Alteration Of Physico Chemical And Morphological Characteristics Of Sod-podzolic Soils In Technogenically-affected Landscapes Of Moscow Brown Coal Basin

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Abstract

Long-term coal mining in the Moscow basin has led to changes in soil properties of landscapes. Spoil heaps of sulphide-bearing overburden rocks and subsidence over the mined space are formed at abandoned mine fields. Acid mine drainage (AMD) of sulfuric acid, Al and Fe sulfate as well as pyritized material, entering from eroded spoil heaps, results in morphological changes in soil properties. This study aimed at evaluation of physico chemical transformation of soil properties, which is adjacent to spoil heaps. Natural soils are sod-podzolic soils. On foreslopes around spoil heaps technogenically transformed soils are common. Technogenically transformed soils are characterized by acidic reaction with a high content of Fe and Al sulfate as well as a considerable amount of exchange and total titratable acidity in soil solid phases and soil solutions, respectively. It is revealed that contaminated sod-podzolic soils, in relation to natural soils, has a specific morphologic features: intensification of eluvial process (bleaching of soil mass) along with intensive accumulation of iron (nodules and patches of Fe oxides and hydroxides) and organic matter of coal origin. Sod-podzolic-gley soils with transformed water regime are formed in mine subsidence.

Keywords: brown sulfur coals, spoil heaps, acid mine drainage, mine subsidence, technogenically transformed soils

Introduction

Coal mining causes substantial environmental alterations of landscapes (terrain, soils and ground waters) (Nordstrom and Alpers 1999). In sulfur brown coal mining areas of Moscow basin, soils are affected by acid mine drainage (AMD), solid sulfide-bearing mine wastes and carbonaceous particles. Solid mine wastes of Moscow basin, which comprise of overburden and host rocks, are stored in conical spoil heaps (40-60 m in height) near mine sites (Solntseva et al. 1992). At present, coal mining is terminated. Abandoned spoil heaps in Moscow basin have not been recultivated and erode intensively due to physico chemical properties of waste rocks. As a result, mine wastes enter the environment.

The toxicity of waste materials for biota is determined by the high amounts of iron sulfides (mostly pyrite and marcasite). Very high total content of sulfur (up to 5%) is connected to marine origin of brown coals in the Moscow basin. Pyrite is subjected to continuous weathering and oxidation in spoil heaps (Lottermoser 2010). Active oxidation of sulfides in waste dumps results in the producing of toxic sulfuric acid and iron sulfate (Nordstrom and Alpers 1999). Aluminosilicates in clay minerals (predominantly kaolinite and illite) of spoil heaps are in contact with acidic pyrite oxidation waters that creates toxic Al sulfate (Younger 2004; Silva et al. 2011). Weathering of spoil heaps led to formation of deluvial and proluvial waste dump tailings of technogenic materials on soil surface. Solid-phase products of chemical weathering and mechanical dispersion of spoil heaps, transported by drainage waters, formed technogenic deposits on the soil surface.

Other environmental concern is the formation of dips and subsidence areas over the mined space due to the dewatering of abandoned coal mines. It results in alteration of the soil water regime (Younger 2004; Wang et al. 2017).

The aim of the study was to examine the post-mining transformation of physico-chemical and morphological soil properties under the effect of supply of technogenic material from the spoil heaps and changes of the terrain in abandoned sulfur coal mining areas.

Study area

Sampling site was located in the Cherepet brown coal deposit of Moscow basin (the Tula Region, Russia). We investigated Glubokovskaya-4 (36°32'17"E, 54°10'43"N) abandoned spoil heap and adjacent areas (fig. 1). According to Geology of coal and oil shales of the USSR (1962), carboniferous strata of Moscow basin belong to the Visean stage of the Lower Carbon. Waste dumps of Cherepet deposit comprise of iron sulfide-bearing carbonaceous black greasy clays with kaolinic clays, brown coal layers, loams, sandy loams and quartz sands, as well as pyrite crystals (Solntseva et al. 1992). There may be $CaCO_3$ (calcite) and $FeCO_3$ (siderite) impurities in clays. At the reference site natural soils are sod-podzolic soils, mainly weakly podzolic (Albeluvisols in WRB 2014 (IUSS Working Group WRB 2015)), sandy-loamy on moraine loams. Sod-podzolic-gley soils prevailed in depressions. The vegetation of the site is represented by mixed forests with birch, aspen and pine.

Methods

Descriptions and soil sampling were carried out at sites with technogenic transformation (soil profiles SUV 2 to SUV 6) and at relatively natural site (soil profile SUV 1). Waste material was sampled at foothill of the spoil heap (SWD point). AMD was sampled from technogenic reservoir at foothill of the spoil heap (SPW point) (fig. 1). Samples of AMD, soils, waste materials and displaced solutions from soils and waste materials were investigated. Fresh soil samples, taken from each genetic horizon and overburden sediments, were used for soil solutions displacement.

Soil solutions were displaced by ethanol (Ishcherekov-Komarova method, Russia) (Snakin et al. 2001). The composition of soil solutions was measured by ion chromatography. The content of Fe^{2+} and Fe^{3+} ions in soil solutions was determined by spectral photometry. The content of H^+ and Al^{3+} ions in soil solutions (the sum of H^+ and Al^{3+} is equal to titratable acidity) was determined by titration to pH 8.2 using a 0.01 M NaOH solution. The pH value was measured by the potentiometric method using Expert 001 ionometer (Econics Expert,

Figure 1 Satellite image of the sampling site and locations of soil, waste dumps, filtrated waters, and AMD sampling.

Russia). Electrical conductivity (EC) was measured using conductometer SevenEasy S30 (Mettler Toledo, Switzerland).

Exchangeable cations (H^+, Al^{3+}, Ca^{2+}, Mg^{2+}) were released upon exchange by 1 M KCl solution at a soil to solution ratio of 1:2.5. Total alkalinity in the aqueous extract was determined by acid-base titration using a 0.01 M H_2SO_4 solution to pH 4.4. The content of Ca^{2+} and Mg^{2+} was determined by titration using a 0.05 M EDTA solution (Vorobyova 2006). The total content of organic carbon was determined by dichromate oxidation.

Results and Discussion

Technogenic deposit (TD) on the soil surface, composed of the waste dump material, had a highly acidic reaction (pH=3.4-3.9) as well as high content of organic carbon of coal origin (up to 18.1%). Aluminum sulfates prevailed among readily soluble salts. The share of Ca^{2+} and Mg^{2+} was also considerable (tab. 1). Clay material of the deposits was very fine, dirty brown in color, with inclusions of silty detrital carbonaceous particles. Dump tailings were covered by white saline crusts composed of Fe and Al-hydrated sulphates. There was no vegetation on the surface of TD.

Technogenic waterlogged reservoir (SPW), filled with highly acidic filtrated waters (pH = 2.7-3.0), had reddish-yellow colour with elevated concentrations of Fe, Al and sulfate (tab. 1), that is typical for coal mining areas (Martin et al. 2008). EC value was about 2920 µS/cm.

At the reference site, natural sod-podzolic soils were characterized by low carbon content (up to 1.5%) and had a weak-acid reaction (pH 5.5-6.3). EC value of soil solutions did not exceed 320 µS/cm. Soils had a homogenous distribution and low content of salts throughout the profile (SUV 1). A predominant cation in the readily soluble salts was Ca^{2+} (tab. 2). The composition of the anionic part was sulfate-bicarbonate (SUV 1). Exchangeable Ca^{2+} prevailed in natural soils (tab. 3).

Soils with technogenic transformation were overlapped by technogenic deposits up to several dozen centimeters in thickness. Buried part of soil profile had the specific chemical and morphological properties (Solntseva et al. 1992). The contaminated soils, affected by technogenic fluxes, were characterized by a strong acidic reaction (pH=3.5-4.5). EC of soil solutions was extremely high (from 940 to 5680 µS/cm). Technogenic fluxes from waste dumps contain fine dispersed fractions of coal material. As a result, organic carbon of coal origin was accumulated in the upper horizons of technogenic soils. Concentrations of organic carbon (up to 10%) exceeded background values by 2.5-5.6 times. The specific feature of the newly formed salt composition in polluted sod-podzolic soils (SUV 4) was the presence of aluminum sulfates in soil solution in very high amounts, especially in the layer of 32-60 cm in EL and BEL horizons. The horizons were bleached (tab. 2) and had homogeneous light-grey colour that might be associated with partial acid hydrolysis of the primary silicates (mainly feldspars and phyllosilicates) (Martin et al. 2008). Sod-podzolic soils at the reference site had no water-soluble aluminum sulfates. There were less Fe^{3+} and Fe^{2+} ions in solutions, because of their precipitation in BTg horizon, mainly in amorphous or poorly crystallized forms (Simon et al. 2001).

Increasing of the concentration of H^+ and Al^{3+} ions in the liquid phase of contaminated soils decreased the amount of exchangeable Ca^{2+} and Mg^{2+} in soil ion-exchange complex by 2.5 times due to the substitution of Ca^{2+}

Table 1 *Chemical properties (pH value, composition of readily soluble salts, titratable acidity, water-soluble Fe) of waste dumps (displaced solutions) and AMD*

Sampling point	pH	composition of readily soluble salts (mmoL/dm³)							titratable acidity (mmoL/dm³)			
		HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	Al^{3+}	Fe^{2+}	Fe^{3+}
SWD[1]	2.9	0.1	1.0	65.3	25.0	16.1	0.2	1.0	0.4	3.4	18.0	4.8
SPW[2]	3	ND[3]	0.2	28.9	14.0	2.1	ND	0.1	9.7	21.6	22.5	0.4

[1]SWD technogenic material of waste dumps [2]SPW filtrated waters and acid mine drainage [3]ND not detected

Table 2 Chemical properties (pH value, composition of readily soluble salts, titratable acidity) of displaced solutions from soils and deposits of waste material

Sampling point	Horizon	Depth, cm	pH	composition of readily soluble salts (mmoL/dm³)							titratable acidity (mmoL/dm³)	
				HCO_3^-	Cl^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	Na^+	H^+	Al^{3+}
SUV 1, reference site	AY	0-13	6.0	0.4	0.2	0.2	5.7	0.9	0.1	0.2	0.5	ND
	EL	13-18	6.3	0.4	0.2	0.3	3.3	0.4	0.1	0.2	0.5	ND
	BEL	18-45	6.2	1.2	0.2	0.3	2.9	0.2	0.1	0.3	1.0	0.1
	BT_1	45-90	5.5	0.7	0.5	0.2	1.1	0.2	ND	0.2	0.8	ND
	BT_2	90-110	5.9	0.6	0.8	0.3	0.6	0.2	ND	0.1	0.4	ND
SUV 4, technogenically-affected site	WTD	0-15	3.8	0.1	0.1	9.0	5.8	1.2	0.1	0.9	0.7	4.5
	TD[1]	15-32	3.7	0.1	0.1	252.1	35.7	6.8	0.2	0.7	49.9	40.4
	EL	32-54	3.8	0.1	0.1	200.9	31.7	10.6	0.4	0.7	4.3	83.7
	BEL	54-60	3.5	0.1	0.2	201.0	25.0	12.7	0.4	0.7	2.8	79.4
	BT	60-110	3.4	0.1	0.2	221.8	28.7	16.3	0.2	0.8	1.8	79.4
SUV 6, subsidence area	TD	0-23	4.1	0.1	ND[2]	0.7	1.7	0.1	ND	0.6	4.8	0.4
	EL	23-34	4.5	0.3	ND	0.8	1.6	0.4	ND	0.5	0.7	0.3
	BELg	34-51	4.3	0.3	0.2	5.8	4.0	1.0	ND	0.3	0.3	1.4
	BTg_1	51-95	4.1	0.2	0.3	25.8	20.6	6.5	0.1	1.1	0.6	2.5
	BTg_2	95-110	4.2	0.3	0.2	20.5	16.0	4.8	ND	1.0	0.7	2.7

[1]TD technogenic deposit, [2]ND not detected

Table 3 Concentrations of exchangeable cations in natural and technogenically transformed soils

Sampling point	Horizon	Depth, cm	pH_{KCl}	Ca^{2+} (cmol$_c$ kg^{-1})	Mg^{2+} (cmol$_c$ kg^{-1})	H^+ (cmol$_c$ kg^{-1})	Al^{3+} (cmol$_c$ kg^{-1})
SUV 1, reference site	AY	0-13	3.3	4.1	1.3	0.1	0.4
	EL	13-18	3.7	4.6	1.9	0.1	0.4
	BEL	18-45	3.8	5.3	1.8	ND[2]	0.4
	BT_1	45-90	3.9	6.5	2.5	0.1	1.3
	BT_2	90-110	4.0	6.9	2.9	0.1	1.3
SUV 4, technogenically-affected site	WTD	0-15	3.5	2.1	0.9	0.2	7.6
	TD[1]	15-32	4.1	1.3	0.5	ND	3.4
	EL	32-54	4.1	1.5	0.5	ND	4.1
	BEL	54-60	3.7	5.8	2.3	0.1	9.6
	BT	60-110	3.7	7.4	4.8	0.1	5.7
SUV 6, subsidence area	TD	0-23	4.0	2.5	1.1	0.1	2.7
	EL	23-34	4.0	1.0	0.6	0.1	2.3
	BELg	34-51	3.7	3.8	2.1	0.1	7.4
	BTg_1	51-95	3.8	4.5	3.1	ND	4.4
	BTg_2	95-110	3.7	4.6	3.3	0.1	4.9

[1]TD technogenic deposit, [2]ND not detected

and Mg^{2+} by H^+, and at low pH values - by Al^{3+} (Snakin et al. 2001; Androkhanov et al. 2004). Al^{3+} was predominant in the ion-exchange complex of soils in the amount of up to 70-80% of the total exchange cations. The share of exchangeable H^+ was also substantial (tab. 3). The content of exchangeable Mg^{2+} exceeded concentrations in natural soil.

The soils in a subsidence area (SUV 6) had excessive moisture, lower pH and lower content of salts in soil solution due to the additional lateral intrasoil runoff of water. Hydromorphic gley and gleyic soils with secondary gley genesis were formed in subsidence areas (fig. 2).

Various morphological alterations were revealed in the sod-podzolic soils influenced by technogenic fluxes of phytotoxic rocks. Filling of pore space with finely dispersed material led to compaction of soil mass and formation of horizons with extremely high bulk density, and low porosity and a substantial amount of technogenic carbonic admixtures (fig. 2). The microaggregation of the contaminated soils was law. Granular and cloggy aggregates were replaced by cloddy, lumpy, and nutty ones.

Due to AMD effects that had destroyed fine clay minerals, numerous clarified areas were formed, composed of quartz and feldspar. Throughout the profile, there were signs of gleying (grayish and smoke blue shades) and ferrugination (ochreous and rusty-brown iron patches, nodules and crusts of Fe oxides and hydroxides) on faces of structural units (Solntseva and Rubilina 1987). In soil genetic horizons specific cutans with the high content of coal particles were formed (fig. 2).

Conclusions

Long-term introduction of sulfide-bearing technogenic material to the environment led to substantial geochemical transformation of sod-podzolic soils. The main changes in morphology of sod-podzolic soils were the intensive ferrugunation of the buried soil profile and the intensification of the eluvial process (formation of carbonaceous films). Chemical properties and morphological features of technogenically altered soils and natural soils differed considerably. Key geochemical processes at mine sites in sod-podzolic soils were: (1) acidification and Fe-

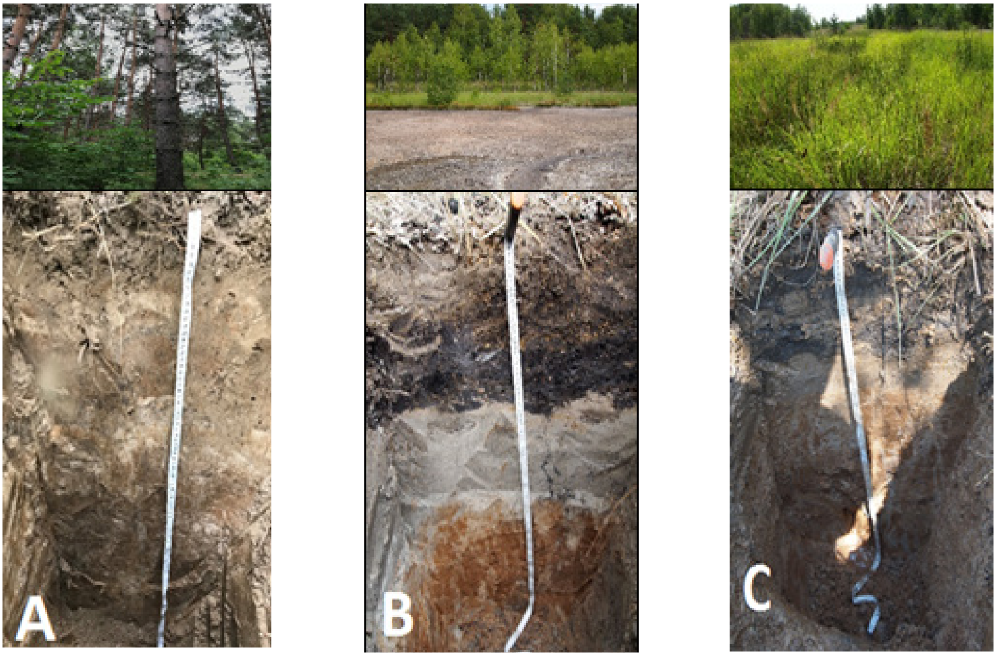

Figure 2 *(A) Reference sod-podzolic soils and transformed soils (B, C - in subsidence area) polluted by acid coal mine wastes*

$Al-SO_4$ salinization of soil profile along with the increasing of H^+ and Al^{3+} ions content; (2) cation exchange, leading to replacement of Ca^{2+} and Mg^{2+} ions by Al^{3+} and H^+ ions, perhaps, and by Fe^{2+} in soil ion-exchange complex; (3) mineral transformations.

Thus, sod-podzolic with technogenic transformation at post sulphur coal mining sites were similar to northern podzolic soils in terms of intensive acid hydrolysis of the layer silicates. The results of this investigation could be used to implement a complex remediation measures in Moscow coal basin, as well as prognosis on the negative effect of mine wastes on soil salinity status.

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