C. Melchiorri and A. Grella. 1970. Polycyclic Aromatic Hydrocarbons From Gasoline-Engine And Liquefied Petroleum Gas Engine Exhausts. Pure and Applied Chemistry 42: 739-748.

WHO (1998) Environmental Health Criteria 202: Selected Non-heterocyclic Polycyclic Aromatic Hydrocarbons. World Health Organization, Geneva, p. 883.

Yang HH, Lee WJ, Chen SJ, Lai SO. PAH emission from various industrial stacks. J. Hazard Mater 1998; 60: 159-174.

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

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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.

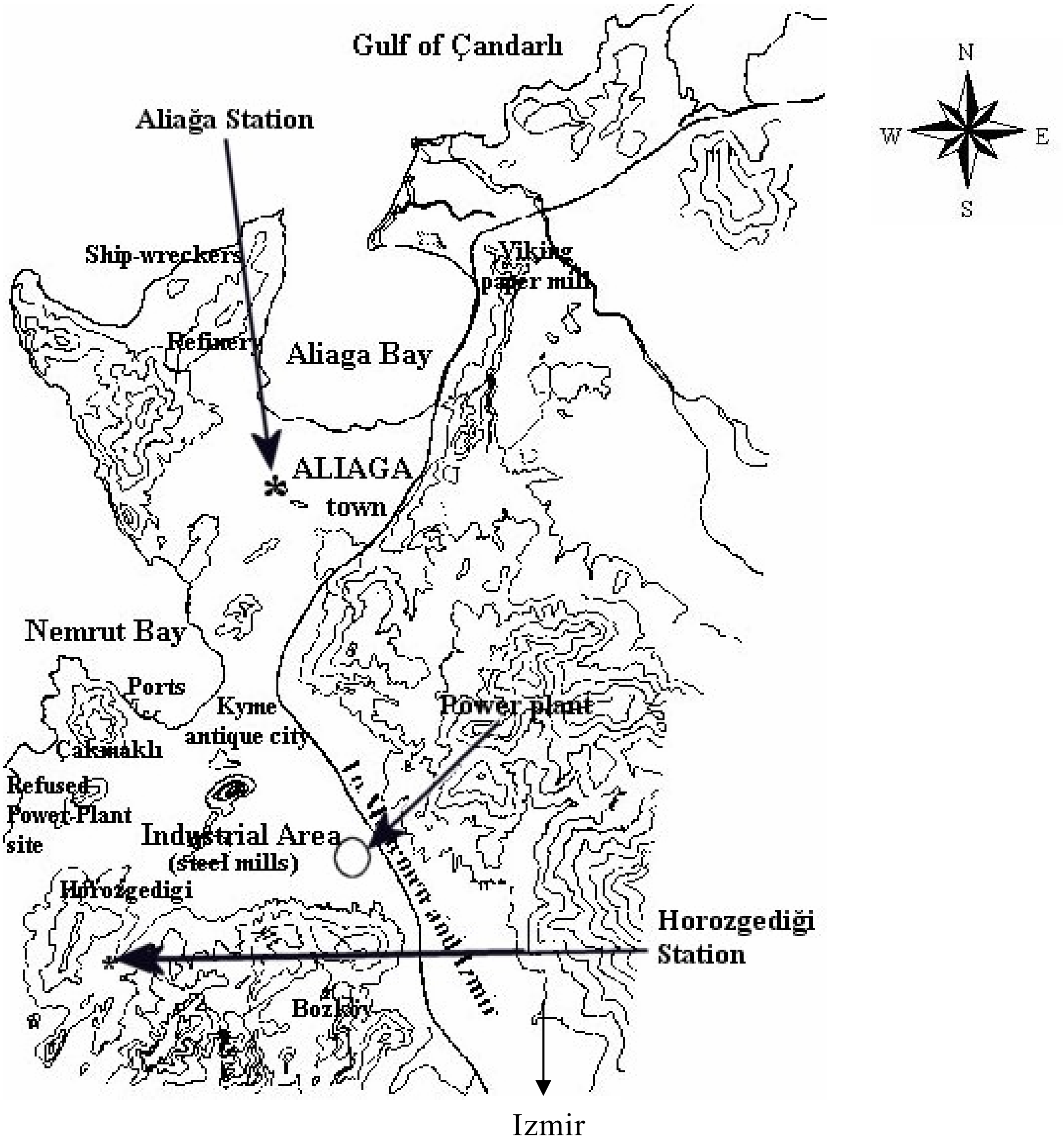

Figure 1. The sampling area.

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 $\mu g\ m^{-3}$ 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.

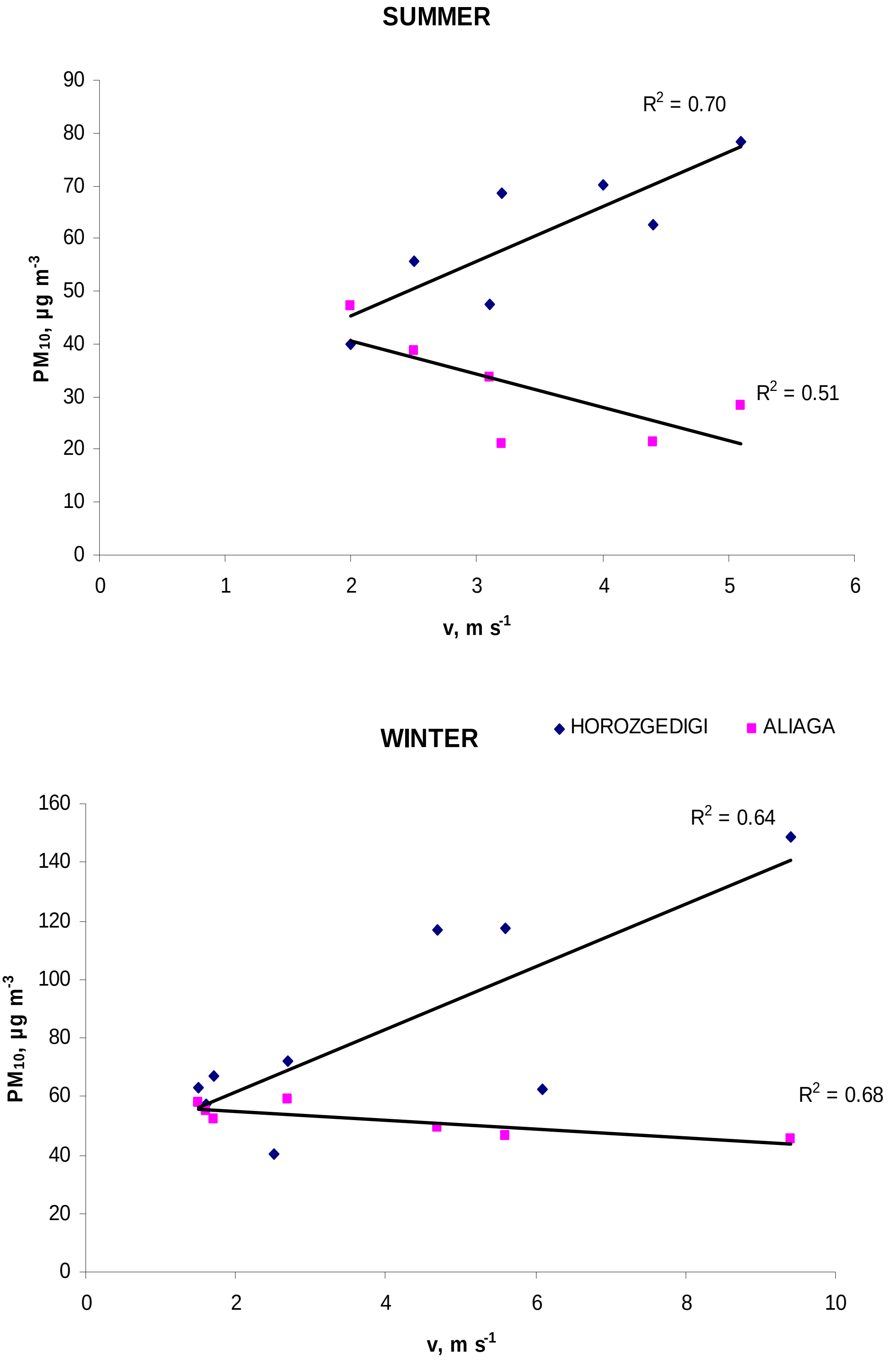

Figure 2. The relationship between PM_{10} and wind direction at two stations

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

	Horozgediği		**Aliağa**		**Horozgediği**		**Aliağa**	
	(ng m^{-3})		**(ng m^{-3})**		**(µg g^{-1})**		**(µg 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.

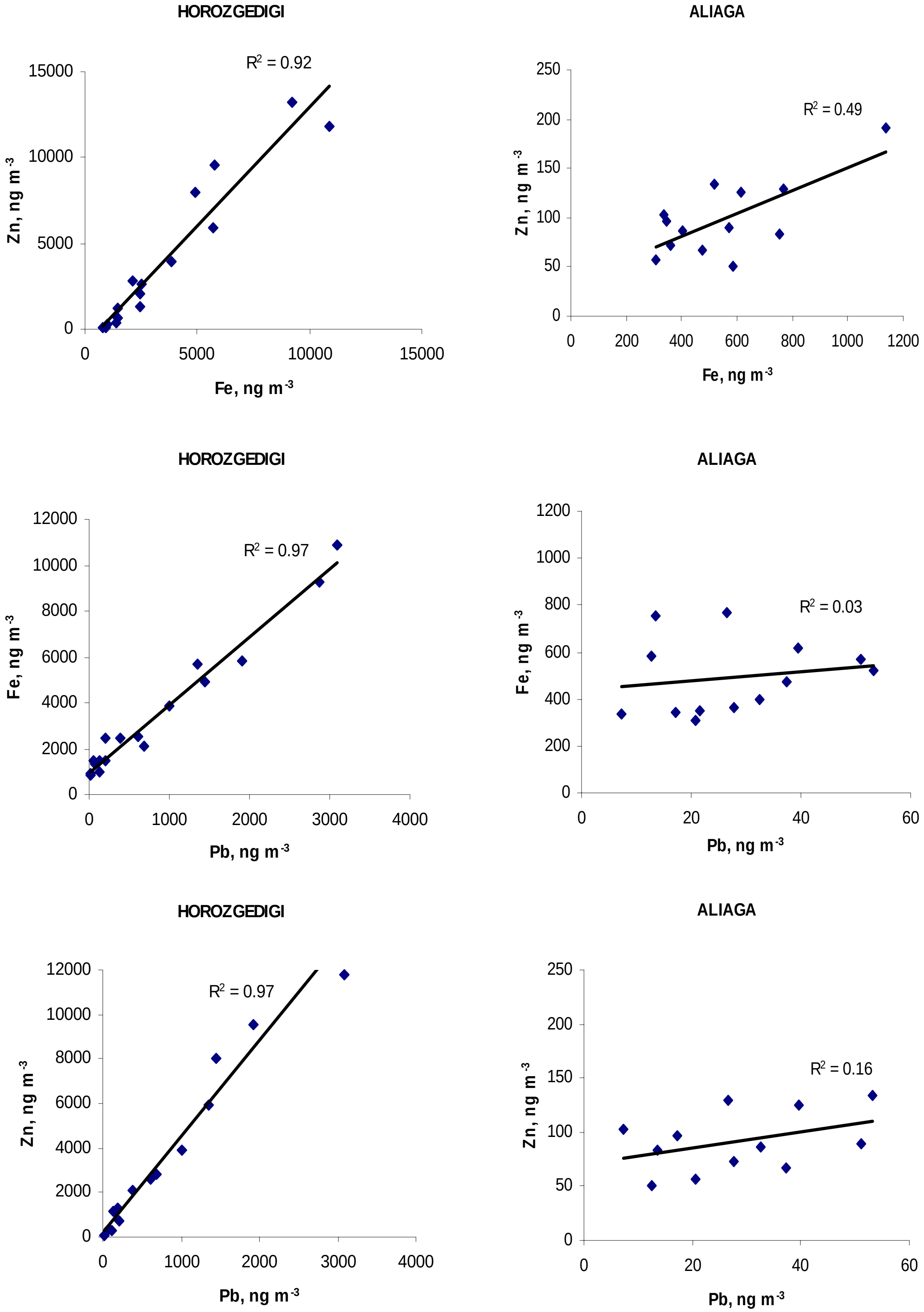

Figure 4. The scatter plots of Zn-Fe, Fe-Pb and Zn-Pb at two stations

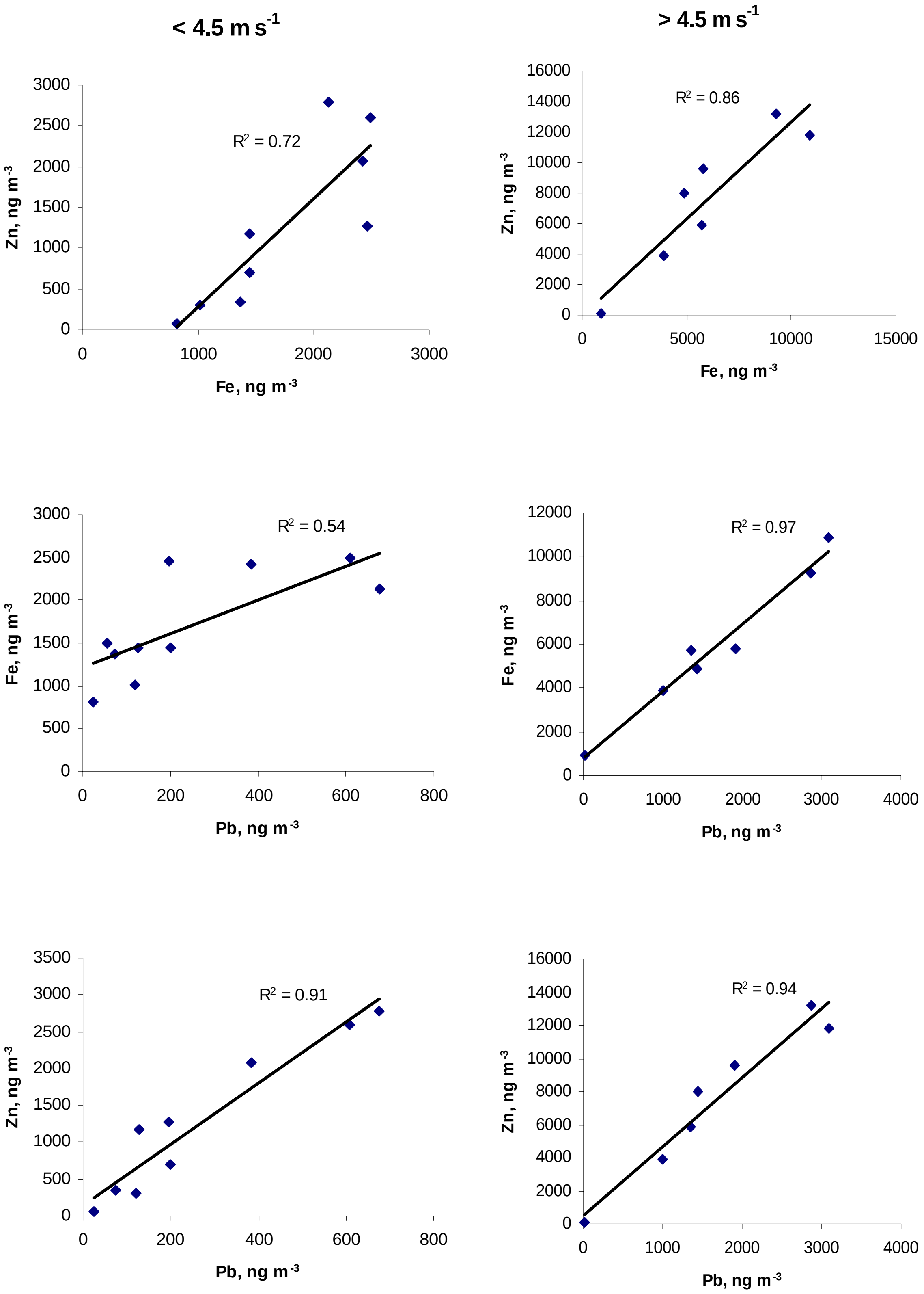

Figure 5. The scatter plots of Zn-Fe, Fe-Pb and Zn-Pb according to the wind speed at Horozgediği station.

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

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AMBIENT AIR CONCENTRATIONS OF VOLATILE ORGANIC COMPOUNDS AROUND THE HEAVY INDUSTRIAL AREA (ALIAGA) IN IZMIR

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ABSTRACT

The concentrations of volatile organic compounds (VOCs) have been studied in Aliaga region in Izmir, Turkey. Aliaga is surrounded by several major industries, mainly petrochemical industry, refinery and iron-steel smelters. These industries significantly contribute to the air pollution in this region.

The sampling was conducted for 10 sequential days in late March, and 7 sequential days in July, 2005 at two sampling stations concurrently. One of the stations is located at the city center of Aliaga, and the other at Horozgedigi industrial area. The results were evaluated in terms of meteorological conditions such as wind speed, wind direction and temperature.

Keywords: Volatile organic compounds, industrial area, petroleum refineries, petrochemical industry.

1. INTRODUCTION

Izmir metropolitan city, with the 2.7 million of population is the center of a highly industrialized area by the Aegean Sea shoreline of Turkey. Particularly, Aliaga region is surrounded by several major industries, mainly petrochemical industry, refinery and iron-steel smelters. Thus, this region is the source of many anthropogenic pollutants. Particulate matter and gaseous pollutants such as SO_2, NO_x and volatile organic compounds (VOCs) are some of these major pollutants.

Volatile organic compounds (VOCs) are a major group of pollutants which significantly affect the chemistry of atmosphere and human health. They play an important role in the stratospheric ozone depletion and formation of highly toxic secondary pollutants, such as tropospheric ozone and peroxyacetylnitrate (PAN), and they enhance the global greenhouse effect. Their toxic and carcinogenic human health effects are also recognized (Dewulf and Langenhove, 1999; Guo et al., 2004; Srivastava et al., 2005). VOCs can be emitted from combustion processes utilizing fossil fuels, petroleum storage and distribution, solvent usage and other industrial processes.

The objective of this work was to determine the ambient concentrations of VOCs at heavy industrialized site, Aliaga, in Izmir, Turkey. The results were evaluated in terms of meteorological conditions such as wind speed and wind direction.

2. MATERIALS AND METHODS

2.1 Sampling Site

Aliaga is located at north of Izmir, approximately 50 km far from the city center in Turkey. Aliaga has many industrial plants very close to the town such as petrochemical complex, refinery, liquid petroleum gas storage plants etc. Horozgedigi Industrial Area is approximately 5 km far from the town and located at south of the town. There are many iron-steel manufacturers, 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 Aliaga town and Horozgedigi village. Horozgedigi 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 site is demonsrated in Figure 1.

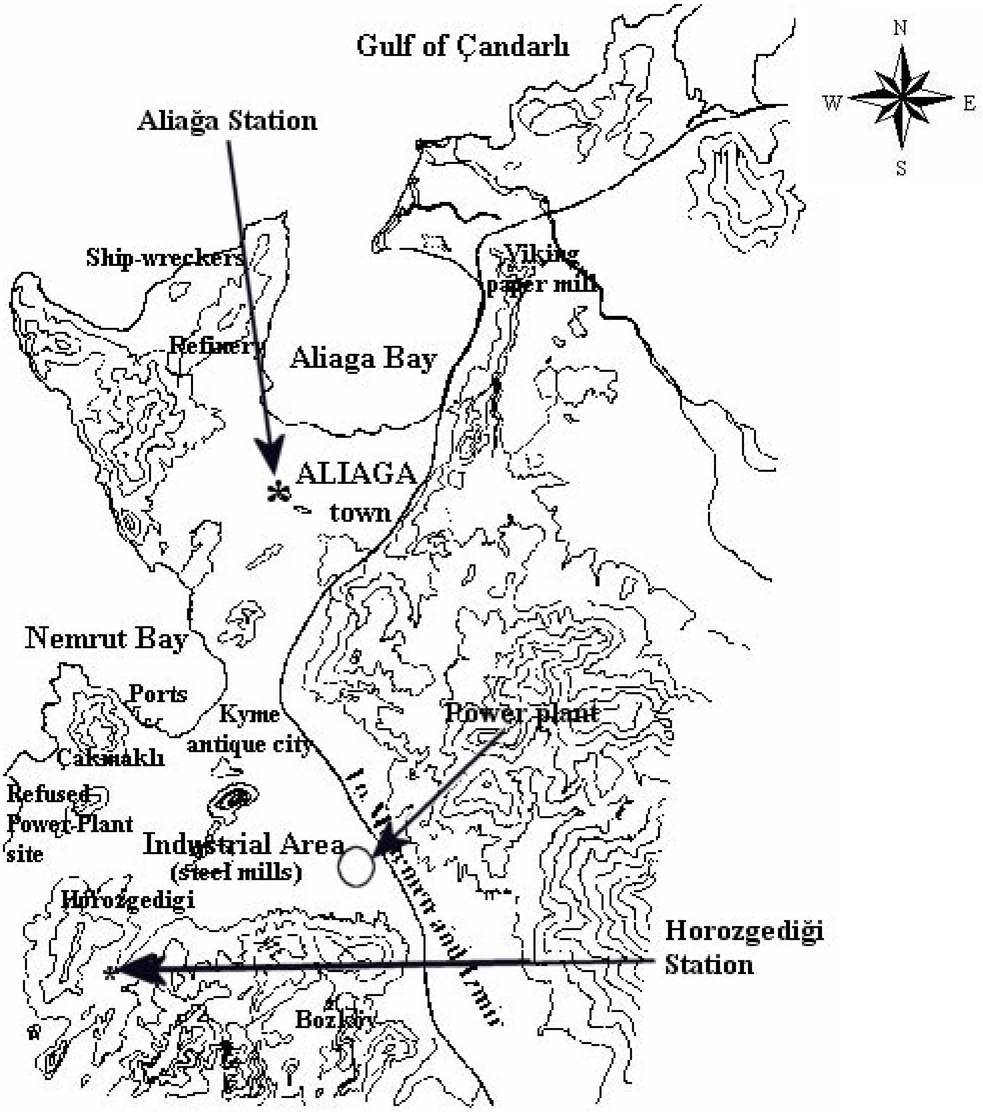

Figure 1. The sampling area.

2.2 Sampling and analysis

The sampling was conducted for 10 sequential days in winter and 7 sequential days in summer periods at two stations, concurrently. The winter period was between 28 March-07 April 2005 and the summer one was 13-19 June 2005.

Ambient VOCs were collected using a sampling train consisted of a moisture trap (calcium chloride), an activated carbon tube, a rotameter, a dry gas meter, and a vacuum pump. Charcoal tubes (Drager-NIOSH) containing 150 mg of activated carbon in two successive sections were used for sampling (ASTM, 1988a). The average sampling flow rate was 0.5 l min^{-1}.

Adsorption tubes were labeled and closed with special caps to avoid contamination and desorption. The samples were placed into tightly closed special plastic bags and kept in a freezer until they were processed. Before analysis, contents of both sections of the adsorber tubes were placed into two different vials in which they were weighed, 1.0 ml carbon disulfide (CS_2) was added as the extraction solvent and they were reweighed (ASTM, 1988b). Samples were extracted in an ultrasonic bath for 15 min. Then they were centrifuged for another 15 min to obtain a clear phase at the top. The extracted samples were stored in a freezer until they were analyzed.

The VOC samples were analyzed with a gas chromatograph (GC) (Agilent 6890N) equipped with a mass selective detector (Agilent 5973 inert MSD). The chromatographic column was HP5-ms (30 m, 0.25 mm, 0.25 µm) and the carrier gas was helium at 1 ml min^{-1} and 36 cm s^{-1} linear velocity with a split ratio of 1:20. The inlet temperature was 240°C. Temperature program was: initial oven temperature 40°C, hold for 3 min, 40°C to 120°C at 5°C/min, hold 1 min. Ionization mode of the MS was electron impact (EI). Ion source, quadropole, and GC/MSD interface temperatures were 230, 150, and 280°C, respectively. The MSD was run in selected ion monitoring. Compounds were identified based on their retention times (within ±0.05 minutes of the retention time of calibration standard), target and qualifier ions. Identified compounds were quantified using the external standard calibration procedure. The calibration for liquid samples was performed injecting (1 µl) five levels (0.02, 0.1, 1.0, 3.0, and 5.0 µg ml^{-1}) of standard solutions in CS_2.

Quality control

Blank activated carbon tubes were extracted and analyzed as process blanks to determine if there was any contamination in the activated carbon tubes. Extraction solvent (CS_2) was also analyzed. None of the compounds included in this study were detected in CS_2 and in process blanks. Back-up sections of adsorbent tubes were also extracted and analyzed. VOC amounts in the back-up sections were below the detection limits indicating that breakthrough was not a problem.

3. RESULTS AND DISCUSSION

Total VOCs refer to sum of the concentrations of 36 compounds analyzed in this study. Total VOC concentrations in summer ranged between 3.31-8.25 (average±SD, 4.61±1.61) and 5.11-109.30 (average±SD, 35.24±36.92) µg m^{-3} in Horozgedigi and in Aliaga regions, respectively. However, in winter the total VOC concentrations were between 3.80-70.97 (average±SD, 20.17±24.99) and 3.18-18.81(average±SD, 8.93±5.83) µg m^{-3} in Horozgedigi and Aliaga, respectively (Fig 2 and 3). Total VOC concentrations in Aliaga were higher than those measured in Horozgedigi in summer period. However, this trend is vice versa in winter period. In Figure 2 and 3, wind speed values were also illustrated and it was clearly seen that as expected, total VOC concentrations were inversely proportional with wind speed. There were three peak days of VOC concentration in Horozgedigi in winter period when the wind speed is very low. Also, in summer there were two days with very high VOC concentrations. As can be seen in the figure, these days, the wind speed was also lower than the other days.

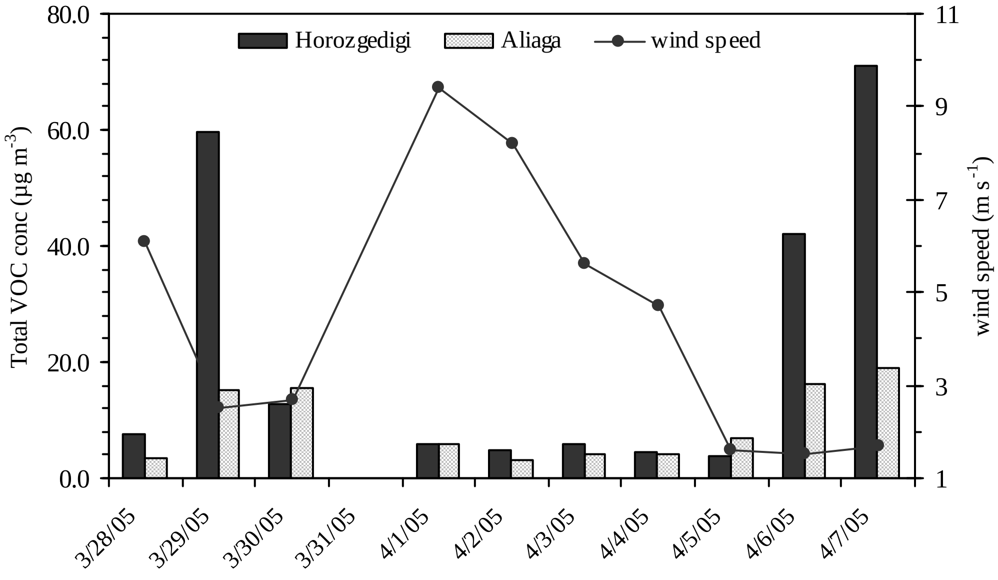

Figure 2. Variation of total VOCs in winter sampling period.

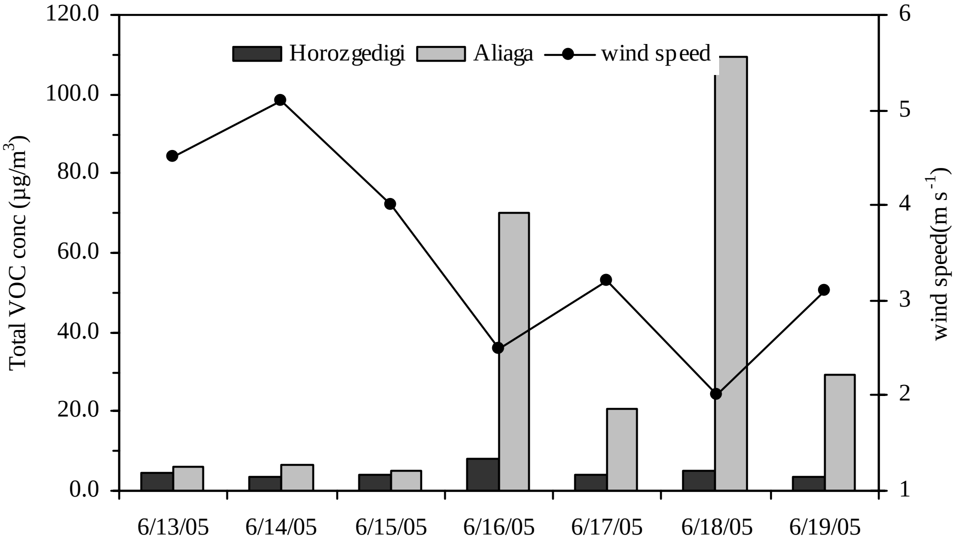

Figure 3. Variation of total VOCs in summer sampling period.

These high concentrations of total VOC concentrations were due to 1.2-Dichloroethane, also called ethylene dichloride, followed by toluene and benzene in Aliaga and Horozgedigi. 1.2 Dichloroethane accounted for %57.0 of total VOCs measured in Horozgedigi and % 21.4 in Aliaga in winter and 16.6 % and 32.4 % of total VOCs measured in Horozgedigi and Aliaga in summer, respectively. A summary of VOC concentrations measured in this study is presented in Table 1.

Table 1. Summary of VOC concentrations (μg m^{-3}, average±SD) measured in this study

	Horozgedigi (μg m^{-3})		**Aliaga (μg m^{-3})**	
	Winter (n=10)	**Summer (n=7)**	**Winter (n=10)**	**Summer (n=7)**
1,1-Dichloroethene	0.06±0.10	0.01±0.01	0.01±0.02	0.07±0.08
Acrylonitrile	0.50±0.97	0.03±0.04	0.11±0.20	0.21±0.37
1,1-Dichloroethane	0.09±0.14		0.03±0.05	0.08±0.11
Vinyl Acetate	1.46±3.53	0.45±0.22	0.37±0.21	0.68±0.30
Butanal		0.04±0.05	0.02±0.04	0.28±0.20
Chloroform	0.20±0.23	0.07±0.06	0.14±0.09	0.31±0.21
2- Butanone	0.13±0.42			0.13±0.34
1,1,1-trichloroethane	0.09±0.01	0.04±0.00	0.07±0.01	0.06±0.01
1,2-Dichloroethane	11.60±19.14	0.74±1.06	1.92±3.25	11.58±17.16
Crotonaldehyde	0.01±0.02			0.07±0.10
Benzene	1.40±0.95	0.52±0.37	1.42±0.68	9.93±12.95
Carbon tetrachloride	0.61±0.19	0.30±0.09	0.37±0.07	0.44±0.21
Pentanal			0.04±0.12	0.85±0.43
Trichloroethene	0.21±0.09	0.06±0.06	0.18±0.25	0.06±0.03
Bromodichloromethane		0.01±0.01	0.03±0.03	0.03±0.01
Buthyl formate	0.13±0.07	0.01±0.01	0.05±0.06	0.05±0.03
4-Methyl - 2 - pentanone		0.06±0.03	0.05±0.06	0.12±0.06
Toluene	1.81±0.71	0.99±0.31	1.92±1.11	6.11±6.53
1,1,2-Trichloroethane	0.02±0.04		0.01±0.02	0.03±0.04
2-Hexanone	0.02±0.03	0.07±0.02	0.64±0.45	0.34±0.24
Dibromochloromethane			0.03±0.04	0.03±0.02
Hexanal	0.14±0.18	0.47±0.18	0.11±0.17	0.91±0.52
Tetrachloroethene	0.10±0.05	0.07±0.03	0.10±0.10	0.07±0.02
Butyl acetate	0.07±0.06	0.07±0.04	0.14±0.19	0.15±0.14
Chlorobenzene		0.02±0.03	0.02±0.01	0.02±0.01
Ethyl benzene	0.11±0.05	0.07±0.02	0.18±0.12	0.29±0.21
p-Xylene	0.44±0.42	0.17±0.16	0.44±0.38	1.37±1.97
Bromoform			0.02±0.03	0.02±0.01
Styrene	0.01±0.01		0.01±0.01	
O,m-Xylene	0.26±0.16	0.10±0.03	0.38±0.24	0.90±0.99
Heptanal	0.03±0.11		0.06±0.11	
1,4-Dichlorobenzene			0.03±0.03	0.03±0.01
1,2-Dichlorobenzene		0.01±0.02		0.01±0.02
Nonanal	0.30±0.48		0.04±0.09	
Decanal	0.15±0.23			

1.2 Dichloroethane is produced in vinyl chloride process of the petrochemical complex located in Aliaga area as an intermediate compound using ethylene and Cl_2. The strong dependency of 1.2 Dichloroethane concentrations on wind direction indicated the association of this compound with the petrochemical complex and the petroleum refinery (Cetin, 2002).

1.2 Dichloroethane is a gasoline additive used as a lead scavenger (Barletta et al., 2002). High concentrations of 1.2 Dichloroethane observed in this study can be also due to the common use of leaded gasoline in this area but probably of minor importance because of significant impact of the petroleum industries.

Benzene is mainly emitted from vehicles. Therefore, benzene is significantly high in Aliaga sampling area, which is in city center (nearly 20 times higher than the samples collected from Horozgedigi in summer period). However, in winter benzene concentrations are nearly the same in both regions.

References

Annual Book of ASTM Standards, Easton, MD, U.S.A., 1983

ASTM. Method D 3686-84: Standard practice for sampling atmospheres to collect organic compound vapors (activated charcoal tube adsorption method). Annual book of ASTM standards 1988a; vol. 11.03:234-240.

ASTM. Method D 3687-84: Standard practice for analysis of organic compound vapors collected by the activated charcoal tube adsorption method. Annual book of ASTM standards 1988b; vol. 11.03:241-246.

Barletta, B, Meinardi, S, Simpson, IJ, Khwaja, HA, Blake DR, Sherwood Rowland F. Mixing ratios of volatile organic compounds (VOCs) in the atmosphere of Karachi, Pakistan. Atmos Environ 2002;36:3429-3443.

Cetin E. Ambient volatile organic compound (VOC) concentrations around a petrochemical plant. MS thesis, Graduate School of Natural and Applied Sciences. Izmir, Turkey: Dokuz Eylul University, 2002.

Chen, B, Hong, C and Kan, H. Exposures and health outcomes from outdoor air pollutants in China, Toxicology, 2004; 198, 291-300.

Dewulf, J, Langenhove, HV. Anthropogenic volatile organic compounds in ambient air and natural waters: a review on recent developments of analytical methodology, performance and interpretation of field measurements. J Chromatogr A 1999; 843:163-177.

Guo, H, Lee, SC, Louie, PKK, Ho, KF. Characterization of Hydrocarbons, Halocarbons and Carbonyls in the Atmosphere of Hong Kong, Chemosphere, 2004; 57:1363-1372.

Srivastava, A, Joseph, AE, Patil, S, More, A, Dixit, RC and Prakash,M. Air Toxics in Ambient Air of Delhi. Atmospheric Environment, 2005; 39: 59-71.