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# INFLUENCE OF ANTHROPOGENIC ACTIVITY TO THE MACRONUTRIENT LOADING IN WATER AND SOIL - CASE STUDY OF INDUSTRIAL AREAS

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**Abstract:**

Mining activities, in combination with accelerated urbanization growth and climate change, constitutes a major challenge for creating a sustainable development. Thus, the monitoring and assessment of mining effect is mandatory in understanding the impact on the primary physico-chemical characteristics of an environment. In this context, the paper presents the evolution of micro- and macro- nutrients in water, soil and sediment from two industrial areas from Romania (Copșa Mică industrial platform and Baia Sprie mining zone), in order to assess the impact of pollutants on ecosystems. Physico-chemical (pH, $NH_4^+$, $NO_3^-$, $NO_2^-$, TN, TP), base cations (Ca, Mg, Na and K) and micronutrients (Fe, Mn and Zn) have been analyzed in order to evaluate the quality of the environment. For some of the analyzed soils, the concentration of Zn, Mn and Fe exceeded the maximum permissible limits (MPL) imposed by the Romanian legislation, falling within the limit for Alert Thresholds for less sensitive soils. The correlation analysis on water quality parameters revealed that all parameters are more or less correlated with each other Person's Correlation matrix. Overall, our results demonstrated that the knowledge of the physico-chemical regime of an environment is of great value in the determination of its productivity, usefulness and other characteristics which can facilitate further vegetation restoration and reconstruction and a sustainable development of the ecological environment in a polluted area.

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## 1. INTRODUCTION

Water, an inexhaustible resource, is the basis of life on the planet with a radically influence on the life cycle and biodiversity (Goher, Ali and El-Sayed, 2019). Therefore, its mineral content is very important, especially when it is exposed to different pollutants (gases and particulate) due to the continuous worldwide urbanization and industrialization (Arefin et al., 2016). This development is unfortunately difficult to control and thus the pollution caused by both greenhouse gases from atmosphere and particulate matter deposited onto ground and trees affect the ecosystem (Satyanarayana et al., 2010). In this context, controlling the water quality from different sources to better understand the contribution of human activities, but also the influence of rainfall, can be a reliable solution for establishing appropriate solutions to reduce pollution and, consequently, mitigate the effects of industrialization. Rainfall water composition is also a significant source of data for assessing the impact of acid deposition on the ecosystem (Satyanarayana et al., 2010).

When discussing on terrestrial ecosystem, the investigation of soil quality is as representative as that of water, since its pollution poses a risk to human health through the soil-crop chain. Soil acts as a filter that retains pollutants from the water, as well as deposits/dust from the atmosphere, which can negatively change its properties by the appearance of the process of mineralization and accumulation (Sponza and Karaoglu, 2002).

The main pollutants encountered in water and soil are the heavy metals, which are toxic and cannot be easily removed from environment. They are continuously accumulating in living organisms, including human body, causing serious diseases (Goher, Ali and El-Sayed, 2019; Harrison, 2001; Paul, 2017; Xu et al., 2018; Azizullah et al., 2011; Fand et al., 2018; Wu et al., 2016). Nevertheless, within some limits, metals such as zinc, iron, copper and manganese, are essential for plant growth and for animal nutrition and human health (Abdu, Abdullahi and Adulkadir, 2017).

The source of this type of elements which are easily spread through air and water is diverse, from industrial activity, farming practices and/or municipal wastes. Acidic rains have also a high contribution to heavy metals spreading through decomposition of contaminated soil (Bagul et al., 2015). Thus, the elemental composition of soil, sediments and water can provide information regarding the migration and behavior of toxic elements in the environment (Iordache et al., 2020).

On the other hand, nutrients content of water and soil is decisive for plants/tree growth having a critical role in the development (enlargement) of forested area which increased with 11 million hectares, from 1990 to 2010, in Europe (Fact Sheets on the European Union, 2020). This aspect is very important due to the influence of forest on the global climate, by storing carbon dioxide and by avoiding soil erosion.

Therefore, cross-correlation maps of water and soil quality were developed by research community as reliable tools to assess the environmental impact of anthropogenic activities, including industry, by supplying data regarding the relationships between water/soil quality parameters and different pollutant sources (Wang et al., 2019). Such a study, conducted in 2018 by the scientists Deng, Ye and Liu, highlighted the significant spatial variation of water quality in rivers due to the differences in catchment characteristics, in terms of industrial development and urbanization (Deng, Ye and Liu, 2018). They explored the spatial and seasonal pattern of nutrients and heavy metals in river waters as quality indicators, emphasizing the impact of dilution effect caused by rainfall and flooding to their concentration. By chemometric analysis based on water quality parameters (80.87% of the total variance), they showed that the main sources of nutrients are the domestic and industrial wastewaters, while industrial activities enrich the water with heavy metals (Deng, Ye and Liu, 2018).

Starting from the foregoing considerations, this paper focuses on evaluating the contribution of certain industrial areas in Romania, namely Copșa Mică and Baia Sprie, well known for their metallurgical activities, on water and soil contamination in the area. The achieved results by examining various environmental samples (soil, water and sediments) provide us useful information for assessing the impact of pollutants to the ecosystems. Hence, having an overview of the impact of anthropogenic activities on the environment and by understanding (evaluating) the migration of pollutants in different natural compartments, measures can be found to remedy and/or prevent "accidental pollution".

## 2. MATERIALS AND METHODS

### 2.1. Study area

For this study, samples of groundwater, surface water, soil and sediments were collected from an area with a history of over 60 years in the industrial activity with non-ferrous metals, namely Copșa Mică industrial platform and Baia Sprie mining zone. The pollutants dispersion is governed by the local climate, one of the most important vectors being the wind regime of the areas that is influenced by the land orography.

The city of Copsa Mica had the reputation of being the most polluted city in Europe until the Chernobyl nuclear accident. This was due to emissions from two factories in the area:

*(i)* CARBOSIN SA, founded in 1935 to produce carbon black from methane gas, and shut down in 1993; its emissions have affected an area of over 20 km in length and almost 6 km in width, leaving traces of ash on houses, trees, animals and the rest. These traces are still visible today.

*(ii)* SOMETRA SA, the other source of pollution, less visible but much more serious in terms of impact on the health of locals. Smelter emissions have contributed to the high incidence of lung cancer and impotence, and a life expectancy nine years lower than the national average. Activity profile: production of lead and zinc from mining concentrates, with the capitalization of other metals, respectively antimony, bismuth, silver and gold.

The second site selected for this study, Baia Sprie, is a mining zone situated in northern Romania, near the Baia Mare town. It is recognized as a “hot spot” in Europe with respect to Cd, Cu, Pb, Zn and As pollution (Cordos et al., 2007). In the east side of Baia Mare city are also located three large ore processing plants (Cupro Company, Romplumb Company and a Flotation facility) and several decantation ponds around the town, representing the most important sources of soil and groundwater pollution.

### 2.2. Sample Collection and Pre-treatment

To assess the influence of selected industrial platforms to the environment, samples were collected from the groundwater, surface water, sediment and soil. The sampling period was during December 2019 – January 2020, from two contaminated areas (see Table 1).

**Table 1.** Sample locations

| **Matrix** | **Sampling Location/Sample Code** | | | |
|---|---|---|---|---|
| | *Copsa Mica* | | *Baia Sprie* | |
| Groundwater | $A1_{CM}$ | $A2_{CM}$ | - | |
| Surface water | $A3_{CM}$ | $A4_{CM}$ | $A5_{BS}$ | |
| Soil | S1-$I_{CM}$ *at 0-20 cm* | S1-$II_{CM}$ *at 20-40 cm* | S2-$I_{BS}$ *at 0-20 cm* | S2-$II_{BS}$ *at 20-40 cm* |
| Sediment | $S3_{CM}$ | | $S4_{BS}$ | |

Water (surface and groundwater) and soil samples were collected and analyzed according to standard sampling guidelines (SR EN ISO 5667-1, 2007). Water sampling was made in clean glass bottles, which were previously rinsed with deionized water and stored to the laboratory for up to 24 h, at 4°C, to retard the microbiological activity as well as the rates of possible physical and chemical reactions. Soil was sampled at depth of 0–20 cm and 20–40 cm; before analysis the soil samples were air-dried, homogenized and then passed through a 20-mesh sieve to obtain very fine particles (MO, 2002).

### 2.3. Analytical procedure

#### *2.3.1. Basic physico-chemical indicators*

Soil pH was potentiometrically measured in $H_2O$ at the ratio soil: $H_2O$ of 1:5 using a pH meter standardized with known buffer solutions. For water samples, the pH measurement was performed at the sampling site.

For anion extraction ($NH_4^+$, $NO_3^-$, $NO_2^-$, TN, TP), the soil samples were extracted into water as follows: air-dried soil samples (10 g) were weighed into 100 ml specimens and 50 ml $H_2O$ was added. The samples were stirred for 15 min and filtered through filter paper into a vial.

The nitrate ($NO_3^-$), nitrite ($NO_2^-$) and ammonium ($NH_4^+$) concentrations in water and soil samples were determined by colorimetric method, using a UV-VIS spectrophotometer type SPECORD 250. The quality control analysis has been tested using Certified Reference Material. The total nitrogen (TN) and total phosphorous (TP) were determined through the measurement of absorbance value, using the UV-Vis spectrophotometer DR3900 (Hatch, Dusseldorf, Germany).

All chemicals and reagents used during the study were of spectroscopic grade; the multielement standard solution CertiPur, with a certified value of 1000 ± 3 mg/L, obtained from Merck (Germany) was used in the quantitative analysis for the calibration curve. Ultrapure water, having a maximum resistivity of 18.2 MΩ/cm, was used for sample treatment and dilution. All the investigated calibration curves were characterized by a high correlation coefficient ($r>0.995$).

#### *2.3.2. Elemental analysis (Ca, K, Mg, Na, Fe, Mn and Zn)*

For cations and micronutrients determination, the soil samples were extracted for exchangeable Ca, K, Mg, Na, Fe, Mn and Zn, using 1 mol/L (M) ammonium chloride ($NH_4Cl$) as follows: air dried soil samples (2.5 g) were weighed into 50-mL test tubes, and 25 mL of 1 M $NH_4Cl$ was added. Samples were shaken for 30 min. After centrifugation the supernatant was filtered through filter paper into a volumetric flask. For the microwave acid digestion procedure, an aliquot of sample to be digested (~1 g) was placed in a clean Teflon digestion vessel. Then, 7 mL concentrated nitric acid (65%) and 21 mL hydrochloric acid (37%) were added. The vessel was closed, placed into the rotor, followed by digestion using a three step temperature program, namely (*i*) power 400 W, ramp 10 min, pressure 35 psi, temperature 160 °C, hold 5 min; (*ii*) idem as (*i*) ; and (*iii*) cooling. After the digestion process, each digest was transferred quantitatively with ultra-pure water to a 50 mL volumetric flask.

Ca, Mg, Na, K, Fe, Mn and Zn concentration determination in water and soil samples was carried out using flame atomic absorption spectroscopy (AAS). Atomic Absorption Spectrophotometer (AAS) NOVAA 300 model with Air-$C_2H_2$ flame type of an average fuel flow rate of between 0.8-4.0 L/min and the support gas flow rate between 13.5-17.5 L/min was used for sample analysis. Hallow cathode lamps of the different metals were used as the radiation sources and the analytical measurements based on time-averaged absorbance.

Resonance lines at 422.7, 285.2, 589.0, 769.0, 248.3, 279.5 and 213.9 nm were employed for Ca, Mg, Na, K, Fe, Mn and Zn. Lamp intensity of 4 - 6 mA and band pass of 0.2 - 0.5 nm were used according to the equipment manufacturer's recommendations. Air/acetylene flow rates were between 0.9 and 1.1 L/min for all the metals. Prior to each series of measurements, a calibration line was created for each element.

## 3. RESULTS AND DISCUSSION

To assess the quality of water and soil around the two selected locations, Copsa Mica and Baia Sprie, samples of groundwater ($A1_{CM}$, $A2_{CM}$), surface water ($A3_{CM}$, $A4_{CM}$, $A5_{BS}$), soil on two levels of depth ($S1\text{-}I_{CM}$, $S1\text{-}II_{CM}$, $S2\text{-}I_{BS}$, $S2\text{-}II_{BS}$) and sediment ($S3_{CM}$, $S4_{BS}$) were collected. The results of groundwater samples (Table 2) were compared with the normal values and thresholds set by the regulation (Law 311, 2004) on drinking water quality, while for surface waters and sediments with the legally prescriptions (MESDR, 2006) approving the norms regarding surface water quality classification, in order to determine the ecological status of water bodies. For soil samples the obtained data were compared with the legally prescriptions (MESDR, 1997).

**Table 2.** Physico-chemical characterization of water (groundwater and surface water) samples

| Sample code/ threshold | | Parameters | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *pH* | *N-$NH_4^+$* | *N-$NO_3^-$* | *N-$NO_2^-$* | *TP* | *TN* | *Ca* | *Mg* | *Na* | *K* | *Mn* | *Zn* | Fe |
| | | (upH) | (mg/L) | | | | | | | | | | | |
| Groundwater | $A1_{CM}$ | 7.47 | 0.035 | 0.79 | 0.09 | 0.181 | 5.64 | 99.20 | 19.20 | 42.90 | 1.31 | <0.05[a] | <0.05[a] | <0.2[a] |
| | $A2_{CM}$ | 7.73 | 0.074 | 9.73 | 0.005 | 0.169 | 35.55 | 207.2 | 65.52 | 73.75 | 62.39 | 0.065 | <0.05[a] | <0.2[a] |
| | MAC[b] | 6.5-9.5 | 0.5 | 50.0 | 0.5 | - | - | - | - | 200 | - | 0.05 | 5.0 | 0.2 |
| Surface water | $A3_{CM}$ | 7.77 | 0.0059 | 0.18 | 0.003 | 0.189 | 1.61 | 101.6 | 21.86 | 32.61 | 7.34 | <0.05[a] | <0.05[a] | <0.2[a] |
| | $A4_{CM}$ | 7.78 | 0.0026 | 0.41 | 0.004 | 0.289 | 1.98 | 129.8 | 37.14 | 30.97 | 3.27 | 0.063 | <0.05[a] | <0.2[a] |
| | $A5_{BS}$ | 7.16 | 1.65 | 0.134 | <0.02[a] | 0.14 | 2.78 | 36.61 | 7.06 | 16.66 | 2.83 | <0.05[a] | <0.05[a] | <0.2[a] |
| | 1st class[2] | 6.5-8.5 | 0.4 | 1 | 0.01 | 0.15 | 1.5 | 50 | - | 25 | - | 0.05 | 0.1 | 0.3 |
| | 2nd class[2] | | 0.8 | 3 | 0.03 | 0.4 | 7 | 100 | - | 50 | - | 0.1 | 0.2 | 0.5 |
| | 3rd class[2] | | 1.2 | 5.6 | 0.06 | 0.75 | 12 | 200 | - | 100 | - | 0.3 | 0.5 | 1 |
| | 4th class[2] | | 3.2 | 11.2 | 0.3 | 1.2 | 16 | 300 | - | 200 | - | 1 | 1.0 | 2 |
| | 5th class[2] | | >3.2 | >11.2 | >0.3 | >1.2 | >16 | >300 | - | >200 | - | >1 | >1 | >2 |

[a] *limit of quantification of the method (LQ)*;
[b] *maximum permissible concentrations according the Law no. 311/2004 for the amendment and completion of Law no. 458/2002 regarding the quality of drinking water*;
[c] *water quality classes according to the Order of Ministry of Environment and Sustainable Development of Romania, no. 161/2006, for the approval of the Norms regarding the classification of surface water quality in order to establish the ecological status of the water body.*

### 3.1. Groundwater and surface water

Two groundwater samples were collected for this study, a spring captured in the forest area located near the Copsa Mica industrial platform ($A1_{CM}$) and a well from the inhabited area ($A2_{CM}$). The registered pH values, of 7.47 and 7.73, falls within the one imposed by the national legislation (Law 311, 2004). Also, to both samples, for N-$NH_4^+$, N-$NO_3$, and N-$NO_2^-$, the resulted values were well below the limits imposed by the legislation for drinking water. Looking to data from Table 2, can be observed that for both samples, $A1_{CM}$ si $A2_{CM}$, concentration below the quantification limit were obtained for Zn and Fe and for Mn in sample $A1_{CM}$. A slightly higher value than the threshold was seen for Mn in sample $A2_{CM}$.

Table 2 highlights the content of macro- and microelements in the surface water samples from Copsa Mica ($A3_{CM}$ and $A4_{CM}$) and Baia Sprie (A5) areas. It was found that in

water samples from Copsa Mica area, the pH values were between 7.77 and 7.80, while for the sample collected in Baia Sprie area, a significantly lower value (7.16) was registered. Across the Copsa Mica catchment the surface water samples are slightly alkaline, versus the Baia Sprie sample that is neutral, a possible explanation being related to the fact that Baia Sprie area could be more affected by pollution compared to Copsa Mica. Most probably, the mineral nature of the soils and shallow rocks from this catchment, but also the substances resulted from human activity, induce changes in the pH value. Furthermore, the pH is one of the main factors that controls the bio-availability and chemical behavior of heavy metals and offers important knowledge and guidance for ecological environment protection and land re-use in polluted area.

To Copsa Mica area, the results showed a content of $N\text{-}NH_4^+$ ranging between 0.0026– 0.0059 mgN/L, $N\text{-}NO_3^-$, from 0.18 to 0.41 mgN/L, and $N\text{-}NO_2^-$, between 0.003 and 0.0035 mgN/L, all within the limits of the 1st class quality for surface water. TN and TP fall within the limit of the 2nd class quality for the analyzed points, with values between 1.61 and 1.91 mgN/L, and from 0.189 to 0.289 mgP/L respectively. Conversely, for water sample from Baia Sprie, the content of $N\text{-}NH_4^+$ falls within the limits of 4th quality class (1.65 mgN/L) while $N\text{-}NO_3^-$, $N\text{-}NO_2^-$ and TP fall within the limits of 1st quality class. TN falls within the 2nd quality class limit (2.7 mgN/L).

The macroelements Ca, Na, Mg, K, Mn, Zn, Fe from the analyzed surface water samples from Copsa Mica area, registered the following values: *Ca* with values between 101.6 and 129.8 mg/L, being assigned to the 3rd quality class, while Na with values between 32.61 and 30.97mg/L, falls within the limit of the 2nd quality class; Mg with values between 21.86-37.14 mg/L, K with values between 3.27- 7.34 mg/L, Mn with values between <0.05 - 0.0626 mg/L (1st and 2nd classes), Zn and Fe with values below the limit of quantification of the method (LQ) (<0.05 and <0.02 mg/ L, respectively). The macroelements Ca, Na, Mg, K, from the analyzed surface water sample from Baia Sprie area, registered a strong decrease towards Copsa Mica, presenting the following results: 36.61, 16.66, 7.06 and 2.83 mg/L, respectively, that may be caused by the toxic effect of Cu and Ni values registered in Baia Sprie, causing subsequently severe disturbances in nutrient uptake. Groundwater contains higher amounts of Ca and Mg versus surface water, yet with no significant differences between them in the case of Copsa Mica. This could be explained by the Baia Sprie enriched subsoil in these two cations, or rainfall water infiltration in the aquifer. The same behavior was observed for Na and K, presenting higher values in the groundwater versus surface water. The concentration of manganese in samples examined from Copsa Mica exhibited the concentration above the permissible value of 0.05 mg/L specified by the WHO. Manganese is a major constituent of ores and rocks that is widely naturally distributed. For the $A2_{\mathbf{CM}}$ sampling site, this exceeding could be due to the groundwater contact with dissolved soil, rock and minerals of manganese in the local aquifer or due to a possible leach of industrial effluents discharge into the soil, whereas the surface water Mn from Copsa Mica could be explained by a leachate from landfill and sewage deposited over time.

The physico-chemical characteristics of water bodies are key parameters in environmental health determination with direct influence upon quality and aquatic life sustainability when affected by pollution. Therefore, in order to determine the relationship between parameters, correlation analysis was performed revealing the existing interaction between a minimum of two continuous variables with values ranging between − 1 and +1 (Figure 1).

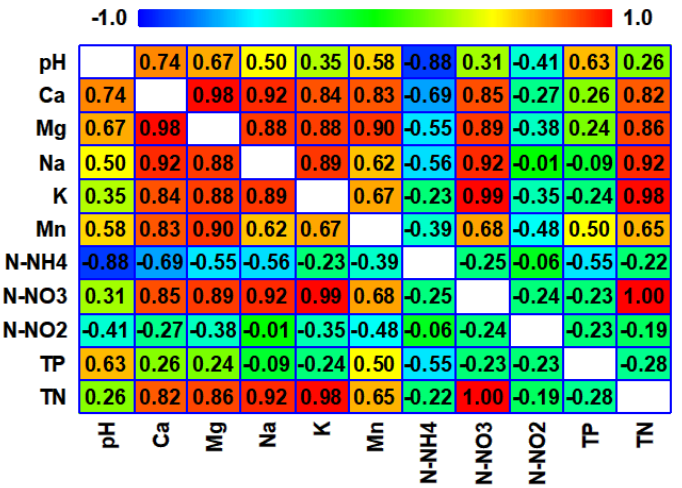


**Figure 1.** Pearson's correlation of physico-chemical parameters of water samples

This statistical tool was used to correlate water parameters in the examined locations. A negative value implies negative correlation, while a positive value implies positive correlation between variables. It was observed that the following pairs of variables presented a strong positive correlation: Ca and Mg, Ca and Na, Mg and Na, Mg and K, Mg and Mn, Mg and N-$NO_3^-$, Na and K, Na and N-$NO_3^-$, Na and TN, K and N-$NO_3^-$, K and TN, N-$NO_3^-$ and TN, while pH and N-$NH_4^+$ exhibited a strong negative correlation. However, majority of the measured physico-chemical parameters correlated with one another at either $p < 0.05$ or $< 0.01$ which is an indication that availability of specified pollution indicators will definitely have an influence on other assessed pollutants in both water sample type (surface or groundwater). The correlation analysis on water quality parameters revealed that all parameters are more or less correlated with each other Pearson's Correlation matrix. It was noticed that some of the parameters do not present significant correlation between them indicating a different origin source of pollution. From correlation analysis, the negative relationship between pH and N-$NH_4$ reveals the high organic pollution with anthropogenic activities in the Baia Sprie area.

### 3.2. Soil and sediment

The nutrient complex of the soil provides plants with macroelements (N, P, Ca, Mg, Na, K) and microelements (Cu, Zn, Mn, etc.) necessary for nutrition, which are selectively absorbed in the form of ions. Sodium, magnesium, calcium by accumulation in the form of chlorides, sulfates or bicarbonates cause soil salting, which has unfavorable effects on specific species that are dependent on the concentration of salts and their degree of tolerance. Excessive salinity, however, makes it difficult to supply water to less adapted plants, causing a physiological drought by increasing the osmotic pressure of the soil solution. The most toxic action is exerted by magnesium cations (Mg). Sodium ion (Na), although less harmful, causes strong alkalization of the soil solution by accumulation in the soil (it is harmful to plant roots and destroys the glomerular structure of the soil). Among the anions in saline soils, the $Cl^-$ ion is more toxic than the $SO4^{2-}$ sulfate ion.

From Figure 2, it can be seen that for the soil in the Copsa Mica area (S1), the pH is slightly acidic both in the surface soil layer (5.35 upH) and at depth (5.26 upH), while in Baia Sprie area (S2)), the pH of the surface soil layer is acidic (3.87 upH) compared to the depth (7.01 upH).

In the sediment samples, the pH is within the normal value (VN) in the sample collected from the Copsa Mica area (S3) (7.48 upH), while in the sample collected in the Baia Sprie area (S4) it is acidic (3.21 upH). This acidity deserves a lot of attention, because very low *pH* values can be dangerous for soil health and could inhibit the development and growth of vegetation. Acidification largely resulted from nitrogen deposition; another acidifying factor is the removal of basic cations from ecosystems by wood extraction (Vanguelova et al., 2010; Radim et al., 2011). One third of the long-term loss of base cations may be wood. Finally, acidifying nitrogen compounds are released from decaying biomass. Acidification thus occurs during the succession of the ecosystem, otherwise the aging of forests is associated with a decrease in soil *pH* even in pollution free conditions (Radim et al., 2011).

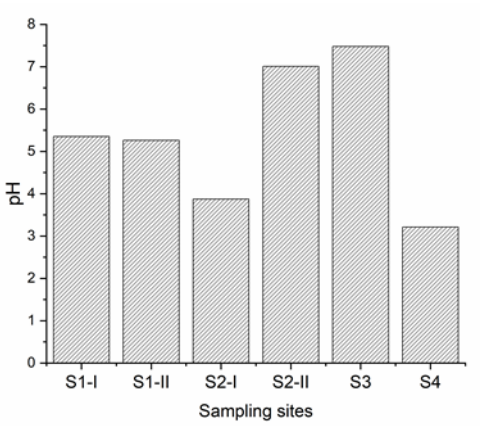


**Figure 2.** Evaluation of pH in the soil and sediment sampling sites

A higher content of macronutrients in the soil sampled from the surface, compared to the deep soil in the Copsa Mica area (S1), was observed (Figure 3). The cause could be that at the surface of the soil the litter is formed, a plant layer, consisting of various organic residues. Following the decomposition of these materials in soil, new portions of humus accumulates. So, the organic part of the soil is presented by the living organic (vegetable) substance, the residues of the organisms and the humus content, which decreases to depth from a few percent of the soil volume to hundreds of percent, at a depth of about 100 cm. There is also a high content of Mn and Fe in the soil harvested at the surface and in the deep soil. Because the processes of reduction predominate in the soil, the reduced compounds of iron and manganese have a harmful influence on the plants, both directly and indirectly by immobilizing phosphorus and nitrogen. The mobile, assimilable forms of phosphorus pass into iron, manganese and aluminum phosphates, which are not assimilable. Nitrogen is no longer oxidized until nitrates are formed. Existing nitrates are consumed by anaerobic microorganisms, or are reduced to elemental nitrogen by the denitrification process. Regarding the Zn content of 529.66 mg/kg in the soil at level I (0-20 cm) and at level II (20-40 cm) (114.25 mg/kg), it exceeds the normal value (VN) of 100 mg/kg imposed by regulations (MESDR, 1997), within the limit Alert thresholds for less sensitive soils (PA - 700 mg/kg). This high concentration of Zn may be due to a historical pollution of a factory that produced Zn and Pb. Although it is considered an essential element for life, in large quantities zinc can be toxic, both to plants and to humans or animals. Excess zinc causes changes in the physical and physicochemical properties of the soil by reducing the biological activity in the soil. Zinc acts on microorganisms both directly and indirectly, disrupting the transformation processes of organic matter in the soil. The toxic action of excess zinc on

microorganisms is to slow down physiological processes. Zinc is easily absorbed by plants in the soil and accumulates to a greater extent in the green organs of the plant.

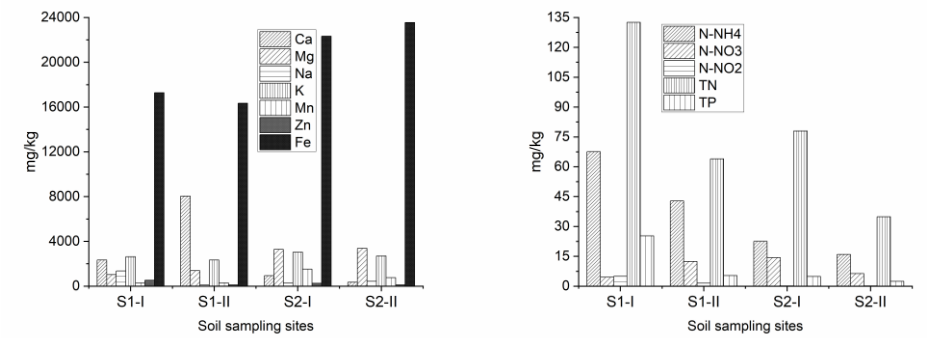


**Figure 3.** Evaluation of macronutrients and micronutrients in the soil sampling sites

Also, Baia Sprie area (S2), a higher content of macronutrients was found in the soil harvested from the surface compared to the soil harvested at a depth between 20 and 40 cm. In the soil surface there is a high content of $N\text{-}NH_4^+$ (22.48 mg/kg), $N\text{-}NO_3^-$ (14.32 mg/kg) and TN (78 mg/kg) and also a high content of Mn and Fe. The Mn content from the soil surface, presenting a value of 1523 mg/kg, falls within the limit for Alert Thresholds for less sensitive soils (PA - 2000 mg/kg) imposed by (MESDR, 1997). Regarding the Zn content both soils presented high concentrations framing in level I (253.38 mg/kg) and at level II (112.77 mg/kg), exceeding the normal value (VN) of 100 mg/kg imposed by (MESDR, 1997), and falling within the limit for Alert Thresholds for less sensitive soils (PA - 700 mg/kg). The high content of Zn, Mn and Fe in the soil may be due to a historical pollution due to the mining industry in the area.

Figure 4 highlight the macronutrient content for the sediment samples in the Copsa Mica (S3) and Baia Sprie (S4) areas.

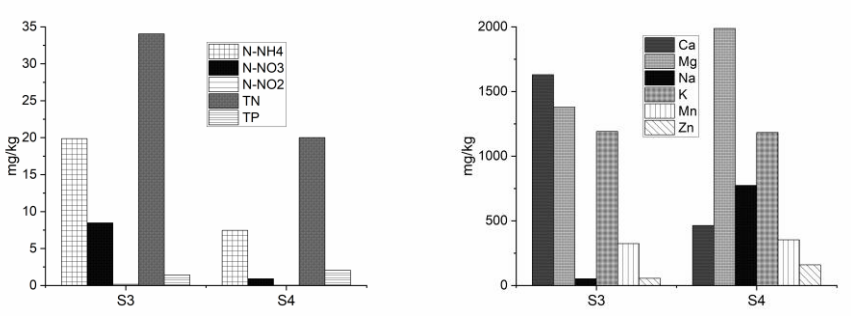


**Figure 4.** Evaluation of macronutrients and micronutrients in the sediment sampling sites

To Copsa Mica area (S3), following the obtained results, it was found a high content of $N\text{-}NH_4^+$ and TN (19.88 and 34.05 mgN/kg). There is also a high content of Ca, Mg, Na, K, Mn, Zn, Fe (1629.3, 1378.4, 51.61, 1190.8, 323.61, 54.9 and 16961 mg/kg). The high content of Ca may be due to the texture of the soil in the area which is mainly of the "clay - sandy" type, rich in carbonates in many places.

In the Baia Sprie area (S4), following the results obtained, it is found: a high content of $N\text{-}NH_4^+$ and TN (7.46 and 20.0 mgN/kg). There is also a high content of Ca, Mg, Na, K, Mn, Zn, Fe (463.3, 1987.6, 774.0, 1182.6, 353.2, 159.12 and 41311 mg/kg). The high content of

Mn, Zn and Fe may be due to a historical soil pollution in the Baia Sprie area due mainly to the extraction and processing of non-ferrous ores and non-ferrous metallurgy.

## 4. CONCLUSIONS

The present study examined different types of water and soil samples from two different industrial locations for some selected physico-chemical parameters which included the main macro- and microelements necessary for the nutrition, that plants selectively absorb in the form of ions ($N\text{-}NH_4^+$, $N\text{-}NO_3^-$, $N\text{-}NO_2^-$, total N, total P, Ca, Na, Mg, K, Mn, Zn, Fe). In the surface water and groundwater samples from the Copsa Mica area, a high load with the macroelements Ca, Na, Mg, K, Mn, Zn, Fe was not found, but in the groundwater higher concentrations of TN, $N\text{-}NO_3^-$ and K, probably due to the infiltration in the groundwater of some fertilizers based on nitrogen and potassium. In the water samples from the Baia Sprie area, there was no high load of compounds with nitrogen ($N\text{-}NO_3^-$, $N\text{-}NO_2^-$, TN) and TP, with the exception of $N\text{-}NH_4^+$ which fall within the limits of the quality 4$^{th}$ class. Pearson correlation matrix was applied to all the collected water samples for identifying the possible statistical relationship between different pairs of ground water quality parameters. A highly strong correlation was observed between pH and $NH_4$ revealing a possible high organic pollution with anthropogenic activities in the Baia Sprie area. In the soil samples collected from the Copsa Mica industrial platform area, a high content of Mn and Fe was obtained both in the soil harvested at the surface and in the deep soil. It was also observed a high content of Zn both in the surface soil and at depth, the values exceeding the normal value (VN) of 100 mg/kg imposed by Order 756/1997, falling within the Alert thresholds for less sensitive soils (PA - 700 mg/kg). The high content of Mn, Fe and Zn may be due to a historical pollution of the factories that operated on the Copsa Mica industrial platform. In the soil samples from the Baia Sprie mining area, a higher content of macronutrients (Ca, Na, Mg, K, $N\text{-}NH_4^+$, TN and TP) was observed in the soil harvested from the surface compared to the soil harvested at depth of 30 cm. In the surface soil there is a high content of $N\text{-}NH_4^+$ (22.48 mg/kg), $N\text{-}NO_3^-$ (14.32 mg/kg) and TN (78 mg/kg). The cause could be that at the surface of the soil is formed litter, plant layer, consisting of various organic residues (living and dead). There is also a high content of Mn and Fe both in the soil harvested at the surface and in the deep soil. The Mn content from the soil surface falls within the value of 1523 mg/kg in the limit for Alert Thresholds for less sensitive soils (PA - 2000 mg/kg) imposed by Order 756/1997. Regarding the Zn content both in the soil at level I (253.38 mg/kg) and at level II (112.77 mg/kg), it exceeds the normal value (VN) of 100 mg/kg imposed of Order 756/1997, within the limit for Alert Thresholds for less sensitive soils (PA - 700 mg/kg). The high content of Zn, Mn and Fe in the soil may be due to a historical pollution due to the mining industry in the area. The results of the current investigation conclude that the water and soil physico-chemical parameters still face the influence of residual pollution.

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**Author Contributions**
Mihaela Iordache set the concept of the paper, draw the draft manuscript; Claudia Sandru performed analysis; Marius Miricioiu contributed to data interpretation; Constantin Nechita collected the samples; Roxana Elena Ionete revised the data and completed the final manuscript; Oana Romina Botoran participated to statistical data interpretation and revised the manuscript.

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**REFERENCES**

Abdu, N., Abdullahi, A.A., Adulkadir, A. (2017). Heavy metals and soil microbes, *Environmental Chemistry Letters*, *15*, 65-84, DOI 10.1007/s10311-016-0587-x.

Arefin, M.T., Rahman, M.M., Wahid-u-Zzaman, M., Kim, J. (2016). Heavy metal contamination in surface water used for irrigation: Functional Assessment of the Turag River in Bangladesh, *Journal of Applied Biological Chemistry*, *59*(1), 83-90.

Azizullah, A., Khattak, M.N.K., Richter, P., Hader, D.P. (2011). Water pollution in Pakistan and its impact on public health-A review, *Environment International*, *37*(2), 479-497, https://doi.org/10.1016/j.envint.2010.10.007.

Bagul, V.R., Shinde, D.N., Chavan, R.P., Patil, C.L., Pawar, R.K. (2015). New perspective on heavy metal pollution of water, *Journal of Chemical and Pharmaceutical Research*, *7*(12), 700-705.

Cordos, E., Roman, C., Ponta, M., Frentiu, T., Rautiu, R. (2007). Evaluation of soil pollution with copper, lead, zinc and cadmium in the mining area Baia Mare. *Revista de chimie*, *58*(5), 470.

Deng, A., Ye, C., Liu, W. (2018). Spatial and seasonal patterns of nutrients and heavy metals in twenty-seven rivers draining into the South China Sea, *Water*, *10*(1), e50, https://doi.org/10.3390/w10010050.

Fang, Q., Wang, G., Xue, B., Liu, T., Kiem, A. (2018). How and to what extent does precipitation on multi-temporal scales and soil moisture at different depths determine carbon flux responses in a water-limited grassland ecosystem?, *Science of the Total Environment*, *635*, 1255-1266, https://doi.org/10.1016/j.scitotenv.2018.04.225.

Goher, M.E., Ali, M.H.H., El-Sayed, S.M. (2019). Heavy metals content in Nasser Lake and the Nile River, Egypt: An overview. *The Egyptian Journal of Aquatic Research*, *45*(4), 301-312. https://doi.org/10.1016/j.ejar.2019.12.002.

Harrison, N. (2001). Woodhead Publishing Series in Food Science, *Technology and Nutrition*, Cambridge, p. 148, ISBN 1-85573-462-1, https://doi.org/10.1533/9781855736320.2.148.

Iordache, A. M., Nechita, C., Pluhacek, T., Iordache, M., Zgavarogea, R., & Ionete, R. E. (2020). Past and present anthropic environmental stress reflect high susceptibility of natural freshwater ecosystems in Romania. *Environmental Pollution*, *267*, 115505.

Law 311/2004 amending and supplementing Law 458/2002 on drinking water quality.

MESDR, (1997), Order of Ministry (Ministry of Environment and Sustainable Development of Romania) no. 756/1997 for the approval of the Regulatory concerning environmental pollution assessment.

MESDR, (2006), Order of Ministry (Ministry of Environment and Sustainable Development of Romania) no. 161/2006, for the approval of the Norms regarding the classification of surface water quality in order to establish the ecological status of the water body.

MO, 2002, Soil-forest vegetation monitoring methodology for forestry.

Paul, D. (2017). Research on heavy metal pollutin of river Ganga: A review, Annals of Agrarian Science, 15, 1-9, https://doi.org/10.1016/j.aasci.2017.04.001.

Radim H, Petr P., Karel B., (2011), Long-term patterns in soil acidification due to pollution in forests of the Eastern Sudetes Mountains, *Environmental Pollution*, *159*, 2586-2593, https://doi.org/10.1016/j.envpol.2011.06.014.

Satyanarayana, J., Reddy, A.K., Kulshrestha, M.J., Rao, R.N., Kulshrestha, U.C., (2010). Chemical composition of rain water and influence of airmass trajectories at a rural site in an ecological sensitive area of Western Ghats (India), *Journal of Atmospheric Chemistry*, *66*, 101-116.

Sponza, D., Karaoglu, K., (2002). Environmental geochemistry and pollution studies of Aliaga metal industry district, *Environment International*, *27*, 541-553.

SR EN ISO 5667-1, 2007, Water quality. Sampling. Part 1: General guide for establishing sampling programs and techniques.

Vanguelova E.I., Benham S., Pitman R., Moffat A.J., Broadmeadow M., Nisbet T., Durrant D., Barsoum N., Wilkinson M., Bochereau F., Hutchings T., Broadmeadow S., Crow P., Taylor P., Durrant Houston T., (2010), *Chemical fluxes in time through forest ecosystems in the UK – Soil response to pollution recovery*, *Environmental Pollution*, *158*, 1857-1869, https://doi:10.1016/j.envpol.2009.10.044.

Wang, P., Yao, J., Wang, G., Hao, F., Shrestha, S., Xue, B., Xie, G., Peng, Y. (2019). Exploring the application of artificial intelligence technology for identification of water pollution characteristics and tracing the source of water quality pollutants, *Science of the Total Environment*, **693**, e133440, https://doi.org/10.1016/j.scitotenv.2019.07.246.

Wu, B., Wang, G., Jiang, H., Wang, J., Liu, C. (2016). Impact of revised thermal stability on pollutant transport time in a deep reservoir, *Journal of Hydrology*, *535*, 671-687, https://doi.org/10.1016/j.jhydrol.2016.02.031.

Xu, J., Chen, Y., Zheng, L., Liu, B., Liu, J., Wang, X. (2018). Assessment of heavy metal pollution in the sediment of the main tributaries of Dongting lake, China, *Water*, *10*(8), 1060, https://doi.org/10.3390/w10081060.

https://www.europarl.europa.eu/factsheets/en/sheet/105/the-european-union-and-forests, accessed in July 24, 2020