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# FRACTIONAL COMPOSITION OF ORGANIC MATTER IN SURFACE HORIZON OF SOILS FROM "BOBOV DOL" VALLEY

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## Abstract

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The paper deals with the content and composition of organic matter of soils polluted with ash from Thermal Power Plant "Bobov Dol". Coal impurities have impact not only on the amount of total carbon but also on the type of humus. Fine ash particles are deposited in the northern part of the valley, and they had change the composition of organic acids, where now humic type of humus dominates. The average amount of organic carbon increases in the surface horizon since 1979. It could be considered that this increase is due to 36 years of TPP "Bobov Dol" operation.

*Key words*: humus, organic carbon, coal ashes, humic and fulvic acids

## Introduction

The content of organic carbon in soils is increasingly important topic in recent years in relation to climate change, greenhouse gas emissions associated with carbon emissions into the atmosphere. Recent years we are talking about sequestration of carbon from the atmosphere and holding in the soil to avoid the negative consequences of climate change. Known fact is the increasing amount of carbon dioxide due to fossil fuels, emitted mainly from transport and Thermal Power Plants (TPP).

One of the main issues of the European Commission is to reduce carbon emissions. Companies that emit large amounts of carbon are sanctioned and required to buy carbon emissions. One of the biggest pollutants emissions in Bulgaria is TPP "Bobov dol", which are frequently imposed with financial sanctions. In 2011 and heat station was threatened with closure. "Bobov Dol has three blocks with a total installed capacity of 630 MWh, started in 1973-1975. Electricity is produced by burning lignite and brown coals. The main suppliers are mines at Stanyantsi, Bobov Dol, Beli Breg and Chukurovo. In 2012, was inserted new FGD installation, which should reduce emissions for ecological standards and requirements for dust, sulfur dioxide etc?

The aim of this study is to examine the present state of soil organic matter and to find out the effect of TPP "Bobov dol", on the humus quality, quantity and composition.

## Material and Methods

The object of our study is Bobov Dol Valley, which is characterized by mining and electricity production in TPP"Bobov Dol". Natural organic carbon in the soils is low (Blagoev et al., 1978). The main soil types in the region are Haplic Luvisols (WRB, 2006), Endocalcic Luvisols, Vertic Luvisols. On the steep parts of the relief, weak developed and eroded soils are found [Cambisols and Leptosols (WRB, 2006)]. In the lowest parts of the valley near the riverbeds, Mollic Fluvisols (WRB, 2006) are spread. Valley slopes, dry bottoms and torrential valleys are made from coluvial materials. In places along to the river Razmetitsa we can find depositions of alluvial materials. All the rest of the valley is spread on the soft Paleogene unstable sediments (Blagoev et al, 1979).

Zdravkov et al. (2012) studied the region for arsenic and organic carbon ($C_{org.}$) in the surface horizon. The authors point that the organic carbon content is similar to that in earlier studies of the area. The highest content of $C_{org}$. is spread in a thin strip, approximately 1.5 - 2 km width in north-south

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direction and close to two deposition spots in the territory of TPP "Bobov Dol". The distribution and content of the arsenic in humus horizon differs significantly from organic carbon content. To study the impact of TPP "Bobov Dol" on the farmlands near the plant 28 soil samples were taken from a depth of 0 - 30 cm from humus horizon. Sampling was taken in irregular network (Zdravkov et al., 2012). The location of soil samples is suitable to cover the maximum area.

Content and composition of soil organic matter in the studied profiles are determined with the modified Tjurin method [oxidation with a solution $K_2Cr_2O_7/H_2SO_4$ in the thermostat at 125°C for 45 min, in the presence of a catalyst $Ag_2SO_4$ and titration with $(NH_4)_2SO_4$. $FeSO_4$ $6H_2O$ and the Kononova - Belichkova method (Kononova, 1966; Filcheva and Tsadilas, 2002)].

## Results and Discussion

Mainly Haplic Luvisols and Endocalcic Luvisols dominate soil cover in the region of the Bobov Dol. Humus formation conditions are conducive to accumulation of significant amounts of organic carbon (Filcheva, 2007). Haplic Luvisols, accumulate more Corg then Endocalcic Luvisols because the humus and basies aren't leached. Amount of total carbon ranged from 0.6 to 1.75% (Table 2) that is low to moderate content (Raytchev and Filcheva, 2011). An exception is sample 81 Bd93-1, where $C_{org}$. is 4.41%, because it is taken frorm the marshy ground of the sludge pond close to Kamenik village.

Estimated amount of organic carbon in the surface horizon on the land of vilage Balanovo and village Golemo selo (Blagoev et al., 1978, 1979) is comparable to the amount of carbon analyzed in this research. Amount of the total carbon (Table 1) varies sharply. The highest amount of total carbon (1.8%) was measured in Mollic Fluvisols (Blagoev et al., 1978).

Haplic Luvisols and Endocalcic Luvisols are the most common soil types. The amount of $C_{org}$ ranged from 0.38% to 1.14 % and the average amount is 1.19 % (Table 2 without sample 81 Bd 93-1). Compared with the content of $C_{org}$ in both tables the average amount of $C_{org}$ increases in the surface horizon with 25 % since 1979 (from 0.95 % to 1.19%). It could be considered that this increase is due to 36 years of TPP "Bobov Dol" operation.

Haplic Luvisols are characterized as fulvic-humic type of humus (Ch/Cf 1-2). Ednocalcic Luvisols presents humic – fulvic type (Ch/Cf 1 - 0.5) (Filcheva, 2007). This relationship was observed in soil samples taken from the southern part of the valley, near the village Balanovo. An exception to this trend makes the point Bd 81-1, where the type of humus is fulvic-humic (Ch/Cf = 1.94), but the sample is taken near the village Palatovo where for agricultural is used probably added organic fertilizer. Soil sample 76 Bd 89-3 is the only one with fulvic type of humus, but there total amount of Corg is low, probably because of the sloping terrain, shallow profile and parent rock.

Highest pH (7.7) was observed in point 57 Bd 72-2 where is unusual the type of organic matter to be humic-fulvic (Ch/Cf = 0.72). In this point, the soils are with anthropogenic formation. This is reclaimed tailing and this point lies on its side sloping side, and on the surface appear fine ash residues from coal combustion of TPP "Bobov Dol".

Humic type of organic matter (Ch/Cf> 2) is characteristic for isohumic soils (Filcheva, 2007), which are neutral and slightly alkaline, and they are saturated with bases. Soil samples from the northern part of the basin are mainly characterized with humic type (Ch/Cf> 2) and fulvic - humic type of humus. It is not typically throughout the land of Golemo Selo village humic type to be predominating in area with majority of acidic soils. According to some authors (Banov et al., 1989; Hristova et al., 2011) coal impurities have impact not only on the amount of total carbon and also on the type of humus and there humic type dominates. It can be assumed that the fine ash particles deposited in the northern part of the valley had change the composition of organic matter. Humic acids are stable and they are 100% in a complex with calcium.

**Table 1**
**Total carbon content in the surface (A) horizon (restated Corg = Humus/1.724)**

| Soil types | $C_{org}$, % |
|---|---|
| *Land of village Golemo Selo (*Blagoev et al.*, 1979)* | |
| Profile 134, Endocalcic Vertic Luvisols | 0.98 |
| Profile 94, Endocalcic Luvisols | 0.83 |
| Profile 84,Epicalcic Luvisols | 1.21 |
| Profile 85, Epicalcic Vertic Luvisols | 1.11 |
| Profile 106, Haplic Cambisols | 1.14 |
| Profile 131, Mollic Fluvisols | 1.02 |
| Profile 80, Mollic Geyic Fluvisols | 1.5 |
| Profile 79, Mollic Geyic Fluvisols | 1.8 |
| *Land of village Balanovo (*Blagoev et al.*, 1978)* | |
| Profile 52, Epicalcic Luvisols | 0.95 |
| Profile 10, Epicalcic Luvisols | 0.77 |
| Profile 21, Haplic Luvisols | 0.48 |
| Profile 41, Haplic Cambisols | 0.38 |
| Profile 37, Haplic Cambisols | 0.56 |
| Profile 80, Haplic Luvisols | 0.39 |
| Profile 65, Mollic Fluvisols | 1.04 |
| Profile 13, Mollic Fluvisols | 0.91 |
| Average amount | 0.95 |

**Table 2**
**Content and composition of the organic matter. Designations: a - % of the sample mass, b - % of the total carbon, mass, c - % of the total humic acids . Optical characteristics: $E_4/E_6$, h - humic acids, f – fluvic acids**

| Horizon Depth, cm | pH | Total carbon Corg, % | Organic carbon, % extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH | | | $C_x/C_ф$ | Organic carbon , % Humic acid fractions | | Unextracted Organic carbon (C res.) % | Extracted C with 0.1N $H_2SO_4$, % | Optical characteristics ($E_4/E_6$) | | Organic carbon NaOH, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Total | Humic acids | Fulvic acids | | Free and $R_2O_3$ complexed | Ca-complexed | | | Total humic acids | Free humic acids | |
| 3 Bd 12-1 | 4.8 | 1.55 | 0.53[a] / 34.19[б] | 0.38 / 24.52 | 0.15 / 9.67 | 2.53 | 0 | 100 | 1.02 / 65.81 | 0.04 / 2.58 | 3.63 | - | 0.22 / 14.19 |
| 6 Bd 14-1 | 6.3 | 1.36 | 0.48 / 35.29 | 0.34 / 25 | 0.14 / 10.29 | 2.43 | 0 | 100 | 0.88 / 64.71 | 0.04 / 2.94 | 3.43 | - | 0.12 / 8.82 |
| 8 Bd 16-1 | 7 | 1.6 | 0.52 / 32.5 | 0.42 / 26.25 | 0.1 / 6.25 | 4.2 | 0.14 / 33.36[в] | 0.28 / 66.67 | 1.08 / 67.5 | 0.03 / 1.87 | 4.8 | 2.74 | 0.22 / 13.75 |
| 11 Bd 25.1 | 5.2 | 0.89 | 0.35 / 39.32 | 0.26 / 29.21 | 0.09 / 10.11 | 2.89 | 0 | 100 | 0.54 / 60.67 | 0.03 / 3.37 | 4.68 | - | 0.14 / 15.73 |
| 12 Bd 26-1 | 4.9 | 1.37 | 0.52 / 37.95 | 0.36 / 26.28 | 0.16 / 11.67 | 2.25 | 0 | 100 | 0.85 / 62.05 | 0.03 / 2.19 | 3.78 | - | 0.26 / 18.98 |
| 17 Bd 36-1 | 7.3 | 0.81 | 0.28 / 34.57 | 0.28 / 34.57 | 0 | - | 0 | 100 | 0.53 / 65.43 | 0.03 / 3.7 | 4.18 | - | 0.08 / 9.88 |
| 20 Bd 38-1 | 4.1 | 1.65 | 0.56 / 33.94 | 0.40 / 24.24 | 0.16 / 9.7 | 2.5 | 0 | 100 | 1.09 / 66.06 | 0.03 / 1.82 | 3.89 | - | 0.23 / 13.94 |
| 22 Bd 39-1 | 6.1 | 0.72 | 0.25 / 34.72 | 0.17 / 23.61 | 0.08 / 11.11 | 2.13 | 0 | 100 | 0.47 / 65.28 | 0.03 / 4.17 | 5.31 | - | 0.1 / 13.89 |
| 25 Bd 47-1 | 5.1 | 1.16 | 0.43 / 37.07 | 0.29 / 25 | 0.14 / 12.07 | 2.07 | 0 | 100 | 0.73 / 62.93 | 0.03 / 2.59 | 4.06 | - | 0.17 / 14.66 |
| 27 Bd 49-1 | 5.9 | 1.3 | 0.37 / 28.46 | 0.22 / 16.93 | 0.15 / 11.54 | 1.47 | 0 | 100 | 0.93 / 71.54 | 0.03 / 2.31 | 5.33 | - | 0.14 / 10.76 |
| 32 Bd 51-2 | 7.2 | 1.15 | 0.36 / 31.3 | 0.22 / 19.13 | 0.14 / 12.17 | 1.57 | 0 | 100 | 0.79 / 68.7 | 0.03 / 2.61 | 4.7 | - | 0.07 / 6.09 |
| 34 Bd 52-1 | 5.6 | 1.42 | 0.55 / 38.73 | 0.4 / 28.17 | 0.15 / 10.56 | 2.67 | 0 | 100 | 0.87 / 61.27 | 0.03 / 2.11 | 2.39 | - | 0.21 / 14.79 |
| 36 Bd 52-3 | 5.9 | 1.01 | 0.38 / 37.62 | 0.24 / 23.76 | 0.14 / 13.86 | 1.71 | 0 | 100 | 0.63 / 62.38 | 0.03 / 2.97 | 4.56 | - | 0.11 / 10.89 |
| 40 Bd 54-1 | 4.8 | 1.13 | 0.5 / 44.25 | 0.29 / 25.66 | 0.21 / 18.58 | 1.38 | 0 | 100 | 0.63 / 55.75 | 0.03 / 2.65 | 2.38 | - | 0.21 / 18.58 |
| 45 Bd 62-1 | 5.3 | 1.02 | 0.44 / 43.14 | 0.29 / 28.43 | 0.15 / 14.73 | 1.93 | 0 | 100 | 0.58 / 56.86 | 0.03 / 2.94 | 4.01 | - | 0.14 / 13.72 |
| 48 Bd 64-2 | 5.9 | 1.38 | 0.55 / 39.85 | 0.31 / 22.46 | 0.24 / 17.39 | 1.29 | 0.14 / 45.16 | 0.17 / 54.84 | 0.83 / 60.15 | 0.03 / 2.17 | 4.28 | 3 | 0.26 / 18.84 |
| 57 Bd 72-2 | 7.7 | 0.72 | 0.27 / 37.5 | 0.13 / 18.06 | 0.14 / 19.44 | 0.93 | 0 | 100 | 0.45 / 62.5 | 0.04 / 5.56 | 3.72 | - | 0.1 / 13.89 |
| 62 Bd 75-1 | 4.7 | 1.27 | 0.44 / 34.65 | 0.18 / 14.17 | 0.26 / 20.47 | 0.69 | 0 | 100 | 0.83 / 65.35 | 0.03 / 2.36 | 4.44 | - | 0.26 / 20.47 |
| 66 Bd 79-2 | 5.9 | 1.05 | 0.27 / 25.71 | 0.11 / 10.48 | 0.16 / 15.23 | 0.69 | 0 | 100 | 0.78 / 74.29 | 0.03 / 2.86 | 3.35 | - | 0.17 / 16.19 |

***continued on next page***

**Table 2 (Continued)**

**Content and composition of the organic matter. Designations: a - % of the sample mass, b - % of the total carbon, mass, c - % of the total humic acids . Optical characteristics: $E_4/E_6$, h - humic acids, f – fluvic acids**

| Horizon Depth, cm | pH | Total carbon Corg, % | Organic carbon, % extracted with 0.1M $Na_4P_2O_7$+0.1M NaOH | | | $C_x/C_\phi$ | Organic carbon , % humic acid fractions | | Unextracted Organic carbon (C res.), % | Extracted C with 0.1N $H_2SO_4$, % | Optical charcterisitcs ($E_4/E_6$) | | Organic carbon NaOH, % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Total | Humic acids | Fulvic acids | | free and $R_2O_3$ complexed | Ca-complexed | | | Total humic acids | Free humic acids | |
| 68 Bd 80-2 | 4.6 | 1.17 | 0.33<br>28.2 | 0.15<br>12.82 | 0.18<br>15.38 | 0.83 | 0 | 100 | 0.84<br>71.8 | 0.05<br>4.27 | 3.41 | - | 0.2<br>17.09 |
| 69 Bd 81-1 | 5.6 | 1.75 | 0.47<br>26.86 | 0.31<br>17.71 | 0.16<br>9.14 | 1.94 | 0 | 100 | 1.28<br>73.14 | 0.04<br>2.28 | 5 | - | 0.28<br>16 |
| 72 Bd 83-1 | 4.5 | 1.41 | 0.35<br>24.82 | 0.15<br>10.64 | 0.2<br>14.18 | 0.75 | 0 | 100 | 1.06<br>75.18 | 0.04<br>2.84 | 3.72 | - | 0.23<br>16.31 |
| 76 Bd 89-3 | 5.4 | 0.59 | 0.26<br>44.07 | 0.08<br>13.56 | 0.18<br>30.51 | 0.44 | 0 | 100 | 0.33<br>55.93 | 0.04<br>6.78 | 5.67 | - | 0.15<br>25.42 |
| 78 Bd 90-3 | 6.4 | 1.29 | 0.28<br>21.71 | 0.13<br>10.08 | 0.15<br>11.63 | 0.87 | 0 | 100 | 1.01<br>78.29 | 0.04<br>3.1 | 5.25 | - | 0.11<br>8.52 |
| 81 Bd 93-1 | 5.9 | 4.41 | 0.93<br>21.09 | 0.42<br>9.52 | 0.51<br>11.56 | 0.82 | 0.29<br>69.05 | 0.13<br>30.95 | 3.48<br>78.91 | 0.08<br>1.81 | 4.82 | 6.17 | 0.59<br>13.38 |
| 84 Bd-100 | 7.6 | 1.19 | 0.35<br>29.41 | 0.22<br>18.49 | 0.13<br>10.92 | 1.69 | 0.13<br>59.09 | 0.09<br>40.91 | 0.84<br>70.59 | 0.04<br>3.36 | 4.04 | 3.64 | 0.24<br>20.17 |

Only in four samples (8, 48, 81 and 84), there are “free” and bind with $R_2O_3$ forms of humic acids. According to the map (Figure 1) soils near rivers and pond of the power plant, have initial process of soil formation. Similar results in other areas of the country with the participation of the coal particles were obtained earlier (Banov et al., 1989; Gencheva et al., 1995; Filcheva et al., 2000; Hristova et al., 2011). Unextracted amount of organic carbon is high. It varies from 55 to 78%, this indicates a stable condition in the insoluble fraction of organic matter. There is a minimal amount of aggressive fulvic acids (Extracted $C_{org}$. with. 0.1N $H_2SO_4$). Similar results were obtained by the aforementioned authors in reclaimed soils from different regions of the country where we can find coal impurities.

The optical soils’ characteristics ($E_4/E_6$) in the valley showed that more than half of the samples have a mean (average) optical density of humic acids from 4 to 5 ($E_4/E_6$). These results are quite typical for Epicalcic and Haplic Luvisols, which have relatively low humus content and formation in acidic environment, continental climate and vegetation typical for the researched area (Artinova, 2007). Humic acids are high condensed and with high optical density at one-third of the samples ($E_4/E_6$, 3 and 4). This is characteristic for Mollic Fluvisols, located in the middle of the valley. In limited places, humic acids with low optical density

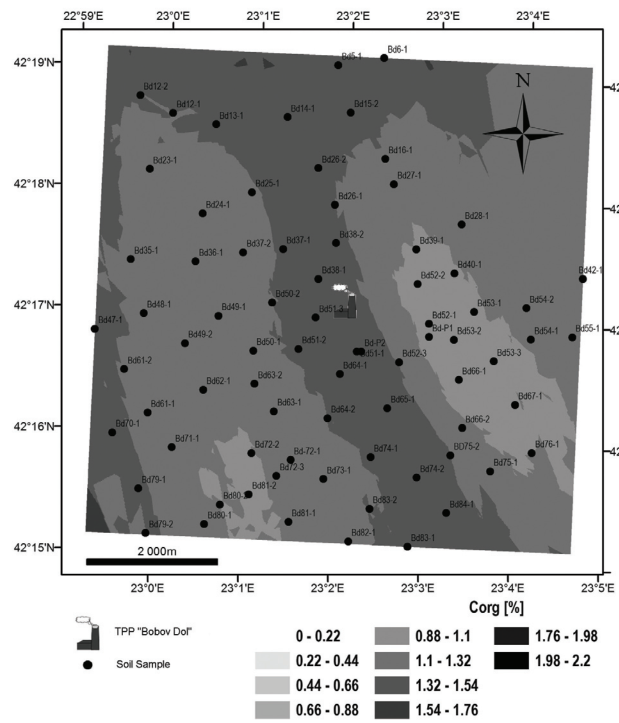


**Fig. 1. Spatial distribution of organic carbon (Corg) of valley Bobov Dol (Zdravkov et al., 2012)**

are spread ($E_4/E_6$ 5 to 6). These data are not typical for the area, because this type of optical characteristic is distributed mainly in the mountains, where conditions of humus formation are more severe. In this case, it cannot be argued that TPP "Bobov Dol" has influence.

## Conclusion

Soil' researches in the Bobov Dol Valley show that the separation of fine particles and transport of combustion residues of TPP "Bobov Dol" have impact on the quantity and composition of soil organic matter. This process can be observed mainly in the northern part of the valley and near to ponds around the villages Kamenik and Palatovo. For 36 years, operation of TPP "Bobov Dol" the total carbon amount has increased average by 25% in the humus horizon. The type of organic matter is predominantly humic. Base elements are associated with humic acids, which favor the quality of soil organic matter. There is no potential risk for export of organic mater and elements along the profile depth. Following soil features differs from representative of soils in the region.

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## References

**Artinova, N.,** 2007. Optical Density of Humic acids in Soils of Bulgaria. - International Conference "60 years Institute of Soil Science "N. Poushkarov ", pp. 124-128 (Bg).

**Banov, M., E. Filcheva and B. Hristov,** 1989. - Humus Accumulation and Qualitative Composition of Humus in Reclaimed Lands. *Soil Science and Agro Chemistry*, **24** (4): 3-8 (Bg).

**Blagoev, H. and S. Mikhailov,** 1978. Soil Characteristics of the Land SONS Balanovo. *Archive ISSAPP "N. Poushkarov* ", 35 pp. (Bg).

**Blagoev, H. and S. Mikhailov,** 1979. Soil Characteristics of the Land SONS Golemo Selo. *Archive ISSAP "N. Poushkarov* ", 28 pp. (Bg).

**Filcheva, E. and C. Tsadilas,** 2002. Influence of Cliniptilolite and Compost on Soil Properties. *Commun. of Soil Sci. and Plant Analysis*, **33** (3-4): 595-607.

**Filcheva, E.,** 2007. Characteristic of Bulgarian Soils with Content, Composition and Stocks of Organic Matter. Grouping of Bulgarian sols. Sustainable Land Management, ISBN: 978-954-8702-11-9, *Advertising and Publishing House Minerva,* 191 pp. (Bg).

**Gencheva, S. and E. Filcheva,** 1995. Composition of Organic Matter in Reclaimed Lands from Open Mining. "Jubilee Scientific Session 70 years Forestry Education in Bulgaria", 7-9 VI 1995, Sofia, **3:** 3-10 (Bg).

**Hristova, M., V. Tsolova and E. Filcheva**, 2011. Extractable Heavy Metals in Organic Matter Fractions of Technogenic Soils. *Soil Science, Agrochemistry and Ecology,* Supplement 1-4: 205-210 (Bg).

**Kononova, M**., 1966. Soil Organic Matter. Its nature and Properties. 2nd Ed. – *Pergammon press, Inc*., M. V., p. 544 (Ru).

**Raytchev, T. and E. Filcheva**, 2011. Soil Organic Matter, Small Terminological Vocabulary, ISBN 978-954-323-878-1, ed. "Avangard Prima", Sofia, 99 pp. (Bg).

**WRB,** 2006. World Reference Base for Soil Resources. *FAO pub*., Rome, 132 pp.

**Zdravkov, A., K. Markov, I. Nikova, B. Hristov, D. Petrov and D. Bakardjiev,** 2012. Presence and Distribution of Arsenic in Humus Horizon in Bobov Dol Valley. *Yearbook UMG "Ivan Rilski",* **55** (1): 40-49 (Bg).

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