CONSIDERATIONS REGARDING THE HISTORICAL POLLUTION FROM THE INDUSTRIAL AREA OF THE CITY OF ORADEA

Costea Monica^{*}, Emilia Pantea^{*}, Carmen Ghergheles^{*}, Ani Moza^{*}, Ciuclea Mihaela Ana^{*}

*University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048, Oradea, Romania, e-mail: <u>costeamonica001@gmail.com</u>
*University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048, Oradea, Romania, e-mail: <u>emipantea@gmail.com</u>
*University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048, Oradea, Romania, e-mail: <u>i carmen g@gmail.com</u>
*University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048, Oradea, Romania, e-mail: <u>i carmen g@gmail.com</u>
*University of Oradea, Faculty of Environmental Protection, 26 Gen. Magheru St., 410048, Oradea, Romania, e-mail: mozaani@yahoo.com
*University of Oradea, Faculty of Construction Cadastre and Arhitecture, 4 Barbu Stefanescu Delavrancea St., 410048, Oradea, Romania, e-mail: <u>costeamonica001@gmail.com</u>

Abstract

There have been significant changes in the types of economic activities in the industrial area of Oradea during the last few years. Economic objectives with significant environmental impact have been closed down and other economic objectives with far less environmental impact have been opened during these years. To establish the evolution of the level of environmental pollution, air, water and soil determinations have been made in the last years.

The current paper shows the investigations made upon the impact area to determine the intensity of pollution by sampling and physico-chemical analyses of environmental factors water, air and soil.

Key words: pollution, economic activities, environmental impact

INTRODUCTION

There were 17,891 active local units in Bihor County in 2015, representing 23.56% of the active local units in the North West Region, ranking second in the region, after Cluj County (28,890 u.i.a.; 38.04%).

Of all the active local units in Bihor County, 87.295% are microenterprises (0 - 9 employees), 10.687% small enterprises (10 - 49 employees), 1.727% medium enterprises (50 -249 employees) and 0.2911% (250 employees and over). 10,458 local units were active in Oradea in 2014, representing 85.65% of the local active units in the Metropolitan Area and 58.74% of all local active units in the Bihor County. (SIDU, 2017)

The representative industrial branches ordered according to the value of their turnover in Oradea in 2016 were: • Food industry • Manufacture of computers and electronic and optical products • Manufacture of footwear • Manufacture of machinery and equipment for general use • Manufacture of rubber and plastic products • Manufacture of furniture • Manufacture of metal products obtained by plastic deformation • Powder metallurgy • Production of tools and articles of ironmongery • Production of parts and accessories for vehicles and motor vehicles • Extraction of crude oil and natural gas • Manufacture of basic chemicals • Other industrial groups.

Oradea Local Development Agency SA (ADLO) had three industrial park property titles for the three locations situated on **Calea Borşului** (130.02 ha) - **Oradea Industrial Park I**, Ogorului Street (83.5 ha) - Oradea Industrial Park II, respectively Uzinelor Street - Oradea Industrial Park III (15 ha).

The quality of environmental factors and sources of pollution

Public policies and legislation in this field must also be taken into consideration, an important environmental factor being the legislative framework, respectively the European / world environmental regulations, rules that must be obeyed by our country as well. Compliance with these rules may also result in public investment being directed to certain types of objective over others.

A. Air quality

Critical areas as regards air pollution are located near high-traffic roads, major intersections, industrial waste dumps, uncontrolled domestic waste dumps, and animal farms. The chemical and petrochemical industries have substantially reduced their production activities. (ANPM, 2008-2017)

Air quality monitoring in Bihor County is carried out through the monitoring network consisting of:

- Automatic stations for monitoring air quality
- Sediment dust collection points
- Precipitation sampling points

The automatic air quality monitoring network in Oradea gathered and processed the data provided by the 3 monitoring stations:

- Station BH 1 (urban station) situated near APM Bihor headquarters, No.25 / A Dacia Boulevard, monitors on-line the following pollutants: CO, SO₂, NO, NO₂, NO_x, PM_{2,5} (dust) gravimetric and nephelometric, BTX (benzene, toluene, xylene), weather parameters.
- Station BH 2 (industrial station) located in the yard of the Secondary School situated in Episcopia Bihor, with the following monitored parameters: CO, SO₂, NO, NO₂, NO_x, O₃, PM₁₀ (dust) gravimetric and nephelometric, weather parameters.
- Station BH 3 (traffic station) located in the Nufarul district near McDonalds drive, monitors on-line the following pollutants: CO,

SO₂, NO, NO₂, NO_x, O₃, PM_{10} (dusts), nephelometric determination, BTX (benzene, toluene, xylene), weather parameters.

B. Water quality

Crişul Repede runs through the administrative territory of Oradea Metropolitan area, on the East-West direction. It springs from an altitude of 710 m, near the locality called Izvorul Crisului, from a hilly area on the northern edge of Huedin basin. The right bank of Crisul Repede is dammed downstream of Oradea, on a length of 23.6 km. After passing by the city of Oradea in a plain area, its course is slow. Crişul Repede represents a heavily modified water body and has been monitored in 3 sections (on the territory of the Oradea Metropolitan Area), on a length of 34.27 km. The quality of water falls within the category of good environmental potential according to indicator groups such as oxygen regime, salinity and toxic pollutants, respectively relevant chemical indicators. biological indicators(http://www.oradea.ro/fisiere/module_fisiere).

C. Soil quality

Soil quality is affected, in various de

grees of pollution, by industrial activities, as follows from the partial inventory data carried out from 2012 to 2015. Generally speaking, in the field of soil protection, pollution means any disruption that affects the soil quality qualitatively and / or quantitatively (D. Mocuta, 2017).

The types of soil pollution are those set out in the Methodology for Pedological Studies, Volume III (1987) and the Romanian Soil Taxonomy System (2003).

The degree of pollution can be assessed on 5 classes, either on the basis of the crop reduction percentage in terms of quantity and / or quality, compared to the production obtained on unpolluted soil (Annex 2), or by exceeding, in different proportions, the thresholds established by the Order of the Ministry of Waters, Forests and Environmental Protection no. 756 of November 3, 1997, for the approval of the Regulation regarding Environmental Pollution Assessment (G. Neață et. all, 2013)

Categories of pollution:

- industrial and agricultural pollution
- pollution through slope processes and other physical processes;
- soil pollution through other natural and / or anthropogenic processes.

MATERIAL AND METHOD

The reference area for establishing the quality of the analyzed environmental factors was the Industrial Park I. Figure.1



Fig. 1. The Industrial Park I

A. Environmental factor: air

The concentrations of CO, SO_2 , NO, NO_2 , NO_x , O_3 , PM_{10} (dust) gravimetric and nephelometric, weather parameters were monitored to analyze the degree of pollution and the air quality in the industrial area. Monitoring was done over a four-year period between 2012 and 2015.



Fig 2. The automatic air quality monitoring station

The hourly limit value for human health protection $350 \mu g / m^3$, which should not be exceeded more than 24 times a year and the daily limit value for the protection of human health $125 \mu g / m^3$, which should not be exceeded more than 3 times a year, were used in order to assess the degree of pollution with SO_2 .

The NO₂ concentrations in ambient air are assessed using the hourly limit value for human health protection $200 \mu g / m^3$, which shall not be exceeded more than 18 times a year, and the annual limit value for the protection of human health $40 \mu g / m^3$.

CO concentrations in ambient air are assessed using the hourly limit value for human health protection $10mg/m^3$, which shall not be exceeded more than 18 times a year and the annual limit value for human health protection calculated as the maximum daily mean value of 8 hours (rolling average position).

The values of suspended particulate concentrations PM_{10} monitored by automatic measurements (using nephelometric method) at the monitoring station are guide values. The reference measurement method, in accordance with the Law on ambient air quality No 104/2011 for this indicator, is the gravimetric method, which is based on the collection of the PM_{10} and $PM_{2.5}$ fractions, of suspended particulate matter in the air and determining their mass using the method of weighing in the laboratory.

The particle concentration in suspension with a diameter of less than 10 microns in ambient air was evaluated using the daily limit value, determined gravimetrically $50 \mu g / m^3$, which should not be exceeded more than 35 times a year, and the annual limit value determined gravimetrically $40 \mu g / m^3$.

B. Environmental factor: water

As Crişul Repede is the running water whose course can be affected by the industrial activity in the analyzed area, we considered it necessary to carry out a monitoring of its quality from 2012 to 2015. The pollutants that could contaminate the surface water in the monitoring area were: chlorides, total organic carbon, suspended matter, CCO - Cr, extractable substances with organic solvents, sulphates, CCO - Mn (Romocea Tamara, et al, 2016)

In view of the above, an investigation on water quality was carried out in the period 2012-2015.

In order to determine the water pollution indexes, during the monitoring period (2012-2015), water samples were taken from the Crişul Repede River, downstream of CET 1, the sampling being carried out quarterly. The temperature indicators, residues filtered at 105°C, chlorides, sulphates, CCO-Cr, and pH were monitored. The analysis methods for each parameter analyzed, the limit values admitted under the specific legislation, are specified in the following table.

Table 1.

	specific registation									
Nr. crt.	Physico - chemical indicators	U.M.	VL / CMA	Analysis methods STAS						
1.	Temperature	⁰ C	< 35	-						
2.	Residue filtered at 105°C	mg / 1	700	STAS 9187/84						
3.	Ph	Unit pH	$(6,5 \div 8,5)$	-						
4.	CCO – Cr	mg/l	70	SR ISO 6060/96						
5	Sulphates	mg/l	600	STAS 8601/70						
6	Chlorides	mg/l	300	STAS 8663/1970						

The analysis methods for each parameter analyzed, the limit values admitted under the specific legislation

C. Environmental factor: soil

Concentrations of activity-specific pollutants that could affect the soil on lands which are likely to be polluted in Industrial Park 1, shall not exceed the limits for less vulnerable land, as provided for in the *MAPPM Order* 756/1997 for the approval of the Regulation on environmental pollution assessment (D. Mocuța, .

The results obtained for the quality indicators determined for the soil samples taken in the years 2012 - 2015, in the Industrial Park 1 (Hg, Cr_{total} , Cr^{6+} , Pb, Cd, HAP, Sulphates and Ni) were below the alert thresholds (PA).

The methods of analysis used by the accredited laboratories were as follows:

- The pH was determined potentiometrically according to SR ISO 10390: 1999;
- The sulphate content was performed with Dionex DX-120 Ion Chromatograph according to EPA method 9056:1994, SR EN 12457-2:2003, SR EN 12457-4:2003, SR EN 16192:2012, SR EN ISO 10304-1:2009;
- Cadmium, Chromium, Nickel, Lead, Hexavalent Chromium and Mercury were determined according to SR ISO 11466: 1999, SR ISO 11047: 1999, using the Perkin Elmer PinAAcle 900T Atomic Absorption Spectrometer
- Polycyclic aromatic hydrocarbons were determined with the HP 69890 Gas Chromatograph, by EPA 8270C: 1996, SR EN 15527: 2008.

Table 2.

Nr. crt.	Physico - chemical indicators	U.M.	Alert thresholds (mg/kg s.u)	Intervention thresholds (mg/kg s.u)	Analysis methods STAS
1.	рН	Unit pH	$(6,5 \div 8,5)$		SR ISO 10390:1999
2.	Sulphates	mg/kg	5 000	50 000	SR EN 16192:2012
3.	Lead	mg/kg	250	1000	SR ISO 11466:1999
4.	Cadmium	mg/kg	5	10	SR ISO 11466:1999
5.	Chromium, Hexavalent Chromium	mg/kg	300 10	600 20	SR ISO 11466:1999
6.	Nickel	mg/kg	200	500	SR ISO 11466:1999
7.	Mercury	mg/kg	4	10	SR ISO 11466:1999
8.	Polycyclic aromatic hydrocarbons	mg/kg	25	150	SR EN 15527:2008

Concentrations of specified pollutants in Order MAPPM 756/1997

RESULTS AND DISCUSSION

A. Environmental factor: air

From the comparison of the results obtained for the SO_2 parameter, from the measurements using the norms established by the air quality law it follows that there were no exceedances during the study period. The values recorded for this parameter are quite high and are mainly due to industries that use fossil fuel combustion to produce heat and electricity. (J. Seinfield, 1986)

For this reason, the measurements made at IMA 2 were analyzed as the main source of pollution in the industrial area. The principles of the analytical methods used are presented in the following table. (E. Boeker, R. van Grondelle, 2011)

Table 3.

	Analytical method used								
Particles	Optical principle								
$[mg/Nm^3]$									
NOx	extractive: GFC principle (correlation of gas filters) of infrared								
$[mg/Nm^3]$	absorption for NO, for total NOx catalytic NO ₂ is converted to NO								
SO ₂	extractive: GFC principle (correlation of gas filters) of infrared								
$[mg/Nm^3]$	absorption								
CO [mg/Nm ³]	extractive: GFC principle (correlation of gas filters) of infrared								
	absorption								
O ₂ %	extractive: the paramagnetic principle								
Gas temp., °C	Heat resistance								

Analytical method used to determine the concentrations measured at source

The obtained results confirm that the highest share in the quantities of pollutants monitored is mainly due to Large Combustion Plants which operate with coal (lignite) with fuel oil.

	Conc.	Conc.	Conc.	Conc.		VLE
Pollutant	(monthly	(monthly	(monthly	(monthly	U.M.	
	average)	average)	average)	average)		
	2012	2013	2014	2015		
SO_2	(5.410÷5.544)	(5.408÷5.420)	(5.408÷5.416)	(5.413÷5.534)	mg/m ³ _N	400
NO_x	(333 ÷ 353)	(332 ÷ 357)	(335 ÷ 351)	(341 ÷ 380)	mg/m ³ _N	200
РМ	(1.053 ÷ 1.333)	(1.004 ÷ 1.132)	(922 ÷ 1.040)	(908 ÷ 999)	mg/m ³ _N	50

Monthly average values measured at the main source of pollution, IMA 2

The monthly average values are presented in the table and it is observed that the concentrations emitted far exceed the VLE, the Emission Limit Values.

From the comparison of the concentrations obtained from the NO_X parameter measurements it follows that there were no exceedances of the established rules. (D. Borota, M Costea, 2000)

Table 5.

	The exceedances of the average daily concentrations									
Number of exceedances of the daily limit value $50 \mu g / m^3$	2012	2013	2014	2015	The maximum number of exceedances allowed					
Nephelometric method	11	2	24	22	35					
gravimetric method	26	9	28	28	35					

During the analyzed period 2012-2015 there were exceedances of the average daily concentrations at the monitoring station, as shown in the following table.

Table 6

					Tuble 0		
Annual average values for PM ₁₀							
Valori medii anuale PM ₁₀							
	valoarea						

					limită anuală
Annual average PM10 nephelometric method	27,01	28,27	25,73	31,02	40
Annual average PM ₁₀ gravimetric method	27,13	23,99	26,44	30,25	40

The sources that contributed to the exceedances are those resulting from the small residential combustion (to a lesser extent), as well as the influence of the large combustion plants (significantly), the exceedances being recorded mainly during the cold season. (M. Costea, 2014)

B. Environmental factor: water

The results obtained for the indicators monitored by water sampling from Crisul Repede River downstream of the Industrial Platform analyzed in this study are outlined in the following table.

Table 7

The results obtained for the indicators monitored by water sampling from Crisul Repede
River

Physico - chemical	U.M.	СМА	Co	ncentratio	Interpretation		
indicators			2012	2013	2014	2015	
Temperature	⁰ C	< 35	(6÷	(3 ÷	(5 ÷	(6÷	_
	C		30)	30)	28)	30)	
Residue filtered at 105°C	mg / 1	700	(93 ÷ 210)	(89 ÷ 168)	(90 ÷ 150)	(92 ÷ 177)	Sub PA
рН	Unit pH	(6,5 ÷ 8,5)	7,4	7,4	7,5	7,6	Sub PA
CCO - Cr	mg/l	70	sldd	sldd	sldd	sldd	-
	(1	COO	(13,6	(15,2	(0,6÷	(18,9	
Sulphates	mg/l	600	÷ 56,4)	÷ 45,3)	1,8)	÷ 48,1)	Sub PA
Chlorides	mg/l	300	(3,0÷	(2,5 ÷	(1,9÷	(1,8÷	Sub PA
Cinorides	1116/1	500	7,5)	7,8)	28,9)	8,0)	540171

Following the results of the specific analyses for the quality indicators determined for water samples, it can be seen that the impact of the industrial activity on the water surface, in this case of Crişul REPEDE, is insignificant. This was mainly due to measures to protect the water sources provided by each economic objective in the studied area. Significant variations were observed in the values of the parameters analyzed according to the sampling site and its vicinity, but also the sampling period, without exceeding the alert threshold.

C. Environmental factor: soil

In order to highlight the approach of the current study regarding the reference to the soil environmental factor it can be observed in the physicochemical determinations of the monitored parameters during the period 2012 -2015.

	period 2012 -2015								
Physico - chemical indicators	U.M.	Alert thresholds	2012	2013	2014 sem I	2014 sem II	2015 sem I	2015 sem II	
	Unit								
pН	pН		6,94	7,8	7,8	7,9	7,1	7,6	
	mg/kg								
Total HAP		25	0,08	0,09	0,07	0,08	0,04	1,48	
Sulphates	mg/kg	5.000	310,8	2317	1450	1370	975	437	
Lead	mg/kg	250	16,5	32	17,3	16,7	15,3	17,2	
Cadmium	mg/kg	5	0,45	0,63	0,87	0,78	0,86	0,79	
Chromium total	mg/kg	300	24,3	39,5	20,9	22,5	22,6	27,8	
	mg/kg								
Chromium 6+		10	0,72	0,01	0,01	0,01	0,01	0,01	
Nickel	mg/kg	200	11,7	12,8	17,9	17,2	18,1	17,2	
Mercury	mg/kg	4	0,01	0,05	0,05	0,05	0,05	0,05	

The physico-chemical determinations of the monitored parameters during the period 2012 -2015

Table 8

Soil quality integrates a number of features such as ability to perform functions within the ecosystem or geosystem, potential in maintaining biodiversity as well as water, air, nutrient cycle.

Soil, as well as air and water, is an environmental factor with a particular influence on health. The formation and protection of water sources, both surface and especially the underground ones, depend on the quality of the soil.

The determined values were compared with the reference values for the heavy metal content in the soil, for less vulnerable lands, according to Order 756/1997.

There were no exceedances of the following indicators: Sulfates, total HAP, Pb, Cd, Total Cr, Hexavalent Cr, Mercury and Ni, compared to

the alert and intervention thresholds provided for by Order 756/1997 for less vulnerablel lands.

The conclusion is that, following the analyses carried out, the area with the highest values of the metal concentrations in the soil are the squares and soils under the impact of the heavy traffic and the Industrial Park 1 area.

CONCLUSIONS

From the comparison of the concentrations obtained from the measurements using the norms established by the air quality law, it results that no exceedances have been recorded. Nevertheless, the values of the SO_2 and PM_{10} concentrations were quite high and were mainly due to the heat and electricity industry. The analysed pollutant concentrations would significantly decrease with the closure of the old Combustion Plants.

As a result of monitoring the quality of Crişul Repede, the main source of surface water present in the analyzed industrial area, we have noticed an insignificant negative influence on its quality of the economic activity carried out in this area.

It is noted that in the Industrial Park 1 area, during the soil monitoring period, there were no significant emissions on the soil over the years. The soil quality in the Industrial Park 1 could be influenced by the activity of CET I, which interfered with the influence areas of other potentially polluting industrial activities such as the Alumina Factory (ALUMINA), organic compounds factory (SINTEZA), the Sugar factory, etc.

REFERENCES

- 1. E. Boeker, R. van Grondelle, 2011, Environmental physics : sustainable energy and climate change, ISBN 978-0-470-66675-3
- D. Borota, Mona Costea, 2000, Poluarea aerului. Editura Univ. din Oradea, ISBN 973-8083-23-0
- 3. M. Costea, 2014, Analiza statistică pentru științele mediului, Editura Univ. din Oradea, ISBN 978-606-10-1457-6
- 4. Huang F, Wang XQ, Lou LP, Zhou ZQ, Wu JP, 2009. Spatial variation and source apportionment of water pollution in Qiantang River (China) using statistical techniques. Water Research 2009;44:1562-72
- Ionescu C.A., Laura Roxana Popovici, Simona Roxana Georgescu, Dorina Mocuta, Cinel Malita, M. Burlibasa, 2009, *The quality of human life from the perspective of sustainable development*, METALURGIA INTERNATIONAL, vol.XIV Special Issue No.2, Editura Științifică F.M.R.,București, http://ebookbrowsee.net/me/metalurgia-international
- Y. Liu, B.H. Zheng, Q. Fu, L.J. Wang, M. Wang, 2012. The Selection of Monitoring Indicators for River Water Quality Assessment. Procedia Environmental Sciences 13, 129 – 139 1878-0296.

doi:10.1016/j.proenv.2012.01.013 Available online at www.sciencedirect.com Procedia Environmental Sciences Proceding

- 7. D. Mocuta, 2017, Influence of the Climate changes on the human life quality, in rural areas, Revista de Chimie, <u>http://www.revistadechimie.ro/</u>
- G. Neață, Elena Stoian, Dorina Mocuța, Georgeta Temocico, Gina Fîntîneru, Mihaela Georgescu, 2013, Nitrates and nitrites as source of n-nitroso compounds, Romanian Biotechnological Letters, Journal Volume: 18, Issue: 5, 2013, www.rombio.eu.
- 9. Richard S., Arnoux A., Cerdan P., 1997, Evolution in physico-chemical water quality in the reservoir and downstream following the filling of Petit-Saut dam, Hydroécol. Appl., Tome 9 Vol. 1-2, 57-83
- Romocea Tamara, Pantea Emilia, Oneț Aurelia, Oneț Cristian, 2016. Influence of dam building on surface water quality. Case study Analele Universității din Oradea, Fascicula Protecția Mediului Vol. XXVII
- 11. Romocea T., 2009, Chimia și poluarea mediului acvatic, Editura Universității din Oradea
- 12. Romocea T., 2011, Practicum pentru determinarea calității apei, Editura Universității din Oradea
- 13. Vega M, Pardo R, Barrado E, Deban L. Assessment of seasonal and polluting effects on the quality of river water by exploratory data analysis. Water Research 1998;32:3581-92
- 14. J. Seinfield, 1986, Atmospheric chemistry and physics of air pollution, publisher: wiley-blackwell ISBN-13: 978-0471828570
- 15. SIDU, Strategia Integrată de Dezvoltare Urbană a Municipiului ORADEA, 2017, Available online at http://www.oradea.ro/fisiere/module_fisiere
- 16. http://apmbh.anpm.ro/ro/rapoarte-anuale