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SULPHATES, NITRATES, AND CHLORIDES IN PARTICLE FRACTIONS OF DIFFERENT SIZE

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This paper describes a pilot study of chloride, nitrate, and sulphate content in thoracic and high-risk respirable fractions of airborne particles. Samples were collected at one measuring site in Zagreb in autumn 1998 and spring 1999. The results showed that almost total chloride, nitrate, and sulphate content was present in the respirable particle fraction. The average mass contribution of these pollutants to the particle mass amounted to 25%. Although chloride mass concentrations were quite low, the findings indicated that all pollutants originated from the same source.

Key words:
ion chromatography, high-risk respirable particle fraction,
thoracic particle fraction

Associations between air pollution, especially particulate matter, and mortality, morbidity, and different adverse health effects in humans were the aim of numerous epidemiological studies (1–4). The inhaled fraction of airborne particles depends on particle properties (size, shape, and electric charge), direction and velocity of air in the breathing zone, pathway (the nose or mouth) of inhalation, and its intensity. Inhaled particles are deposited inside the respiratory tract or exhaled. The deposition site, as well as the probability for a particle to deposit depend on its properties, breathing pattern, and other factors (5).

Liquid and soluble components of solid particles can become absorbed by body tissues. Corrosive or radioactive particles can cause damage at the deposition site. Insoluble particles can travel to all over the respiratory tract, reach other organs, and start adverse biological processes there.

Even though significant association between total suspended particulate matter (TSP) and health adverse health effects have been reported, much higher correlation levels were found for thoracic particle fraction (PM_{10} : equivalent aerodynamic diameter $< 10 \mu\text{m}$) and high-risk respirable particle fractions ($PM_{2.5}$: equivalent aerodynamic diameter $< 2.5 \mu\text{m}$). *In vitro* and *in vivo* experiments performed by *Li and co-workers* (6)

confirmed a PM_{10} -induced oxidant stress caused by free radical activity at the cellular level, resulting in lung inflammation and epithelial injuries. *Lippman and Thurston* (4) reported significant correlation between TSP, PM_{10} , $PM_{2.5}$, sulphates and mortality, morbidity, and adverse health effects in large populations, as follows: $TSP < PM_{10} < PM_{2.5} < SO_4^{2-}$.

It is evident that aerosol acidity is the crucial factor in adverse health effects of particulate matter, and that sulphates are the best routinely available surrogate metric for H^+ ions. This paper brings the results of a pilot study of sulphate, nitrate, and chloride content in PM_{10} and $PM_{2.5}$ particle fractions in the air in the city of Zagreb, Croatia.

MATERIALS AND METHODS

Sampling

Twenty-four-hour samples of PM_{10} and $PM_{2.5}$ particle fractions were collected in the northern, residential part of Zagreb with moderate to high traffic density during the heating season (autumn 1998 and spring 1999). A fraction coarser than defined by instrument parameters was removed from the air stream by inertial impactors, whereas fine particles were collected on membrane filters (Millipore SSWP09025 and AAWP09025, pore size $0.8 \mu m$) at the average air flow rate of 70 L/min from approximately $100 m^3$ of ambient air.

Sample analysis

Filters were preconditioned to constant humidity ($1.25 g/m^3$, $30.5 ^\circ C$) in a desiccator containing $CaCl_2$ for 24 hours before and after sampling. Mass concentrations of PM_{10} and $PM_{2.5}$ fractions were determined by gravimetry (7). Only 1/4 of each sample was used for chemical analysis. After extraction in an ultrasonic bath (10 ml, 1 h, $40 ^\circ C$) and centrifugation, mass concentrations of water-soluble chloride, nitrate, and sulphate content, were determined by ion chromatography in both particle fractions (column: IonPac AS14 Analytical and AG14 Guard, eluent $3.5 mM Na_2CO_3/1.0 mM NaHCO_3$, flow rate 1.2 ml/min, suppressor: Anion Self-Regenerating Suppressor, recycle mode, detection: conductivity, injection volume: $50 \mu l$) (8).

RESULTS AND DISCUSSION

Table 1 summarises the results of mass concentration for chlorides, nitrates, and sulphates in both particle fractions. Since the distribution of concentrations tended to be asymmetric and skewed towards lower concentration values, medians and quartile ranges were chosen as the measures of a central tendency. The regression analysis (Figure 1) showed that differences in mass concentrations were small between anion

Table 1 Mass concentrations of chlorides, nitrates, and sulphates in airborne particles ($\mu\text{g}/\text{m}^3$)

	N	Average	Minimum	Maximum	Median	C25	C75
Cl ⁻ -10	122	0.384	0.000	1.967	0.343	0.089	0.561
Cl ⁻ -2.5	125	0.334	0.000	1.567	0.293	0.072	0.499
NO ₃ ⁻ -10	122	4.858	0.216	22.865	3.150	1.917	6.073
NO ₃ ⁻ -2.5	125	4.335	0.575	24.221	2.790	1.499	4.990
SO ₄ ²⁻ -10	122	6.378	0.928	26.069	4.700	3.124	7.962
SO ₄ ²⁻ -2.5	125	6.231	0.921	23.539	4.620	3.052	7.712

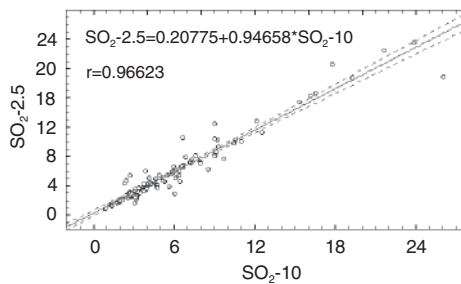
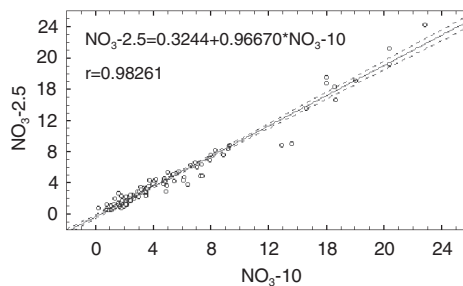
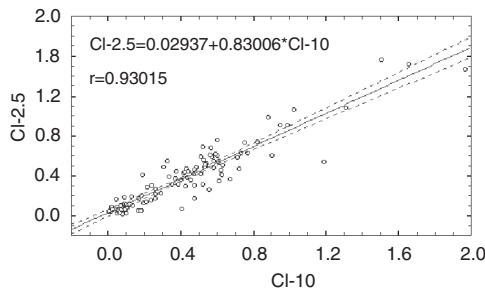


Figure 1 Regression between mass concentrations of chlorides, nitrates and sulphates in PM₁₀ and PM_{2.5} particle fractions ($\mu\text{g}/\text{m}^3$)

contents in the two particle fractions, indicating that chlorides (86%), nitrates, and sulphates (95%) were mainly present in the PM_{2.5} particle fraction.

The relative content of anions in PM_{2.5} mass ranged from 20.2% to 41.6%, with median value of 28.7%. In PM₁₀ mass the anion content ranged from 17.4% to 35.4, with the median of 25% (Table 2). Medians and quartile ranges were again used as a better measure of the central tendency for the same reasons as described above.

Table 2 *Relative content of chlorides, nitrates, and sulphates in overall particle mass*

	N	Average	Median	C25	C75
Cl ⁻ -10 content	110	0.016	0.010	0.006	0.013
Cl ⁻ -2.5 content	112	0.020	0.011	0.006	0.015
NO ₃ ⁻ -10 content	120	0.117	0.099	0.068	0.147
NO ₃ ⁻ -2.5 content	120	0.124	0.106	0.072	0.160
SO ₄ ²⁻ -10 content	121	0.173	0.141	0.100	0.194
SO ₄ ²⁻ -2.5 content	120	0.205	0.170	0.124	0.241

Table 3 shows t-e relations between pollutant concentrations for both particle fractions. Highly significant correlation was found between nitrate and sulphate concentrations for both fractions (65–70% of common variance), indicating that both pollutants may have originated from the same source or that the intensity of the pollution source is relatively constant. The lower correlation between chloride and nitrate and chloride and sulphate concentrations could partly be a consequence of low chloride concentration levels and the fact that only 1/4 of the sample was used for chemical analysis.

Table 3 *Correlations between pollutant mass concentrations*

	Cl ⁻ -10	NO ₃ ⁻ -10	SO ₄ ²⁻ -10		Cl ⁻ -2.5	NO ₃ ⁻ -2.5	SO ₄ ²⁻ -2.5
PM-10	0.5176**	0.8691**	0.7955**	PM-2.5	0.5530**	0.8740**	0.8159**
Cl ⁻ -10		0.4672**	0.2005*	Cl ⁻ -2.5		0.4474**	0.1944*
NO ₃ ⁻ -10			0.8118**	NO ₃ ⁻ -2.5			0.8448**

* P<0.01

** P<0.001

To confirm these findings, we ran a factor analysis with 14 variables. Three extracted factors account for 86% of the variance (Table 4). The first factor describes nitrate and sulphate contribution to the overall particle mass, expressing thus the intensity of the source. The second factor concerns the relative contribution of chlorides, nitrates, and sulphates to the overall particle mass. It does not depend on pollutant concentrations and shows the stability of the source in time. The third factor is related to chlorides only, probably as a consequence of the reasons explained above. If we limit the analysis to the extraction of two factors only, then chlorides are incorporated into the first factor, confirming the above conclusions.

Table 4 Factor loadings

	Factor 1	Factor 2	Factor 3
PM10	0.867*	-0.237	0.354
PM2.5	0.889*	-0.200	0.348
Cl ⁻ -10	0.378	0.102	0.850*
Cl ⁻ -10-content	-0.259	0.825*	0.364
Cl ⁻ -2.5	0.358	-0.011	0.861*
Cl ⁻ -2.5-content	-0.274	0.781*	0.382
NO ₃ ⁻ -10	0.942*	0.023	0.235
NO ₃ ⁻ -10-content	0.144	0.762*	-0.032
NO ₃ ⁻ -2.5	0.933*	0.027	0.235
NO ₃ ⁻ -2.5-content	0.012	0.897	0.049
SO ₄ ²⁻ -10	0.958*	-0.017	-0.006
SO ₄ ²⁻ -10-content	0.007	0.709*	-0.502
SO ₄ ²⁻ -2.5	0.969*	-0.005	-0.011
SO ₄ ²⁻ -2.5-content	-0.101	0.812*	-0.366
% Variance	0.400	0.282	0.178

*factor loading >0.7

CONCLUSIONS

The average contribution of chlorides, nitrates, and sulphates to the total particle mass amounts up to 25%. The results show that almost total chloride, nitrate, and sulphate content is found in the PM_{2.5} particle fraction. Highly significant correlation found between nitrate and sulphate concentrations for both particle fractions (65–70% of common variance) suggests that both pollutants may have originated from the same source or/and that the intensity of the source of these pollutants is relatively constant.

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Sažetak

SULFATI, NITRATI I KLORIDI U FRAKCIJAMA RAZLIČITIH VELIČINA LEBDEĆIH ČESTICA

Istraživanja pokazuju da praćenje razina koncentracija samo ukupnih lebdećih čestica nije dostatno te da je povezanost negativnih zdravstvenih učinaka bolja s razinama koncentracija pojedinih frakcija veličina čestica i njihovih sastojaka. Prikazani su početni rezultati određivanja sadržaja klorida, nitrata i sulfata u inhalabilnoj i respirabilnoj frakciji lebdećih čestica mjerenih na jednome mjernom mjestu u Zagrebu tijekom jeseni 1998. i proljeća 1999. godine. Frakcije PM₁₀ i PM_{2.5} lebdećih čestica skupljane su na membranskim filtrima uz izdvajanje nerespirabilnog dijela čestica iz uzorka uporabom impaktora. Masene koncentracije frakcija lebdećih čestica određene su gravimetrijski, dok su masene koncentracije u vodi topljivih sulfata, nitrata i klorida u frakcijama lebdećih čestica određene metodom ionske kromatografije. Rezultati pokazuju da se pretežni dio navedenih onečišćenja nalazi u respirabilnoj frakciji lebdećih čestica te da njihov doprinos ukupnoj masi čestica iznosi oko 25%. Iako su koncentracije klorida bile pretežito niske, moguće je zaključiti da sva navedena onečišćenja potječu pretežito iz istog izvora.

Ključne riječi:

inhalabilna frakcija čestica, ionska kromatografija, respirabilna frakcija čestica

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