Romanian Journal of Petroleum & Gas Technology
VOL. IV (LXXV) • No. 2/2023

A SCREENING OF THE HYDROGEN SULFIDE LEVELS IN PLOIEȘTI CITY, ROMANIA

Mia Nuta Stancu (Sanda) [1*]

Dorin Bombos [1]

Ion Onutu [1]

[1] Petroleum-Gas University of Ploiesti, Romania
email (corresponding author): mia.sanda@upg-ploiesti.ro

DOI: 10.51865/JPGT.2023.02.19

ABSTRACT

Oil refineries and petrochemical facilities contribute to the pollution of the environment either air, water, or soil releasing hazardous and toxic air pollutants into the atmosphere. These include nitrogen oxides (NO_x), carbon monoxide (CO), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), and particulate matter (PM), affecting both environment and human health. In the range of air pollutants, hydrogen sulfide is less monitored and reported despite its importance in determining adverse effects. Background H_2S concentrations in air were found to range commonly from 0.11 ppb to 0.33 ppb. The concentrations in urban areas can reach 1 ppb (~1.4 µg m^{-3}) up to more than 90 ppb (~125 µg m^{-3}) near sources of H_2S emissions. In Romania, the standard for the air in protected areas for the hydrogen sulfide pollutant provides an admissible concentration, over a maximum interval of 30 minutes, of 15 µg/m³. Everything that exceeds this value is considered harmful to human health. The statistics for the H_2S time series recorded in Ploiești City by the mobile laboratory of the Environmental Protection Agency Prahova between 2019 and 2021 with a sampling rate of 30 minutes showed that the mean ranged between 1.51 and 3.74 µg/m³, while the maximum reached 59.36 µg/m³ in the east of Ploiești in 2019. Overall, the highest variance occurred in the East and North parts due to the presence of the concentration peaks. Hydrogen sulfide must be considered on the public health agenda, both from the occupational perspective and for the ambient concentrations near significant H_2S sources and in background urban areas. The monitoring infrastructure needs to be improved to allow continuous surveillance to ensure reliable databases that support research regarding the health effects of H_2S across the concentrations occurring in the urban environment.

Keywords: hydrogen sulfide, mobile monitoring, central tendency, variance, environmental impact.

INTRODUCTION

Many health issues were reported to be related to exposure to air pollutants, including birth defects and cardiovascular and respiratory diseases, some of which are carcinogenic [1]. For example, a recent study performed for Ploiești City conditions reported values for the *Integrated Lifetime Cancer Risk* (ILTCR) in winter 14.1×10^{-5}, in spring 9.04×10^{-5}, in summer 8.74×10^{-5}, and in autumn 10.6×10^{-4}, considering the recorded outdoor benzene concentrations [2]. The ILTCR annual averages fitted very risky conditions for the population matching the definite cancer risk category established by U.S.E.P.A (year 2019: 1.08×10^{-4}; year 2020: 1.07×10^{-4}; year 2021: 1.04×10^{-4}; whole period: 1.06×10^{-4}) [2].

In the natural cycle of sulfur in the environment, hydrogen sulfide **(**H_2S**)** has an important role [3]. The main sources of hydrogen sulfide are:

- In somewhat larger quantities, hydrogen sulfide occurs in volcanic eruptions.
- Some mineral waters, the so-called sulfurous springs, contain dissolved hydrogen sulfide.
- Hydrogen sulfide has been detected in high quantities on the bottom of the Black Sea and in some areas of the Baltic Sea;
- Hydrogen sulfide is produced also by bacteria through direct sulfate reduction [3]. Natural gas fields and areas with geothermal features can present important amounts of hydrogen sulfide [3].
- Hydrogen sulfide can form at high temperatures, elemental sulfur or certain sulfur compounds coming into contact with organic substances [3].

In industry, hydrogen sulfide is generally an unwanted by-product, even though it is a key reagent in various industrial processes [3]. Hydrogen sulfide is produced from sulfur-containing coal, the production of carbon disulfide, the hydro-refining of petroleum products, which contain sulfur, the production of viscose, etc. [3].

Among anthropogenic sources, H_2S is present in high concentrations in or near sewage systems, slaughterhouses, and animal containment facilities [4]. Regarding industrial sources, H_2S is emitted at elevated levels from oil and gas processing sites, geothermal power plants, coke ovens, food processing facilities, tanneries, and pulp/paper mills [4].

Background H_2S concentrations in air were found to range commonly from 0.11 ppb to 0.33 ppb, respectively from 0.15 to 0.45 μg m^{-3} (based on conversion formula *Concentration (μg/m³) = molecular weight × concentration (ppb) ÷ 24.45* and the molecular weight of H_2S of 34.081 g/mol). The concentrations in urban areas can reach 1 ppb (~1.4 μg m^{-3}) up to more than 90 ppb (~125 μg m^{-3}) near sources of H_2S emissions [4]. In Romania, the standard for the air in protected areas for the hydrogen sulfide pollutant provides an admissible concentration, over a maximum interval of 30 minutes, of 15 μg/m³ (STAS 12574-87). Everything that exceeds this value is considered harmful to human health [5].

Hydrogen sulfide odor starts to be detectable at concentrations as low as 0.005 ppm, but the sense of smell is lost after 2–15 minutes at 100 ppm [6]. This renders the odor of the gas an ineffective hazard warning. In some situations that involve extremely high H_2S levels in the air, potential victims run the risk of experiencing "*knockdown*" or passing out in the area [6].

Knockdown severely diminishes survival rates due to trauma sustained during the fall and/or inability to escape [6]. Collapsed victims also endanger responders as they entice would-be rescuers into locations with dangerously high toxicant levels [6]. Probably due to cardiopulmonary paralysis, at > 500 ppm H_2S (cases of severe acute toxicity), unconsciousness, and death may result almost very fast [6].

The main knowledge on the effects of hydrogen sulfide on health refers to:

- Inhalation of hydrogen sulfide is very dangerous for health due to high toxicity [7].
- Exposure to hydrogen sulfide harms most organs resulting in important health risks, and, consequently, it is a broad-spectrum toxicant.
- Short exposure to hydrogen sulfide affects the central nervous system causing nausea, headache, skin irritation, and negative effects on the respiratory tract, eyes, and membranes with mucous [7].
- Acute exposure to high concentrations of hydrogen sulfide can cause tearing, photophobia, and painful conjunctivitis [7].
- Air concentrations high enough to exceed the body's detoxification threshold lead to poisoning and cellular respiratory asphyxiation [8].
- Respiratory arrest determines the death due to exposure to excessive hydrogen sulfide [8].
- Acute exposure to hydrogen sulfide has several sensitive endpoints such as nausea and headache in human volunteers, reported at concentrations below the odor threshold [9].
- Headache, nausea, low blood pressure, loss of appetite, weight loss, ataxia, inflammation of the eye membrane, and chronic cough are chronic effects provoked by hydrogen sulfide [9].

Hydrogen sulfide must be considered a relevant public health risk that should be carefully addressed from an occupational perspective, and the monitoring infrastructure currently in place could be improved. Incomplete databases and inadequate research regarding the health effects of H_2S across the range of levels to be found in the environment, as well as the potential for the gas to be used for malicious purposes [6].

In this context, the paper aimed to present the trend of concentrations that occurred in Ploiesti City, Romania during various periods from 2019 to 2021 using statistical indicators. These are the only available data obtained through mobile monitoring by the EPA Prahova.

MATERIALS AND METHODS

The available data on concentration monitoring were collected, analyzed, and interpreted for H_2S in Ploiesti Municipality. They were monitored by the Environmental Protection Agency in the following years and points, respectively: **2019** (Catina Alley nr.1, Catina Alley nr.2, Apelor Street, Mihai Bravu Street), **2020** (Ploiesti Nord District, Vest District, Bereasca District), and **2021** (Evo Casa District, “Lazar Edeleanu” High School) [5].

EPA Prahova [5] considered it necessary to supplement the air quality monitoring network (compared to the automatic network consisting of 6 stations) with:

- The auto-laboratory is equipped with analyzers for SO_2 / H_2S, NO_2 / NH_3, VOC (Benzene and Toluene), weather data instrumentation (temperature, wind direction, wind speed), which was purchased in December 2017;

- A mobile station for indicators: hydrogen sulfide and sulfur dioxide, weather data.

The collected data were statistically analyzed by calculating the indicators of central tendency and of the variance (Average, Minimum, Maximum, Standard deviation, Coefficient of variation (%), Skewness, and Kurtosis).

RESULTS AND DISCUSSIONS

The hydrogen sulfide showed various time series with different evolutions regarding the peak values and trends. Figures 1, 2, and 3 highlight the trend of each time series monitored in Ploiesti city and the exceeding of the limit value mentioned in the Romanian standard STAS 12574-87 (average of short duration – 30 minutes i.e., 15 µg m^{-3}).

Compared to the 15 µg m^{-3} maximum admissible concentration, there were two periods in which the concentrations exceeded this threshold namely in April 2019 at Mihai Bravu Street, in the eastern part of Ploiesti City, with five peaks (Fig. 1b), and in August 2020 at Ploiesti Nord point, in the north of Ploiesti City with four peaks (Fig. 2b). The remaining monitoring periods performed in various points showed values that did not exceed the limit value. The highest concentrations were recorded at Mihai Bravu Street in 2019.

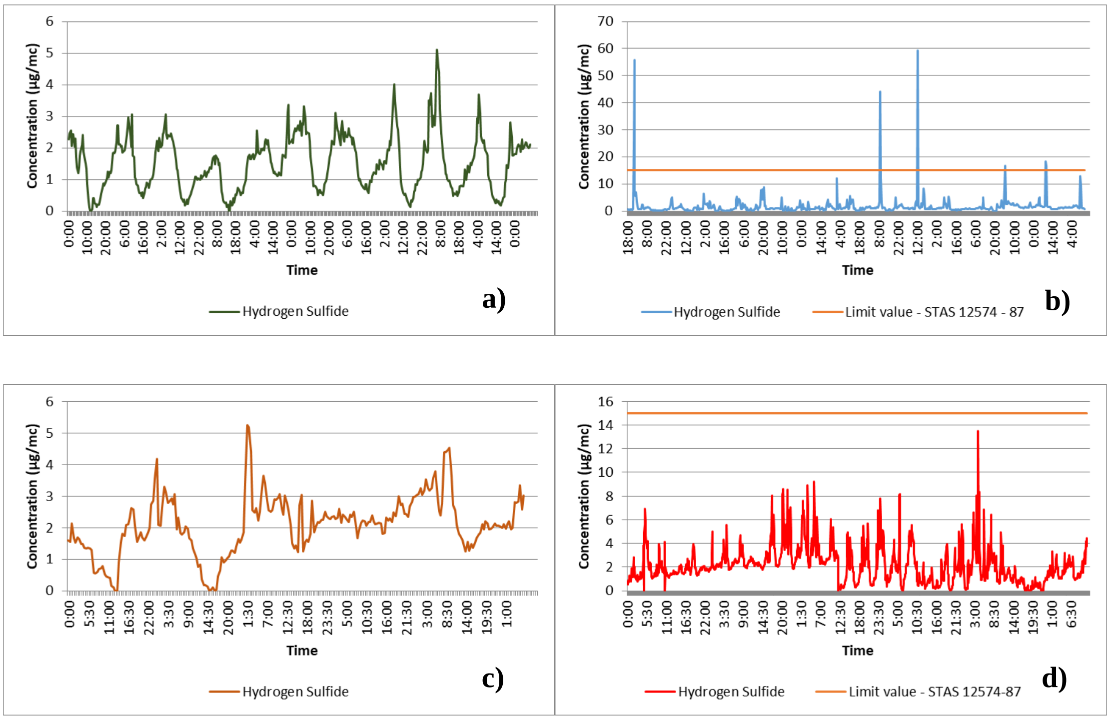

Fig. 1 *Hydrogen sulfide time series monitored in various points of Ploiesti City in 2019: a) Str. Apelor (8.03-18.03.2019); b) Str. Mihai Bravu (2.04-16.04.2019); c) Aleea Cătinei 1 (28.11-3.12.2019); d) Aleea Catinei 2 (24.12.2019-22.01.2020), the interval between ticks is 30 minutes.*

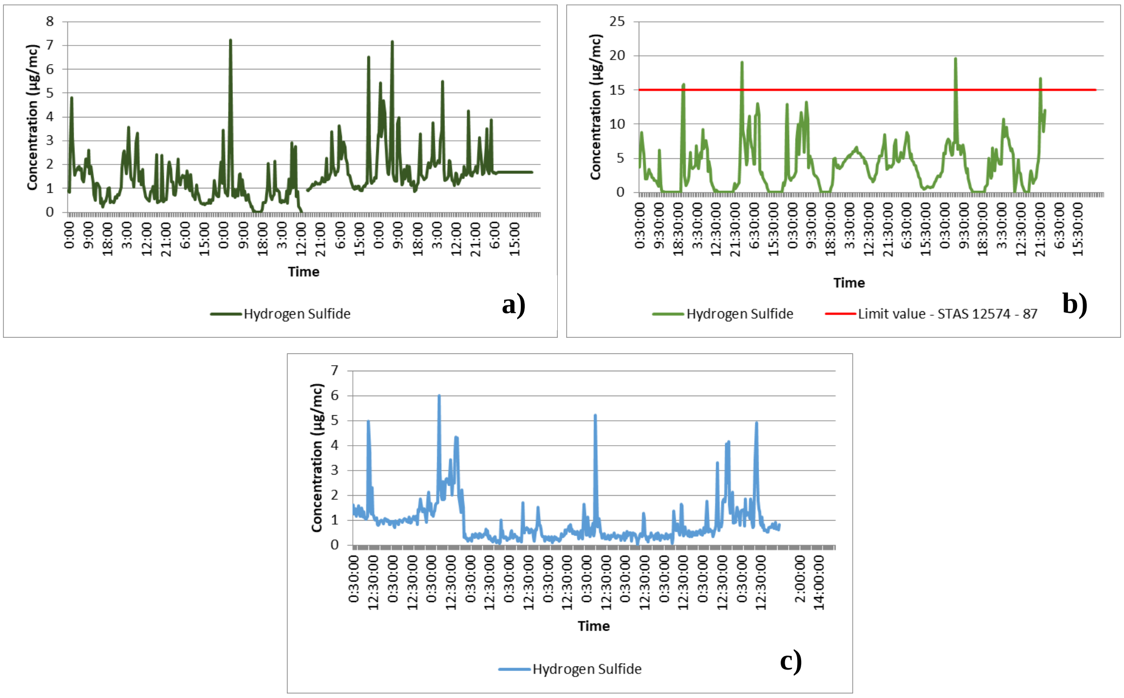

Fig. 2 *Hydrogen sulfide time series monitored in various points of Ploiesti City in 2020: a) Cartier Vest (20.02-27.02.2020); b) Ploiesti Nord (21.08-28.08); c) Cartier Bereasca (12.12-22.12.2020) - the interval between ticks is 30 minutes.*

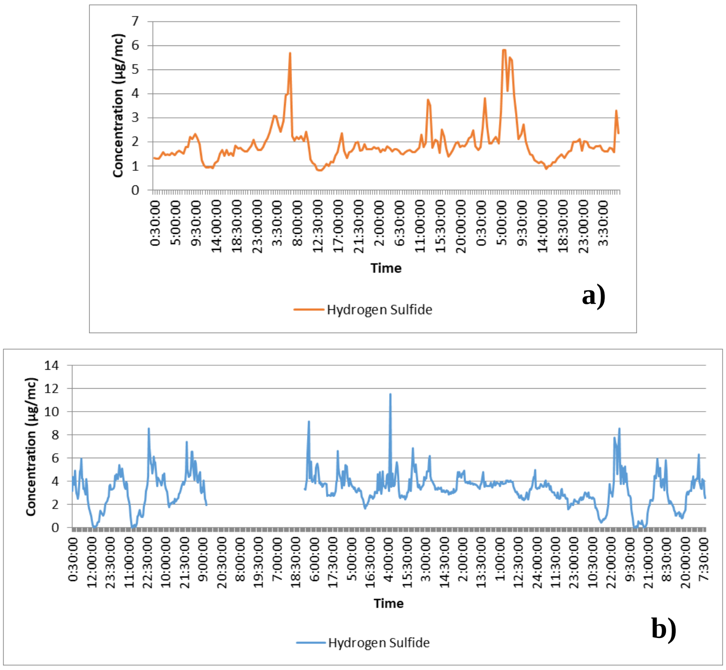

Fig. 3 *Hydrogen sulfide time series monitored in various points of Ploiesti City in 2021: a) Cartier Evo Casa (14.01-18.01.2021); b) Lazar Edeleanu (22.05-7.06.2021); the interval between ticks is 30 minutes.*

Table 1 shows the statistics for the H_2S time series recorded in Ploiești City by the mobile laboratory of the Environmental Protection Agency Prahova between 2019 and 2021 with a sampling rate of 30 minutes [5].

Table 1. *Statistics of hydrogen sulfide concentrations (µg/m³) recorded in Ploiești City between 2019 and 2021 by the mobile laboratory of the Environmental Protection Agency Prahova (sampling rate – 30 minutes)*

	2019				2020			2021	
Monitoring point	Str. Apelor	Str. Mihai Bravu	Aleea Catinei 1	Aleea Catinei 2	Cartier Vest	Ploiesti Nord	Cartier Bereasca	Cartier Evo Casa	Lazar Edeleanu
Relative position	East	East	North	North	West	North	North-East	North-West	South
Period	8.03-18.03	2.04-16.04	28.11-3.12	24.12-22.01.2020	20.02-27.02	21.08-28.08	12.12-22.12	14.01-18.01	22.05-7.06
Average (µg/m³)	**1.51**	**1.74**	**2.08**	**2.15**	**1.49**	**3.74**	**0.90**	**1.90**	**3.25**
Minimum (µg/m³)	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.81	0.00
Maximum (µg/m³)	5.10	59.36	5.25	13.52	7.23	19.64	6.00	5.81	11.47
Standard deviation	0.87	4.07	0.94	1.52	0.99	3.45	0.84	0.84	1.46
Coefficient of variation (%)	57.80	234.58	45.13	70.38	66.69	92.25	93.18	44.03	44.98
Skewness	0.54	10.38	0.15	1.56	2.00	1.27	2.51	2.56	0.32
Kurtosis	0.27	128.31	0.84	4.51	7.17	2.34	8.15	8.39	2.17

The mean ranged between 1.51 and 3.74 µg/m³, while the maximum reached 59.36 µg/m³ in the east of Ploiești in 2019. Overall, the highest variance occurred in the East and North parts due to the presence of the concentration peaks.

The municipality of Ploiesti and the neighboring areas are included in the list of localities where the quality of air was permanently questioned due to the three refineries in function, but also of the thermal and electrical energy production units, the factory of solid detergents, to which the traffic pollution is also added.

The analysis of the dataset based on the computed statistical indicators showed that despite the occurrence of high concentrations that exceeded the limit value of 15 µg m^{-3} in the identified points and periods, high average concentrations occurred at Lazar Edeleanu point (3.25 µg/m³) in 2021, and Aleea Catinei area (2.08 and 2.15 µg/m³) in 2019. This suggests that the concentrations recorded at 30 minutes were relatively constant varying less evidently, but maintaining a concentration that could be harmful to health. In other cases, the concentration reached high values for a shorter period dropping to 0 afterwards. These situations should be further investigated in detail to determine the patterns and the cycles in correlation with the emission times that can be established using remote sensing resources.

Near the industrial emission sources, the concentrations are much higher than in background areas (for example, the airborne H_2S concentrations in Aydin and Manisa, Turkey, where the power plants are located, ranged between 11.2 and 66.7 μg m^{-3} compared to 0.61 μg m^{-3} and 0.60 μg m^{-3} in the background area, respectively) [9].

The petroleum industry, through its particularly diverse and complex activities, produces a variety of compounds and pollutants in all stages of processing, transport, and storage of raw materials [10].

Thus gas emissions, liquid effluents, solid waste, and oil waste are recorded during stages of processing, storage, transport, or use.

Hydrogen sulfide emissions from oil refineries are resulting in the time of the removal of sulfur compounds from petroleum products. These emissions occur from heaters, boilers, headers, storage tanks, FCC plants, incinerators, and wastewater treatment [7].

Hydrogen sulfide is very frequently mentioned in reports of refinery incidents having a distinct odor [7].

As in the case of ammonia, H_2S appears in the complaints of the residents from Ploiesti as the worst scenario of toxic release.

In Romania, the field of "air quality" is mainly regulated by: "Law no. 104/15.06.2011 regarding the quality of the surrounding air published in the Official Gazette of Romania, Part I, no. 452 of June 28, 2011, which transposes the Directives 2008/50/CE and 2004/107/CE adopted by the European Parliament and Council".

The compliance with European and national legislation leads to an intensification of the activities of monitoring, maintaining, and improving air quality in the municipality of Ploiesti. International environmental regulations for gas emissions by industries have become strict regarding the release of sulfur-containing gases. Most gas detectors for industrial personnel are set at 20 ppm of H_2S in the air as the limit for evacuation from a contaminated area. To meet the regulatory requirement, it is necessary to use appropriate technologies for purification and reduction of H_2S concentrations [11]. Furthermore, continuous monitoring campaigns and deployment of modern cyber infrastructures with expert algorithms for exposure to air pollutants and health effect assessments are key factors in ensuring suitable information for the inner residents of urban areas to protect their health [12].

CONCLUSIONS

Hydrogen sulfide must be considered on the public health agenda, both from the occupational perspective and for the ambient concentrations near the significant H_2S sources and in background urban areas, including Ploiesti City. In this study, the statistical analysis of the available dataset showed the variance of the concentrations with exceedances of the maximum admissible concentrations determined at Mihai Bravu Street, in the eastern part of Ploiesti City, with five peaks and the maximum concentration (59.36 μg m^{-3}), and at Ploiesti Nord point, in the north of Ploiesti City with four peaks. The remaining monitoring periods performed at various points recorded values that did not exceed the limit value, but further investigations are required to establish the potential adverse effects of lower concentrations that are however constant for long periods not dropping to 0.

The monitoring infrastructure needs to be improved to allow continuous surveillance to ensure reliable databases that support research regarding the health effects of H_2S across the concentrations occurring in the urban environment.

ACKNOWLEDGEMENTS

We thank the Environmental Protection Agency Prahova, Romania, for the support provided to Stancu (Sanda) Mia Nuţa in her Ph.D. program.

REFERENCES

[1] Filonchyk M., Peterson M.P., NO2 emissions from oil refineries in the Mississippi Delta. Science of the Total Environment, 898, 65569, 2023. https://doi.org/10.1016/j.scitotenv.2023.165569

[2] Sanda M., Dunea D., Iordache S., Pohoata, A. Glod-Lendvai A.M., Onutu I., A Three-Year Analysis of Toxic Benzene Levels and Associated Impact in Ploieşti City, Romania. Toxics, 11 (9), 748, 2023. https://doi.org/10.3390/toxics11090748

[3] IPCS International Programme On Chemical Safety, Environmental Health Criteria 19, Hydrogen Sulfide. https://www.inchem.org/documents/ehc/ehc/ehc019.htm

[4] National Center for Biotechnology Information. PubChem Compound Summary for CID 402, Hydrogen Sulfide, 2023. https://pubchem.ncbi.nlm.nih.gov/compound/Hydrogen-Sulfide.

[5] EPA Prahova, State of the Environment – Annual Report - https://apmph.anpm.ro/

[6] Malone Rubright S.L., Pearce L.L., Peterson J., Environmental toxicology of hydrogen sulfide. Nitric Oxide. 71, pp 1-13, 2017. doi: 10.1016/j.niox.2017.09.011.

[7] Riveles K., Nagai Al. Analysis of Refinery Chemical Emissions and Health Effects, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, 2019. https://oehha.ca.gov/media/downloads/faqs/refinerychemicalsreport032019.pdf

[8] Skrtic L., Energy and Resources Group. University of California, Berkeley; Berkeley, CA: Hydrogen Sulfide, Oil and Gas, and People's Health; p. 77, 2006.

[9] USEPA Agency for Toxic Substances and Disease Registry (ATSDR) Hydrogen Sulfide Fact Sheet, 2016. https://www.epa.gov/sites/default/files/2017-12/documents/appendix_e-atsdr_h2s_factsheet.pdf

[10] Dumanoglu Y., Monitoring of hydrogen sulfide concentration in the atmosphere near two geothermal power plants of Turkey. Atmospheric Pollution Research, 11(12), pp 2317-2326, 2020. https://doi.org/10.1016/j.apr.2020.08.015.

[11] Onutu I., Manufacturing ecological petroleum fuels. Complex refinery schemes, UPG Publishing House, 2001.

[12] Oprea M., Dunea D., Liu H.Y. Development of a knowledge-based system for analyzing particulate matter air pollution effects on human health. Environmental Engineering and Management Journal, 16 (3), pp 669-676.

Received: November 2023; Accepted: November 2023; Published: November 2023