

RESEARCH ON POTENTIAL ACIDIFICATION OF SOILS, DUE TO ACID RAINS, IN THE INFLUENTIAL AREAS OF THE POWER PLANT PAROȘENI

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Abstract. *Acid rains are precipitations that have a pH level lower than 5.6, thus having strong acidic characteristics. Usually this phenomenon takes place after a considerable amount of sulfur dioxide or nitrogen oxide reach the atmosphere, where they go through a series of transformations and are absorbed by water droplets in clouds. A means by which these gases can reach the atmosphere in significant quantities are the emissions generated by power plants. This paper is aimed at highlighting the potential acidification of soils, due to acid rains in the influential areas of the power plant Paroșeni, and includes a number of methods of sampling and testing of water and soil samples to determine the effect of acid rains in these regions.*

Key words: *power plant; acid rain, emissions, acidification, soil, labor analysis*

1. INTRODUCTION

Paroșeni thermoelectric plant is located in the center of Petroșani basin, on the right bank of the river west Jiu in town Paroșeni, county Hunedoara, is bordered to the east by the access road to the mining Paroșeni, to the west by the river Jiu, and to the north by the railroad Livezeni-Lupeni, and it's aimed at providing the necessary heat and energy, for urban consumers in cities Petroșani, Vulcan, Lupeni and Aninoasa and to supply electricity in the National Power Grid /11/.

Combustion of fossil fuels in steam boilers result in various emissions such as sulfur dioxide (SO₂), nitrogen oxides (NO_x), particulate matter (PM₁₀ and PM_{2,5}), carbon monoxide (CO), of which those that pose a serious risk to both human health and the environment are sulfur dioxide and nitrogen oxides, because once released into the atmosphere have the ability to produce a number of negative effects over the environment of which the most important may be their capacity to produce acid rain have a negative effect on the flora and fauna of the area affected, but also the structures present in the area /3, 7/.

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2. ESTABLISHING RESEARCH DIRECTIONS

In order to determine the potential soil acidification, in the influential areas of C.E.T Paroşeni, a series of studies are required. Studies needed include sampling and laboratory analysis of soil samples and rain water in areas where concentrations of pollutants reach maximum concentrations, and thus the probability of acid rain is greater.

Analyses will include determination of pH, salt content, nitrites, chlorides, aluminum and other substances that can accumulate in the soil due to acid rain. To establish these sampling points, dispersion maps will be used (fig. 1 and fig. 2), since these maps provide information on the direction of the movement these gases and also their concentration. To highlight a soil acidification values obtained in laboratory tests will be compared with results obtained from an adjoining area, which is not under the power plant's influence.

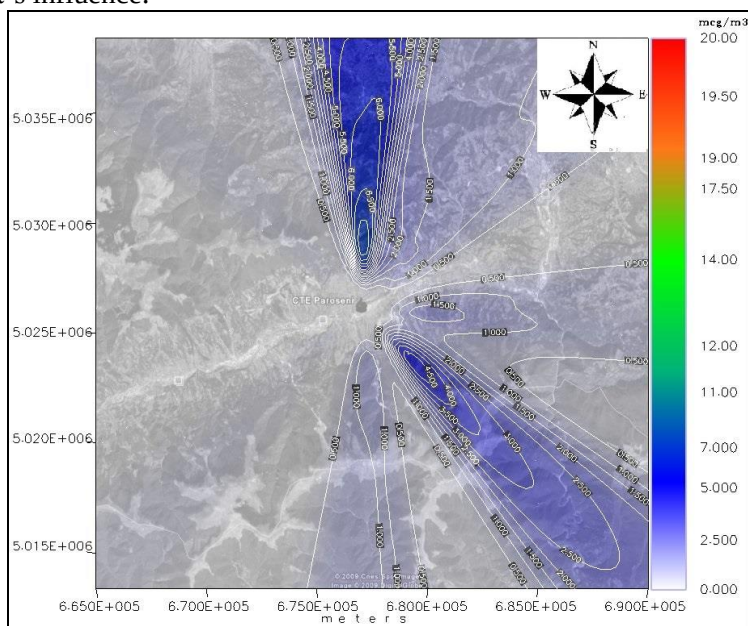


Fig. 1 Dispersion map with annual SO₂ concentration, expressed in g/m³

2.1. Establish sampling points for the soil and water samples

Upon analyzing the dispersion maps it was determined that the pollution plume is being dispersed to the North and South-East, with SO₂ concentrations reaching a maximum of 6.5 µg/m³ in the "Dealul Babii" area to the North and 4.5 µg/m³ in the "cable car" area to the South-East, therefore the sampling point will be in number of two to the north in the "Dealul Babii" area and one to the South-East in the "cable car" area. The control samples will be taken from the "Valea Arsului" area to the north east, being the adjoining area, which is not under the power plant's influence (fig. 3).

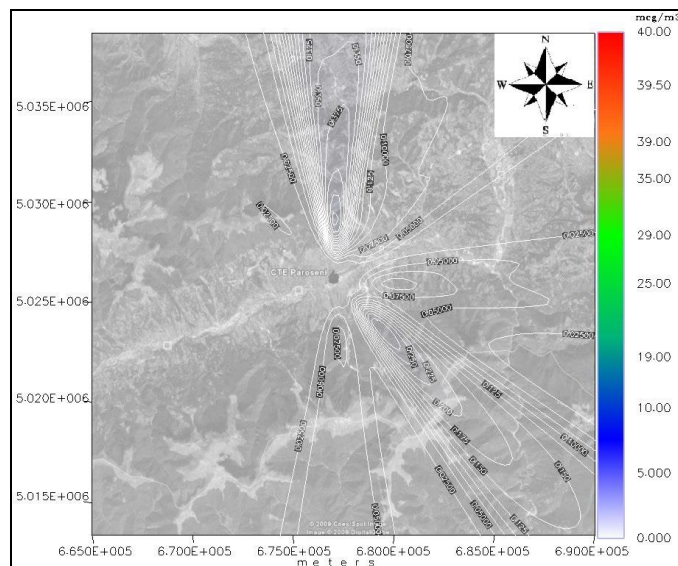


Fig. 2 Dispersion map with annual NO_x concentration, expressed in g/m^3



Fig. 3 Sampling points locations.

2.2. Water and soil sampling

For the collection of water samples, in every area containers were placed in order to collect rain water for the exception of the “Dealul Babii” area where because of the relative small distance between the points “Dealul Babii I” and “Dealul Babii II” was decided that placing a single container was sufficient. To ensure that a sufficient amount of rain water was collected, the containers were placed two days before a

major rain, and were collected no later than 24 hours after the rain stopped to minimize evaporation.

Also from the “Dealul Babii” area water samples were collected from stagnant surface waters and from temporary springs caused by surface leakage.

In order to perform lab analysis, from each area soil samples were collected using the envelope method [4], from a depth of 10 centimeters, the distance of the envelope corners being approximately 10 meters (fig. 4).

The soil samples taken from all 5 points of the envelope, that have a dimension of 20 cm², were placed in individual airtight plastic bags, that have been placed in black plastic bags with a note that contains data regarding the date, time and area where the sampling took place.

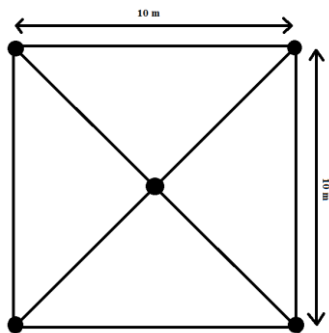


Fig. 4 Envelope method for sampling

3. CHEMICAL ANALYSIS OF SOIL AND WATER SAMPLES

3.1. Determining soil pH and conductivity

To determine the conductivity and soil pH the first step is to homogenize soil samples. After homogenization, 20 grams of soil from each area was weight using an analytical scale and mixes with 200 ml of distilled water in Erlenmeyer flasks and left for 24 for the salts to dissolve. The pH was measured with a HANNA HI 9023 pH meter and the conductivity was measured with a HANNA 1032 conductivity meter. After measuring the pH and conductivity, the solution was filtered for later use in the nitrate and chloride analysis.

3.2. Determining soil cation exchange capacity

The cation exchange capacity represents the maximum quantity of cations absorbed in colloidal complex. Cation exchange capacity values depend on the nature of the soil absorption complex and soil reaction. In general, the organic part of the adsorption complex, represented by humic acids, possesses a higher retention capacity than the mineral part [4].

Higher cation retention also occurs when the soil pH rises, because it increases the ionization of the functional groups of humic acids and clay minerals. The most common exchangeable cations found in soils, that gives it basic properties are: Ca²⁺,

Mg^{2+} , K^+ , Na^+ , Al^{3+} , while the H^+ cation in large quantities will raise the soil's pH level considerably /5/.

To determine the cation exchange capacity of hydrogen ions (SH) /6, 9/, 10 grams of soil that was dried and sifted was mixed with 100 ml of distilled water in a Erlenmeyer flask, 2-3 drops of phenolphthalein indicator will be added, and then the solution was titrated using NaOH 0,1 n solution until the content of the flask is colored a steady pink.

The cation exchange capacity of hydrogen ions is calculated using the following relation:

$$\text{SH} = V_{\text{NaOH}} * 10 [\text{m.echil/Kg sol}] \quad (1)$$

The process used to determine the cation exchange capacity of metal ions (SMe) is similar to the one use for the hydrogen ions with the exception that the color indicator will be methyl orange and for the titration a HCl 0,1 n solution was used until the contents of the flask was a steady orange.

The cation exchange capacity of metal ions is calculated using the following relation:

$$\text{SMe} = V_{\text{HCl}} * 10 [\text{m.echiv/Kg sol}] \quad (2)$$

3.3. Determining the soil's nitrate content

Nitrites are naturally present in soil, water and food and regularly testing their concentrations is essential for many applications, in this case serving as an indicator since due to acid rains they can accumulate in soils in significant quantities. To establish the soil's nitrate content an AQUAQUANT Nitrit 114424 kit will be used, this kit being equipped with two test tubes, Color indicator reagent AH and a color scale.

To determine the soil's nitrate content, in both of the test tubes will be filled to the 25 ml mark with the left over solution from the pH and conductivity determination, after which in one of these test tubes was added a measure of AH reagent, and then placed in the Styrofoam stand next the test tube with no reagent. Using color scale ... the two test tubes will be compared until the colors match. The nitrite content will be displayed on the right side of the color scale.

3.4. Determining the soil's chloride content

In order to establish the soil's chloride content an AQUAQUANT Cl 114401 kit will be used, this kit being equipped with two test tubes, two types of reagents Cl 1A and Cl 2A.

The testing method is similar to that used for the nitrates with the exception that the test tubes will be filled with only 2.5 ml and in one of these tubes will be added 3 drops of Cl 1A followed by 3 drops of Cl 2A reagent. Like with the nitrate determination the chloride concentration will be displayed in the right side of the color scale.

3.5. Determining the soil's aluminum content

To determine the soil's aluminum content 500 grams of soil were mixed with one liter of distilled water and left for 24 hours in order for all the salts and minerals present in the soil to dissolve. Afterwards the samples will be filtered repeatedly until all the solid particles will be removed, and the remaining solution will be placed in thermo resistant vessels which will be placed in an oven 105 degrees Celsius for 26 hours in order to evaporate.

The remaining salts will be scraped using a steel wool, weighed, and then analyzed using a spectrophotometer.

3.6. Soil spectrophotometric analysis

For the spectrophotometric analysis 20 grams of soil that were dried and sifted through a 1 mm test sieve were stored in a special aluminum containers after they were placed in plastic ones and covered with transparent foil, and are placed inside the spectrophotometer.

The samples go through an x-ray source that excites atoms, and the output rays produced pass through a prism and decompose the radiation into components and are received by a detector. Determination of elements that make up the soil samples will be based on the wavelength of the radiation components.

3.7. Chemical analysis of water samples

Water sample analysis includes pH determination, nitrite and chloride content and will be performed using the same methods as in the case of the soil samples.

4. BIOINDICATORS ANALYSIS

Plants can adapt to various conditions, but some species prefer more specific conditions, among them being the acidophilic plants, that can provide information on acid rain /1, 2/. Investigations on bioindicators and observations made in the areas of influence of the power plant that may indicate acidification of soils were found following species of flora:

Athyrium filix-femina is a species of pteridophytes from the Athyriaceae family which includes about 180 species of ferns. It is found mainly in the northern hemisphere temperate zones where it grows abundantly, being one of the most common ferns. It prefers humid environments and shaded forest. The plant prefers sandy soils, clay and heavy soils, but requires well-drained soil. It can adapt to acidic, neutral and alkaline soils but prefers an acidic soil with a pH of 5.5 - 6.5.

Genistella sagittalis is a genus of flowering plants in the legume family Fabaceae. The stem is a cladodie with yellow flowers, presenting flattened arch, and reduced leaves. It's commonly found in temperate climates in Europe and grows in areas with hayfields, pastures and bushes. This plant prefers a soil with a pH of 4.0-4.5.

Petasites ablus (White Butterbur) is a perennial herb belonging to the family Asteraceae genus Petasites. The petals of this plant are white and elongated and the

flowers are grouped on top of the stem. White Butterbur is a plant native to Europe and Southwest Asia thriving in hilly areas and mountain forests with relatively high moisture or areas close to flowing or standing water sources. This species of plants prefers a slightly acidic soil with a pH between 6.0-6.8.

Leucanthemum waldsteinii (daisy) is a plant of the family Asteraceae, genus *Leucanthemum*, which includes about 70 species. They are herbaceous plants with a specific type of inflorescence called calathidium. Though the calathidium is made up of many flowers, the inflorescence is like a single flower. The flowers that make this type of inflorescence often have tubular or ligulate shaped petals. They are found in Europe, Northern Africa and the temperate regions of Asia. This plant grows in a weakly acidic type of soil with a pH value of 6.0-6.8.

Serpyllum Thymus (field thyme) is a species of angiosperms belonging to the Lamiaceae family. The stems are cylindrical, hairy, with a reddish-green color, on top of which are piles of flowers. The leaves are small, oval, and sometimes bent down. The field thyme is an herb native to Europe and northern Africa, which grows even in arid areas, in soils with low fertility and low to medium humidity. Being an unpretentious plant regarding growing conditions it can adapt to almost any soil with proper drainage but it thrives in a soil with a pH value of 5.5-7.0.

Vaccinium myrtillus (blueberry bush) is a shrub of the genus *Vaccinium* species belonging to the family Ericaceae. It prefers moderate temperatures but in winter can last up to maximum of -20° C. Behaves well in areas with average annual rainfall ranging from 800-1000 mm. Grows on, well structured, with a high humus content acidic soils (pH values between 4.5 - 6.5). The species is native to Europe, northern Asia, Canada and the United States.

5. THE RESULTS OF ANALYZES

Laboratory tests conducted on soil samples taken from the areas of influence near power plant have obtained a series of values. These values are shown in tables 1, 2, 3.

Table 1 Soil chemical analysis

Sampling area Chemical Characteristics	Dealul Babii I	Dealul Babii II	Cable car	Valea Arsului
pH	7.15	7.05	6.85	6.94
Nitrites [mg/kg]	4	5	3	3
Chlorides [mg/kg]	750	550	400	400
Conductivity [μ s]	111.5	79.4	85.9	75.4
Aluminum (Al^{3+}) [mg/kg]	8.97	6.36	11.25	1.57

Table 2 Cation exchange capacity

Sampling area Exchange capacity	Dealul Babii I	Dealul Babii II	Cable car	Valea Arsului
Hydrogen ions [m.echiv]	82	70	95	48
Metal ions [m.echiv]	210	190	170	310

Analyzing data obtained from measurements made in the laboratory, included in table 1, can be observed that a higher concentration of nitrates and chlorides is higher in sampling points “Dealul Babii I” and “Dealul Babii II” then in the control point “Valea Arsului” what may indicate their accumulation due to acid rains, these chemicals being released into the atmosphere from the processes carried out at the power plant. Aluminum also can give us indications of soil acidification, it being more soluble under acidic conditions, and as the results show, in all three sampling points the numbers are higher than the control point. Conductivity can also provide information regarding the activity of acid rains in the region, due to the potential of acid rains to dissolve most salts and minerals, therefore the lower values of the conductivity in the control point could point out a certain soil acidification due to acid rains.

As it can be seen in table 2 exchange capacity of hydrogen ions is higher in the “Dealul Babii I”, “Dealul Babii II” and “cable car” areas compared to the control area “Valea Arsului”, which could indicate a soil acidification in those areas. Also the exchange capacity of metal ions is higher in the control point (the most common cations found in soils are Ca^{2+} , Mg^{2+} , K^{+} , Na^{+} , Al^{3+}) , giving the soil alkaline characteristics.

Table 3 Spectrophotometric analysis

Sampling area Chemical Characteristics	Dealul Babii I	Dealul Babii II	Cable car	Valea Arsului
Na_2O [g/kg]	1.48	1.08	0	0
MgO [g/kg]	3.82	3.49	3.32	3.87
SiO_2 [g/kg]	412.3	418.6	532.3	427.1
P_2O_5 [g/kg]	4.68	4.34	0	2.23
SO_3 [g/kg]	3.89	5	3.85	4.46
Cl [g/kg]	0.94	0.7	0.5	0.5
K_2O [g/kg]	48.1	49.8	23.6	27
Al_2O_3 [g/kg]	121.5	120	74.9	99.7
CaO [g/kg]	31.74	15.97	11.87	18.98
TiO_2 [g/kg]	21.3	16.66	26.89	22.98
V_2O_5 [g/kg]	0.3	0	0	0
Cr_2O_3 [g/kg]	2.1	0.6	4.19	4.55

MnO [g/kg]	4.26	4.89	3.61	5.08
Fe ₂ O ₃ [g/kg]	177.9	197.82	159.4	194.64
Co ₂ O ₃ [g/kg]	0	0	0.6	0
NiO [g/kg]	0.78	0.66	0.42	0.54
CuO [g/kg]	0.72	0	0	0
Ga ₂ O ₃ [g/kg]	0	0	0.42	0
GeO ₂ [g/kg]	0	0	0	0.39
As ₂ O ₃ [g/kg]	0.92	0.87	0.13	0
SeO ₂ [g/kg]	0	0.39	0	0
Rb ₂ O [g/kg]	1.5	1.72	0.53	2.08
SrO [g/kg]	0.55	0.76	0.58	0.74
ZrO ₂ [g/kg]	2	1.81	0.21	0
Nb ₂ O ₅ [g/kg]	0	0	0	0.2
BaO [g/kg]	6.15	7.74	0	3.96
CaCO ₃ [g/kg]	56.6	28.43	21.2	32.71
Humus [g/kg]	88.7	111.47	119.79	139.89

Following the analysis of water samples made in the laboratory, the following data was obtained:

Table 4 Chemical analysis of rain and surface water

Sampling area Chemical Characteristics	Dealul Babii			Cable car	Valea Arsului
	Rain water	Surface water	Temporary spring	Rain water	Rain water
pH	5.97	5.91	6.14	5.94	6.17
Nitrites [mg/l]	0.3	0.3	0.4	0.3	0.2
Chlorides [mg/l]	20	15	15	15	10
Conductivity [μS]	67.7	55	77.6	59.1	46.9

As in the case of soil samples, a difference can be observed between the values of the results from the two sampling areas “Dealul Babii I” and “Cable car”, compared to the ones obtained from the control area “Valea Arsului”. The presence of nitrates and chlorides in water samples taken indicate the existence of these compounds in the atmosphere as a result of processes performed at C.T.E Paroșeni which even in relatively small amounts can lead to their accumulation in the soils due to the presence of humus.

6. CONCLUSIONS

From gaseous pollutants discharged into the atmosphere by power plant Paroseni, the significant negative influence on soil acidification potential are sulfur dioxide and nitrogen oxides. These gases have synergistic effects on local and regional scale, and their quantity depends on the quality of the used fuel and of the characteristics of burning process.

After chemical analyzing the data obtained in the laboratory and observations made on bioindicators in the areas of influence of the power plant, it has been established that there is a slight acidification of soils due to the activities undertaken at C.T.E Paroșeni.

Therefore, further research is recommended by a pedological study of the affected soils in areas to determine the ability of buffering and neutralizing of the acidic soil by humic acids. Also, these studies can provide information on the accumulation of nitrates in the soil. It is proposed sampling of the lichens and their spectrophotometric analysis, which can provide information's on pollution from affected areas by their property to absorb harmful substances.

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