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Correlation Between Metallic and Acidic Components in High-Risk Particle Fraction in Zagreb Air

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Chemical analysis of aerosol particles has gained increasing importance because of the effects of these particles on the environment (Schwartz, 1994, Gamble and Lewis, 1996, Lippmann and Thurston, 1996, Harisson et al. 1997). Epidemiological studies have shown that the exposure to urban particles is associated with an increase in mortality and morbidity, mainly of cardiopulmonary origin (Levy et al. 1999). Particle size and chemical composition play a major role in defining the relative toxicity of particles (Lippmann and Thurston, 1996, Magari et al. 2002, Okeson et al. 2003).

This paper presents the results of measurements of metallic (lead, manganese, cadmium) and acidic (chloride, nitrate, sulphate) components in high-risk particle fraction ($PM_{2.5}$ particles with equivalent aerodynamic diameter less than 2.5 μm) in the city of Zagreb, Croatia.

MATERIALS AND METHODS

Twenty-four hour samples of $PM_{2.5}$ particle fraction were collected in the northern, residential part of Zagreb, at the distance of approximately 20 m from the road with moderate to high traffic density. The sampling was carried out continuously over the one-year period (21 March 2001 - 20 March 2002). Samples of $PM_{2.5}$ were collected on cellulose membrane filters from approximately 100 m^3 of ambient air. The coarser particle fraction was removed from air stream using inertial impactor. Before and after sampling filters were dried to constant humidity in desiccator for 24-hour periods. Particle mass concentration was determined by gravimetry. After that all the filters were cut into two parts. One half of the sampling filter was used to analyze acidic anions. Water-soluble inorganic anions were extracted from the filter media by use of an ultrasonic bath for one hour at 40 °C. Ultra-pure water (specific resistance ≥ 18.3 MΩcm) was used. Undisolved part was separated by centrifugation. Acidic anions (chloride, nitrate and sulphate) were analysed using ion chromatography. Dionex DX 120 chromatograph equipped with suppressed conductivity detection, Dionex AS14: 4mm Analytical Column + AG14: 4mm Guard Column was used. Another half of the sampling filter was used to analyze metallic components lead, manganese, and cadmium. Samples were extracted in nitric acid and metallic components were determined by flame atomic absorption spectrometry. Pye

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Unicem SP 9 flame atomic absorption spectrometer was used. All AAS measurements were carried out in an air/acetylene flame.

For preparation of calibration curves, commercial anion standard mix solution (Dionex) and commercial metal ion standard mix solution (Merck) were used. Correlation coefficient of calibration curve for each species was > 0.999. In order to check for possible background contamination, blank samples (unexposed filters) were used and processed simultaneously with field samples. The method detection limit was calculated for each investigated ion based on average of 10 repeatedly measuring of blank sample ($\gamma \pm 3\sigma$). The detection limits were: 0.05 $\mu g\ m^{-3}$ for chlorides, 0.13 $\mu g\ m^{-3}$ for nitrates, 0.01 $\mu g\ m^{-3}$ for sulphates, 0.0015 $\mu g\ m^{-3}$ for lead, 0.0013 $\mu g\ m^{-3}$ for manganese and 0.0001 $\mu g\ m^{-3}$ for cadmium. For evaluation of the efficiency of the method recovery two series of filters were analysed after being spiked with known amount of ions. The results of recovery were 99.3 – 101.2 % with relative standard deviation RSD < 5%.

RESULTS AND DISCUSSION

Table 1 summarises the statistical parameters: number of samples (N), average values (C_{avg}), standard deviations (SD), median (C_{50}), and maximum values (C_{max}) of mass concentrations of measured pollutants for the overall measuring period, as well as for each season. Results show that the concentration levels of all pollutants showed significant seasonal differences ($P<0.001$, ANOVA, one-way), with high values during winter, which may be due to great emissions of pollutants and their precursors from anthropogenic sources, combustion of fossil fuels and motor vehicle exhaust with high incomplete combustion in cooler period, except manganese with high value in summer. The lower chloride, sulphate and manganese concentrations were found during the spring, nitrates and lead in summer and $PM_{2.5}$ and cadmium in autumn.

In Table 2 the correlation coefficients (* $P < 0.05$; ** $P < 0.01$) between pollutant mass concentrations for entire year are presented, as well as for each season.

The lower correlation was found between chlorides and $PM_{2.5}$ in summer and autumn, which may be due to lower chloride concentration levels. Correlation between nitrates and chlorides were not significant in summer when the concentration levels of both pollutants were lower. Sulphates significantly correlated with $PM_{2.5}$ in spring, summer and winter, and nitrates in all seasons which may be due to the higher contribution of nitrate and sulphate mass to overall particle mass. More significant correlations were found between lead and chlorides, lead and nitrates in spring, summer and winter, and lead and $PM_{2.5}$, in winter indicated that the pollutants might be originated from the same sources. Significant higher correlations between manganese and $PM_{2.5}$, and manganese and chlorides, and manganese and nitrates, and manganese and lead, indicated that the pollutants might be originated from the same source, probably traffic. The lower correlation between cadmium and $PM_{2.5}$ in autumn indicated that the cadmium might originate from separate source.

Table 1. Mass concentration of pollutants ($\mu g\ m^{-3}$).

Measuring period	Statistical parameters	$PM_{2.5}$	Cl^-	NO_3^-	SO_4^{2-}	Pb	Mn	Cd
Spring	N	81	81	81	81	81	81	81
	$C_{avg} \pm SD$	42.2 ± 21.1	0.28 ± 0.27	1.62 ± 1.11	3.33 ± 2.07	0.05 ± 0.02	0.0055 ± 0.004	0.00059 ± 0.0004
	C_{50}	39.0	0.20	1.30	2.81	0.05	0.0048	0.00051
	C_{max}	100.3	1.15	6.09	13.53	0.14	0.0214	0.00226
Summer	N	85	93	93	93	93	93	93
	$C_{avg} \pm SD$	27.9 ± 17.3	0.30 ± 0.19	0.95 ± 0.44	3.30 ± 2.15	0.04 ± 0.02	0.0069 ± 0.004	0.00079± 0.0006
	C_{50}	24.1	0.24	0.87	2.72	0.04	0.0064	0.0008
	C_{max}	83.0	1.20	2.22	9.47	0.10	0.0231	0.00427
Autumn	N	88	89	89	88	89	89	89
	$C_{avg} \pm SD$	27.2 ± 17.3	0.39 ± 0.25	3.69 ± 2.50	4.22 ± 2.52	0.08 ± 0.04	0.0083 ± 0.004	0.00053 ± 0.0005
	C_{50}	21.5	0.34	3.33	3.50	0.08	0.008	0.00043
	C_{max}	92.2	1.73	11.40	11.48	0.16	0.028	0.00211
Winter	N	90	90	90	90	90	90	90
	$C_{avg} \pm SD$	42.8 ± 21.1	0.57 ± 0.48	6.10 ± 3.69	6.05 ± 4.15	0.10 ± 0.06	0.0126 ± 0.007	0.00066 ± 0.0005
	C_{50}	38.6	0.50	5.19	4.80	0.10	0.0114	0.00061
	C_{max}	101.6	4.53	19.08	20.76	0.32	0.0344	0.00198
Overall	N	345	363	363	362	364	364	364
	$C_{avg} \pm SD$	34.6 ± 20.5	0.39 ± 0.34	3.05 ± 3.03	4.16 ± 3.06	0.07 ± 0.04	0.0083 ± 0.006	0.00064 ± 0.0005
	C_{50}	31.1	0.32	1.77	3.37	0.05	0.0071	0.00058
	C_{max}	101.6	4.53	19.08	20.76	0.32	0.0344	0.00427

N – number of samples C_{avg} – average values SD – standard deviation C_{50} – median C_{max} – maximum values

Table 2. Correlation coefficients between pollutant mass concentrations.

Measuring Period	Correlated components	Cl^-	NO_3^-	SO_4^{2-}	Pb	Mn	Cd
Spring (N = 81)	$PM_{2.5}$	-0.316**	-0.074	0.357**	-0.041	0.391**	0.413**
	Cl^-		0.528**	-0.071	0.311**	-0.036	-0.126
	NO_3^-			0.531**	0.431**	-0.055	0.033
	SO_4^{2-}				0.010	0.142	0.266*
	Pb					-0.004	-0.006
	Mn						0.319**
Summer (N = 85)	$PM_{2.5}$	0.099	0.021	0.523**	-0.072	0.021	0.266*
	Cl^-		0.120	-0.022	-0.051	0.213*	-0.002
	NO_3^-			0.465**	0.183	-0.027	0.037
	SO_4^{2-}				0.159	0.069	-0.019
	Pb					0.275*	-0.126
	Mn						0.082
Autumn (N = 87)	$PM_{2.5}$	0.151	0.024	0.049	0.065	0.311**	-0.049
	Cl^-		0.276**	0.082	0.247*	0.492**	0.316**
	NO_3^-			0.578**	0.344**	0.451**	0.499**
	SO_4^{2-}				0.189	0.333**	0.219*
	Pb					0.493**	0.327**
	Mn						0.389**
Winter (N = 90)	$PM_{2.5}$	0.278**	0.705**	0.618**	0.568**	0.462**	0.306**
	Cl^-		0.264*	0.033	0.312**	0.224*	0.183
	NO_3^-			0.465**	0.492**	0.420**	0.312**
	SO_4^{2-}				0.054	0.013	0.110
	Pb					0.849**	0.285**
	Mn						0.276**
Overall (N = 343)	$PM_{2.5}$	0.125*	0.316**	0.419**	0.272**	0.342**	0.197**
	Cl^-		0.419**	0.144**	0.395**	0.349**	0.083
	NO_3^-			0.564**	0.628**	0.506**	0.128*
	SO_4^{2-}				0.258**	0.248**	0.092
	Pb					0.667**	0.076
	Mn						0.217**

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

Figure 1 presents the anion (chlorides, nitrates and sulphates) mass content (%) in the high-risk particle fraction during the overall measuring period, as well as for each season. The metal (lead, manganese and cadmium) mass content (%) in the high-risk particle fraction during the overall measuring period, as well as for each season was shown in Figure 2.

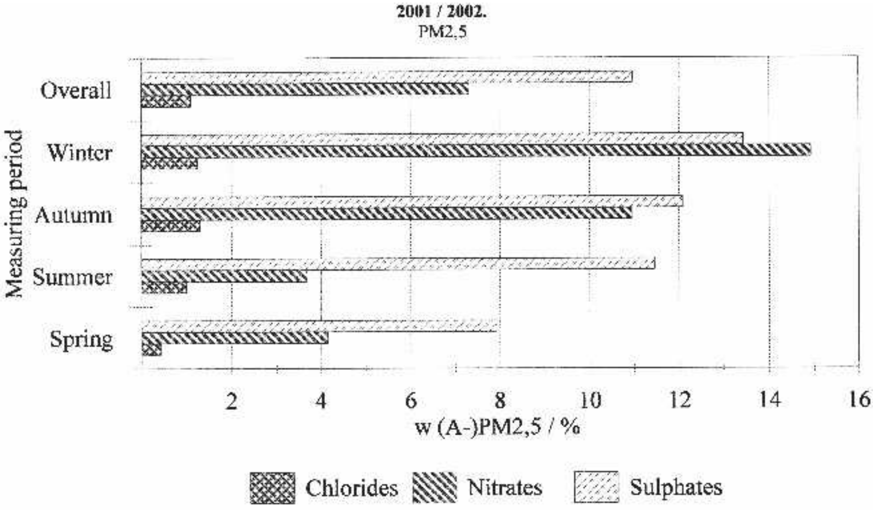

Figure 1. Anion mass content (%) in $PM_{2.5}$ particle fraction

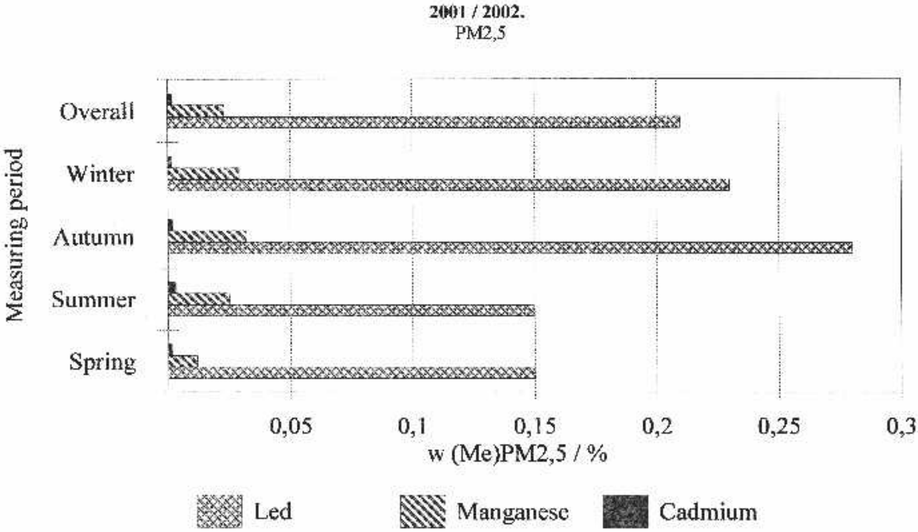

Figure 2. Metal mass content (%) in $PM_{2.5}$ particle fraction

The content of all components in $PM_{2.5}$ particle fraction also showed significant seasonal differences ($P<0.001$, ANOVA, one-way). Marked seasonal variations of chloride and nitrate content in the fine particle fraction could be attributed to the variation in volatility of the ammonium salts leading to lower summertime values. Ammonium chloride and nitrate are unstable under normal atmospheric conditions, and there content depends on the temperature, relative humidity and chemical composition of the aerosols and gaseous precursors (Willson et al. 1985, Solomon et al. 1992, Kaneyasu et al. 1995). The high sulphate content in summer may be due to the strong solar radiation in summer, and photochemical gas-phase oxidation of gas precursor pollutant. During the winter period the aqueous-phase oxidation of gas precursor pollutant to secondary aerosols mainly take place (Van Der Zee et al. 1998). The overall anion content median in high-risk particle fraction amounted to 19%, ranging from 12.4% during spring to 29.7% during winter period. The higher metal content was found during the autumn (lead) and summer (manganese and cadmium) period. The lower contents of all metals were measured in spring. The overall metal content median in high-risk particle fraction was 0.22%, ranging from 0.16% in spring to 0.30% in autumn period.

The most abundant species contributing to the $PM_{2.5}$ mass were: sulphates > nitrates > chlorides > lead > manganese > cadmium.

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