

SPATIAL AND TEMPORAL VARIATIONS OF MAJOR ACIDIC SPECIES IN PM_{2.5} PARTICLE FRACTION IN ZAGREB AIR

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ABSTRACT

This paper presents the spatial and temporal mass concentration variations of major acidic species (chlorides, nitrates and sulphates) in high risk particle fraction PM_{2.5} in Zagreb air. The sampling was carried out at four measuring sites during the summer of 2002 (June – July) and winter 2002-2003 (November – January).

The results show no significant differences in pollutant concentration levels between the measuring sites in the winter, while significant differences were found for nitrates and sulphates in the summer. Higher mass concentrations of all pollutants were measured in the winter. The mass concentrations of investigated anions showed significant seasonal differences, except for chlorides at two sampling sites. The most abundant species contributing to the PM_{2.5} mass were: sulphates > nitrates > chlorides.

Key Words: Chlorides, Nitrates, Sulphates, Sampling sites, Ion chromatography

1. INTRODUCTION

Acid aerosols in the air are formed primarily from the oxidation of sulphur oxides, nitrogen oxides, and hydrocarbons, mainly originating from combustion sources. In the atmosphere the primary pollutant sulphur dioxide is oxidised by both homogenous and heterogeneous reactions forming a sulphuric acid aerosol, which can react with other components present in the air mainly with gaseous ammonia, leading to various molecular forms of sulphates (Khoder 2002, Brook et al. 1997). Nitrogen dioxide (mainly the secondary pollutant) is readily oxidised to nitrates (Khoder 2002). Nitrates may be present in the gaseous phase as nitric acid vapour, while the sulphates are mainly found in the aerosol phase (Wyers and Duyzer 1997). Aerosol acidity and concentrations of each species are seasonally dependable, varying with the time of the day and location. Strong acids are more frequently present in fine (high-risk) particle fraction. Chemical analysis of aerosol particles has gained increasing importance because of the effects of these particles on the environment (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).

This paper presents the spatial and temporal mass concentration variations of major acidic species (chlorides, nitrates and sulphates) in high risk particle fraction PM_{2.5} in Zagreb air measured at four sampling sites during the summer and winter period.

2. MATERIALS AND METHODS

The sampling of high-risk particle fraction was carried out at four measuring sites in Zagreb during the summer of 2002 (June – July) and winter 2002-2003 (November – January). The measuring sites are designated here as NR (northern residential part of the city with moderate traffic density and numerous green areas), CC (city centre with high traffic density and individual heating), RW (residential-industrial area in western part of the city with high traffic density) and RE (residential-industrial area in eastern part of the city).

Twenty-four hour samples of high-risk particle fraction were collected by means on quartz filters. The coarse particle fraction was removed from air stream using inertial impactor. Filters were dried to constant humidity in a desiccator for 24-hours before and after sampling. Particle mass concentration was determined using the gravimetric method. Samples were extracted from the filter media with an ultrasonic bath. Dionex DX-120 ion chromatograph equipped with suppressed conductivity detection, Dionex AS14: 4mm analytical column + AG14: 4mm guard column was used to measure anion content.

3. RESULTS AND DISCUSSION

Table 1 summarises the descriptive statistics, including the number of samples (N), average values ($\bar{\gamma}$), minimum (γ_{\min}), and maximum (γ_{\max}) of chloride mass concentrations in PM_{2.5} particle fraction measured at four sampling sites in summer and winter, as well as the ratio between the mass concentration measured in winter and summer ($\bar{\gamma}_w / \bar{\gamma}_s$). The same parameters for nitrate mass concentrations are shown in Table 2, and for sulphates in Table 3.

Table 1. Mass concentration of chlorides ($\mu\text{g m}^{-3}$) in PM_{2.5} particle fraction

Statistical parameters	CC		NR		RE		RW	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
N	21	37	35	48	22	25	24	32
$\bar{\gamma}$	0,61	0,55	0,21	1,01	0,87	0,86	0,28	1,00
γ_{\min}	0,02	0,00	0,00	0,00	0,00	0,07	0,00	0,03
γ_{\max}	6,83	1,99	1,94	8,58	16,22	2,58	2,78	10,72
$\bar{\gamma}_w / \bar{\gamma}_s$	0,90		4,81		0,99		3,57	

Table 2. Mass concentration of nitrates ($\mu\text{g m}^{-3}$) in $\text{PM}_{2.5}$ particle fraction

Statistical parameters	CC		NR		RE		RW	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
N	21	37	35	48	22	25	24	32
$\bar{\gamma}$	0,97	6,76	0,79	6,28	0,72	11,25	0,90	7,11
γ_{\min}	0,22	1,33	0,11	0,63	0,09	1,75	0,17	0,41
γ_{\max}	1,45	18,63	1,68	18,61	1,48	34,10	1,73	19,73
$\bar{\gamma}_w / \bar{\gamma}_s$	6,97		8,61		15,63		7,9	

Table 3. Mass concentration of sulphates ($\mu\text{g m}^{-3}$) in $\text{PM}_{2.5}$ particle fraction

Statistical parameters	CC		NR		RE		RW	
	Summer	Winter	Summer	Winter	Summer	Winter	Summer	Winter
N	21	37	35	48	22	25	24	32
$\bar{\gamma}$	6,54	9,65	6,53	9,59	5,52	15,86	6,77	10,60
γ_{\min}	1,28	1,67	0,41	0,72	0,98	2,07	0,61	0,99
γ_{\max}	16,63	22,97	17,24	26,24	17,20	34,51	14,24	25,44
$\bar{\gamma}_w / \bar{\gamma}_s$	1,48		1,47		2,87		1,57	

The measurements of acidic components (chlorides, nitrates, and sulphates) in high-risk particle fraction $\text{PM}_{2.5}$ at four sampling sites show no significant difference ($P > 0.05$, ANOVA, one way analyses of variance) in pollutant concentration levels between the measuring sites in the winter, while significant differences ($P < 0.05$) were found for nitrates and sulphates in the summer.

Higher mass concentrations of all pollutants were measured in the winter which may be due to high emissions of pollutants and their precursors from anthropogenic sources, combustion of fossil fuels and motor vehicle exhaust. The mass concentrations of investigated anions showed significant seasonal differences (one-tailed t -test), except for chlorides at sampling sites CC and RE. More pronounced differences were found for nitrates at all sampling sites, sulphates at sampling site RE, and chlorides at sampling site RN.

Chloride, nitrate, and sulphate content (%) in $\text{PM}_{2.5}$ particle fraction measured in the summer 2002 and the winter 2002/3 at the sampling site NR are shown in Figure 1. The same parameters measured at sampling site CC are shown in Figure 2, for sampling site RW in Figure 3, and for sampling site RE in Figure 4.

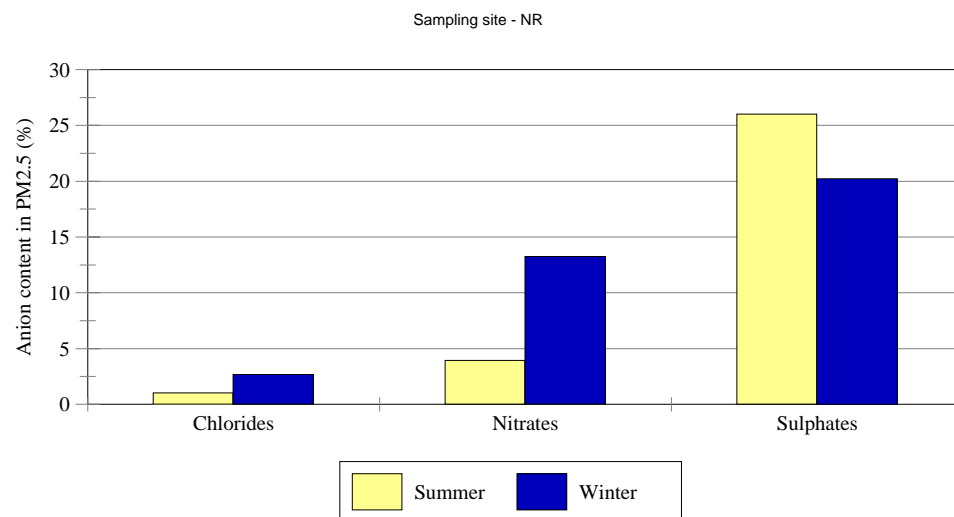


Figure 1. Anion mass content (%) in PM_{2.5} particle fraction measured at sampling site NR in the summer 2002 and winter 2002/3

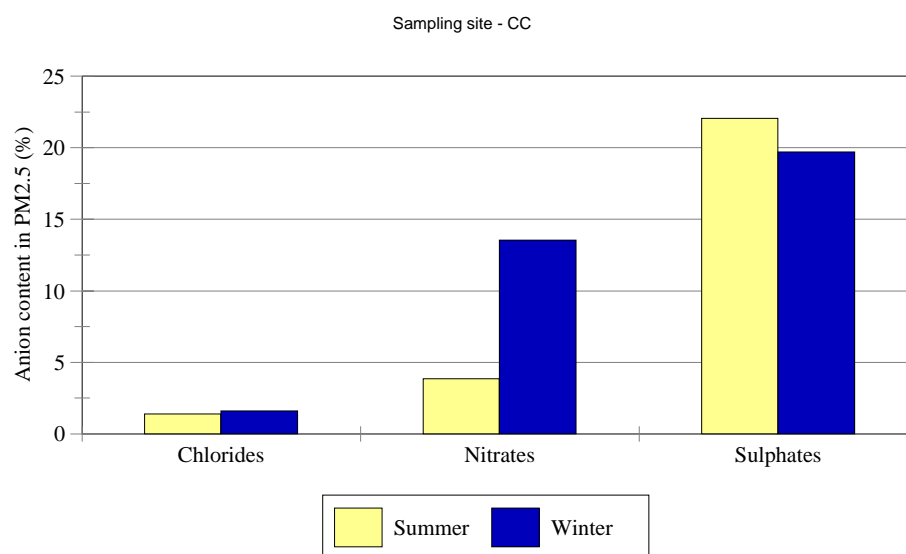


Figure 2. Anion mass content (%) in PM_{2.5} particle fraction measured at sampling site CC in the summer 2002 and winter 2002/3

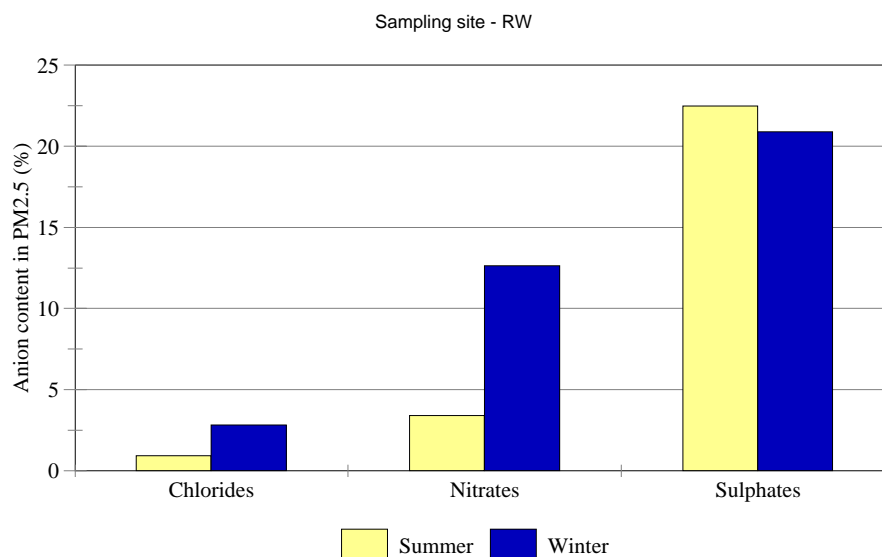


Figure 3. Anion mass content (%) in PM_{2.5} particle fraction measured at sampling site RW in the summer 2002 and winter 2002/3

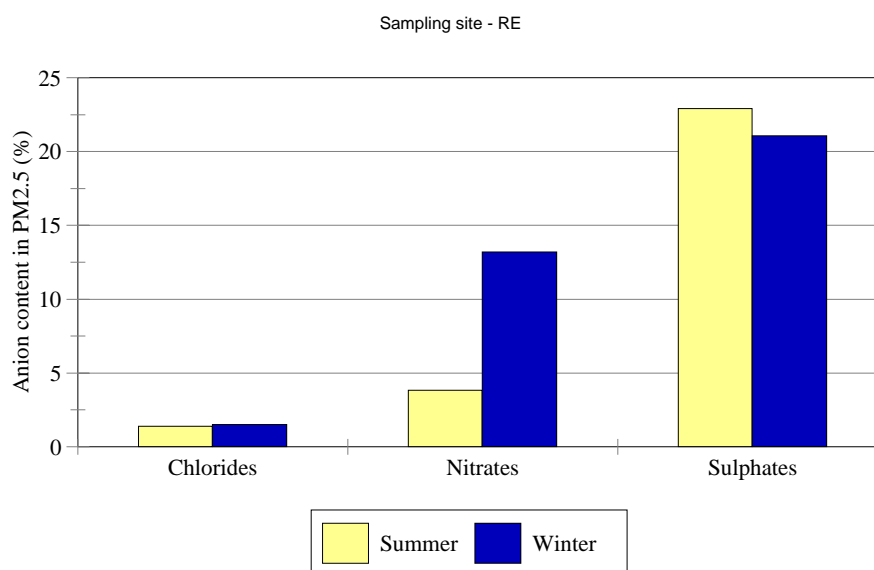


Figure 4. Anion mass content (%) in PM_{2.5} particle fraction measured at sampling site RE in the summer 2002 and winter 2002/3

The content of acidic components nitrates and sulphates in PM_{2.5} particle fraction showed significant differences ($P < 0.01$, ANOVA, one-way analysis of variance) between sampling sites in the summer and winter, while the chloride content showed no significant difference ($P > 0.05$).

The nitrate content in PM_{2.5} particle fraction showed significant seasonal difference (one-tailed *t*-test) at all sampling sites, while chloride and sulphate content in PM_{2.5} particle fraction showed significant seasonal difference only at sampling sites NR. Higher contributions of nitrates and chlorides to particle mass were in winter period at all sampling sites, while the sulphates contribution in the summer.

The high level of nitrate content in the winter has been observed by Kaneyasu et al. (Kaneyasu et al., 1995). This phenomenon has been accounted for by the shifting of the $\text{NH}_4\text{NO}_3 (\text{s}) \leftrightarrow \text{HNO}_3 (\text{g}) + \text{NH}_3 (\text{g})$ equilibrium to the aerosol phase (Solomon et al., 1992). The high level of chloride content in winter could be attributed to the thermodynamic equilibrium of $\text{NH}_4\text{Cl} (\text{s}) \leftrightarrow \text{NH}_3 (\text{g}) + \text{HCl} (\text{g})$ reaction (Willson et al., 1985). The high sulphate content in the summer may be due to strong solar radiation in the 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. This process is slower than photochemical gas-phase oxidation (Van Der Zee et al., 1998).

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

4. CONCLUSION

Mass concentration of major acidic species (chlorides, nitrates and sulphates) in high-risk particle fraction PM_{2.5} in Zagreb air show no significant differences in pollutant concentration levels between the measuring sites in the winter, while significant differences were found for nitrates and sulphates in the summer.

The mass concentrations of investigated anions showed significant seasonal differences, except for chlorides at two sampling sites. Higher mass concentrations of all pollutants were measured in the winter.

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