

Size-Resolved Water-Soluble Ionic Composition of Ambient Particles in an Urban Area in Southern Poland

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ABSTRACT

The ambient concentrations of PM-related anions (Cl^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}), total and contained in the PM fractions, were investigated in a typical urban area within the Silesian Agglomeration. A DEKATI low pressure impactor (DLPI) was used to sample PM and separate it into 13 fractions. The PM concentrations were determined gravimetrically, the ion content of the PM water extracts—by means of ion chromatography (Herisau Metrohm AG ion chromatograph). In general, sulfate, nitrate, and ammonia had the greatest ambient concentrations. PM_1 contained over 60% of the PM-related sulfate and nitrate mass and 90% of the ammonia mass. Also the majority of Na^+ and Cl^- were bound onto fine particles. Instead, more of the PM-related K^+ , Ca^{2+} and Mg^{2+} mass were in $\text{PM}_{2.5-10}$ than in $\text{PM}_{2.5}$. In the fine particles (sub-fractions of $\text{PM}_{1.6}$) sulfate, nitrate and ammonia occur mainly as $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 . In the sub-fractions of $\text{PM}_{1.6-10}$ sulfate and nitrate might also occur as K_2SO_4 , CaSO_4 , $\text{Ca}(\text{NO}_3)_2$ or NaNO_3 .

Keywords: Ambient Aerosol; DEKATI; Mass Size Distribution; SIA; Ammonium Sulfate; Ammonium Nitrate; Neutralization Ratio; Upper Silesia

1. Introduction

To assess the impact of atmospheric aerosol on the environment, including air quality, ecosystems, human health and climate change, it is necessary to know its concentration, chemical composition and mass size distribution of PM (ambient particulate matter) components [1-8]. Knowledge of the mass size distribution of PM components is helpful in determining mechanisms of aerosol formation, as well as physical and chemical changes, it is subjected to on a given area [9-13].

Besides the obvious and relatively well-recognized relation between the content of various toxic compounds in ambient dust and human health [14-17], another example of a dust chemical composition impact on the environment, is the effect of some water-soluble inorganic compounds on the acidity and conductivity of aerosols. Under certain conditions, the water-soluble sulfur and nitrogen compounds contained in the dust, contribute to

acidification of precipitation and/or deposition, whereas the deposition of particles rich in the water-soluble calcium, magnesium, potassium or sodium compounds, increases the alkalinity of the environment [18-21].

Water-soluble ions, next to elemental carbon and organic matter, dominate the mass of PM. In urban areas, mass of sulfates (SO_4^{2-}) and nitrates (NO_3^-) associated with particulate matter is even ~80% of all water extracted ions (**Table 1**, [22]) and ~15% - 50% of the total mass of $\text{PM}_{2.5}$ (fine particles, with aerodynamic diameters not exceeding 2.5 μm) [23-26].

Sulfates, nitrates and ammonia are used to determine the share of secondary inorganic aerosol (SIA) in the mass of ambient dust. Oxidation of SO_2 in the air, then a binary nucleation of $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ and ternary $\text{H}_2\text{SO}_4\text{-H}_2\text{O-NH}_3$, results in the formation of dust particles, mostly smaller than 1 μm [19,21,27,28]. These particles, together with nitrate (V) ammonium emerging in the analogous reaction of nitric acid (V) with ammonia, form

Table 1. Ambient concentrations of water-soluble ions ($\text{ng}\cdot\text{m}^{-3}$) related to various PM fractions at various sites in Europe.

City (Country); description of the measuring point; [references]	Averaging period	Fraction	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
Bern (Switzerland); kerbside in the city center; [33]	04.1998-03.1999	$\text{PM}_{2.5}$	102	3000	2800	94	1600	180	132	8.5
		$\text{PM}_{2.5-10}$	1012	1100	700	746	0	48	1420	37
Basel (Switzerland); suburban; [33]	04.1998-03.1999	$\text{PM}_{2.5}$	145	3100	4100	111	2000	218	71	13
		$\text{PM}_{2.5-10}$	111	700	100	128	100	28	279	26
		$\text{PM}_{0.11}$	-	1	48	-	40	46	-	-
K-puszta (Hungary); rural site; [34]	Summer 1999	$\text{PM}_{1.05}$	-	64	2590	-	1139	198	-	-
		$\text{PM}_{2.60}$	-	95	2655	-	1173	240	-	-
		$\text{PM}_{10.77}$	-	133	2667	-	1194	286	-	-
Bemantes (Spain); seaside background; [35]	Whole year 2001	PM_{10}	1259	862	-	-	1329	-	-	-
		$\text{PM}_{2.5}$	555	399	-	-	1152	-	-	-
Barcelona (Spain); impact of industry; [36]	Whole year 2001	PM_{10}	-	7200	-	-	3900	-	-	-
		$\text{PM}_{2.5}$	-	5200	-	-	3700	-	-	-
Tarragona (Spain); impact of road traffic; [36]	Whole year 2001	PM_{10}	-	6000	-	-	2200	-	-	-
		$\text{PM}_{2.5}$	-	3800	-	-	1600	-	-	-
Helsinki (Finland); urban background; [37]	08.2002-09.2002	$\text{PM}_{2.5}$	11.9	303	1850	61.6	791	47.1	24.1	9.35
		$\text{PM}_{2.5-10}$	124	445	146	122	20.8	15.4	191	27.8
Menen (Belgium); suburban; [38]	Spring 2003	$\text{PM}_{2.5}$	260	8120	4760	-	2340	120	80	20
	Summer 2003	$\text{PM}_{2.5}$	250	4170	3230	-	1920	130	60	20
	Autumn 2003	$\text{PM}_{2.5}$	370	4100	3700	-	1740	210	50	30
	Winter 2003	$\text{PM}_{2.5}$	890	5280	4990	-	1880	250	70	30
	1999/2000	PM_{10}	-	-	-	-	-	-	-	-
	2000/2001	PM_{10}	-	-	-	-	-	-	-	-
	2001/2002	PM_{10}	-	-	-	-	-	-	-	-
Zagreb (Croatia); residential-industrial-traffic site; [39]	2002/2003	PM_{10}	-	-	-	-	-	-	-	-
	2003/2004	PM_{10}	-	-	-	-	-	-	-	-
	2004/2005	PM_{10}	-	-	-	-	-	-	-	-
	2006/2006	PM_{10}	-	-	-	-	-	-	-	-
	Summer season (2004-2008)	PM_{10}	160	-	-	300	-	120	140	50
		$\text{PM}_{2.5}$	50	-	-	110	-	80	80	20
Melpitz (Germany); rural background; [40]	Winter season (2004-2008)	PM_1	30	-	-	40	-	60	50	10
		PM_{10}	570	-	-	430	-	180	110	70
		$\text{PM}_{2.5}$	240	-	-	160	-	140	70	30
near Chania (Crete, Greece); urban background; [41]	08.2007	PM_{10}	3295	4946	18,725	3397	720	668	511	136
	07.2008	PM_{10}	2649	1620	6353	4432	1466	669	2459	314
Zabrze (Poland); urban background; [this study]	08-12.2008	PM_1	567	715	1284	157	775	163	146	36
		$\text{PM}_{2.5}$	684	880	1706	220	956	184	210	51
		PM_{10}	775	1046	1927	273	962	191	345	79

the SIA. In the air poor in NH_4^+ , sulfuric acid H_2SO_4 can react with mineral dust or sea salt components, generally creating coarse particles of CaSO_4 or $(\text{Na})_2\text{SO}_4$.

The goal of the work was to determine concentration and mass size distribution of eight water-soluble ions (Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+}) related to thirteen PM fractions in a typical urban area of southern Poland. Possible chemical composition of secondary inorganic aerosol in 13 dust fractions was also estimated.

2. Material and Methods

The site of experiment (Zabrze, Poland, **Figure 1**) is located in area representative of the air pollution conditions for the central part of Upper Silesia and it meets the criteria of urban background site (Directive 2008/50/EC). Conditions at this point, characterize well dust concentration in residential areas exposed to municipal and industrial emissions in the Upper Silesia [29].

Samples have been collected from August to December 2008. Fourteen measurements were carried out and each lasted about a week. Dust was collected using a thirteen stage DEKATI low pressure impactor (DLPI) [13].

Masses of dust collected on aluminum substrates, were determined by weighing substrates before and after exposure, on a Mettler Toledo microbalance (accuracy 2 μg). Before weighing the substrates were kept in weighing room for 48 hours (temperature $20^\circ\text{C} \pm 2^\circ\text{C}$, relative air humidity $48\% \pm 5\%$). Concentrations of PM fractions were calculated by dividing each fraction's mass by the volume of air, from which it was collected. Dust samples were kept in a refrigerator in tight and lightproof containers until the analysis.

Thirteen samples were fixed for chromatography analysis - for each fraction, a collective sample from 14 weeks was prepared. Samples were placed in ROTH extraction containers. For the extraction, 50 cm^3 of deionized water was added to each container and the containers were tightly capped to prevent leaking during the extraction. Extracts were then placed in an ultrasonic

bath (60 min), at a temperature not exceeding 15°C . Then, the extraction containers were placed in a vortex mixer and shaken overnight at about 18°C and 60 cycles per minute. Extracts were then filtered through a CRONUS microporous filter with a PES membrane with a porosity of 0.2 microns.

The ion content in the extracts was determined using Metrohm ion chromatograph (Metrohm Herisau AG, Switzerland), equipped with 818 IC Pump, 819 IC Detector, 837 IC Eluent Degasser, 830 IC Interface, 820 IC Separation Center, Metrodata 2.3 programme). The method was previously validated on the basis of certified reference material (CRM Fluka products nos. 89316 and 89886, the standard recovery ranged in 92% - 109%). Detection limits were at the level of: $0.02 \text{ mg}\cdot\text{l}^{-1}$ for NH_4^+ , $0.05 \text{ mg}\cdot\text{l}^{-1}$ for Cl^- , SO_4^{2-} and K^+ , $0.07 \text{ mg}\cdot\text{l}^{-1}$ for NO_3^- and Na^+ , $0.12 \text{ mg}\cdot\text{l}^{-1}$ for Ca^{2+} and Mg^{2+} .

3. Results and Discussion

PM-related Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Ca^{2+} , Mg^{2+} concentrations from Zabrze, were compared with concentrations of these ions from various sites in Europe (**Table 1**). The concentration of the PM_{10} -related ion was calculated by summing its concentrations in following fractions: 0.03 - 0.06 μm , 0.06 - 0.108 μm , 0.108 - 0.17 μm , 0.17 - 0.26 μm , 0.26 - 0.40 μm , 0.40 - 0.65 μm and 0.65 - 1.0 μm . In the case of ions associated with $\text{PM}_{2.5}$, additionally concentrations from fractions: 1.0 - 1.6 μm and 1.6 - 2.5 μm were included and in case of PM_{10} , besides previously mentioned, ion concentrations of 2.5 - 4.4 μm ; 4.4 - 6.8 μm and 6.8 - 10.0 μm range were summed.

Most of ions' concentrations in Zabrze were comparable to concentrations noted between 1998-2008 in Europe. For example, concentration of sulfates in particulate matter in Zabrze, was comparable to the concentration recorded at two sites in Switzerland, suburban station in Menen (Belgium) and urban background station in Helsinki (Finland). Generally, higher concentrations than in Zabrze are listed in Asian countries [13,30, 31]. Concentration of Cl^- associated with fine dust in Zabrze was extraordinarily high comparing to values recorded in other parts of Europe and similar to concentrations of chlorine in Menen and Melpitz, recorded in these cities during the winter season (**Table 1**).

Sulfates, nitrates and ammonia associated with PM_{10} , $\text{PM}_{2.5}$ and PM_{10} , had the highest concentration of the eight analyzed ions in Zabrze (**Tables 1 and 2**). Average mass shares of SO_4^{2-} and NO_3^- in the $\text{PM}_{2.5}$, are about 80% of the total mass (the sum of the masses in all 13 fractions) of sulfates and nitrates, and the average mass share of NH_4^+ is even up to 98% of the total mass of ammonia. More than 60% of sulfates and nitrates mass were related to particles with an aerodynamic diameter

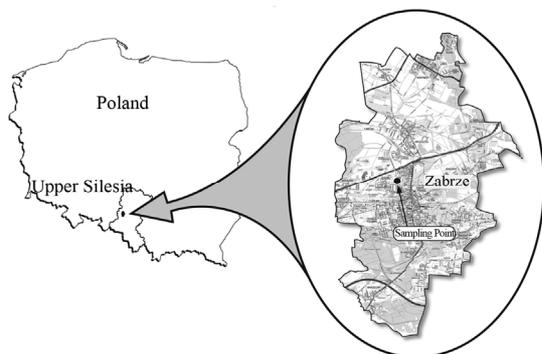


Figure 1. Location of the sampling point.

Table 2. Ambient concentrations of PM ($\mu\text{g}\cdot\text{m}^{-3}$) and PM-related ions ($\text{ng}\cdot\text{m}^{-3}$) from 13 original DLPI fractions of PM at the urban background site.

Fraction	PM	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	Mg^{2+}
1a)	0.34	19.89	20.34	33.97	5.14	28.70	1.66	28.74	3.04
2	0.52	22.59	17.52	44.97	7.46	22.63	7.83	11.38	4.25
3	1.09	29.27	14.34	39.30	13.00	18.36	12.35	17.23	4.81
4	3.05	71.35	35.52	123.07	20.16	54.52	25.28	22.76	5.59
5	5.15	103.79	89.70	221.89	44.91	199.32	46.04	22.72	4.46
6	7.76	171.91	275.77	445.88	35.28	267.35	43.16	18.62	7.02
7	7.65	148.60	261.54	374.47	31.08	184.05	26.25	24.96	6.46
8	5.04	78.80	85.48	245.70	28.25	169.68	12.74	29.35	7.16
9	2.75	38.30	80.20	176.48	34.49	11.81	8.22	34.62	8.66
10	2.35	45.77	88.84	111.14	26.84	2.28	4.46	40.90	9.56
11	1.56	27.52	51.63	67.24	14.19	1.00	2.67	40.68	8.00
12	1.28	16.77	25.46	43.02	12.65	2.39	<i>bl d b)</i>	52.82	10.01
13	1.54	29.30	44.16	97.43	8.06	1.37	2.67	35.55	6.16

a. 1—0.03 - 0.06 μm ; 2—0.06 - 0.108 μm ; 3—0.108 - 0.17 μm ; 4—0.17 - 0.26 μm ; 5—0.26 - 0.40 μm ; 6—0.40 - 0.65 μm ; 7—0.65 - 1.0 μm ; 8—1.0 - 1.6 μm ; 9—1.6 - 2.5 μm ; 10—2.5 - 4.4 μm ; 11—4.4 - 6.8 μm ; 12—6.8 - 10.0 μm ; 13—>10.0 μm ; b. below limit of detection.

$\leq 1 \mu\text{m}$. As to NH_4^+ , it was close to 90%. SO_4^{2-} , NO_3^- and NH_4^+ concentrations were highest in the range of 0.26 - 1 μm . Very similar, bimodal mass size distribution of SO_4^{2-} and NO_3^- , with a maximum occurring between 0.4 - 1 μm (**Figure 2(a)**), means that these ions are parts of the same compounds in the dust. The main mechanism of their formation are presumably the transformation processes of PM gaseous precursors occurring in the atmosphere. PM-related NH_4^+ had multimodal mass size distribution, with a one maximum occurring in the range of 0.4 - 1 μm and two maxima between 1.6 - 10 μm (**Figure 2(b)**).

On the areas where sea spray or sea water evaporation (marine aerosols) and road salt are main sources of sodium and chloride, ambient concentrations of Na^+ and Cl^- related to $\text{PM}_{2.5-10}$ (coarse dust, ambient particles with aerodynamic diameters exceeding 2.5 and not greater than 10 μm) are generally higher than the concentrations of PM_1 - and $\text{PM}_{2.5}$ -related Na^+ and Cl^- (**Table 1**). It is clear that in Zabrze, Na^+ and Cl^- are related mostly with fine dust particles [26,32]. $\text{PM}_{2.5}$ -related Na^+ and Cl^- were respectively 80 and 85% of their total concentration in the air of Zabrze. The highest concentrations of PM-related Na^+ and Cl^- , occurred in similar particle sizes range, as in the case of highest SO_4^{2-} , NO_3^- and NH_4^+ concentrations (**Table 2**). Both, Na^+ and Cl^- , were characterized by unimodal mass size distribution and its maximum occurred in the range of 0.4 - 1 μm (**Figures 2(a)** and **(b)**). This indicates the anthropogenic origin of these ions (combustion processes). It is most likely that Na^+ and Cl^- , occur in the dust mainly

as a sodium chloride.

The concentration of K^+ , Mg^{2+} and Ca^{2+} associated with each of 13 fractions, did not exceed $53 \text{ ng}\cdot\text{m}^{-3}$ (**Table 1**). Masses of these cations were distributed differently among PM fractions. More than 95% of the total mass of K^+ was concentrated in the $\text{PM}_{2.5}$, over 25% of which were $\text{PM}_{0.26-0.4}$ and $\text{PM}_{0.4-0.65}$. Distribution of Ca^{2+} and Mg^{2+} masses among 13 fractions was more variable, although the share of $\text{PM}_{2.5-10}$ -related ions' mass, was much bigger than their contribution in the fine dust particles amount, and was more than 50% of total mass of these ions in the Zabrze air.

Potassium and calcium were characterized by unimodal mass distribution with a maximum—as in the case of SO_4^{2-} , NO_3^- , Na^+ and Cl^- —in the range of 0.26 - 0.65 μm (**Figure 1(b)**), whereas magnesium was determined with multimodal size mass distribution, without clearly dominant maximum. Highest potassium concentrations occurred for particles in the range of 0.17 - 1 μm (**Table 2**). However, higher Mg^{2+} and Ca^{2+} concentrations occurred for particles with an aerodynamic diameter larger than 2.5 μm . Therefore, it seems that K^+ and Ca^{2+} may be present in the compounds with SO_4^{2-} , NO_3^- , Na^+ and Cl^- ions, and their most probable source in Zabrze air are combustion processes. Relatively high proportion of Mg^{2+} in the coarse fraction of particulate matter, proves that mechanical processes, including re-suspension of the soil and road dust could have had an influence on these ions concentration levels.

To assess the neutralizing capacity of occurring simultaneously in the air sulfates and nitrates by ammo-

anium ion, neutralizing ratio (NR) was calculated for each fraction of particulate matter. NR is the ratio of NH_4^+ concentration (in normal equivalent, $\text{neq}\cdot\text{m}^{-3}$) and the sum of NO_3^- and SO_4^{2-} concentrations (in $\text{neq}\cdot\text{m}^{-3}$)—**Table 3**.

For particles not greater than $1.6\ \mu\text{m}$, NR values ranged from ≈ 1 ($\text{PM}_{0.65-1}$, $\text{PM}_{0.17-0.26}$, $\text{PM}_{0.108-0.17}$ and $\text{PM}_{0.06-0.108}$) to 1.82 ($\text{PM}_{0.26-0.4}$). It means that the amount of NH_4^+ related to these dust fractions, was sufficient to neutralize sulfuric and nitric acid completely. This result also proves that ambient fine dust ($\text{PM}_{1.6}$) in Zabrze is alkaline ($\text{NR} \geq 1$).

Stoichiometric ratio for $(\text{NH}_4)_2\text{SO}_4$ of $\text{SO}_4^{2-}/\text{NH}_4^+$ is 2.67. In all fractions of particles $\leq 1.6\ \mu\text{m}$, the ratio of SO_4^{2-} and NH_4^+ (in $\text{neq}\cdot\text{m}^{-3}$) is much lower than 2.67. It confirms the previous deduction, that $\text{PM}_{1.6}$ -related

NH_4^+ in Zabrze occurred in a greater amount than needed to react with the $\text{PM}_{1.6}$ -related SO_4^{2-} completely. Also the condition $\text{NH}_4^+ > \text{SO}_4^{2-}$ (in $\text{neq}\cdot\text{m}^{-3}$) is satisfied. Therefore, the concentration of $(\text{NH}_4)_2\text{SO}_4$ may be estimated from the formula:

$$[(\text{NH}_4)_2\text{SO}_4] = 1.38[\text{SO}_4^{2-}] \quad (1)$$

The concentration of $(\text{NH}_4)_2\text{SO}_4$ associated with particles $\leq 1.6\ \mu\text{m}$, fit within the limits of $615.31\ \text{ng}\cdot\text{m}^{-3}$ ($\text{PM}_{0.4-0.65}$) to $46.88\ \text{ng}\cdot\text{m}^{-3}$ for $\text{PM}_{0.03-0.06}$. The amount (concentration) of NH_4^+ , remaining after reaction with SO_4^{2-} (ammonium ion excess $[\text{ex-NH}_4^+]$) and ammonium nitrate concentration associated with each fractions of particles $\leq 1.6\ \mu\text{m}$, was calculated from the following formulas:

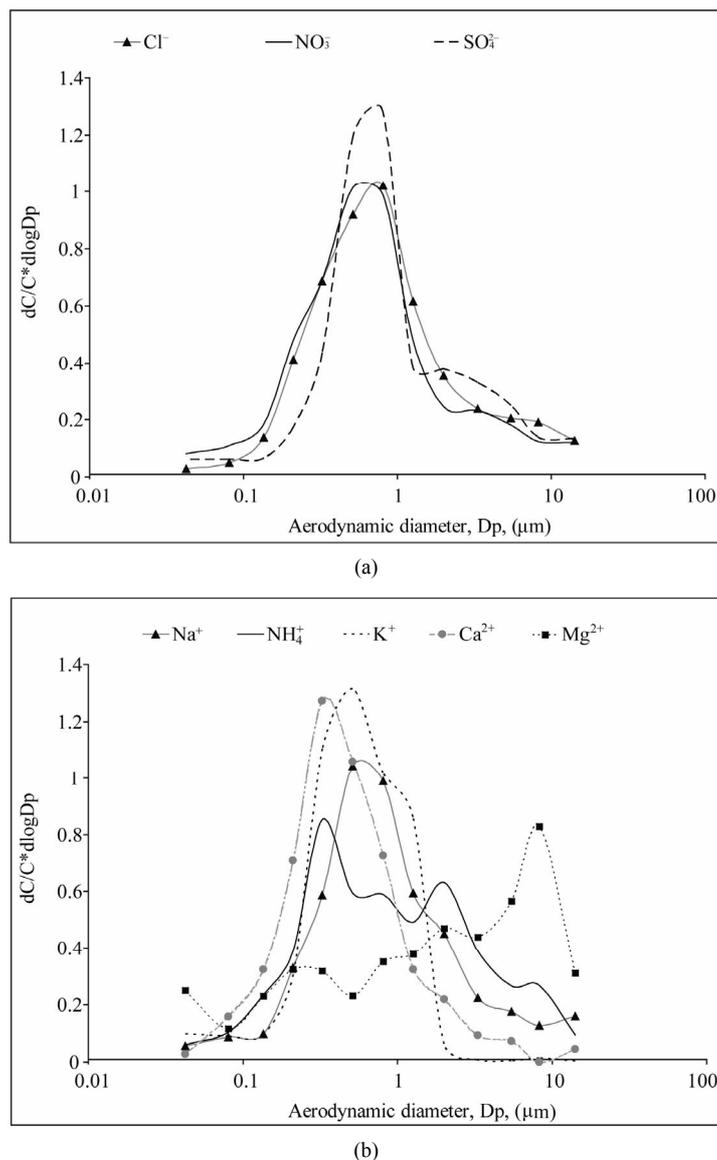


Figure 2. Mass size distribution of PM-related ions in Zabrze, Poland.

Table 3. Proportions of the ionic equivalent concentrations and probable composition of secondary inorganic aerosol in 13 original DLPI fractions of PM at the urban background site in Zabrze, Poland.

Fraction	$\Sigma_{\text{cations}}/\Sigma_{\text{anions}}$												
	neq.m ⁻³	neq.m ⁻³	neq.m ⁻³	neq.m ⁻³	ng.m ⁻³	ng.m ⁻³	ng.m ⁻³	ng.m ⁻³	%	ng.m ⁻³	ng.m ⁻³	ng.m ⁻³	ng.m ⁻³
		NR=NH ₄ ⁺ /(SO ₄ ²⁻ +NO ₃ ⁻)	SO ₄ ²⁻ /NH ₄ ⁺	NH ₄ ⁺ >SO ₄ ²⁻ or NH ₄ ⁺ <SO ₄ ²⁻	[(NH ₄) ₂ SO ₄]=1.38[SO ₄ ²⁻] if NH ₄ ⁺ >SO ₄ ²⁻	[ex-NH ₄ ⁺]=[NH ₄ ⁺]-0.27[(NH ₄) ₂ SO ₄]	[NH ₄ NO ₃]=4.44[ex-NH ₄ ⁺]	[SIA]=[NH ₄ ⁺]+[NO ₃ ⁻]+[SO ₄ ²⁻]	(NH ₄) ₂ SO ₄ +NH ₄ NO ₃ /SIA×100%	[(NH ₄) ₂ SO ₄]=3.67[NH ₄ ⁺] if NH ₄ ⁺ <SO ₄ ²⁻	[ex-SO ₄ ²⁻]=[SO ₄ ²⁻]-0.73[(NH ₄) ₂ SO ₄]	[ex ⁻ SO ₄ ²⁻]=[ex-SO ₄ ²⁻]-0.55[K ₂ SO ₄] ^{a)}	[ex ⁻ SO ₄ ²⁻]=[ex ⁻ SO ₄ ²⁻]-0.71[CaSO ₄] ^{b)}
>10	0.76	0.03	26.76	<	-	-	-	-	-	5.01	93.79	90.5	-0.76
6.8 - 10	2.25	0.1	6.75	<	-	-	-	-	-	8.77	36.64	36.64	-0.30
4.4 - 6.8	1.11	0.02	25.21	<	-	-	-	-	-	3.67	64.57	61.29	-0.52
2.5 - 4.4	0.83	0.03	18.28	<	-	-	-	-	-	8.37	105.05	99.56	-0.85
1.6 - 2.5	0.79	0.13	5.6	<	-	-	-	-	-	43.34	144.95	134.84	-1.18
1 - 1.6	1.49	1.45	0.54	>	339.06	169.68	753.38	500.86	218.11	-	-	-	-
0.65 - 1	0.92	0.89	0.76	>	516.76	44.52	197.69	820.06	87.12	-	-	-	-
0.4 - 0.65	1.02	1.08	0.63	>	615.31	101.22	449.4	988.99	107.66	-	-	-	-
0.26 - 0.4	1.75	1.82	0.42	>	306.2	116.64	517.91	510.91	161.3	-	-	-	-
0.17 - 0.26	1.19	0.97	0.85	>	169.83	54.52	242.07	213.1	193.29	-	-	-	-
0.108 - 0.17	1.68	0.97	0.8	>	54.23	18.36	81.52	72	188.55	-	-	-	-
0.06 - 0.108	1.45	1.03	0.74	>	62.05	22.63	100.4772	85.12	190.95	-	-	-	-
0.03 - 0.06	2.22	1.54	0.44	>	46.88	28.7	127.43	83.01	209.98	-	-	-	-

^{a)}[K₂SO₄]=1.8[ex-SO₄²⁻]; ^{b)}[CaSO₄]=1.42[ex⁻SO₄²⁻].

$$[\text{ex-NH}_4^+] = [\text{NH}_4^+] - 0.27[(\text{NH}_4)_2\text{SO}_4] \quad (2)$$

$$[\text{NH}_4\text{NO}_3] = 4.44[\text{ex-NH}_4^+] \quad (3)$$

NH₄NO₃ concentration ranged from 753.38 ng·m⁻³ (for PM_{1-1.6}) to 81.52 ng·m⁻³ (for PM_{0.108-0.17}).

(NH₄)₂SO₄ and NH₄NO₃ concentrations sum share, in a total SIA concentration $([\text{SIA}] = [\text{NH}_4^+] + [\text{NO}_3^-] + [\text{SO}_4^{2-}])$ for fractions of particles ≤ 1.6 μm, is shown in **Table 3**. For the fraction with ((NH₄)₂SO₄+NH₄NO₃)/SIA value exceeding 1, the share is overestimated. Still, stoichiometric calculations that have been carried out, show that these two compounds constitute the entirety of SIA in ambient particles not greater than 1.6 μm. The most probable distribution of (NH₄)₂SO₄ and NH₄NO₃ concentrations between the sum of these compounds concentrations were obtained for PM_{0.65-1} and PM_{0.4-0.65}, where the share of ((NH₄)₂SO₄+NH₄NO₃) in the SIA did not exceed 100%. There are also these two fractions, in which the predominant part in the SIA takes ammonium sulfate, while the concentra-

tions of these two dust fractions in the air are the highest of all 13 (**Table 2**).

NR for particles greater than 1.6 μm, was much smaller than 1 (**Table 3**). However, it doesn't mean that ions associated with these particles are not fully neutralized. The concentration sum ratio of anions to cations ($\Sigma_{\text{cations}}/\Sigma_{\text{anions}}$, in neq·m⁻³) is in the range of 1, for all fractions.

In all fractions of particles greater than 1.6 μm, the concentration ratios of SO₄²⁻ and NH₄⁺ (in neq·m⁻³) is considerably higher than 2.67. Also the relation NH₄⁺<SO₄²⁻ is satisfied (concentrations in neq·m⁻³). It means that in these PM fractions, NH₄⁺ could neutralize some part of SO₄²⁻, forming (NH₄)₂SO₄ but there was not enough of NH₄⁺ to react the whole SO₄²⁻. Thus, there was not enough of NH₄⁺ to form ammonium nitrate. Therefore, the (NH₄)₂SO₄ concentration for particles greater than 1.6 μm, can be calculated from the formula:

$$[(\text{NH}_4)_2\text{SO}_4] = 3.67[\text{NH}_4^+] \quad (4)$$

The concentration of $(\text{NH}_4)_2\text{SO}_4$ associated with particles greater than $1.6 \mu\text{m}$, ranged from $3.67 \text{ ng}\cdot\text{m}^{-3}$ ($\text{PM}_{4.4-6.8}$) to $43.34 \text{ ng}\cdot\text{m}^{-3}$ for $\text{PM}_{1.6-2.5}$.

It is impossible to determine precisely concentrations of all compounds constituting the secondary inorganic aerosol in Zabrze, still, estimating on the basis of stoichiometric relations. However, it can be shown that the amount of SO_4^{2-} in the particles greater than $1.6 \mu\text{m}$ is enough to react the whole NH_4^+ .

The rest of the SO_4^{2-} (sulfate ion excess $[\text{ex-SO}_4^{2-}]$) could react i.a. with potassium and calcium ions, forming K_2SO_4 and CaSO_4 . This would prove specific, similar to SO_4^{2-} , mass size distributions of K^+ , Ca^{2+} (**Figures 2(a)** and **(b)**). The concentration of the rest of SO_4^{2-} , that remained after:

- reaction with NH_4^+ forming $(\text{NH}_4)_2\text{SO}_4$; $([\text{ex-SO}_4^{2-}])$,
- reaction with NH_4^+ forming $(\text{NH}_4)_2\text{SO}_4$ and K^+ forming K_2SO_4 ; $([\text{ex}'\text{-SO}_4^{2-}])$,
- reaction with NH_4^+ forming $(\text{NH}_4)_2\text{SO}_4$, K^+ forming K_2SO_4 and Ca^{2+} forming CaSO_4 ; $([\text{ex}''\text{-SO}_4^{2-}])$

can be calculated (in $\text{PM}_{1.6-2.5}$, $\text{PM}_{2.5-4.4}$, $\text{PM}_{4.4-6.8}$, $\text{PM}_{6.8-10}$, $\text{PM}_{>10}$) from the following formula:

$$[\text{ex-SO}_4^{2-}] = [\text{SO}_4^{2-}] - 0.73[(\text{NH}_4)_2\text{SO}_4] \quad (5)$$

$$[\text{ex}'\text{-SO}_4^{2-}] = [\text{ex-SO}_4^{2-}] - 0.55[\text{K}_2\text{SO}_4] \quad (6)$$

$$[\text{ex}''\text{-SO}_4^{2-}] = [\text{ex}'\text{-SO}_4^{2-}] - 0.71[\text{CaSO}_4] \quad (7)$$

Using values listed in **Table 3**, it can be concluded that for $\text{PM}_{>1.6}$, there was not enough sulfate ion to complete reaction of calcium ions ($[\text{ex}''\text{-SO}_4^{2-}] < 0$).

Therefore, it can be concluded, that the secondary inorganic aerosol in Zabrze, in the case of compounds occurring in particles greater than $1.6 \mu\text{m}$, is mainly composed of ammonium sulfate, potassium sulfate and calcium sulfate. Certainly, there are also nitrates in these particles, however, in contrast to particles not greater than $1.6 \mu\text{m}$, there is no ammonium nitrate but probably NaNO_3 and/or $\text{Ca}(\text{NO}_3)_2$.

4. Conclusions

Most of ions' concentrations in Zabrze were comparable to concentrations presented in the literature. Generally, higher concentrations than in Zabrze are listed in Asian countries, this concerns particularly to SO_4^{2-} , NH_4^+ , K^+ , Mg^{2+} and Ca^{2+} . Concentration of Cl^- associated with fine dust in Zabrze was extraordinarily high, comparing to values recorded in other parts of the world.

Sulfates, nitrates and ammonium had the highest concentration of the eight analyzed ions in Zabrze. More

than 60% of SO_4^{2-} and NO_3^- and 90% of NH_4^+ mass, was concentrated in particles with an aerodynamic diameter ≤ 1 micron. Na^+ and Cl^- were also mostly associated with fine dust particles. Ions mentioned above, as well as K^+ and Ca^{2+} , had similar mass size distributions, and generally, maxima of these distributions were in the same particle size ranges. This indicates the anthropogenic origin of seven of eight analyzed ions (combustion processes), associated with dust in Zabrze.

Relatively high proportion of Mg^{2+} in the coarse fraction of particulate matter, proves that mechanical processes, including re-suspension of the soil and road dust could have had an influence on Mg^{2+} concentration in the air.

In particles not greater than $1.6 \mu\text{m}$, the amount of ammonium ion is sufficient to neutralize sulfuric and nitric acid, therefore, in dust precursors gas conversions, ammonium sulfate and nitrate are formed. In fractions of particles greater than $1.6 \mu\text{m}$, the amount of ammonium ion is not sufficient to neutralize the nitric acid. Therefore, in these fractions, inorganic aerosol is composed of ammonium sulfate and other compounds, including K_2SO_4 and CaSO_4 , and also NaNO_3 and/or $\text{Ca}(\text{NO}_3)_2$.

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