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# MINERALOGICAL AND GEOCHEMICAL CHARACTERISTICS OF PARTICLE $PM_{10}$ IN TIKVEŠ AREA AND THEIR INFLUENCE IN THE ENVIRONMENT

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In this work the results of investigation of the geochemical and mineralogical characteristics of particulate matters below 10 μm ($PM_{10}$) collected from Tikveš area, Republic of Macedonia, are presented. For that purpose, $PM_{10}$ samples were collected from the city of Kavadarci and from the area close to the ferronickel smelter plant. As well as the concentration of $PM_{10}$, the chemical content and mineral phases of dust samples and their relations to some anthropogenic sources are investigated. Determination of the content of various elements was performed by using inductively coupled plasma–mass spectrometry (ICP-MS). Scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS) was used for the determination of mineralogical phase content. From the obtained results, it can be concluded that the concentration of $PM_{10}$ in the vicinity of the ferronickel smelter is much higher than those from the city of Kavadarci. It was found that $PM_{10}$ samples collected close to the ferronickel smelter plant have a higher content of some elements present in higher concentrations in the ore processed in the ferronickel smelter plant (Fe, Ni, Cu, Zn, Ag, Cr) than those from the town of Kavadarci, showing their anthropogenic origin. The investigations performed by applying electron microscopy (SEM-EDS) unequivocally confirmed the results obtained using X-ray diffraction and ICP-MS. Namely, mineral phases present in the particulates were found to be those which are present in the ore used in the process in the metallurgical plant, including chlorite, amphibole, pyroxene, magnetite, chromites, quartz, calcite or plagioklas clay minerals.

**Keywords:** $PM_{10}$; Tikveš area; Republic of Macedonia; air pollution; chemical characterization; mineralogical characteristics

## МИНЕРАЛОШКИ И ГЕОХЕМИСКИ КАРАКТЕРИСТИКИ НА ЧЕСТИЧКИТЕ $PM_{10}$ ВО ОБЛАСТА НА ТИКВЕШ И НИВНО ВЛИЈАНИЕ ВРЗ ЖИВОТНАТА СРЕДИНА

Во овој труд се презентирани резултатите од истражувањата на геохемиските и минералошките карактеристики на цврстите честички под 10 μm ($PM_{10}$) земени во областа на Тиквеш, Република Македонија. Примероци од $PM_{10}$ се земени во градот Кавадарци и во околината на топилницата за фероникел. Освен определување на концентрацијата на $PM_{10}$, истражуван е и хемискиот состав и минералните фази во примероците на прав и нивниот однос со некои антропогени извори. Определувањето на содржината на различни елементи е извршено со примена на масена спектрометрија со индуктивно спрегната плазма (ICP-MS). За определување на минералошките фази е применет скенирачки електронски микроскоп со енергетски дисперзивна спектроскопија (SEM-EDS). Од добиените резултати може да се заклучи дека концентрацијата на $PM_{10}$ во околината на топилницата за фероникел е многу повисока од онаа во градот Кавадарци. Утврдено е дека во примероците од $PM_{10}$ земени во близина на топилницата за фероникел содржината на некои елементи чијашто содржина е висока и во рудата која се преработува во топилницата (Fe, Ni, Cu, Zn, Ag, Cr), е повисока во споредба со примероците земени од градот Кавадарци, што укажува на нивното антропогено потекло. Истражувањата извршени со примена на електронска миктроскопија (SEM-EDS) недвосмислено ги потврдуваат резултатите добиени со XRD и ICP-MS. Имено, најдено е дека минерални фази присутни во честичките прав се присутни и во рудата која се користи во металуршките процеси: хлорити, амфиболи, пироксен, магнетит, хромити, кварз, калцит, плагиоклас и глинени минерали.

**Клучни зборови:** $PM_{10}$; Тиквеш; Република Македонија; загадување на воздухот; хемиска карактеризација; минералошка карактеризација

## 1. INTRODUCTION

Particulate matters that are the product of anthropogenic sources are extremely hazardous substances. They are increasingly present in the environment, affecting the quality of air, water, soil and plant products. To define the origin and characteristics of particles, very different terms are used [1]. Particulate matters (PM) are used for the determination of air pollution with fine particles, mainly those with a size below 10 μm ($PM_{10}$), but those below 2.5 μm ($PM_{2.5}$) are also useful for air pollution monitoring.

The finest metallurgical gases consist of condensed volatile ingredients that are of molecular size, although they are often quickly grouped into long chains. The secondary particles are generated in the atmosphere because of photochemical reactions between the primary gases. The real distribution of particle size in the atmosphere is a result of several competitive processes including condensation, sedimentation, evaporation, agglomeration, conversion of gas into particles etc. Therefore, it can be expected that their distribution will be very variable [2, 3].

Particles as air pollutants are either emitted into the air or can be formed in air. They spend some time in the air before being deposited from the air naturally or artificially. The particles are deposited on the surface by three main mechanisms: sedimentation, Brown diffusion and impaction [4, 5]. Each of these mechanisms is effective for a different size range of particles [4, 5].

Due to specific characteristics, dust shows a wide range of harmful effects on the human organism. Practically every dust at higher concentrations and longer periods of exposure have fibrogenic properties leading to disruption of the functions of the human respiratory system. Certain types of dust are toxic and have harmful influences to the inner human organs (stomach, liver, kidneys, etc.), while others have irritating effects and damage the skin and eyes of exposed workers. However, toxic and irritation effects, compared with harmful effects on the respiratory system are almost negligible and can be controlled (both in terms of their prevention and medical terms). For these reasons, the emphasis for defining the physiological effects of dust is to commence a study of the adverse effects that occur in the human respiratory system. The nasal and oral routes through which people breathe merge in the trachea, and from there lead to the bronchus through the throat [6–10].

In this study, a detailed mineralogical and geochemical determination of particulate matters below 10 μm ($PM_{10}$) collected in Tikveš area, Republic of Macedonia, was performed. The quality of the environment in the Tikveš area, as well as in the city Kavadarci is affected by several important factors: industrialization of the area, usage of fertilizers in the agriculture and local infrastructure. The highest impact on the environment in the area was registered after the ferronickel smelter plant started production. This impact is manifested differently in various environmental media.

## 2. MATERIALS AND METHODS

### 2.1. *General characteristics of the investigated area*

Among the valleys in Macedonia, Tikveš valley stands out in particular as a separate geographic entity with its own geomorphological and anthropogeographical characteristics [11]. With an area of 2120 km$^2$, this valley occupies a substantial part of the territory of Republic of Macedonia. It is bounded to the south by the Mariovo-Magelanian Mountains, ranging up to 1700 m. Other mountains are Konečka Mt. on the east and Dren and Babuna on the west. The Tikveš valley is cut by the Vardar river on its north side and on the west side by the Crna Reka river, while the Luda Mara river passes through the middle of the valley (Fig. 1).

The climate has a major influence on the development of vines and other crops, as well as in the production and quality of agricultural products. It controls the air temperature, sunlight, humidity and air currents present in the given area. Each of these factors has a specific effect, and the overall result of their influence could be seen in the growth of the vine, the degree of ripening of the grapes and the creation of high quality ingredients which passes into the wine.

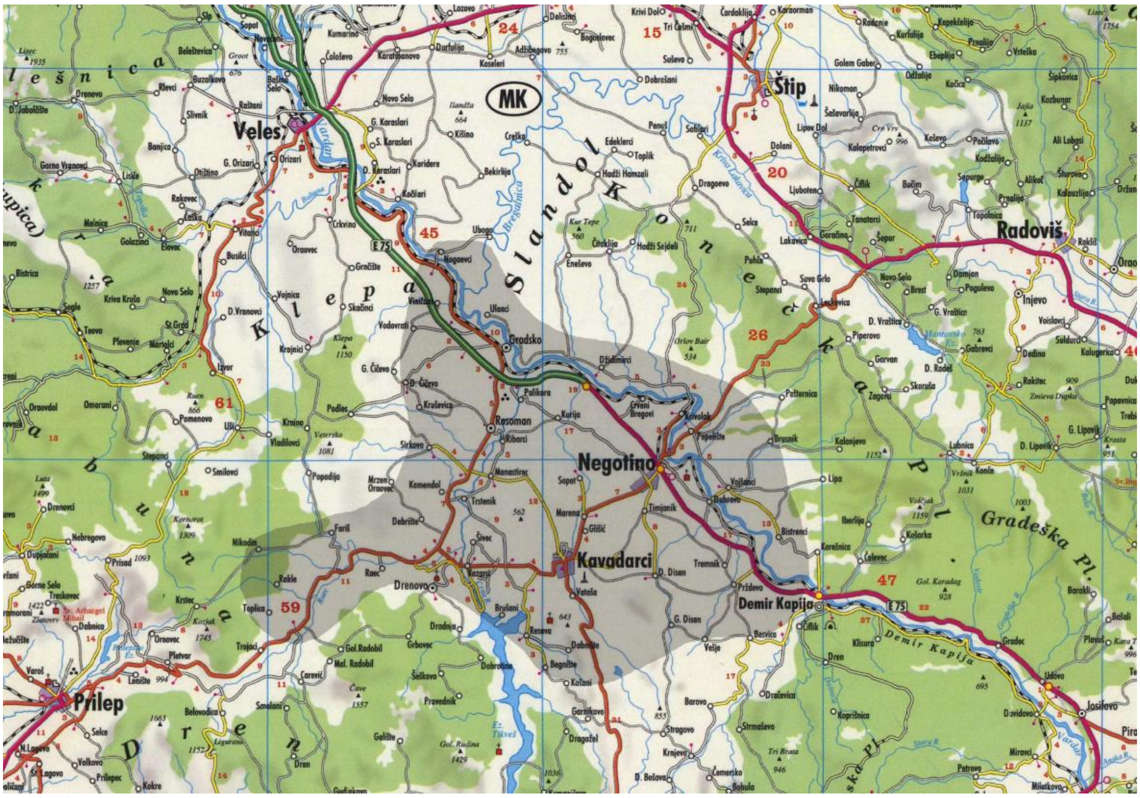


**Fig. 1.** Geographic map of the Tikveš area

The Tikveš valley is an area where two zonal climates, continental and Mediterranean, intersect and influence the local climate [12]. The influence of the continental climate spreads from the north and continues along the Vardar and Bregalnica rivers. As a result of its impact, there are brief very cold periods. The Mediterranean climate in turn flows in from the south and the Aegean Sea into the Vardar river valley, and because of its influence there are beneficial winters with relatively high temperatures. The impact of the local mountain climate is limited and greater expression does not occur. Under the influence of these climate impacts, a special modified Mediterranean climate developed in this region. As a result, the Tikveš region is rich with diverse flora.

Most of the Tikveš region is an area with a small amount of rainfall, with the area in the vicinity of the village of Gradsko being considered the area with the least rainfall per square meter in the Republic of Macedonia. The average rainfall in Kavadarci is 484 mm. In Kavadarci, the most arid summer months (July and August) have an average monthly amount of 23 to 27 mm. The average annual days with precipitation in Kavadarci range from 63 to 112 days. If the total amount of rainfall is divided by the number of rainy days, the average is 5 mm on a rainy day.

### 2.2. *The quality of the environment in Tikveš area*

The quality of the environment in the Tikveš area, as well as in the city of Kavadarci is affected by several factors: industrialization of the area, use of fertilizers in the agriculture and communal infrastructure. The highest impact on the environment in the area was registered after 1982 when the ferronickel smelter plant was started with the production with an annual processing of about 1.5 million tons of laterite type nickelous ore. Starting in 2005, in total, about 900,000 tons of ore was retrieved from the Ržanovo mine annually (southern parts of Kožuf Mountain), and the smelter plant has since begun processing ore originating from Albania, Turkey, Indonesia and Guatemala. Data concerning the composition (chemical and mineralogical) of these types of ores are presented in several publications [13–16]. The operation of this plant effects changes in the composition (mineralogical) of urban dust in the Tikveš valley. This factory processes a laterite nickelous ores, with a yearly capacity of 2 million tons of ore and the smelter plant capacity of about 16,000 tons of nickel in the form of ferro-nickel per year.

Based on studies of mineral associations, as well as the major mineral phases, the major nickel-bearing minerals in the ores include magnetite, hematite, clinochlore, talc, sepiolite, magnesioriebeckite, lizardite, antigorite, actinolite, tremolite, chrysotile, dolomite, phlogopite, stilpnomelane, muscovite, quartz, albite, pyrite, maghemite, pirotine, digenite and millerite. Only five of the mentioned minerals are constantly present: magnetite, hematite, clinochlore, talc and magnesioriebeckite [15].

Based on these processes, it can be concluded that, during the processing of nickel ore, a certain amount of dust is generated and emitted into the air in the Tikveš region. Legal norms existing in the Republic of Macedonia specify 50 μg $m^{-3}$ or less. It must be noted that the emission of dust, as observed from a factory producing nickel, in fact exceeds this limit [17–19].

### 2.3. *Sampling*

The dust samples (particulate matters, $PM_{10}$) were collected in 2012 by the standard procedures by setting up two mobile stations, one in the area of the village of Vozarci (near the iron ferronickel smelter plant) and the other in the urban part of the town of Kavadarci. Ten samples were collected in the area of the village of Vazarci, and 13 from the urban part of Kavadarci.

The sampling device consists of three integral, conductive plastic cassette sampling heads, with a design that does not allow a significant spilling around the filter. The sampling head consists of a cylindrical protective casing and filter holder with an auxiliary filter. The protective layer of the filter holder is made of stainless material. The filter should be tight so that no significant leakage occurs around the filter at various pressures up to approximately 50 kPa with a flow from 8 to 30 l/min. Within 2 minutes of the start of sampling, the flow should be adjusted to 2 l/min per square centimeter. The volume of 1000 liters per square centimeter of effective filter area was passed through the filters in a sampling period of about 8 hours.

### 2.4. *Chemical analysis*

For the digestion of dust samples, open wet digestion with a mixture of acids was applied. The digestion was carried out in this order: precisely measured mass of dust samples (0.500 g) with the accuracy of 0.0001 g was placed in teflon vessels. After this, 5 ml $HNO_3$ was added, until brown vapors came out of the vessels. For the total digestion of inorganic components, 5–10 ml HF and 2 ml of $HClO_4$ were added. After cooling the vessels for 15 min, 2 ml of HCl and 5 ml of $H_2O$ were added and the vessels were cooled, before digests were quantitatively transferred to 50 ml calibrated flasks [19].

Determination of the concentration of investigated elements was performed by the method of mass spectrometry with inductively coupled plasma (ICP-MS), using the Agilent model 7500 in the laboratory of the Goce Delčev University from Štip [20].

### 2.5. *Determination of mineral phases*

For the determination of the phase and mineralogical content of $PM_{10}$ collected from Kavadarci and Vozarci areas, the filters were cut and mounted on 25 millimeter Cambridge-style SEM stubs using double sided carbon tape, and graphite coated to prevent charging. The coated samples were analyzed by Quanta 650F SEM, fitted with a Back-scattered electron detector (BSED) and a Bruker 5030 X-ray detector. The Esprit Quantax 1.9 EDS Analysis System was used to determine the elemental composition of particulate matter. Point analysis was used to characterize the samples in high-vacuum mode, using an accelerating voltage of 15 kV and a spot size of 6. Back-scattered electron (BSE) images of selected fields of view were taken to examine SEM-based characteristics [21]. The SEM-EDS analyses were performed at the Actlabs from Ancaster, Ontario.

## 3. RESULTS AND DISCUSSION

### 3.1. *Distribution of $PM_{10}$*

The results of the concentrations of $PM_{10}$ show that the concentration of $PM_{10}$ in the vicinity of the village Vozarci (close to the ferronickel smelter) was much higher than in the urban area of the city of Kavadarci [20]. It was found that the average concentration of $PM_{10}$ determined in the vicinity of the village of Vozarci is 630 $\mu m/m^3$, while in the area of the city of Kavadarci it is 210 $\mu m/m^3$ measured in the same 12 days period [20]. The distribution of $PM_{10}$ collected in the vicinity of the village of Vozarci for the period of 24 hours is shown in Figure 2. From the obtained diagrams it can be concluded that the emissions of particulate matter $PM_{10}$ during a 24 hour period is highly variable and ranges from 50 $\mu g/m^3$ to 800 $\mu g/m^3$. The average concentration of $PM_{10}$ is from 100 to 300 $\mu g/m^3$, while in some short periods, the concentration increases to over 500 $\mu g/m^3$. It is obvious that the concentration of $PM_{10}$ in this area is up to 10 times higher than the maximal permitted concentration of 50 $\mu g/m^3$, according to the national regulation [22].

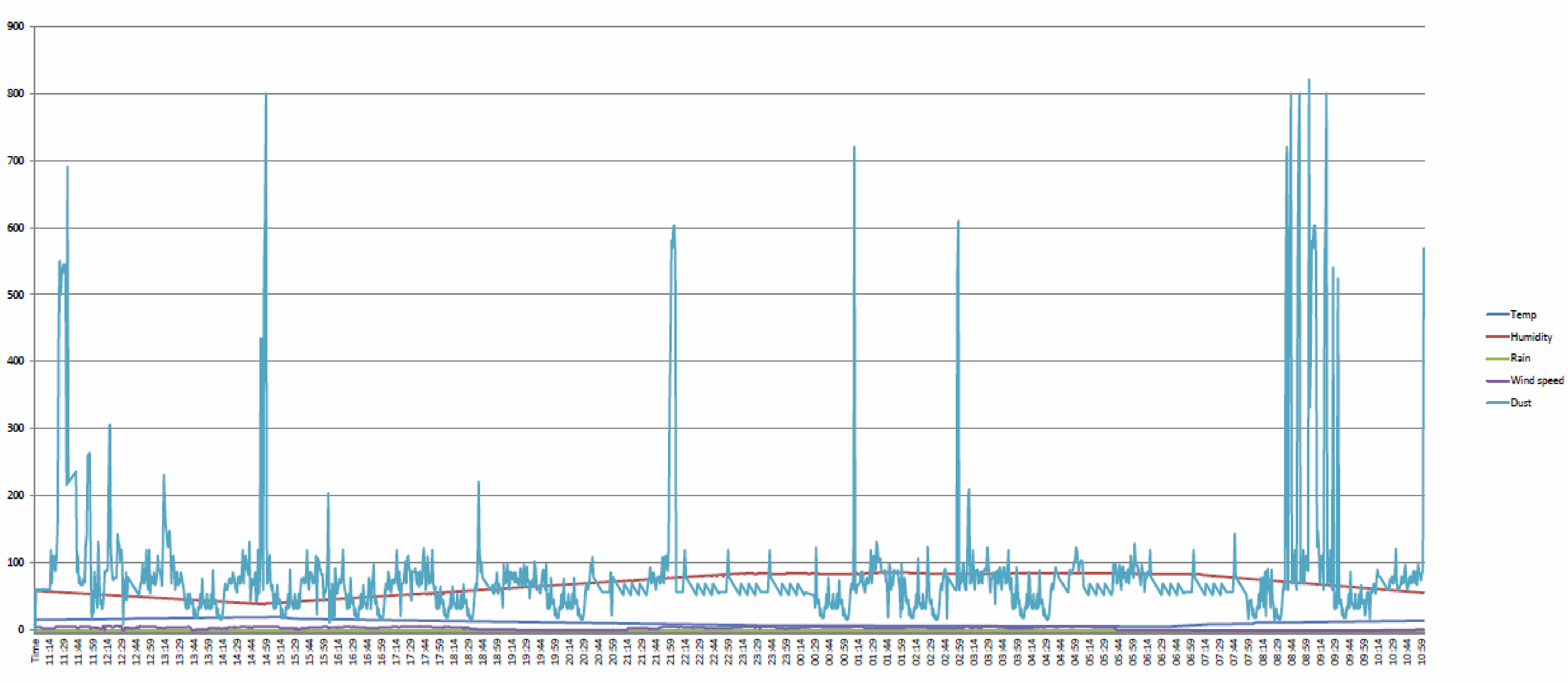


**Fig. 2**. Daily distribution of $PM_{10}$ particulate matter in the Tikveš area

3.2. *Macro- and microelements distribution*

The results obtained for the content of 36 elements in $PM_{10}$ samples collected from the urban part of Kavadarci and the village of Vozarci, close to the smelter plant are presented in Table 1. In comparison of the results for the content of nickel in $PM_{10}$, it can be seen that its content is much higher in dust samples collected close to the ferronickel smelter plant than in those collected in the city of Kavadarci. The higher content of Al and Fe was also found in the samples from the village of Vozarci. Slightly increased contents were also found for some other elements (Cu, Mn, Pb, Zn) in $PM_{10}$ from Vozarci compared with those from Kavadarci [20]. In general, it was found that the total content of the analyzed elements (Al, Fe, P, B, Ba, Ti, Cr, Mn, Pb, Bi, Ni, Cu, Zn, Ga, Sr) is higher in $PM_{10}$ from Vozarci than in those from Kavadarci. These differences are especially expressed for the contents of aluminum, iron, manganese, barium and nickel (Table 1).

T a b l e 1

*The mean, median, minimal and maximal content of trace elements in thirteen $PM_{10}$ samples collected in the urban area of the city of Kavadarci (in mg/kg) [20]*

| Element | $PM_{10}$ from the city of Kavadarci | | | | $PM_{10}$ from the vicinity of the village of Vozarci | | | |
|---|---|---|---|---|---|---|---|---|
| | Mean | Median | Min | Max | Mean | Median | Min | Max |
| Ag | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 |
| Al | 4649 | 2911 | 679 | 13140 | 25262 | 22364 | 13727 | 44755 |
| As | 15 | 14.5 | 12 | 17 | 31 | 16 | 5 | 141 |
| B | 5008 | 5045 | 1225 | 8675 | 2757 | 1405 | 228 | 7747 |
| Ba | 612 | 197 | 10 | 4145 | 10302 | 3722 | 558 | 26391 |
| Be | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 |
| Bi | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 |
| Cd | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 |
| Ca | 427 | 67 | 8 | 4563 | 86 | 78 | 35 | 144 |
| Co | <10 | <10 | <10 | <10 | 33 | 27 | 11 | 63 |
| Cr | 1000 | 958 | 750 | 1440 | <10 | <10 | <10 | <10 |
| Cs | <10 | <10 | <10 | <10 | 337 | 376 | 10 | 930 |
| Cu | 1505 | 971 | 307 | 2855 | 2341 | 1709 | 1309 | 6409 |
| Fe | 23226 | 22887 | 1136 | 71783 | 1081 | 802 | 481 | 2450 |
| Ga | 22 | 19 | 10 | 46 | 71 | 64 | 27 | 126 |
| Ge | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| K | 48 | 37 | 1 | 115 | 55 | 37 | 4 | 160 |
| Li | 97 | 65 | 37 | 272 | 71 | 62 | 12 | 168 |
| Mg | 394 | 132 | 97 | 3212 | 600 | 570 | 377 | 1009 |
| Mn | 323 | 249 | 40 | 1144 | 1272 | 297 | 11 | 8247 |
| Mo | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Na | 1473 | 1608 | 687 | 2159 | 1046 | 989 | 788 | 1621 |
| Ni | 1896 | 917 | 288 | 9571 | 5904 | 5821 | 2270 | 11510 |
| P | 6107 | 1244 | 94 | 60202 | 1928 | 1902 | 65 | 6437 |
| Pb | 139 | 54 | 5 | 442 | <10 | <10 | <10 | <10 |
| Pd | <10 | <10 | <10 | <10 | 276 | 231 | 2 | 927 |
| Rb | 28 | 27 | 12 | 53 | 36 | 28 | 4 | 98 |
| Sb | 118 | 118 | 13 | 222 | 68 | 68 | 68 | 68 |
| Sn | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Sr | 161 | 151 | 55 | 484 | 444 | 464 | 224 | 745 |
| Th | <10 | <10 | <10 | <10 | <10 | <10 | <10 | <10 |
| Ti | 161 | 151 | 55 | 484 | 725 | 572 | 193 | 1453 |
| Tl | <5 | <5 | <5 | <5 | <10 | <10 | <10 | <10 |
| U | 7 | 6 | 2.5 | 15 | 10 | 9 | 8 | 15 |
| V | 21 | 10 | 10 | 45 | 48 | 48 | 28 | 68 |
| Zn | 1007 | 871 | 287 | 1847 | 921 | 1037 | 329 | 5646 |

The results show that the presence of Mg, Li, Th, Na, Ca, U Sr, Ti and V which have lithogenic origin is almost identical in the samples from both locations due to the similar geological structure. The increased presence of Rb, K, Cs, Fe, P, Ba, Mn, Ni, Cr, Co, Zn, Sn, Pb, Cu, Mo, Cd, As, Ag, Sb in dust from Vozarci could be considered of anthropogenic origin due to the increased presence in the ore processed in the smelter plant [16–19, 21, 23, 24].

### 3.3. *Mineralogical characterization*

By the application of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction, mineralogical phases in the $PM_{10}$ samples were also determined. By using SEM-EDS it was found that the $PM_{10}$ particles contain several alumosilicate phases, including quartz, illite, plagioclase, and possibly amphibole/pyroxene and chlorite [21, 25, 26]. In some of the $PM_{10}$ particles, a high content of Ca observed on and around clay minerals is probably due to the presence of calcium carbonate. The particles of manganochromite and stainless steel were also observed in the samples as well. From the backscattered electron (BSE) images and EDS spectra the following minerals were determined: manganochromite, stainless steel, metals, metal oxides, and metal oxyhydroxides. Minor particles of nickel were found associated with metal oxides and stainless steel. Also, metals, metal oxides, and metal oxyhydroxides were found with clay minerals. Hydrated phases, observed to be volatile under the electron beam, presumably produced water vapor or carbon dioxide as an effect of heating. Minor nickel was found associated with metal oxides. All of these minerals are present in the ore processed in the ferronickel smelter plant situated in this area. We can conclude that the content of these particles in the analyzed samples come from human activities in the ferronickel metallurgical plant.

Beside the application of SEM-EDS, all of the $PM_{10}$ collected samples were analyzed by X-ray diffraction method. X-ray diffractograms for 25 $PM_{10}$ samples were also recorded. X-ray diffractograms for some of the samples are presented in Figures 3–8. The most abundant minerals in each sample are listed in each figure. It was found that the most present minerals in $PM_{10}$ from Tikveš area are: actinolite, albite, anhydride, anorthite, antigorite, augite, barite, bassanite, biotite, calcite, clinochlore, dolomite, fluorite, gypsum, halloysite, hematite, microcline, muscovite, quartz, tremolite, etc.

The investigations performed by applying electron microscopy (SEM-EDS technique) unequivocally confirmed the results obtained by X-ray diffraction and the results from the determination of chemical composition of $PM_{10}$ particles with the application of ICP-AES and ICP-MS. From the results performed with all of the applied techniques, it can be concluded that the presence of specified mineral phases that have typically anthropogenic origin are registered as well as the mineral phases that have lithogenic origin or the origin of the present geological structure.

Therefore, it can be concluded that the urban dust with a sizes below 10 μm ($PM_{10}$) in the Tikveš area originated from lithogenic and anthropogenic processes. The phase composition of $PM_{10}$ particles from Tikveš area consists of mineral phases which have anthropogenic origin, confirmed by the high content of Fe, Ni, Cu, Zn, Ag, Cr (present in higher content in the ore processed in the ferronickel smelter), and by the presence of the minerals like: chlorite, amphibole, pyroxene, magnetite, chromites, Ag-minerals, metallic forms of Mn-Cr, Cu-Zn (also present in the ore processed in the smelter plant). The lithogenic origin of the part of $PM_{10}$ is confirmed by the presence of minerals such as quartz, calcite, plagioclase and clay.

## 5. CONCLUSION

In this work, the results of the mineralogical and geochemical characteristics of particles $PM_{10}$ from Tikveš area, Republic of Macedonia, and their influence on the quality of the environment are presented. For that purpose, $PM_{10}$ samples are collected from the city of Kavadarci and from the area close to the ferronickel smelter. Beside the concentration of $PM_{10}$, the chemical content and mineral phases of the dust samples and their relation to some anthropogenic sources are investigated. The investigations performed by applying electron microscopy (SEM-EDS) unequivocally confirmed the results obtained using X-ray diffraction and the results from the determination of chemical composition of particles $PM_{10}$ with the application of the ICP-AES and ICP-MS. From the results obtained by all of the applied techniques, it can be concluded that the presence of specified mineral phases that have a typically anthropogenic origin are registered as well as the mineral phases that have a lithogenic origin or an origin in the present geological structure. Therefore, it can be concluded that the urban dust with a sizes below 10 μm ($PM_{10}$) in the Tikveš area originated from lithogenic and anthropogenic processes. The phase composition of $PM_{10}$ particles from Tikveš area consists of mineral phases which have anthropogenic origin, confirmed by the high content of Fe, Ni, Cu, Zn, Ag, Cr (present in higher content in the ore processed in the ferronickel smelter), and by the presence of the minerals like: chlorite, amphibole, pyroxene, magnetite, chromites, Ag-minerals, metallic forms of Mn-Cr, Cu-Zn (also present in the ore processed in the smelter plant).

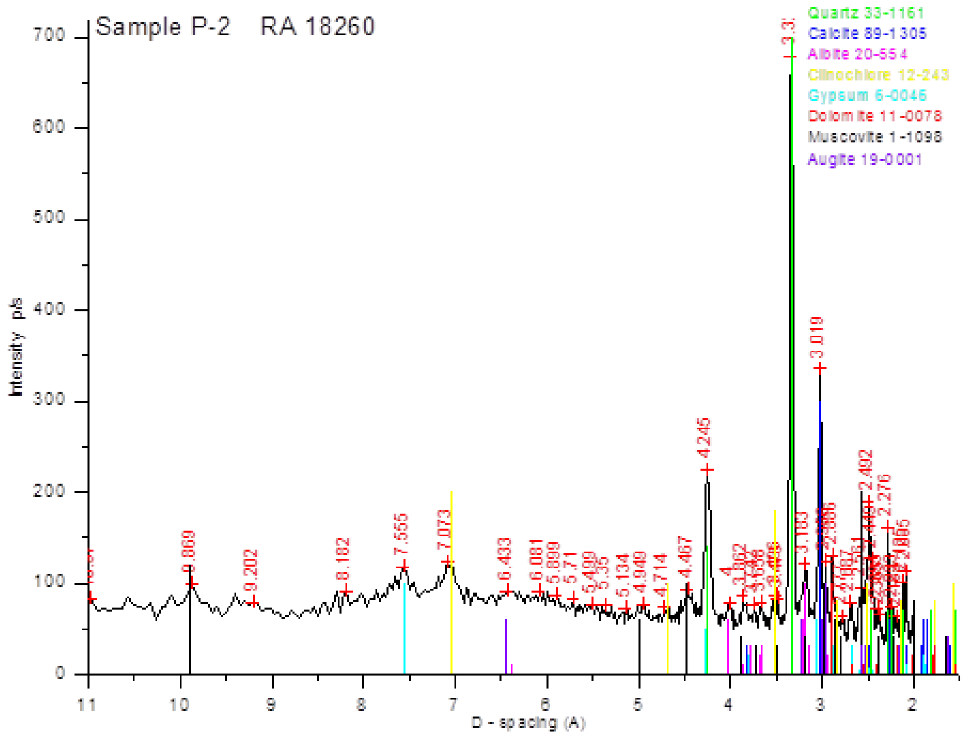


**Fig. 3**. X-ray diffractogram of $PM_{10}$ (sample No. 2)

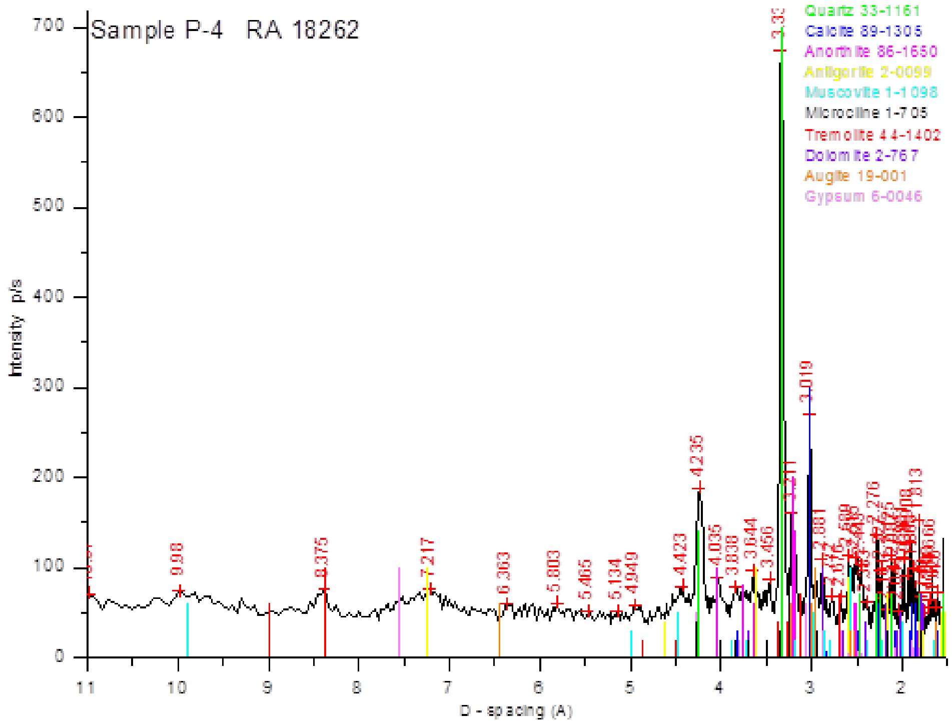


**Fig. 4.** X-ray diffractogram of $PM_{10}$ (sample No. 4)

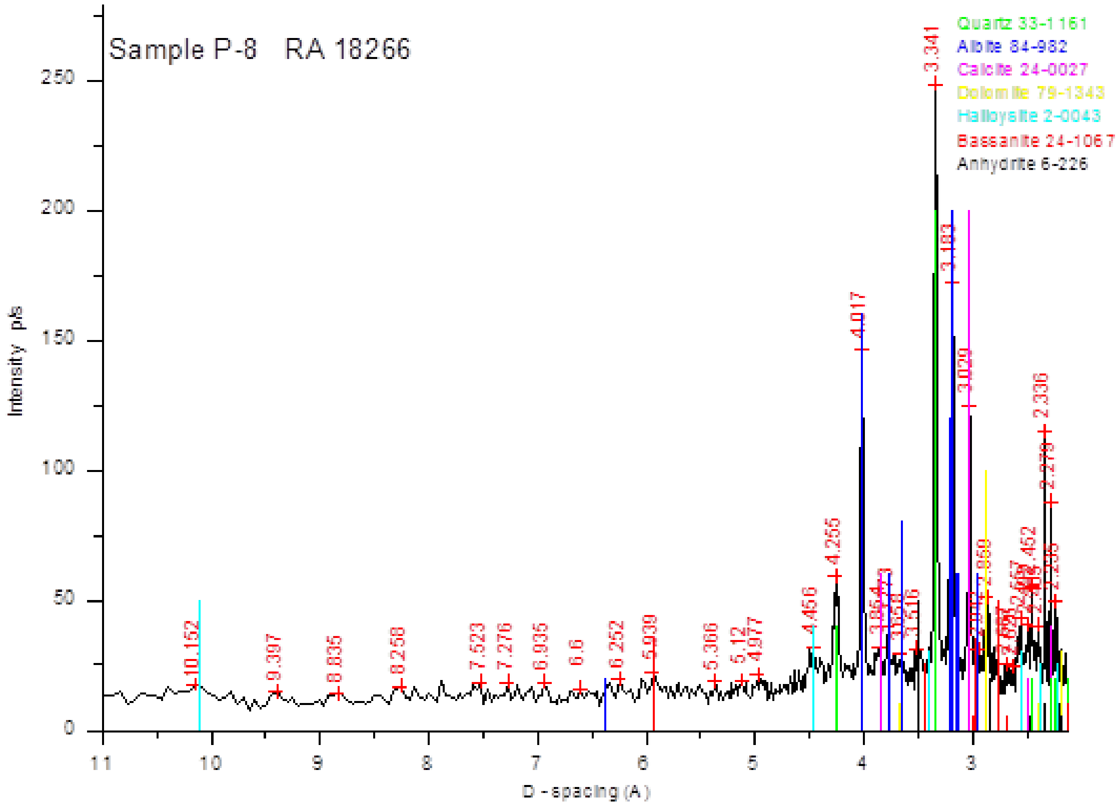


**Fig. 5**. X-ray diffractogram of $PM_{10}$ (sample No. 8)

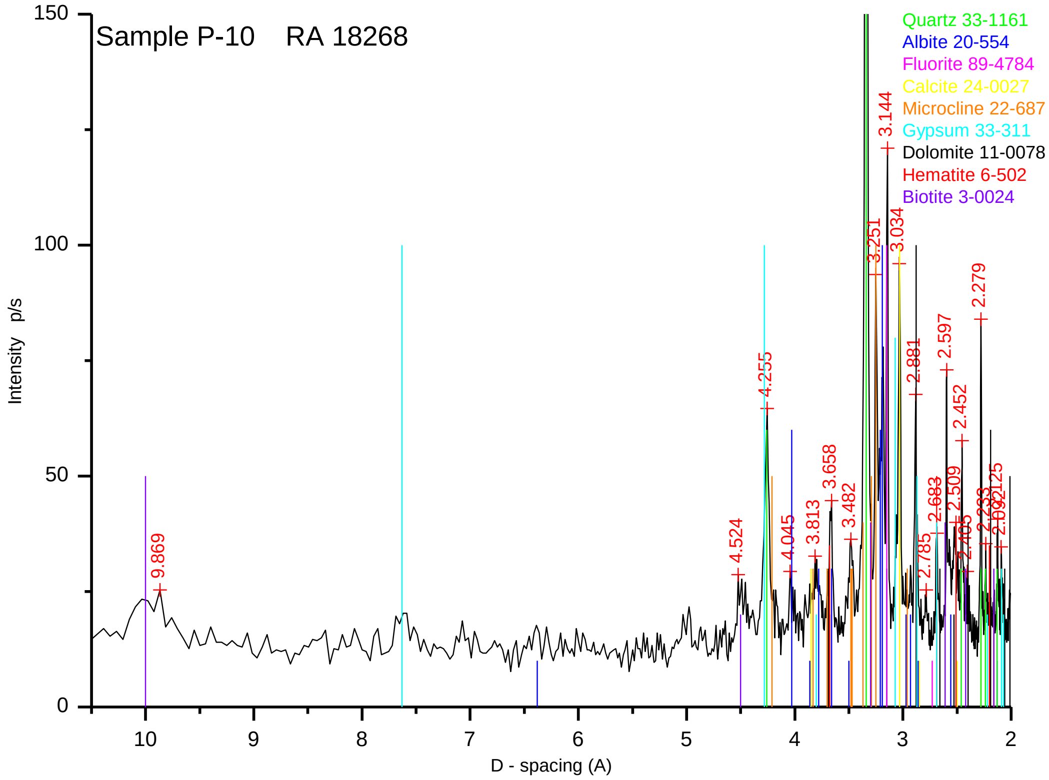


**Fig. 6**. X-ray diffractogram of $PM_{10}$ (sample No. 10)

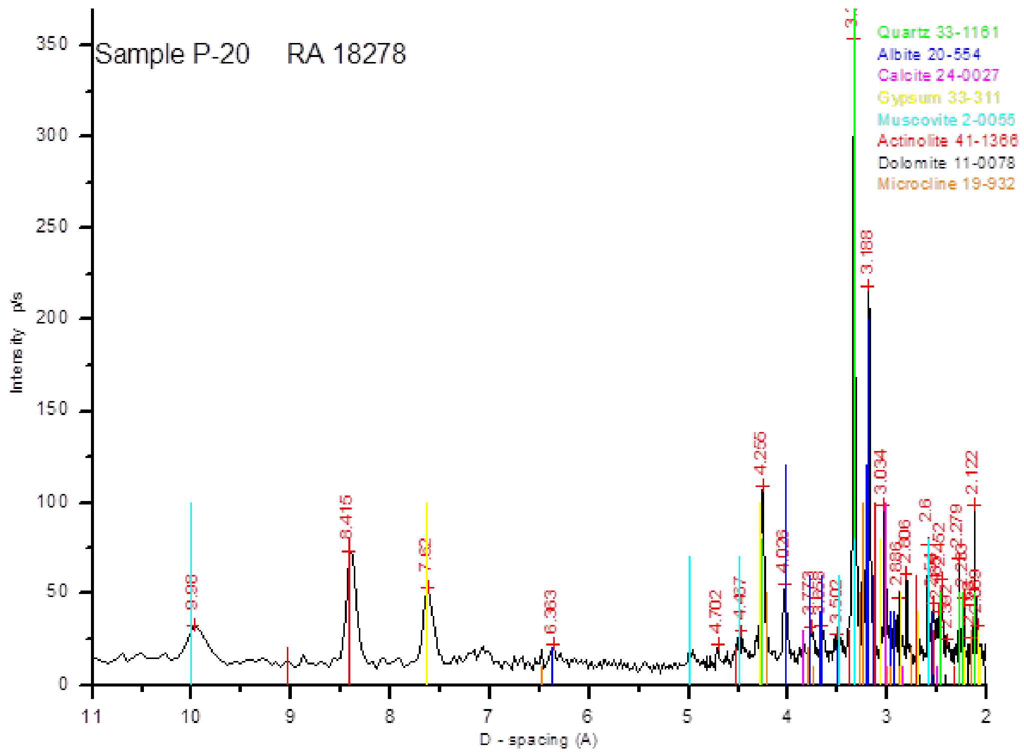


**Fig. 7**. X-Ray diffractogram of $PM_{10}$ (sample No. 20)

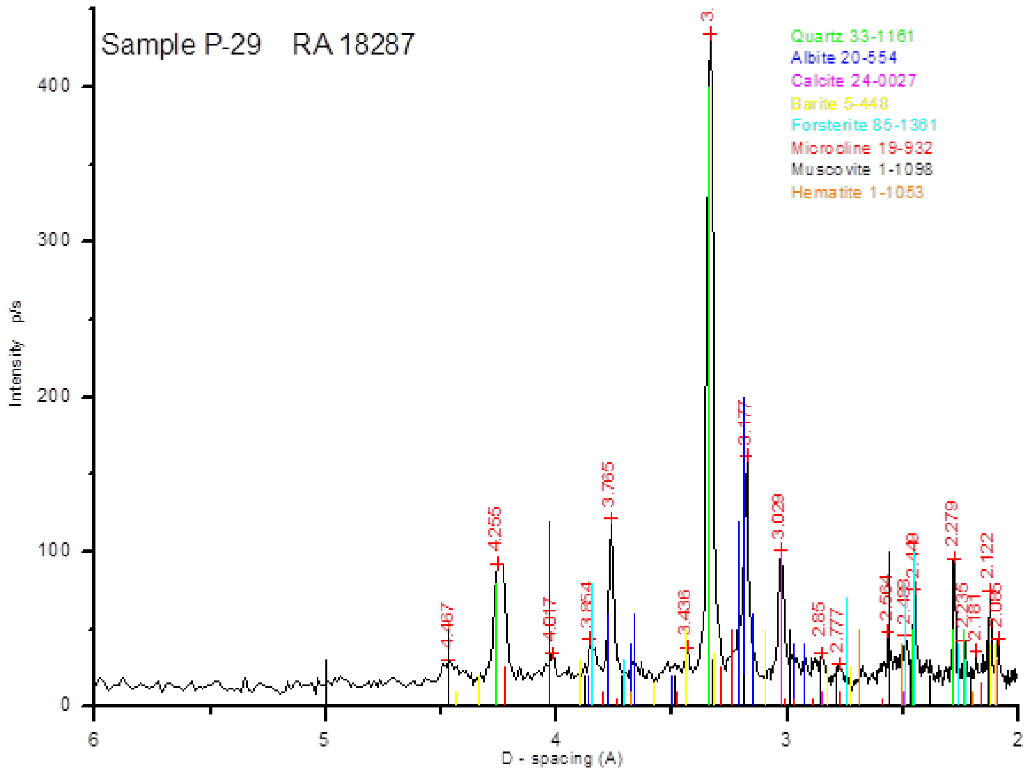


**Fig. 8**. X-ray diffractogram of $PM_{10}$ (sample No 29)

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