

WIOLETTA ROGULA-KOZŁOWSKA^{1,2}, TOMASZ MACH³,
PATRYCJA ROGULA-KOPIEC², JUSTYNA RYBAK³, KATARZYNA NOCÓN²

CONCENTRATION AND ELEMENTAL COMPOSITION OF QUASI-ULTRAFINE PARTICLES IN UPPER SILESIA

The ambient concentrations and elemental composition of particles with aerodynamic diameters between 30 and 108 nm (quasi-ultrafine particles, q-UFP) were studied. The data came from 6 sites in Katowice and Zabrze, big cities in Upper Silesia, where particulate matter was sampled at urban background site and crossroads in Katowice and Zabrze, at highway in Katowice, and at urban road in Zabrze. The ambient concentrations of q-UFP and of 24 q-UFP-bound elements at these six sampling sites have been discussed in the paper. The q-UFP mass concentrations in Upper Silesia did not appear high, they were not higher than in other areas. The percentages of the total mass of the examined elements in the q-UFP mass suggest that in Upper Silesia, within a typical residential area, q-UFP consist mainly of primary matter. At the sites under strong influence of road traffic emissions, where the contributions of the examined elements to the q-UFP mass were small, most probably, carbonaceous matter and elemental carbon build the core q-UFP mass. The majority of the elements in q-UFP are anthropogenic. Clear effects of local PM sources can be seen on the ambient concentrations of q-UFP-bound Al, Si, S, Cl, K, Sc, Ti, V, Cd, Cr, Mn, Co, and Sb.

1. INTRODUCTION

Although ultrafine particles (UFP), i.e., particles with the aerodynamic diameter not greater than 0.1 μm (PM_{0.1}), make only a small part of the total mass of atmospheric particulate matter (PM) [1–3], they significantly outnumber other airborne particles in urban areas [4–7]. Because of their great number concentrations and tiny sizes their

¹The Main School of Fire Service, Faculty of Fire Safety Engineering, ul. Słowackiego 52/54, 01-629 Warsaw, Poland.

²Institute of Environmental Engineering, Polish Academy of Sciences, ul. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland.

³Wrocław University of Science and Technology, Faculty of Environmental Engineering, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland, corresponding author J. Rybak, e-mail address: justyna.rybak@pwr.edu.pl

correlation with the adverse health effects in humans are stronger than those of coarser PM fractions. The great pulmonary deposition efficiency of UFP, their toxicity due to their large surface area and the amounts of transition metals they adsorb can cause serious cardiopulmonary issues [8, 9]. Their presence in the air is linked with exacerbation and promotion of asthma, chronic obstructive pulmonary disease, atherosclerosis and hypertension [10, 11]. There is general agreement among the scientists about the importance of investigating the UFP for their properties and the relations of their presence in the air with health effects [4–6]. The monitoring of (most often number) UFP concentrations has become routine in some European regions [4–7].

UFP are either emitted directly from high-temperature processes or they are formed in the air as secondary particles. They come mainly from road traffic (those with the median diameters between 20 and 100 nm), from combustion of coal, fuel oil (35–100 nm), and natural gas (15–30 nm) for residential heating, and from nucleation (1 nm, the smallest measurable particles) [4].

Health effects of PM in humans are due to the combination of its ambient concentrations and chemical composition [12–16]. In Poland, the chemical composition of PM₁, PM_{2.5}, and PM₁₀ is recognized quite well, e.g., [1–3, 16–18]. PM contains trace elements (metals), including those toxic, in PM_{2.5}, organic and elemental carbon and secondary inorganic compounds (ammonium sulfate and nitrate) prevail [17, 18]. In Polish urban areas, not only the concentrations but also some toxic element content of PM_{2.5} are alarmingly high compared to other urban areas worldwide. The issue is especially severe in the southern part of the country, where not only emissions from traffic and coal combustion are high, but also very high industrial emissions contribute to PM-bound elements [1, 17, 18].

The mass contribution of UFP to total PM is very small, they are mainly secondary and they dynamically change in the air, therefore, in general, they are investigated using automatic samplers [5, 6]. However, although the UFP mass possible to receive from direct sampling is extremely small, besides mere forecasting and modeling of UFP composition and origin [19], some attempts have been made recently to use the classical sampling of UFP directly from the air and then determining their chemical composition in laboratory [12].

Two papers discussing the chemical composition of UFP in Poland, both presenting classical approach [2, 3] have been published so far. The results were used in the discussion concerning some human health issues due to the mass size distributions of PM and its components [20]. The present work presents the data that they contain on the particles having aerodynamic diameters between 30 and 60 nm and between 60 and 108 nm, directly sampled in the southern part of Poland, to present the properties of the particles having aerodynamic diameters between 60 and 108 nm (called quasi-ultrafine particles, q-UFP). Our technical possibilities did not allow to sample smaller particles, however, the particles we sampled contain a greater part of the UFP mass and their diameters

cover about 2/3 of the diameter interval of UFP. Besides, the q-UFP are of special importance in the area of sampling because very intense emissions of UFP from industry and combustion of coal, gasoline, and diesel oil present within this area.

2. MATERIALS AND METHODS

The q-UFP samples were collected in southern Poland, in two Upper Silesian cities, Zabrze and Katowice, at three sites in each (Fig. 1). In each city, one measuring site was situated within the area representing urban background air pollution [21]. The urban background sites were located in the central parts of the cities, close to residential and commercial buildings, both surrounded by lawns.

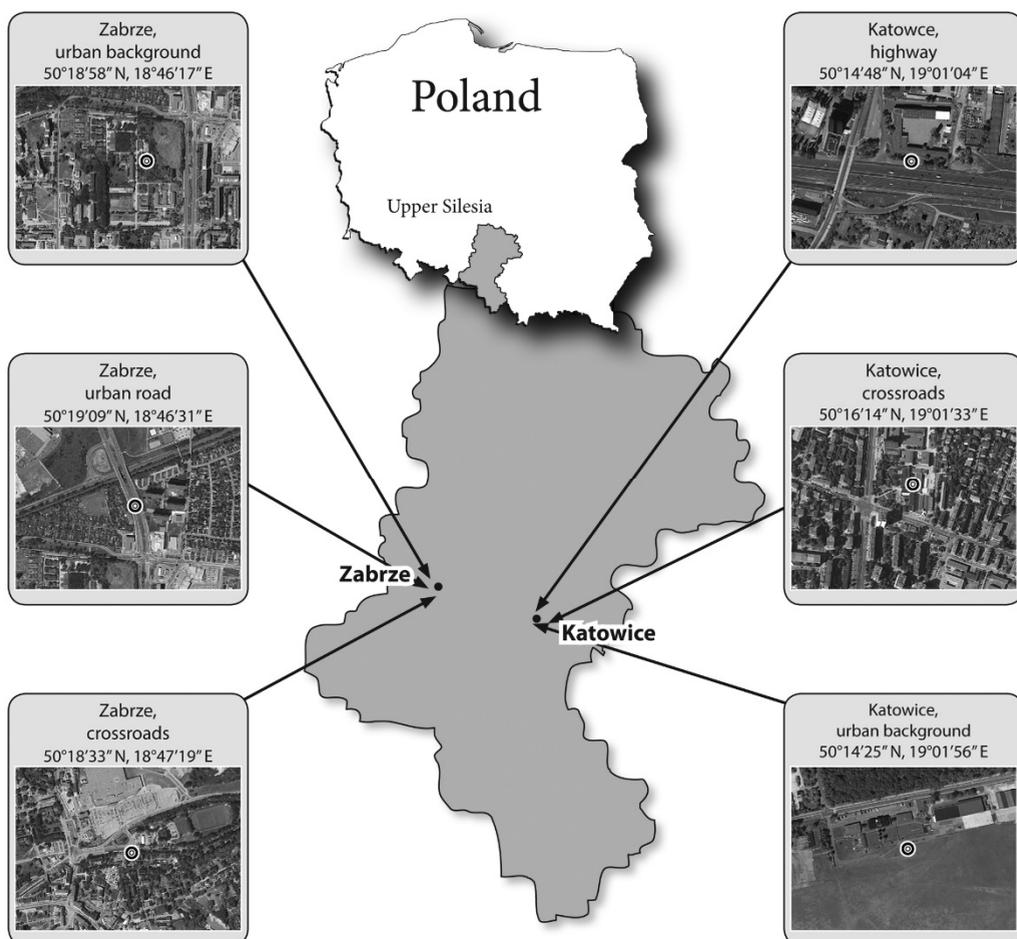


Fig. 1. Sampling sites (map source: Google Earth)

One measuring site in each city was situated at a crossroads in the city center. The direct neighborhood of the sites were the crossing roads. The traffic intensities on the crossroads were about 40 000 vehicles per day in Zabrze and 28 000 vehicles per day in Katowice.

In Zabrze, the third measuring site was located at a grassy side of a busy six-lane urban road, about 800 m away from the city center and 350 m from the urban background site. The traffic intensity on the road was about 30,000 vehicles per day. The third sampling site in Katowice was located on the shoulder of the highway A4, about 1500 m south of the city center and 1200 m northwest of the urban background site. Average traffic density through the highway was 30 000 cars per day. The meteorological conditions at the measuring sites were typical of the region during all the measuring period.

The samples of q-UFPs were taken using two thirteen-stage low pressure impactors from DEKATI (DLPI, Dekati low pressure impactor) and Nylon substrates (Whatman, nylon membrane filters 0,2 μm , \varnothing 25 mm, Cat. No. 7402-002). They were collected in the period from the middle of March to the end of August in Katowice (16 sample-takings, 4 at the highway, 4 at the crossroads, and 8 at the urban background site), and from the beginning of May to the middle of October in Zabrze (21 sample-takings, 6 at the urban road, 6 at the crossroads, and 9 at the urban background site). The particular sample-takings lasted from about 3 to 5 days (the shortest lasted 62 hs, the longest – 128 h). The impactors and gravimetric analyses applied to the sample development have been described elsewhere [1–3].

The elemental composition of q-UFPs was determined by means of energy dispersive X-ray fluorescence (EDXRF). An Epsilon 5 (PANalytical B.V.), calibrated with the use of the thin-layer single-element standards (Micromatter) was used to measure the total concentrations of the elements. The NIST SRM2873 samples were measured to control the performance of the analytical procedure [1–3, 18]. To control the performance of the analytical procedure, the NIST SRM2873 samples were measured weekly (except 52% and 39% recoveries of V and Co, the recoveries were between 85 and 120% of the certified values) and the X-ray tube and detector drift were monitored monthly. The detection limits (from the statistical development of the blank results) were from 0.15 ng/cm^2 (Ti, Pb) to 16.8 ng/cm^2 (Si).

The results were analyzed for statistical significance of the differences of the concentration of q-UFP and of q-UFP-bound elements among the sampling sites using Statistica 8 (Stat Soft) (one-way ANOVA with post hoc Tukey HSD test, $p < 0.05$).

3. RESULTS AND DISSCISSION

On average, the q-UFP mass concentration slightly exceeded 800 ng/m^3 at the highway in Katowice. It was the greatest q-UFP concentration among all the sampling

sites. In Zabrze, at crossroads, it was 620 ng/m^3 , and at the rest of the sites the q-UFP mass concentrations were in the range of $290\text{--}370 \text{ ng/m}^3$, being close to one another, (Fig. 2). These concentrations are relatively low. In small Alpine town of Morbengo (Sondrio), northern Italy, average UFP concentrations were 2 and $2.23 \text{ }\mu\text{g/m}^3$ [12], and at ten sites in the USA they were between 200 and 1000 ng/m^3 [20]. Yu et al. [22] showed that traffic emissions (diesel and gasoline) contribute relatively little to UFP mass concentrations at the sites or time periods of enhanced natural gas and wood combustion. In summer, when the emissions from residential heating ceases, traffic contributes to the UFP mass concentrations more. They also showed that at all the sites very few UFP came from nucleation [22].

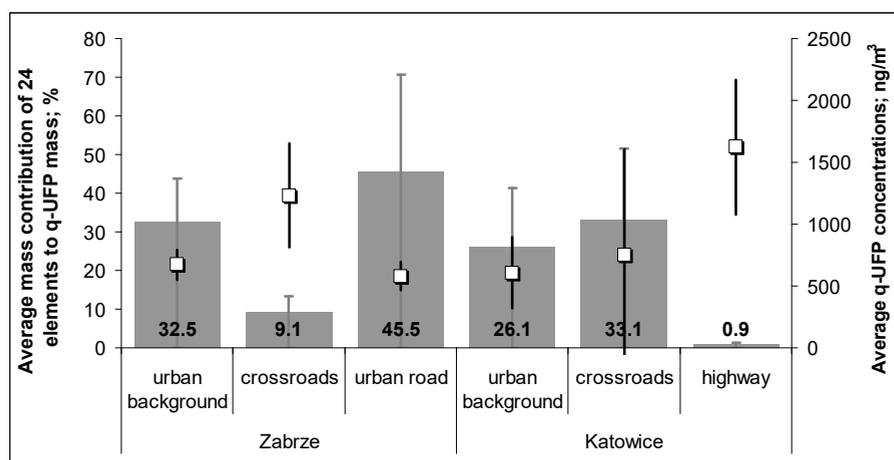


Fig. 2. Average q-UFP concentrations (the squares, black vertical line represents standard deviation from mean) and average mass contribution of 24 elements to q-UFP mass (grey bars, grey vertical line represents standard deviation from mean) at six sites in Upper Silesia

Here, the periods for the PM sampling were selected so that the emissions from combustion for residential heating (low-quality coal, wood, wastes) could be avoided. These emissions, very intense in heating periods in Upper Silesia, efficiently suppress emissions of PM from other sources [1, 18]. Nonetheless, in the heating season, the low concentration of q-UFP (around 500 ng/m^3) was also observed at the urban background in Zabrze. Therefore, according to results received by Yu et al. [22], the differences in q-UFP concentrations among the six sites investigated here seem to depend on the differences in road traffic intensities at these sites.

The highest q-UFP concentrations were observed in the sites under influence of heavy road traffic, i.e. at the highway in Katowice and the very busy crossroads in Zabrze (Fig. 2). In Katowice, the q-UFP concentrations at the crossroads were higher than at the urban background site not being effected directly by road traffic (Fig. 2). Statisti-

cally significant differences in the q-UFP concentrations were noted between the highway in Katowice and each of the urban background site in Katowice, urban road in Zabrze, urban background site in Zabrze, and between the crossroads and urban background in Zabrze (Fig. 2). Also, the average total element contents of q-UFP make q-UFP at the highway in Katowice and at the urban background site in Zabrze essentially different from q-UFP at the remaining sites. The average mass contribution of the investigated elements to the q-UFP mass at the highway in Katowice does not exceed 1%, and at the crossroads in Zabrze it is about 9%. At the remaining sites it is much higher, the highest being at the urban road in Zabrze (more than 40%). At the urban background sites, the examined elements are no more than 30% of q-UFPs mass (Fig. 2). Therefore, these two sampling sites, the highway in Katowice and background site in Zabrze, are specific among all the six sampling sites.

According to the earlier investigations of the effects of road traffic emissions on 13 PM fractions at the highway in Katowice [2], at this site, the carbonaceous matter, including hydrocarbons and elemental carbon, contributes more to the finest PM fraction than other components together do, and this contribution is greater than it is to PM sampled at the urban background site in Katowice at the same time. The small contribution of the investigated elements (among which there are not carbon, oxygen, or hydrogen) to q-UFP proves that at heavily affected by road traffic both the highway in Katowice and crossroads in Zabrze the chemical composition of q-UFP is shaped by road traffic emissions. It is highly probable that q-UFP at these sites are composed primarily of elemental carbon and organic compounds comprising, besides carbon, also oxygen and hydrogen.

Instead, at the two other traffic sites, the urban road in Zabrze and crossroads in Katowice, the mass q-UFP concentrations and the contribution of the element sum to the q-UFP mass were close to those at the urban background sites in these cities (Fig. 2). Although affected by road traffic, the urban road in Zabrze and crossroads in Katowice are surrounded by residential and commercial housing that affects these sites by releasing emissions from combustion of natural gas and wood, and periodically of oil or coal, for heating and cooking. Most probably these municipal sources affect stronger q-UFP than road traffic. The phenomenon of concealing road traffic effect on PM concentrations by municipal emissions was already observed in Upper Silesia earlier [1–3]. Besides, the traffic of heavy lorries, which probably are the most efficient sources of q-UFP, especially of those carbonaceous, e.g., [23], is practically banned from the road in Zabrze and crossroads in Katowice, while the traffic of heavy vehicles on the highway in Katowice and the crossroads in Zabrze is very intense.

Among 24 examined q-UFP-bound elements, Al, Si, S, Cl, K, Ca, Ti, Mn, Fe, and Sb had the greatest ambient concentrations at each site (Table 1). In a small Alpine town of Morbegno (Sondrio, Northern Italy), almost all these element concentrations were also highest, but the concentrations of Co, As, Cd, V, and Sr were visibly lower [12]. The latter can originate from industry [24, 25] or energy production from coal [26–28],

and in Poland, almost the whole of electric power and heat are produced from combustion of coal.

Table 1

Mean ambient mass concentrations [$\mu\text{g}/\text{m}^3$]
of q-UFP-bound elements at six sites in Upper Silesia

Zabrze												
Site	Element											
	Al	Si	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe
Urban background	8324	10014	23510	22736	3314	11000	2592	58334	8844	266	16034	6934
Crossroads	14490	15572	18794	6402	7464	7064	778	128	66	952	428	5834
Urban road	11362	11908	21598	21704	3632	11630	2988	68302	10070	298	19182	7788
	Co	Ni	Cu	Zn	As	Rb	Sr	Cd	Sn	Sb	Ba	Pb
Urban background	1244	116	1062	480	336	104	1024	1104	932	29808	5504	900
Crossroads	62	786	770	12858	2648	92	950	712	392	358	1648	3272
Urban road	1306	176	1440	424	378	164	1336	1570	944	36756	6856	1032
Katowice												
Site	Element											
	Al	Si	S	Cl	K	Ca	Sc	Ti	V	Cr	Mn	Fe
Urban background	3842	3898	22416	19610	3144	3060	958	27778	3494	1234	7644	3144
Crossroads	3796	4152	25902	15662	3198	3198	1096	31310	3924	1530	8444	4536
Urban road	318	348	2746	2168	456	372	92	2668	336	122	736	490
	Co	Ni	Cu	Zn	As	Rb	Sr	Cd	Sn	Sb	Ba	Pb
Urban background	564	60	900	596	674	88	578	764	674	14346	3416	1900
Crossroads	458	60	1270	700	314	54	480	878	596	15726	3764	754
Urban road	56	6	94	160	48	4	46	64	48	1402	336	126

The element concentrations differed significantly between some sites. For Sc, Ti, V, Cr, Mn, Co, and Sb, the pairs of the sites between which the difference was statistically significant outnumbered a half of all the 15 pairs of sites. For Al, Si, S, Cl, K, Rb, Cd, and Ba, there were from 4 to 6 such pairs, and for Ni, Zn, As, and Pb there was none. The rest of the elements had only from 1 to 3 such pairs (Table 2).

Therefore, Zn, As, Pb, Cu, and Sr, whose presence in the atmosphere can be linked with coal combustion, e.g., because of the seasonal variability of their ambient concentrations [1, 18], have quite uniform ambient concentrations over Upper Silesia, what means that their main sources cannot be local. The concentrations of other elements, as well the PM microcomponents Al, Si, S, Cl, and K as the trace elements Sc, Ti, V, Cd, Cr, Mn, Co, and Sb, are explicitly affected by sources local to the considered sites.

The mass contributions of particular q-UFP-bound elements to the mass of all the 24 elements determined in q-UFP are very similar among five sites (Fig. 3), where the contributions (%) of Al, Si, S, Cl, K, Ca, Sc, Ti, V, Mn, Fe, Sb and Ba are greatest.

Despite the pointed out earlier differences, the site at the highway in Katowice is among these five sites (Fig. 3).

Table 2

q-UIP-bound elements and the pairs of sites between which their ambient concentrations statistically significantly differ (one-way ANOVA with post hoc HSD Tukey test, $p < 0.05$)

	Pairs of sites with statistically significant difference between the element concentration
Al	CZ-CK, CZ-HK, CZ-UBK, HK-URZ
Si	UBZ-HK, URZ-HK, URZ-UBK, CZ-CK, CZ-HK, CZ-UBK
S	UBZ-HK, URZ-HK, CZ-HK, CK-HK, HK-UBK
Cl	UBZ-CZ, UBZ-HK, URZ-CZ, URZ-HK, CZ-UBK, HK-UBK
K	UBZ-CZ, URZ-CZ, CZ-CK, CZ-HK, CZ-UBK
Ca	UBZ-CK, UBZ-HK, UBZ-UBK, URZ-CK, URZ-HK, URZ-UBK, CZ-HK
Sc	UBZ-CZ, UBZ-CK, UBZ-HK, UBZ-UBK, URZ-CZ, URZ-CK, URZ-HK, URZ-UBK
Ti	UBZ-CZ, UBZ-CK, UBZ-HK, UBZ-UBK, URZ-CZ, URZ-CK, URZ-HK, URZ-UBK, CZ-CK, CK-CZ, CK-HK, HK-UBK
V	UBZ-CZ, UBZ-CK, UBZ-HK, UBZ-UBK, URZ-CZ, URZ-CK, URZ-HK, URZ-UBK, CZ-CK, CZ-UBK
Cr	UBZ-CZ, UBZ-CK, UBZ-UBK, URZ-CZ, URZ-CK, URZ-UBK, CZ-CK, CZ-HK, CZ-UBK, CK-HK, HK-UBK
Mn	UBZ-CZ, UBZ-HK, UBZ-UBK, URZ-CZ, URZ-CK, URZ-HK, URZ-UBK, CZ-CK, CZ-UBK
Fe	UBZ-HK, URZ-HK, CZ-HK
Co	UBZ-CZ, UBZ-CK, UBZ-HK, UBZ-UBK, URZ-CZ, URZ-CK, URZ-HK, URZ-UBK
Ni	–
Cu	URZ-HK, CK-HK
Zn	–
As	–
Rb	UBZ-HK, URZ-CK, URZ-HK, URZ-UBK, CZ-HK
Sr	URZ-HK
Cd	UBZ-HK, URZ-CZ, URZ-HK, URZ-UBK
Sn	UBZ-HK, URZ-HK
Sb	UBZ-CZ, UBZ-HK, UBZ-UBK, URZ-CZ, URZ-CK, URZ-HK, URZ-UBK, CZ-UBK
Ba	UBZ-CZ, UBZ-HK, URZ-CZ, URZ-HK
Pb	–

UBZ – urban background in Zabrze, UBK – urban background in Katowice, CZ – crossroads in Zabrze, CK – crossroads in Katowice, URZ – urban road in Zabrze, HK – highway in Katowice.

The crossroads in Zabrze differs explicitly from the other five sites with the high contributions of Zn and As (very low everywhere else except the highway in Katowice), contributions of Al and Si higher than at other sites, and almost lacking contributions of Ti and Sb that are relatively high at other sites. Because Zn share is considerably high also at the highway in Katowice (Fig. 3) and it is known that Zn occurs in cars (e.g., lubricating oil or tires), the Zn high contribution to the mass of the 24

are high (Fig. 3, Table 1). The Ti concentrations differ significantly among the sites. This unusual Ti abundance can be due to the multiplicity of industrial Ti sources dispersed over Upper Silesia. Ti can be emitted in TiO_2 from various high-temperature processes. Ti is used as a component of alloys with other metals for stainless steel production [31]. TiO_2 is used as a pigment in paints (nearly 70% of all its production), it is also used as a pigment in glazes, enamels, plastics, paper, fibers, foods, pharmaceuticals, cosmetics, and toothpastes. Other TiO_2 uses include antimicrobial applications, catalysts for air and water purification, medical applications, and energy storage [32]. The global production of TiO_2 for all uses is in millions of tons per year.

Table 3

24 q-UFP-bound elements ordered by their enrichment factors increasing from the top to the bottom in columns at six sites in Upper Silesia

Zabrze			Katowice		
Urban background	Crossroads	Urban road	Urban background	Crossroad	Highway
Si	Ti	Si	Si	Si	Si
Al	Si	K	Al	Al	Al
K	Al	Al	Fe	Ca	Ca
Fe	Fe	Fe	Ca	K	Fe
Ca	Ca	Ca	K	Fe	K
Rb	K	Rb	Rb	Rb	Rb
Sr	Mn	Sr	Sr	Sr	Sr
Ni	Rb	Zn	Ni	Ni	Ni
Cr	V	Cr	Ba	Ba	Ba
Ba	Ba	Ni	Ti	Ti	Ti
Zn	Sr	Ba	Zn	Zn	Sn
Ti	Co	Ti	Mn	Sn	Mn
Sn	Sn	S	Sn	Mn	S
S	Cl	Sn	S	Cl	Zn
Mn	S	Cl	Cl	S	Cl
Cl	Cr	Mn	Cr	Co	Cr
Pb	Ni	Pb	Co	Cr	Co
Cu	Cu	Cu	Cu	Pb	V
Co	Sc	Co	V	V	Cu
V	Pb	As	Pb	Cu	Pb
As	Zn	V	Sc	Sc	Sc
Sc	Sb	Sc	As	As	As
Cd	As	Cd	Cd	Cd	Cd
Sb	Cd	Sb	Sb	Sb	Sb

The background: white $EF \leq 10$, light gray $10 < EF \leq 100$, dark gray $100 < EF \leq 1000$, black $1000 < EF \leq 10\ 000$, bold symbols $EF > 10\ 000$.

To distinguish between anthropogenic or natural origin of the elements, their enrichment factors (EF) were computed for all the sites [1–3] (Table 3). The enrichment factor EF_x for the element x is defined as:

$$EF_x = \frac{\left(\frac{C_x}{C_{ref}} \right)_{PM}}{\left(\frac{C_x}{C_{ref}} \right)_{crust}} \quad (1)$$

where C_x and C_{ref} are the concentrations of the element x and the reference element, and $(C_x/C_{ref})_{PM}$ and $(C_x/C_{ref})_{crust}$ are the proportions of these concentrations in PM and in the Earth crust, respectively. Here, Al is selected as the reference element, i.e., $EF_{Al} = 1$. The chemical composition of the upper continental crust was taken from [33].

The closer EF of an element to 1, the weaker the anthropogenic effect on the element ambient concentrations is. In Table 3, for each site, the symbols of elements are ordered by the element EF increasing from the top to the bottom in the columns. In general, q-UFP-bound Si, Al, K, Fe, Ca, and Rb, having EF s not greater than 10, are of natural origin, their presence can be linked with the presence of soil, sand, etc., at all the sites. At all the sites, excluding the crossroads in Zabrze, Sr and Ni had EF greater than 10, but much lower than other elements had. The majority of the q-UFP-bound elements should be considered anthropogenic because of their high EF . As, Cd, and Sb had the greatest EF s at all the sites (Table 3).

4. CONCLUSIONS

The paper presents the analysis of the elemental composition of ambient ultrafine particles in urban environment which was done in Poland for the first time. The data from PM measurements, earlier used by the authors to determine the mass size distributions of PM-bound elements, are here applied to characterize ambient mass concentrations and elemental composition of ultrafine particles with aerodynamic diameters between 30 and 108 nm (q-UFP) which are the least recognized subfraction of the fine PM fraction.

The average ambient concentrations of q-UFPs vary within Upper Silesia depending on the site. They depend on local sources of primary q-UFP such as road traffic and municipal sources, their values vary widely at a big crossroads or highway. They are quite uniform within area of residential and commercial housing. High contribution of the investigated elements to the mass of q-UFP proves the prevalence of primary matter content in q-UFP at four sites, the urban background site and road in Zabrze and the urban background site and crossroads in Katowice. At the big crossroads in Zabrze and

the highway Katowice, the prevalence of carbon, oxygen, and hydrogen, not investigated here, is expected. Most probably, also secondary matter contributes significantly to ultrafine particles at these two sites.

The chemical composition of q-UFP in Upper Silesia is quite uniform over its area. The ambient concentrations of Zn, As, Pb, Cu, Sr and their contributions to the mass of the 24 q-UFP-bound elements are comparable among sites, probably because they are influenced mainly by the same global factors such as coal combustion for energy and power production. The ambient concentrations of such q-UFP-bound elements as Al, Si, S, Cl, K, Sc, Ti, V, Cd, Cr, Mn, Co, and Sb are affected by local sources. Majority of elements bound to q-UFP are anthropogenic.

REFERENCES

- [1] ROGULA-KOZŁOWSKA W., MAJEWSKI G., CZECHOWSKI P.O., *The size distribution and origin of elements bound to ambient particles: A case study of a Polish urban area*, Environ. Monit. Asses., 2015, 187 (5), 240.
- [2] ROGULA-KOZŁOWSKA W., *Traffic-generated changes in the chemical characteristics of size-segregated urban aerosols*, B Environ. Contam. Tox., 2014, 93 (4), 493.
- [3] ROGULA-KOZŁOWSKA W., *Size-segregated urban particulate matter: mass closure, chemical composition, and primary and secondary matter content*, Air Qual. Atmos. Health, 2016, 9 (5), 533.
- [4] SALMA I., BORSOS T., WEIDINGER T., ALTO P., HUSSEIN T., DAL MASO M., KULMALA M., *Production, growth and properties of ultrafine atmospheric aerosol particles in an urban environment*, Atmos. Chem. Phys., 2011, 11, 1339.
- [5] KUMAR P., MORAWSKA L., BIRMILI W., PAASONEN P., HUG M., KULMALAE M., HARRISON R.M., NORFORD L., BRITTER R., *Ultrafine particles in cities*, Environ. Int., 2014, 66, 1.
- [6] MA N., BIRMILI W., *Estimating the contribution of photochemical particle formation to ultrafine particle number averages in an urban atmosphere*, Sci. Tot. Environ., 2015, 512, 154.
- [7] DAMETO DE ESPANA C., WONASCHÜTZ A., STEINER G., ROSATI A., DEMATTIOA A., SCHUHA H., HITZENBERGER R., *Long-term quantitative field study of New Particle Formation (NPF) events as a source of Cloud Condensation Nuclei (CCN) in the urban background of Vienna*, Atmos. Environ., 2017, 164, 289.
- [8] OBERDORSTER G., SHARP Z., ATUDOREI V., ELDER A., GELEIN R., LUNTS A., KREYLING W., COX C., *Extrapulmonary translocation of ultrafine carbon particles following whole-body inhalation 700 exposure of rats*, J. Toxicol. Environ. Health A, 2002, 65, 1531.
- [9] WILSON M.R., LIGHTBODY J.H., DONALDSON K., SALES J., STONE V., *Interactions between ultrafine particles and transition metals in vivo and in vitro*, Tox. Appl. Pharmacol., 2002, 184, 172.
- [10] GWINN M.R., VALLYATHAN V., *Nanoparticles. Health effects – pros and cons.*, Environ Health Perspect., 2006, 114 (12), 1818.
- [11] LU S., ZHANG W., ZHANG R., LIU P. WANG Q., SHANG Y., WU M., DONALDSON K., WANG Q., *Comparison of cellular toxicity caused by ambient ultrafine particles and engineered metal oxide nanoparticles*, Part. Fibre Tox., 2015, 12 (5).
- [12] CORSINI E., VECCHI R., MARABINI L., FERMO P., BECAGLI S., BERNARDONI V., CARUSO D., CORBELLA L., DELL'ACQUA M., GALLI C.L., LONATI G., OZGEN S., PAPALE A., SIGNORINI S., TARDIVO R., VALLI G., MARINOVICH M., *The chemical composition of ultrafine particles and associated biological effects at an alpine town impacted by wood burning*, Sci. Tot. Environ. 2017, 587, 223.

- [13] VINZENTS P.S., LOLLER P., SORENSEN M., KNUDSEN L., HERTEL O., JENSEN F.P., SCHIBYE B., STEFFEN-LOFT S., *Personal exposure to ultrafine particles and oxidative DNA damage*, Environ. Health Perspect., 2005, 113, 1485.
- [14] CORLIN L., WOODIN M., HART J.E., SIMON M.C., GUTE D.M., JOANNA STOWELL J., TUCKER K.L., DURANT J.L., BRUGGE D., *Longitudinal associations of long-term exposure to ultrafine particles with blood pressure and systemic inflammation in Puerto Rican adults*, Environ. Health, 2018, 17 (1), 33.
- [15] BADYDA A., GAYER A., CZECHOWSKI P. O., MAJEWSKI G., DĄBROWIECKI P., *Pulmonary function and incidence of selected respiratory diseases depending on the exposure to ambient PM10*, Int. J. Mol. Sci., 2016, 17 (11), 1954.
- [16] SÓWKA I., CHLEBOWSKA-STYŚ A., PACHURKA Ł., ROGULA-KOZŁOWSKA W., *Seasonal variations of PM2.5 and PM10 concentrations and inhalation exposure from PM-bound metals (As, Cd, Ni). First studies in Poznań (Poland)*, Arch. Environ. Prot. 2018, 44 (4), 86.
- [17] ROGULA-KOZŁOWSKA W., KLEJNOWSKI K., ROGULA-KOPIEC P., LESZEK OŚRÓDKA L., EWA 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 (1), 41.
- [18] ROGULA-KOZŁOWSKA W., MAJEWSKI G., BŁASZCZAK B. KLEJNOWSKI K., ROGULA-KOPIEC P., *Origin-oriented elemental profile of fine ambient particulate matter in central European suburban conditions*, Int. J. Environ. Res. Publ. Health, 2016, 13 (7), 715.
- [19] POSNER L.N., PANDIS S.N., *Sources of ultrafine particles in the Eastern United States*, Atmos. Environ., 2015, 111, 103.
- [20] WIDZIEWICZ K., ROGULA-KOZŁOWSKA W., *Urban environment as a factor modulating metals deposition in the respiratory track and associated cancer risk*, Atmos. Pollut. Res., 2018, 9 (3), 399.
- [21] EC 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, 2008.
- [22] YU X., VENECEK M., HU J., TANRIKULU S., SOON S.-T., TRAN C., FAIRLEY D., KLEEMAN M., *Sources of airborne ultrafine particle number and mass concentrations in California*, Atmos. Chem. Phys. Discuss., 2018.
- [23] CHINA S., SALVADORI N., MAZZOLENI C., *Effect of traffic and driving characteristics on morphology of atmospheric soot particles at freeway on-ramps*, Environ. Sci. Technol., 2014, 48 (6), 3128.
- [24] TIAN H., LIU K., ZHOU J., LU L., HAO J., QIU P., GAO J., ZHU C., WANG K., HUA S., *Atmospheric emission inventory of hazardous trace elements from China's coal-fired power plants. Temporal trends and spatial variation characteristics*, Environ. Sci. Technol. 2014, 48 (6), 3575.
- [25] ZHANG K., CHAI F., ZHENG Z., YANG Q., ZHONG X., FOMBA K.W., ZHOU G., *Size distribution and source of heavy metals in particulate matter on the lead and zinc smelting affected area*, J. Environ. Sci., 2018, 71, 188.
- [26] KOLKER A., *Minor element distribution in iron disulfides in coal. A geochemical review*, Int. J. Coal Geol., 2012, 94, 32.
- [27] IZQUIERDO M., QUEROL X., *Leaching behavior of elements from coal combustion fly ash. An overview*, Int. J. Coal Geol., 2012, 94, 54.
- [28] VEJAHATI F., XU Z., GUPTA R., *Trace elements in coal. Associations with coal and minerals and their behavior during coal utilization. A review*, Fuel, 2010, 89 (4), 904.
- [29] PENKAŁA M., OGRODNIK P., ROGULA-KOZŁOWSKA W., *Particulate matter from the road surface abrasion as a problem of non-exhaust emission control*, Environ., 2018, 5 (1), 9.
- [30] JOHANSSON C., NORMAN M., BURMAN L., *Road traffic emission factors for heavy metals*, Atmos. Environ., 2009, 43 (31), 4681.
- [31] ELREFAEY A., TILLMANN W., *Brazing of titanium to steel with different filler metals. Analysis and comparison*, J. Mat. Sci., 2010, 45 (16), 4332.

- [32] WEIR A., WESTERHOFF P., FABRICIUS L., GOETZ N., *Titanium dioxide nanoparticles in food and personal care products*, Environ. Sci. Technol., 2012, 46 (4), 2242.
- [33] WEDEPOHL K.H., *The composition of the continental crust*, Geochim. Cosmochim. Acta, 1995, 59, 1217.