

WIOLETTA ROGULA-KOZŁOWSKA<sup>1</sup>, GRZEGORZ MAJEWSKI<sup>2</sup>,  
PIOTR O. CZECHOWSKI<sup>3</sup>, PATRYCJA ROGULA-KOPIEC<sup>1</sup>

## 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

---

<sup>1</sup>Institute of Environmental Engineering, Polish Academy of Sciences, ul. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland, corresponding author, e-mail: wioletta@ipis.zabrze.pl

<sup>2</sup>Warsaw University of Life Sciences, Faculty of Civil and Environmental Engineering, ul. No-woursynowska 166, 02-776 Warsaw, Poland.

<sup>3</sup>Gdynia Maritime University, Information Systems Department, ul. Morska 83, 81-225 Gdynia, Poland.









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).

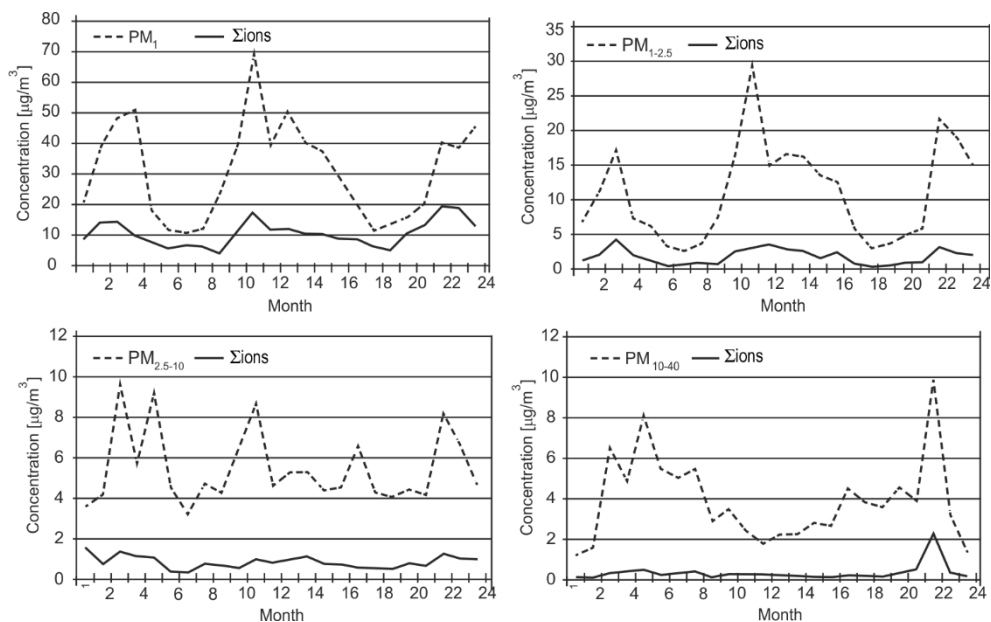


Fig. 3. Monthly ambient concentrations of the four PM fractions and their total ion contents

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].

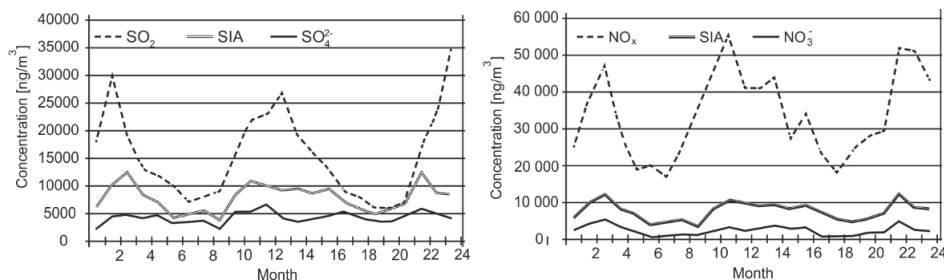


Fig. 4. Monthly ambient concentrations of  $\text{SO}_2$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_x$ ,  $\text{NO}_3^-$ , and SIA

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 PM<sub>1</sub>-bound F<sup>-</sup> and K<sup>+</sup>, but positively. Therefore, salts Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> probably occur in PM<sub>1</sub> in the heating period and various potassium salts in the non-heating period [25]. PC2 for the heating period was highly (negatively) correlated with PM<sub>1</sub>-bound SO<sub>4</sub><sup>2-</sup> and Na<sup>+</sup> (possible PM<sub>1</sub>-bound Na<sub>2</sub>SO<sub>4</sub> 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 PM<sub>1</sub>-bound NH<sub>4</sub><sup>+</sup>.

The PC1 for the heating period was strongly correlated with the monthly concentrations of PM<sub>1-2.5</sub>-bound NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, suggesting the presence of NH<sub>4</sub>NO<sub>3</sub> in this PM fraction in the heating period. Probably, also (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> occurred in PM<sub>1-2.5</sub> in the non-heating, and NH<sub>4</sub>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 PM<sub>1-2.5</sub>-bound SO<sub>4</sub><sup>2-</sup>-PM<sub>1-2.5</sub> could contain not neutralized H<sub>2</sub>SO<sub>4</sub>, and be acidic [3, 8, 17].

Table 3

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

PM <sub>1</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>	0.57	0.15	-0.61	0.42	-0.08	-0.80	0.88	-0.13	-0.22	
Cl <sup>-</sup>	0.87	-0.37	0.20	0.74	-0.42	0.39	0.70	-0.54	0.38	
NO <sub>3</sub> <sup>-</sup>	0.77	-0.42	0.11	0.47	-0.33	-0.05	0.30	-0.67	0.43	
PO <sub>4</sub> <sup>3-</sup>	-0.43	-0.80	-0.29	-0.88	-0.34	-0.05	-0.51	-0.60	-0.60	
SO <sub>4</sub> <sup>2-</sup>	-0.07	-0.74	0.14	-0.45	-0.74	0.41	-0.31	-0.53	0.29	
Na <sup>+</sup>	0.61	-0.44	-0.58	0.20	-0.89	-0.35	0.54	-0.59	-0.58	
NH <sub>4</sub> <sup>+</sup>	0.53	-0.38	0.70	0.23	0.24	0.84	-0.21	-0.44	0.87	
K <sup>+</sup>	0.81	-0.14	-0.04	0.63	-0.63	0.22	0.76	-0.14	0.01	
Ca <sup>2+</sup>	-0.41	-0.81	-0.23	-0.90	-0.30	0.01	-0.46	-0.63	-0.58	
Mg <sup>2+</sup>	-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	
PM <sub>1-2.5</sub>	HP + NHP			HP				NHP		
	PC 1	PC 2	PC 3	PC 1	PC 2	PC 3	PC 4	PC 1	PC 2	PC 3
F <sup>-</sup>	0.61	-0.28	-0.36	-0.58	-0.27	0.14	-0.53	0.92	0.16	0.12
Cl <sup>-</sup>	0.89	0.03	-0.08	-0.78	0.06	0.38	0.25	0.93	0.15	0.23
NO <sub>3</sub> <sup>-</sup>	0.80	-0.06	-0.12	-0.71	0.04	0.01	-0.51	0.96	0.08	0.04
PO <sub>4</sub> <sup>3-</sup>	-	-	-	-	-	-	-	-	-	-
SO <sub>4</sub> <sup>2-</sup>	0.44	0.40	0.72	-0.05	0.74	-0.58	0.14	0.94	-0.10	-0.17
Na <sup>+</sup>	0.61	-0.17	-0.42	-0.02	-0.68	0.46	0.32	0.61	0.60	-0.07
NH <sub>4</sub> <sup>+</sup>	0.91	-0.16	0.29	-0.85	0.09	-0.38	0.06	0.92	-0.15	0.30
K <sup>+</sup>	0.59	-0.48	0.37	-0.54	-0.37	-0.42	0.54	0.44	-0.76	0.25
Ca <sup>2+</sup>	0.50	0.56	-0.20	-0.57	0.53	0.52	0.22	0.51	0.16	-0.77
Mg <sup>2+</sup>	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.

#### ACKNOWLEDGMENTS

The work was carried out within the project No. 2012/07/D/ST10/02895 (ID 202319) financed by the National Science Centre, Poland (NCN). Results from the IEE PAS own projects, realised in 2009–2011, were used.

#### REFERENCES

- [1] CHOW J.C., *Measurement methods to determine compliance with ambient air quality standards for suspended particles*, J. Air. Waste. Manage., 1995, 45, 320.
- [2] HINDS W.C., *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, Wiley, 2012.
- [3] SEINFELD J.H., PANDIS S.N., *Atmospheric Chemistry and Physics. From Air Pollution to Climate Change*, Wiley, 2012.
- [4] HARRISON R.M., YIN J., *Particulate matter in the atmosphere: which particle properties are important for its effects on health?*, Sci. Total. Environ., 2000, 249, 85.
- [5] DAHER N., SALIBA N.A., SHIHADAH A.L., JAAFAR M., BAALBAKI R., SHAFER M.M., SCHAUERD J.J., SIOUTAS C., *Oxidative potential and chemical speciation of size-resolved particulate matter (PM) at near-freeway and urban background sites in the greater Beirut area*, Sci. Total. Environ., 2014, 470, 417.
- [6] SCHLESINGER R.B., *The health impact of common inorganic components of fine particulate matter (PM<sub>2.5</sub>) in ambient air. A critical review*, Inhal. Toxicol., 2007, 19, 811.
- [7] DUVAL R.M., MAJESTIC B.J., SHAFER M.M., CHUANG P.Y., SIMONEIT B.R.T., SCHAUER J.J., *The water-soluble fraction of carbon, sulfur, and crustal elements in Asian aerosols and Asian soils*, Atmos. Environ., 2008, 42, 5872.
- [8] PATHAK R.K., WU W.S., WANG T., *Summertime PM<sub>2.5</sub> ionic species in four major cities of China. Nitrate formation in an ammonia-deficient atmosphere*, Atmos. Chem. Phys., 2009, 9, 1711.

- [9] BANZHAF S., SCHAAP M., WICHINK K.R.J., DENIER VAN DER GON H.A.C., STERN R., BULTJES P.J.H., *Impact of emission changes on secondary inorganic aerosol episodes across Germany*, Atmos. Chem. Phys., 2013, 13, 11675.
- [10] TANG A., ZHUANG G., WANG Y., YUAN H., SUN Y., *The chemistry of precipitation and its relation to aerosol in Beijing*, Atmos. Environ., 2005, 39, 3397.
- [11] ZHANG L., VET R., WIEBE A., MIHELE C., SUKLOFF B., CHAN E., MORAN M.D., IQBAL S., *Characterization of the size-segregated water-soluble inorganic ions at eight Canadian rural sites*, Atmos. Chem. Phys., 2008, 8, 7133.
- [12] SHEN Z., ZHANG L., CAO J., TIAN J., LIU L., WANG G., ZHANG R., LIU S., *Chemical composition, sources, and deposition fluxes of water-soluble inorganic ions obtained from precipitation chemistry measurements collected at an urban site in northwest China*, J. Environ. Monitor., 2012, 14, 3000.
- [13] CHEN J., QIU S., SHANG J., WILFRID O.M., LIU X., TIAN H., BOMAN J., *Impact of relative humidity and water soluble constituents of PM 2.5 on visibility impairment in Beijing, China*, Aerosol Air Qual. Res., 2014, 14, 260.
- [14] MAJEWSKI G., CZECHOWSKI P.O., BADYDA A., BRANDYK A., *Effect of air pollution on visibility in urban conditions. Warsaw case study*, Environ. Prot. Eng., 2014, 40, 47.
- [15] SILLANPÄÄ M., HILLAMO R., SAARIKOSKI S., FREY A., PENNANEN A., MAKKONEN U., SPOLNIK Z., GRIEKEN R.V., BRANIS M., BRUNEKREEF B., CHALBOT M.C., KUHLEBUSCH T., SUNYER J., KERMINEN V.M., KULMALA M., SALONEN R.O., *Chemical composition and mass closure of particulate matter at six urban sites in Europe*, Atmos. Environ., 2006, 40, 212.
- [16] BELIS C.A., KARAGULIAN F., LARSEN B.R., HOPKE P.K., *Critical review and meta-analysis of ambient particulate matter source apportionment using receptor models in Europe*, Atmos. Environ., 2013, 69, 94.
- [17] ROGULA-KOZŁOWSKA W., KLEJNOWSKI K., ROGULA-KOPIEC P., OŚRÓDKA L., KRAJNY E., BŁASZCZAK B., MATHEWS B., *Spatial and seasonal variability of the mass concentration and chemical composition of PM2.5 in Poland*, Air Qual. Atmos. Health, 2014, 7, 41.
- [18] ROGULA-KOZŁOWSKA W., KLEJNOWSKI K., ROGULA-KOPIEC P., MATHEWS B., SZOPA S., *A study on the seasonal mass closure of ambient fine and coarse dusts in Zabrze, Poland*, Bull. Environ. Contam. Toxicol., 2012, 88, 722.
- [19] *Technical report on measurements of fine PM in urban areas, IEE PAS own project 2009–2011*, IEE PAS, Zabrze 2012 (in Polish).
- [20] *Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe*.
- [21] CZECHOWSKI P.O., *Mechanisms for evaluation of data quality in the concept of analytical system Eco Data Miner*, Institute of Maritime Transport, Gdańsk 2009 (in Polish).
- [22] CZECHOWSKI P., BADYDA A., MAJEWSKI G., *Data mining system for air quality monitoring networks*, Arch. Environ. Prot., 2013, 39, 123.
- [23] SÓWKA I., ZWOŹDZIAK A., TRZEPLA-NABAGLO K., SKRĘTOWICZ M., ZWOŹDZIAK J., *PM2.5 elemental composition and source apportionment in a residential area of Wrocław, Poland*, Environ. Prot. Eng., 2012, 38, 73.
- [24] ZWOŹDZIAK A., SAMEK L., SÓWKA I., FURMAN L., SKRĘTOWICZ M., *Aerosol pollution from small combustors in a village*, Sci. World J., 2012, 1–8, ID 956401.
- [25] ROGULA-KOZŁOWSKA W., BŁASZCZAK B., SZOPA S., KLEJNOWSKI K., SÓWKA I., ZWOŹDZIAK A., JABŁOŃSKA M., MATHEWS B., *PM2.5 in the central part of Upper Silesia, Poland: concentrations, elemental composition, and mobility of components*, Environ. Monit. Assess., 2013, 185, 581.