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Investigation of Suspended and Settled Particulate Matter in Indoor Air

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1. Introduction

Particulate matter is a natural part of the atmosphere, where the solid or liquid particles are suspended in the air. These suspended particles, also known as suspended particulate matter represents a dispersion aerosol system. In the air there are many types of microscopic airborne particles originated from both natural and anthropogenic processes, such as atmospheric clouds of water droplets, photochemically generated particles, re-suspended particulates, fumes arising from the production of energy, etc. They are present in various forms, eg. mists, fumes, dust. The atmosphere contains particles of the size ranging from slightly larger than molecules up to hundreds of micrometers, which consists of a variety of chemical compounds [1]. Depending of their lifetime, the particulates observed at a location can be both of local origin or the product of the transport over distances of hundreds to thousands kilometres.

Particulate matter is mainly classified by particle size distribution as follows [2]: Coarse Particles (CP) include all particles with an aerodynamic diameter (diameter of a sphere with unit density and mass equal to the mass of the provided particle) greater than 2.5 micrometers and less than 10 micrometers. These particles are identified as PM$_{2.5-10}$. PM$_{10}$ is an abbreviation used for so called „thoracic" particles with the diameter under 10 μm. Fine Particles (FP) include all particles having an aerodynamic diameter less than 2.5 micrometers and greater than 0.1 micrometers (PM$_{2.5}$). Ultrafine Particles (UFP) include all particles the aerodynamic diameter of which is less than 0.1 micrometers. These size limits are not sharp; the cyclone and impactor pre-separators remove half of the particles at the cut size and larger particles with increasing efficiency.

Increase in particulate matter air contamination and its negative impact on human health have resulted in efforts to monitor and identify the pollutants. The particulate mass concentrations in a very clean urban environment are about 10 μg.m^{-3}, which correspond to

2.10^7 particles in 1 m^3. In the polluted urban air the particle concentrations are higher than 10^{11} particles in 1 m^3 and their mass concentrations may be higher than 100 µg.m^{-3} [1,3]. In the Slovak Republic, the average annual outdoor PM$_{10}$ concentrations ranged from 11.6 –18 µg.m^{-3} in 2009 [4].

Danger of toxic inhalation exposure depends on both the physical and chemical characteristics of particulate matter and thus the study of its properties is essential to assess the health risks. Exposure to PM in ambient air has been linked to a number of different health outcomes, ranging from modest transient changes in the respiratory tract and impaired pulmonary function, through increased risk of symptoms requiring emergency room or hospital treatment, to increased risk of death from cardiovascular and respiratory diseases or lung cancer. The elderly, children, and people with chronic lung disease, influenza, or asthma, are especially sensitive to the effects of particulate matter [5]. Multiple studies have showed that a short-term exposure to particulate matter may associated with increased cardiovascular mortality [6-8]. The occurrence of particulate matters in the air interferes with human health not only due to its composition but also due to its specific properties. The large specific particle surface takes a share on the catalysis of heterogeneous chemical reactions and on adsorption of other pollutants and their transport [9].

Sources of particulate matter occur in the outdoor air as well as in the indoor environment. Ambient air concentrations are strongly dependent on meteorological factors in contrast to the indoor environment which is much more stable. The suspended particulate matter present in the indoor air is cumulated and as reported by [10-12] the indoor particulate concentrations are often measured to be higher than those outdoors. With the emphasis on both energy conservation and efficiency, mainly new home construction can create the problem of indoor air pollution. Vapour barriers, tight windows, weather-stripping and caulk have reduced or stopped fresh air from infiltrating and replacing stale air. Special attention must be paid to indoor air contamination because people spend a substantial portion of their time in indoor environment [13].

If indoor air pollution is investigated, both outdoor and indoor sources have to be considered, because the outdoor air is an important source of indoor particles pollution. Indoor particle concentration depends on penetration of outdoor particles into the indoor environment and on intensity of indoor aerosol sources [2]. Indoor particulate matter sources include building materials, cooking, heating and all activities related to combustion processes, smoking, cleaning and moving of inhabitants [14,15]. The importance of indoor sources depends significantly also on the number and habits of the inhabitants. It was noted [16] that the concentration of PM$_{2.5}$ was 2.8 times higher in houses where people smoked.

The behaviour of indoor aerosols is affected by the structural system of a building, material characteristics, the way of air exchange, the operating mode of indoor environment in the presence of inhabitants. The structural systems of a building along with the physical properties of the outdoor air (wind direction and intensity, the difference in the density of the indoor/outdoor air, the difference in the indoor/outdoor air temperatures etc.) determine interzonal transport of pollutants [17]. In multi-floor buildings, the flow induced by

buoyancy influences the motion of contaminated air within the building. Mechanical and/or natural ventilation and infiltration define air exchange rate, and thereby the amount of outdoor particles penetrating into the building interior. The efficiency of filters integrated in mechanical ventilation systems and natural ventilation by open windows allows the estimations of particle penetration in the dependence on outdoor aerosol concentration, whereas infiltration through cracks in the building envelope is uncontrolled and depends not only on physical properties of contaminated air but mainly on particle deposition on surface cracks [18,19].

Operation, the number and behaviour of inhabitants, i.e. type, emission intensity and amount of indoor contamination sources determine temporal and spatial variations of indoor aerosol distribution. In addition, wet processes such as cleaning, washing, drying and ironing increase relative humidity which can lead to variations in particle size distribution [20]. Physical properties of employed building materials such as thermal conductivity influence surface-to-air temperature difference, thermal convection and thermophoresis (or thermoprecipitation). This process is significant in the winter season when constructions separate heated from unheated areas. Chemical composition of particulate matter can influence the appearance of the electrostatic charge. The total aerosol concentration is determined by the balance between source emissions and aerosol decay due to indoor air chemical processes and aerosol loss mechanisms [2].

This chapter aims to present the results of the investigation of both suspended and settled particulate matter occurring indoors. The mass concentration and surface concentration measured were monitored for suspended and settled particulate matter, respectively. The chemical composition with special regard to the metals content as well as the morphology of indoor particulates was studied.

2. Indoor particulate matter decay

The aerosol particulate decay in indoor environment occurs by two mechanisms - ventilation and deposition. In general, ventilation is a positive mechanism for the loss of particles from indoor air. However, in real conditions, it often may cause entering the outdoor pollutants with supplied air into the indoor environment. The extent which ventilation contributes to the reduction of the indoor concentrations depends on the way of air exchange which can be carried out by natural air change, infiltration or ventilation systems. If the ratio of indoor and outdoor concentrations I/O reaches a value more than 1, the positive venting mechanism will result in a reduction of particulate matter concentration due to dilution. Otherwise, the contamination of indoor air increases by addition of outdoor particulate matter, mainly by natural air change. Ventilation systems should ensure the particulate matter concentration in the indoor environment is not increasing due to utilization of special filters in the inlet. In addition, coarse particles in ventilation system are often deposited by gravitational process which also leads to the removing of particles from the air supplied. On the other hand, particles deposited in the pipes can be re-suspended in dependence on the air flow speed [21].

Particle deposition is an important factor affecting indoor particle concentrations in all types of buildings and is considered to be a dominant mechanism of the aerosols concentration level decreasing [22-23]. The largest incidental losses occur as a result of particle deposition onto the surfaces. Due to the relatively large surface-to-volume ratio indoors, deposition has a much larger effect on reducing concentrations indoors than it does outdoors [19].

Particle deposition on indoor surfaces strongly depends on particle size and is governed by the processes of particle diffusion toward the surfaces, which is of particular significance for very small particles, and of gravitational sedimentation, which is significant for larger particles. In addition, the presence of airflows induced by convection currents or the action of fans, as well as air turbulence, can increase particle transport towards the surface a thus the deposition. Deposition is also dependent on the surface area and on its characteristics, with sticky surfaces resulting in higher deposition than smooth one. The larger surface area, the higher probability of particle deposition, and therefore furnished rooms, with lots of surface area, will have a higher deposition rate than bare rooms. Additional factors affecting particles deposition are: the presence of surface charge, which leads to the deposition rate increasing; temperature gradient, resulting in convective currents and thermophoretic deposition; and room volume [2].

Aerosol particles adhere when they collide with a surface. The aerosol concentration at the surface is zero and the concentration gradient is established in the region near the surface. The concentration gradient causes a continuous diffusion of aerosol particles to the surface, which leads to a gradual decay in concentration. Applying Fick´s first law of diffusion, deposition rate J is defined as a number of particles depositing per unit surface area per unit time and is given by equation (1)

$$J = n_0 \left(\frac{D}{\pi t} \right)^{1/2} \tag{1}$$

where n_0 is the uniform initial concentration and D is the particle diffusion coefficient [12]. The deposition can be also characterized in terms of deposition velocity V_{dep}, which is defined as the deposition rate divided by concentration in the equation (2)

$$V_{dep} = \frac{J}{n_0} = \frac{number\ deposited\ /\ m^2.s}{number\ /\ m^3} = m\ /\ s \tag{2}$$

The number of particles depositing on the total surface per unit time is expressed by the deposition loss rate coefficient β [1/s, 1/h]. This coefficient includes all the processes that remove the particle in enclosure (e.g. diffusion loss, gravitational settling loss and other loss mechanisms by external forces). In the context of regular geometry, β can be evaluated from the deposition velocity on different orientation of surfaces and their particular surface area, and can be expressed as

$$\beta = \frac{V_{dw} A_w + V_{du} A_h + V_{dd} A_d}{V} \tag{3}$$

where A_w, A_h and A_d are the total areas for the vertical wall, upward-facing and downward-facing horizontal surfaces, respectively. V_{dw}, V_{du} and V_{dd} are the deposition velocities for the vertical wall, upward-facing and downward-facing horizontal surfaces, respectively, and V is the volume of the enclosure [13].

Diffusion deposition is primaryly observed on vertical and downward-facing surfaces (ceilings). Deposition induced by gravitational force is observed onto upward-facing surfaces (wear layer of floor constructions, upward-facing areas of furnishing). Air drag force compared with settling particle is determined by airflow. For settling observed in still air (i.e. Re < 1 laminar airflow) the Stoke's low is valid. If airflow is turbulent (Re > 1000), Newton resistant low is valid for settling particle. Terminal settling velocity VTS of the particle settling due to gravitational force is results of balance drag and gravity. V_{TS} is expressed in equations (4, 5) [1].

$$V_{TS} = \frac{\rho_p d_p^{\,2} g}{18\eta}, \; \text{for Re} \, < \, 1 \text{ laminar airflow} \tag{4}$$

$$V_{TS} = \left(\frac{4\rho_p d_p g}{3 C_D \rho_g} \right)^{1/2}, \; \text{for Re} \, > \, 1000 \text{ turbulent airflow} \tag{5}$$

where η is the viscosity of the air, ρ_p a ρ_g are the density of the particle and the density of the air, d_p is the particle diameter, g is the gravitational acceleration and C_D the drag coefficient. Indoor particle deposition can be induced also by thermophoretic forces which results in thermoprecipitation, or by ventilation and air conditioning use which lead to the eddy diffusion. Thermoprecipitation may be significant in the winter season because of heating. The presence of a heating device seems to be related to lower concentrations of a number of components, such as particle mass, Cr, Zn, Ca^{2+}, SO_4^{2-} and NO_3^{-} and other as noted in reference [45].

Particles deposited on indoor surfaces create a potential reservoir from where they can be re-suspended whereby the secondary contamination is increased. This re-suspension effect can be caused by mechanical vibration, aerodynamic or electrostatic forces.

3. Indoor air monitoring – A case study

The monitoring of aerosol particulate matter (PM) was carried out in three rooms of the selected flat building in the city of Košice, Slovakia. Kitchen, living room and working room as representative indoor environments with different indoor sources were chosen for PM monitoring. Environmental tobacco smoke was considered a major source of the particles in the living room; cooking on the gas stove was considered a major indoor source of particulate matter in the kitchen. None significant indoor source was identified in the working room. However, a penetration of outdoor particles through large openings (windows, doors) or cracks and gaps through building envelope and interzonal transport from other rooms cannot be neglected.

Settled particulate matter sampling was carried out by passive methods during 28 days. The adjusted sampling method for ambient air was used for indoor environment. The aerosol particulates were captured into Petri dishes (8.5 cm diameter), installed at three height levels: on the floor, at height of 0.8 m from the floor and at height of 2.2 m from the floor. The settling of particles proceeded onto both by water filled Petri dishes (wet gravitational settling) and empty Petri dishes (dry gravitational settling) at each monitored level. The particle total mass was calculated by gravimetric method from the Petri dish mass increases; the surface particle concentrations were determined by standard way.

Suspended particulate matter investigation was focused on total suspended particles (TSP) and thoracic fraction PM_{10}. Investigation was carried out in the same rooms in the investigated flat building in the city of Košice. Measurement have included integral particles sampling onto a collection material (membrane filter Synpor 0.83 µm pore size, 35 mm in diameter and PTFE filter for TSP and PM_{10}, respectively) by sampling equipment VPS 2000 (Envitech, Trenčín) at the constant air flow of 600 litres/hour during a sampling period of approximately 24 hours. Because of minimization of humidity interference and volatile organic matters elimination, the filters were dried at a temperature of 105°C for 8 h before sampling than equilibrated at a constant temperature and humidity (e.g. 20°C and 50% RH) for 24 h before and after sampling. The particulate mass concentrations were determined by gravimetric method from the increase of filter weight (measured by analytical balance fy Mettler Toledo within 0.00001 g). The average concentrations of measured particulate matter in studied rooms are presented in Table1.

	Mean
Settled particulate matter - surface concentration [$\mu g.cm^{-2}$]	44.8
Total suspended particulates - mass concentration [$\mu g.m^{-3}$]	84.7
PM_{10} - mass concentration [$\mu g.m^{-3}$]	45.4
PM_{10} / TSP ratio	0.5

Table 1. The mean concentrations of settled and suspended particulate matter

The surface concentrations of settled particulate matter measured in selected rooms were in the range 7.0 to 86.6 $\mu g.cm^{-2}$ while the average surface concentrations for the rooms were calculated from 32.7 to 63.9 $\mu g.cm^{-2}$ (Table 2). The percentage of non-dissolved portion of settled particulate matter was calculated by dividing of the non-dissolved mass separated by filters by total deposited mass [47].

Room	Total deposited mass [μg]	Average surface concentration [$\mu g.cm^{-2}$]	Non-dissolved mass [μg]	Percentage of non-dissolved [%]
Kitchen	44.8×10^3	63.9	17.06×10^3	38.1
Living room	27.6×10^3	37.8	19.70×10^3	71.4
Working room	21.7×10^3	32.7	7.36×10^3	33.9

Table 2. Settled particulate matter and percentage of non-dissolved particles in total deposited mass

The highest total deposited mass was detected in the kitchen, the lowest in the working room (Table 2). The highest non-dissolved mass was expected as well. However, there was detected the highest percentage of non dissolved particulate matter in the living room. Fibres from carpets, textile and upholstered furniture represented the essential part of non-dissolved from the total deposited mass (Figure 1).

Figure 1. Non-dissolved particles captured on the filter

The results of indoor particle deposition monitoring considering the three high levels in all monitored rooms are summarized in Table 3. Besides the standard wet deposition, the dry deposition was included in the study in order to investigate the re-suspension processes. The surface concentrations of particles ranged from 21.0 to 86.6 $\mu g.cm^{-2}$ by wet gravitational settling and from 7.0 to 39.5 $\mu g.cm^{-2}$ by dry gravitational settling in all monitored rooms.

Surface concentration [$\mu g.cm^{-2}$]	Distance from the floor		
	0.0 m	0.8 m	2.2 m
Kitchen			
wet gravitational settling	86.62	53.50	51.59
dry gravitational settling	39.49	27.39	24.84
Living room			
wet gravitational settling	42.68	38.22	32.48
dry gravitational settling	27.39	21.02	14.01
Working room			
wet gravitational settling	47.77	29.29	21.02
dry gravitational settling	17.19	15.92	7.01

Table 3. Surface concentration of particulate matter

The highest surface concentrations of particulate matters were measured in the kitchen at all monitored levels. The surface concentration values were expected to be the highest in the kitchen because of the most intensive indoor particulate sources. The surface concentrations determined in the other rooms reached the comparable values.

The particles surface concentration was found to be decreased with the height of the room from the floor to the ceiling construction at wet gravitational settling in all monitored rooms

(Figure 2), as well as at dry gravitational settling (Figure 3). That means the lowest surface concentrations of particulates were measured at the height level of 2.2 m in all monitored rooms.
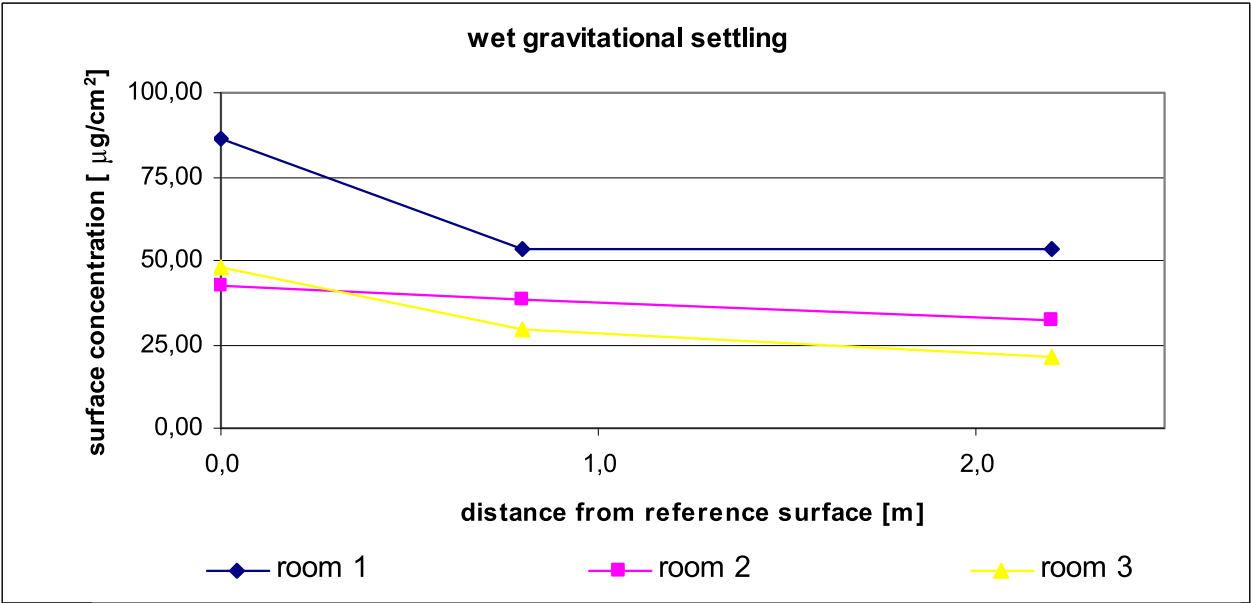

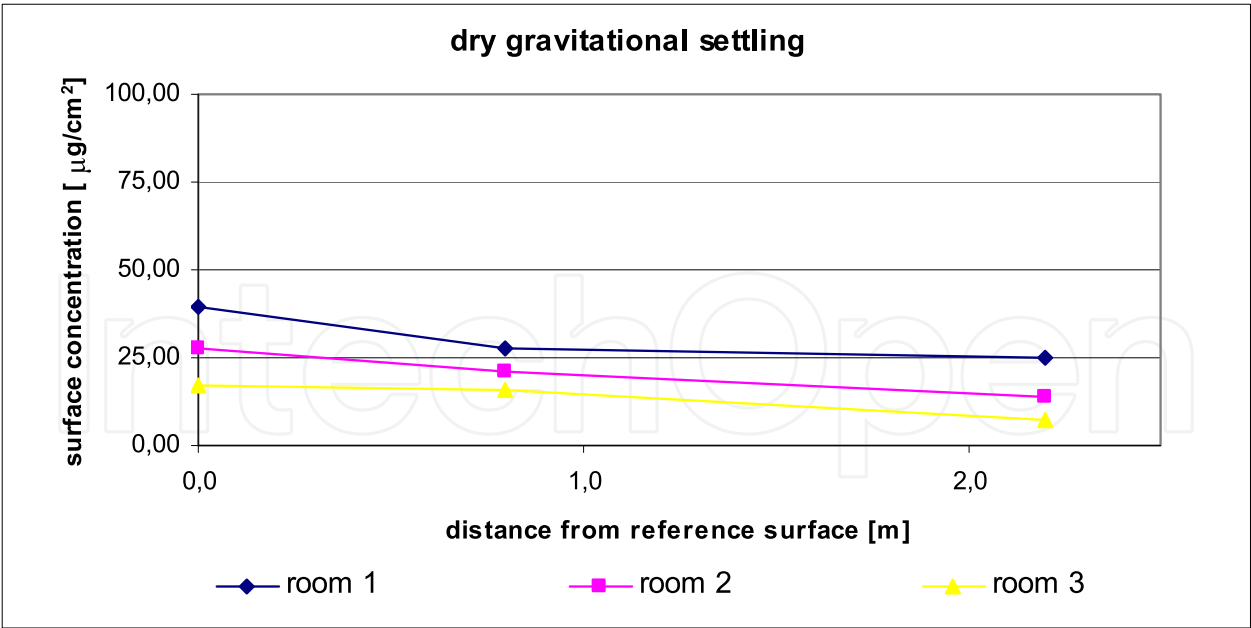**Figure 2.** Particles surface concentration versus height level at wet gravitational settling

Figure 3. Particles surface concentration versus height level at dry gravitational settling

Particles re-suspension effect was studied in real conditions without boundary conditions providing for any effect elimination. The particles release was expressed in percentage; the amount of particulates settled into water filled Petri dishes was represented by 100%.

The proportion of particles (re-suspended) released into the air after sedimentation settling was calculated as a difference between surface concentrations at both wet and dry settling for each height level and all monitored rooms [48]. The particles portions in relation to the height level in monitored rooms are illustrated in Figure 4.
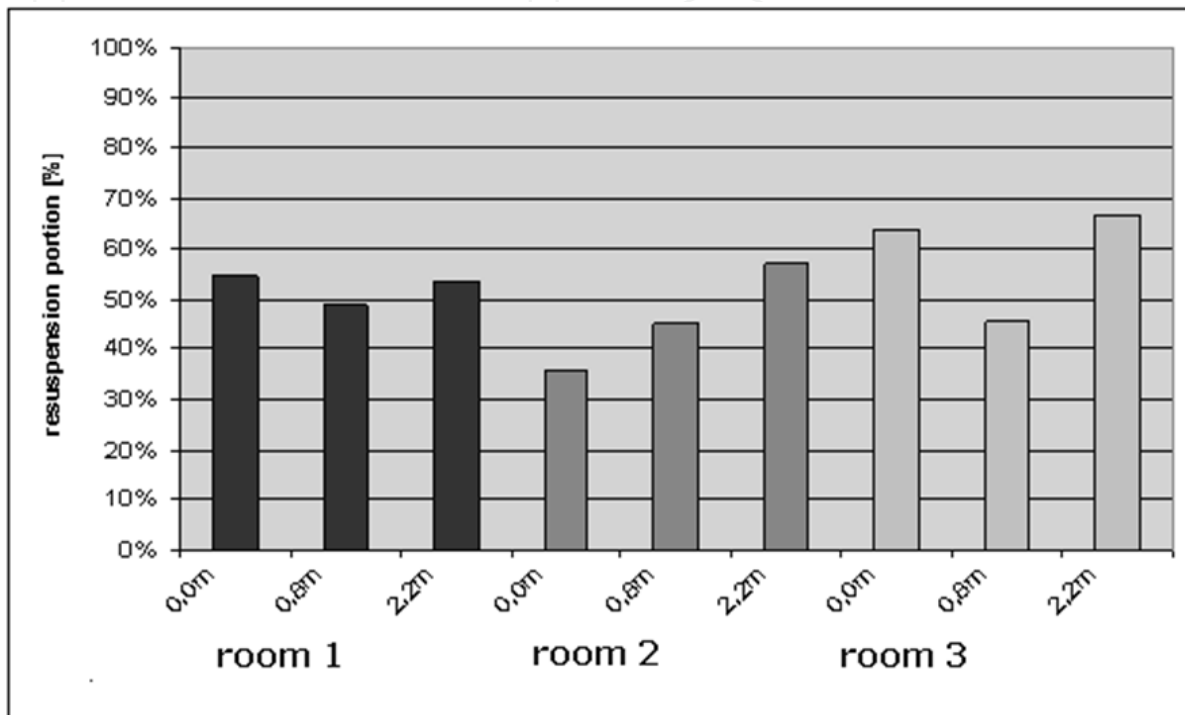

Figure 4. The particles portions in relation to the height level

The values of re-suspension particles portions ranged from 45.6 to 58.7% in monitored rooms. The results of particles re-suspension effect were not consistent with our expectations. None trend of particles release in relation to the height level was confirmed (Figure 4). The wide differences in particle re-suspension portions were achieved at monitored height levels in studied rooms: from 35.8 to 64 % on the floor and from 56.8 to 66.7 % at the height level of 2.2 m from the floor. The comparable portions for particles release was achieved only at the height level of 0.8 m from the floor (48.8, 45.0 and 45.7 %).The average values of re-suspended particles portion in all monitored rooms are presented in Table 4.

Room	Re-suspended portion [%]
Kitchen	51.69
Living room	45.89
Working room	58.77

Table 4. The re-suspended portions of particulate matter in monitored rooms

The non-expected conclusion has resulted from comparison of the average values of resuspension portions in monitored rooms. The highest portions of released particles were found out in the working room with a minimum operating mode (minimum people activity).

The mass concentrations of total suspended particulate matter (TSP) in studied rooms were detected in the range 59.028 to 114.583 $\mu g.m^{-3}$; PM_{10} mass concentrations measured ranged from 31.94 to 55.56 $\mu g.m^3$ (Table 5). Unlike settled particulate matter monitoring, the highest concentration of total suspended particles as well as PM_{10} fraction were measured in the living room.

Room	TSP [$\mu g.m^{-3}$]	PM_{10} [$\mu g.m^{-3}$]	PM_{10}/TSP
Kitchen	80.556	48.611	0.60
Living room	114.583	55.556	0.48
Working room	59.028	31.944	0.54

Table 5. Suspended particulate matter concentration

The PM_{10} hygienic limit (50 $\mu g.m^{-3}$) for indoor air in the Slovak Republic was exceeded in one measured room; the mean mass concentration detected was close to the limit. PM_{10} concentration values reached about half of TSP concentration values (PM_{10}/TSP ratio 0.48 for the living room, 0.60 for the kitchen and 0.54 for the working room).

The similar mean concentration value of 63.3 $\mu g\ m^{-3}$ monitored in 34 homes in Hong Kong has been reported in [25]. The lower indoor PM_{10} concentration levels were measured in Athens (mean values for all residences was 35.0 ± 10.7 $\mu g.m^{-3}$ during the warm period and 31.8 ± 7.8 $\mu g.m^{-3}$ during the cold period), presenting no exceedance above the 50 $\mu g.m^{-3}$ limit value [26]; whereas the authors in the study [27] referred much higher mean concentrations of 202 and 215 $\mu g.m^{-3}$ in poor Bangladeshi households. The very high PM_{10} levels were caused by using wood, dung and other biomass fuels for cooking.

4. The morphology of settled and suspended particulate matter

The morphology of settled as well as suspended particulate matter was investigated by electron scanning microscopy (SEM) with equipment Jeol JSM-35CF (Japan) at various extensions ranging from 90 to 5500. The scanning electron microscopy (SEM) micrographs represent the morphology of selected particles. As shown in Figures 5 to 9, the particles of irregular shapes and various sizes were observed in the sample of settled particulate matter.
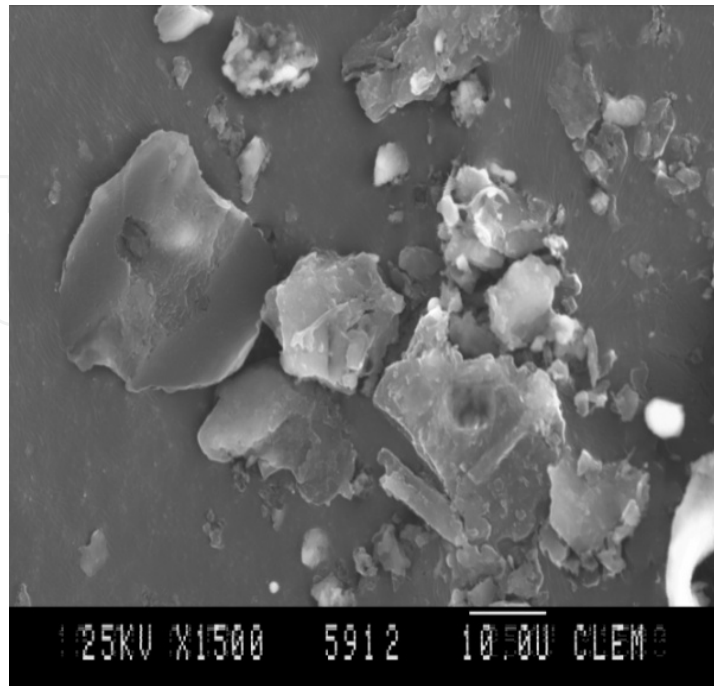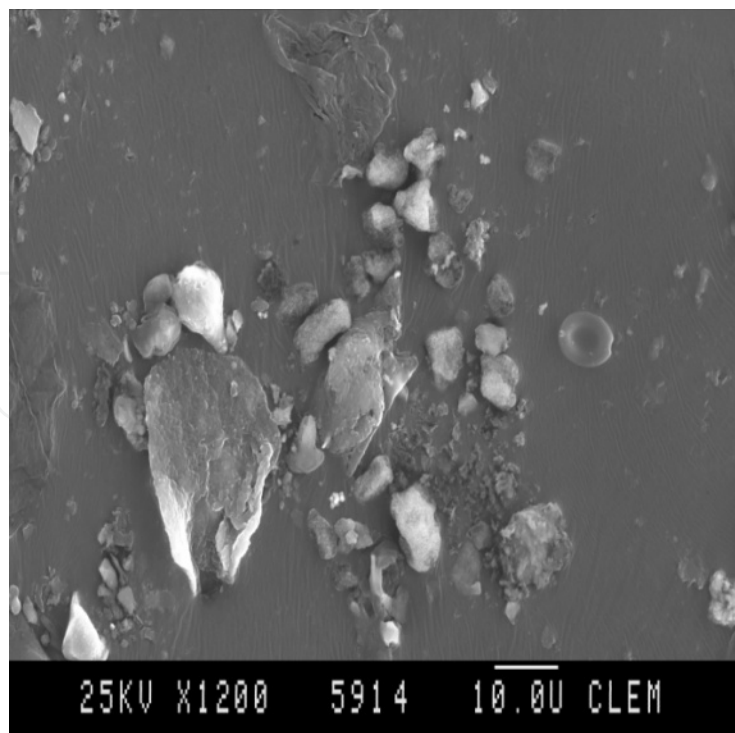
Figure 5. Settled particulate matter morphology

Figure 6. Settled particulate matter morphology

Figure 7. Detail of various shapes of settled particulate matter
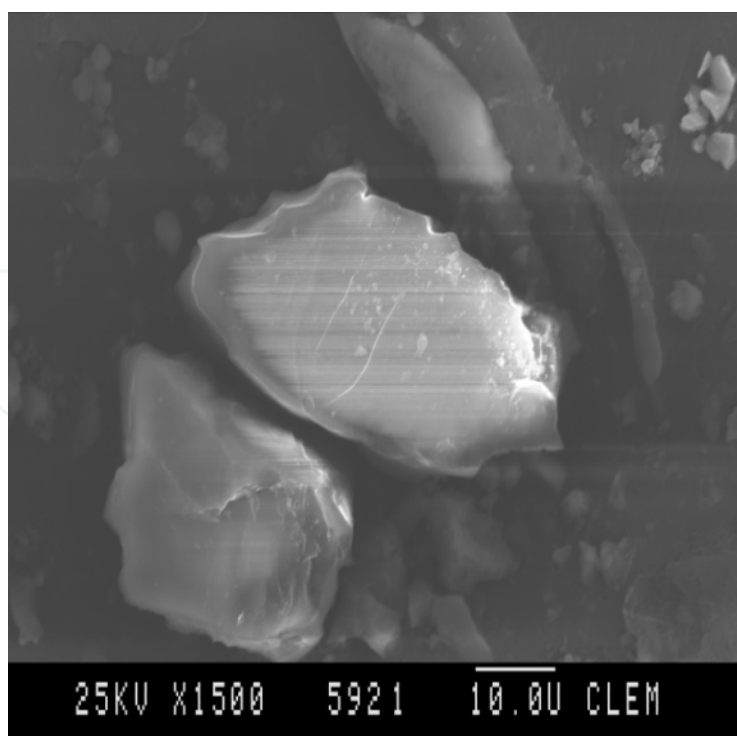

Figure 8. Detail of various shapes of settled particulate matter

The majority of particles are non-spherical in shape with strong division of the surface. The occurrence of spherical as well as fibrous particles was not obvious.
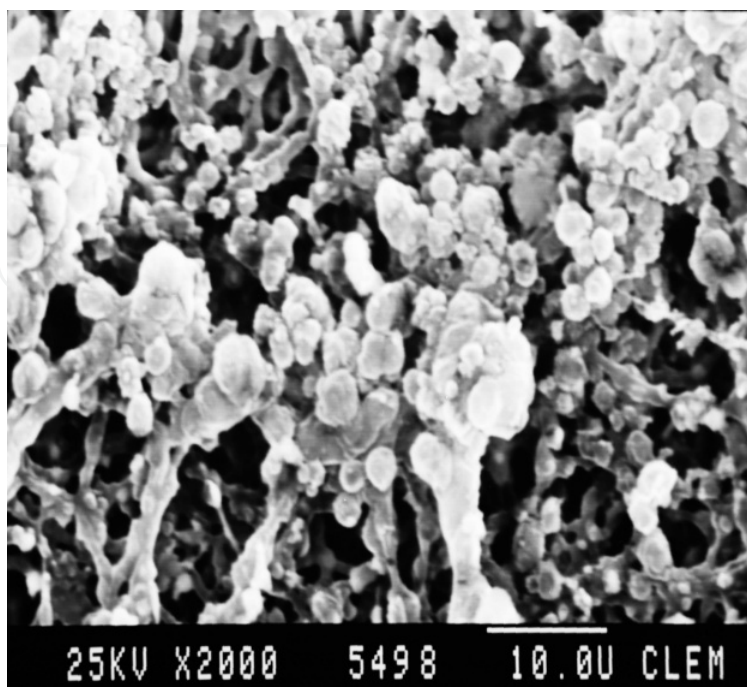

Figure 9. PM$_{10}$ particulate matter morphology

Individual particles along with the aggregates of fine particles were observed in PM$_{10}$ suspended particulate matter (Figure 9). The evaluation of SEM micrographs of the total suspended particulate samples showed that 80 - 90 % of the particles are smaller than 10 μm. In case of some samples, the particle size distribution was even shifted in the range of particle size under 5 μm. As referred by authors in the Chinese study [24], the analysis of the settled dusts collected in typical resident buildings showed that the volume percent for the fine particles (particle size < 10.5 μm) of the settled dusts ranged from 26 % - 38 %.

Seasonal variations and variations due to location were observed in both the morphological measurements and chemical analysis of settled dust collected inside the main foyers of three University buildings in Wolverhampton City Centre, U.K. [28].

5. The chemical composition of settled and suspended particulate matter

The elemental EDX analyses were carried out on the micro-analytical system LINK AN 10 000 operating in secondary mode at a potential 25 kV. The energy-dispersion X-ray system provided preliminary information on the elemental composition of the samples. The EDX spectra were very similar for majority of collected particulate matter samples. Principal inorganic elements constituting the particles calcium, silicon, aluminium, potassium, iron, chlorine, magnesium as well as titan and manganese were confirmed. The EDX spectrum in Figure 10 represents the elemental chemical composition of the settled particulate matter sample.
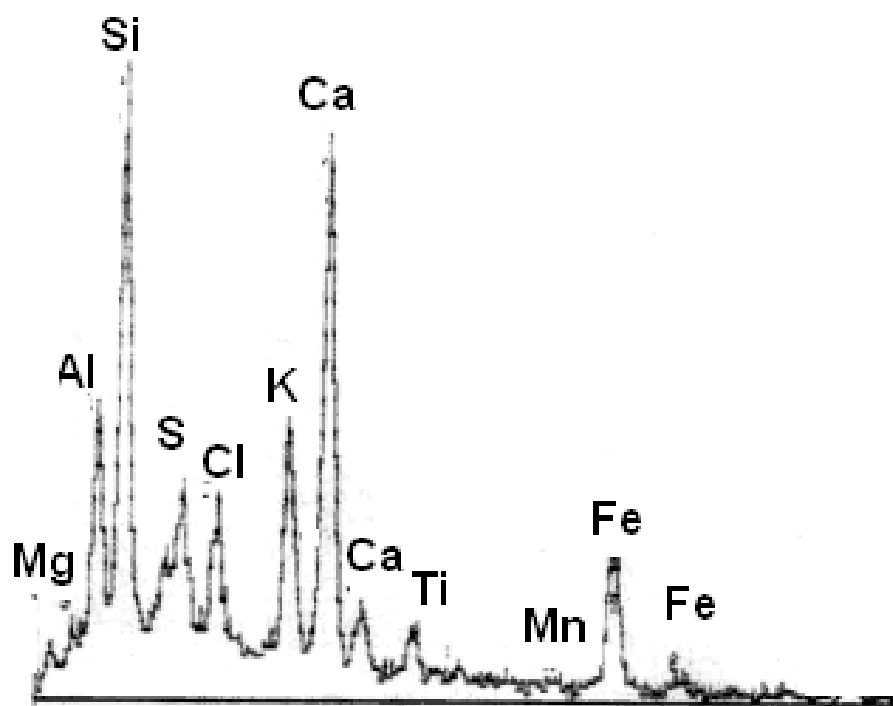
Figure 10. EDX spectrum of elemental chemical analysis of settled particulate matter

The energy-dispersive X-ray system interfaced to the SEM provides preliminary information on the elemental composition of the samples. Figure 11 presents the EDX spectrum of the suspended particulate matter sample.

In all samples discussed here, the EDX spectra were very similar for majority of collected particulate samples. The principal inorganic elements constituting the particles in order of peak intensity decreasing were Ca $\approx$ Si > O > Al > C > Mg > Fe > Cl > Na $\approx$ K. The presence of both carbon and oxygen, which can originate from organic compounds as well as from inorganic oxides, acids and/or salts, was confirmed [29].

The elements observed by EDX were confirmed also by using X- ray fluorescence analysis (XRF). The total amount of inorganic elements (except for carbon, oxygen and other elements with proton number under 11) in settled particulate matter measured by XRF was found very low and was about 2.23 %. In [30] organic carbon and elemental carbon made up 29 % and 2.5 % of the particulate matter, respectively. Water-soluble total carbon content in PM_{10} corresponds to 16% of the total particle masses measured in India. Organic matter is by far the major PM_{10} component besides mineral oxides. As observed in [31] major individual organic compounds quantified included series of alkanes, n-alkanoic acids, n-alkanals, alkan-2-ones and PAHs. Alkanes and ketones make up a significant fraction of particle-phase organic compounds, ranging from C_{11} to C_{26}, and C_9 to C_{19}, respectively. In addition, other organic compound classes have been identified, such as alkanols, esters, furans, lactones, amides, and nitriles [28]. The measured percentage content of measured elements is summarised in Table 6.
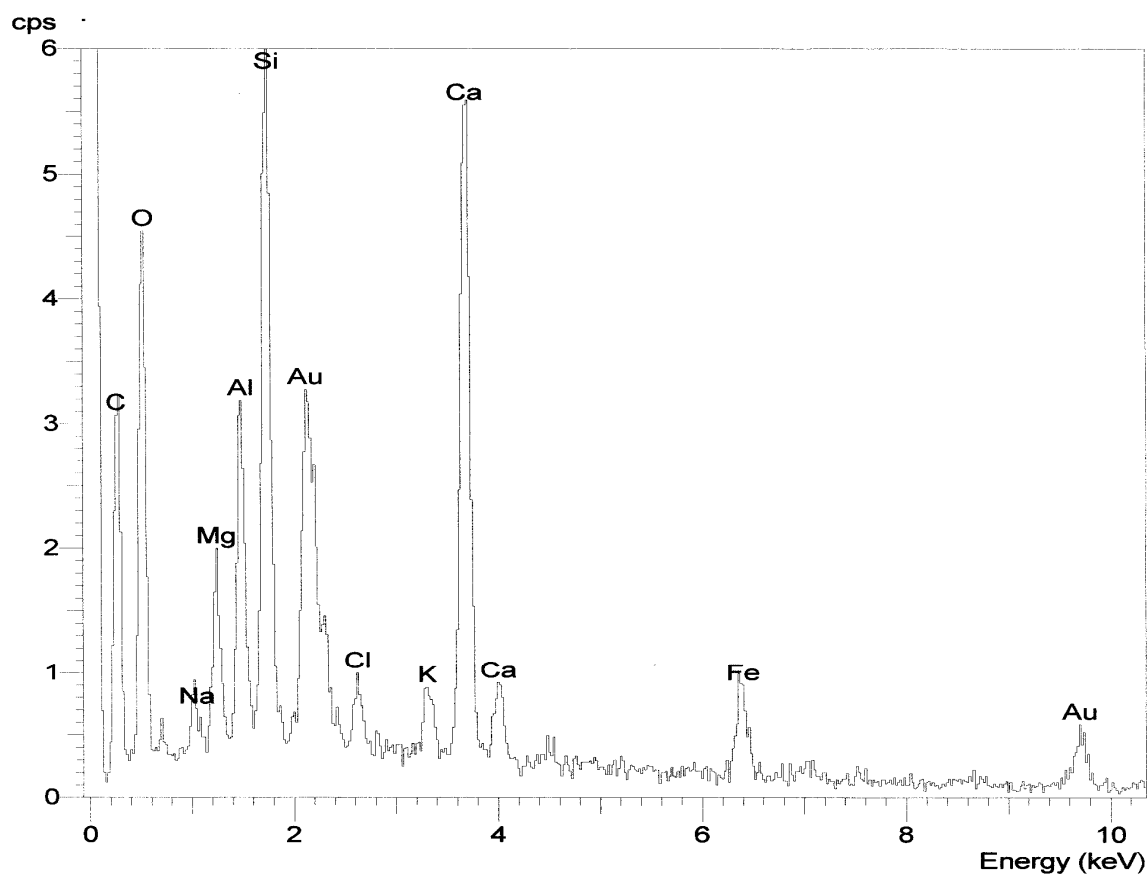
Figure 11. EDX spectrum of elemental chemical analysis of suspended particulate matter

Element	Minimum [%]	Maximum [%]	Mean [%]
Aluminium	0.14	0.18	0.159
Silicon	0.33	0.37	0.350
Phosphorous	0.02	0.03	0.021
Sulphur	0.30	0.31	0.306
Chlorine	0.48	0.66	0.570
Potassium	0.25	0.37	0.310
Calcium	0.33	0.51	0.420
Titane	0.02	0.03	0.025
Cromium	0.01	0.01	0.010
Manganese	0.004	0.006	0.005
Iron	0.01	0.03	0.020
Zinc	0.01	0.01	0.01
Bromium	0.002	0.0007	0.0014

Table 6. The percentage of basic inorganic elements measured by XRF in settled particulate matter

Chlorine, calcium, silicon, potassium and sulphur were found to be dominated; the concentrations of the other elements were quite lower as resulted from the quantitative XRF analysis (Table 6). The results of qualitative analysis by XRF correlated with those reported in [32]. The percentage of calcium and chromium measured by XRF is consistent with that measured by AAS (Table 9): 0.42 versus 0.43 % in case of calcium; 0.01 % by both XRF and AAS analysis in case of chromium. The XRF measured concentrations of iron and zinc were detected to be much lower than those detected by AAS (Table 9).

The principal component analysis shows the existents of three associations of the elements in settling particles: a) lithogenic (As, Co, Cr, Fe, lantanides and Sc); b) biogenic (Sr and Ca); c) authigenic (U and Se). The average element enrichment factors were higher in the first period of settled particulate matter sampling from: Se (739)> Zn (523)> Cr(105)> Br(104)> Sb(97)> As (69) [33]. The As, Br, Cr, Sb, Se, Sr and U average concentrations in the settled particulate matter were measured higher than their average crustal abundances [33].

Qualitative estimation of various functional groups in particulate matter proceeded with Fourier transformed infrared analysis FTIR (Figure 12).
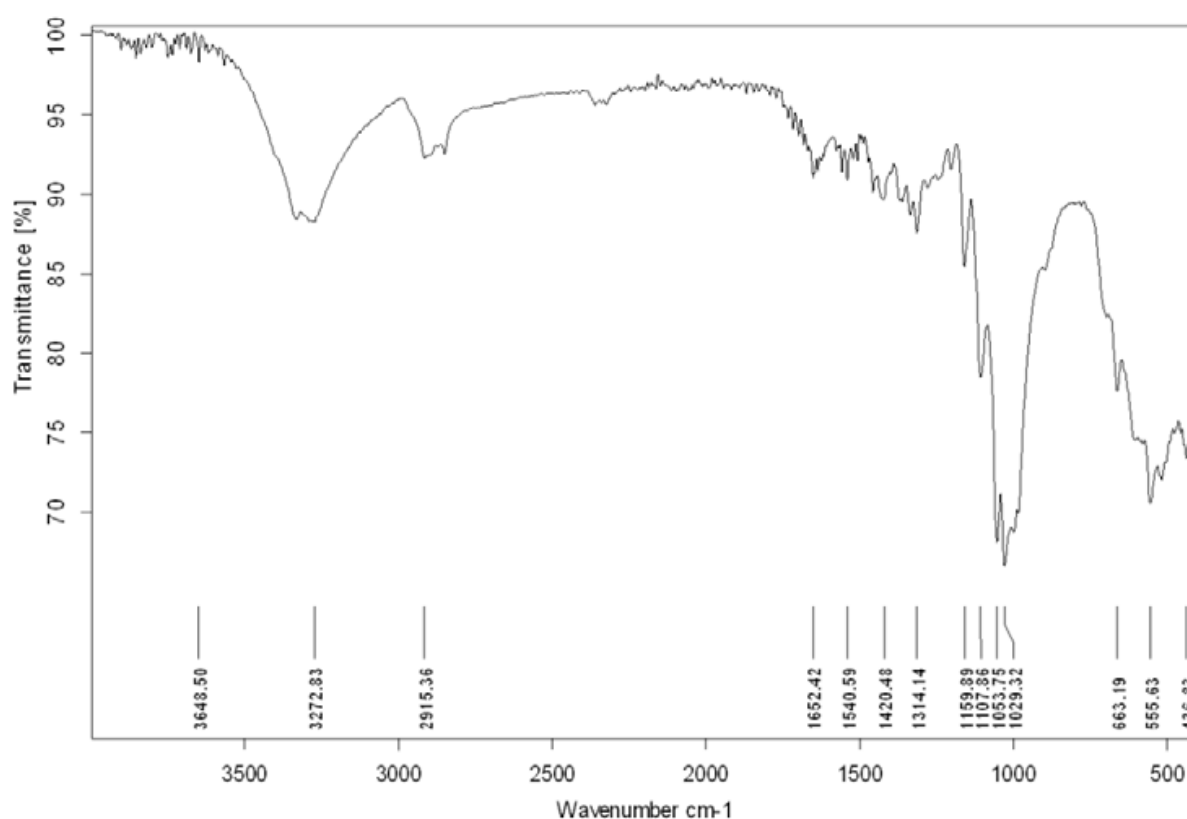

Figure 12. FTIR spectrum of settled particulate matter

Transmittances associated with particulate sulphate (near 618 and 1110 cm^{-1}), ammonium (2900–3200, 1430 cm^{-1}), hydroxyl (3200–3500 cm^{-1}), aliphatic carbon (2920 and 2850 cm^{-1}) and carbonyl (1650–1800 cm^{-1}) functional groups were observed. FTIR also identified several organic functional groups, although specific organic molecules could not be identified. In addition, there was also noticed the presence of inorganic nitrate (835 cm^{-1}) in [34].

Absorbances associated with sulphate, nitrate, ammonium, aliphatic carbon-hydrogen, and carbonyl functional groups as main constituent of particulate matter were observed also in the FTIR spectra of diesel generated PM_{10} [35]. The mass concentrations of sulphate, nitrate, ammonium, organic carbon (OC), elemental carbon (EC) were primarily measured in [36] in small particulate matter of size 0.1–3.0 µm.

The sum of Cl^-, NO_3^- and SO_4^{2-} concentrations represents a contribution of approximately 24% to the total mass in ambient PM_{10} as noticed in [37]. Compared to outdoors, indoor PM contained more silicate (36% of particle number), organic (29%, probably originating from human skin), and Ca-carbonate particles (12%) [38]. Indoor PM_{10} was elevated, chemically different and toxicologically more active than outdoor PM_{10} [38]. Suspended and settled particulate matter sampled in the child's bedroom was investigated in terms of mouse allergen in [39]. Airborne mouse allergen was detected in 48 of 57 (84%) bedrooms, and the median airborne mouse allergen concentration was 0.03 $ng.m^{-3}$. The median PM10 concentration was 48 $mg.m^{-3}$ [39].

6. Metals content in suspended and settled particulate matter

The presence of selected metals in particulate matter samples was detected by atomic absorption spectrometry (SpectrAA-30, Varian, Austrália). Fe, Zn, and Cu were detected by a standard process in acetylene – air flame, Cd, Cr, Ni, Pb and Co were detected in graphite cell in the GTA 96 add-on equipment. Arsenic content was detected by hydride method in the VGA 76 add-on equipment.

Metals content was investigated in both settled and suspended particulate matter samples. Because of low quantity in the suspended particles samples, the metals concentrations were detected for TSP and PM_{10} filters all at once.

The results of AAS analysis of selected metals content in settled and suspended aerosols for each monitored room are presented as metal concentrations in Tables 7 and 8. The average concentrations of metals measured in insufficient amount for individual concentration detection for each room are presented for arsenic, cadmium, chromium, nickel and lead.

Metal	Kitchen	Living room	Working room
Calcium	0.64	1.46	2.06
Copper	0.04	0.06	0.07
Iron	2.56	1.78	4.73
Magnesium	0.22	0.50	0.67
Zinc	0.29	2.80	0.91
	Average concentration		
Arsenic	0.10		
Cadmium	0.03		
Chromium	0.04		
Nickel	0.05		
Lead	0.09		

Table 7. Surface metal concentrations in settled particulate matter [$µg.cm^{-2}$]

Metal	Kitchen	Living room	Working room
Calcium	2.16	2.47	1.56
Copper	0.18	0.10	0.16
Iron	0.14	0.51	1.71
Magnesium	0.41	0.51	0.37
Zinc	0.20	0.21	0.20
	Average concentration		
Arsenic	0.28		
Cadmium	0.07		
Chromium	0.10		
Nickel	0.14		
Lead	0.24		

Table 8. Mass metal concentrations in suspended particulate matter [$\mu g.m^{-3}$]

The surface metal concentrations of settled particulate matter were detected in the range from 0.03 (cadmium) to 4.73 $\mu g.cm^{-2}$ (iron). The high concentrations were measured also in case of calcium and zinc. The highest concentrations were measured in case of iron, calcium and zinc. There were no significant differences of metal surface concentrations found out in all measured rooms. The metal concentration of the other investigated metals (Cr, Ni, Pb, Cd, As) in settled particulate matter were close to the detection limit (Table 7). The significant high concentrations of cadmium, chromium, arsenic and lead as tobacco smoke emissions were not confirmed in settled particulate matter.

The mass metal concentrations in suspended particulate matter range from 0.07 (cadmium) to 2.47 $\mu g.m^{-3}$ (calcium). Similarly to settling PM metal concentrations, no significant differences were measured for the monitored rooms.

The percentage of studied metals content was calculated in settled as well as suspended particulate matter as the ratio of measured metal concentration to the particulate matter concentration (Table 9).

Metal	Settled PM [%]	Suspended PM [%]	Suspended/ settled metals
Arsenic	0.03	0.46	15.3
Cadmium	0.01	0.11	11.0
Chromium	0.01	0.17	17.0
Nickel	0.02	0.23	11.5
Lead	0.03	0.40	13.3
Calcium	0.43	3.25	7.6
Copper	0.02	0.26	13.0
Iron	0.88	0.33	0.4
Magnesium	0.14	0.68	4.9
Zinc	1.50	0.34	0.2

Table 9. The metals percentage content in settled and suspended particulate matter

The higher percentage of metals content was detected in suspended particulate matter in comparison to the settled particles. This finding may result from the fact that most of metals are cumulated in the finest fraction of aerosols [40] represented by suspended PM_{10} in this study. As reported in [41] Na, Al, Ca, Fe, Mg, Mn and Ti were found in coarse particles, while K, V, Cr, Ni, Cu, Zn, Cd, Sn, Pb, As and Se occured more in fine particles. In reference [44] there is noted that elements mostly concentrated in coarse mode including Al, Mg, Ca, Sc, Ti, Fe, Sr, Zr and Ba; elements mostly concentrated in accumulation mode including S, As, Se, Ag, Cd, Tl and Pb; and the elements having muti-mode distribution including Be, Na, K, Cr, Mn, Co, Ni, Cu, Zn, Ga, Mo, Sn and Sb.

The measured values of metals content in suspended particulate matter were 4.9 – 15.3 times higher for all metals except for iron and zinc. The comparison of the percentage content of arsenic, cadmium, chromium, nickel and lead in settled and suspended indoor particulate matter is presented in Figure 13.
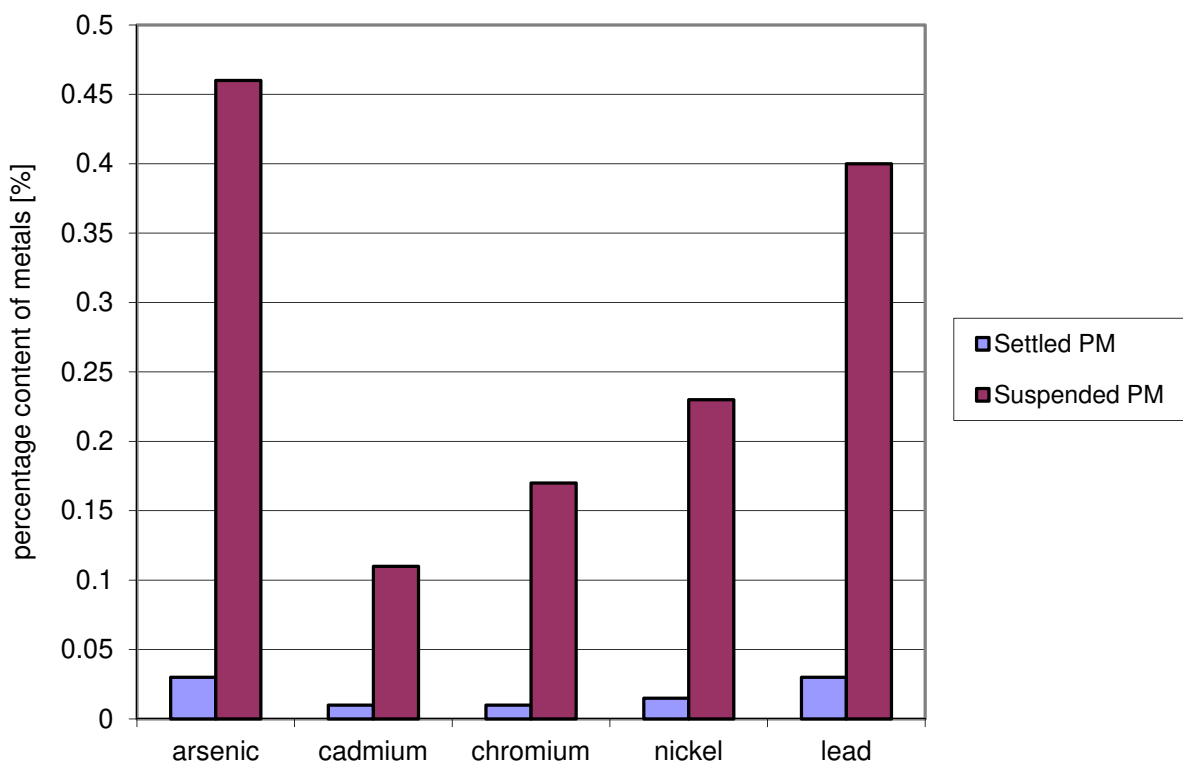

Figure 13. The percentage content of metals in settled and suspended particulate matter

The measured mass of metals contents in the samples of settled as well as suspended particulate were compared to the total mass of monitored particulate matter for each monitored room. Figures 14 and 15 represent the percentage content of metals in settled and suspended particulate matter for each monitored room, respectively.
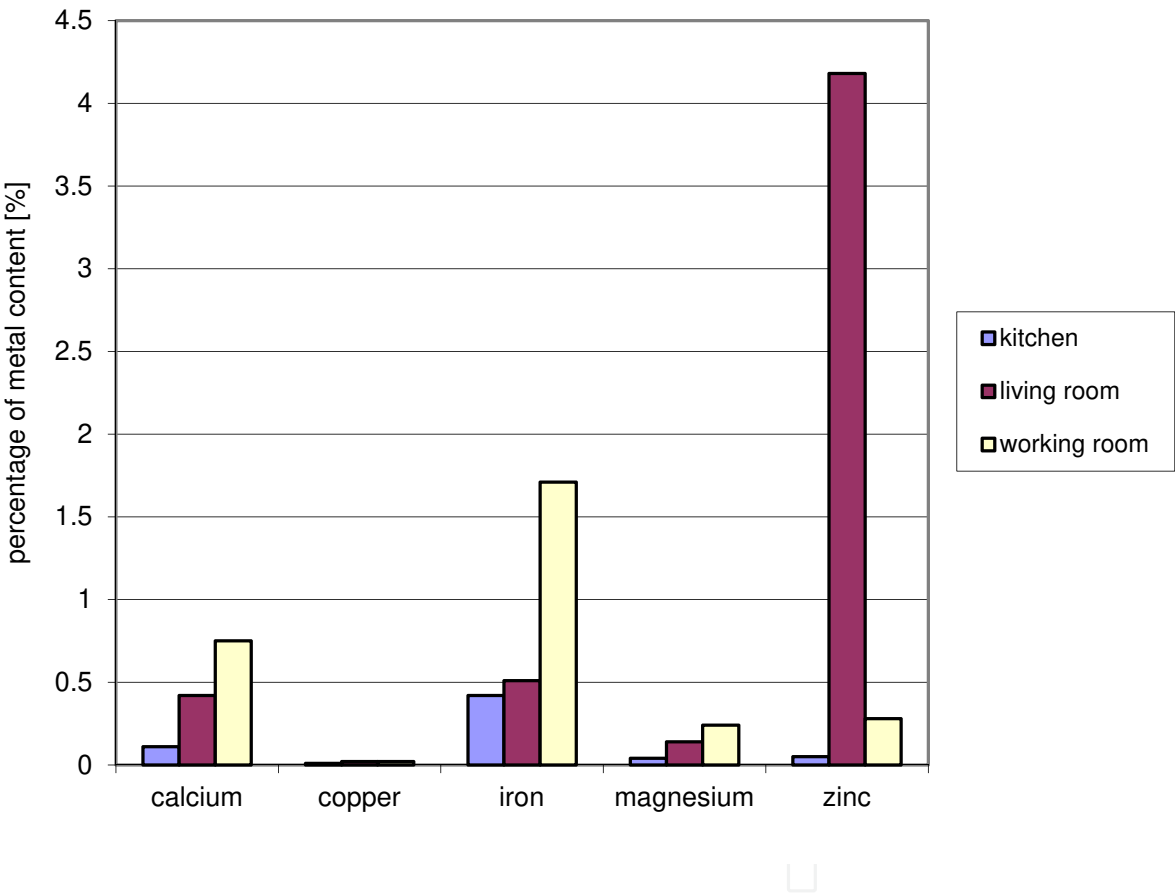
Figure 14. The percentage content of metals in settled particulate matter for monitored rooms
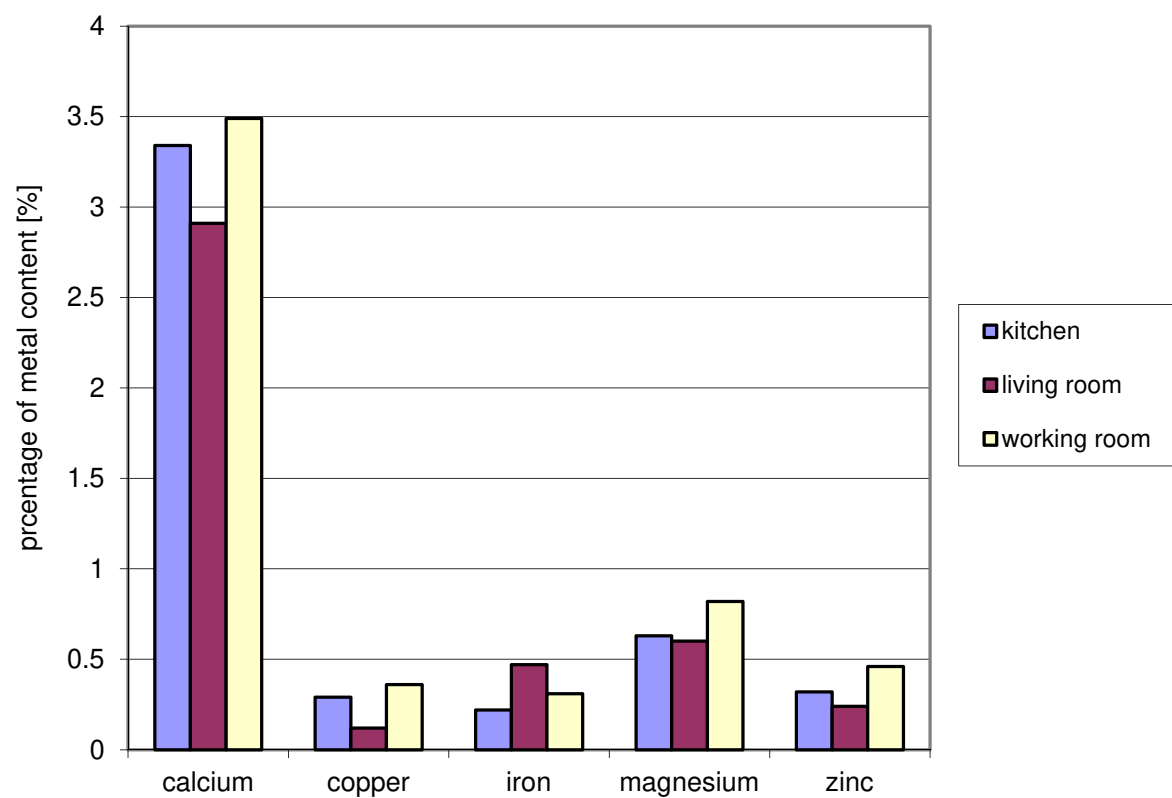
Figure 15. The percentage content of metals in suspended particulate matter for monitored rooms

The obtained mass concentrations of metals in indoor particle samples correspond with those in the typical urban aerosol [42,43]. The average indoor concentrations of total

elements were lower than or comparable to those measured outdoors, suggesting that indoor elements originated mainly from outdoor emission sources. On the contrary, the authors in [24] reported the metal elements concentrations analyzed were 3-15 times higher relative to soil background values in China.

Anthropogenic sources include fossil fuel combustion, industrial metallurgical processes, vehicle emission and waste incinerations. Natural sources include a variety of processes acting on crustal minerals, such as volcanism, erosion and surface winds, as well as from forest fires and the oceans. Some elements are potentially toxic trace metals, such as Pb, Cd, V, Fe, Zn, Cr, Ni, Mn and Cu.

7. Conclusion

Particulate matter exposure that occurs indoors probably constitutes a significant fraction of the overall exposure to hazardous particles since typically people spend most time indoors. The indoor settled as well as suspended particulate matter was monitored and particles morphology and chemical composition with special regard to metal content investigation was performed.

- Particles of irregular shapes and various sizes were observed in settled as well as suspended particulate matter.
- Principal inorganic elements constituting the particulate matter such as calcium, silicon, aluminium, potassium, iron, chlorine, magnesium as well as titan and manganese was confirmed. The percentage of inorganic elements mentioned was detected very low in the range of 2.23 %.
- Higher percentage of metals content was detected in suspended particulate matter in comparison to the settled particles except for iron and zinc. The measured values of metals content were 4.9 – 15.3 times higher in suspended particulate matter when comparing to the settled one.
- There were found out no significant differences of metal surface concentrations in the measured rooms in spite of the various indoor particulate matter sources.

The results demonstrate the complexity of indoor particulate matter nature affecting their surface properties. The results also emphasise the need for further research to a more complete understanding of the chemical nature of indoor particulate matter in connection with their surface reactivity. Due to the negative biological influence of particulate matters and their specific properties resulting in synergic effect of the other pollutants in the indoor air it is necessary to investigate the ways of indoor particulate matters occurrence minimization and/or elimination.

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