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Characterisation of Major Acidic Anions in TSP and PM_{10} in Zagreb Air

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Abstract This article presents the results of mass concentration of major acidic anions (chlorides, nitrates and sulphates) in TSP and PM_{10} particle fraction in Zagreb air measured continuously at one measuring site in 2004. The annual average mass concentrations of the investigated anions followed the order chloride < nitrate < sulphate. Significant correlations were obtained between TSP and investigated anions and between PM_{10} and investigated anions, the latter showing a higher correlation coefficient. The annual average mass ratio of $(NO_3^-)/(SO_4^{2-})$ obtained in TSP and PM_{10} was >0.8, which suggests that mobile source emission was an important contributor to particle mass.

Keywords Chlorides · Nitrates · Sulphates · Source emission

Airborne particulate matter is a complex mixture of solid particles and liquid droplets suspended in the air. They vary in size, chemical composition and origin. Epidemiological studies have shown that 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). Even though significant association between total suspended particulate matter (TSP) and adverse health effects have been reported, much higher correlation levels were found for thoracic particle fraction (PM_{10}—particle with equivalent aerodynamic diameter <10 μm) and high-risk respirable particle fractions ($PM_{2.5}$—particle with equivalent aerodynamic diameter <2.5 μm) and their constituents (Lippmann and Thurston 1996). It is evident that aerosol acidity is the crucial factor in adverse health effects of particulate matter. Acid aerosols in the air are formed primarily from the oxidation of sulphur oxides, nitrogen oxides, and hydrocarbons, mainly originating from combustion sources (Khoder 2002; Brook et al. 1997; Wyers and Duyzer 1997).

This article presents the results of mass concentration of major acidic anions (chlorides, nitrates and sulphates) in TSP and PM_{10} particle fraction in Zagreb air measured over a year.

Materials and Methods

Twenty-four-hour samples of TSP and PM_{10} 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. Sampling was carried out continuously throughout the year 2004. Samples of TSP and PM_{10} particle fraction were collected on quartz filters at the average sampling flow rate of 70 Lpm, from approximately 100 m^3 of ambient air. For collecting of PM_{10} particle fraction inertial impactor was used. Filters were dried to constant humidity in a desiccator for 24 h before and after sampling. Particle mass concentration was determined by gravimetry. Mettler Tolledo MX5 microbalance was used. After that all the filters were cut into two parts. One half of the sampling filter was used to analyse acidic anions.

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Samples were extracted from filters using an ultrasonic bath for 1 h at 40°C. The undissolved part was separated by centrifugation. For anion content measurement we used a Dionex-120 ion chromatograph equipped with suppressed conductivity detection, a Dionex AS14: 4 mm Analytical Column and AG14: 4 mm Guard Column. For preparation of calibration curves, commercial anion standard mix solution (Dionex) was 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, 0.06 $\mu g\ m^{-3}$ for nitrates and 0.20 $\mu g\ m^{-3}$ for sulphates. 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), medians (C_{50}), and maximum values (C_{max}) of mass concentrations of measured pollutants, as well as the mass ratio of $[NO_3^-]/[SO_4^{2-}]$ obtained in TSP and PM_{10}.

Results show that annual average mass concentrations of TSP and PM_{10} were: 43.9 $\mu g\ m^{-3}$ and 36.2 $\mu g\ m^{-3}$, respectively. The annual average mass concentrations of the investigated anions in TSP and PM_{10} particle fraction followed the order chloride < nitrate < sulphate, and their concentrations were 0.71, 5.30 and 6.29 $\mu g\ m^{-3}$ in TSP, and 0.49, 4.70 and 6.64 $\mu g\ m^{-3}$ in PM_{10}, respectively. The regression analysis (Table 2) showed that the 88.6% of TSP mass was present in PM_{10} particle fraction, as well as (25.9%) of chlorides, (67.2%) of nitrates, and (84.2%) of sulphates were present in the PM_{10} particle fraction.

Table 3 shows the correlation coefficients between pollutant mass concentrations in TSP for entire year. The same parameters for PM_{10} particle fraction are presented in Table 4.

Significant correlations were obtained between TSP and investigated anions and between PM_{10} and investigated anions, as well as between nitrates and sulphates, and nitrates and chlorides in TSP and PM_{10}, indicating that pollutants may have originated from the same sources or that the intensity of the pollutant source is relatively constant. No significant correlation was found between chlorides and sulphates in either TSP, or PM_{10} particle fraction.

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

Statistical parameters	N	$C_{avg} \pm$ SD	C_{50}	C_{max}
TSP	362	43.9 ± 21.9	39.8	134.4
Cl^-	359	0.71 ± 0.67	0.44	6.83
NO_3^-	360	5.30 ± 4.53	3.64	28.7
SO_4^{2-}	360	6.29 ± 4.64	5.17	35.04
$[NO_3^-]/[SO_4^{2-}]$	360	0.96 ± 0.63	0.80	3.77
PM_{10}	359	36.2 ± 20.4	32.5	134.0
Cl^-	353	0.49 ± 0.44	0.38	4.40
NO_3^-	353	4.70 ± 4.18	3.31	24.46
SO_4^{2-}	354	6.64 ± 4.96	5.37	38.48
$[NO_3^-]/[SO_4^{2-}]$	352	0.84 ± 0.62	0.68	3.40

N, number of samples; $C_{avg,}$ average values; SD, standard deviation $C_{50,}$ median; C_{max}, maximum values; $[NO_3^-]/[SO_4^{2-}]$, mass ratio

Table 2 Relationship between mass concentrations of pollutants ($\mu g\ m^{-3}$) in TSP (*x*) and PM_{10} (*y*) particle fractions

Pollutant	N	*r*	*p*	$y = a + bx$
TSP (*x*) PM_{10} (*y*)	356	0.948	**	$y = -2.964 + 0.886x$
$(Cl^-)_{TSP}$ (*x*) $(Cl^-)_{PM10}$ (*y*)	347	0.514	**	$y = 0.305 + 0.259x$
(NO_3^-) $_{TSP}$ (*x*) $(NO_3^-)PM_{10}(y)$	349	0.731	**	$y = 1.103 + 0.672x$
$(SO_4^{2-})_{TSP}$ (*x*) $(SO_4^{2-})_{PM10}$ (*y*)	349	0.792	**	$y = 1.326 + 0.842x$

N, number of samples; *r*, correlation coefficient; $^{**}p < 0.01$; $y = a + bx$, linear regression

Table 3 Correlation coefficients between pollutant mass concentrations in TSP

Correlated components	Cl^-	NO_3^-	SO_4^{2-}
TSP	0.398**	0.597**	0.493**
Cl^-		0.464**	0.012
NO_3^-			0.477**

** $p < 0.01$

Table 4 Correlation coefficients between pollutant mass concentrations in PM_{10} particle fraction

Correlated components	Cl^-	NO_3^-	SO_4^{2-}
PM_{10}	0.442**	0.621**	0.521**
Cl^-		0.499**	0.072
NO_3^-			0.397**

$^{**}p < 0.01$

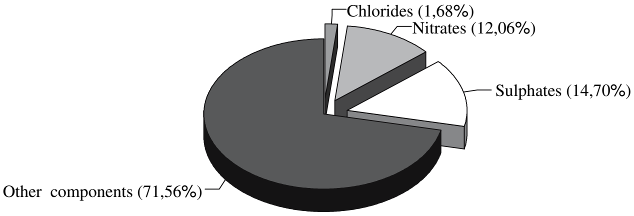

Fig. 1 Anion mass content (%) in TSP in 2004

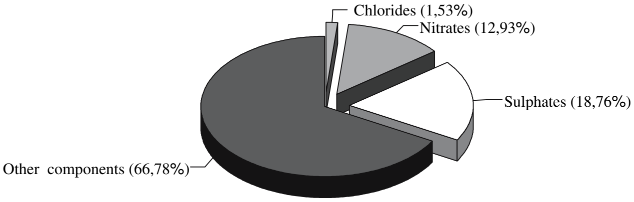

Fig. 2 Anion mass content (%) in PM_{10} particle fraction in 2004

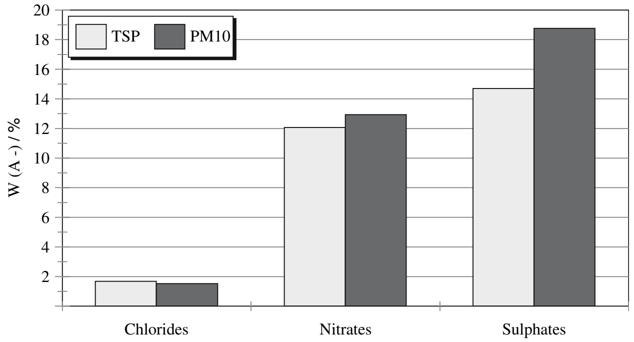

Fig. 3 Comparison of anion mass content (%) in TSP and PM_{10} particle fractions

The mass ratio of $[NO_3^-]/[SO_4^{2-}]$ is therefore used as an indicator of the relative importance of pollutant sources (Xiao and Liu 2004). Annual average mass ratios of $[NO_3^-]/[SO_4^{2-}]$ obtained in TSP and PM_{10} (Table 1) were: 0.96 and 0.84, respectively, which suggests that mobile source emission was an important contributor to particle mass.

Figure 1 shows anion (chlorides, nitrates and sulphates) mass content (%) in TSP, and Fig. 2 in PM_{10} particle fraction. The most contributing to the TSP and PM_{10} mass were sulphates, then nitrates, and then chlorides. Our results show evidently higher contribution of nitrates and sulphates to overall PM_{10} particle mass compared to TSP, while chlorides contributed slightly to the overall TSP mass (Fig. 3).

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