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ИДЕНТИФИЦИРАНЕ НА ЗАПЛАХИ ЗА ПОЧВИТЕ В РАЙОНА НА ПРОУЧВАНЕ В ДОЛИНАТА НА ЗЛАТИЦА–ПИРДОП
IDENTIFICATION OF SOIL THREATS FROM THE SURVEY AREA IN THE ZLATITSA–PIRDOP VALLEY

Тома Шишков*, Бисер Христов
Toma Shishkov*, Bisser Hristov

Институт по почвознание, агротехнологии и защита на растенията
”Никола Пушкаров”, София
Institute of Soil Science, Agrotechnology and Plant Protection
“Nikola Poushkarov”, Sofia

***E-mail: toma_shishkov@yahoo.com**

Abstract

Soil is a basic natural resource and therefore farms, livestock, forests and waters from watersheds resolve their problems on the soil. The Zlatitsa-Pirdop valley forms a closed air pool which is crucial for the distribution of harmful substances (emitters). The selected soil survey area is linked directly to the threats to soil identified in the EU Thematic Strategy for Soil Protection. The threats such as erosion, soil contamination and sealing were identified during the soil survey. The authentic information obtained on the Deluvial (Colluvial) meadow soil tended to be more suited to characterise specific soil features, including morphological conditions, while the data on the Undeveloped cinnamonic forest (shallow) soils, Alluvial-meadow and Alluvial soils from the flooded zone provided more detailed spatial information on the particular soil varieties.

Key words: soil threats, heavy metals, soil protection, soil survey.

INTRODUCTION

All of degradation and hazardous processes which have negative impacts on the soil (land), are divided into three groups according to the degree of danger: a) the processes proceeding with the destruction of the soil and land take off; b) changing the structure of the soil cover, leading to soil degradation and reduce soil fertility; d) reducing the productivity of the land.

In Zlatitsa-Pirdop valley prevailing north-easterly winds in combination with the relief are crucial for distribution, diffusion and precipitation of harmful substances (emitters). Air quality is determined primarily by the sources, located in the vicinity: large industrial sources and tailings with dust emissions; heavy metals (Cu, As, Pb, Cd); sulfur dioxide SO_2; also sulfuric-acid mist (sulfur dioxin SO_2 and sulfur trioxide SO_3; nitrogen oxides; CO; CO_2 hydrogen sulphide H_2S). Processing of concentrates to metals has been done in Copper Plant in the town Pirdop (“Aurubis” today) with all obligations in cases when were registered past pollution and for termination new burst and current pollution. Pollution of rivers Luda Yana and Topolnitsa with heavy metals and reagents is a few kilometres from their sources in the Sredna Gora Mountain.

The study area of the survey is localized close to village Chavdar on the nearest slope of lower part of watershed of Topolnitsa River, beneath the vast tailing pond. The aim of the survey is to identify the soil threats based on the sound field and analytical data obtained in 2014-2015 year.

MATERIALS AND METHODS

The study area is characterized by the Deluvial (Colluvial) meadow soil (medium thick) located in the village Chavdar, Municipality Pirdop with ele-vation 520 meter and coordinates N 42°37’47.2’’ E 24°03’32.1’’ (Fig. 1). The parent materials are colluvial gneisses and schist deposits, and the vegetation is composed of meadow grasses associations.

Fig. 1. *Landscape and localization of the soil survey area in the Zlatitsa-Pirdop valley*

Climate is characterized with mean annual temperature 9.4°C (mean January temperature -1.7° C and mean July temperature 19.8°C); mean annual precipitation is 590 mm. The soil moisture and temperature regime is mesic-udic.

Morphological description is performed after The Guidelines for soil description (FAO, 2006). Soil samples from the genetic horizons are analyzed to determine total organic soil carbon, the cation exchange capacity and texture. Soil organic carbon content was determined using the modified Turin's method (Kononova, 1966; Filcheva et al., 2002) (dichromate digestion at 120°C, 45 min, in presence of Ag_2SO_4 and $(NH_4)_2$ SO_4 $FeSO_4$ $6H_2O$ titration, phenyl anthranilyc acid as indicator).

The cation exchange capacity was determined after the method of Ganev and Arsova (1980). The texture or particle size distribution was determined according to method of Kachinskiy (1965) revised. The the harmful levels of heavy metals content in the soil is discussed according to the Ordinance No 3 (2008). The harmonization of classification of the terrain soil units is after Shishkov (2011).

RESULTS AND DISCUSSION

Geomorphologicaly Zlatitsa-Pirdop valley is referred to the Sub-Balkans valleys province. The surrounding relief is mountain-valley of middle-height. In the transition zone between steeper mountain slopes and valley floors along the river beds, rivers and steams accumulate deposited material like large cones. The Quaternary sediments cover the lover parts of the valley and are deposited products of weathering of Palaeozoic mica schist (muscovite), gneiss or granite-gneiss and granite. Many of the foot slopes are covered with colluvium.

The soil profile is localized on the foot slope and the classification is: Deluvial (Colluvial) meadow soil (medium thick) (Bulgarian classification 1976, 1983); Haplic Cambisols (Colluvic, Eutric, Siltic) (WRB, 2006); Humic Eutrudepts (Soil Taxonomy USDA, 2010), Eutric Cambisol (FAO, 1990).

Morphological description of the Deluvial (Colluvial) meadow soil (medium thick) is, as follows:

A1 0-10 cm. Colour brown 10YR 4/3 (dry) and dark yellowish-brown 10YR 3/4 (moist), silty loam textural class, friable granular structure of medium size 2-5 mm, occurrence of many fine roots, weak presence of biological activity, gradual smooth boundary to the lower horizon;

A2 10-30 cm. Colour yellowish-brown 10YR 5/3 (dry) and dark yellowish-brown 10YR 3/4 (moist), silty clay loam textural class, friable granular structure of medium size 2-5 mm and coarse 5-10 mm, many fine roots, abundance of quartz grains and micas fragments, gradual smooth boundary to the lower horizon;

AC1 30-35 cm. Colour yellowish-brown 10YR 5/3 (dry) and brown 10YR 4/3 (moist), sandy loam textural class, friable subungular blocky structure of medium size 10-20 mm single aggregates of coarse size 20-50 mm, abundance of quartz grains and micas fragments, gradual smooth transition;

AC2 35-45 cm. Colour yellowish-brown 10YR 5/4 (dry) and brown 10YR 4/3 (moist), silty clay loam textural class, friable subungular blocky structure of medium size 20-50 mm, abundance of quartz grains and micas fragments, gradual smooth transition;

Fig. 2. *Deluvial (Colluvial) meadow soil (medium thick), from region village Chavdar*

AC3 45-55 cm. Colour yellowish-brown 10YR 5/4 (dry) and brown 10YR 4/3 (moist), silty clay loam textural class, friable subungular blocky structure of medium size 10-20 mm, many small pebbles and stones, sharp boundary to the lower horizon;

C1 55-70 cm. Colour yellowish-brown 10YR 5/4 (dry) and dark yellowish-brown 10YR 4/4 (moist), silty loam textural class, massive structure, abundance of quartz grains and micas fragments, many pebbles and stones of different size, gradual smooth transition;

C2 70-85 cm. Colour yellowish-brown 10YR 5/4 (dry) and dark yellowish-brown 10YR 4/4 (moist), silty clay loam textural class, not homogeneous, semi weathered parent rock, compacted, massive, abundance of rock fragments.

The surface horizons 0-20 cm of the spatial characteristic of the texture in the survey area (Table 1) shows that the Undeveloped cinnamonic forest soils (shallow, medium and severely eroded) are composed of skeletal part and fine earth. The latter is referred to the silty loam textural class followed by silty clay loam; in the Deluvial (Colluvial) meadow soil (medium thick) developed on the foot slope and the Alluvial meadow soils formed on the terrace the textural class is loam; and in the Alluvial soils from flooded zone it is sandy loam. In the fine earth, the content of clay (or particles with diameter less than 0.001 mm) is very low 1.5-6.5 % at the upper slope and gradually increases downward up to 19 % in the foot slope zone.

According to the texture data (Table 2), the selected site with the Deluvial (Colluvial) meadow soil (medium thick) is composed of colluvium mixed layers of different textural classes - silty loam, silty clay loam, sandy loam.

The ratio of the cations exchange capacity identified in the different parts of soil profile and soil forming materials indicates the nature and development of soil colloids. The cations exchange adsorptions capacity ($T_{8.2}$) shows the chemical reactivity and status of organic-mineral nature of colloids of the studied soil (Table 3). The Deluvial (Colluvial) meadow soil (medium thick), is characterized with well developed cation exchange capacity ($T_{8.2}$ = 30.4-32.8 cmol/kg soil) throughout the profile. The relevant share of the ions exchange positions on the surfaces of clay structures is evidence of high non-equivalent isomorphic substitutions of clay crystal lattice. The soil colloids are not differentiated in the profile according to their crystal-chemistry of clay structures. The relative share of the cation exchange capacity of the strongly acidic ions exchanger (T_{CA}) is 76.0-78.7 % of ($T_{8.2}$) in the humus (A) horizon and is 81.0-86.5 % at the depth 85 cm.

Table 1. Spatial characteristic of the soils particle size distribution from the survey area (% to air dry soil) (according method of Kachinskiy revised)

Horizon and depth, cm	Munsell soil colour, (dry)	Hygros. mois-ture, %	Particle size (mm), %							
			>1.0	1.0-0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001	Σ ≤ 0.01
Undeveloped cinnamonic forest soils (shallow, medium and severely eroded), on the upper and middle slope										
1. AC 0-20	10YR5/4	2.98	0.0	44.1	24.8	18.3	5.9	4.4	2.5	12.8
2. AC 0-20	10YR5/4	3.62	0.0	38.5	19.0	23.4	12.4	3.8	2.9	19.1
3. AC 0-20	10YR5/4	2.43	0.0	50.6	20.8	9.3	8.8	6.1	4.4	19.3
4. AC 0-20	10YR5/4	1.74	0.0	45.6	27.6	7.4	9.3	4.4	5.7	19.4
5. AC 0-20	10YR5/4	2.48	0.0	78.8	3.2	6.4	7.3	2.3	2.0	11.6
6. AC 0-20	10YR6/4	2.67	0.0	70.1	12.1	5.0	9.5	1.8	1.5	12.8
7. AC 0-20	10YR5/4	2.99	0.0	43.0	27.8	6.1	12.1	4.5	6.5	23.1
8. AC 0-20	10YR5/4	2.32	0.0	59.2	22.8	4.9	6.1	4.8	2.2	13.1
9. AC 0-20	10YR6/3	1.93	0.0	72.0	13.4	4.0	4.7	4.1	2.1	10.6
10. AC 0-20	10YR5/4	4.32	0.0	21.8	35.2	18.0	12.3	5.8	6.9	25.0
11. AC 0-20	10YR5/4	3.35	0.0	49.6	21.0	11.9	3.9	3.5	10.1	17.5
12. AC 0-20	10YR5/4	2.95	0.0	71.8	1.3	7.6	3.9	3.7	11.7	19.3
13. AC 0-20	10YR6/3	3.78	0.0	40.2	16.7	14.6	9.6	6.6	12.3	28.5
14. AC 0-20	10YR5/4	2.77	0.0	48.9	14.6	2.6	16.0	4.2	13.7	33.9
Deluvial (Colluvial) meadow soil (medium thick) on the foot slope										
15. AC 0-20	10YR5/4	4.28	0.0	33.4	22.6	11.0	10.1	3.8	19.1	33.0
16. AC 0-20	10YR5/3	4.68	0.0	29.8	21.6	9.0	13.8	7.6	18.2	39.6
Alluvial meadow soils from the terrace										
17. AC 0-20	10YR5/4	3.54	0.0	20.8	13.7	26.1	10.9	13.7	14.8	39.4
18. AC 0-20	10YR5/3	4.13	0.0	39.9	19.0	7.7	14.0	4.1	15.3	33.4
Alluvial soils from the flooded terrace										
19. AC 0-20	10YR6/4	1.22	0.0	70.9	17.2	3.3	2.8	3.3	2.5	8.6
20. AC 0-20	10YR6/3	2.72	0.0	56.2	25.3	5.3	3.6	3.4	6.2	13.2

Table 2. Particle size distribution of the selected site with Deluvial (Colluvial) meadow soil (medium thick) (% to air dry soil, according to method of Kachinski revised)

Horizon and depth, cm	Hygros. moisture, %	Particle size (mm), %							
		>1.0	1.0-0.25	0.25-0.05	0.05-0.01	0.01-0.005	0.005-0.001	<0.001	Σ ≤ 0.01
A1 0-10	3.98	0.0	50.2	13.1	14.3	5.5	3.3	13.6	22.4
A2 10-30	4.74	0.0	29.3	24.1	11.7	13.1	5.7	16.1	34.9
AC1 30-35	2.88	0.0	30.4	26.4	24.4	6.7	3.6	8.5	18.8
AC2 35-45	2.34	0.0	49.3	9.9	7.5	14.2	3.6	15.5	33.3
AC3 45-55	2.28	-	38.0	14.3	17.3	11.2	3.4	15.8	30.4
C1 55-70	2.64	-	46.0	13.0	13.6	6.4	4.0	17.0	27.4
C2 70-85	2.61	-	34.4	18.0	12.4	11.1	4.4	19.7	35.2

Table 3. Cation exchange capacity (meq/100 g soil = cmol/kg soil) and base saturation (%) in the selected site with Deluvial (Colluvial) meadow soil (medium thick) after the method of Ganev and Arsova (1980)

Horizon and depth, cm	pH H_2O	Exchange cations, (cmol/kg soil)							Exchange cations, $T_{8.2}$ (%)						Base saturation, V %
		$T_{8.2}$	T_{CA}	T_A	$H_{8.2}$	Al+H	Ca	Mg	T_{CA}	T_A	$H_{8.2}$	Al+H	Ca	Mg	
A1 0-10	5.3	30.4	23.1	7.3	8.5	1.2	17.5	4.3	75.99	24.01	27.96	3.95	57.57	14.14	72.04
A2 10-30	5.4	32.8	25.8	7.0	8.0	0.9	20.8	4.2	78.66	21.34	24.39	2.74	63.41	12.80	75.61
AC1 30-35	5.5	33.5	27.2	6.3	7.1	0.8	22.6	4.2	81.19	18.81	21.19	2.39	67.46	12.54	78.81
AC2 35-45	5.5	32.7	26.7	6.0	6.6	0.7	21.8	4.2	81.65	18.35	20.18	2.14	66.67	21.84	79.82
AC3 45-55	5.6	31.3	26.5	4.8	5.4	0.6	21.5	4.1	84.66	15.34	17.25	1.91	68.69	13.10	82.75
C1 55-70	5.65	31.3	27.1	4.2	4.8	0.6	22.0	4.3	86.58	13.42	15.34	1.92	70.29	13.74	84.66
C2 70-85	5.65	31.2	27.0	4.2	4.8	0.6	21.9	4.2	86.54	13.46	15.38	1.92	70.19	13.46	84.62

Note: ($T_{8.2}$) – cation exchange adsorption capacity of soil; (T_{CA}) – cation exchange capacity of the strongly acidic ions exchanger; (T_A) - slightly acidic ions exchanger.

The base saturation is 72 % in the humus (A) horizon and higher 84 % in the parent materials. The value of acidification is high (exch. $H_{8.2}$ = 24-28 % of $T_{8.2}$) in the surface humus (A) horizon where presence of exchangeable aluminum is (exch Al+H = 3-4 % of $T_{8.2}$). The destructive processes occur at the colloid surfaces of the slightly acidic ions exchanger of the soil.

All over the survey area the very high levels of Mn concentration were identified (Table 4). Relatively high total metal content can be of natural origin. The total content of elements in soil forming rocks is possible to display the background content. In many cases these concentrations are less mobile and biologically unavailable. Soil reaction is an important factor affecting mobility of elements (pH determined in water or electrolyte ISO 10390). There is evidence that organic matter affects the mobility of potentially toxic elements (Filcheva et al., 2014). The commitment of elements with whose from different backgrounds as atmospheric transport, of sludge and other waste should be taken under the consideration.

The high concentrations of Cu (87-318 mg/kg) and Zn (80-135 mg/kg) that exceed the permitted toxic levels in soil are identified in the Alluvial soils from flooded zone and also in Alluvial meadow soils from terrace. The high level of exchangeable Mn of 72 mg/kg was identified in the Alluvial soils from the flooded zone.

The significant variation of the soil organic matter content in the survey area was established (Table 4). The surface horizons of shallow Undeveloped cinnamonic forest soils are with properties inherited from the hard rock limited to the 20-25 cm depth. These soils are with weak pronounced humus horizon and homogeneous distribution of the total organic carbon, which content varies from 0.8 to 3.5 %.

In the organic matter composition of the Deluvial (Colluvial) meadow soil (medium thick) the content of the extractable organic carbon in the surface horizons shows that the organic matter is bounded to the soil mineral part. The weathering is more advanced and affects also the (C) horizons, where amount of organic carbon was found. Humic acids are characterized with low degree of humification. The data of organic matter contend and low content of clay is evidence of prone to the erosion process.

In the most northern part in the flooded zone occupied with alluvial soils the disposal of construction waste, inert and other materials as well as asphalt residues was established.

Table 4. Spatial characteristic of the total content of heavy metals in soil samples from the survey area (in mg/kg dry weight) decomposed with Aqua regia and mobile forms extracted with 1 M NH_4NO_3

№	Opr.C, %	pH (H_2O)	Extracted with 1 M NH_4NO_3, (mg/kg)						Decomposed with HNO_3 + 3 HCl, (mg/kg)					
			Cupper (Cu)	Zink (Zn)	Cadmium (Cd)	Lead (Pb)	Manganese (Mn)	Iron (Fe)	Cupper (Cu)	Zink (Zn)	Cadmium (Cd)	Lead (Pb)	Manganese (Mn)	Iron (Fe)
Undeveloped cinnamonic forest soils (shallow, medium and severely eroded), on the upper and middle slope														
1	2.96	5.73	0.100	0.55	0	0	14.00	0.33	44.0	67.0	<0.50	29.0	1058	38800
2	3.46	5.55	0.100	0.68	0	0	16.25	0.43	53.0	74.0	<0.50	35.0	733	-
3	3.05	5.33	0.100	1.00	0	0	24.25	0.35	50.0	72.0	<0.50	31.5	790	40500
4	2.12	5.42	0.050	0.55	0	0	13.75	0.18	40.0	66.0	<0.50	24.0	605	39600
5	2.33	5.38	0.275	1.43	0	0	16.50	0.38	72.0	57.0	<0.50	57.0	485	-
6	0.81	5.56	0.175	0.63	0	0.5	15.25	0.50	26.5	56.5	<0.50	12.0	408	45500
7	3.24	5.07	0.150	0.78	0	0	18.00	0.35	45.5	53.5	<0.50	27.5	533	-
8	3.17	5.01	0.175	1.05	0	0.13	20.25	0.43	46.0	51.5	<0.50	27.5	475	29700
9	1.26	5.07	0.800	1.33	0	0	21.00	0.53	50.0	61.0	<0.50	23.5	535	-
10	3.52	5.40	0.100	0.88	0	0	18.50	0.35	44.0	60.0	<0.50	21.5	620	31000
11	2.47	5.41	0.075	0.93	0	0	19.50	0.38	45.0	57.0	<0.50	27.0	480	34700
12	2.48	5.24	0.150	0.85	0	0	19.50	0.38	47.0	49.0	<0.50	25.0	703	-
13	1.29	5.18	0.150	1.45	0	0	26.75	0.47	50.0	56.0	<0.50	28.5	510	31300
14	2.07	5.56	0.025	0.45	0	0	18.00	0.35	38.0	53.0	<0.50	18.5	493	32400
Deluvial (Colluvial) meadow soil (medium thick) on the foot slope														
15	2.98	5.29	0.100	1.18	0	0	23.00	0.53	43.5	57.5	<0.50	21.0	583	-
16	4.09	5.07	0.050	0.70	0	0	18.50	0.50	49,0	60.5	<0.50	39.0	625	32600
Alluvial meadow soils from the terrace														
17	2.72	6.67	0.175	0.23	0	0	14.25	0.75	72,5	79.5	<0.50	31.0	650	-
18	4.06	6.67	0.100	0.28	0	0	22.75	0.45	87,0	135.0	<0.50	38.5	825	38200
Alluvial soils from the flooded terrace														
19	0.60	7.03	0.150	0.23	0	0	12.25	0.25	117,0	78.5	<0.50	7.50	593	37900
20	1.08	6.34	0.300	0.70	0	0	72.00	0.35	318,0	117.5	<0.50	16.0	665	33700

Soil forming processes tend to be slow and occur over long period of time even under the permanent grasslands in temperate climate. Soil that is lost due to the degradation processes (e.g. erosion, pollution) would need many years to recover naturally. This is a case when compare to the human's life, the soils must be regarded as non-renewable recourse.

CONCLUSIONS

1. The high susceptibility and vulnerability of soils was identified in the survey area of Zlatitsa-Pirdop valley. Most soils are with silty loam, silty clay loam and sandy loam textural classes. The soil colloids are not differentiated in the soil profile according to their clay structures. The destructive processes occur only at the colloids surface. Soils are with weak pronounced humus horizon and distribution of the organic carbon from 0.8 to 3.5 %. The very high level of Mn concentration was identified in the survey area which is possible to display the background content in the rock. The area occupied by the alluvial soils nearby the Topolnitsa River is contaminated also with Cu and Zn.

2. The terrain survey identified basic pedoge-netic processes established in the area of Zlatitsa-Pirdop valley like leaching, weathering "in situ", erosion and contamination with Mn, Cu and Zn. However, there were established processes induced by human activities like erosion, contamination and soil sealing as disposal of construction waste, inert and other materials on the surface of alluvial soils.

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