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Original Research

Influence of Vehicular Traffic on Concentration and Particle Surface Composition of PM10 and PM2.5 in Zabrze, Poland

W. Rogula–Kozłowska [1,2], J. S. Pastuszka [2]*, E. Talik [3]

[1] Polish Academy of Sciences, Institute of Environmental Engineering,
M. Skłodowska-Curie 34, 41-890 Zabrze, Poland
[2] Silesian University of Technology, Division of Energy and Environmental Engineering,
Department of Air Protection, Akademicka 2, 44-100 Gliwice, Poland
[3] University of Silesia, August Chełkowski Institute of Physics, Uniwersytecka 4, 40-007 Katowice, Poland

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Abstract

The results of the PM10 and PM2.5 study in Zabrze, Upper Silesia, Poland, near a very busy city street intersection and in a site representing urban background air are presented. Airborne particles were sampled at both sites in parallel, three or five times a month from April to December 2005. Concentration of the ambient aerosol was determined gravimetrically. It has been found that the mean of the 24-hour concentration of PM10 and PM2.5 near the crossroads was 55 μg/m^3 and 32 μg/m^3, respectively; significantly higher than at the background site, where the mean concentration of PM10 and PM2.5 reached the level of 37 μg/m^3 and 22 μg/m^3, respectively. Five pairs of PM10 and four pairs of PM2.5 samples were selected for analysis of elemental composition of surface layer of collected particles. This analysis, performed using X-ray photoelectron spectroscopy (XPS), showed that the main components of the surface layer of all studied airborne particles were carbon, nitrogen and oxygen. Besides, the typical surface layer is composed of sodium, potassium, silicon, magnesium and aluminum. In some samples zinc and calcium also occurred. It has been documented that the surface layer of the airborne particles near the crossroads contained more carbon and less oxygen compared with particles from the background site.

Keywords: atmospheric aerosol, PM10, PM2.5, traffic aerosol, surface chemical composition, X-ray photoelectron spectroscopy (XPS)

Introduction

Numerous epidemiological studies have demonstrated positive association between ambient concentrations of airborne particulate matter and increased adverse respiratory and cardiovascular events [1-11], including morbidity and mortality [12-15]. Despite insufficient knowledge on the exposure-effect relationships between PM10 and human health, the PM10 (thoracic fraction) standards have been developed. In 1999 the European Commission included the PM10 monitoring and limit values in the Air Quality Directive. It should be remarked, however, that the World Health Organization concluded that health risks are present at any level of particles [16]. For instance, an increase of PM10 concentration by 10 μg/m^3 causes a several percent increase of upper respiratory tract diseases in exposed population, even in unindustrialized and not urbanized Polar Regions [17]. On the other hand, it is well documented that

*e-mail: Jozef.Pastuszka@polsl.pl

health effects are more strongly associated with exposure to particulate matter less than 2.5 μm (PM2.5) than with the coarse fraction of PM10 [18, 19]. Recently, the USEPA has promulgated air quality standards for both PM10 and PM2.5 mass and is moving towards standards for PM2.5 and coarse particles PM (2.5–10). In the European Union, the Clean Air for Europe [20] process currently is recommending a change to PM2.5 standard. It should be noted that the fine particles may also transport many toxic substances into the deeper regions of lungs. For example, various carcinogenic substances were often found in such particles [21, 22]. Lately, the updated review of relations between human health and exposure to atmospheric aerosols has been published by Englert [23] and by Kappos et al. [24].

Significant political and economical transformations in Poland during the last twenty years have changed the sources of anthropogenic pollution. The reduction of emissions of air pollutants from the metallurgical, chemical, and coal mining industries have taken place, especially in Upper Silesia. Although these traditional industrial, as well as municipal sources, are still very important there, the present sources are also related to rapid development of vehicular traffic along the streets. Traffic has been recognized as a significant source of fine/respirable particles because mainly fine and ultra-fine particles are emitted by compression-ignition (diesel) engines, although other sources of aerosols, including vehicle wear and street surface erosion, as well as dirt and materials which fall from vehicles, can be important. Therefore, particulate matter originating from mobile sources is thought to be responsible for various health outcomes, ranging from asthma to lung cancer and cardiopulmonary disease, and environmental problems (for example, acid rain) [25-29].

To clarify the effect of the changes in the hierarchy of emission sources of particulate pollutants on the atmospheric aerosol in Upper Silesia, intensive studies are required. The chemical characterization of the surface of atmospheric particles is crucial to identify particulate sources because new species produced from chemical reactions in the atmosphere occur on the particle surface. Although the toxicity of airborne particles is still not clearly understood, it should be noted that the chemical composition of the surface of particles also plays an important role in determining health effects, because the surface is directly accessible to biological fluids after inhalation. X-ray photoelectron spectroscopy (XPS) is a surface analysis technique and in recent years, a number of researchers have used XPS to analyze particulate matter collected onto filters [30-37]. However, the surface composition of airborne particles from the vicinity of busy roads and crossroads has not yet been investigated. Such investigations seem to be important because long-term emissions from motor vehicles may essentially change physicochemical properties of the atmospheric aerosol near the roads, perhaps even in downtowns.

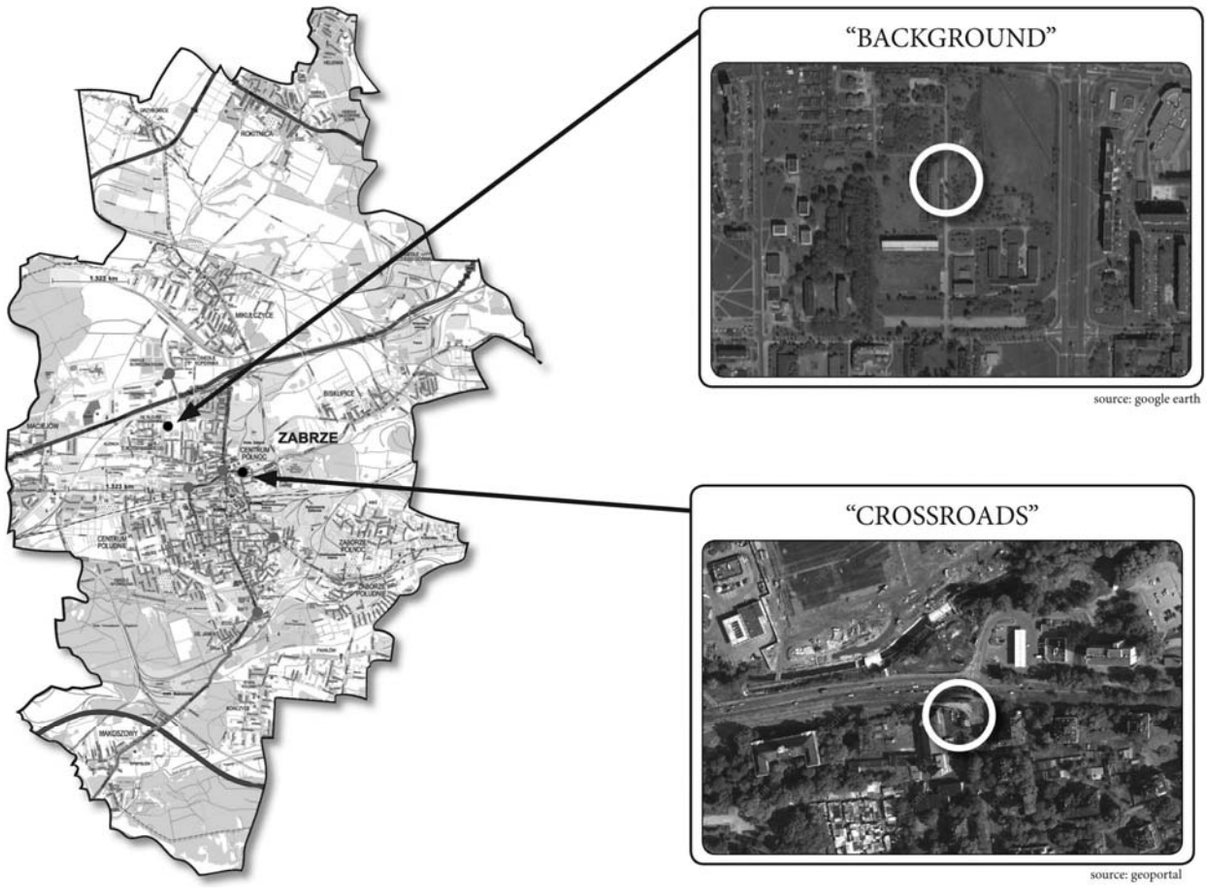

Fig. 1. Location of the "BACKGROUND" and "CROSSROADS" sampling points.

The aim of this paper was to compare the PM10 and PM2.5 concentrations near a very busy crossroads in Zabrze with their urban background concentrations and to determine the elemental composition of the surface layer of particles of these aerosol fractions. This work is the first application of XPS to the study of surface composition of airborne particles of traffic origin in Poland (and certainly one of the first in the world).

Methods

The aerosol particles were collected simultaneously at the roadside and in the urban background site in Zabrze, an industrial town in Upper Silesia, Poland, extending in the area of 80.5 km^2, and densely populated (2,363 persons/km^2). The roadside site ("CROSSROADS") was located in the downtown, at a crossing of two busy roads while the reference site ("BACKGROUND") was about 1,400 m away, in the Institute of the Environmental Engineering of the Polish Academy of Sciences (Fig. 1), near the air quality monitoring station belonging to the regional network. This point is an official urban background site, although it can be influenced in specific circumstances by emissions from radial motorways and the industrial-urban plume from other parts of the Upper Silesia Industrial Zone. Therefore, the urban background aerosol level is typically higher than background levels in other Polish and European towns. However, it should be stressed that no industrial emissions affect directly both these sites because there is no heavy industry and no power generation plant in this territory. Apart from vehicular traffic what is an important source of airborne particles for the roadside sampling point, only domestic furnaces emitting pollutants from hard coal burning are significant emitters of particulate matter in the studied area.

Cars passing the crossroads were counted to determine the traffic density at the roadside site during the first 25 minutes of each hour on the sampling days. The result, multiplied by the factor 60/25, was assumed as the hourly traffic density for this hour.

The aerosol particles were collected 3-4 times a month on randomly selected days over the period April to December 2005 using two MVS6D samplers (ATMOSERVICE, Poznań, Poland), certified for compliance with the CEN EN 12341 European Standard. Each sampler could collect PM10 or PM2.5, depending on the selected exchangeable sampling head, at the constant volumetric air flow 2.3 m^3/h. The sampling time was 24 hours. The samples were taken in pairs consisting of two samples of the same aerosol fraction (PM10 or PM2.5) taken simultaneously at the roadside site and at the background site. To obtain the PM2.5/PM10 ratio, some additional measurements of the PM10 and PM2.5 aerosol fractions were carried out in both sites (first in the roadside and next in the background because only two samplers could be used in this study).

The particulate matter masses were determined gravimetrically by subtracting the initial average mass of the blank filter (Teflon for PM2.5 and glass fiber for PM10) from the final average mass of the sampled filter; the difference was then divided by the total volume of air that passed through filter. The steps of pre- and post-sampling gravimetric mass determinations were the following: 48 hours to equilibrate filters before weighing at temperature 21ºC and relative humidity of 50%, followed by weighing during 24-48 hours. The certified Mettler Toledo AG245 microbalance was used for weighing all the filters. The Mettler Toledo gate was applied to neutralize electrostatic charges on the filter surface.

Basic meteorological parameters such as wind speed and direction, relative air humidity and precipitation for Zabrze were taken from a Web page of the Regional Inspectorate of Environmental Protection in Katowice.

The surface elemental composition was determined for 5 selected pairs of parallel exposed PM10 filters and 4 pairs of parallel exposed PM2.5 filters, by applying the X-ray photoelectron spectroscopy (XPS) technique. The PHI 5700/660 Photoelectron Spectrometer (Physical Electronics, USA) with the monochromatic Al K_α source of X rays (1486 eV) was used. Spectra of energy distribution of photoelectrons were analyzed by a hemispherical analyzer having resolution of approximately 0.3 eV. The area 0.8 × 2 mm of a filter surface was analyzed. Each analysis lasted 12 hours. The measurements were performed in ultra high vacuum (10^{-8} Pa). A low energy electron gun was used to neutralize electric charge which occurs for non-conducting samples.

In the selected samples the elements in a collected particles` surface were identified and relative amounts of the detected elements were determined from the XPS spectra in the energy range 0–1400 eV. The results were developed with the use of the Multipak computer program. Binding energies of particular elements were referred to the C 1s (284.6 eV) level.

The XPS spectrum for the clean Teflon and glass fiber filters were also obtained. Besides, for some filters covered with very thin layer of collected airborne particles only, the influence of the filter surface on the spectrum lines of detected elements was determined.

Results and Discussion

PM10 and PM2.5 Concentrations

Before the discussion of the obtained results it should be mentioned that during the study period weather varied from typical summer to winter.

The analysis of traffic flows at the studied crossroads indicated two daily peaks, both ranging from 2,500 to 2,850 light vehicles per hour: the first maximum of the traffic density appeared between 7 and 9 a.m., the second - between 2:30 and 4:30 p.m. The highest number of trucks (and buses) ranged from 250 to 350 per hour, and appeared about 3:00 p.m., keeping at this level till late evening. The daily averaged traffic density was 1,200 light cars and 120 trucks per hour. Assuming that all light cars had petrol

engines and the trucks had diesels, it means that the daily traffic flow on the crossroads was 28,800 and 2,900 vehicles per day for the petrol and diesel vehicles, respectively. Therefore, the traffic densities of petrol engine vehicles are roughly one order of magnitude higher than those for diesel-powered vehicles.

The daily concentration levels of PM10 and PM2.5 for both studied sites are shown in Figs. 2 and 3, while the mean and other statistical parameters are presented in Table 1. It can be seen that at the crossroads site the mean concentration of PM10 and PM2.5 was 55 and 32 μg/m^3, respectively, while at the background site these aerosol fractions reached only the level of 37 and 22 μg/m^3, respectively.

Detail analysis of the difference between roadside and corresponding urban background samples indicates (Table 2) average mass increments of 17.7 μg/m^3 of PM10 and 10.2 μg/m^3 of PM2.5 for these two site pairs. The relative increase of PM10 at the roadside (comparing to background) ranged from 22.5 to 144.2% (Table 2) while such an increase of PM2.5 ranged from 7.1 to 103.2%. It can also be seen from Fig. 2 that the greatest difference between PM10 concentrations monitored at both sites was 45.9 μg/m^3 (May 12–13, Thursday/Friday, air temperature 19–25ºC, no precipitation nor wind) while the smallest was equal to 7.6 μg/m^3 (August 19–22, weekend, air temperature 18–30ºC, weak wind). For PM2.5 concentrations the greatest difference was 25.6 μg/m^3 (April 21–22, Thursday/Friday, air temperature 10–19ºC, weak wind) while the smallest - 1.3 μg/m^3 (August 5–10, weekend, air temperature 20–28ºC, strong wind).

It is important to note that at both sites concentrations of airborne particles increased in the heating season (Fig. 2). Such seasonal variability of PM10 and PM2.5 occurring in urbanized areas does not occur in rural regions [38]. This is one of the reasons for locating a background site within an urban area rather than beyond the city. Because the only important difference in the sets of sources of emission of PM10 and PM2.5 in both studied sites is the traffic, the differences in the concentrations of PM10 and PM2.5 obtained for these sites may be considered the vehicular traffic contribution.

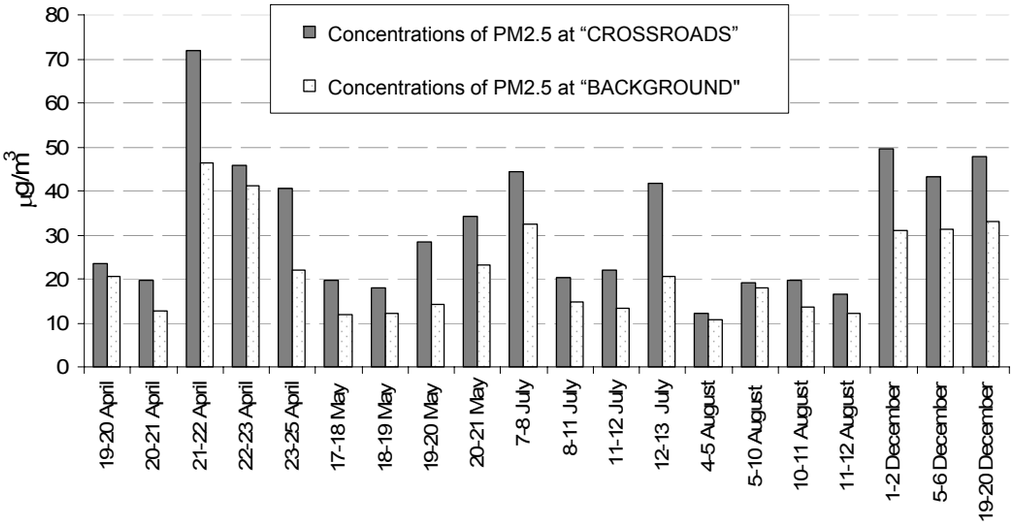

Fig. 2. PM2.5 concentrations at the "BACKGROUND" and "CROSSROADS" sampling points.

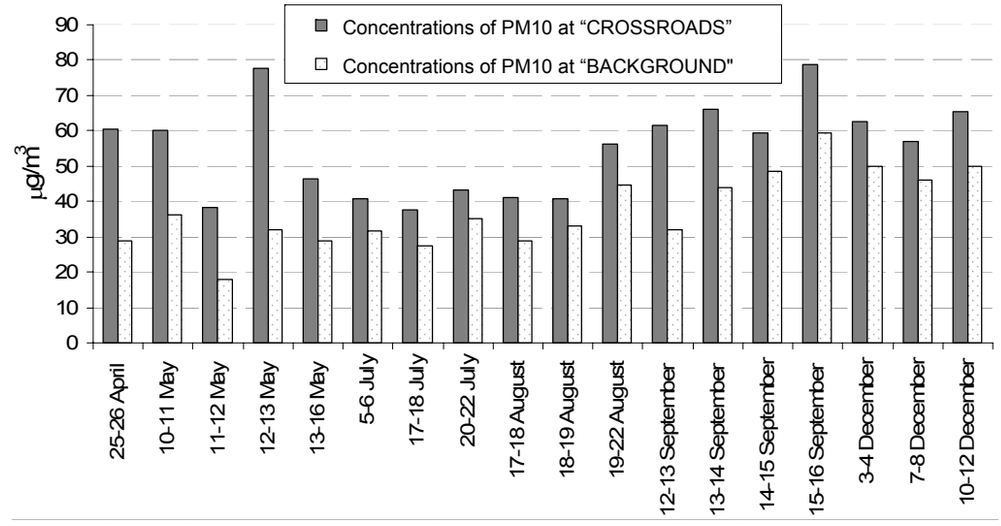

Fig. 3. PM10 concentrations at the "BACKGROUND" and "CROSSROADS" sampling points.

These results, obtained in Zabrze, are in opposition to the intuition suggesting that emissions of fine particles should be the dominating process of traffic emissions. This expectation could be supported by some previous research, mostly focused on vehicle exhaust particulate emissions, because it is generally assumed that fuel combustion is the primary mechanism by which the particles are formed [39-40]. On the other hand, present studies are often oriented towards ultrafine particles emitted from diesel engines (see, for example [41]). However, tire, brake and clutch, as well as a resuspended dust also contribute to atmospheric particulate matter [42]. In fact, some other authors have independently confirmed this conclusion. For example, a Swedish study showed that street PM10 and PM2.5 is 2.5 times and 1.5 times, respectively, higher than background [43]. Our results, however, with the roadside/background ratio equal to 1.5 for both PM10 and PM2.5 fit very well, especially to the British data. Harrison et al. [44] examining, in London and Birmingham, UK, the difference between roadside and corresponding urban background aerosol samples, obtained average mass increments of 11.5 μg/m^3 of PM10 and 8.0 μg/m^3 of PM2.5. It can be calculated from their data that the street PM10 is 1.5 times higher than background, while street PM2.5 is 1.6 times higher than background.

Our preliminary assessment of PM2.5/PM10 ratio indicates that the estimated level of this parameter is 0.63 and 0.75 for roadside and background, respectively. Although the PM2.5/PM10 proportions were not measured simultaneously at both sampling points and it is not possible to assert that the differences between the means of the ratios at traffic and background sites were statistically significant, the PM2.5/PM10 ratio seems to be slightly higher at the background site in Zabrze. It is interesting to note that similar PM2.5/PM10 ratios, contained within a range of 0.73 ±0.15 were obtained by Van Dingenen [45] for various sites over Europe. Especially, the averaged proportion of fine particles to PM10 determined for 25 sites in Middle and Eastern Europe was equal to 0.68 (including 0.75 for 4 cities in southern Poland) [46]. Besides, this ratio was 0.67 in 4 Austrian sites [38], and 0.76 in Thessalonica, Greece [47]. However, more detailed analyses of this ratio in Zabrze needs further study.

Since it is known from the epidemiological investigations that increasing PM10 concentration by 10 μg/m^3 causes 2–5% more cases of upper respiratory tract diseases, it could be concluded that 4 or even 10% more people living in the vicinity of the studied crossroads are expected to complain of such diseases, compared to the population living at the urban background area in Zabrze.

Table 1. Comparison of mass concentrations of airborne particulate matter near the crossroads and in the background site in Zabrze, Poland.

	Concentration [μg/m^3] of			
	PM2.5		PM10	
	CROSSROADS	BACKGROUND	CROSSROADS	BACKGROUND
Mean	31.9	21.7	55.2	37.4
Standard deviation	15.5	10.6	13.0	10.6
Minimum	12.2	10.6	37.5	17.8
Maximum	71.9	46.3	78.6	59.4
n	20	20	18	18

Table 2. Increment of concentrations of PM2.5 and PM10 near the crossroads compared to the background level.

	Increment of concentration of			
	PM2.5		PM10	
	INCREMENT [μg/m^3]	REL. INCREMENT [%]	INCREMENT [μg/m^3]	REL. INCREMENT [%]
Mean	10.2	48.4	17.7	52.9
Standard deviation	6.8	26.7	10.0	37.6
Minimum	1.3	7.1	7.6	22.5
Maximum	25.6	103.2	45.9	144.2
n	20	20	18	18

INCREMENT = concentration at “CROSSROADS” – concentration at “BACKGROUND”;

RELATIVE INCREMENT = (concentration at “CROSSROADS” – concentration at “BACKGROUND)” / concentration at “BACKGROUND”) * 100%

Elemental Composition of Surface of Airborne Particles

The XPS analysis of the aerosol samples was performed for the pairs of filters with airborne particles collected in the following days: April 25–26, May 10–11, May 11–12, May, 12–13 and May 13–16 for PM10 as well as August 10–11, August 11–12, December 1–2 and December 5–6 for PM2.5. The PM10 concentration levels at the roadside were significantly higher than at the background site for all selected samples. The differences ranged from 17.5 μg/m^3 (May 13–16, weekend) to 45.9 μg/m^3 (May 12–13). The differences between roadside and corresponding background concentrations of PM2.5 for the selected pairs ranged from 4.4 μg/m^3 (August 11-12) to almost 19 μg/m^3 (December 1-2).

Examples of the XPS spectra for the roadside and background aerosol in Zabrze are shown in Figs. 4-7. Before detailed analysis of these data it should be noted that XPS yields information on the particle surface rather than the average composition of the whole particles. An important limitation is also the loss of volatile species under UHV conditions, particularly organic species from soot [31]. As shown in Figs. 4-7, the spectra indicate strong peaks of carbon and oxygen, which seem to be the typical picture for urban aerosol because similar results have been obtained in different towns around the world [31, 32, 34-36, 48, 49]. The relative content of the elements determined from XPS analysis is presented in Table 3. It can be seen that the surface layer of PM2.5 and PM10 from the roadside contains significantly more carbon and less oxygen than the airborne particles collected at the background site, which might be explained by the high emission of carbon, mainly soot, from vehicles. It is interesting to note that the relative concentration of silicone in the surface of airborne particles decreases near the crossroads in comparison with the background, which confirms the considerable contribution of particle traffic origin in the aerosol near the crossroads.

It is worth analyzing the December data in more detail. The average relative concentration, presented in Table 3 was mainly caused by the results from December 1-2, when air temperature was between -2 and -2.5 ºC. There was 2.3% more of the elemental carbon in PM2.5 surface at the roadside than in the background site during these days,

Table 3. Surface elemental composition of PM2.5 and PM10 collected near crossroads and in the background site in Zabrze, Upper Silesia, Poland.

Element	Concentration [%at.]					
	PM10 (April, May)		PM2.5 (December)		PM2.5 (August)	
	"CROSSROADS"	"BACK-GROUND"	"BACK-GROUND"	"CROSSROADS"	"BACK-GROUND"	"CROSSROADS"
C	77,24	58,27	82.68	83.51	74.59	82.53
N	1,89	2,4	2.59	2.52	2.27	1.29
O	17,16	29,5	13.41	12.55	20.78	12.41
Na	0,18	0,45	0.1	0.245	0.215	0.215
Mg	0,06	0,03	0.08	-	-	0.015
Al	0,51	0,47	-	-	-	0.415
P	-	0,04	-	-	-	-
Si	1,86	7,63	0.33	0.1	1.76	1.0451
S	0,47	0,52	0.43	0.485	0.135	0.275
K	0,02	0,05	-	-	-	0.38
Cl	0,22	0,19	0.375	0.43	0.1	0.39
Zn	0,08	0,14	-	0.055	-	-
Pb	-	-	-	-	0.005	0.02
Ca	0,2	0,2	-	-	0.09	0.265
Fe	0,12	0,07	-	0.105	-	0.40
Co	-	0,05	-	-	-	-
Ti	-	-	-	-	0.055	-
I	-	-	-	-	0.01	-
Cr	-	-	-	-	-	0.35

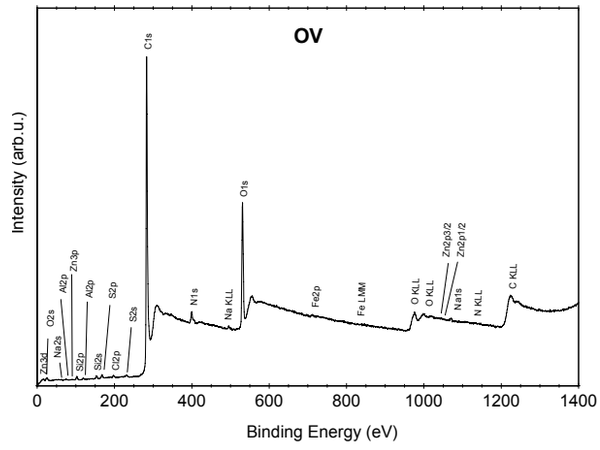

Fig. 4. Example of the XPS spectrum for the PM10 sample from "CROSSROADS" (May10-11).

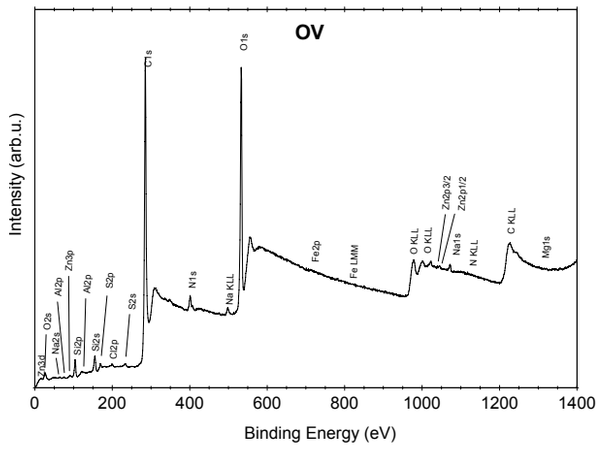

Fig. 5. Example of the XPS spectrum for the PM10 sample from "BACKGROUND" (May10-11).

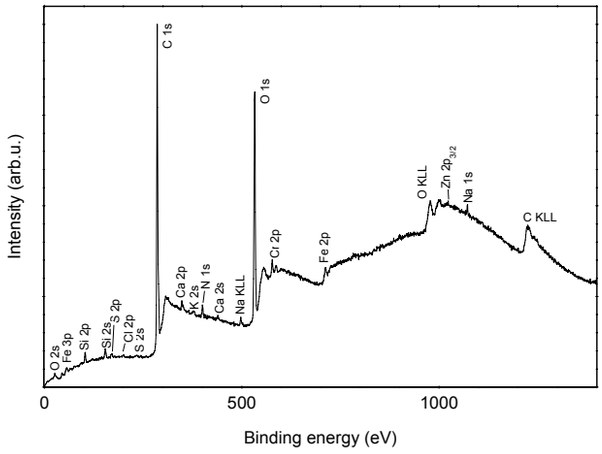

Fig. 6. Example of the XPS spectrum for the PM2.5 sample from "CROSSROADS" (August 10-11).

whereas in December 5-6, when the air temperature significantly decreased, the relation was inverted, indicating 0.64% less carbon in fine particles at the roadside in comparison with the background. This phenomenon appeared probably due to the rapid increase of carbon emission from the domestic furnaces and other heating utilities in this period.

Figs. 8a and 8b show the carbon spectral lines in the narrow energy bandwidth. It may be seen that carbon occurs mainly in compounds with hydrogen, oxygen, silicon and nitrogen. Its bond with fluoride also occurs (Fig. 8a). Determining the carbon lines in a narrow energy bandwidth: 280–290 eV (Fig. 8b) allows us to find a peak corresponding to the coal – chlorine bond. This result could indicate that some dioxins were present in the surface layer of studied particulates at the roadside. Generally, our issues agree well with the results obtained by Paoletti et al. [33] who indicated that various forms of carbon, detectable within the energy range 286-290 eV, participate in the total carbon present in the surface layer of fine airborne particles.

From Table 3 it also may be observed that the surface layer of PM2.5 near the crossroads comprises more sulfur and chloride than at the background site. On the other hand, analyzing Fig.6 where the sulfur peak appears for the binding energy of about 170 eV, it can be concluded, according to Paoletti's study [33], that sulfur in the surface layer of airborne particles (PM2.1) occurs mainly in the form of anion SO_4^{2-}.

In contrast to PM2.5 the surface relative concentration of sulfur in PM10 is lower near the crossroads than at the background site (Table 3). This suggests that, generally, in Zabrze urban area sulfur occurs mostly in coarse particles (PM10 – PM2.5) and comes from municipal sources, mainly domestic furnaces. On the other hand, the roadside aerosol is enriched by sulfur emitted from vehicles. Therefore the surface concentration of sulfur is elevated there in fine particles.

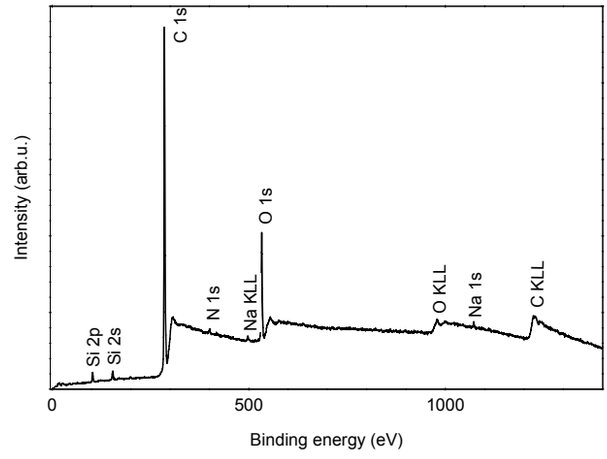

Fig. 7. Example of the XPS spectrum for the PM2.5 sample from "BACKGROUND" (August 10-11).

It is also interesting to analyze the relative concentration of iron and chromium in the surface of fine particles. Table 3 shows that Fe was detected in PM2.5 only near the crossroads. Chromium also appeared only in the PM2.5 sample collected near the crossroads (only in August 10-11). It can be seen that both these metals occurred in oxide compounds: Cr_2O_3 (Fig. 9) and Fe_2O_3 (Fig. 10). This result can be partially explained by the recent study carried out by Geller et al. [50]. They found that car exhaust gases contain some amounts of chromium and iron. Besides, in the case of iron it is possible that the detected Fe_2O_3 comes mostly from mechanical processes (abrasion, corroded iron parts).

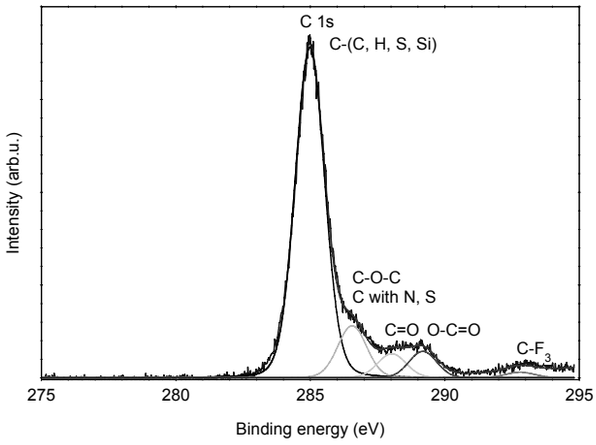

Fig. 8a. Carbon spectral line in narrow energy bandwidth 275 – 295 eV for PM2.5 sampled on August 10-11, 2005, at "BACKGROUND."

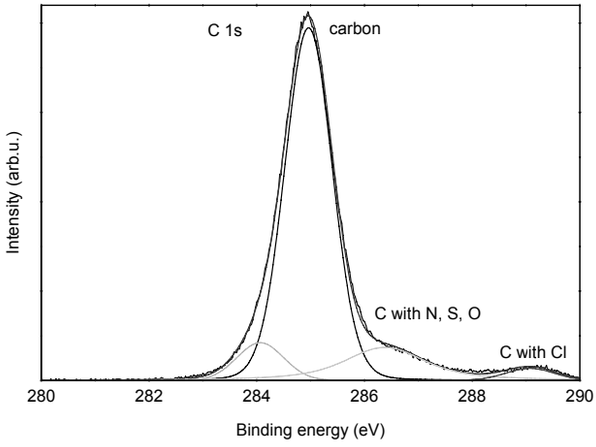

Fig. 8b. Carbon spectral line in narrow energy bandwidth 280 – 290 eV for PM2.5 sampled on August 10-11, 2005, at "CROSSROADS."

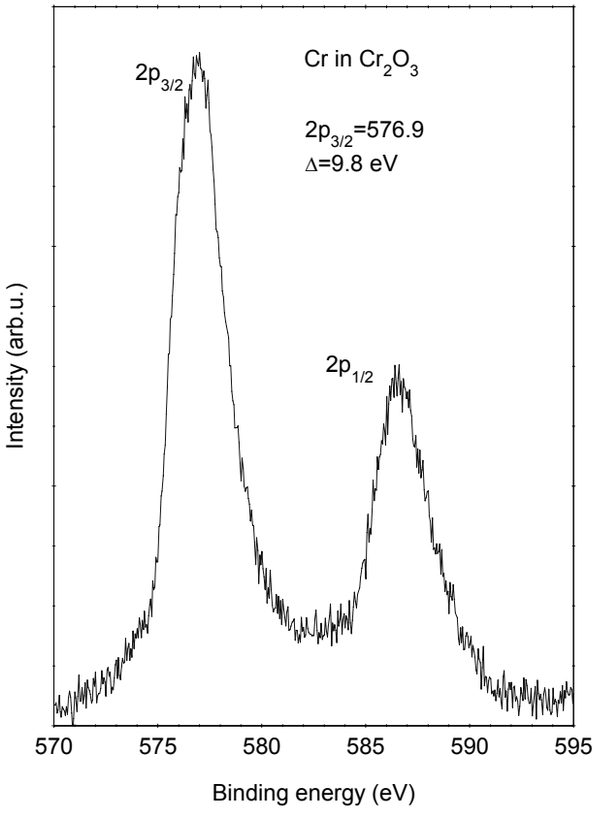

Fig. 9. Chromium spectral line in narrow energy bandwidth 570 – 595 eV for PM2.5 sampled on August 10-11, 2005, at "CROSSROADS."

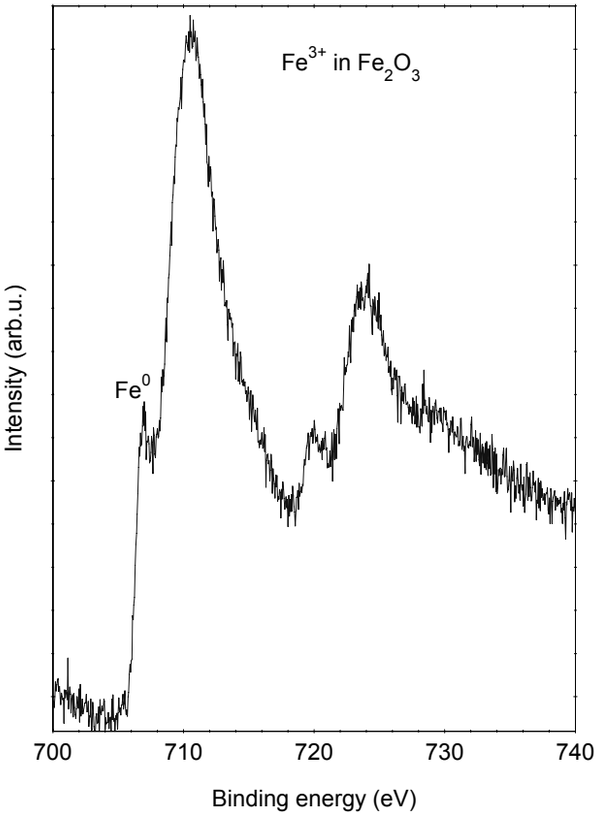

Fig. 10. Iron spectral line in narrow energy bandwidth 700 – 740 eV for PM2.5 sampled on August 10-11, 2005, at "CROSSROADS."

Conclusions

Analysis of the difference between roadside and corresponding urban background aerosol concentration in Zabrze, Upper Silesia, in the period April-May 2005 indicated average mass increments of 17.7 μg/m^3 of PM10 and 10.2 μg/m^3 of PM2.5. Therefore, it has been demonstrated that the crossroads is a significant source of airborne particles, even in the heavily industrialized and urbanized city; where *per capita* (for all the area of the town) the major emissions come from industrial and municipal sources.

When applying the epidemiological data to our results it can be expected that the number of upper respiratory tract diseases of the Zabrze population living near the crossroads will be elevated by 4–10% in comparison with the population living in the urban background area of Zabrze.

The XPS analysis of the PM10 and PM2.5 surface at the background site concludes that elemental carbon is the major component of these two particle fractions, accounting for about 58% and 79%, respectively, increasing in winter. The roadside site shows a strong elevation in elemental carbon in comparison with simultaneously collected urban background samples. An increase of the surface concentration of Cl in aerosol particles near the crossroads compared with the background aerosol has been also observed. On the other hand, the surface layer of the airborne particles contained less O and Si than particles collected at the urban background site.

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