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LONG TERM SULPHUR SOIL POLLUTION CAUSED BY EMISSIONS FROM THERMAL POWER PLANT DOICEŞTI

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Abstract

Some of the most complex polluters of the environment are the Thermal Power Plants that use coal as energy source. There are two types of environmental pollution sources: the main are baskets exhaust gases of coal combustion, so called high sources, and the secondary sources that are ash dumps resulted from the coal combustion activities, so called low sources. Thermal Power Plant Doicesti, located in the area of the Sub-Carpathian hills, on the Ialomița Valley, is a major source of environmental pollution with sulfur, since 1952 when was built.

Geographically, the studied territory can be included into the Sub-Carpathians Curvature, more specifically in the Prahova Sub-Carpathian subunit. Pedogenetic factors: rock, topography and parent material, have led to the evolution of isolated, lythomorphic soils. In the investigated territory four soil classes: Luvisols, Cambisols, Vertisols and Protisols were identified, each of them with types and subtypes mentioned in the paper.

The subject of this paper is to analyze the loading degree of sulphur of the soils affected by emissions from Thermal Power Plants Doiceşti. Soil samples collected from 23 soil profiles distributed in all cardinal directions, were analyzed for total, organic and mobile sulphur contents. In the investigated area, sulphur pollution of soils, caused by sulphur emissions from Thermal Power Plant Doiceşti, were recorded. The sulphur pollution phenomenon gathering way by changing the normal content of soil, plant, and consequently, could affecting the health of the inhabitants of this territory.

INTRODUCTION

The thermal Power Plant Doiceşti is the oldest power plant in Romania, dating since 1952. Those 57 years of its operation left their mark on the characteristics of soils developed in the area of emissions influence.

Sulphur from the burning gases reaches on soils and vegetation under the form of aerosols or acid rain. Up to date, expeditionary field research, performed in the areas of the main power stations could not show significant changes in the soil reaction caused by emissions from coal thermal power plants. This fact is due to the large height of exhaust chimney of burned gasses, which allows distribution of gaseous pollutants in large territory. Secondly, many of the soils developed in the influence area of emissions are buffered by carbonates which prevent leaching and depletion of bases processes. Generally, the sulphur content in the form of SO_4^{-2} is less than 450 mg·kg-1 in unpolluted soils. Determination of sulfur loading degree is very difficult, because each soil is a separate entity characterized by specific chemical properties. However, large quantities of sulphur present in burned coal is often found in the A horizon of soils located in the area of influence of power plants emissions. The thermal power plant Doicesti is located in the Carpathian hills, on Ialomita Valley. South of town Pucioasa valley enlarges its width exceeding 2 km in Doicesti area. Doiceşti, Cornetu and Brăneşti Hills have different sizes and orientations, their height varying between 375-518 m. Most of the ridges have heights lower than those of Thermal Power Plant chimney exhaust gases, its superior part can be seen from the side Forest Balteanu located on the second line of hills behind the Doiceşti Hill [1].

MATERIAL AND METHODS

In preparing this study, field research was required for observation on materials that make up the slopes and terraces around Doiceşti Thermal Power Plant and soil sampling. Soil sampling was done on the depth of 0-20 cm and the sampling points were placed on the map. 23 soil samples were collected, which are subject to the following set of tests: SO_4^{2-} content, total sulphur content and organic sulphur content.

The total sulphur content was determined by gravimetric method as barium sulphates. The principle of the method: ion sulphates precipitated with barium ion in acidic solutions, forming a white precipitate, insoluble crystalline barium sulphate in hydrochloric and nitric acid. Solubility in water at normal temperature is $1x10^{-5}$g/l. The precipitate is separated by filtration, cremated and then weighed.

Organic and mobile sulphur content was determined by the method of Bardsley and Lancester (1960-1965). In this method, organic sulphur is oxidized into sulphates by incineration of soil mixed with sodium bicarbonate. Sulphates are extracted from the soil cremated with a phosphate solution of acetic acid, and then are dosed through turbidity or colorimetric. The method requires a prior procedure of decomposition of sulphide, and easily soluble sulphates removal from the soil.

RESULTS AND DISCUSSION

The study of soil pollution in the area of the Thermal Power Plant Doiceşti requires an extensive analysis of soil properties that make up soil covering of great complexity, determined by the diversity of relief, groundwater, rock and parental materials.

In the area influenced by emissions of the Thermal Power Plant (TPP) Doiceşti, soil samples were taken from 23 soil profiles, mostly located on both sides of the Ialomiţa River, between localities Pucioasa and Târgovişte and western side of the Dâmboviţa River between localities Izvoarele and Drăgăeşti-Ungureni.

The location of soil profiles from the Doiceşti TPP, is the following: on Ialomita Valley to 0.8-9.5 km N from 0.8 to 6.7 km E, at 1.7 to 6.3 km S-SSE; on the left side of Dambovita to Târgovişte, at 1,6-9 km S-SW-V away from TPP, and 6.9-9.1 km away from TPP, respectively.

About 50% of soil profiles are located in meadow, on Entisols (majority Eutric Fluvisols, Haplic, Skeletic and Gleyc). The remaining soils are: 17.65% Cambisols (Eutric Cambisols, Lepti-Eutric Cambisols, and Stagnic-Eutric Cambisols), 17.65 % Luvisols (Haplic Luvisols and Stagnic Luvisols) 8.82% Regosol, 2.94% Mollisols (Rendzic Leptosols) and 2.94% Vertisols (Pellic Vertisols) [2].

In the following the analysis of each pollutant, is presented separately.

A feature of soils from Doiceşti area is low-medium supplying with humus; however, coal dust, rich in organic carbon, has a direct influence on its content in soils located in the area of influence of emissions. Although, to characterize the state of organic matter soil supply, generally used humus content, we considered inappropriate to use as a means of comparison, this parameter. This feature is imposed by the processes of bioaccumulation which, for various reasons, did not allow accumulation of large amounts of humus. Climatic conditions and natural vegetation are the main reasons which prevent the accumulation on the soil surface and the profile of large amounts of plant debris. Many of the soils studied are affected by erosion processes that have the effect of transport of material from the upper soil profile. All these soils can have up to 1.8-3.0% humus under natural conditions. In the investigated soil profiles organic carbon content varied widely, from 0.89 to 4.78% (Figure 1).

The behavior of any chemical element is influenced by soil reaction. There is a relationship of proportionality between the acidity of the soil and the mobility of sulphur. In the area investigated, the analysis revealed a variation of pH values from 6.09 to 8.17, respectively, a variation of soil reaction from slightly acid to slightly alkaline (Figure 2).

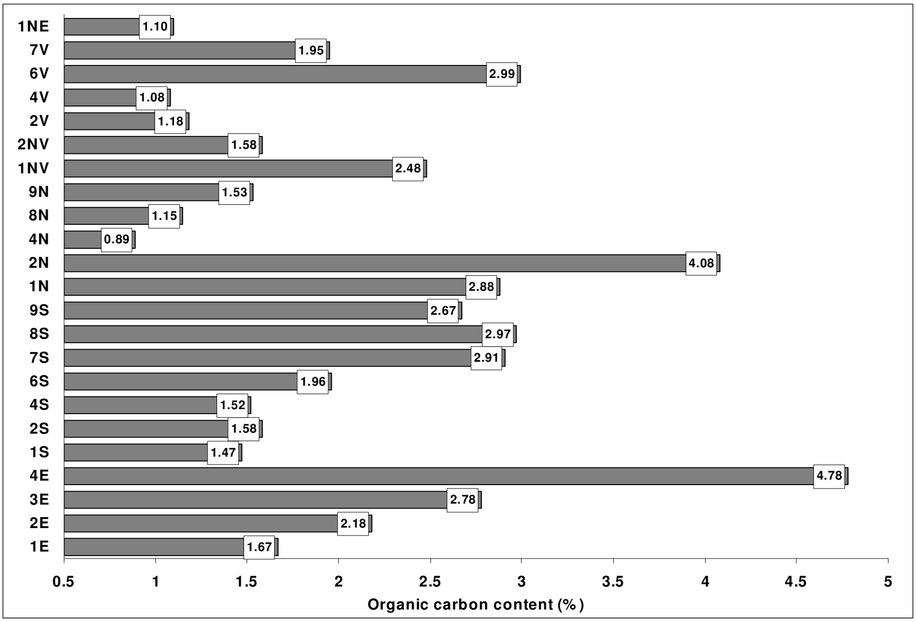

Fig. 1. Amplitude variation of organic carbons content in soil profiles located in the area of the thermo-electric power station Doicesti

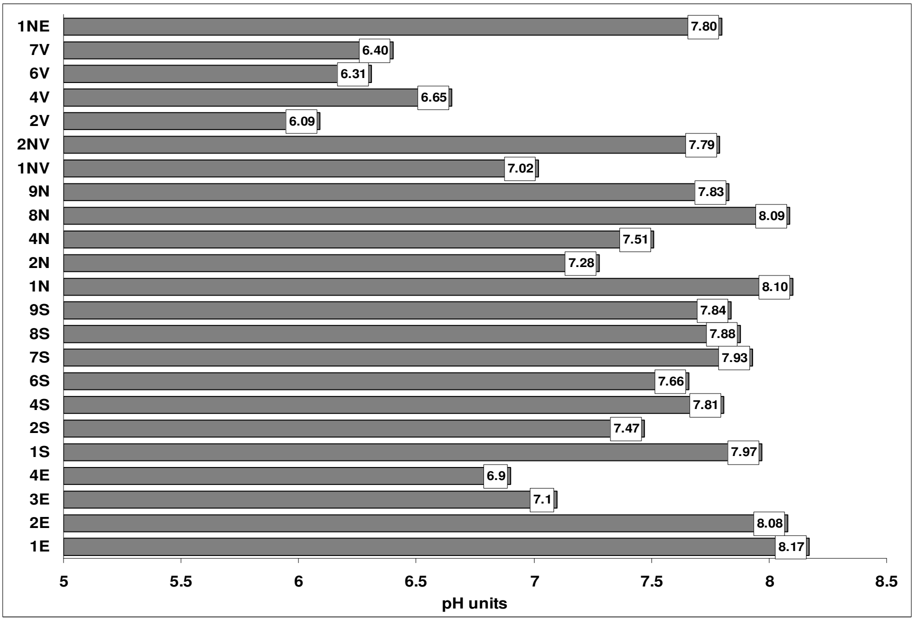

Fig. 2. Amplitude variation of pH values in soil profiles located in the area of the thermo-electric power plant Doicesti

Evaluation of soil degree loading with sulphur derived from the Thermal Power Plant Doiceşti is, however, the subject of this paper. Samples were collected from 23 soil profiles performed on all cardinal directions. Soil samples were analyzed for determination of total sulphur, organic sulfur and mobile sulfur.

Total sulfur content.

Loading degree of soil is low when the total sulphur content is less than 200 mg·kg^{-1}, medium between 201-800 mg·kg^{-1}, and high between 801 and 1600 mg·kg^{-1} (figure 3). In our determination, total sulphur content presented values ranging from 275 mg·kg^{-1} (Profile 2S) and 3350 mg·kg^{-1} (9S profile).

The analysis revealed that in the entire investigated territory, only 5 of 23 soil profiles had values over 801 mg·kg^{-1}, reflecting high total sulphur content. Of these, two profiles showed excessive contents of over 3000 mg·kg^{-1} (Figure 3).

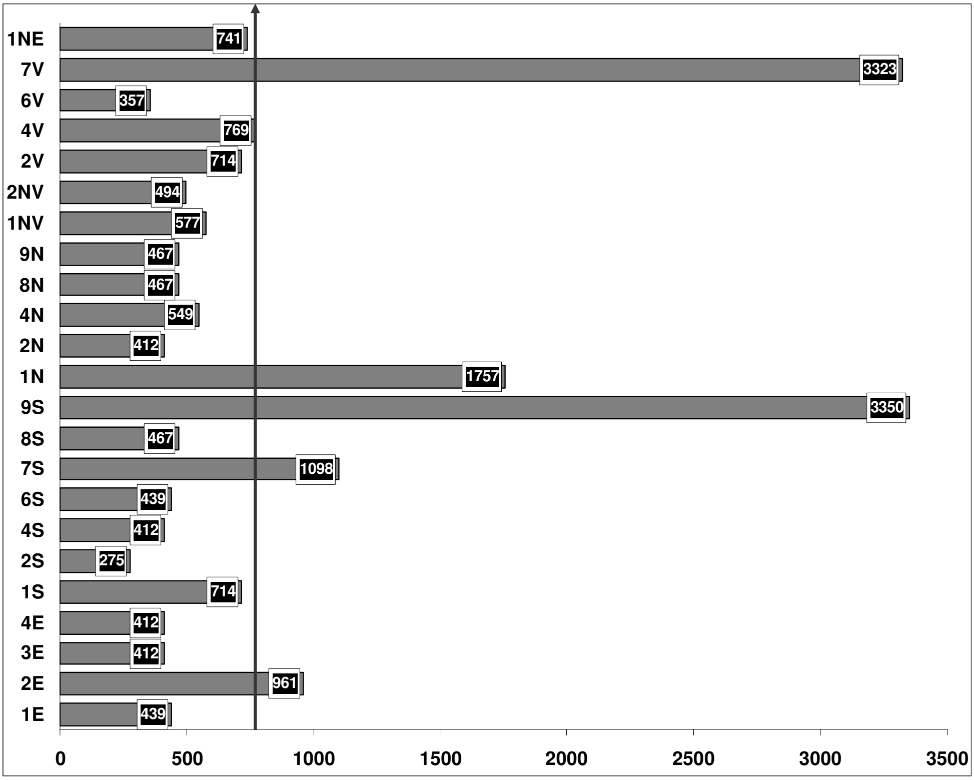

Fig. 3. Total sulphur content in soil profiles located in the area of the thermo-electric power plant Doiceşti (mg·kg^{-1})

On the east direction there were 4 soil profiles with values between 412 $mg \cdot kg^{-1}$ and 961 $mg \cdot kg^{-1}$. Only profile 2E recorded a high load level, 961 $mg \cdot kg^{-1}$, due to the small distance from Thermal Power Plant.

In the southern direction there are 7 soil profiles with values between 275 and 3350 $mg \cdot kg^{-1}$. 7S and 9S profiles have the highest values of the entire studied area, because their location quite close to the Thermal Power Plant Doiceşti.

On the north there were tested 5 soil profiles, profile 1N been quite close to the Thermal Power Plant having the highest value (1757 $mg \cdot kg^{-1}$). On the western direction there are 4 soil profiles, with values between 357 (6V) and 3323 $mg \cdot kg^{-1}$ (7V). On the direction of NV there are two soil profiles with values between 494 and 577 $mg \cdot kg^{-1}$, corresponding to the middle class content.

The total sulphur pollution is relatively high in a southern direction in the 7S and 9S profiles, to the north in the profile 1N, and in a western direction in the profile 7V. The remaining profiles have values ranging into the middle class of content (201-800 $mg \cdot kg^{-1}$).

Organic sulphur content

There are three classes for soil organic sulfur content: low - when the sulphur content is less than 160 $mg \cdot kg^{-1}$, medium - sulphur content is between 161-320 $mg \cdot kg^{-1}$, and high - sulphur content is over 320 $mg \cdot kg^{-1}$.

Organic sulphur content ranged from 134 to 606 $mg \cdot kg^{-1}$ in the investigated area (Figure 4). Eight entire soil profiles had values over 320 $mg \cdot kg^{-1}$, the limit that marks the high content class.

Only a single profile (4S) had a low organic sulfur content value, about 134 $mg \cdot kg^{-1}$ belongs to the low class content.

The amount of organic sulphur content recorded in 1E, 3E, 4E, 1S, 2S, 4S, 1N, 2N, 4N, 9N, 1 NV, and 1 NE profiles belong to the middle class. Soil profiles 2N, 7V, 8V, and 2 NV had values at the border between medium and high-content classes. Profiles 2E, 7, 8, 9S, and 4V showed very high values of between 426 and 606 $mg \cdot kg^{-1}$.

The wide variation of organic sulphur content was influenced by a multitude of factors, less the distance from the source. Stable relationships, highly significantly correlated, between organic C, N and S for different groups of soils, have been reported in spite of great variations in climate and parent material by G. Koptsik, C. Alewell [4]. The relatively weak relationship between air emissions of S and S content in soil is due to the fact that most of the SO_2 is emitted by high chimneys which favor emissions rather transport distances than local deposits.

The previous studies from the surroundings of Nikel and Zapolyarnyy did not find any relationship between the distribution of total soil S and atmospheric S load [6, 10]. The results of geochemical mapping of the Central Barents region did not reveal the anthropogenic enrichment of the organic horizon of the podzols with S despite the S input from the Kola smelters [3].

Novák et al. [7] for Central Europe and Novák et al. [8] for a NW-SE European transect reported statistically significant straight-line positive relationships between the atmospheric S input and total the S concentration in the topsoil. A significant correlation was also found between total S content in the soil organic and mineral layers and the input of S from atmosphere in forest ecosystems of the USA [5]. The impact of 40 a of S emissions from a sour gas processing plant in Alberta (Canada) has also lead to the increase in soil S pools caused by accumulation of organic S in the forest floor and accumulation of inorganic SO_4^{2-} in the mineral soil [9].

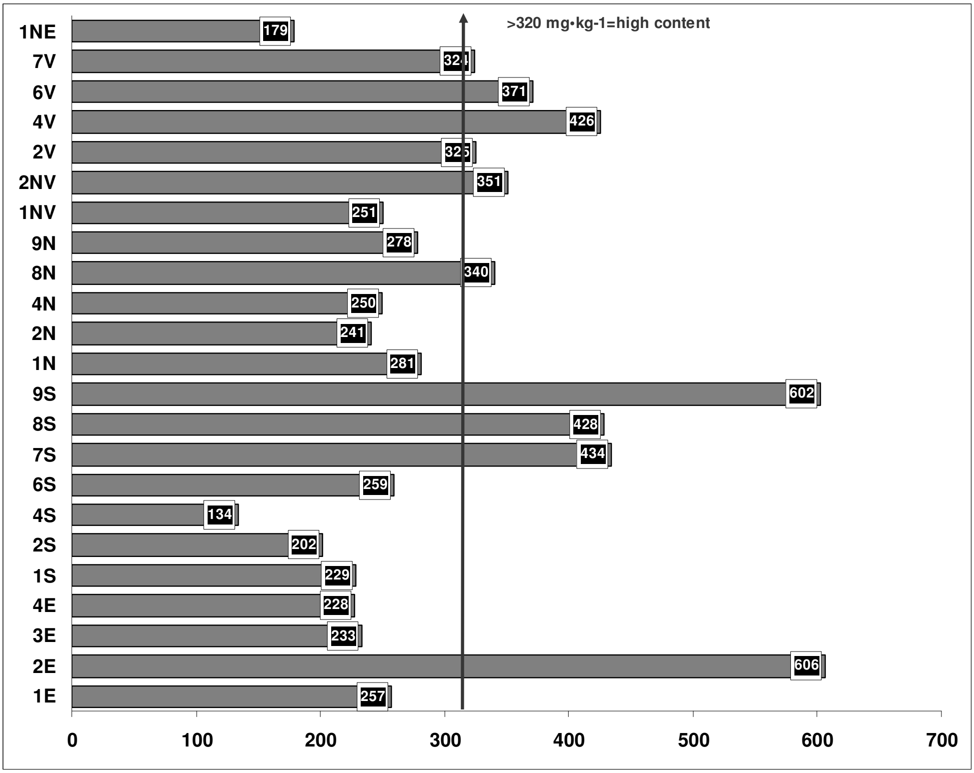

Fig. 4. Organic sulphur content variation in soil profiles located in the area of the thermo-electric power plant Doicesti (mg·kg^{-1})

The research of Mitchell and Lindberg [5] revealed that the sulphur in the O horizons was mainly present as organic S. Organic S, calculated from total S by subtracting inorganic S represented 99% of the median of total S content [5]. Mineral horizons contained significantly lower amounts or organic S. The latter is due to the combined effects of catabolism and chemical precipitation of dissolved organic S in the mineral soil. Nevertheless, the dominant form of S in most mineral soils was also organic [5].

Mobile sulphur content

There are three classes of content for this form of sulphur, namely: low - for values ≤ 5 mg·kg^{-1}, medium for values between 6-15 mg·kg^{-1} and high for values > 16 mg·kg^{-1}. Of the 23 soil profiles investigated, only one profile 4S, recorded a sulphur content value which belongs to the middle class (8.4 mg·kg^{-1}), all other profiles with values well above 16 mg·kg^{-1}, which marks the crossing in high class content (Figure 5).

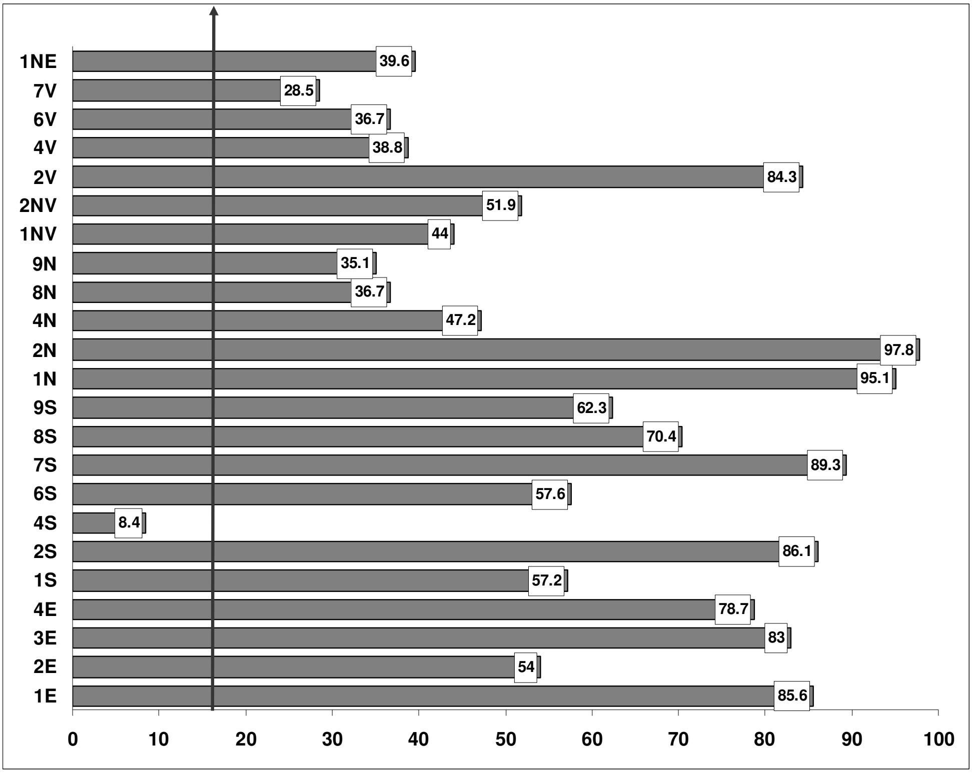

Fig. 5. Mobile sulphur content variation in soil profiles located in the area of the thermo-electric power plant Doicesti (mg·kg^{-1})

Mobile sulfur contents range from 28.5 mg·kg^{-1} to 97.8 mg·kg^{-1}, the highest values, above 95 mg·kg^{-1}, recorded in profiles 1 N and 2 N. Other soil profiles with high mobile sulphur content, over 80 mg·kg^{-1}, were profiles 1E, 3E, 2S, 7S and 2V. Among these soil profiles with high mobile sulphur content, only profiles 1N and 7S had, also, high content of total sulphur. So, a feature of the investigated area is that although total sulphur contents do not always reach levels that could generate pollution problems, mobile forms of sulphur, soluble, highly chemical and biochemical reactive, reaches alarming levels in the soil.

CONCLUSIONS

1. Total sulphur pollution is relatively high in the southern direction in the 7S and 9S profiles, to the north in the profile 1N, and in the western direction in the profile 7V. The remaining profiles have values ranging in the middle class of content (201-800 $mg \cdot kg^{-1}$).
2. The organic sulphur content recorded a large variation from 134 to 606 $mg \cdot kg^{-1}$ in the investigated area. Eight of the entire soil profiles had values over the limit that marks the high content class. The wide variation of organic sulphur content was influenced by a multitude of factors, less the distance from the source.
3. Of the 23 soil profiles investigated, only one profile, 4S, recorded mobile sulfur content value which belongs to the middle class, all other profiles recorded values well above limit which marks the crossing in high class content.
4. The concentrations in soil of total, organic and mobile S tended to be higher in profiles located near the thermal power plant; however, no relationship between distance to emissions source and S contents was found.
5. In the area of influence of the Thermal Power Plant pollution by sulphur Doiceşti is caused by emissions from thermal power station. A feature of the investigated area is that, although total sulphur contents do not always reach levels that could generate pollution problems, mobile forms of sulphur, soluble, highly chemical and biochemical reactive, reaches alarming levels in the soil.

REFERENCES

1. Căpitanu V., M. Dumitru, M. Toti, Daniela Răducu, Daniela Popa, M. Motelică, 1999. *Impactul emisiilor termocentralelor asupra mediului ambiant – Recultivarea haldelor de cenuşă*. Ed. Risoprint, Cluj-Napoca.
2. Florea N., I. Munteanu, 2003. *Sistemul roman de taxonomie al solurilor-SRTS*. Ed. Estfalia Bucureşti.
3. Kashulina G., C. Reimann, 2002. *Sulphur in the Arctic environment (2): results of a multi-medium regional mapping*. Environ. Pollut. 116 (pp. 337-350).
4. Koptsik Galina, Christine Alewell, 2007. *Sulphur behaviour in forest soils near the largest SO_2 emitter in northern Europe*. Applied Geochemistry 22 (pp. 1095-1104).
5. Mitchell M.J., S.E. Lindberg, 1992. *Sulphur chemistry, deposition and cycling in forests.* In: Johnson, D.W., Lindberg, S.E. (Eds.), Atmospheric Deposition and

Forest Nutrient Cycling. A Synthesis of the Integrated Forest Study (Ecological Studies S.), vol. 91. Springer-Verlag Inc., New York (pp. 2-149).

6. Niskavaara H., C. Reimann, V. Chekushin, 1996. *Distribution and pathways of heavy metals and sulphur in the vicinity of the copper-nickel smelters in Nikel and Zapoljarnij, Kola Peninsula, Russia, as revealed by different sample media*. Appl. Geochem. 11 (pp. 25-34).
7. Novák M., S.H. Bottrell, D. Fottová, F. Buzek, H. Groscheová, K. Žák, 1996. *Sulfur isotope signals in forest soils of Central Europe along an air-pollution gradient.* Environ. Sci. Technol. 30 (pp. 3473-3476).
8. Novák M., S.H. Bottrell, E. Prěchová, 2001. *Sulfur isotope inventories of atmospheric deposition, spruce forest floor and living Sphagnum along a NW-SE transect across Europe*. Biogeochem. 53 (pp. 23-50).
9. Prietzel J., B. Mayer, A.H. Legge, 2004. *Cumulative impact of 40 years of industrial sulfur emissions on a forest soil in westcentral Alberta (Canada).* Environ. Pollut. 132 (pp. 129-144).
10. Räisänen M.L., G. Kashulina, I. Bogatyrev, 1997. *Mobility and retention of heavy metals, arsenic and sulphur in podzols at eight locations in northern Finland and Norway and the western half of the Russian Kola Peninsula*. J. Geochem. Explor. 59 (pp. 175-195).