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## ANALYSIS OF THE DATA SET FROM A TWO-YEAR OBSERVATION OF THE AMBIENT WATER-SOLUBLE IONS BOUND TO FOUR PARTICULATE MATTER FRACTIONS IN AN URBAN BACKGROUND SITE IN SOUTHERN POLAND

Ten water-soluble ions ( $F^-$ ,  $Cl^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ ,  $SO_4^{2-}$ ,  $Na^+$ ,  $NH_4^+$ ,  $K^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ), distributed among four fractions of particulate matter, PM, were investigated in an urban background site. The PM was sampled twice a week during a two-year sampling period. Mass distribution among the PM fractions and ambient concentrations of the ten PM-bound ions in the heating and non-heating periods, the seasonal effects in the PM fraction-bound ion concentrations (generalized regression model), and the principal components of all the resulting sets of ambient concentrations (principal component analysis) were determined, discussed, and interpreted in the terms of source apportionment of PM emissions. The formation of secondary inorganic aerosol in transformations of gaseous precursors (e.g.,  $SO_x$ ,  $NO_x$ ,  $NH_3$ ) appeared to be most probable and significant source of  $PM_{2.5}$ , especially of its sub-fraction  $PM_{1-2.5}$ , in the non-heating period. In the heating period, PM and  $PM_{2.5}$  bound water-soluble ions originated mainly from combustion of coal and other solid fuels, or waste. Coarse particles ( $PM_{2.5-10}$  and  $PM_{10-40}$ ) and some  $PM_{2.5-40}$ -bound ions (e.g.  $Na^+$ ,  $K^+$ ,  $Mg^{2+}$ ) may come from re-suspension of mineral matter and road dust. In some part, coarse PM may consist of mineral and salt particles containing gaseous and semi-volatile compounds.

### 1. INTRODUCTION

Dispersed phase of atmospheric aerosol (ambient particulate matter, PM) is a mixture of primary and secondary particles, the former coming directly from the source, the

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latter resulting from various physicochemical processes involving precursor gases and ambient particles [1, 2]. The smallest primary particles come from combustion, their aerodynamic diameters are not greater than 0.3  $\mu\text{m}$ . The mechanically formed primary particles such as particles of eroded rocks, soils, volcanic dust, particles from abrasion of car parts and road surface, or dust re-suspension, usually have diameters greater than 1–2  $\mu\text{m}$ . The particles with diameters between 0.1 and 2.5  $\mu\text{m}$ , which arise from  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$  in chemical transformations, and volatile organic compounds are the secondary particles [1–3].

Although the ways of the PM impact on the environment are not well-recognized, the effects of the toxic content of PM on human health are obvious [4, 5]. Less obvious are the effects of other PM-bound chemicals, often involved as mere catalysts in a chain of chemical reactions yielding a toxic output, or whose less direct environmental effects depend on, for example, their water solubility.

Often, some PM-bound water-soluble inorganic compounds account for important chemical properties of PM [6–9]. Their content in PM can decide on the acidity or conductivity of PM. The PM-bound water-soluble sulfur and nitrogen compounds can make precipitation and PM deposition acidic [3, 10, 11]; the deposition of PM rich in water-soluble compounds of calcium, magnesium, potassium or sodium increases the environmental alkalinity [3, 9–12]. Dispersing sun light, particles of these compounds affect visibility; acting as cloud condensation nuclei, they influence the climate [3, 13, 14].

The amounts of secondary inorganics in PM can be derived from the amounts of sulfate, nitrate, and ammonium ions in PM water-extract; the amounts of sodium in PM water extracts allow us to assess the amounts of marine salt in the air; the potassium amounts – the biomass combustion contribution to PM. This way, the water-soluble compound content of PM, derived from the amounts of ions in PM water extracts, points to the PM source [5–17].

The first in Poland long-term (two-year) investigation of size-resolved PM for water-soluble ions is presented. The goal of the work was to closely examine the seasonal variability of the ambient concentrations, the chemical compounds of occurrence in PM, and the origins of ten water-soluble ions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) distributed among four PM fractions ( $\text{PM}_1$ ,  $\text{PM}_{1-2.5}$ ,  $\text{PM}_{2.5-10}$ ,  $\text{PM}_{10-40}$ , particles with aerodynamic diameters:  $\leq 1 \mu\text{m}$ , 1–2.5  $\mu\text{m}$ , 2.5–10  $\mu\text{m}$ , 10–40  $\mu\text{m}$ , respectively) in a typical urban area in Southern Poland.

## 2. MATERIALS AND METHODS

PM was sampled at the urban background site in Zabrze, Upper Silesia in Southern Poland [17–20]. Samples of PM were taken twice a week during two calendar years; a single sample-taking lasted 48 h. A four stage DEKATI low pressure impactor (DEKATI-PM10) was used, which collects three PM fractions ( $\text{PM}_{1-2.5}$ ,  $\text{PM}_{2.5-10}$ ,

PM<sub>10-40</sub>) onto three aluminum foil substrates (Ø25 mm) and one fraction (PM<sub>1</sub>) onto a PTFE afterfilter (Ø47 mm). The principle of the DEKATI-PM10 operating, description of the measuring site, and technical details of the measurements can be found elsewhere [19]. Before and after exposing, all the filters and substrates were conditioned in a weighing room (48 h, relative air humidity 45±5%, air temperature 20±2 °C), and weighed twice, with 24 h period between, on a Mettler Toledo microbalance (resolution 2 µg). The samples were kept in a refrigerator in tight and lightproof containers.

For each of the calendar month in the sampling period, a collective sample of each PM fraction was made by merging all this PM fraction samples from this month together (in total, 24 monthly samples for each PM fraction were obtained). Water extracts of PM were made by ultrasonizing the monthly samples in 50 cm<sup>3</sup> of deionized water for 60 min at 15 °C, then shaking them for about 12 h (18 °C, 60 r/min).

The ion content in the extracts was determined using a Metrohm ion chromatograph (Herisau Metrohm AG). The chromatographic analysis, the validation process of the whole method, and the values of the validation parameters (standard recoveries, detection limits, etc.) have been presented elsewhere [19]. Existence of a possible time dependence of the fraction-bound ion concentration was examined (yes–no) by applying the generalized regression model (GRM) to the concentration set of each of the ions and for each PM fraction separately. Further analysis of data consisted in the application of principal component analysis (PCA) to each of the four PM fraction-associated 10×24 data matrices (10 ions monitored×24 monthly concentrations) of ion concentrations, and to 10×24 data matrix of the ion concentrations summed over four fractions and representing the monthly total PM-bound ion concentrations. For each PM fraction with the GRM output yes, i.e. showing a clear seasonal effect, PCA was additionally applied to the two 10×12 matrices of the monthly ion concentrations associated with the seasons of the year (the heating and non-heating periods). All the computations were performed by using the Statistica 8.0 and customized Eco Data Miner [21, 22].

### 3. RESULTS AND DISCUSSION

#### 3.1. AMBIENT PM-BOUND ION CONCENTRATIONS AND MASS DISTRIBUTIONS OF THE IONS AMONG THE PM FRACTION

The high linear correlation between monthly concentrations of total cations ( $\Sigma\text{cations}$ , neq/m<sup>3</sup>) and total anions ( $\Sigma\text{anions}$ , neq/m<sup>3</sup>) in total PM (the sums of the concentrations in PM<sub>1</sub>, PM<sub>1-2.5</sub>, PM<sub>2.5-10</sub>, and PM<sub>10-40</sub>) (Fig. 1) suggests that the determined anions are bound to the determined cations and both occur in the same chemical compounds in PM. The ratios  $\Sigma\text{cations}/\Sigma\text{anions}$  between 0.7 and 1.2, only four being greater than 1, mean acidity of PM; sulfates and nitrates might have partly come from sulfuric and nitric acids [3]. Averaged in the periods (non-heating period, NHP, from April to

September, heating period, HP, from October to January), these proportions were also similar (Table 1).

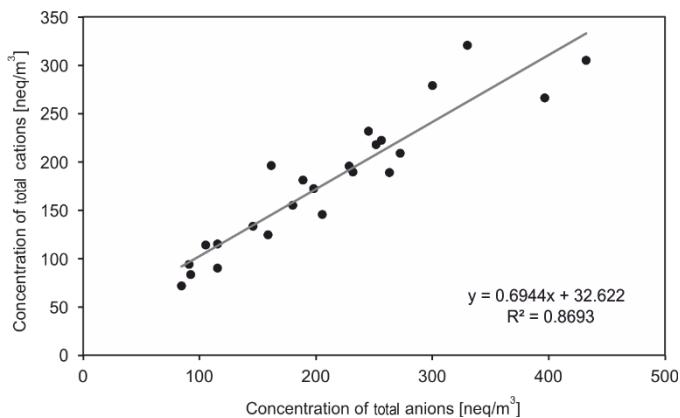


Fig. 1. Correlation between monthly concentrations ( $n = 24$ ) of PM-related total cations and total anions

Table 1

Ambient concentrations [ $\text{ng}/\text{m}^3$ ] of PM-bound fraction-resolved ions and the ratios of average concentration of total cations ( $\Sigma\text{cat}$ ) [ $\text{neq}/\text{m}^3$ ] to total anions ( $\Sigma\text{an}$ ) [ $\text{neq}/\text{m}^3$ ]

Fraction	$\text{F}^-$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{PO}_4^{3-}$	$\text{SO}_4^{2-}$	$\text{Na}^+$	$\text{NH}_4^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\frac{\Sigma\text{cat}}{\Sigma\text{an}}$	
Non-heating period (NHP) from April to September												
$\text{PM}_{10}$	mean	8	345	1041	637	3296	1463	345	296	299	107	0.9
	st. dev.	9	286	644	1317	760	495	283	153	478	117	
$\text{PM}_{1-2.5}$	mean	1	91	350	bdl	403	65	78	44	56	30	0.7
	st. dev.	1	115	216	bdl	145	24	118	20	54	25	
$\text{PM}_{2.5-10}$	mean	1	44	300	bdl	175	56	9	27	56	38	0.7
	st. dev.	3	53	102	bdl	50	29	10	19	52	27	
$\text{PM}_{10-40}$	mean	bdl	13	72	bdl	90	19	5	21	53	29	1.2
	st. dev.	bdl	16	38	bdl	23	8	6	21	49	22	
Heating period (H) from October to January												
$\text{PM}_{10}$	mean	16	2318	2511	919	3487	2127	1111	590	480	85	0.9
	st. dev.	18	712	642	1882	736	806	513	404	860	110	
$\text{PM}_{1-2.5}$	mean	2	709	608	bdl	721	127	331	88	70	65	0.7
	st. dev.	2	239	325	bdl	525	44	223	70	60	49	
$\text{PM}_{2.5-10}$	mean	1	191	267	bdl	264	107	84	33	47	39	0.9
	st. dev.	3	84	119	bdl	88	43	208	28	52	25	
$\text{PM}_{10-40}$	mean	1	59	78	bdl	140	39	6	8	49	26	0.8
	st. dev.	2	109	204	bdl	121	35	8	19	107	27	

mean – arithmetic mean, st. dev. – standard deviation, bdl – below detection limit.

The ambient monthly concentrations of sulfates, nitrates, sodium, and chlorides were the highest and varied widely (Table 1, Fig. 2). In particular fractions, the concentrations of sulfates were higher than the concentrations of nitrates, sodium, and chlorides.

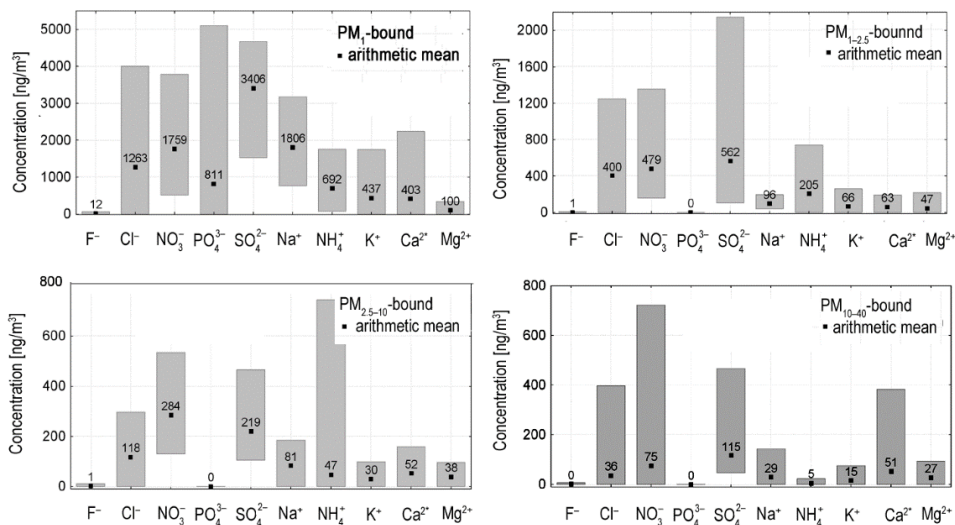


Fig. 2. Monthly concentrations of PM fraction-resolved ions and their arithmetic means; the range of ion concentrations corresponds to the positions of the grey rectangles

The concentrations of these ions were higher rather in the heating period than in non-heating one. The differences between their seasonal concentrations are most clear among PM<sub>1</sub>- and PM<sub>1-2.5</sub>-bound ions. The remaining PM<sub>1</sub>- and PM<sub>1-2.5</sub>-bound ion seasonal concentrations, except for magnesium, had also very wide value intervals. The ambient concentrations of total ion ( $\Sigma$ ion) associated with PM<sub>1</sub>- and PM<sub>1-2.5</sub> behaved similarly to the concentrations of PM (Fig. 3), and were lower in summer and higher in winter. Greater parts of the NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> masses were in PM<sub>2.5</sub>. The average HP and NHP mass contributions of PM<sub>1</sub>-bound SO<sub>4</sub><sup>2-</sup> to the total PM-bound SO<sub>4</sub><sup>2-</sup> mass were 75 and 83%, respectively; for PM<sub>1</sub>-bound PO<sub>4</sub><sup>3-</sup> it was 100%. In average, the PM<sub>1</sub>- and PM<sub>1-2.5</sub>-bound NO<sub>3</sub><sup>-</sup> contributed 72 and 17% in the heating and 59 and 20% in the non-heating periods to the total PM-bound NO<sub>3</sub><sup>-</sup> mass. The NH<sub>4</sub><sup>+</sup> like SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> also accumulated in PM<sub>2.5</sub> in both the heating and non-heating periods.

In European urban and rural areas, the collective mass of PM-bound SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> is between 20 and 56% of the total mass of PM<sub>2.5</sub> [17, 18]. In Zabrze, it was less than 10% in the heating period and almost 40% in the non-heating one.

Usually, ammonium ions are the main neutralizer of ambient SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> ions [3, 7–16]. Sulfate, nitrate and ammonium ions together constitute secondary inorganic

aerosol (SIA). SIA is this part of PM that arises from transformations of gaseous precursors such as  $\text{SO}_2$  and  $\text{NO}_x$ . In the air,  $\text{SO}_2$  is oxidized to gaseous  $\text{SO}_3$  or liquid  $\text{H}_2\text{SO}_4$ , then neutralized to ammonium sulfate ( $(\text{NH}_4)_2\text{SO}_4$ ) or ammonium bisulfate ( $\text{NH}_4\text{HSO}_4$ ).  $\text{NO}_x$  oxidize photochemically to  $\text{HNO}_3$  that is neutralized to ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) [3]. In Zabrze, the monthly concentrations of  $\text{SO}_2$  and  $\text{NO}_x$  were linearly correlated with the monthly concentrations of SIA<sup>4</sup> ( $R^2 = 0.52$  and  $0.56$ , respectively for  $\text{PM}_{10}$ -bound SIA).

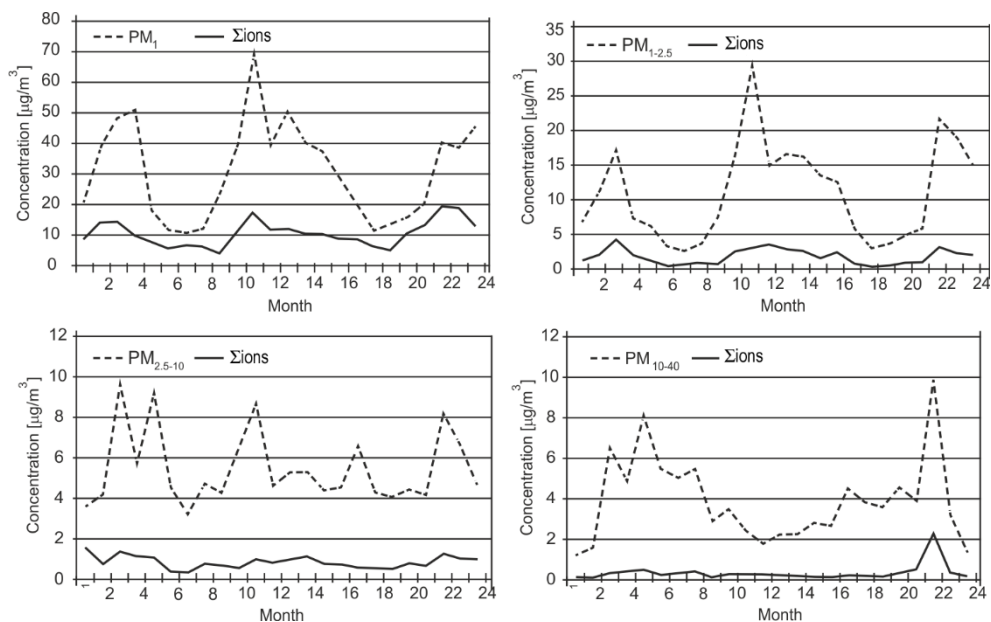


Fig. 3. Monthly ambient concentrations of the four PM fractions and their total ion contents

Meteorological conditions in a hot period are not favorable to ammonium nitrate formation in the air because ammonium tends to neutralize sulfates first. When it is cold, ammonium is more probable to occur in the amount sufficient to neutralize sulfuric and nitric acids, and then to give rise to ammonium nitrate (cf. Fig. 4). In the hot periods, the monthly ambient concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$  and SIA were very close, and probably majority of  $\text{SO}_2$  was first oxidized to sulfuric acid and then neutralized to ammonium sulfate or ammonium bisulfate. The concentrations of  $\text{NO}_x$ ,  $\text{NO}_3^-$  and SIA behaved similarly to each other in cold periods; it may point to  $\text{NH}_4\text{NO}_3$  formation as the source of the ambient  $\text{NO}_3^-$ . However, during the whole year, some, or even total, nitric acid might be neutralized by cations, e.g.  $\text{Na}^+$  or  $\text{Ca}^{2+}$ , through the formation of  $\text{NaNO}_3$  and

<sup>4</sup>The SIA concentration is here the sum of the concentrations of  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ .

$\text{Ca}(\text{NO}_3)_2$ , especially in summer. Also, some sulfate ions could react with sodium and calcium ions to form  $\text{K}_2\text{SO}_4$  and  $\text{CaSO}_4$ , respectively [3, 11, 15, 17].

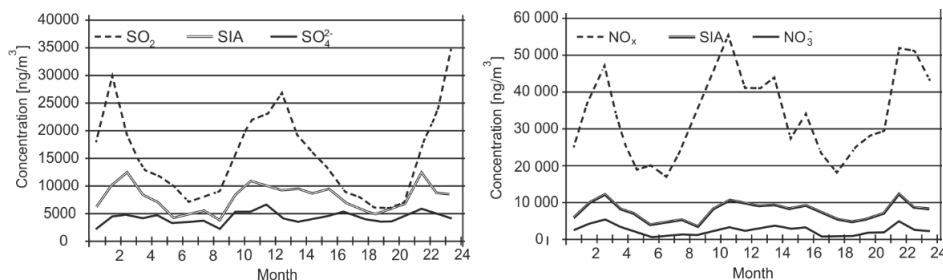


Fig. 4. Monthly ambient concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_x$ ,  $\text{NO}_3^-$ , and SIA

For each PM fraction, the monthly ambient concentrations of  $\text{Cl}^-$  were from 4 to 8 times higher in the heating than in the non-heating periods (Table 1). The mass of  $\text{PM}_{2.5}$ -bound  $\text{Cl}^-$  was about 90–96% in the monthly PM-bound  $\text{Cl}^-$  masses in the heating period, and 85–90% in the non-heating one. The monthly mass shares of the of  $\text{PM}_{2.5-10}$  and  $\text{PM}_{10-40}$ -bound  $\text{Cl}^-$  in the PM-bound  $\text{Cl}^-$  monthly masses were greater in the non-heating periods than in the heating ones, but never exceeded 20%.

$\text{Na}^+$  had also high concentrations in the heating period. It accumulated mainly in  $\text{PM}_1$ , the monthly masses of  $\text{PM}_1$ -bound  $\text{Na}^+$  being more than 90% of the monthly masses of PM-bound  $\text{Na}^+$  in both periods. The  $\text{PM}_{2.5}$ -bound  $\text{Cl}^-$  higher ambient concentrations and higher  $\text{Cl}^-$  and  $\text{Na}^+$  shares in the  $\text{PM}_{2.5}$  mass in the heating period suggest that local  $\text{NaCl}$  sources, such as combustion of fossil fuels, biomass, and house garbage in household stoves, have considerable share in  $\text{Cl}^-$  and  $\text{Na}^+$  emissions [17, 18].  $\text{Cl}^-$  and  $\text{Na}^+$  in coarse PM were secondary, they came mainly from the salt used to deice roads in winter [15, 18].

The high  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  contents of  $\text{PM}_{2.5}$  suggest that these ions are anthropogenic, like  $\text{Cl}^-$  and  $\text{Na}^+$ , especially in winter. The mass shares of  $\text{PM}_1$ -bound  $\text{K}^+$  in the samples were 82 and 76% of the mass of PM-bound  $\text{K}^+$  in the heating and non-heating periods, respectively; for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  they were 64 and 74% and 52 and 40%, respectively. The mass shares of  $\text{PM}_{2.5}$ -bound  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$  in the samples were higher: 94 and 87%, 85 and 76%, and 70 and 67% of their mass in PM, respectively in the heating and the non-heating periods.

### 3.2. QUANTITATIVE ANALYSIS

The GRM trials revealed seasonal effects in ambient concentrations of at least several water-soluble ions from each  $\text{PM}_1$ ,  $\text{PM}_{1-2.5}$ , and  $\text{PM}_{2.5-10}$ , and of none from  $\text{PM}_{10-40}$  (Table 2). PCA was applied separately to each of the two sets of the seasonal monthly

concentration of PM<sub>1</sub>-, PM<sub>1-2.5</sub>-, and PM<sub>2.5-10</sub>-bound ions and to each two-year monthly concentration set of PM<sub>1</sub>-, PM<sub>1-2.5</sub>-, PM<sub>2.5-10</sub>-, and PM<sub>10-40</sub>-bound ions (Table 3).

The first three principal components, PC1, PC2, and PC3 for the two-year set of PM<sub>1</sub>-bound ion monthly ambient concentrations accounted for 81% of the transformed set variance. Among all the correlations between the PCs and the observed variables (monthly ion concentrations), the correlations of the concentrations of (PM<sub>1</sub>-bound) Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and K<sup>+</sup> with PC1 (eigenvalue = 3.78, 38% of total variance) were the strongest, those of the concentrations of PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, and Ca<sup>2+</sup> with PC2 (eigenvalue = 2.91) the second strongest, and of the concentrations of NH<sub>4</sub><sup>+</sup> with PC3 (eigenvalue = 1.45) – the third strongest (Table 3). For PM<sub>1-2.5</sub>, similarly to PM<sub>1</sub>, the strongest relationships occurred between PC1 (Eigenvalue = 3.92) and the concentrations of Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>, but also for the concentrations of NH<sub>4</sub><sup>+</sup>. These high correlations between PC1 and the PM<sub>1-2.5</sub>-bound NH<sub>4</sub><sup>+</sup> concentrations may mean the presence in PM<sub>1-2.5</sub> of one of the main constituents of secondary inorganic aerosol, NH<sub>4</sub>NO<sub>3</sub>. In PM<sub>1</sub>, instead, NH<sub>4</sub><sup>+</sup> (NH<sub>3</sub> in the air), the main H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> neutralizer, almost solely makes PC3, and PM<sub>1</sub>-bound NO<sub>3</sub><sup>-</sup> probably occurred in compounds with K<sup>+</sup>, both being highly correlated with PC1. Besides, the possible PM<sub>1</sub>-bound compounds were KCl, CaSO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (K<sup>+</sup> and Cl<sup>-</sup> correlated with PC1 for the two-year period, and Ca<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup> with PC2).

Table 2

Results from GRM  
– seasonal effects in the four PM fractions

Ion	PM <sub>1</sub>	PM <sub>1-2.5</sub>	PM <sub>2.5-10</sub>	PM <sub>10-40</sub>
F <sup>-</sup>	no	no	no	no
Cl <sup>-</sup>	yes	yes	yes	no
NO <sub>3</sub> <sup>-</sup>	yes	yes	no	no
PO <sub>4</sub> <sup>3-</sup>	no	no	no	no
SO <sub>4</sub> <sup>2-</sup>	no	yes	yes	no
Na <sup>+</sup>	yes	yes	yes	no
NH <sub>4</sub> <sup>+</sup>	yes	yes	no	no
K <sup>+</sup>	yes	yes	no	no
Ca <sup>2+</sup>	no	no	no	no
Mg <sup>2+</sup>	no	yes	no	no

Each two-year set of monthly ion concentrations for PM<sub>1</sub>, PM<sub>1-2.5</sub>, and PM<sub>2.5-10</sub>, according to GRM clearly affected by a season, was split into two seasonal sets to which PCA was applied separately. The seasonal effects appeared also in the virtual sources of PM<sub>1</sub>, PM<sub>1-2.5</sub>, and PM<sub>2.5-10</sub> determined by using PCA [23, 24].

The PC1 (eigenvalue = 4.1) for the heating period was correlated with the ambient concentrations of PM<sub>1</sub>-bound Mg<sup>+</sup>, Ca<sup>2+</sup>, and PO<sub>4</sub><sup>3-</sup> the strongest, negatively. For the



non-heating period PC1 is correlated the strongest with the  $\text{PM}_1$ -bound  $\text{F}^-$  and  $\text{K}^+$ , but positively. Therefore, salts  $\text{Ca}_3(\text{PO}_4)_2$  and  $\text{Mg}_3(\text{PO}_4)_2$  probably occur in  $\text{PM}_1$  in the heating period and various potassium salts in the non-heating period [25]. PC2 for the heating period was highly (negatively) correlated with  $\text{PM}_1$ -bound  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  (possible  $\text{PM}_1$ -bound  $\text{Na}_2\text{SO}_4$  occurrence); in the non-heating period these correlations were much weaker. Both PC3s, for the heating and the non-heating periods, were equally highly correlated with the concentrations of  $\text{PM}_1$ -bound  $\text{NH}_4^+$ .

The PC1 for the heating period was strongly correlated with the monthly concentrations of  $\text{PM}_{1-2.5}$ -bound  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , suggesting the presence of  $\text{NH}_4\text{NO}_3$  in this  $\text{PM}$  fraction in the heating period. Probably, also  $(\text{NH}_4)_2\text{SO}_4$  occurred in  $\text{PM}_{1-2.5}$  in the non-heating, and  $\text{NH}_4\text{Cl}$  in both periods. The PC3 for the whole measuring period and the PC2 for the heating period were highly correlated with the concentrations of  $\text{PM}_{1-2.5}$ -bound  $\text{SO}_4^{2-}$ - $\text{PM}_{1-2.5}$  could contain not neutralized  $\text{H}_2\text{SO}_4$ , and be acidic [3, 8, 17].

Table 3

The PCA of the sets of  $\text{PM}$ -bound ion concentrations in the HP, NHP, and in the whole measuring period (HP + NHP)

$\text{PM}_1$	HP + NHP			HP			NHP			
	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	
$\text{F}^-$	0.57	0.15	-0.61	0.42	-0.08	-0.80	0.88	-0.13	-0.22	
$\text{Cl}^-$	0.87	-0.37	0.20	0.74	-0.42	0.39	0.70	-0.54	0.38	
$\text{NO}_3^-$	0.77	-0.42	0.11	0.47	-0.33	-0.05	0.30	-0.67	0.43	
$\text{PO}_4^{3-}$	-0.43	-0.80	-0.29	-0.88	-0.34	-0.05	-0.51	-0.60	-0.60	
$\text{SO}_4^{2-}$	-0.07	-0.74	0.14	-0.45	-0.74	0.41	-0.31	-0.53	0.29	
$\text{Na}^+$	0.61	-0.44	-0.58	0.20	-0.89	-0.35	0.54	-0.59	-0.58	
$\text{NH}_4^+$	0.53	-0.38	0.70	0.23	0.24	0.84	-0.21	-0.44	0.87	
$\text{K}^+$	0.81	-0.14	-0.04	0.63	-0.63	0.22	0.76	-0.14	0.01	
$\text{Ca}^{2+}$	-0.41	-0.81	-0.23	-0.90	-0.30	0.01	-0.46	-0.63	-0.58	
$\text{Mg}^{2+}$	-0.66	-0.61	0.17	-0.94	-0.12	0.05	-0.88	-0.31	0.22	
Eigenvalue	3.78	2.91	1.45	4.10	2.32	1.83	3.62	2.45	2.28	
Variance	0.38	0.29	0.14	0.41	0.23	0.18	0.36	0.25	0.23	
$\text{PM}_{1-2.5}$	HP + NHP			HP				NHP		
	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	PC 4	PC 1	PC 2	PC 3
$\text{F}^-$	0.61	-0.28	-0.36	-0.58	-0.27	0.14	-0.53	0.92	0.16	0.12
$\text{Cl}^-$	0.89	0.03	-0.08	-0.78	0.06	0.38	0.25	0.93	0.15	0.23
$\text{NO}_3^-$	0.80	-0.06	-0.12	-0.71	0.04	0.01	-0.51	0.96	0.08	0.04
$\text{PO}_4^{3-}$	-	-	-	-	-	-	-	-	-	-
$\text{SO}_4^{2-}$	0.44	0.40	0.72	-0.05	0.74	-0.58	0.14	0.94	-0.10	-0.17
$\text{Na}^+$	0.61	-0.17	-0.42	-0.02	-0.68	0.46	0.32	0.61	0.60	-0.07
$\text{NH}_4^+$	0.91	-0.16	0.29	-0.85	0.09	-0.38	0.06	0.92	-0.15	0.30
$\text{K}^+$	0.59	-0.48	0.37	-0.54	-0.37	-0.42	0.54	0.44	-0.76	0.25
$\text{Ca}^{2+}$	0.50	0.56	-0.20	-0.57	0.53	0.52	0.22	0.51	0.16	-0.77
$\text{Mg}^{2+}$	0.35	0.74	-0.17	0.20	0.59	0.62	0.09	0.33	-0.75	-0.43

Table 3

The PCA of the sets of PM-bound ion concentrations in the HP, NHP,  
and in the whole measuring period (HP + NHP)

Eigenvalue	3.92	1.40	1.14	2.85	1.86	1.69	1.07	5.31	1.62	1.04
Variance	0.44	0.16	0.13	0.32	0.21	0.19	0.12	0.59	0.18	0.12
PM <sub>2.5-10</sub>	HP + NHP			HP			NHP			
	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	
F <sup>-</sup>	-0.05	-0.83	0.24	-0.23	-0.63	0.67	0.84	0.41	-0.15	
Cl <sup>-</sup>	0.50	-0.55	-0.56	0.37	-0.75	-0.41	0.89	0.21	0.36	
NO <sub>3</sub> <sup>-</sup>	-0.13	-0.81	0.41	-0.31	-0.80	0.36	0.78	-0.08	-0.49	
PO <sub>4</sub> <sup>3-</sup>	-	-	-	-	-	-	-	-	-	
SO <sub>4</sub> <sup>2-</sup>	-0.06	-0.34	-0.66	-0.70	0.29	0.39	0.81	-0.05	0.42	
Na <sup>+</sup>	0.77	-0.29	-0.36	0.78	-0.27	-0.22	0.78	-0.38	0.26	
NH <sub>4</sub> <sup>+</sup>	0.78	0.15	0.16	0.83	0.10	0.28	-0.04	0.68	-0.24	
K <sup>+</sup>	0.82	0.06	0.32	0.86	0.00	0.29	0.15	-0.74	-0.53	
Ca <sup>2+</sup>	-0.30	-0.77	0.14	-0.32	-0.80	-0.26	0.61	0.58	-0.39	
Mg <sup>2+</sup>	0.74	-0.09	0.32	0.79	-0.04	0.37	0.49	-0.68	-0.09	
Eigenvalue	2.80	2.47	1.35	3.53	2.40	1.31	4.02	2.17	1.15	
Variance	0.31	0.27	0.15	0.39	0.27	0.15	0.45	0.24	0.13	
PM <sub>10-40</sub>	HP + NHP									
	PC 1	PC 2								
F <sup>-</sup>	-0.88	0.21								
Cl <sup>-</sup>	-0.94	0.25								
NO <sub>3</sub> <sup>-</sup>	-0.96	0.07								
PO <sub>4</sub> <sup>3-</sup>	-	-								
SO <sub>4</sub> <sup>2-</sup>	-0.85	0.37								
Na <sup>+</sup>	-0.87	0.37								
NH <sub>4</sub> <sup>+</sup>	-0.58	-0.42								
K <sup>+</sup>	-0.62	-0.62								
Ca <sup>2+</sup>	-0.95	-0.14								
Mg <sup>2+</sup>	-0.72	-0.50								
Eigenvalue	6.19	1.22								
Variance	0.69	0.14								

The discussion concerning PM-bound ions in the previous section and these observations prove the term favorable having its meaning when applied to the meteorological conditions for SIA formation in the non-heating period.

According to PCA, the two finest PM fractions in Zabrze, PM<sub>1</sub> and PM<sub>1-2.5</sub>, consist partly of SIA. The transformations of the SIA gaseous precursors are probably a significant PM<sub>1-2.5</sub> source, especially in a non-heating period. They are also a source of PM<sub>1</sub>, but not so important.

The correlations of PC1 and Cl<sup>-</sup> point to the combustion of coal or solid waste as a source of fine PM in the heating period. Very much of PM<sub>1</sub> came from combustion

also in the non-heating period, but the correlations between PC1 and the PM<sub>1</sub>-bound K<sup>+</sup> concentrations indicate biomass combustion or combustion of liquid fuels in car engines as the sources. It agrees with the sampling point location within the living quarter, where houses are heated individually with obsolete ovens or boilers in winter, and biomass is combusted in garden parcels in spring and autumn; also the traffic emissions were present in the area in the whole measuring period.

The monthly PM<sub>2.5-10</sub>-bound Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup> concentrations were strongly correlated with the PC1s for both the whole two-year period and the heating period. This coincidence proves PC1 rather an anthropogenic than natural source, although coarse PM is concerned. Instead, correlations of the PM<sub>2.5-10</sub>-bound Ca<sup>2+</sup> concentrations with the PC2s for the two-year and the heating periods suggest PC2 representing natural source, most probably mineral soil re-suspension. In the non-heating period, the PC1, accounting for 40% of the data variance, was highly correlated with the concentrations of PM<sub>2.5-10</sub>-bound F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup>, while PC2 (eigenvalue = 2.17) was correlated only with the K<sup>+</sup> concentration. As far as coarse PM is considered, it may mean both PC1 and PC2 representing re-suspension of mineral matter or road dust [1, 15, 17, 23, 24].

For PM<sub>10-40</sub>, PCA was applied to the whole two-year data set only. The PC1 accounts for more than 69% of the data set variance, and is highly correlated with the monthly concentrations of all PM<sub>10-40</sub>-bound ions except for K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>. The lack of seasonal effects in the observed ion concentrations, mutual relations between them, and the PC1 correlations with the PM<sub>10-40</sub>-bound ion concentrations suggest that PM<sub>10-40</sub> consists of coarse mineral particles and particles of salts covered with gaseous and semi-volatile compounds.

#### 4. CONCLUSIONS

The detailed analysis of the ambient concentrations of water soluble ions distributed among four PM fractions in a typical urban area of Southern Poland can be concluded as follows:

- Independent of the PM fraction, the highest ambient concentrations among ten PM-bound water-soluble F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, SO<sub>4</sub><sup>2-</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, and Mg<sup>2+</sup> were those of Cl<sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>3</sub><sup>-</sup>,
- Each of the ten PM-bound water-soluble ions has the greater part of its mass in PM<sub>2.5</sub>, especially in a heating period; the concentrations of the ions bound to coarse PM are low and do not change with PM concentrations nor seasons (according to GRM, there is no statistical dependence on a season),

- The collective mass of PM<sub>2.5</sub>-bound SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> is less than 10% of the PM<sub>2.5</sub> mass in the heating period and almost 40% in the non-heating period; it may mean 10–40% of PM<sub>2.5</sub> coming from chemical transformations of the SIA gaseous precursors,
- Transformations of the SIA gaseous precursors are probably a significant PM<sub>1–2.5</sub> source; in this PM fraction, in a heating period, NH<sub>4</sub>NO<sub>3</sub> can occur, in a non-heating period – NH<sub>4</sub>NO<sub>3</sub> and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>,
- Salts, such as Na<sub>2</sub>SO<sub>4</sub>, Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, can occur in PM<sub>1</sub> in a heating period and various potassium salts in a non-heating one, and also KCl and NH<sub>4</sub>NO<sub>3</sub> in both periods; it may mean primary/anthropogenic origin of these compounds, so also of the ions into which they dissociate (combustion of solid fuels in ovens and of liquid fuels in car engines),
- In a heating period, PM<sub>2.5–10</sub>-bound Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup> are most probably anthropogenic; PM<sub>2.5–10</sub>-bound ions in a non-heating period, and PM<sub>10–40</sub>-bound ions in both periods, may originate from chemical compounds present in mineral matter or road dust, and also from semi-volatile compounds adsorbed on coarse mineral particles and particles of salts.

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