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Mineral composition of the airborne particles in the coal dust and fly ash of the Kolubara basin (Serbia)

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Abstract

The airborne particles were collected near the power plant and the opencast coal mine of the Kolubara basin. This paper represents the part of the one-year project aiming to collect, characterize and then determine the mineralogical composition of the airborne particles. Samples of deposited particulate matter from the air were collected between March 2007 and March 2008. Mean concentrations content of soluble, insoluble and total deposited matter measured annually exceed 200 mg/m^2 per day (U-1 and U-3). The particle distribution at all sites was classified in three classes: the particles larger than 10 µm, the particles from 10 to 2.5 µm and the particles below 2.5 µm. Such a division gave the ratio of inhaled and respiratory particle concentrations by the measuring points. Scanning electron microscopy showed that dust from coal mines and power plant largely consists of the group of mineral grains and coal particles. SEM-EDS analysis also showed that the mineral composition of the deposited particulate matter was heterogeneous but uniform throughout the investigated area. These findings were also supported by X-ray powder diffraction analytical studies, which gave a similar mineral composition for all samples (quartz, feldspar, clays, gypsum, dolomite, calcite, micas, chlorite and hematite). This paper shows that both concentration and mineralogical characterization of airborne particles from mine and power plant are essential for quantification of the fractions that are inhaled and for the identification of potentially dangerous (hazardous) components in the deposited matter.

Key words: mineral dust; particulate matter; fly ash; deposited material; Kolubara.

Introduction

The air of the atmosphere always contains a certain amount of aerosol particles found in solid or liquid state. Besides the natural aerosols, significant amounts of so-called industrial aerosols are found in the atmosphere. They have a negative effect on the development of flora and fauna and also pose a serious threat to human health. One of the greatest dangers is connected with inhaling industrial dusts which contain free silicon dioxide (SiO_2). Mining dusts are industrial dusts as well, formed as a result of exploitation and processing of non-metallic mineral raw materials and coal, and also due to the release of ash through coal combustion in thermal power plants. Particles in the air may also appear due to natural processes, during interactions in the very air. Merefield et al. (1995) carried out analyses of environmental dust from the area of opencast mining excavation site in south Wales. Using the combination of X-ray diffraction and the SEM (scanning electron microscopy) analysis they singled out ten most common minerals: quartz, basanite, halite, calcite, illite, chlorite, kaolinite, montmorillonite, dolomite and feldspar. The level and mineral composition of dust generated in the open pits were determined by local geology and mining operations. Jones et al. (2002) have determined the mineralogical composition of particles from the Park Slip West opencast coal mine. Mineralogical associations were variable in dependence of local geology and mining activities.

According to the effect they make industrial dusts can be toxic, aggressive and inert. Toxic dusts while dissolving create toxic components which, after a certain amount of time, cause physiological changes in the body. Aggressive dusts have the mechanical effect on human body, causing physiological changes (lung fibrosis), dissolve difficult or not at all, and after a while, depending on the component, create a certain disease.

Inert dusts are present in the working environment and even after prolonged inhalation does not cause any specific disease, i.e. do not cause physiological changes (limestone, magnesite, gypsum, etc.). Some insoluble substances are classified as inert (e.g., the iron dust, steel dust, cement dust, coal dust). Inert dusts that are easily dissolved can be rapidly eliminated from the body. Over time, insoluble inert components might be accumulated in the respiratory organs, creating the so-called pockets, thus reducing the capacity of the lungs.

Through coal combustion, practically only organic matter is lost while the inorganic part remains in the ashes. Flying ash contains incombustible inorganic matter present in coal that during the combustion is partly transformed into a glassy, amorphous substance. Flying ash particles are generally spherical in shape and from 0.5 μm up to 100 μm in size, and mainly contain SiO_2, Al_2O_3 and Fe_2O_3. Minerals from the clay group, quartz, feldspar, hematite and micas are most common. The other minerals, such as calcite, dolomite and chlorite, are rare (Djordjević, 2005).

It is well known that workers working in coal mines are more susceptible to respiratory diseases compared to employees in other areas. The possibility that the dust from coal mines with a coal and quartz content along with smoking, depending on individual sensitivity, can cause lung diseases were studied by many authors (Love et al., 1997; Munro and Crompton, 1999; Jones et al., 2002).

In this paper attention was paid to the mineralogical composition of airborne particles and their effect on human health. According to Richards and Wusteman (1974), particles less than 10 μm in diameter are called inhalational, or those that can be inhaled, while those less than 2.5 up to 3 μm in diameter are considered respiratory, or the ones that can remain in respiratory organs such as lungs. The fact is that not all particles have an equal effect on human health and that it is important to know the shape, size and whether they have bioreactive surface. Thus, frequent exposure to particles rich in silica, which are considered highly bioreactive, can cause lung silicosis. According to that, from the aspect of health, it is important in which mineralogical form the particles are present. Particular attention is paid to the mineralogical aspect of these particles.

Earlier works on the impact of the inhalation of mineral dust and flying ash on human health can roughly be divided into four groups. The first is the study of dust from the sites consisting of many types of rocks. The study of opencast mines with the presence of sedimentary rocks that, together with coal, can contain sandstones, shales as well as a number of associated minerals, falls into that category (Munro and Crompton, 1999; Pless-Mulloli et al., 2000). David et al. (1981) have studied the biological activity of the dust from mines as well as the quartz content. Merefield et al. (1995) specified the mineral composition of dust from the opencast, mainly from a geological aspect but not from the aspect of its potential influence on human health.

The second group encompasses studies related to one type of rocks, assuming that these rocks may contain various minerals. The examples are given by El Ghawabi et al., (1985) who studied the pneumoconiosis caused by basalt.

The third group involves the study of certain toxic minerals. The examples include silica (Fubini et al., 1999; Ivanović, 2002), kaolinite (Lapenas et al., 1984), talc (Henderson et al.,1975), micas (Shanker et al., 1975) and asbestos (Ivanović, 2002).

The fourth group includes morphological, chemical and structural studies of free ash particles and their impact on the environment and human health (Gieré et al., 2003).

The form of the particles, from almost spherical to very irregular, can be determined by using an electron microscope. Furthermore, particles can consist of primary particle aggregates, i.e. of a central particle with relatively tightly associated smaller particles. Due to large difference in particle forms, their size is often presented by the Stokes radius, which is defined as the radius of a sphere which has the same falling speed and density as the particle observed. The Stokes radius of particles of mist, steam and smoke are almost identical to the real, geometric radius of a particle. The geometric radius of particles produced by friction as well as of complex particles can be much smaller than Stokes.

Materials and methods

The samples have been collected within the range of Kolubara coal basin, which is situated about 50 km southwest of Belgrade, and is one of the largest coal basins in Serbia with an area of about 600 km^2. Its productive area is reduced to about 170 km^2. It covers an area limited from the west by the Cer Mountain, from the south by the slopes of Bukulja and Venčac mountains, the Mesozoic serpentine rocks of Šumadija from the east, while towards the north it is open to the Pannonian Basin. The productive part of the basin is divided by the Kolubara River on the eastern and western parts. In geological terms the deposit represents a single unit where deposition of organic matter took place over a long period of time in a wide area (Janković and Janković, 1998). The present appearance of the relief is largely the result of the geological composition of the background. More intensively dispersed relief is located on the border areas of the basin, built of Palaeozoic and Mesozoic solid creations. The geographic map of the Kolubara basin area is shown in Figure 1.

Figure 1. Geographical position of the Kolubara basin. (Modified from Tourist-road map of Serbia and Montenegro, published by Company "Novosti", Belgrade, 2004).

During 2007 (March - December) and January - February 2008, systematic sampling of deposited aero sediments was carried out on four sampling locations: one in the town of Ub and three in rural areas outside the settlement. Geographical position of the Ub municipality and location of the sampling points, occupying north-western part of the Kolubara basin, is presented in the Figure 2. Locations for sampling were chosen based on vicinity and impact of potential pollution sources, which are numerous in the Kolubara basin of the Ub municipality. The first location U-1 covers a wide area encompassing the place Brgule. Due to the multiple sources of airborne particles (Kolubara A-TPP (Thermal Power Plant), Tamnava-west coal mine (Figure 3), Kolubara B-TPP, vicinity of the railway line), this location is interesting because of the potential presence of both primary and secondary minerals. The location U-2 is the westernmost point in the study area. Results from that point showed how much Obrenovac-TPP and the Tamnava-west opencast influenced the pollution. Closeness of the highway and the individual furnaces are also significant sources of the airborne particles. The presence of both primary and secondary particles-minerals was expected. Point U-3 is located in a heavily populated urban area of Ub. This point is important because of its very position, as it is located on one of the top elevations in town, so it represents the whole place. Potential sources of dust and fly ash are numerous: Kolubara B -TPP and Obrenovac-TPP, individual home furnaces, industry, the impact of the industry of the towns in the surroundings. Location U-4 is unique because it is located in the sheltered, forested area far from the source of the contamination. It is situated in the central, rural part of the investigated area. This point was chosen to determine whether the mineral composition of dust varies in relation

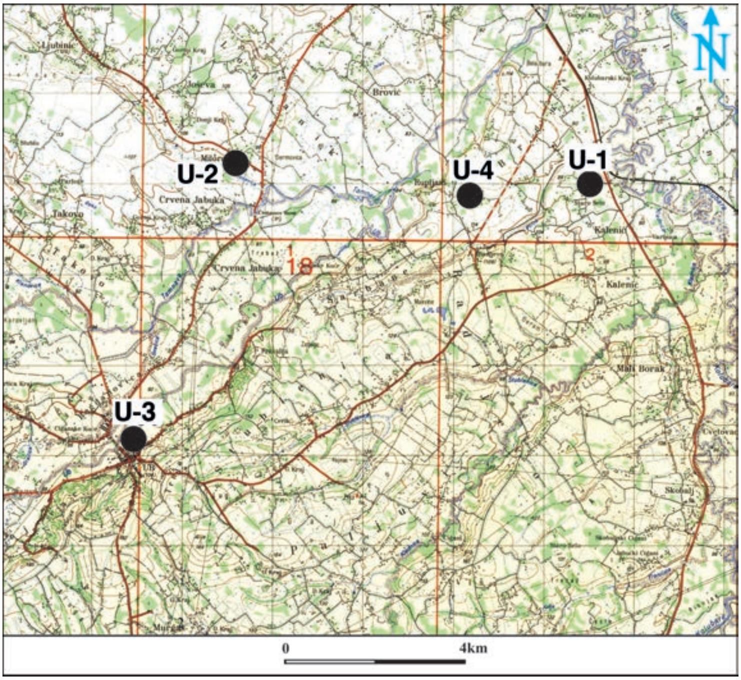

Figure 2. Position of the sampling places within the Kolubara basin. (Modified from Topographic maps 1:50.000, sheets Lazarevac 1 and Beograd 3, published by The Military Geographical Institute, Belgrade, Serbia, 1970).

to other locations and whether the mineral dust is present in these areas and to what extent.

From the four selected measurement locations, samples were collected monthly. Sampling of deposited substances was carried out in the winter and summer period. The winter period included 180 days from 28th of August 2007 to 26th of February 2008 (98,90 %), while the summer period included 176 days from 05th of March 2007 to 28th of August 2007 (95,65 %) of the planned period. Sampling included a total of 356 days, i.e. 97.27% of the year. As far as the individual measuring points are concerned, no breakage of the deposition tanks or loss of samples was registered, so, all measuring points were active all the time. Hence, during one year of sampling, 12 samples from each measuring point were gathered. Samples collected during six winter months were merged into one. The same was done for the summer period. In that way, two samples were obtained from each measuring points: one for the winter and one for the summer period, which make total of eight samples.

The equipment on the field was in accordance with the current regulations in the field of measuring immission (Directive, 2008) and this included placing deposition tanks for the sampling of aero sediments. Particles were gathered by the sedimentation method, due to their property to deposit on certain surface as a result of their own weight. This method was used to determine the quantity of liquid pollutants, and also the quantity of solid matter diluted by the rainwater and swilled into the deposition tank on its way to the ground. The deposition tanks for aero sediment sampling were made of chemically inactive materials (plastics). The deposition tank is a container for aero sediment collecting with a capacity of three litters with a funnel of the prescribed minimal diameter (210 mm). The deposition tanks were placed outdoors, in the courtyards of individual households. The deposition tank supporting holder was metallic column, with a concrete foot buried into the ground, about 2 m high, with a metal basket (bearing) on top (Figure 4).

The initial method, used primarily for the introduction with the material the samples were made of, was the examination of microscopic thin sections prepared in the xylol immersion on glass. This was followed by taking photographs

Figure 3. View of the Tamnava opencast mine and coal exploitation. Removal of the overburden generates large amounts of dust, whereas in the case of actual coal mining (middle bottom) no visible dust is generated.

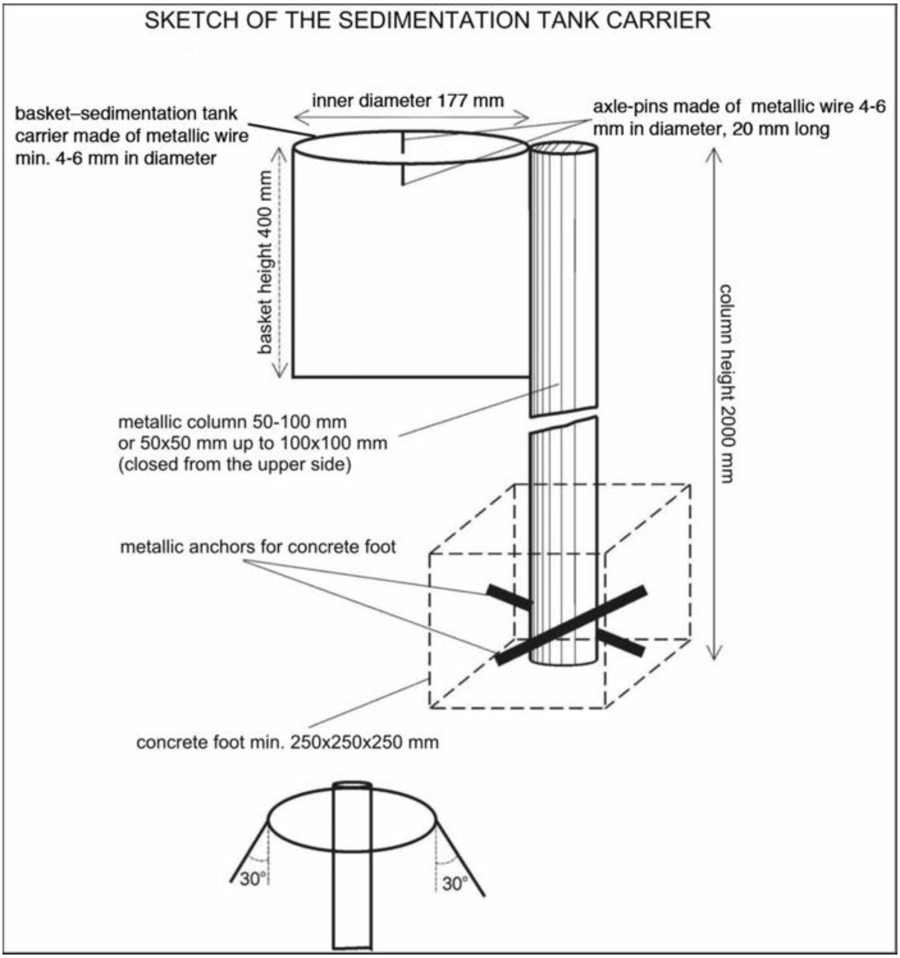

Figure 4. Schematic diagram of the columnar supporting holder of deposition tank for aero sediment sampling (Ločkić, 2003).

of particles in the thin sections in order to determine their granulometric composition. Thin sections were observed using a Zeiss transmitted-light microscope with 6x, 16x and 40x magnification lenses. Photographs were taken using a JVC, GC-X3E digital camera.

For the determination of particle size (granulometric composition) a MAUD (Mineral Analysis Using Diffraction) software package which contains a program for digital image analysis was used (Lutterotti, 2002). Photomicrographs of the particles in thin sections for image analysis were taken by a digital camera affixed to the microscope ocular. Besides the photos of the particle, scale recordings for each lens magnification used were also made. One notch on the scale is 10 microns. The program itself is based on integration, or summation of grain areas which are later placed in the given granulometric classes. For the integration, it is important that the contrast between the grains and the matrix is as strong as possible. The best contrast is obtained when the grains are black and the matrix is white, which can be achieved by adjusting the eight bit tone scale.

The output data from the MAUD software package were: number of analyzed grains, their size and the coordinates. Such data were processed in MS-Excel and graphically presented in histograms as the representation of relative surface of grains (%). Sizes of the sample particles have been determined by applying picture analyses.

Samples of deposited aero sediments were investigated by X-ray powder diffraction method. Analyses were carried out on the Philips automatic X-ray powder diffractometer, type PW-1710. Copper anticathode with CuK_α radiation (λ = 1.54128 Å) and graphite monochromator were used. Data were collected in the 2θ angle range from 5 ° to 50 ° with a 0.02 ° step. The precision of the diffractometer was controlled before and after the experiments, using the Si standard. The tests were performed in the Laboratory for Crystallography of the Faculty of Mining and Geology in Belgrade. The identification of the existing mineral phases was performed by comparing interplate distances (d) and relative intensity (I) with literature data, or the appropriate standard card from the JCPDS files. Samples of aero sediments of 0.5 to 2 grams were placed into aluminium frames and photographed on the instrument. Size of the particles present in aero sediments did not require any sample powdering.

Scanning electron microscopy (SEM) analyses were carried out on the instrument JEOL JSM-6610LV. This scanning electron microscope achieves high resolution pictures with magnifications of 5 to 100.000 x, works in the low and high vacuum conditions. Tungsten filament or LaB_6 crystal were used as the electron source (cathode), at accelerating voltage of 0.3-30 kV. Besides the detectors for secondary electrons (SE) and backscattered electrons (BSE), this microscope uses energy-dispersive spectrometer (EDS) – detector X-Max large area analytical silicon drift connected with INCEA Energy 350 microanalysis system, and cathodoluminescence detector (CL). For sample preparation, carbon tape was used, with sample adhered to one side and the other fixed to glass plate 10 mm large. Samples fixed in such mode were coated with gold. Semi-quantitative chemical analyses were obtained by using 64 standard minerals and synthetic compounds.

Results

Morphology and the characterization

The distributions of particles photographed under a microscope and processed using the MAUDE program, for all measuring points, in the period from March 2007 to March 2008, were presented in histograms. Histograms (Figure 5) represent the distribution of particles for the entire sample > 25 μm large in steps of 2.5 μm. Similarity of the most of the histograms can be noticed: the largest number of particles distributed by classes is up to 2.5 μm in the summer and 10 μm in the winter period. The exception is the histogram of the location U-4, with class maximums for the particle size up to 2.5 μm in July and for the classes of particles up to 10 μm in February. This site is characterized by an increased content of particles larger than 10 μm in January. At the location in the forested rural area, with the highest impact of individual furnaces, presence of large fractions dominates in January. At the location directly next to the open pit (U-1) presence of fractions > 10 μm dominates in February. The presence of the largest fraction at the other locations depends on the point position. At the point U-2, placed in the westernmost part of the exploration area, influence of the Obrenovac power plant and the vicinity of the highway were registered, so the presence of the largest fractions was dominant in the October. Closer to the open pit (point U-1) the frequency of large fractions is larger. Particles with diameter less than 10 µm were divided into two categories: class below 2.5 µm and class from 2.5 up to 10 µm. Such classification is important because it shows the relationship between the concentrations of inhaled and respiratory particles on the measuring points. The concentration of respiratory particles is higher in the summer (March to September) at all sites, while the concentration of inhaled particles is larger in the winter period (from October to February) at the locations U-1, U-2 and U-3. At the location U-4 the distribution of respiratory particles is dominant from March to December (less than 2.5 µm) which makes this location specific (Figure 5d).

The concentration of deposited material was measured throughout the entire test period, on all four measuring points. The results represent monthly concentrations of the measuring sites. According to the standard for the deposited material (Directive on permissible levels, measuring methodology and criteria from immission monitoring sites and collecting data, 2008), in order to evaluate the air quality it is necessary to determine the concentration of soluble, insoluble and total deposited matter, to observe their mean values through the periods and compare them with the maximal allowed concentrations on a daily, six month and annual basis. Mean values of total deposited matter per measurement point (Table 1) show that the two measuring points (U-2, U-4,) do not exceed the annual limit value of 200 mg/m^2 per day. Two measuring places U-1 and U-3 show the average values of total deposited matter between 200 and

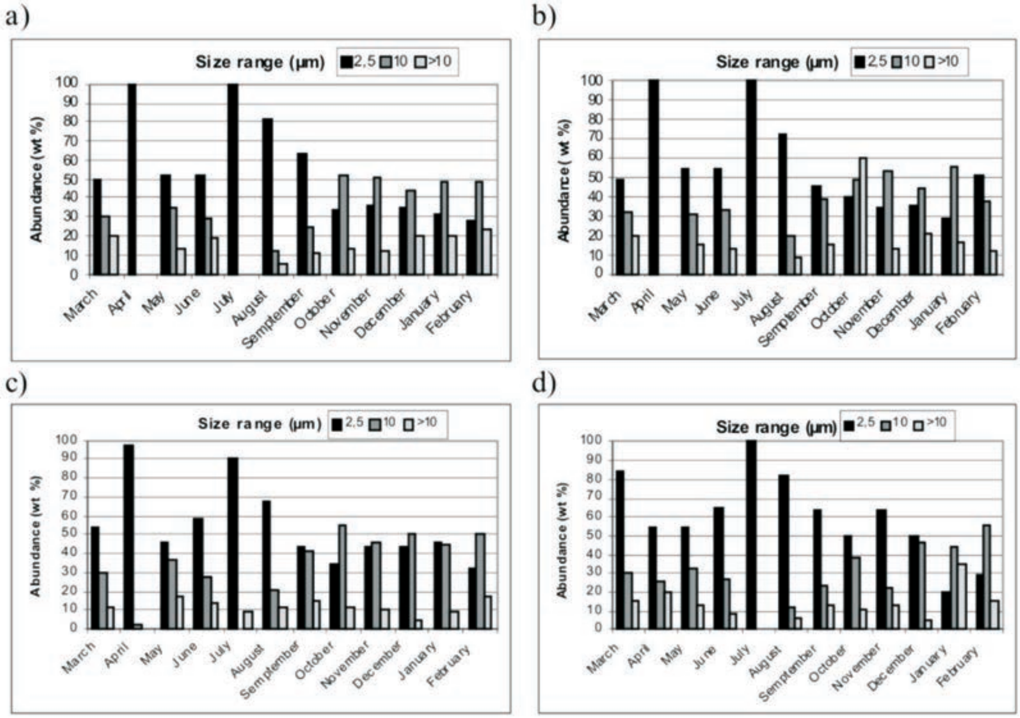

Figure 5. Histograms of aero sediment particles distribution: a) location U-1, b) location U-2, c) the location U-3, d) the location U-4.

450 mg/m^2 per day, while none of measuring points belong to the category with values above 450 mg/m^2 per day.

Aerosol and dust particles generally have a complex shape. Photomicrographs of the analyzed various shaped particles representative for samples of all measuring points are presented on the Figure 6, and the spectra of distribution of elements showing the chemical composition of corresponding particles are presented on the Figure 7. SEM EDS provides basic information and cannot determine the presence of the elements of low atomic weight (Table 2). At SEM microscopy some misidentifications were inevitable (especially of complex minerals such as clay, slightly less for simple minerals such as quartz, gypsum and feldspar). For some particles only content of certain elements were determined, and some particles were not identified at all (unknown). In the case of complex particles consisting of two or more minerals (Figure 6 b), identification of individual minerals is usually problematic. The particles that do not give a signal are considered to be made of organic carbon (microorganism) or coal, or it is the exhaust particle from vehicle (Figure 6g, h). Analyzed spherical particle is shown in the Figure 6a. The emission spectrum of elements showed the largest share of oxygen, aluminium and silicon, less iron, calcium and the subordinate content of magnesium (Figure 7a). This particle, due to the fusion, gained the form of sphere originating from several mineral kinds, mostly of alumosilicate composition. Calcium, magnesium and potassium may be an integral part of the structure of alumosilicates. Iron is probably of the limonite or the hematite origin. The particle of the porous morphology is shown on the Figure 6b. The emission spectrum of elements showed the largest content of oxygen, aluminium and silicon, less calcium, potassium, iron and magnesium (Figure 7b). Similar to the previous particle, element distribution of potassium, magnesium, calcium indicates the presence of at least two alumosilicate phases. Iron content indicates the presence of hematite, magnetite or limonite amalgamated into the particle. The Figure 6c shows the platy-shaped particle. The main forming parts of the particles are oxygen, calcium and sulphur, while aluminium, silicon and potassium are subordinate (Figure 7c). Present elements indicate that the particle is of sulphate composition, and its form corresponds to the gypsum. Tiny particles of alumosilicate composition are adhered on the surface of gypsum particle. Irregular shape of the particle with adhered smaller particles on the surface can be seen on the Figure 6d. The emission spectrum of elements shows the largest share of oxygen and silicon, less aluminium and sodium (Figure 7d). Present elements indicate that the particle is of the feldspar composition. Figure 6e shows the particle in the form of twisted flakes. The spectrum shows that the main elements forming

Table 1. Mean concentration values of deposited matter.

Measure point	Total deposited matter			Soluble deposited matter			Insoluble deposited matter		
	mg/m^2 per day			mg/m^2 per day			mg/m^2 per day		
	Winter	Summer	Year	Winter	Summer	Year	Winter	Summer	Year
U-1	406.0	399.7	402.9	86.0	120.3	146.2	320.0	279.3	299.7
U-2	137.3	180.3	158.8	56.7	58.0	57.4	80.7	122.3	101.5
U-3	296.8	258.5	277.7	84.2	90.2	87.2	212.7	168.3	190.5
U-4	198.5	192.0	195.3	82.8	33.3	58.1	115.7	158.7	137.2

Table 2. Distribution of elements in the deposited matter (in %) obtained by SEM-EDS analysis.

element	6 a	6 b	6 c	6 d	6 e	6 f	6 g	6 h
O	48.40	46.64	45.43	49.68	39.84	30.17	71.85	71.81
Na	-	-	-	6.65	-	-	0.54	-
Mg	1.82	1.43	-	-	-	-	-	-
Al	12.79	14.2	1.00	9.59	9.65	-	-	0.31
Si	29.48	25.39	2.92	34.09	16.69	-	-	0.84
K	0.92	1.45	1.06	-	-	-	-	-
Ca	1.48	7.35	30.98	-	22.59	-	0.26	0.36
Cl	-	-	-	-	-	-	0.50	0.11
Fe	5.10	3.72	-	-	11.23	69.60	-	0.16
C	-	-	-	-	-	-	26.86	26.42
S	-	-	19.16	-	-	0.23	-	-

the particle are oxygen and silicon, less aluminium, calcium and iron. Such distribution of elements and form of the particle indicates that flakes consist of at least two types and of chlorite (Figure 7e). Figure 6f shows the particle with well-developed form of octahedral shape. The inner part of the particle is analyzed and the emission spectrum shows a dominant share of iron and oxygen, while the sulphur is present in subordinate amounts (Figure 7f). The main phase is the iron oxide, so on the basis of its morphological form it can be concluded that it is magnetite. The presence of the sulphur points to the coal combustion and the soot content on the surface of particle. Elongated, spear-shaped particle can be seen on the Figure 6g. The elements the particle consists of are oxygen and carbon, while the sodium, chlorine and calcium occur in subordinate amounts (Figure 7g). Present elements imply that the particle is of organic origin and it represents the coal. Presence of sodium, chlorine and calcium indicates the coal combustion and the soot content on the surface of particle. Figure 6h shows the presence of microorganisms, which may occur in aero sediments. The emission spectrum shows the dominant presence of oxygen and carbon while aluminium, chlorine, silicon, calcium, and iron occur in subordinate amounts (Figure 7h). The presence of carbon and oxygen as well as the morphological form of the tested particle indicates the microorganism. Other elements that appear in traces indicate the presence of alumosilicate, carbonate and ferrous phase in the form of fine particles adhered on the surface of microorganism.

In summary, the results obtained by SEM indicate the existence of the particles of various shapes, from rounded, welded, spherical, mostly of soot, quartz, magnetite and hematite (quite comparable to Hower et al., 1999; Sokol et al., 2002; Gieré et al., 2003 and Kutchko and Kim, 2006), to irregular, complex particles of various shapes that form aggregates of several minerals (quite comparable to Jones et al., 2002 and Kutchko and Kim, 2006).

Mineralogy

After examining thin sections in the microscope, characteristic particles that occur in the samples of measuring points were photographed. The particles of regular carbonate form that are, next to quartz, dominant on the site U-4, are interesting. The particles of irregular forms and different sizes mostly prevail in the thin sections. Quartz and micas (biotite and muscovite) can be identified, while gypsum and feldspar cannot be determined reliably. The

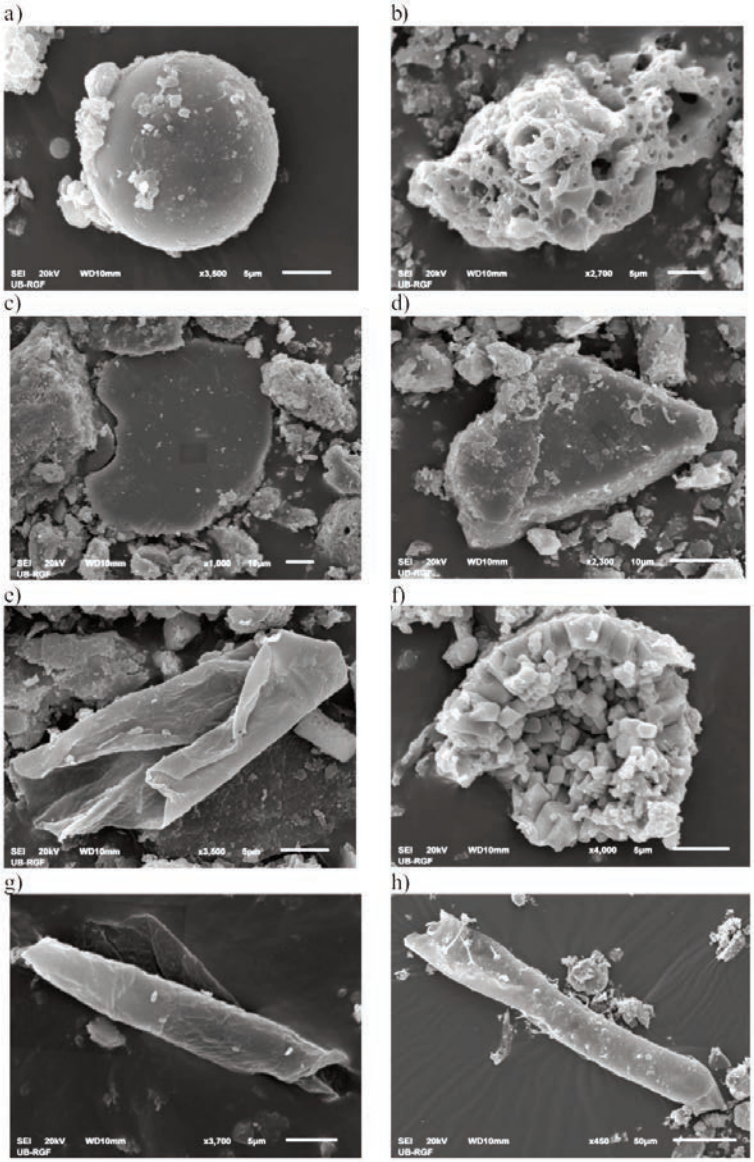

Figure 6. SEM images of the airborne particles from Kolubara basin. All samples were coated with gold. a) Spherical particle formed by merging, with particles of clay and Fe minerals adhered to the surface b) A particle which has gained porous form due to the fusion and represents an aggregate of several minerals with major alumosilicate phase. c) A gypsum particle which is a common mineral in the aero sediments. d) The feldspar particle with the finer particles adhered to the surface. e) Twisted chlorite flakes. f) Well developed octahedral form of magnetite in the inner part of the particle. g) Elongated spear-shaped coal particle. h) The presence of microorganisms in the deposited sediment.

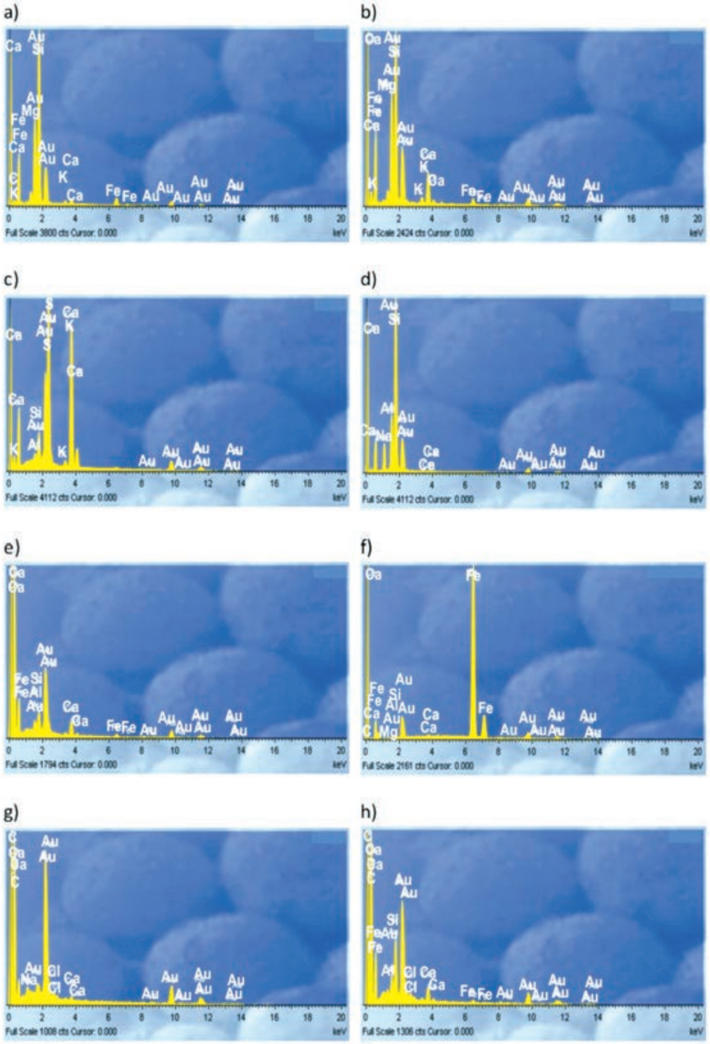

Figure 7. SEM-EDS spectra of the airborne particles from Kolubara basin. a) Emission spectrum of the spherical particle. b) Emission spectrum of composite, porous particle. c) Emission spectrum of the gypsum particle. d) Emission spectrum of feldspar particle. e) Emission spectrum of chlorite particle. f) Emission spectrum of the magnetite in the inner part of the particle. g) Emission spectrum of the coal particle. h) Emission spectrum of the microorganism from the deposited matter.

particles of coal and metallic mineralization were more dominant in samples taken next to the edge of the mine (sample U-1) and in the urban area of Ub town (sampleU-3), while the soot particles are usually adhered to the surface of quartz, carbonate and micas (Figure 8a, b). Besides the particles of minerals and coal, various forms of plants (leaf, flower, branch) were present in the thin sections.

Mineralogical analysis of deposited material at the location U-1 showed a similar mineral composition in summer and the winter period. The presence of quartz was dominant, while the other minerals were less frequent. The difference in mineral composition is reflected in the presence of anhydrite and clay minerals in the summer. The identified particles from deposited material at the location U-2 were similar in the summer and winter period. Presence of quartz was dominant. Also, feldspar, micas and clay minerals appeared in both periods. The difference in mineral composition was noticeable only in the presence of dolomite and anhydrite in the summer. The composition of particles in the deposited material on the location U-3 was similar in summer and the winter period as well. The presence of quartz was dominant in both periods, and then gypsum, feldspar, dolomite, micas and chlorite. Anhydrite, which occurs in trace amounts, is related to the summer period. Mineralogical composition identified at the location U-4 differed in the summer and winter periods. In addition to the dominant presence of quartz, dolomite was the next most frequent mineral only in the summer, while the other minerals were present in small amounts. Besides quartz, feldspar was present in both periods studied. The other minerals occurred only during the summer and that is why this location is specific compared to the previous ones. The data obtained from the X-ray diagrams for the locations U-1, U-2, U-3 and U-4 are shown in Tables 3 and 4.

The results of mineralogical compositions identified at all four sites (proximate to the open pit, power plant and the proximity of the railway U-1; the impact of power plant and open pit U-2; urban area of the city U-3; the sheltered part of the terrain U-4), correspond to the mineral dust composition given in the study of Merefield et al. (1995) and Jones et al. (2002), at the coal opencast mine in south Wales. Mineral composition of the ash presented by Gier et al. (2003) is mostly in accordance with the mineral composition of the aero sediments in the points of U-1, U-2, U-3 and U-4.

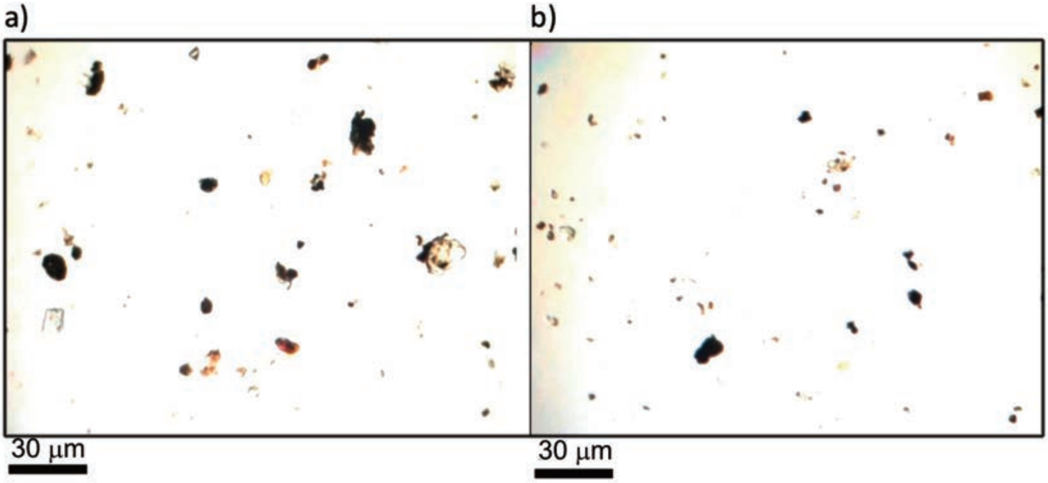

Figure 8. Photomicrographs of particles taken at magnification of 40 x, a) coal and mineral particles of irregular shape (U-1) and b) the increased presence of metallic minerals and soot particles adhered on the surface of mostly quartz and carbonate grains(U-3).

Table 3. X-ray diffraction data of powder samples (U-1 and U-3).

U – 1						U – 3					
SUMMER U–1			WINTER U–1			SUMMER U–3			WINTER U–3		
I_{ctg}	d Å	minerals	I_{ctg}	d Å	minerals	I_{ctg}	d Å	minerals	I_{ctg}	d Å	minerals
17	9.96	M	14	10.07	M	20	10.03	M	17	10.07	M
25	7.62	G	12	7.59	G	22	7.63	G	23	7.67	G
15	7.13	Cl	14	4.98	M	18	7.06	Co	13	7.06	Co
11	6.03	F	23	4.47	M	16	5.75	F	16	6.02	F
15	5.11	M	73	4.25	Q	23	4.67	F,H,Co	27	4.47	M
16	4.99	M	19	4.04	F,D	31	4.45	M	68	4.27	Q,G
29	4.46	M,Cl	21	3.68	D	72	4.27	Q,F,G	23	4.05	F,D,Co
91	4.27	Q,G	272	3.34	Q,M	24	4.14	F,M	228	3.35	Q,M
23	4.05	F,D	50	3.21	F	50	4.05	F,D	24	3.25	F
25	3.80	G,Cl	16	3.06	G	25	3.79	G	30	3.20	F,M
24	3.66	M,H	18	2.88	G,D	24	3.67	F,D	29	3.07	G
20	3.56	M,Cl,A	17	2.59	M,G	25	3.54	F,Co	20	3.02	F
244	3.35	Q,M	20	2.56	M,D	27	3.49	F,M,A	29	2.88	G
36	3.20	F,M	17	2.50	F,M,G	184	3.35	Q,M	18	2.69	G,F
29	3.07	G	34	2.46	Q,M	31	3.19	F	20	2.57	M,Co
30	2.88	D,G	23	2.28	Q,F	28	3.06	G	22	2.53	F,D,Co
20	2.68	G,H	19	2.24	Q,F,M	21	2.99	F,M	32	2.46	Q,M
22	2.57	M,Cl	27	2.13	Q,F,M	30	2.88	D,G	22	2.29	Q,G,Co
18	2.49	F,M,G,Cl	11	2.07	F,D	19	2.82	Co,A	23	2.13	Q,M
33	2.46	Q,M	8	2.05	G	19	2.68	H,G,Co,D	17	1.99	Q,G
23	2.28	Q,F,H	16	1.98	Q,F,M	21	2.59	M,H			
18	2.24	Q,F,M,Cl				23	2.57	M			
13	2.21	F,G,H,A				29	2.46	Q,M			
23	2.13	Q,F,M,Cl				24	2.29	Q,F,H			
15	2.08	G,H				18	2.24	Q,F,M,A			
14	1.98	Q,F,M,Cl				24	2.13	Q,F,M			
13	1.90	G,Cl,M				15	2.09	F,G			
14	1.88	F,M,G,A				19	1.98	Q,F			

Legend : Q = quartz, F = feldspar, G = gypsum, M = mica, D = dolomite, Cl = clay minerals, A = anhydrite, H = hematite, Co = chlorite.

Discussion

Association of minerals gathered at specific locations may be related to geology, mining, coal combustion and opencast mining works. Constant improvements in analytical methods results in better physicochemical characterization and mineralogical identification of airborne particles.

Due to the proximity of pollution sources, the highest mean concentrations of deposited material were noticed on the location U-1 (annual value of 402.9 mg/m^2 per day), as well as the larger presence of the inhalational particles. At the location U-1, closest to the opencast mine, the frequency of the larger

Table 4. X-ray diffraction data of powder samples (U-2 and U-4).

U – 2						U – 4					
SUMMER U–2			WINTER U–2			SUMMER U–4			WINTER U–4		
I_{ctg}	d Å	minerals	I_{ctg}	d Å	minerals	I_{ctg}	d Å	minerals	I_{ctg}	d Å	minerals
14	10.00	M	16	9.94	M	22	9.98	M	14	10.07	M
22	7.63	G	19	7.63	G	23	7.64	G	11	7.67	G
11	7.07	Co	16	4.98	M	21	7.07	Co	22	4.47	M
71	4.27	Q,G,M	21	4.47	M	23	5.32	D	64	4.27	Q,G
26	4.07	F,D	73	4.25	Q,A	18	4.98	M	26	4.01	D
26	3.80	G	24	4.04	F	37	4.53	M	244	3.35	Q,M
22	3.68	H,D	20	3.95	M	66	4.25	Q	37	3.19	F
23	3.53	Co,A	31	3.78	F,G	30	4.05	D,F	19	3.03	C
227	3.35	Q,M	32	3.73	F,M	30	3.95	M	22	2.89	D
31	3.20	M,F	23	3.67	D	29	3.50	M,Co,A	17	2.56	D,M
27	3.07	G	262	3.35	Q,M,A	27	3.48	F,M	29	2.46	Q,M,G
35	2.88	G,D	32	3.18	F	181	3.34	Q,M	22	2.28	Q,F,C
17	2.69	H,G	19	3.06	G	39	3.20	F,M	22	2.13	Q,F,M
18	2.57	M,Co	19	2.99	F,M,A	26	3.05	G,C	17	1.98	Q,F,M
25	2.46	Q,M,F	24	2.89	G	80	2.89	D	12	1.88	C,G
20	2.29	H,Q,F	17	2.83	F	25	2.83	F,Co,A			
14	2.24	Q,M,F,C	14	2.69	G,A	21	2.72	G			
13	2.20	H,M,F,A	21	2.57	M	25	2.58	Co,M			
20	2.14	Q,G,M	18	2.54	D	29	2.46	Q,G,M			
10	2.09	G,F	32	2.46	Q,M	22	2.39	D,F,M			
11	2.02	F,Co,D	26	2.28	Q,F,A	26	2.28	Q,F,C			
12	1.99	G,M,F,Co	20	2.24	Q,F,M	22	2.23	Q,G,M,A			
10	1.90	G	15	2.16	F,A	35	2.19	D,M			
6	1.88	G,M,F,Co,A	24	2.13	Q,M,F	26	2.13	Q,F,M			
			13	2.09	F,G	18	2.07	C,G,Co,M			
			18	1.98	Q,F,M	23	2.02	D,F,Co			
						23	1.98	Q,F			
						16	1.89	C,G,M			
						17	1.85	F,M,A			

Legend: Q = quartz, F = feldspar, G = gypsum, M = mica, D = dolomite, C = calcite, H = hematite, A = anhydrite, Co = chlorite.

fractions (>10 μm) is higher, especially in the winter period. Mineral composition of aero sediments shows the dominant presence of quartz, then feldspar, chlorite and micas. Almost all mineral phases are of primary origin, generated by coal combustion and release of mineral particles into the atmosphere. Exceptions are the secondary dolomite, derived from tailings, and then anhydrite and gypsum resulting from large concentrations of volatile gases with sulphur and free calcium (thermal power plant effect), and clay minerals, which are an integral part of intercalations between the layers of coal. On the basis of mineral association and concentration of particles, the dominant effect of dust from the open pit was confirmed as the primary source of mineral particles.

Mean concentration values of aero sediments on the location U-2 were significantly lower than from the previous location U-1, especially in winter period, with the dominant presence of particles up to 2.5 μm in the summer and up to 10 μm in the winter. Presence of larger particles in winter period is understandable because of the impact of individual home furnaces in the rural part of the municipality where this point is located. Concentration of minerals in the deposited material indicates the dominant presence quartz in both periods (as part of quartz sands, which are present as barren interlayers in coal), then feldspar and micas as primary minerals in both research periods. Gypsum and anhydrite, as the secondary minerals, were formed in the atmosphere at precisely defined processes (Song et al., 2008). The presence of dolomite during the summer indicates the impact of dust from the open pit.

Location U-3 is placed in the urban part of the Ub town. Due to the distance of main pollutants (power plant and open pits), the mean concentrations of total deposited material for summer and winter period were approximately the same. The presence of particles under 10 μm in the winter and 2.5 μm in the summer were dominant. The mineral composition of this site depends on a number of potential sources (power plant, roads, individual home furnaces and opencast coalmine). The presence of quartz, feldspar, dolomite, chlorite and micas is related to the geology of the surrounding terrain. These minerals were formed in the process of coal combustion as fly ash and/or dust caused by excavation of coal tailings. Gypsum and anhydrite, as secondary minerals, were present like the smallest particles as unavoidable mineral phases. The increased presence of mineral particles points to the equal participation of both dust and ash from the Tamnava opencast, power plant and individual home furnaces.

Location U-4 monitors impact of the coal dust brought from the open pit on the wider environment in the central rural investigated area. Average values of aero sediment concentrations were uniform in the summer and winter time, which was directly related to climatic parameters of the given area (small influence of rainfall) for the investigated period (especially for the class below 2.5 μm). In this regard, the concentration of particles smaller than 10 μm was dominant in the deposited material. This location was characterized by increased content of particles larger than 10 μm in January. The composition of particle deposited material is different compared to the previous locations, especially if we observe through the periods. The presence of only quartz and feldspar in the winter period indicates the influence of fly ash from individual home furnaces, while the share of dolomite, micas and chlorite in the summer indicates the impact of dust from the open pit. Gypsum as secondary mineral was an integral part of any aero sediment and is concentrated among the smallest particles. Almost approximate concentration values in the winter and summer point to equal participation of fly ash and dust from the mine.

It is shown that the mineral composition of dust and fly ash largely depends on the sampling locations. Thus, secondary, well-crystallized minerals and organic matter are more abundant at the locations closer to the edges of pits (U-1, U-3). Deposited material from locations closer to the power plant and the individual home furnaces, is composed of the larger amounts of soot, and therefore the larger content of poorly crystallized minerals and amorphous matter (U-2, U-4). In the diagrams this is manifested by an increase background in the form of hump. These phenomena were studied and presented in the papers of (Hubbard et al., 1984; McCarthy, 1988; Enders 1995; Bosbach and Enders, 1998; Hower et al. 1999; Gieré et al., 2003).

At the locations where large amounts of amorphous matter and slightly crystallised mineral phases are present in deposited substance, dominant share of the fly ash was noted (U-2 and U-4). A larger share of carbon and urban dust reduces the presence of amorphous matter, which was the most distinctive at the sites U-1 and U-3.

Measuring of dust and quartz contents in and next to the Tamnava opencast was presented in study of Ivanović (2002). Data on the analysed samples of flying dust from the Tamnava-east opencast mine gave an average participation of crystalline SiO_2 from 3.5 to 20 %. Potential danger of the aggressive floating mineral dust arising from the exploitation and crushing of coal was studied, measured and analyzed for the year 1996. The samples analyzed on the content of free crystalline SiO_2 in all locations, correspond with the results presented in the research of Ivanović (2002).

Variations in mineral composition reflect the geology of the locations next to the opencast mine (U-1) and the impact of fly ash from thermal power plant (U-2) and individual home furnaces (U-4). Quartz is the dominant mineral in all locations and is estimated to be potentially the most dangerous mineral for human health. A large number of studies was made on this subject and is given through the papers (Richards and Wusteman, 1974; Murphy et al., 1998; Fubini et al., 1999; Ivanović, 2002). The other mineral components are significantly less common and do not affect human health.

Conclusion

This work is part of a one-year project of collecting particles from the atmosphere near the power plant, in the urban area of the town and opencast coal mine in the Kolubara basin and analyzing their shape, size and mineral composition. The average annual concentrations of total deposited material on the sites ranged from 158.8 to 402.9 mg/m^2 per day. So 50% of the measured values were above the recommended daily limits on an annual level of 200 mg/m^2 per day (U-1 and U-3). The dominant presence of particles below 2.5 μm in the summer and 10 μm in winter has also been determined. Such distribution of particle size depends on the location of the area. The SEM method and X-ray examination showed that the collected dust samples from the vicinity of the coal mine and power plant to a great extent consist of associations of a larger number of minerals and organic matter particles. The mineral composition of the particles of aero sediments was complex but uniform throughout the investigated area. In both of the studied periods, the most common minerals were quartz, feldspar, amorphous inorganic and organic matter, which was confirmed by X-ray powder diffraction, while other minerals were less frequent. Nevertheless, differences appear if the points are observed through certain periods. The summer period is characterised by the increased presence of secondary minerals (clay minerals, gypsum, carbonates, chlorite, anhydrite, micas), that were lifted up from the opencast coalmine and transferred to larger distances under the influence of wind, while in the winter the opencast mining areas were usually covered with snow. Since quartz is a dominant mineral component in all of the sites, in future research more attention should be paid to the toxicological properties of this mineral.

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