INFLUENCE OF CLIMATE CHANGE ON AQUATIC ECOSYSTEM CONTAMINATED WITH TOXIC SUBSTANCES ORIGINATING FROM HISTORICAL MINING ACTIVITIES

Ana-Maria REŞETAR-DEAC[1], Elena DIACU[2]

The main purpose of this study was to establish the link between the transport of heavy metals (Ni, Cr, Mn and Fe) in the surface waters of a mining area located in Romania and climate change during four successive years. The heavy metals concentration values were high, in the sequence: Fe>Mn>Ni>Cr. A comparison between the variations of rainfall of 2011-2014 period recorded in the studied area and the climatological norms of 1961-1990 was performed. The Gaussian index of 0.073 was calculated, leading to the fact that 2011-2014 was a period of excessive drought, when the sampling campaigns were conducted with difficulty.

Keywords: climate change, contaminated surface water, mining activities

1. Introduction

Life on earth depends on a clean and healthy water environment. With the development of human society, has become clear that human activity affects the environment and is, in turn, influenced by it [1]. Water Directive 2000/60/EC of the European Parliament and of the Council stipulated that: "water is not a commercial product like some, rather, a heritage which must be protected, defended and treated as such." Therefore, the water policy must be coherent and efficient, and to take account of the vulnerability of aquatic ecosystems, otherwise their equilibrium will be negatively influenced [2].

Climatic changes registered in recent decades have been the main cause of the increase of the global temperature with $0,5^0$C in the 20th century, in this way it was intimated that the present climate is quite different from that of the past. Research studies on the atmospheric deposition of dust and greenhouse gas emissions bring comprehensive data on climate changes and their consequences on the planetary waters. As a result of disturbance of the planet climate has sparked numerous catastrophes, such as the persistent drought, which causing

[1] PhD student, Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: ana6209@yahoo.com
[2] Prof., Faculty of Applied Chemistry and Materials Science, University POLITEHNICA of Bucharest, Romania, e-mail: elena_diacu@yahoo.co.uk

large fires in some regions of the globe, or floods (rainfall) in others, and also a different distribution of environmental pollution.

As a consequence in the latest period, in Romania territory were recorded either flooding accompanied by landslides or long periods of drought that affected agricultural and forest ecosystems, situation attributed to massive cutting of large areas of forest, through deforestation or irrational exploitation.

It is well known that there is a close relationship between temperature and rainfall, at higher temperature the amount of rainfall is increasing. If this is not uniformly distributed, generates conditions of drought in some areas, which will lead to major imbalances that will decisively change the structure and dynamics of ecosystems, including the distribution of environmental pollutants [3].

The issues related above regarding environmental transformation influence also the surface water contamination with unpredicted effects on the human health on short and long term. First, there can be included the agriculture, which is without any doubt, the most affected by climate change [4-8].

Changes in rainfall regime are much stronger in those regions affected by mining activities, where there is a high level of heavy metal contamination, in the last period, metal type contaminants receiving special attention due to its persistence, biochemical recycling and risk to the environment [9-12].

Because in mining there are diffuse sources of pollution with heavy metals, small rivers are natural receptors, which play a critical role in the transport of metals to other river systems. Due to the diffuse nature of the contamination, metals can be transported and deposited in the form of particles in the banks and floodplains at distances of hundreds of kilometers of mining area, there is a direct correlation between the pollutant transport rate and abundant rainfall [13-15].

In the contaminated sites a series of chemical processes can take place. The precipitation of metal sulfides can act as a "sink" for metal contaminants. Metals such as lead, zinc and copper may co-precipitate or adsorb with iron mono-sulphide and may also precipitate directly as distinct phases. Although, in general insoluble, the relative solubility of different metals sulfides ranging from largest to smallest: manganese sulfide (MnS) > mono-sulphide (FeS) > nickel sulphide (NiS) > sphalerite (ZnS) > cadmium sulphide (CdS) > galena (PbS) > copper sulfide (CuS) > pyrite (FeS2). Metal Sulfides are highly resistant to the effects of the desorption process. However, when the sediment is re-exposed to the dissolved oxygen, the oxidized metal sulphide could be a secondary source of trace metal contamination. Pyrite is reported to be thermodynamically more stable and more resistant to oxidation than amorphous precipitates mono-sulphide-type, although the environmental consequences regarding oxidation are more severe.

The freshly precipitated metal oxides and sulfides may be more “reactive” (more adsorbent and prone to dissolution when conditions change) than older crystalline forms. Fluctuations at the oxic-anoxic interface brought about through changes in the frequency and duration of flood and drought episodes may therefore influence the reactivity of secondary minerals [13, 16].

Studies on toxic contaminants response in surface water due to climatic factors are reported increasingly in the last years. The authors of these studies have shown that each contaminant behave differently to climate change [17-20].

This paper presents a study regarding the influence of climate change on aquatic ecosystem contaminated with toxic substances originating from historical mining activities in the northwestern Romania.

The objectives of this paper were: (I) selection and monitoring of chosen area historically contaminated with metals due to closed mining activities and located near surface waters with national and international importance; (II) link assessment between metals transport in Socea Valley, with a background of anthropogenic contamination of more than 20 years and climate change occurring in a period of four years (2011-2014); (III) presentation of climatological changes of parameters (precipitation-monthly average values) in the period 2011-2014, recorded at Satu Mare weather station, Romania, in respect to the 1961-1990 climatological norm.

2. Experimental

2.1 Investigated area description

The location map of the studied area was performed using ArcGIS Explorer Desktop platform and represents the north-western part of Romania, which is an area with a long tradition in the field of mining with consequences on the quality of the environmental. Specifically, the study was conducted in the mining perimeter Socea, Tarna Mare Commune, Satu Mare County (Fig. 1).

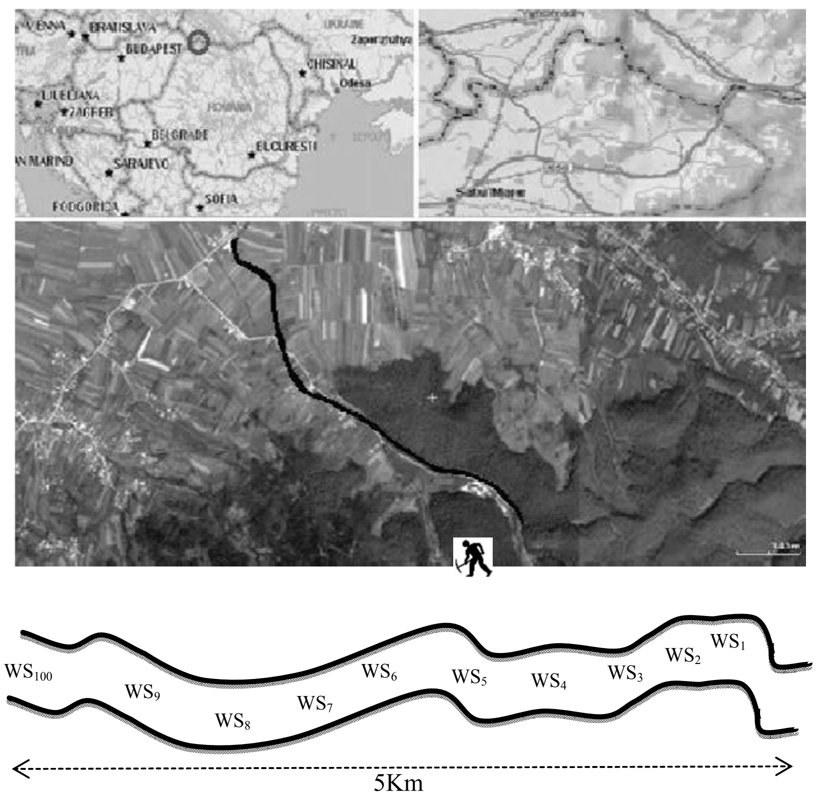


Fig.1. Mining area map and location of sampling points

The selection of sampling points was based on concern of the spread of toxic pollutants identified at large distances from the source through surface water outside the Romanian borders [21].

The climate, being temperate-continental in this region, with warm summers and high rainfalls, has to be considered as an essential factor in the influence on distribution of pollutants in respective aquatic environment. Generally, in the County of Satu Mare, the average annual rainfall totals a quantity of 600-700 mm in the plain region, over 800 mm in Culmea Codrului and over 1000 mm in mountainous region. Extreme temperatures - the highest being the 39-40°C, registered in August 1952 at Carei (absolute maximum), and the lowest, of 30.4°C recorded at Satu Mare in December 1961 (absolute minimum). In the territory of Satu Mare County, water courses of the Tisza basin have a length of 429 km and an area of 1327 km^2. In evaluating of the distribution of pollutants for studied area, it also must be also taken into account that in the period 1978-1981 were landscaped the streams Bătarci, Tarna Mare, Tarna Mică and Dobruța, courses that are part of the Tisza basin [22].

2.2 Water sampling

10 surface water samples were collected from the Socea Valley, which is the nearest water from the pollution source. Sampling points were selected from the mining area toward to downstream until near the human settlements, according to the sampling points shown in the map in Fig.1. For each sampling point, three replicates of water sample have been taken and stored separately in metal-free 2L polypropylene recipients. The sampling recipients were washed thoroughly to remove impurities that may distort the sample composition. The washing was done, first, with detergent solution, and then rinsed thoroughly with tap water, distilled and double distilled water. The sampling campaign took place in the period of 2011-2014, in different days between the 15 and 20 of August, for each year of assessment.

To maintain all characteristics, water samples were subjected immediately to preservation by acidification with nitric acid, and transported to laboratory in order to be analyzd in respect to the content in Ni, Cr, Mn, and Fe.

All water samples were carried out according to the methodologies specified by SR EN ISO 5667-1:2007 Water quality. Sampling. Part 1: Guidance on the design of sampling programmes and sampling techniques, SR EN ISO 5667-3:2013 Water quality. Sampling. Part 3: Preservation and handling of water samples.

Water samples (WS) were identified as follows: WS_1 - in the vicinity of mining perimeter, WS_2 - 50 m from the source, WS_3 - 500 m from the source, WS_4 - 1 km from the source, WS_5 - 1.5 km from the source, WS_6 – 2 km from the source, WS_7 - 2.5 km from the source, WS_8 – 3 km from the source, WS_9 – 4 km from the source, WS_{10} - 5 km from the source (Fig.1)

2.3 Materials and methods

All solutions were prepared using double distilled water and the reagents were of analytical purity, nitric acid 65% being purchased from Merck.

The analysis was performed by a VARIAN AA240 flame and furnace atomic absorption spectrometer, using the standardized methods depicted in Table 1. The pH was determined "on site", being performed with a CONSORT C830 portable multi-parameter, able to measure both the temperature in the range 0...100^0C and also the conductivity between 0...100 mS cm^{-1}.

Table 1

Standardized methods used to determine the pollution with metals

Element	Used Method	
	Index	*Title*
Ni	SR ISO 8288:2001	Water quality. Determination of cobalt, nickel, copper, zinc, cadmium and lead. Flame atomic absorption spectrometric methods
Cr	SR EN 1233:2003	Water quality. Determination of chromium. Atomic absorption spectrometric methods
Mn	SR 8662-2:1996	Water quality. Manganese determination. Spectrometric method of atomic absorption
Fe	SR 13315:1996	Water quality. Iron determination. Spectrometric method of atomic absorption

3. Results and discussion

The fact that climatological changes can have a significant contribution to the transportation/distribution and loading of surface waters with heavy metals is evidenced from the representations of Fig. 2-5, that have been carried out by using OriginPro 8.6 software. The data sets were obtained by calculating the average metal concentration of the three replicates samples at each sampling point (results were expressed in µg of metal per L).

3.1. Influence of climatology on heavy metal distribution

The relationship between the air temperature and rainfall is shown in Fig. 2, where it can be seen that the rainfall rise when the temperature rises. This dependence is more evident at the average high temperature (34.15^0C), when for rainfall the average value was high (2.5 mm), and at the average minimum temperature (14.65^0C) when the rainfall was low (0.3 mm). For temperature, it took into account the average daily temperature and for the rainfall, the daily average rainfall from 15 to 20th of August in the four years (2011-2014) of the present monitoring period. In this study, the meteorological data source comes from the site "Weather Underground", free for the public since 1993 [23].

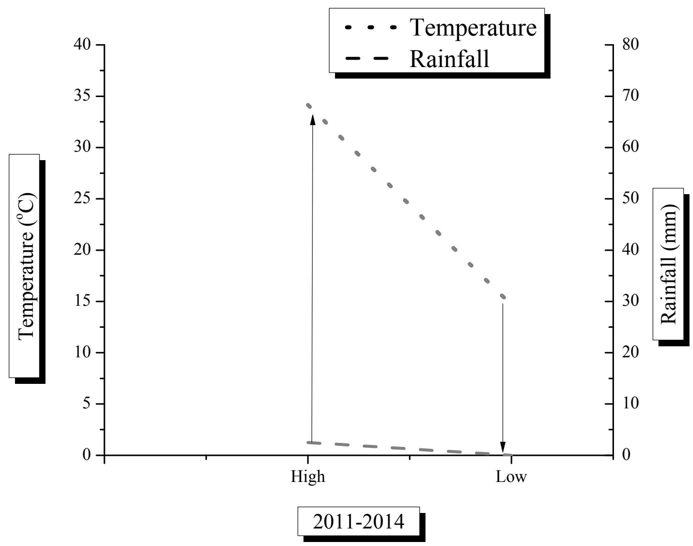


Fig. 2. Ombrothermic diagram - dependency of average air temperature and precipitation averages over the period of 15-20 of August, 2011-2014 period

Fig. 2, also known as ombrothermic diagram, correlates in a minimal way two main climatic factors (temperature and rainfall) by the Gaussen index expression. So if the ratio $p/t < 2$ (where *p* is precipitation and *t* is temperature) within a certain time of year, it is considered dry [24]. In order to achieve the ombrothermic diagram have used the scale of temperature and precipitation values in the ratio of 1:2. The Gaussen index was calculated and the obtained value was 0.073 (in the case of maxima), leading to the fact that there has been a period of excessive drought. Due to this fact the sampling campaigns were conducted with some degree of difficulty because the water surface depth was very low (below 20 cm of water surface).

Diurnal variations (from day 15 to day 20, D_{15}-D_{20}) of the average temperature registered during the four sampling campaigns are depicted in Fig. 3 for each year. This analysis is based on climatological records hourly that highlights differences depending on the time of day and the spatial distribution of the survey points (here the Satu Mare weather station). In general, the highest values of the trend are recorded in the course of the day, between 12 and 18 GMT, followed by those registered in the morning and at night. The samples were taken between 4.00-6.00 PM.

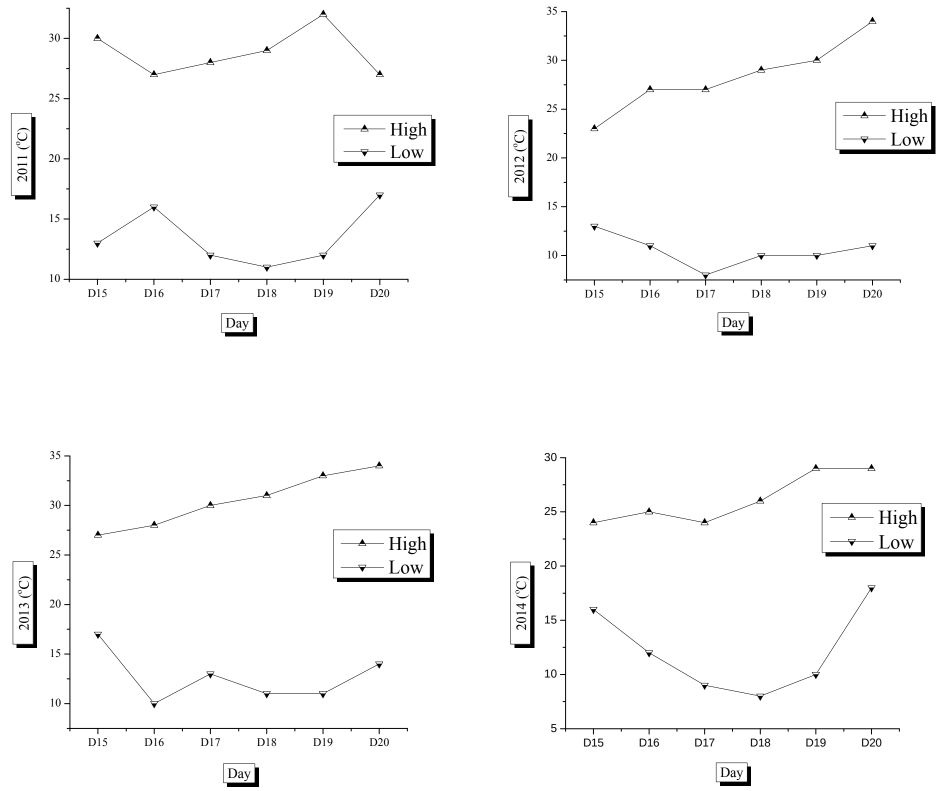


Fig. 3. Daily variations in the average daily temperature recorded during performance of the four sampling campaigns

Compared to the 1961-1990 climatological norm (ANM source - National Administration of Meteorology), in Fig. 4 it was analyzed the main climatological parameters trend – precipitation, in August 2011-2014 period.

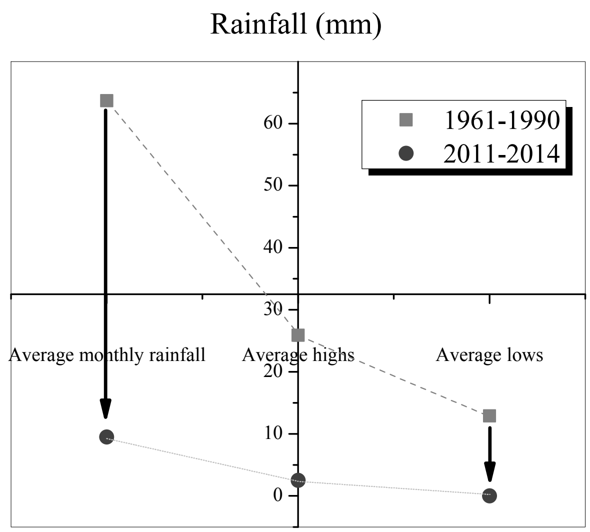


Fig. 4. Climatological parameters main trend - rainfall - in the period 2011-2014 compared to the climatological norm 1961-1990

Thus, it appears that the monthly average rainfall as well as the maximum and minimum a major decreasing trend compared to the climatological norm. This trend has led to conclusion that during the monitored period and region was recorded for drought.

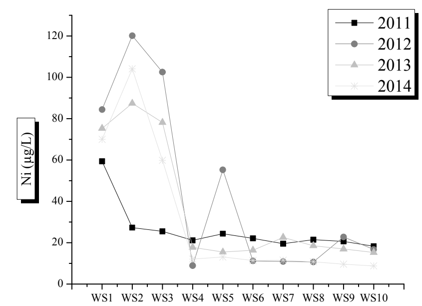
3.2 Heavy metal distribution trend

Starting from the conclusion of the study on the variation of precipitation for 2011-2014, the trend of distribution of heavy metals in surface water in the area mentioned above was established. The concentration for the four metal ions: Ni^{2+}, total Cr (Cr^{3+} + Cr^{6+}), total Mn (Mn^{2+} + Mn^{7+}) and total Fe (Fe^{2+} + Fe^{3+}) were determined and their variation during 2011-2014 was represented. From Fig. 5.a it can observe a large variations in the concentration of nickel in water samples from points WS_2 and WS_3, while for the other sampling points nickel concentrations did not vary too much. For manganese (Fig.5.b) there was not found significant variation for the four years. This behaviour could be explained because the manganese was found in high concentrations and at higher concentrations, more than 200 μg/L, in the presence of oxygen, the manganese can precipitate in the form of oxides.

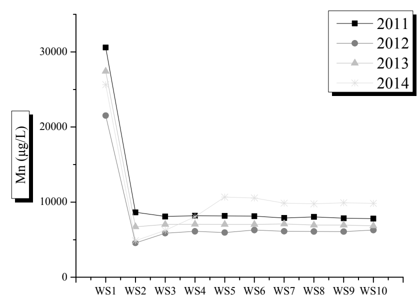
However, in Fig. 5.c it was found the opposite of the variation referred to Ni^{2+}. The concentration variation of total Cr was present downstream of point source, starting from the WS_4 to WS_{10}.

It can be said that there is an equal distance between the four sampling campaigns.

Maximum concentration values obtained experimentally were in 2012. Year in which, during the sampling period the biggest differences noticed was between day/night, reaching up to 23^0C difference (minimum 11^0C, maximum 34^0C in 20 August at 6.00 PM).



a)



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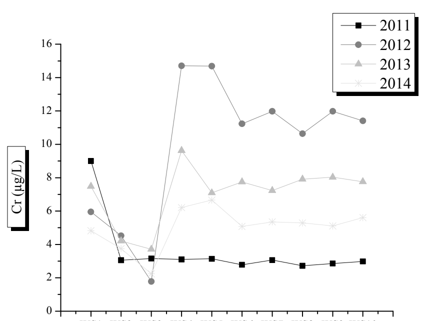
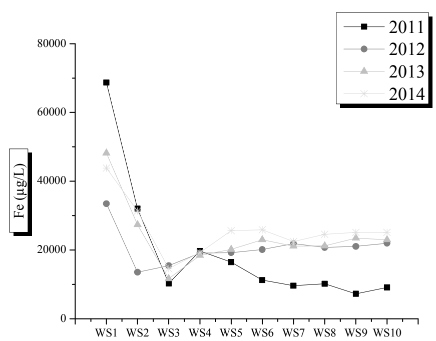


c)



d)

Fig. 5. Variation of the metal ions concentration monitored over four consecutive years: a) Ni, b) Mn, c) Cr, d) Fe

For Fe was found a difference between 2011 and the rest (2012-2014) with the highest concentration around the source WS_1 reaching close to the value of 70000 µg/L, which falls heavily to WS_3 and then downstream to WS_{10} which does not show significant variations (Fig. 5.d).

The ferruginous acid discharges have made their mark in the content of surface water, which pose significant changes: high turbidity, rusty color, taste-smell modified and especially an acid pH. For the 10 samples analysed, water pH values were framed within 2.5 and 6.5.

3.3 Climate-metal relationship

As outlined above, the concentrations values of selected metals are high in the period of drought around the source, limiting the transport of contaminants in the surface water. Thus, for the four metals assessed, in sample WS_1 were found the following maximum concentration values: 84.4 µg/L Ni (2012), 9.0 µg/L Cr (2011), 30588.0 µg/L Mn (2011), and 68705.0 µg/L Fe (2011). Therefore, the research results indicate that climate change can affect both the water quantity and quality, including the water level, temperature and pH value.

However, in this study cannot be provided experimental data relating to periods with intense precipitation, when it is assumed that the metals accumulated over the years in the sediment and those deposited on shore or soil are carried, so that the quantities of toxic elements increase in surface water. Worrying is the fact that the water of the Socea Valley is maintained at a high level of contamination that affect the environment and nearby population both at present and in the future.

4. Conclusions

The results of this study reveal that, in years 2011-2014, the north-western part of Romania, more precisely, Tarna Mare Commune is experiencing a prolonged severe drought. Issue that has led to a decrease in groundwater levels - the drying up of wells and surface water. Low waters adversely affect the prediction of the metal pollutants concentration along the course of the Socea Valley..

Regarding to the four selected metals, it was observed a uniform variation of concentration (the shape of the graph can be associated with the letter L), with the exception of chromium to which there are annual fluctuations. Environmental data obtained may bring a substantial contribution to the development of an integrated monitoring for the region studied. The hydrological changes increase/decrease the processes of pollutant transport strongly influencing the environment away from the contamination source. Because of these sudden climate changes (diurnal and annual differences in temperature/precipitation) the pollution degree is different every year.

The study showed the persistence of metals Ni^{2+}, Cr^{3+}+Cr^{6+}, Mn^{2+}, Fe^{2+} and Fe^{3+} in surface waters, metals from acidic water drainage from abandoned mines in relation to meteorological variations.

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