Environmental
Contamination
and Toxicology

Seasonal Distributions of Acid Components in PM$_{2.5}$ Fraction of Airborne Particles in Zagreb Air

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It is well known that airborne particles and their constituents are associated to adverse health effects, reduction of visibility and the soiling of buildings (Schwartz 1994; Gamble and Lewis 1996, Lippmann and Thurston 1996; Harrison et al. 1997). The acidity of the particle has been supposed to be the crucial factor (Lippmann and Thurston 1996). 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 oxidized by both homogenous and heterogenous reactions forming a sulphuric acid aerosol, which can react rapidly with other components present in the air mainly with gaseous ammonia, leading to various molecular forms of sulphates (Brook et al. 1997). Nitrogen dioxide (mainly the secondary pollutant) is readily oxidized to nitrates. Nitrates may be present in the gaseous phase as nitric acid vapor, 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. Summer aerosols are more acid compared to those collected during winter period. Strong acids are more frequently present in fine (high-risk) particle fraction compared to the coarse one.

This paper presents seasonal mass concentration and content distributions of acid anions (chlorides, nitrates, sulphates) in high-risk particle fraction (PM$_{2.5}$ – particles with equivalent an aerodynamic diameter less than 2.5 μm) in Zagreb ambient air.

MATERIALS AND METHODS

The sampling site was located in the northern residential part of Zagreb, at a distance of approximately 20 meters from the road with moderate to high traffic density. Sampling was carried out continuously during one-year period (21st March 1999 - 20th March 2000). Twenty-four hour samples of high-risk particle fraction were collected by means of cellulose membrane filters (Millipore SSWP09025 or AAWP09025, pore size 0.8 μm) at the average sampling flow rate of 70 Lpm, from approximately 100 m^3 of ambient air. The coarser particle fraction was removed from the air stream using inertial impactor. Filters were dried to constant humidity in a desiccator for 24-hour periods before and after sampling. Particle mass concentration

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was determined by gravimetric method. Samples were extracted with deionized water from the filter media by use of an ultrasonic bath for one hour at 40 °C. Undissolved parts were separated by centrifugation, and than analysed for anions: chlorides, nitrates and sulphates. Blank samples were analysed simultaneously together with the field samples. Dionex DX-120 ion chromatograph was used. Operating conditions are shown in Table 1.

Table 1. Operating conditions of ion chromatography system

Apparatus: Dionex DX-120
Column: AS14: 4mm Analytical Column + AG14: 4mm Guard Column
Eluent: 3,5 mM Na_2CO_3/ 1mM $NaHCO_3$
Eluent flow rate: 1,2 mL/min
Injection loop: 50 μL
Pressure: 1200 PSI
Detector: ED40 Conductivity cell
Suppressor: Anion Self-Regenerating Suppressor ASRS-II-4mm
Background conductivity: 16-17 μS

RESULTS AND DISCUSSION

Number of samples, average values and standard deviations of mass concentrations for each pollutant, during overall measuring period, as well as for each season are shown in Table 2.

Table 2. Average mass concentrations of pollutants (μgm^{-3})

	Spring	Summer	Autumn	Winter	Overall
	N M±SD	N M±SD	N M±SD	N M±SD	N M±SD
$PM_{2.5}$	87 25.5±15.3	93 32.6±20.6	86 32.1±23.1	90 52.4±31.5	356 35.8±25.4
Cl^-	92 0.25±0.22	93 0.20±0.14	89 0.33±0.25	91 0.51±0.60	365 0.32±0.37
NO_3^-	92 2.16±1.42	93 0.92±0.69	89 3.49±2.80	91 6.10±4.81	366 3.14±3.46
SO_4^{2-}	92 4.02±2.04	93 5.18±2.99	89 5.02±4.37	91 6.87±6.22	366 5.26±4.31

Concentration levels of all pollutants showed significant seasonal differences ($p<0.05$), with elevated values during winter, and lower concentration levels during spring ($PM_{2.5}$, sulphates) or summer (chlorides, nitrates) period. Seasonal dependence of fine particulate chloride mass concentrations was reported earlier . During the winter period fine chlorides are mainly present as NH_4Cl aerosol. Their concentrations are highly dependent on the ambient temperature levels. It could be

attributed to the thermodynamical equilibrium of $NH_4Cl \rightleftharpoons HCl + NH_3$ reaction and relatively low concentration levels and to both gaseous HCl and NH_3 (Willison et al. 1985). Low nitrate mass concentration levels during summer period could be the possible consequence of intensive dissociation of labile particulate NH_4NO_3 to gaseous NH_3 and HNO_3. This dissociation depends on temperature, relative humidity and aerosol composition (Stelson and Seinfeld 1982).

Number of samples, average values and standard deviations of anion content (%), during overall measuring period, as well as for each season are shown in Table 3.

Table 3. Average anion content P_a (%) in $PM_{2.5}$ particle fraction

|	Spring	Summer	Autumn	Winter	Overall
	N M±SD	N M±SD	N M±SD	N M±SD	N M±SD
Cl^-	83 1.02±1.01	91 0,90±0.89	84 1.22±1.09	88 1.14±1.02	346 1.07±1.00
NO_3^-	83 9.70±6.44	91 3.19±2.64	84 12.18±2.58	89 12.25±6.37	347 9.22±7.23
SO_4^{2-}	83 19.0±12.1	91 18.7±11.1	84 17.6±11.2	89 12.8±7.5	347 17.0±10.8

The chloride content showed no significant seasonal difference, while nitrate content was significantly lower during summer period. Sulphate content showed significant seasonal difference, with lower values during winter period when the aqueous-phase oxidations of gaseous precursor pollutants to secondary aerosols mainly take place. This process is slower compared to the photochemical gas-phase oxidation which is the predominating oxidation mechanism during summer (Van Der Zee et al. 1998).

High-risk particle, chloride, nitrate and sulphate mass concentration distributions (minimum, maximum, median and inter quartile range) for overall measuring period, as well as for each season are shown in Figures 1-2. The same parameters for chloride, nitrate and sulphate content in high-risk particle mass (%) are shown in Figures 3-4.

Results show that the distributions of all investigated pollutants could be approximated to the lognormal distribution (p<0.001).

Figure 5. presents the total anion mass content (%) in the high-risk particle fraction during the overall measuring period, as well as for each season. The overall anion content median in the high-risk particle fraction amounted to 22.3 %, ranging from 20,0% during summer to 24.7% during spring period. Sulphates dominated in all seasons. Nitrate and sulphate content varied with the season, while chloride content showed no significant seasonal dependence.

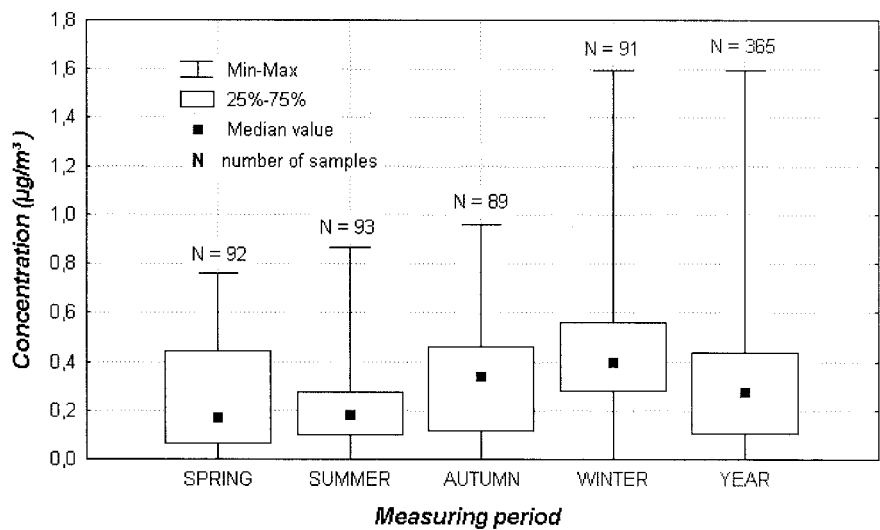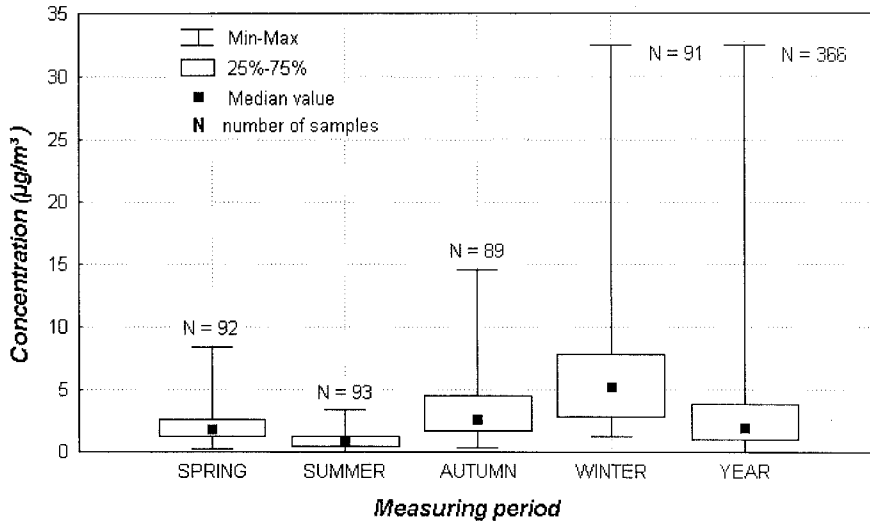# Suspended particle fraction - PM$_{2.5}$
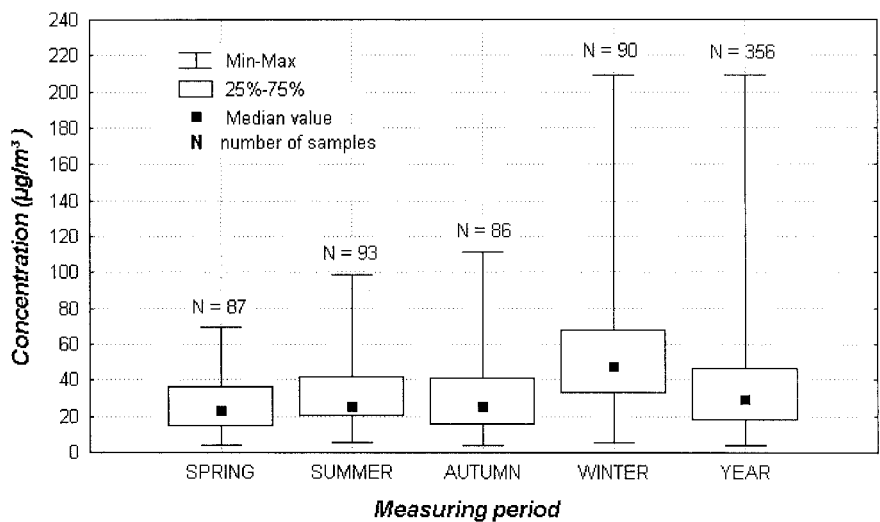
Chlorides

Figure 1. Summarized mass concentration distributions of PM$_{2.5}$ and chlorides (μgm^{-3})
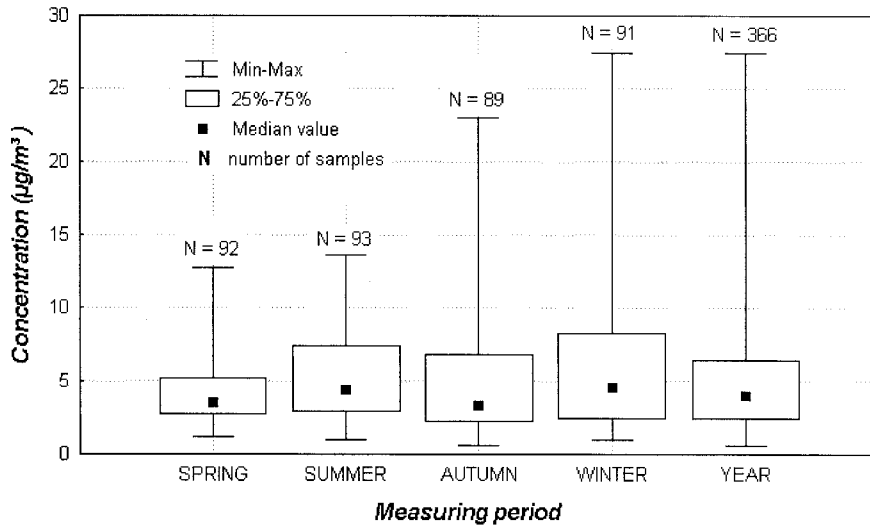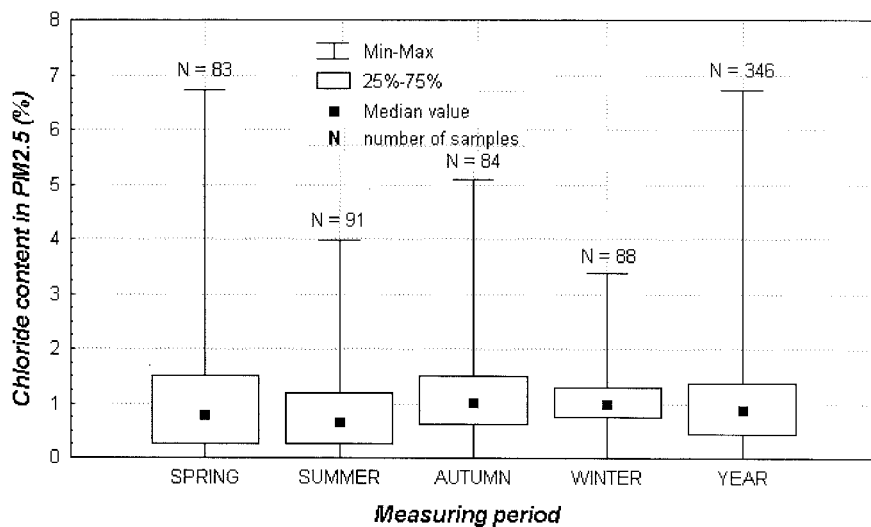
Nitrates

Sulphates

Figure 2. Summarized mass concentration distributions of nitrates and sulphates (μgm^{-3})
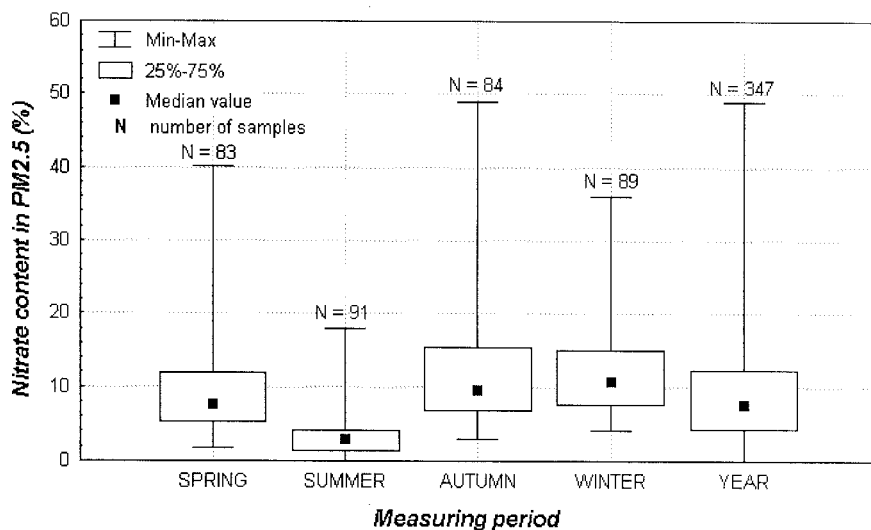
Chlorides

Nitrates

Figure 3. Distribution of chloride and nitrate content (%) in $PM_{2.5}$ particle fraction
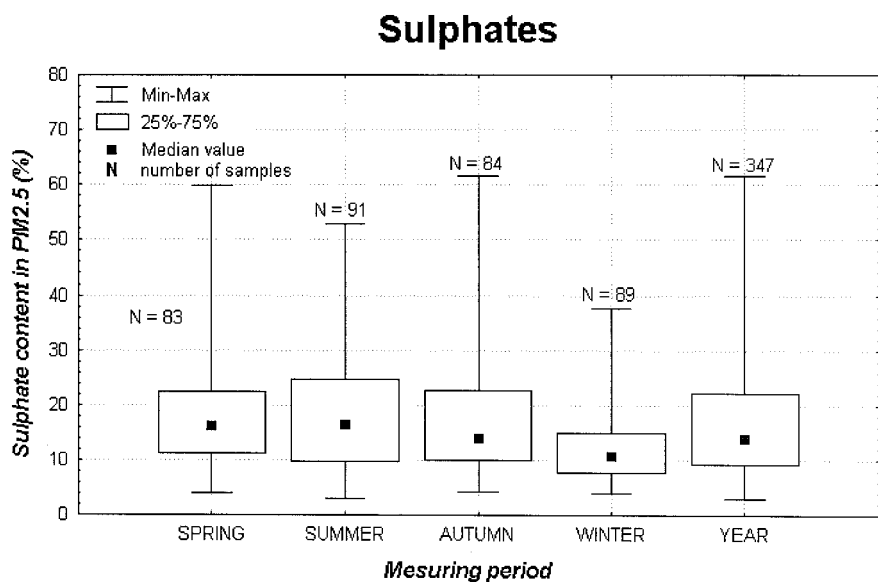
Sulphates

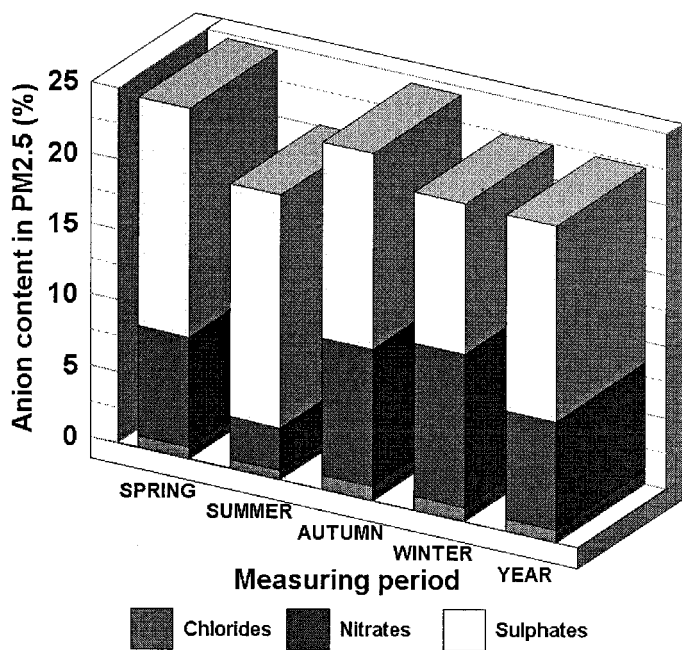**Figure 4.** Distribution of sulphate content (%) in $PM_{2.5}$ particle fraction

Figure 5. Overall anion mass content (%) in $PM_{2.5}$ particle fraction

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