

ANALYSIS OF ARSENIC CONTENT IN THE AIR OF THE CITY OF ZENICA FOR THE PERIOD 2020-2024

Farzet Bikić, Halim Prcanović, Mirnes Duraković, Naida Bikić, Sanela Beganović
University of Zenica
Bosnia and Herzegovina

ABSTRACT

The aim of the research conducted in this research is to analyze the arsenic content in PM10 particulate matter for the period 2020-2024, providing an objective assessment of whether there has been a significant reduction in arsenic emissions into the atmosphere of the city of Zenica during this period. This timeframe was selected for analysis due to changes that may have influenced arsenic emissions into the atmosphere. The key changes include the transition from fossil fuels to gas for the heating needs of Zenica in the ArcelorMittal company, where coal was officially replaced by gas in 2022. Additionally, the coking plant at ArcelorMittal Zenica ceased operations. Finally, there was the installation of hybrid filters on agglomachines in the Agglomeration department of Arcelor Mittal. The results of the conducted research and subsequent analyses confirm that arsenic emissions into the atmosphere decreased in the period 2022–2024 compared to the period 2020–2021. This research will also examine the possible reasons that contributed to the reduction of arsenic emissions in the atmosphere of Zenica.

Keywords: PM10, arsenic emissions, fuels, gas, atmosphere of Zenica

1. INTRODUCTION

Ambient particulate matter could affect human health due to its various chemical constituents [1, 2]. Some of the most toxic species of particulate matter are heavy metals. Although the elemental mass fraction of PM is small, heavy metallic elements, such as Pb, Cd, Cr(VI), Hg and As, pose serious threats to human health [3]. Atmospheric heavy metals absorbed on to the particles may cause inflammation, lung and heart disease, or DNA damage via ingestion, inhalation exposure and dermal contact [4, 5]. Arsenic can also cause serious disturbances of the cardiovascular and central nervous systems [6]. The principal route of entry arsenic into the human body is by low-dose intake via foods and drinks, where it accumulates in the gastroin testinal tract before being released into circulation. During chronic poisoning, arsenic is transformed by the hepatic into a less dangerous form, which is subsequently primarily eliminated in the urine. Indeed, albeit very high levels of exposure result in detectable bioaccumulation; nonetheless, small alternative routes of entry via inhalation and cutaneous exposure are found [7]. The highest degree of toxicity is observed in inorganic forms of arsenic, while organic base arsenics are typically fewer toxic than arsenic species that are inorganic [8]. Arsenic (As) is a highly toxic element, metalloid, that is widely distributed in the biosphere, including the atmosphere, soil, natural water, and living organisms [9]. It can attach to PM2.5 in various compounds and be transported over long distances in the atmosphere, ultimately depositing on the surface [10]. Accurately analyzing the sources of As emissions is crucial to reducing the uncertainty of As dry and wet deposition and effectively controlling As pollution. Some scholars have analyzed the sources of As deposition

and found that the sources of As are categorized into natural and anthropogenic sources. Natural sources mainly include volcanic emissions, soil wind erosion and biological activities [11]. Anthropogenic sources mainly come from the combustion of fossil fuels such as coal, mining and smelting of As-containing minerals, mobile source emissions, and biomass burning [11, 12]. Arsenic is the 53rd most abundant substance and comprises around 1500 ppb of the Earth's core. Traditional reference arsenic levels in the atmosphere do not reach 3 ngm^{-3} , in soil 100 mgkg^{-1} , and in freshwater 10 ppb [13].

The Rulebook on air quality limit values of the Federation of Bosnia and Herzegovina ("Official Gazette of FBiH", number: 12/05) does not cover the limit values of arsenic concentrations in the atmosphere. For assessment purposes, data for UK shows that in 2020 annual mean concentrations of arsenic in the UK rural environment are typically in the range of 1 - 4 ngm^{-3} , whilst annual mean urban concentrations are higher, in the range of 5 - 7 ngm^{-3} . Typically, the highest concentrations of arsenic in the UK are found at sites located in the immediate vicinity of industrial processes such as smelters, incinerators and cement works [14]. For example, the highest reported concentrations of arsenic in the UK have been found in the vicinity of a smelter in Walsall, West Midlands. For the monitoring period covering 1975-1990, the highest annual mean concentration of arsenic reported at the site was 223 ngm^{-3} , whilst for other urban sites, during the same period, annual mean values were found to vary from 1 - 18 ngm^{-3} . The highest reported concentration (quarterly mean) of arsenic found at the Walsall site was 573 ngm^{-3} [14].

2. EXPERIMENTAL PART

This study analyzes the results of average arsenic concentration in the air, obtained from PM10 content data collected by automatic monitoring stations AMS Tetovo, AMS Centar, and AMS Radakovo. The objective of the research conducted in this study is to perform a thorough mathematical and statistical analysis of the results on average arsenic concentrations in the air, originating from suspended PM10 particles, for the period from 2020 to 2024. The aim is to provide a realistic assessment of whether there has been a significant reduction in arsenic emissions into the atmosphere in the specified period. Namely, in March 2022, a new heating plant was officially commissioned within the ArcelorMittal company. Unlike the old system, which relied on decades-long coal combustion for heating Zenica, the new system generates thermal energy by burning coke oven gas and blast furnace gas, with an additional option for natural gas combustion. In the mentioned period, more precisely during 2024, the Coke plant in the ArcelorMittal company stopped operating. Also, there was the installation of hybrid filters on agglomeration machines in the Agglomeration department of Arcelor Mittal. The last hybrid filter on the agglomeration machine was installed in 2019, according to data obtained from ArcelorMittal Zenica. The flue gases were gradually released through these filters. After the filter installation, the flue gases were partially discharged through the filter and partially through the chimney. A prolonged period of adjustment and fine-tuning was required to ensure that the entire volume of flue gases was discharged through the hybrid filter. Air monitoring methods are regulated by the Rulebook on the Method of Air Quality Monitoring and the Definition of Pollutant Types, Limit Values, and Other Air Quality Standards of the Federation of Bosnia and Herzegovina (FBiH). According to the provisions of this Rulebook, air quality is monitored, including the measurement of PM10 suspended particle concentrations using automatic measuring instruments. Arsenic concentration is determined from the extract of suspended particle deposits in the laboratory of the Kemal Kapetanović Institute at the University of Zenica. The arsenic concentration is measured using the atomic absorption spectrometry (AAS) method with a Perkin Elmer 3110 atomic absorption spectrometer. Three automatic monitoring stations (AMS) are located in the area of the City of Zenica, at the sites of Centar, Radakovo, and Tetovo. These automatic monitoring stations form the Cantonal Network of Air Quality Monitoring Stations in the Zenica-Doboj Canton and are simultaneously integrated into the Federal Air Quality Monitoring

Network. The locations of the Tetovo, Centar, and Radakovo automatic monitoring stations are shown in Figure 1.

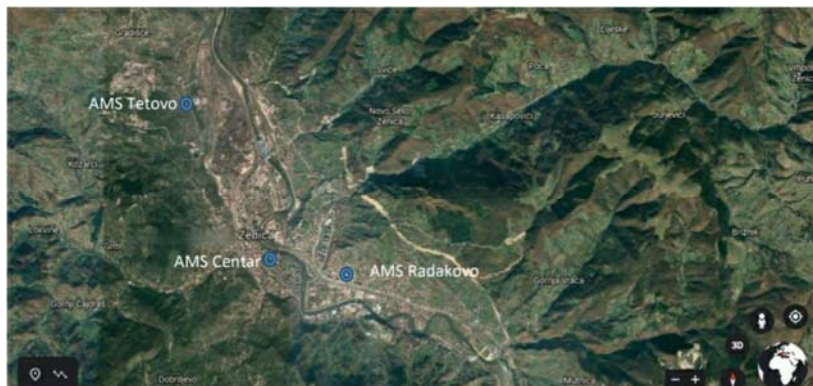


Figure 1. Locations of the stationary automatic monitoring stations Tetovo, Centar, and Radakovo

The AMS Tetovo monitoring station is located in the suburban settlement of Tetovo, on Tetovska Street bb, in close proximity to the industrial zone housing metallurgical facilities. This stationary automatic monitoring station is designed to monitor air quality in the suburban area of the city of Zenica. The AMS Centar monitoring station is situated on the rooftop of the "Bosanka" department store, located in the very center of Zenica. This stationary automatic station is primarily intended for monitoring air pollution levels in the urban environment of Zenica. The AMS Radakovo monitoring station is placed on the rooftop of the "Skender Kulenović" Elementary School in Radakovo. This stationary automatic station is also designated for air quality monitoring in the urban area of Zenica.

3. RESULTS AND DISCUSSION

In this study, after determining arsenic concentrations from the extracts of PM10 suspended particle deposits using the atomic absorption spectrometry (AAS) method, the recalculated average arsenic concentrations in the air for the period 2020–2024 were mathematically and statistically analyzed. The values of average arsenic concentrations in the air, expressed quarterly and as annual average values (Table 1), were recalculated based on the results of daily arsenic concentration measurements in the air for the period 2020–2024.

Table 1. Mean values of arsenic concentration in the air ($\mu\text{g m}^{-3}$)

Year		AMS Tetovo	AMS Radakovo	AMS Centar
2020	Mean	5,207	4,022	4,461
	N	156	181	184
	Std. Deviation	3,829	2,608	2,495
2021	Mean	3,788	2,747	2,619
	N	332	282	365
	Std. Deviation	3,934	3,378	2,690
2022	Mean	0,625	0,062	0,0234
	N	305	263	273
	Std. Deviation	1,185	0,146	0,039
2023	Mean	0,0375	0,029	0,0112
	N	359	355	354
	Std. Deviation	0,0395	0,049	0,0191
2024	Mean	0,0187	0,0124	0,005
	N	182	352	366
	Std. Deviation	0,038	0,023	0,008

Figures 2, 3, and 4 present the average arsenic concentrations in the air, expressed quarterly for the period 2020–2024, derived from PM10 content data collected by the automatic monitoring stations Tetovo, Centar, and Radakovo. Figures 2, 3, and 4 present the results for the quarters in which measurements were available. From the perspective of analyzing arsenic concentrations released into the atmosphere due to fossil fuel combustion, it is essential to focus on the first and fourth quarters, which correspond to the heating season in the city of Zenica.

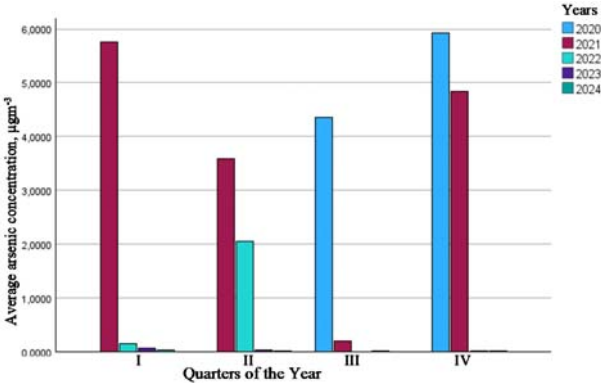


Figure 2. Average arsenic concentrations expressed quarterly for the period 2020-2024 year (AMS Tetovo)

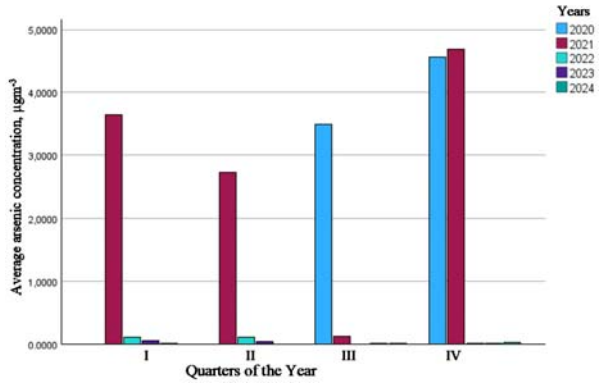


Figure 3. Average arsenic concentrations expressed quarterly for the period 2020-2024 year (AMS Radakovo)

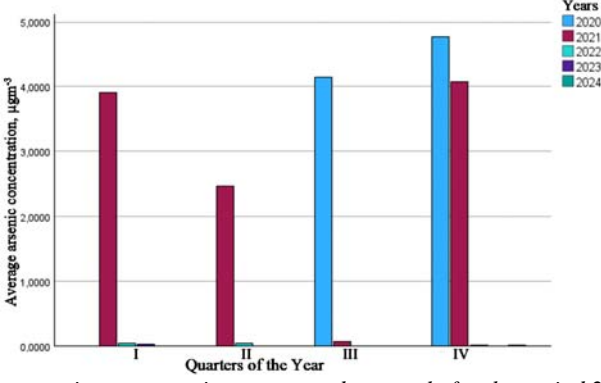


Figure 4. Average arsenic concentrations expressed quarterly for the period 2020-2024 year (AMS Centar)

Analyzing the first and fourth quarters for the period 2020-2024, the results presented in Figures 2, 3, and 4 confirm a significant decrease in the average arsenic concentration in the air during the first and the fourth quarters of 2022, 2023 and 2024 years, compared to the corresponding quarters in the period 2020-2021. As stated in the second chapter of this study, in March 2022, a new heating plant was officially commissioned within the ArcelorMittal company. Unlike the previous system that used coal, the new plant burns coke oven gas and blast furnace gas, with an additional option for natural gas combustion. The reduction in arsenic emissions into the atmosphere during the first and fourth quarters of 2022, 2023 and 2024, compared to the same periods in previous years, may be attributed and to the replacement of coal with coke oven and blast furnace gas or natural gas in the Zenica Heating Plant.

Figures 2, 3, and 4 also present the average arsenic concentrations for the second and third quarters during the period 2020-2024. Analyzing these quarters, the results shown in Figures 2, 3, and 4 indicate a significant decrease in the average arsenic concentration in the air during the second and third quarters of 2022, 2023 and 2024 years, compared to the corresponding quarters in the period 2020-2021. This period falls outside the heating season, meaning there is no combustion of fossil fuels for heating the city of Zenica. However, the results presented in Figures 2, 3, and 4 confirm that the reduction in arsenic concentration in the air also occurred during the non-heating season. This clearly indicates that the replacement of fossil fuels in the heating system of the city of Zenica is not the sole factor contributing to the decrease in arsenic concentration in the air during the analyzed period. The reduction in arsenic emissions into the atmosphere during the second and third quarters of 2022, 2023 and 2024, compared to the same periods in previous years, may be attributed and to installation of hybrid filters on agglomachines in the Agglomeration department of Arcelor Mittal.

Figure 5 shows the average annual arsenic concentrations in the air, recalculated from PM10 content data obtained from the automatic monitoring stations Tetovo, Centar, and Radakovo for the period 2020-2024.

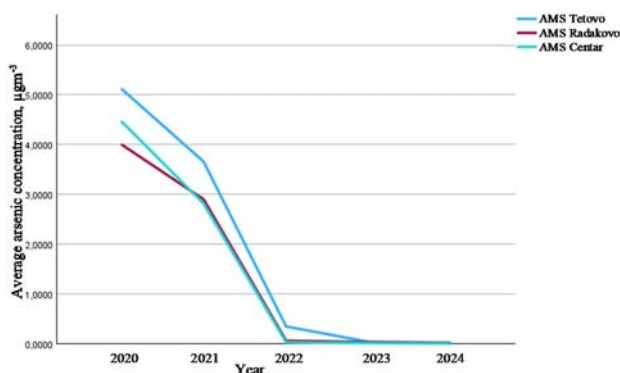


Figure 5. Average annual arsenic concentrations expressed for the period 2020-2024 year

Analyzing the average annual arsenic concentrations in the air for the period 2020–2024, the results presented in Figure 5 show a downward trend in average arsenic concentrations from 2021 to 2024 at all monitoring stations.

Figure 5 also indicates that the average annual arsenic concentrations in the air for the period 2020–2024 are higher at AMS Tetovo compared to AMS Centar and AMS Radakovo. The reason for the increased arsenic emissions at AMS Tetovo, compared to AMS Centar and AMS Radakovo, could be its proximity to the industrial zone housing metallurgical facilities.

It is possible that this trend can be attributed to:

- replacement of coal with coke oven gas and blast furnace gas, or natural gas, in the Zenica Heating Plant,

- installation of hybrid filters on agglomachines in the Agglomeration department of Arcelor Mittal.

4. CONCLUSIONS

Based on the conducted research, which confirms:

- significant decrease in the average arsenic concentration in the air during the all quarters of 2022, 2023 and 2024 compared to the same in the period 2020-2021,
- downward trend in the average annual arsenic concentrations in the air from 2021 to 2024, it can be concluded that arsenic emissions into the atmosphere decreased during the period 2022-2024 compared to the period 2020-2021.

It is possible that this trend can be attributed to:

- replacement of coal with coke oven gas and blast furnace gas, or natural gas, in the Zenica Heating Plant,
- installation of hybrid filters on agglomachines in the Agglomeration department of Arcelor Mittal.

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