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# Concentration Fluctuations and Location Variability of Total Suspended Particles in Zanjan Zinc Industrial Park, Iran

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**Background:** Zinc production due to applying mineral soils as raw material and high rate of tailings and wastes lead to environmental and health challenges, such as total suspended particle (TSP) emissions. This was the first study to monitor TSP concentration fluctuations and location variability in Zanjan zinc industrial park (ZZIP), Iran.

**Methods:** Nine stations equipped with an LVS were selected for TSP sampling from air simultaneously, from Feb. 2018 to Dec. 2018. Sample analysis was performed in the laboratory using gravimetric methods and data depicted by ArcGIS to recognize spatial distribution.

**Results:** Changes in TSP concentrations were within the range of 30.17-2,692.82 $\mu g/m^3$ and exceeded the EPA/WHO guidelines in more than 98% of the cases. Spring and winter showed the highest levels. The main influential factors in the TSP concentration were industrial activities, vicinity to the depot site and main streets, the speed of passing vehicles, and the dominant wind direction.

**Conclusion:** Despite recent attempts to control TSP, the concentrations remain high and alarming. Therefore, special attention must be paid to the health issues affecting staff and residential groups and implementation of more effective control mechanisms.

## 1. Introduction

Air pollution has historically been considered a health and environmental challenge, and human communities have not been able to tackle the issue so far. The impact assessment of air pollution regarding population health has revealed direct and positive associations between the concentration of air pollutants and mortality, adverse health effects, and hospital admissions; the crisis seems to be more critical in developing countries [1-5].

Particulate matter (PM) is a criterion pollutant, which disperses into the air through various natural and anthropogenic activities. Particles have the potential to suspend in the atmosphere for a long time or travel long distances. Particle size is a key indicator that influences the motion behavior of a particle by overcoming gravity or buoyancy forces. In addition, this feature may be involved in health problems. Total suspended particles (TSP) are a measure of the mass concentration of PM in the air, including particles with different sizes, affecting human health, plants, and even visibility. $PM_{2.5}$ (PM with a smaller aerodynamic diameter than 2.5 $\mu m$) and $PM_{10}$ (PM with a smaller aerodynamic diameter than 10 $\mu m$) are the target groups that penetrate the respiratory system. Fine and ultrafine



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particles (dp ≤ 2.5 μm) may behave similar to gas and reach the alveoli in the lungs, while the health effects of inhalable coarse particles (2.5 ≤ dp ≤10 μm) remain unknown and should be further investigated [6].

Particles could be composed of hundreds of chemicals. This variability is a function of the proximity of the emission sources and transformations that particles might be subject to in the atmosphere. According to the literature, inorganic ions (e.g., nitrate, sulfate, ammonium), organic mass (e.g., dioxins, alkanes, PACs), elemental/organic carbon, silicon, sodium ion, soil dust, sea salt, and heavy metals are most commonly detected in the composition of particles and have been studied extensively. PM is formed as a result of construction operations, smokestacks/fires, industrial processes, and unpaved roads. In some cases, they are resulted from the complex reactions between chemicals such as sulfur dioxide and nitrogen oxides, which are emitted into the atmosphere [7, 8].

Industrial processes such as grinding, melting, mixing, fuel combustion, and traffic mainly contribute to the anthropogenic PM emissions in industrial areas. Recently, more research has been focused on the activities associated with the particulate emissions from urban and industrial activities. For instance, a distinct body of research concentrates on particle sizes, confirming that the particle number size distribution is a reliable indicator to identify the source, atmospheric processing, and regional lung dose of airborne particles [9].

The measurement and analysis of the elemental composition and source apportionment of fine and coarse particles in the urban environment of London indicated that roadsides are enriched by elements associated with traffic emissions, accounting for the highest rate of contribution in this regard [10]. In addition, the evaluation of the concentrations of 23 chemical species and elements and their source apportionment in Harbour industrial area of Brindisi (Italy) resulted in the identification of eight main sources, including crustal, aged marine, crustal carbonates, ammonium sulfate, biomass burning fires, traffic, and industrial and ship emissions in the studied area [11]. Similar research has investigated the chemical characterization of the particles in the vicinity of a steelmaking industry by using 94 PM samples and analyzing 22 elements using $k_0$-Instrumental Neutron Activation Analysis ($k_0$-INAA) and Particle Induced X-ray Emission (PIXE). In addition, the source apportionment of $PM_{10}$ identified seven main source groups based on chemical composition and mass contribution [12]. Heavy metal exposure (especially in the vicinity of an industrial district) has also been the subject of a study conducted in Huludao city (China). According to the findings, atmospheric deposition due to metal smelting at the first stage and traffic density at the second stage were the most significant contributing factors to heavy metal contamination. The cancerous and non-cancerous effects of heavy metal exposure were determined in two target groups (children and adults) based on the hazard index (HI) [13]. The mentioned study continued with an emphasis on different particle sizes and their effects on the health risks of residents. The findings indicated significant positive correlations between heavy metal concentration, particle size, and higher elemental concentration, and the non-carcinogenic health risks were expected with smaller particles [14].

Non-ferrous metal industries are a key source of large amounts of $CO_2$, gaseous pollutants, and fine particle emissions into the air and atmosphere due to the high rate of fuel consumption, process type, and use of mineral soils in the production process. Therefore, extensive research has been focused on these concerns. Non-ferrous metals do not contain iron and are widely used owing to properties such as high conductivity, low weight, non-magnetism, and resistance to corrosion. During the primary and secondary processes of these industries, materials from complex sources are used, and metals are separated and sufficiently purified for specific purposes. From an environmental perspective, these processes are associated with significant environmental challenges, such as evaporations from the ore matrix in the form of PMs, which mainly contain anthropogenic heavy metals [13, 15, 16].

Some examples of commonly used non-ferrous metals are aluminum, nickel, lead, tin, brass, silver, and zinc. Zinc (Zn) is a metallic element with the density of 7.13 g/cm3 and is highly resistant to corrosion. In contact with iron, zinc provides sacrificial protection by corroding in place of iron. Therefore, it is widely used as a protective coating for iron, and the process is referred to as galvanization.

Non-ferrous metal industries are a key sector in Iran. Consequently, the population living in the vicinity of these industries or those working inside the production plants and sites are at the risk of numerous environmental and health issues.

Based on a research published by the US Geological Survey (USGS) on the nonfuel mineral industry of Iran, Iran is the second leading producer of lead and zinc in the Middle East and North Africa. The most important zinc mines in Iran are Mehdiabad (400 million tons of ore grading at 2% zinc) and Angouran, which reserves nine million tons of ore grading at 26% zinc and 6% lead. Angouran is located in Zanjan province, and its ore is processed by the zinc and lead plants located in the vicinity of the mine. Three large processors, including Calcimin Company, Zangan Zinc Industry, and Zanjan Zinc Khales Sazan Industries, have the zinc production capacity of as much as 500,000, 250,000, and 200,000 tons per year, respectively. In addition, lead production capacity has been estimated at 30,000 ton/year in Calcimin and 20,000 ton/year in Khales Sazan. In addition, approximately 75 small industries use the ore of this mine for producing zinc and lead and are located in Zanjan Zinc Industrial Park (ZZIP) [17].

Two well-established processes are used to cover the world's demand for zinc, including pyrometallurgical and hydrometallurgical processes. The hydrometallurgical process is the most common method of zinc extraction, and roughly 90% of zinc is produced through this process, which involves roasting, leaching, purification, electrolysis, and melting. This production method is frequently used in Iran and the active industries in ZZIP. Figure 1 shows the hydrometallurgical production process and the associated environmental impacts [18].

The hydrometallurgical process produces high levels of liquid waste, smelter slag, and other residues, which contain significant amounts of heavy metals [19, 20]. The present study aimed to investigate the dispersal and patterns of PM transmission in the point and area source in a zinc industrial zone and assess the exposed population. Previous studies have been mainly focused on soil pollution, and our study is among the first attempts to evaluate the pollutant concentrations in the atmosphere. In addition, the critical parameters interfering with the high concentration of TSP were determined. Another objective of the research was to identify the hot spots, seasonal variations, and effects of some factors (e.g., position and dominant wind direction) on the concentration of the pollutants. It is expected that our findings would be practical for the evaluation of health hazards, controlling emission resources, and selection of proper abatement technologies.

## 2. Materials and Methods

### *2.1. Site Description and Sampling*

The area of ZZIP is about 168 hectares, located in the southwest of Zanjan city within the five-kilometer distance of Zanjan-Bijar road. A wide area placed at the southeast of the industrial park is considered as the depot site. About 2.5 million tons of waste and tailings (mostly toxic elements such as lead, zinc, and cadmium) is produced during zinc purification [21], transfer from the industries to this site by trucks, and kept in exposed and unprotected conditions.

To evaluate the concentration of PMs in ZZIP, nine sampling stations were selected (Table 1). The full coverage of the study site, logical distance from the pollution sources, protection of instruments during rainy seasons, security, and access to the electricity grid were the most important factors considered in the selection of the sampling points [22, 23]. Notably, the selected stations (active industries in the region) met requirements such as security and electricity for sampling purposes, while the amount of emissions and reported concentrations were not necessarily related to these industries and their activities.

The meteorological statistics during 2008-2018 reported the minimum and maximum temperature of Zanjan station to be -12.8°C (January 2008) and +35.8°C (August 2015, July 2018), respectively. The mean 10-meter wind speed with the return periods of 2, 5, 10, and 25 years was estimated at 9.7, 15.12, 4.5, and 21.18 meters per second, respectively, and the dominant wind direction was from the west to the east. Figure 2 depicts the wind direction in different seasons (2008-2018) due to the effects on the emission dispersion and TSP concentration [24].

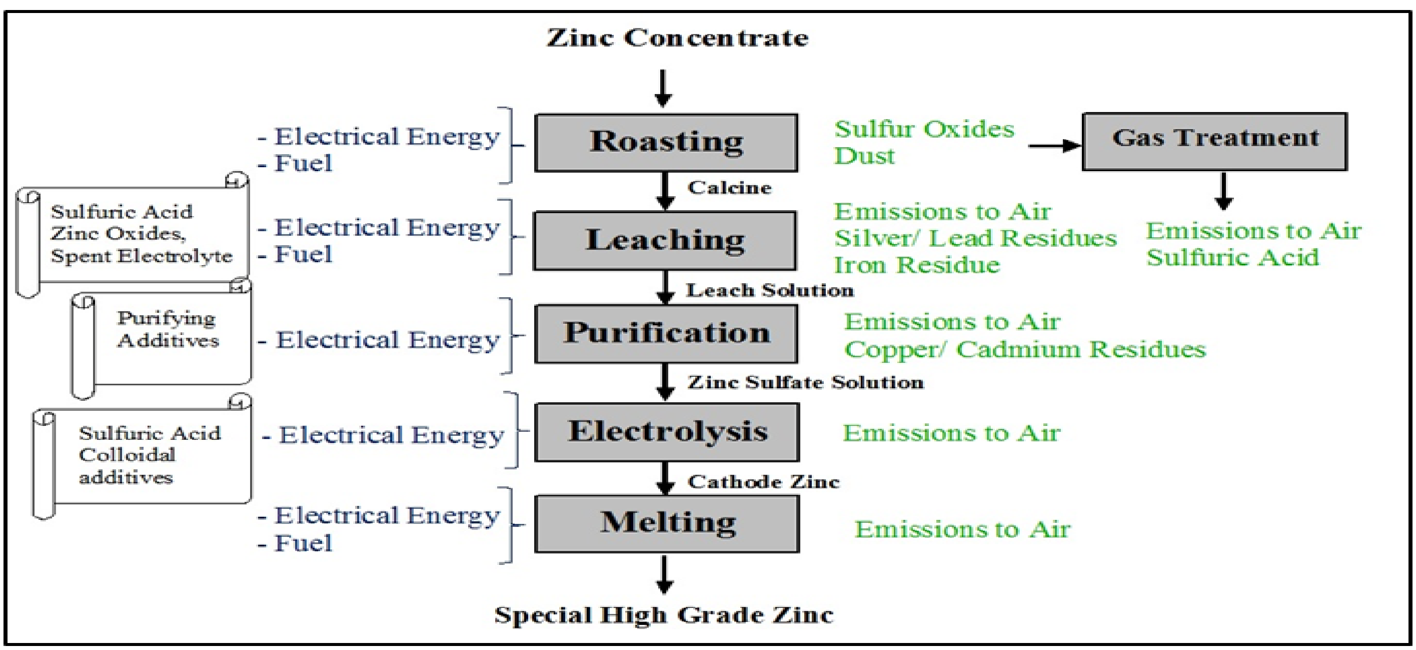


**Figure 1:** Hydrometallurgical process, energy consumption, and environmental aspects [18]

**Table 1:** Geographical position of sampling site in ZZIP

| No. | Station | Location | |
|---|---|---|---|
| | | Longitude | Latitude |
| 1 | Kani Pajoh Mizan | 270219,96 | 4057364,22 |
| 2 | Sadid Zinc | 269975,57 | 4057117,14 |
| 3 | Katalist Parsian | 270001,73 | 4056888,09 |
| 4 | Kane Araei Aria | 269401,34 | 4056717,31 |
| 5 | Khales Sazan | 270145,63 | 4056165,46 |
| 6 | Rouy Parvar | 269500,91 | 4056158,99 |
| 7 | Iran's Lead and Zinc | 270878,94 | 4056564,74 |
| 8 | Milad Zinc | 270273,92 | 4056752,46 |
| 9 | Kosar Zinc | 269553,93 | 4056535,03 |

### *2.2. Sampling Method and Specifications*

Sampling was performed for the measurement of PM in the form of TSP using the gravimetric method. In addition, a low-volume air sampler was developed to collect the particulate phases in the form of TSP at the flows of up to 16 lit/min. The pump of the sampler operated with 750 W, voltage of 220, and single-phase electricity. The mean air flow in the current research was 14.1 lit/min. The pump, which was inside the sampler device, drew a specific volume of air through a pre-weighted filter for 24 hours; the filter selected for this purpose was micro-glass fiber GF/1 (47 mm) with the pore size of 1.6 micrometers (MMP, India).The air volume was recorded by a calibrated ultrasonic gas meter, which was embedded in the sampler and equipped with a temperature sensor, with the ability to determine the volume of the passing air. The use of a gas meter instead of a flow meter had some advantages; in case of a power outage, the measurement of the passing flow would still be accurate, and in common circumstances, the results would be more feasible.

After sampling, the filters were sent to the laboratory of Zanjan Department of Environment for weight measurement. MGF filters are hygroscopic and must be dried at the temperature of 105°C in an oven for two hours before and after sampling. They remained in a desiccator for a minimum of one hour to be conditioned again and re-weighed using a Semi-Micro Lab Sartorius balance with the readability of 0.01 milligram or 10 micrograms (Sartorius Company, Göttingen, Germany).

By subtracting the weight of the blank filter and considering the flow rate of the gas/air sample, the PM concentration in ambient air could be calculated. The PM sampling at ZZIP was performed during January 2018-2019 twice per month, starting at 10:00 AM and continuing for 24 hours. In a few cases, sampling had to be cancelled due to meteorological conditions and atmospheric precipitation (snow/rain). In total, 207 samples were collected during this period. In addition, the PM concentrations in the air were calculated using Equations 1 and 2, as follows:

$$C = \frac{(W_2 - W_1) - (B_2 - B_1)}{V} \quad (1)$$

where C shows the concentration of PMs in standard conditions (μg/m³), $W_2$-$W_1$ is the difference between the secondary and primary weight of the filter (μg), $B_2$-$B_1$ represents the difference between the secondary and primary weight of the blank filter (μg), and V shows the air volume at the corrected or standard condition (m³).

The following formula was also used for the correction of the volume of the air samples:

$$V_S = \frac{V \times P_a}{1013 \times (1 + (\frac{t}{273}))}$$

where Vs is the volume of the air sample in standard conditions (m³), $P_a$ shows the air pressure in the sampling site (mbar), V denotes the volume of the air sample at the site (m³), and t is the air temperature at the sampling site (ºC).

## 3. Results and Discussion

In the present study, we performed the sampling and measurement of the PM concentrations in the form of TSP in ZZIP during one year (2018) at nine stations twice per month. The analysis of the obtained results has been presented as annual and seasonal sections.

### *3.1. Annual Statistics*

Evaluation of the annual results indicated that the concentration of particle changed within the range of 30.17-2,692.82 μg/m³. Table 2 shows the simple statistics regarding the mean annual concentration of PMs in the selected stations.

According to the results of the present study, PM concentration was higher in the stations of Khales Sazan, Rouy Parvar, and Milad Zinc. Figure 3 shows the further analysis of the dispersion patterns of the mean annual concentration of TSP in ZZIP.

**Table 2**: Statistics on annul concentration of TSP in stations

| No. | Station | Concentration (μg/m³) | | | | |
|---|---|---|---|---|---|---|
| | | Min. | Max. | Mean | SD | Median |
| 1 | Kani Pajoh Mizan | 259.33 | 1,771.58 | 624.08 | 360.26 | 526.66 |
| 2 | Sadid Zinc Co. | 120.29 | 1,386.87 | 663.94 | 324.73 | 585.20 |
| 3 | Katalist Parsian | 30.17 | 1,218.59 | 434.64 | 314.32 | 377.22 |
| 4 | Kane Araei Aria | 127.13 | 1,185.95 | 550.72 | 253.50 | 532.28 |
| 5 | Khales Sazan | 161.39 | 2,465.83 | 870.96 | 652.79 | 640.11 |
| 6 | Rouy Parvar | 90.07 | 2,692.82 | 842.51 | 554.31 | 814.77 |
| 7 | Iran's Lead and Zinc | 175.80 | 1,488.99 | 694.93 | 360.38 | 560.69 |
| 8 | Milad Zinc | 202.21 | 2,100.44 | 789.24 | 453.31 | 461.56 |
| 9 | Kosar Zinc | 268.27 | 1,352.54 | 674.12 | 320.95 | 552.63 |
| | ZZIP | 30.17 | 2,692.82 | 682.79 | 430.33 | 566.24 |

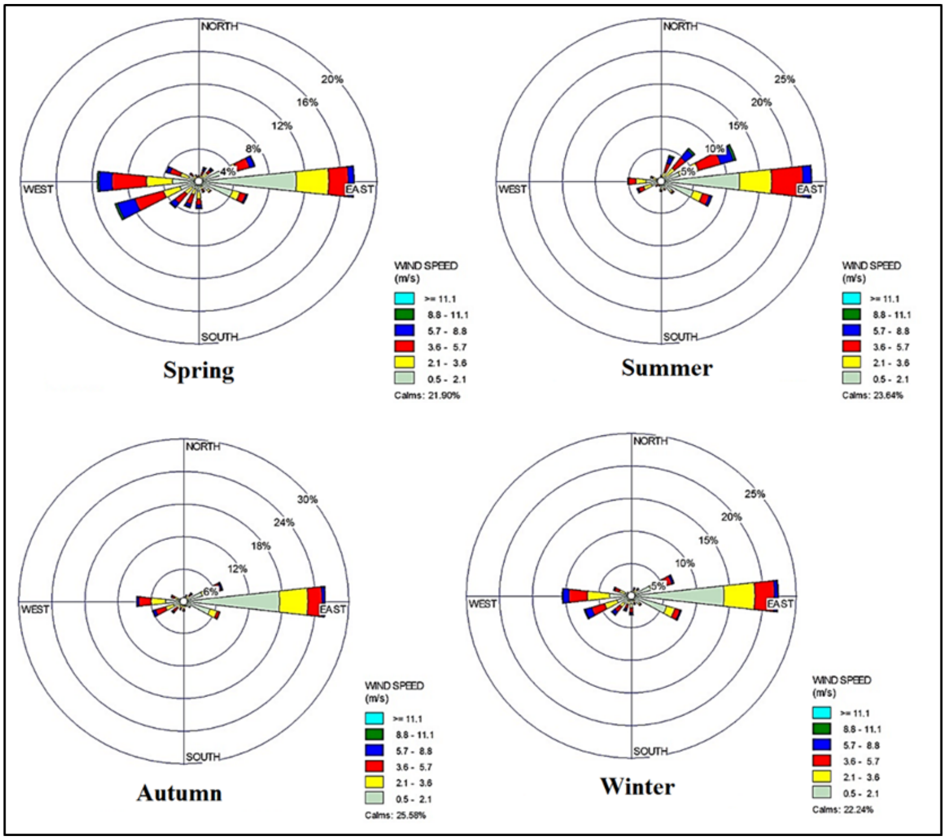


**Figure 2:** Long-term wind rise changes in different seasons (2008-2018)

As can be seen, the highest concentrations were observed in the southern and eastern regions of the industrial park in the vicinity of the depot site.

Our findings indicated that increased distance from the depot led to the reduction of the particle concentrations. Considering the direction of the dominant wind (west to east), the lowest concentration was observed in the western regions, and the intensity of the particles exacerbated from the west to the east. Notably, Iran's air quality national standards are retrieved from the USEPA and WHO standards and guidelines. The annual and 24-hour primary (secondary) standards for TSP are 75 (60) and 260 (150) $\mu g/m^3$, respectively [25]. The comparison of the measured data with these standards in the current research indicated that the mean concentrations in ZZIP were significantly higher than the standards.

### *3.2. Seasonal Statistics*

For the accurate estimation of the changes and influential factors, our data were evaluated in more detail at the seasonal scale. The comparison of four seasons revealed that the highest mean concentrations were in the spring and winter (Table 3).

The statistical analysis of the seasonal data was carried out by comparing the mean values using Tukey's honestly significant difference test under a null hypothesis ($\alpha$ =0.05), and the results indicated that spring and autumn had a significant difference with the other seasons, while no significant difference was observed between different months.

The first season of measurement in the present study was the winter of 2018. During this period, only 5% of TSP concentrations were below the standards, and the maximum and minimum concentrations were 1,495.23 and 219.91 $\mu g/m^3$, respectively (both observed in station eight of Milad Zinc).

**Table 3**: Statistics on seasonal concentrations of TSP in ZZIP

| Season | Obs. | Concentration (μg/m³) | | | |
|---|---|---|---|---|---|
| | | Min. | Max. | Mean | SD |
| Winter 2018 | 54 | 219.91 | 1,495.23 | 751.472 | 329.42 |
| Spring 2018 | 45 | 90.07 | 2,692.82 | 793.27 | 538.70 |
| Summer 2018 | 54 | 30.17 | 2,465.83 | 688.94 | 491.38 |
| Autumn 2018 | 54 | 152.32 | 1,313.46 | 538.80 | 260.96 |
| 2018 | 207 | 30.17 | 2,692.82 | 682.79 | 430.33 |

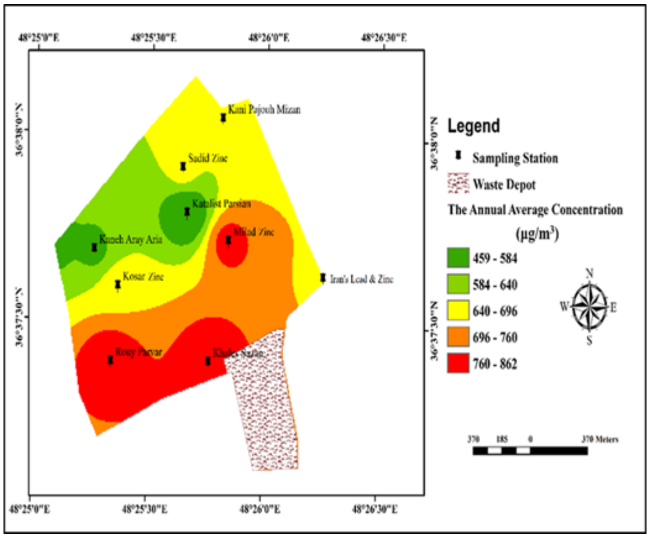


**Figure 3:** Mean annual concentration of particles in ZZIP

In addition, approximately 42% of the winds in this season blew toward the east. Two critical stations (Rouy Parvar and Milad Zinc) are located in the vicinity of the main streets and routes toward the depot site. Consequently, a large number of the trucks carrying tailings toward the depot site pass through this area, releasing PM from the load or the returning particles deposited on the floor to the air stream.

In the spring, sampling was performed from nine stations and five time sections, and the results showed that in 98% of the cases, the estimated concentrations were higher than the standards. About 34% of the winds blew toward the east (dominant wind), and the minimum and maximum concentrations were observed in station six (Rouy Parvar). Figure 4 depicts the dispersion pattern of TSP in the spring.

During summer, only 2% of the data were at an acceptable level, and 98% exceeded the standards. The minimum and maximum changes were also estimated at 30.17 $\mu g/m^3$ (Katalist Parsian) and 2,465.83 $\mu g/m^3$ (Khales Sazan), respectively. Katalist Parsian is located at the side-street and far from the depot site, while Khales Sazan is within the minimum distance from the depot and may completely be affected by TSP dispersion. More than 50% of the winds in this season are from the west to the east. In Figure 4, the north sides are shown in green, and the particles were mostly detected in the vicinity of the depot.

Autumn 2018 was the last season of TSP measurement in the present study, and 54 samples were prepared in this period. According to the analysis, only 3% of the samples were acceptable and standard. Dominant winds (52%) were from the west, and the highest and lowest levels were observed in Rouy Parvar (1,313.46 $\mu g/m^3$) and Katalist Parsian (152.32 $\mu g/m^3$), respectively. Compared to other seasons, autumn had a better condition in terms of air quality owing to the sequential rains in this season.

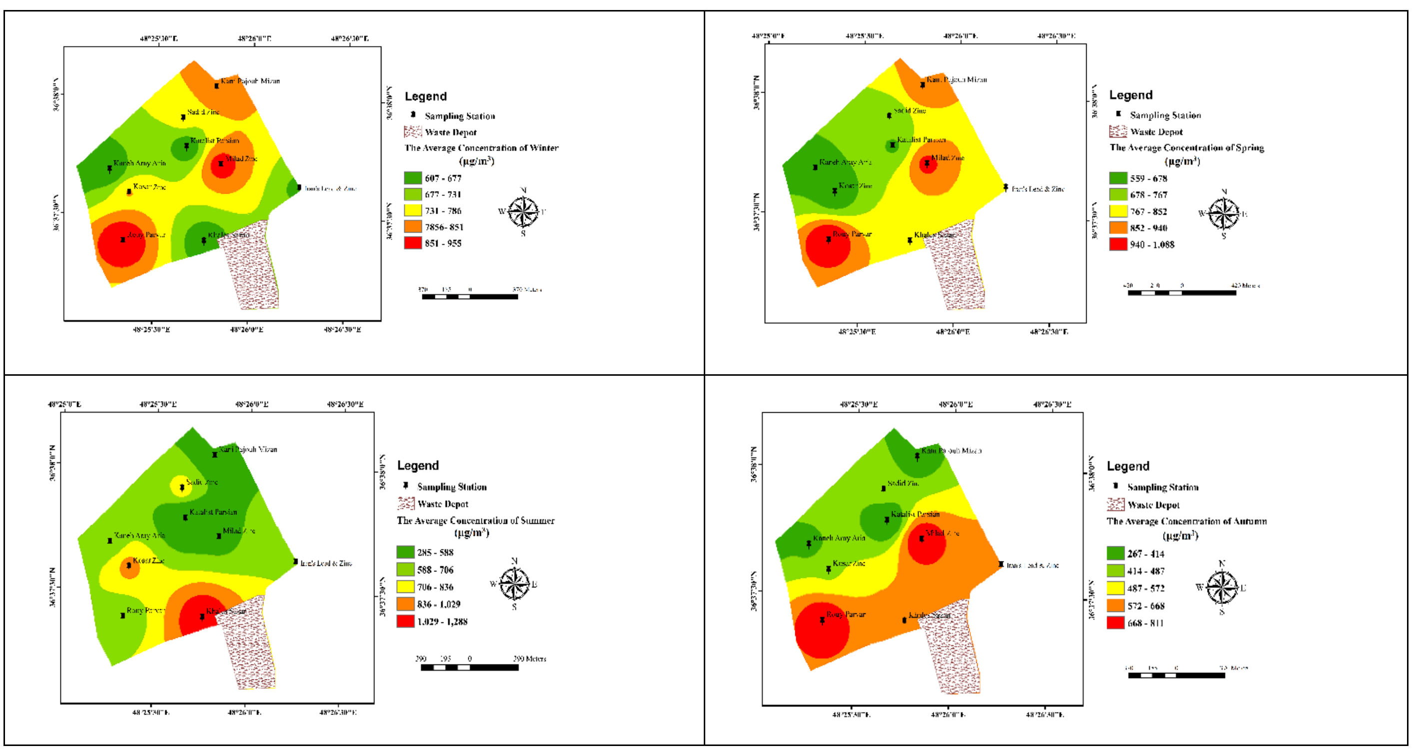


**Figure 4:** Mean seasonal concentration of particles in ZZIP

## 4. Conclusion

During the one-year evaluation of the PM concentrations in ZZIP, it was observed that Khales Sazan station had the highest level of particles, followed by Rouy Parvar and Milad Zinc stations. These industries were adjacent to the roads toward the depot site. At the beginning and end of the route, vehicles travel at a low speed, while in the middle (close to these industries), the concentration of TSP was extremely high due to the high speed of the passing and return of suspended particles to the atmosphere. Furthermore, the most important causes of the high concentrations in these stations could be summarized, as follows:

• The production process (hydrometallurgical process);

• The application and depot of raw materials (mineral soils) and tailings (leach cake) in these industries;

• The vicinity to other zinc production companies and the main streets leading to the depot site;

• High speed of the vehicles passing in the vicinity of these stations;

• A short distance between these industries and the main depot site.

According to the results of this study, Katalist Parsian, Kane Araei Aria, and Sadid Zinc had the minimum TSP concentrations during the evaluation period, respectively. These stations are in the vicinity of side streets and far from the depot site. Production of anode and cathode sheets, zinc and lead concentrate, and zinc ingots constitute the main activities of these three industries.

The inappropriate location of ZZIP, negligence of the direction of the dominant wind, extents of Zanjan city toward this industrial zone, and several other factors have led to the dispersion of air pollutants in the urban zone, thereby giving rise to numerous health complications. Evidently, the proper recognition of the particulate emission sources, concentration fluctuations, dispersion patterns, and the influential factors in this regard could help to control and reduce these emissions.

In the case of Zanjan city, further evaluation (especially in urban areas) seems essential to determine the proportion of urban and residential areas based on the produced PM in ZZIP. Considering the TSP levels inside ZZIP, the health issues threatening the staff in the area must be properly addressed through effective strategies, which are primarily aimed at the reduction of emissions. On the other hand, the chemical analysis of PM composition and the spatial distribution of various heavy metals is highly recommended in this area.

## Authors' Contributions

A.T., and N.A.A., conceived and planned the experiments; A.A., cooperated in the provision of the instruments, selection of the stations, and making the necessary arrangements; N.A.A., performed the measurements and processed the experimental data; A.T., and A.A., were involved in the review and supervision of the research; A.T., drafted the manuscript. All the authors discussed the results and commented on the manuscript.

## Conflicts of Interest

The Authors declare that there is no conflict of interest.

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