ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI
MATHEMATICS, PHYSICS, THEORETICAL MECHANICS
FASCICLE II, YEAR XIV (XLV) 2022, No. 2
DOI: https://doi.org/10.35219/ann-ugal-math-phys-mec.2022.2.06

Study of the evolution of heavy metals emissions in the southeastern part of Romania

Drasovean Romana Maria *, Condurache-Bota Simona

"Dunarea de Jos" University of Galati, Faculty of Sciences and Environment,
111 Domneasca Street, 800201 Galati, Romania
** Corresponding author: rdrasov@ugal.ro*

Abstract

Heavy metals emitted from anthropogenic activities can be transported into the atmosphere over long distances and can have significant negative effects on human health and the environment. Heavy metals are toxic pollutants that act on various organs and systems of the human body, their effects being specific to each substance. Because of their reduced mobility, heavy metals are concentrated at each trophic level, the highest concentration being reached at the ends of food chains, where, most of the times, humans stand. This paper presents the spatial and temporal evolution of heavy metals concentrations in the Southeastern part of Romania. The Southeastern region we studied included the counties of: Braila, Buzau, Constanta, Galati and Tulcea, respectively. The database of the Romanian National Air Quality Monitoring Network (RNMCA) was used for this study.

The data taken from the RNMCA network consisted in the concentrations of As, Cd, Ni and Pb, respectively, which were recorded between January 2020 and May 2022. The monthly evolution of the chosen pollutants was studied. Pearson and Spearman correlations were used in order to study the influence of climatic factors on the heavy metals pollutants.

Keywords: atmospheric pollution, heavy metals, Romania.

1.INTRODUCTION

Air pollution affects human health and the environment [1, 2]. In Europe, in recent years, due to the legislative measures that were taken, the emissions of many atmospheric pollutants have decreased causing an improvement in air quality in the region [3, 4]. The developed countries realized that in order to combat air pollution there was a need for an improvement of the legislation, a continuous and strict monitoring and last but not least, sustained investments and research [4, 5]. With all the measures taken and the sanctions given, air quality problems still persist [6, 7].

Some of the most toxic pollutants are heavy metals: arsenic, boron, cadmium, chromium, copper, lead, mercury and zinc [1, 2, 6, 7]. Heavy metals come from the combustion of coal, fuels, household waste, car batteries and paints, as well as from other industrial processes [7, 8].

These pollutants act on human body and on whole environment [8]. Some of these heavy metals such as lead and inorganic arsenic are considered to belong to the category of hazardous air polluting substances. These air pollutants can have a strong effect on the skin, eye, throat, nervous system, cardiorespiratory system and ultimately can lead to the death of the body [3,7]. Heavy metals cannot be degraded naturally, they have a long retention time in the environment, they can be transported into the atmosphere over long distances and can be accumulated in the food chain.

This paper presents the spatial and temporal evolution of heavy metals concentrations in the Southeastern part of Romania. The Southeastern region contains the counties of: Braila (BR), Buzau

(BZ), Constanta (CT), Galati (GL) and Tulcea (TL) (Fig.1.). The database of the Romanian National Air Quality Monitoring Network (RNMCA) was used for this study.

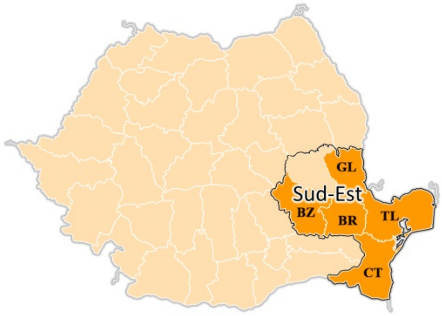

Fig. 1. The southeastern part of Romania

2. EXPERIMENTAL

Measurements from RNMCA database were made with a resolution of 1 hour, from 12 monitoring stations, in these five counties. The daily values taken from the database were averaged per month.

The monitoring period included the pandemic period. The data taken from the RNMCA network consisted of the concentrations of some heavy metals such as: arsenic (As), cadmium (Cd), nickel (Ni) and lead (Pb). The heavy metals concentrations were recorded between January 2020 and May 2022. Heavy metals spatial and monthly distribution was built. Pearson and Spearman correlations were used.

Description of the studied area

As specified, the counties of Constanta, Braila, Buzau, Galati and Tulcea were chosen for the study of atmospheric pollution with heavy metals. In general, the monitoring stations are located in the county seats:

Galati is located in the eastern part of Romania on the right bank of the Danube. This city is the county seat of county with the same name. Data from 4 monitoring stations were used: GL-1, GL-2, GL-3 and GL-4. GL1 monitoring station is used to evaluate traffic pollution. GL-2 monitoring station is an urban background station situated in green area, behind buildings. GL-3 monitoring station is a suburban type station, for the assessment of the exposure of the population and vegetation at the edge of the agglomeration. The main emission sources near the station: non-industrial combustion installations, car traffic, natural factors. Monitoring station GL-4 is a suburban industrial type station for the assessment of air quality in industrial areas and the assessment of the exposure of the population and vegetation on the outskirts of the agglomeration. The main emission sources near the station: non-industrial combustion plants, combustion from the processing industry, car traffic, natural factors.

Braila is an old settlement on the left bank of the Danube, near the town of Galati. Braila is the seat of Braila County. There are three monitoring stations in the city of Braila. Out of the 3 stations in the town of Braila, only one is working, namely station BR2. BR2 is located in the city center, near the County Council, in an area far from traffic or industrial areas.

Buzau is the seat of the county with the same name. Only one traffic station operates in this city.

In Constanta County, there are three functional stations in the city of Constanta and one station in the city of Medgidia. Constanta is a port on the Black Sea and one of the oldest attested cities in Romania. The air monitoring stations CT1, CT2 and CT3 in Constanta are located in green areas or behind buildings. Thus, these stations are far from traffic or industrially polluted areas and the measured values can be better than in reality. The CT7 monitoring station is located in the city of Medgidia in Constanta County, 41 km from Constanta.

In Tulcea County, only one monitoring station operates in the city of Tulcea. Tulcea is a port city on the Danube in the south-east of Romania. Out of the three monitoring stations, two of them are for traffic, TL1 being on a first class artery.

3. RESULTS AND DISCUSSION

In Galati, at all monitoring stations, the measurements of As, Cd, Ni and Pb were made only in January 2020 when the highest values of the entire studied period were recorded. In the rest of the monitored months, measurements were recorded only at the GL2 station.

In figure 2 the monthly average values of temperature and As concentrations, recorded in Galati, are graphically represented. The values of arsenic concentrations did not exceed the target value of 6 ng/m^3 [10], value averaged per year. At GL2 station the values were in the range of 0.03-0.22 ng/m^3. At GL2 station, no arsenic measurements were made in April, July and October 2020, February, May, August 2021 and March, May 2022.

From the same figure, it can be seen that the temperature variation graphs have the same shape for all four stations. The lowest average temperatures were recorded at GL4 station. Average values higher than the climatological norms were not recorded.

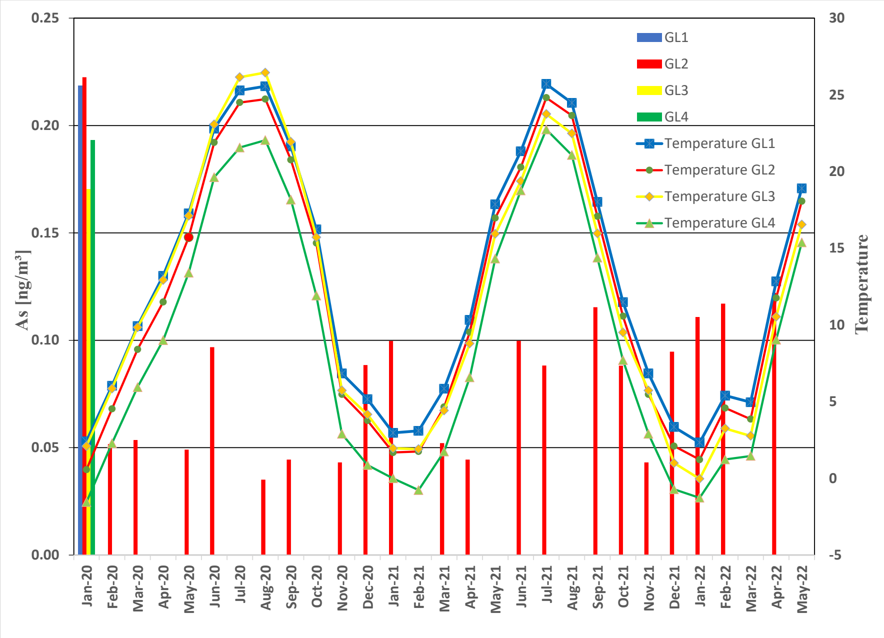

Fig.2.Monthly evolution of temperature and As concentrations in Galati

In the city of Galati, during the studied period, a general low trend of monthly and annual precipitation amounts is highlighted (Fig. 3.). At GL2 station, the recorded values were higher than the ones at the other two stations. The highest amount of precipitation (5.2 mm) was recorded in June 2021, at GL2 station.

The number of data being too small, the influence of climatic factors cannot be seen. For this purpose, the Pearson and Spearman matrices will be constructed. Usually high temperature values favor the dispersion of the pollutant and atmospheric precipitation contributes to cleaning the atmosphere.

Figures 4, 5 and 6 represent the monthly evolution of Cd, Ni and Pb concentrations in the atmosphere of the city of Galati. For all three pollutants, the limit values were not exceeded. The limit values and target values for heavy metals in the atmosphere are given by law of LAW no. 104 of June 15, 2011(Table1).

From figures 4, 5 and 6, it can be also seen that Cd, Ni and Pb were monitored only at one station, GL2. Only in January 2020 the measurements were recorded at all four stations from the city. The highest values were obtained at GL1 and GL2.

Fig.3. The daily rainfall values [mm] recorded at ANPM Galati stations

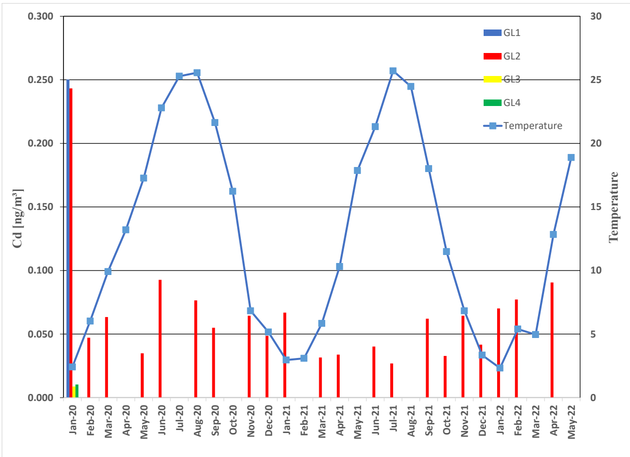

Fig.4. Monthly evolution of temperature and Cd concentrations in Galati

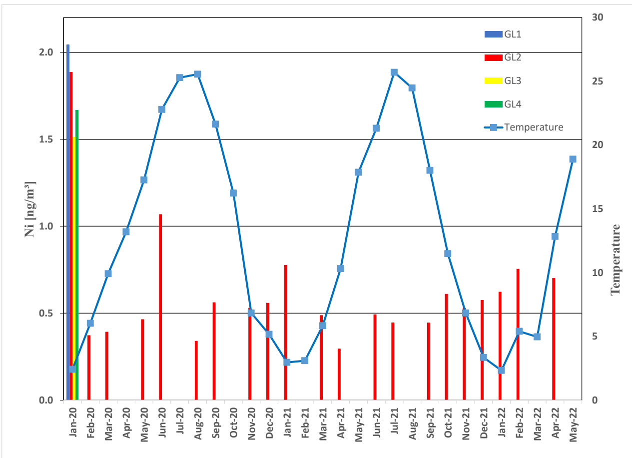

Fig.5. Monthly evolution of temperature and Ni concentrations in Galati

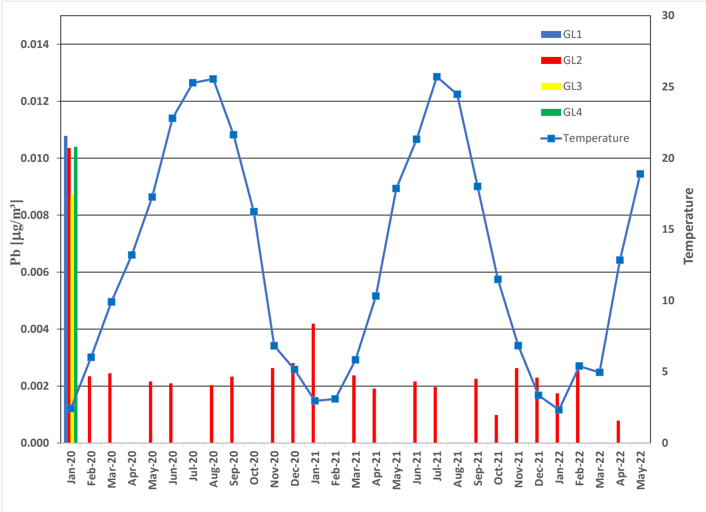

Fig.6. Monthly evolution of temperature and Pb concentrations in Galati

Table 1. Limit Values from Law No. 104 of June 15, 2011

As	6 ng/m^3 - the average target value for a year
Cd	5 ng/m^3 - the average target value for a year
Ni	20 ng/m^3 - the average target value for a year
Pb	0.5 µg/m^3 - the annual limit value for the protection of human health

Figure 7 shows the evolution of arsenic concentrations in the cities of Buzau and Braila, figure 8 the evolution in Constanta County and figure 9 in Tulcea.

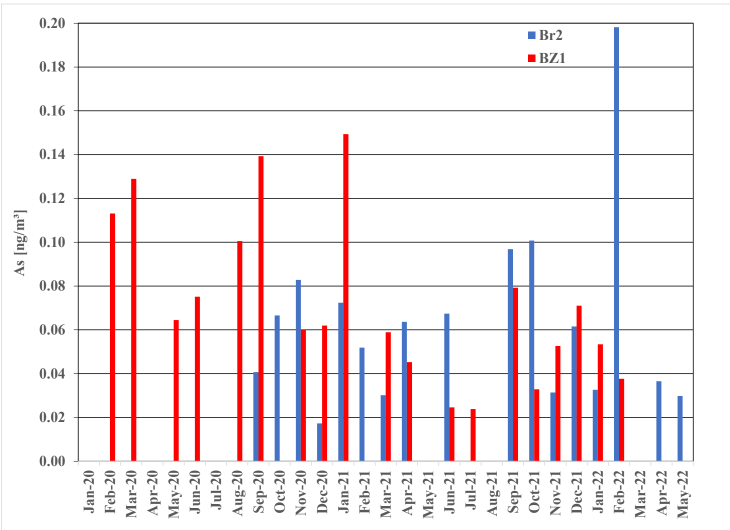

Fig.7. Temporal evolution of arsenic concentrations in Buzau and Braila

The limit values (Table 1) have not been exceeded at any of the stations from Braila, Buzau, Constanta or Tulcea. The highest values were obtained at station CT3 in August 2020 (Fig.8) and TL2 in March 2020 and in December 2021.

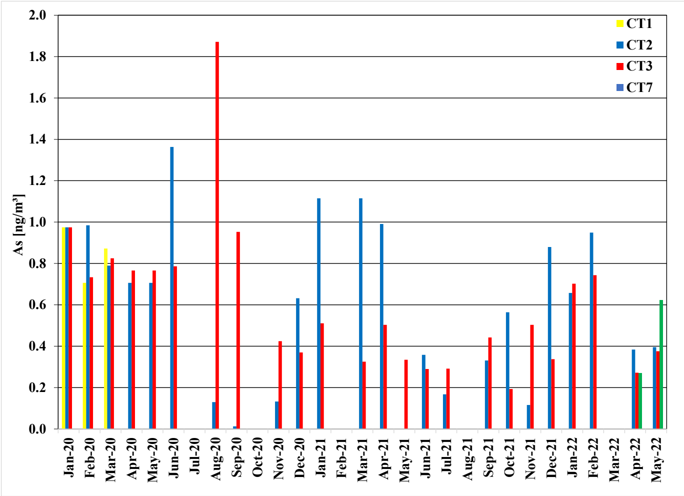

Fig.8. Temporal evolution of arsenic concentrations in Constanta (CT1, CT2, CT3) and Medgidia (CT7)

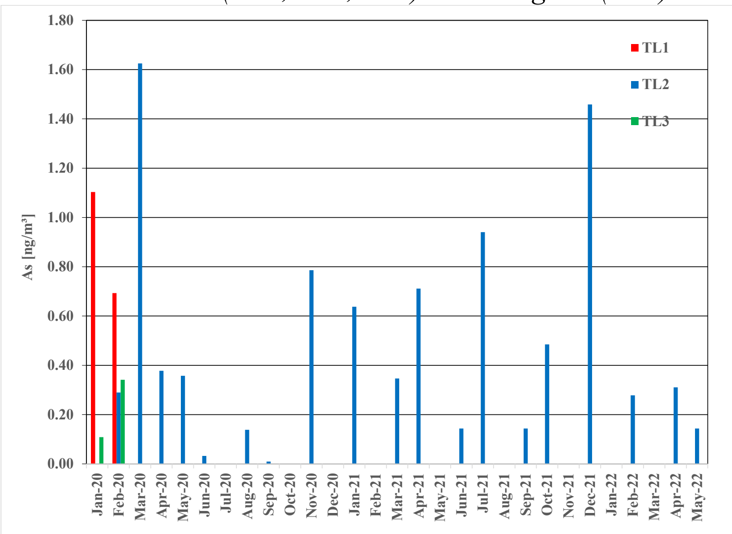

Fig.9. Temporal evolution of arsenic concentrations in Tulcea

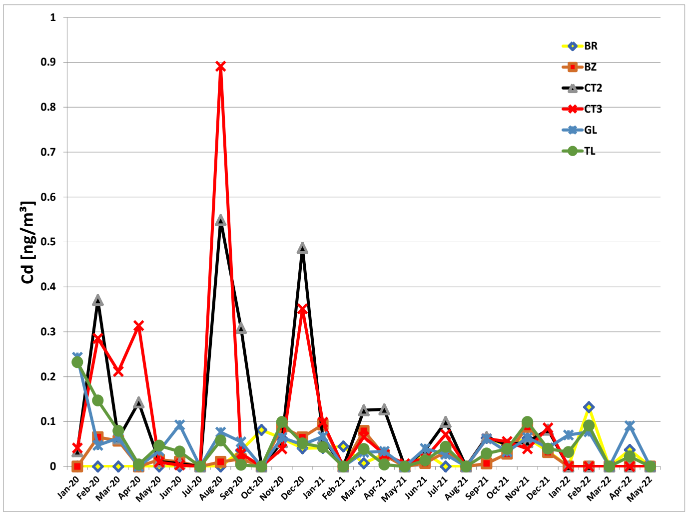

Fig.10. Temporal and spatial evolution of cadmium concentration

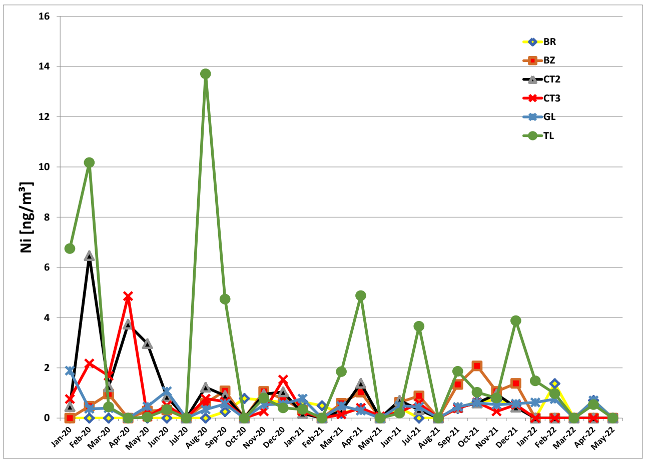

Fig.11. Temporal and spatial evolution of nickel concentration

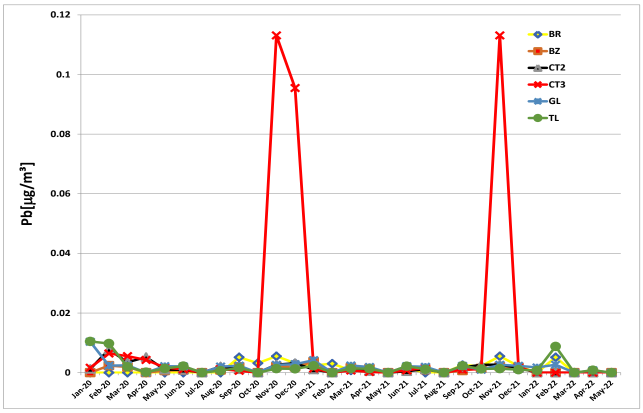

Fig.12. Temporal and spatial evolution of lead concentration

Figures 10, 11 and 12 show temporal and spatial evolution of cadmium, nickel and lead concentration in the Southeastern part of Romania, respectively. Throughout the studied period, the recorded values were much lower than the limit values from Romanian Law No. 104 of June 15, 2011. There is no significant decrease in the concentration of these metals during the pandemic.

From the point of view of the presence of heavy metals in the atmosphere, can it be said that the air quality in these cities is good? It's hard to say because these stations are far from traffic or industrially polluted areas and the measured values may be better than in reality. In addition, the measurements were not made every day and at all stations.

The Pearson (Table 2) and Spearman Matrix (Table 3) was built in order to see what the influence of climatic factors on the heavy metals pollutants was.

Pearson correlation coefficient measures and describes the degree of linear association between two variables while Spearman coefficient reflects the non-linear correlation between the variables [11]. The Pearson coefficient was denoted by R (Table 2.), the Spearman coefficient by r_s and with p confidence factor (Table 3.).

From Pearson matrix (Table 2.) appears that there is a weak negative strength of the linear relationship between parameters temperature-heavy metals and rainfall-heavy metals.

Instead, a statistically significant nonlinear negative correlations (Table 3.) between heavy metals-temperature and heavy metals-precipitation is observed. The values obtained for r_s and p indicate greater relevance for precipitation. High temperature favors the dispersion of the pollutant and atmospheric precipitation contributes to cleaning the atmosphere.

Table 2. Pearson Matrix for climatic parameters-heavy metals

R	Temperature	Rainfall
As	-0.2673	-0.4497
Cd	-0.116	-0.0255
Ni	-0.2736	-0.0935
Pb	-0.0866	-0.0331

Table 3. Spearman's Correlation between climatic parameters-heavy metals

Correlation	r_s	p (2-tailed)	Meaning
As-Rainfall	-1	0	the association between the two variables would be considered statistically significant.
As-Temperature	-0.2641	0.01661	
Cd-Rainfall	-0.38118	0.027549	
Cd-Temperature	-0.18528	0.02567	
Ni-Rainfall	-0.48	0.0022	
Ni-Temperature	-0.2427	0.027978	
Pb-Rainfall	-0.29408	0.01215	
Pb-Temperature	-0.02239	0.030824	

4. CONCLUSIONS

This paper presents the spatial and temporal evolution of heavy metals concentrations in the Southeastern part of Romania. For all the studied pollutants (As Cd, Ni, Pb), the limit values have not been exceeded. These values, below the limit, may be either due to the lack of pollution or to the location of these stations far from any source of pollution or to the absence of daily measurements.

There are nonlinear negative correlations between concentration of heavy metals- temperature and concentration of heavy metals-precipitation. The values of the parameter p, also called the confidence factor, are less than 0.05, which indicates that the associations between the variables would be considered statistically significant.

Analysis of the correlations between heavy metal concentrations and meteorological parameters showed that the association with temperature was the least relevant.

ACKNOWLEDGEMENTS

This work was carried out in the framework of the project:" Internal research grant in the field of environmental engineering regarding the study of the distribution of pollutants in the south-eastern part of Europe" (14886/11.05.2022).

References

1. Wang F., Zhou Y.Y., Meng D., Han M.M., Jia C.Q., Heavy metal characteristics and health risk assessment of PM2.5 in three residential homes during winter in Nanjing, China, Build. Environ. 143 (2018) 339-348.

2. Zheng X.B, Xu X.J., Yekeen T.A., Zhang Y.L., Chen A.M., Kim S.S., Dietrich K.N., Ho S.M., Lee S.A., Reponen T., Huo X., Ambient air heavy metals in PM2.5 and potential human health risk assessment in an informal electronic—waste recycling site of China, Aerosol Air Qual. Res. 16 (2) (2016) 388-397.
3. Declet-Barreto J., Goldman G.T., Desikan A., Berman E., Goldman J., Johnson C., Montenegro L., A.A. Rosenberg, Hazardous air pollutant emissions implications under 2018 guidance on U.S. clean air act requirements for major sources, J. Air Waste Manage. Assoc. 70 (2020) 481-490.
4. Samet J.M., The Clean Air Act and health--a clearer view from 2011, N. Engl. J. Med. 365 (2011) 198-201.
5. Environmental Protection Agency, Guidelines for determining Best Available Control Technology (BACT) https://www.epa.gov/sites/production/files/2015-07/documents/bactupsd.pdf.
6. https://www.eea.europa.eu/ro/articles/
7. Benin A. L., Sargent J. D., Dalton M., and Roda S., High concentrations of heavy metals in neighborhoods near Ore Smelters in Northern Mexico, Environ. Health Perspect. 107 (4) (1999) 279–84.
8. Briffa J., Sinagra E, Blundell R, Heavy metal pollution in the environment and their toxicological effects on humans, Heliyon 6 (e04691) (2020) 1-26.
9. Romanian National Air Quality Monitoring Network (RNMCA).
10. Romanian LAW no. 104 of June 15, 2011.
11. Drasovean R., Murariu G., Water Quality Parameters and Monitoring Soft Surface Water Quality Using Statistical Approaches, Promising Techniques for Wastewater Treatment and Water Quality Assessment,(Moujdin A. and Kevin Summers J., editor), Intechopen, 2021.