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Pedo-chemical Perturbations in Soils from Green Ecosystems of the Sofia City (Bulgaria)

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Abstract. In view of the role of cities for ensuring a favorable living environment, it is important to study the urban soils since they are formed and developed under the impact of different by degree and type anthropogenic perturbations. Pedo-chemical studies of urban soils may capture the evolution of different soil components and reveal the different stages of soil matrix transformation. Using pedogenic and chemical analyses, the present article aims to present the trends of perturbations of the mineral and organic matrix of urban soils located along the direction of increasing gradient of urbanization in cursory investigated soil zones belonging to the residential and industrial districts of the Sofia city (Bulgaria). The results obtained show that anthropogenic alterations are predominantly associated with morphological reorganization of some soils rather than soil compaction and structure loss. The increase of exchangeable hydrogen content provoked by fulvic acid production and leaching can be attributed to the current natural perturbations. Anthropogenically induced chemical changes could be linked with increase of the mineral N flux and high ammonium content which will influence the existing acid-base status of Sofian soils.

Key words: urban soils; exchange capacity; aqua regia; humic acids specification; nitrogen fluxes.

Introduction

Globalization processes that started in the beginning of the 20th century transformed cities in a unique assemblage of natural, ethnic, aesthetic, production, commercial, social and tourist symbols but also contributed to the increase of chemical vulnerability of soils. The enormous gathering of population in the cities influences all the environmental components and substantially changes the soil cover. Usually, urban soils significantly differ in properties and organization from natural soils and should be properly managed (Lehmann & Stahr, 2007). Specific features of urban soils are related to the variation of soil acidity and sorption capacity, enrichment with organic matter mostly in the form of

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non-hydrolysed carbon, low water holding capacity, strong compaction and heavy metals contamination (DOICHINOVA, 2006; DOICHINOVA & ZHYANSKI, 2013).

Metrics such as pH and cation exchange capacity are the most preferable and accessible indicators for initial assessment of chemical status of soils (THOMAS, 1996; DINEV, 2011; NIKOVA, 2009). It is a well-known fact that the interpretation of data on physico-chemical processes running in the soil adsorbent is a key tool for the sustainable management and protection of soils (HENGLEIN, 1993). Organic matter accumulation and transformation as prime soil-forming processes in the pedosphere are also widely discussed (SARDANS *et al*., 2012; CHENU *et al*., 2015; BŁONSKA & LASOTA, 2017; PIERSON, 2017; FROUZ & VINDUŠKOVÁ, 2018; ABDELRAHMAN *et al*., 2018; FILCHEVA, 2018; STUMPF *et al*., 2018). The issue of global warming forces the studies, which increase the knowledge of domains, resistance and cycling of chemical elements in and out of ecosystems (FINZI *et al*., 2011; DELGADO-BAQUERIZO *et al*., 2013; TSOLOVA *et al*., 2014; PARTON *et al*., 2015; YUAN & CHEN, 2015; TAN & WANG, 2016; JIAO *et al*., 2016).

The scarce data on urban soils in Bulgaria has aroused the interest in studying their pedochemical characteristics as information carriers on modern and relict processes of soil formation and transformation. By studying the cation exchange capacity, base saturation level, content of main exchangeable cations, content and forms of essential nutrients including organic carbon, the present article aimed to present the trends of transformation of mineral and organic matrix of urban soils located along the direction of increasing gradient of urbanization in cursory investigated soil zones belonging to the residential and industrial districts of the Sofia city (Bulgaria).

Materials and Methods

Location and morphogenesis of studied soils

Data on 6 soil types, located at the Eastern part of the Sofia city are represented in present publication. All soils form ecosystems with recreational significance and some of them have not been previously studied. They are distinguished for the following morphogenesis:

Anthropogenically overlapped moderately leached Smolnitsa, loamic is characterized by profile 1 located in "Mladost" residential region (Fig. 1). This soil was formed as a result of urbanization and occupies previously unexplored soil zone. In fact, moderately leached Smolnitsa borders this highly urbanized zone according to the previous studies (ACHKOV *et al.* 1972). The original soil, Smolnitsa (named after organic clays, smolnitsas composing soil) is overlapped by layers of earth calcaric masses, mixed with urban waste, pebbles and gravel. Profile development and morphological organization of new soil includes differentiation of organic matter, which resulted in a bimodal distribution and 3 representative horizons for soil morphogenesis: A_{hk} (0-15 cm) - C_{1k} (15-65 cm) - A_b (65-110 cm).

WRB classification of soil: Urbic Technosol (Eutric, Loamic, Humic, Transportic) over Pellic Vertisol (Chernic, Endocalcaric). Profile 2 characterizes Technogenic soil, moderately deep, loamic, moderately stony (15% coarse surface fragments' content in A_h horizon, Fig. 2), classified as *Urbic Technosol (Amphyskeletic, Calcaric, Mollic, Transportic)*. This soil is formed by massive pilling of earth calcaric materials onto the moderately leached Smolnitsa, loamic during the "Mladost" district construction. Profile development and morphological organization are results of surface accumulation of organic matter and slow weathering of subsoil that is strongly mixed with urban building artefacts – these processes lead to the formation of a three-layered profile: A_{hk} (0-21 cm) - C_{1k} (21-52 cm) - C_{2k} (52-85 cm). Parent materials are Quaternary brown alluvial clays and Pliocene sands, usually calcaric (YANEV *et* *al.,* 1992; 1995; BOJINOVA-HAAPANEN, 2014). Profile 3 illustrates the morphogenesis in moderately leached Cinnamon forest soil, loamic, slightly to moderately eroded /*Chromic Endocalcic Luvisol (Clayic, Differentic, Humic, Profondic)*/ located in the periphery of the "Mladost" residential region (Fig. 3). Profile development is a result of pedogenetic differentiation (illuviation) of clay content by depth and leaching of base cations. Morphologically, these processes form the following horizons: A_h (0-10 cm) - B_t (10-35 cm) - B_{t2} (35-72 cm) - B_{tk} (72-86 cm) - C_k (86-120 cm). The soil-forming materials according to YANEV *et al.,* (1992; 1995) and BOJINOVA-HAAPANEN, (2014) are Quaternary diluvial-colluvial materials (non-sorted gravel, boulders and clay-sandy deposits) and Pliocene sediments (yellow-rusty clays with layered structure, usually calcaric, clays with sandy matrix and gravel). Profile 4. Alluvial soil, moderately deep, slightly stony /*Hypereutric Fluvisol (Loamic, Somerimollic)*/ distributed in "Drujba" industrial region (fig 4). This soil is located in an over flooded terrace of the Iskar River, in a virgin district, next to the "Sofia Iztok" Thermal-electric Power Plant. Profile development is limited by coarse fragments abundance in subsoil and therefore the soil formation processes involve only the uppermost 15 cm. They resulted in morphologically simple profile organization: A_h (0-15 cm) – C_1 (15-40 cm) – C_2 (40-80 cm). Parent materials are mostly large gravels and boulders with a sandy matrix which lie onto a Pliocene stratum composed of sands and grey or green coloured clays (YANEV *et al.,* 1992; 1995; BOJINOVA-HAAPANEN, 2014). Fig. 5 shows profile 5 and Alluvial meadow soil, deep /*Hypereutric Fluvisol (Epiclayic, Endoloamic, Pachic)*/ located in "Drujba" residential region. It is formed within the flooded terrace of the Iskar River by fine-particle alluvial sediments of a Quaternary and Pliocene origin (ACHKOV *et al.,* 1972). Profile development and morphological organization is also marked by surface accumulation of organic matter and lithological clay differentiation by depth: A_h (0-30 cm) – A_2 (30-55 cm) – C_1 (55-105 cm) – C_2 (105-155 cm).Profile 6 is in strongly leached Smolnitsa, super deep, moderately clayey /*Pellic Vertisol (Pantochernic, Hypereutric, Relictigleyic)*/ distributed in "Mladost" residential region (fig 6). This soil occupies the higher part of the previously unexplored soil zone and neighbours the moderately leached Smolnitsa. This pedon also consists of organic clays (Smolnitsa), which foster the super deep A-horizon development (reaching up to 165 cm depth). Humus horizon directly lies on parent materials - grey-brown Pliocene clays containing calcareous nuts (YANEV *et al.,* 1992; 1995; BOJINOVA-HAAPANEN, 2014).

Chemical studies

The cation exchange capacity

The cation exchange capacity (Equation 1), the base saturation level and the content of the main exchangeable cations in soils were determined under the GANEV & ARSOVA (1980) method . This method determines the contribution of both the permanent, preferential charges (on basal surfaces, T_{CA}) and variation charges of soil colloids (basically pH dependent exchange including the lateral surfaces, T_A) to the cation exchange capacity by titration of soil extracts (obtained by mixed solution of 1.0 n sodium acetate and 0.2 n potassium maleate having pH 8.25) with 0.04 n sodium hydroxide solution in the presence of phenolphthalein to determine T_A and subsequent titration of the above eluate with 0.04 n complexon III (after dilution up to 200 cm^3 with deionized water and addition of 10 cm^3 of triethanolamine and 2 cm^3 of 5.0 n potassium hydroxide solution, non-carbonate to achieve pH 12-13) in the presence of chromium-blue to determine T_{CA} (Equation 1):

$$T_{8.2}=T_{CA}+T_A \text{ (cmol/kg)} \quad (1)$$

Exchangeable Al: in 1.0 n calcium chloride filtrate obtained as a soil:extractant ratio 1:25 by titration with 0.04 n sodium hydroxide in the presence of phenolphthalein. When soil pH <4.0, exchangeable hydrogen ions, H_A, should be determined first - 1 drop of methyl orange is added to the calcium chloride filtrate and titrated with 0,04 n sodium hydroxide and then this solution is treated to determine the exchange aluminium.

Total acidity (exchange $H_{8.2}$) is calculated by the Equation 2:

$$exch.Al + H_A = exch.H_{8.2}\ (cmol/kg) \qquad (2)$$

Exchangeable calcium: 50 cm^3 of the mixed sodium-acetate and potassium-maleate solution is diluted with deionized water to 100 cm^3. Then 5 cm^3 of triethanolamine (1: 1), 1 cm^3 5.0 n potassium hydroxide solution and a chromium blue (calcon) are added to achieve intensive purple-red colouring. The solution is titrated slowly with 0.01 n complexon III to a deep blue colour.

Sum of exchangeable calcium and magnesium: A new 50 cm^3 of the filtrate is filled up with deionized water to about 100 cm^3. Five cm^3 of triethanolamine (1: 1) and a solid mixture of eriochrome black are added to reach pH of 9.5-10.0 and titrated slowly with 0.01 n complexon III to a deep blue colour. Exchange magnesium is determined by the difference between the sum of two alkaline earth cations and exchange calcium.

The base saturation level (V) is calculated in percentages as the difference between the magnitude of total cation exchange capacity ($T_{8.2}$) and total acidity (exchange $H_{8.2}$) relative to the magnitude of total cation exchange capacity.

Humic substances content and composition

The content of extractable humus fractions was determined using the Kononova-Belchikova method (FILCHEVA & TSADILAS, 2002) in four extracts at soil: solution ratio 1:20.

Total organic carbon was determined by the modified dichromate oxidation method (the oxidation of the soil sample with 0.4 N $K_2Cr_2O_7$ and concentrated H_2SO_4 in a ratio 1:1 at 120 ^{0}C for 45 min. in the presence of Ag_2SO_4 followed by a titration with 0.2 N Mohr's salt). Humus content is calculated by multiplication of organic carbon content with the coefficient 1.724.

Content of humic (HA) and fulvic (FA) acids – in a mixed solution of 0,1 M $Na_4P_2O_7$ and 0,1 M NaOH, and separation of FA by 0,5 M H_2SO_4 as an acidifying agent.

Content of free or linked to sesquioxides humic and fulvic acids representing the potentially mobile HA and FA – extracted with 0,1 M NaOH.

Content of the low molecular (aggressive) fraction of fulvic acids – in extracts with 0,05 M H_2SO_4.

Optical hallmarks (E_4/E_6) are determined in HA-fraction as a ratio of the optical densities at 465 and 665 nm.

Elemental and speciation assays

Content of ferromagnesian trace elements was determined after sample mineralization with aqua regia (ISO 11466:1995) via AAC (ISO 11047:1998) on a Perkin-Elmer 2100.

Total nitrogen content was quantified by the modified Kjeldahl method (BDS ISO 11261:2002) and the main mineral nitrogen forms – by procedure of BREMNER & KEENEY (1965).

Carbonate content was measured following ISO 10693:1995 protocol which reproduces the Scheibler method.

Sample pre-treatment and pH determination

Soil samples were pre-treated according to BDS ISO method (11464:2012) and pH was measured in 2.5:1 water soil suspension (1 part soil and 2.5 parts deionized water) according to the protocol given by GANEV & ARSOVA (1980).

Fig. 1. View and location of profile 1 in overlapped moderately leached Smolnitsa.

Fig. 2. View and location of profile 2 in Technogenic soil.

Fig. 3. View and location of profile 3 in moderately leached Cinnamon forest soil.

Fig. 4. View and location of profile 4 in Alluvial soil.

Fig. 5. Location and view of profile 5 in Alluvial meadow soil.

Fig. 6. Location and view of profile 6 in strongly leached Smolnitsa.

Results and Discussion

Soils created as a result of urbanization (profiles 1 and 2) are characterized with very slightly alkaline reaction (Table 1) and middle content of carbonates (in the interval 3-5%). They have middle colloidal activity ($T_{8,2}$ from 30 to 45 cmol/kg), according to the classification given by GANEV (1990) and sorption interactions, transforming the slightly acidic positions of mineral colloids into the hydrogen-acidic complex. Due to the presence of carbonates, this acidic-hydrogen form of T_A, i.e., exchangeable retention of hydrogen cations upon the slightly acidic positions of mineral colloids can be considered physico-chemical characteristic of soils, which originated from the hydromorphic stage in their genesis and water self-ionization catalytic effect. Signs of hydromorphism are evident in many soil characteristics (clay mineralogy, organic carbon state and transformation) and leave a mark on their current genesis. Concerning clay mineralogy, the predominance of mixed-layered smectite-vermiculite structures was found in Pliocene clays distributed in the "Mladost" residential district (BOJINOVA-HAAPANEN, 2014) which confirm our data and suggestions. This mineral might be indirectly identified through the typically high total magnesium content (or "pseudo" total content determined in the aqua regia extract, Table 1). The sorption capacity which is not very high also suggests a lack of pure smectites and together with transformation of biotite (that is present in Smolnitsas) into vermiculite could explain CEC values. Magnesium, despite of its high content, is not the main exchangeable cation and does not cause magnesium salinization.

Hydromorphism and further transformation of the mineral matrix turn hydrogen in the second abundant exchange ion after calcium. As a result of high hydrolytic acidity (exch. $H_{8,2}$) the base saturation level is under 93%, which is considered a critical minimum for lack of deleterious acidity in soils (PALAVEEV & TOTEV, 1985; TRENDAFILOV, 1992). The deleterious acidity in soils is not accompanied by toxic aluminium availability (exch. Al) and possibility for Al desorption in the soil solution – it is limited only to destabilizing role and chemical activity of exchangeable hydrogen.

The content of hydrolytic acidity in Technogenic soils (profile 2) sharply decreases under 21 cm depth (over 2 times) and that positively influences subsoil base saturation status (V). Although the sorption potential in surface horizon of Technosol is generally lower, its hydrolytic acidity content is close to that in topsoil of the overlapped Smolnitsa. Obviously, the hydrolytic acidity in topsoil of these newly-formed soils originated from biogenic processes associated with well-developed meadow vegetation (TSOLOVA & TOMOV, 2018) rather than clay mineralogy, because this is the only profile wherein the vermiculite is not occurred (as we mentioned above the higher content of magnesium than calcium is indicative for vermiculite presence).

The carbonates in the A_h horizon of moderately leached Cinnamon forest soils (profile 3) take part in neutralization of acid products generated by biodegradable processes. This gradually leads to their depletion and acidification of soil environment to pH 5.9. The strong linear correlations shown on fig 7 reveal the prevalence of exchange hydrogen cations onto slightly acidic positions and pH dependence on the exchange hydrogen content.

The exchangeable acidity (exch. Al) also occurs in topsoil in a concentration that could be toxic for many pasture species (CORANGAMITE REGION "BROWN BOOK"). It usually appears as a result of acid destruction of clay minerals, which can be seen in the ratios: $T_{8,2}$ in A_h/ $T_{8,2}$ in C_k < 1 and $T_{8,2}$ in $B_{t\kappa}$/$T_{8,2}$ in C_k > 1 (GANEV, 1990). The colloid degradation in A_h is moderate according to the classification given by GANEV (1990) and shows that this process is still running slowly. The moderately leached Cinnamon forest soil also has moderately high sorption capacity but smaller buffer potential which, as it was mentioned above, decreases as a result of increasing acidity in surface horizons.

Alluvial soils from the Iskar river valley (profiles 4 and 5) are formed of sediments with different coarse fragments contents. The stonier soils (profile 4) are moderately colloidal ($T_{8,2}$ from 20 to 30 cmol/kg) with high neutralizing potential (V over 80 cmol/kg). Their acidic systems also saturate the variation charges on colloidal surfaces with hydrogen and evoke slightly acidic reaction (according to ATANASOV *et al.*, 2009 classification) - 6.1-6.9. Studied parameters decrease downwards the profile depth, resembling the distribution in some normally developed, genetically old soils and do not follow the lithological differences between separate horizons.

Alluvial-meadow soils (profile 5) are moderately colloidal ($T_{8,2}$ from 30 to 45 cmol/kg) and mostly moderately acidic (pH 5,1-6,0). They have the highest hydrolytic acidity among studied soils and respectively the lowest base saturation level within the whole depth (Table 1). The base saturation level in the interval 77-86% defines a middle range of deleterious acidification of soils according to the classification scheme set by Bulgarian legislation (ORDINANCE № 4).

The features of strongly leached Smolnitsa (profile 6) reveals the evolution of soils distributed in the peripheral part of this previously unexplored soil zone. They are neutral, highly colloidal soils with high neutralizing potential which is slightly lower in A′ and A′′ as a result of the listed hypergenic processes. These soils are distinguished with small amount of slightly acidic charges (T_A) in the humus horizon which is presumably due to the slow *in situ* transformation of biotite into vermiculite, which suggests a lack of defects in the crystal structures (due to the lack of transportation) and a small formation of lateral surfaces yet. These processes can be more clearly observed in the last sub-horizon where the content of slightly acidic positions is the smallest and the content of exchangeable magnesium – the highest (Table 1). The content of "pseudo-total" magnesium (from 565 to 607,5 mg/kg) is higher than the content of calcium (420-560 mg/kg) within the whole profile depth which evidences for the strong leaching of carbonates probably in the form of iron carbonates due to the low content of "pseudo-total" iron too (from 1,06 to 1,30%). These data support the opinion of STRANSKI (1936) that a hidden process of podsolization takes place in the black Sofian soils, since it can't be diagnosed by usual morphological features. This phenomenon is also observed by NIKOVA & TSOLOVA (2018) in arable Smolnitsas from the Sofia valley.

Organic matrix hallmarks

Surface horizon of the Overlapped (Buried) Smolnitsa (profile 1, Table 1) is very rich in organic matter (5.52% humus), despite of soil recent creation (about 45 years ago). The humus is of Mull type, abundant in humic acids ($C_{HA}/C_{FA} > 2,0$) which dominated along the entire depth. Humic acids are strongly condensed (E_4/E_6 = 3.87), very hydrophobic and slightly mobile polymers. They are strongly bound to the mineral matrix having in mind the dominance of Ca-humates (100%). The low molecular (aggressive) fraction of fulvic acids is also present in descending concentrations (from 0,8 in topsoil to 0,4 g/kg in buried horizon). The ratios of C:N (14.04-10.40) in this epipedon indicate middle to high enrichment of hydrocarbons with N (Fig. 8). These N-dressed compounds are active source of ammonium-N and may provoke the soil toxicity (BRITTO & KRONZUCKER, 2002). Values obtained for main mineral forms of N illustrate this trend (fig 8) considering a principally low content of nitrate-N in soils.

The basic features of organic matter (OM) in surface horizon of Technogenic soils (profile 2) are: morphologically homogeneous humus system of well humificated organic matter (C_{HA}: C_{total} x 100, in % = 17.3%) formed by soil-biomes interactions and medium humus content (2.59%); Rhizomull type of humus wherein the very strongly condensed and stable humic acids (C_4/E_6 = 3,50) are absolutely prevalent (C_{HA}/C_{FA} = 3,25). The content of organic carbon (OC) sharply drops (up to 1.8 g/kg) in subsoil, where potentially mobile OM is only composed of FA (up to 33% of total C). The degree of OC enrichment with N is very low especially in topsoil (C:N 21.74) and could be primary attached to the features of newly formed organic matter originated from cereal plant species which are dominant in this ecosystem (TSOLOVA & TOMOV, 2018), soil biota activity and low atmospheric inputs of N.

The humus-accumulative horizon (A_h) of Cinnamon forest soil (profile 3, Table 1) is altered by erosion and this affected carbon stocks - it is moderately rich in organic matter (2.86% humus) likewise Technogenic and Alluvial soils. The prevalence of humic acids is slightly pronounced there (C_{HA}/C_{FA} = 1.17) and the degree of condensation of their aromatic nuclei is lower (E_4/E_6 = 4.08), although this does not change HA hydrophobicity and structure. FA content sharply drops beneath 35 cm and positively influenced the OM humification rate. The increase content of humus acids fractions evokes the naturally occurring leaching process and acidification of pH (5.9). The interaction between pH and potentially mobile fractions of humus acids, respectively fulvic acids is evidenced by the statistically significant correlation between them (R^2 = 0.73 for both fractions and R^2 = 0.85 for fulvic acids).

C:N ratios (10.44-12.29) in this epipedon indicates high degree of organic matter enrichment with nitrogen and respectively similar rate of release of NH_4-N.

The status of organic matter in the next three profiles (№№ 4, 5 and 6) differentiates from described above. All of them are characterized with almost equal amount of HA and FA or lack of HA (like in Alluvial soils - profiles 4 and 5). Fulvic acids are mainly mobile and partially aggressive having in mind the aggressive fractions contents (up to 25% of the total FA fraction). HA are stable, strongly condensed polymers mostly bound to Ca. Organic matter is highly abundant in nitrogen but mineral N content is lower than in profiles 1, 2 and 3 (C:N values fluctuate in the interval 8.6-20.2 with average value 11.54 mg/kg, Fig. 8). The low variation of C:N values by depth reveals the ancient age of humic substances and their stability in diverse soil environments. On the other hand, the older organic colloids have low reactivity (MCBRIDE *et al.*, 1997; BRADL, 2004; COUTRIS *et al.*, 2012) and high resistance to biodegradation and therefore play a minor role in CEC.

The results obtained confirm the fundamental finding that transformation processes of biogenic products in soils are much more intense than those of the mineral components. The presented study shows that biogenic transformation in the modern urban environment is a multifactorial process, dependent on all environmental components.

The elevated NH_4 and NO_3 contents in profiles 1, 2 and 3 can be related to human induced urea saturation of soils (they are also used for strolling pets) which may entail a higher rate of ammonification and amplify the nitrogen cycling. In areas where organic matter is more abundant in nitrogen (profile 4, 5 and 6) the main additional source of N is greenhouse gas emissions (or their precursors - NOx, CO and NMVOCs) which may also affect the cycle of nitrogen transformations. All profiles are located in close proximity to bustling traffic arteries and simultaneously in the direction of prevailing winds (from the north and northeast) which distribute the contamination from the industrial zone known with its strong negative impact on the environment (UZUNOV *et al.*, 1996; FAITONDJIEV *et al.*, 2000; DIMITROVA *et al.*, 2010). The higher temperature of topsoils of profiles 4, 5 and 6 (up to 3-4 ºC) supports the assumption for differentiation of mineral nitrogen fluxes during the anthropogenic impact, although the significant correlation between organic nitrogen and carbon (fig 9) shows that humus is the major source of nitrogen. This is also among reasons for alkaline pH values in profiles 1, 2 and 3 regardless of photochemical smog and nitrous oxide (dinitrogen monoxide, N_2O) acidifying effect.

In urban environments carbon and nitrogen cycles are still coupled (Fig. 9), although the plant diversity in studied ecosystems does not imply substantial nitrogen revenues.

Some more important statistic data regarding the organic carbon abundance can be noted: the established average content of organic carbon in the surface layer of studied urban soils, 19.3 g/kg is almost 2-fold lower than the content of organic carbon in virgin leached Smolnitsas of Bulgaria - 35 g/kg (FILCHEVA, 2007). This content is equivalent to the average content (19.1 g/kg) in the surface horizon of grasslands in Bulgaria (TÓTH *et al.*, 2013) but higher than the content in topsoil of grasslands in the Sofia valley - 12.5 g/kg (LUCAS 2015).

Comparing the results for the mean value of CEC in topsoil of Bulgarian grasslands, extracted for LUCAS (2015) - 36,7 cmol/kg shows a close average value only for moderately leached Cinnamon forest soils (profile 3) and Alluvial-meadow soils (profile 5). The lower content of clay fraction and smectite-vermiculite as well, can explain these lowest CEC values in normally supplied with organic carbon Alluvial soils (profile 4).

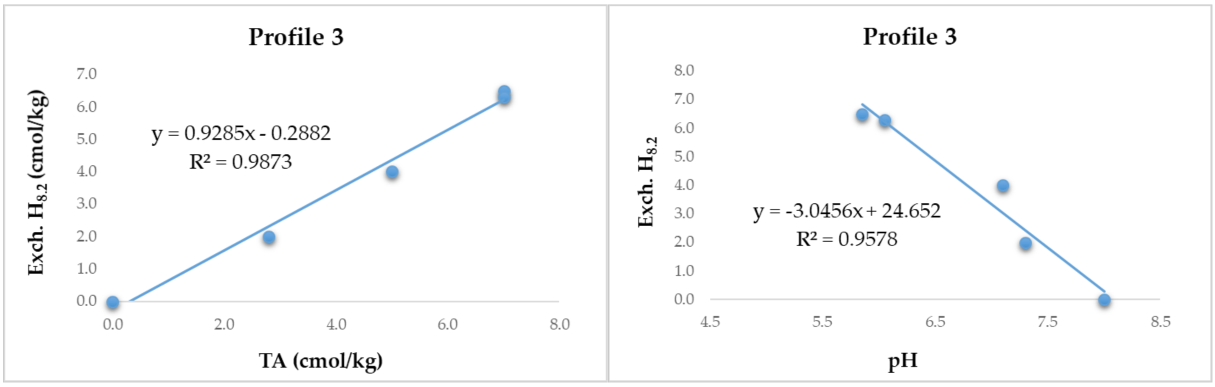

Fig. 7. Correlations between hydrolytic acidity and variation charges T_A (left), and hydrolytic acidity and pH (right) in moderately leached Cinnamon forest soil.

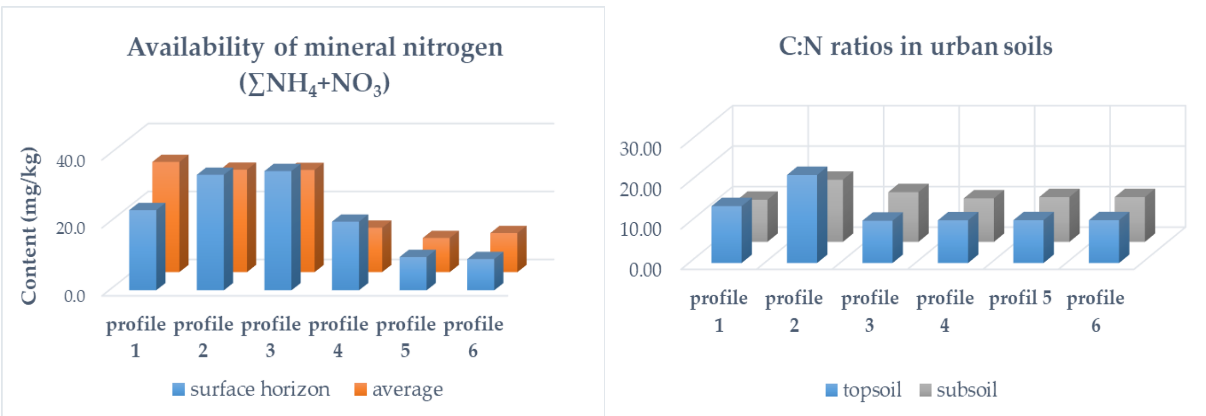

Fig. 8. Mineral nitrogen content and C:N ratios in urban soils.

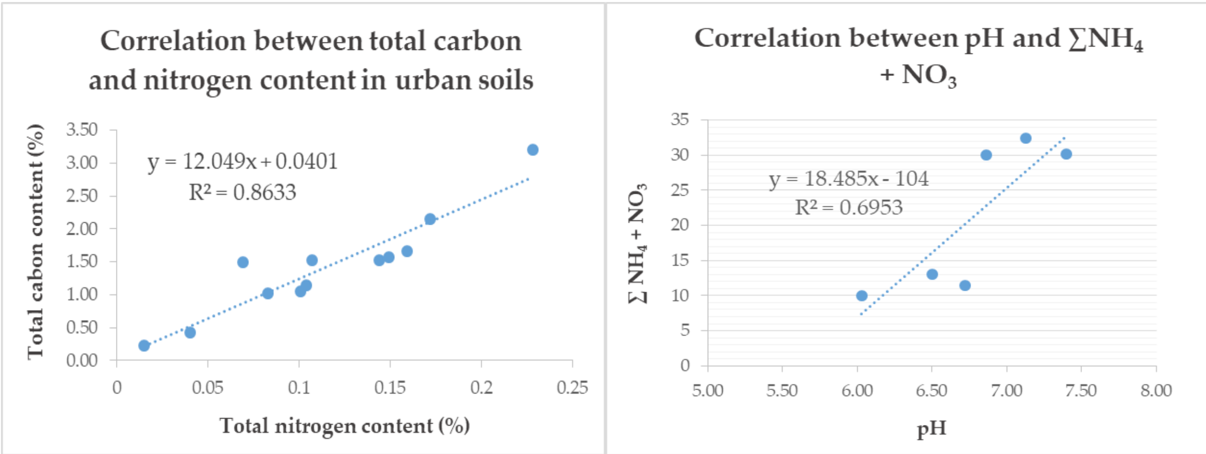

Fig. 9. Correlations between total N and C content in root layers of urban soils, and mineral N and pH (average values).

Table 1. Chemical data on studied urban soils in the city of Sofia.

Horizons and depths (cm)	pH	$T_{8.2}$	T_{CA}	T_A	exch. $H_{8.2}$	exch. Al	exch. Ca	exch. Mg	V (%)	Total C	Humic acids	Fulvic acids	Aggr. FA	Easily mobile HA+FA	C_{HA}/C_{FA}	E_4/E_6	Ca	Mg
		cmol/kg								(%)							AR extracts	
Overlapped moderately leached Smolnitsa (profile 1)																		
Ahk 0-15	7.10	40.40	34.20	6.20	5.00	0.00	32.50	3.10	88.10	3.20	0.56	0.27	0.08	0.33	2.04	3.87	295.0	700.0
C1k 15-65	7.30	41.20	37.90	4.40	3.00	0.00	34.80	3.20	92.30	1.05	0.21	0.08	0.05	0.07	2.63	3.65	1990.0	800.0
A1b 65-110	7.00	41.10	34.50	6.60	6.00	0.00	32.10	3.40	86.40	1.66	0.40	0.20	0.04	0.16	2.00	3.56	1445.0	675.0
Average	***7.13***	***40.90***	***35.53***	***5.73***	***4.67***	***0.00***	***33.13***	***3.23***	***88.93***	***1.97***	***0.39***	***0.18***	***0.06***	***0.19***	***2.22***	***3.69***	***1243.33***	***725.00***
Technogenic soil, moderately deep (profile 2)																		
Ahk 0-21	7.25	33.40	28.40	5.00	4.60	0.00	26.00	2.80	86.20	1.50	0.26	0.08	0.04	0.11	3.25	3.50	2700.0	900.0
C1k 21-52	7.45	31.80	-	-	2.10	0.00	26.50	3.20	93.30	0.23	0.00	0.07	0.02	0.04	-	-	2510.0	900.0
C2k 52-85	7.50	32.70	-	-	2.00	0.00	27.50	3.20	93.90	0.18	0.00	0.06	0.02	0.03	-	-	1935.0	880.0
Average	***7.40***	***32.63***	***28.40***	***5.00***	***2.90***	***0.00***	***26.67***	***3.07***	***91.13***	***0.64***	***0.09***	***0.07***	***0.03***	***0.06***	***1.08***	***1.17***	***2381.67***	***893.33***
Moderately leached Cinnamon forest soil (profile 3)																		
Ah 0-10	5.85	35.80	28.80	7.00	6.50	0.30	24.50	4.80	81.80	1.66	0.28	0.24	0.04	0.30	1.17	4.08	270.0	575.0
Bt 10-35	6.05	40.00	33.00	7.00	6.30	0.00	29.50	4.60	85.25	1.02	0.22	0.15	0.04	0.14	1.47	4.12	210.0	590.0
Bt2 35-72	7.10	38.00	33.00	5.00	4.00	0.00	29.00	4.60	88.40	0.65	0.18	0.00	0.02	0.08	-	3.64	295.0	600.0
Btк 72-86	7.30	38.00	35.20	2.80	2.00	0.00	31.80	4.30	95.00	0.48	0.17	0.00	0.02	0.04	-	3.96	835.0	450.0
Ck 86-120	8.00	37.50	0.00	0.00	0.00	0.00	33.10	4.40	100.00	0.37	0.12	0.00	0.02	0.04	-	4.28	5010.0	525.0
Average	***6.86***	***37.86***	***26.00***	***4.36***	***3.76***	***0.06***	***29.58***	***4.54***	***90.09***	***0.84***	***0.19***	***0.08***	***0.03***	***0.12***	***0.53***	***4.02***	***1324.00***	***548.00***

Horizons and depths (cm)	pH	$T_{8,2}$	T_{CA}	T_A	exch. $H_{8,2}$	exch. Al	exch. Ca	exch. Mg	V (%)	Total C	Humic acids	Fulvic acids	Aggress. FA	Easily mobile HA+ FA	C_{HA}/C_{FA}	E_4/E_6	Ca	Mg
				cmol/kg								(%)					AR extracts	
Alluvial soil, moderately deep (profile 4)																		
Ah 0-15	6.30	21.80	16.50	5.30	4.00	0.00	15.00	2.80	81.65	1.57	0.21	0.20	0.04	0.24	1.05	4.06	470.0	552.5
C1 15-40	6.50	21.80	17.60	4.20	3.00	0.00	15.80	2.90	85.78	0.43	0.00	0.15	0.01	0.09	-	-	285.0	585.0
C2 40-80	6.70	21.40	17.70	3.70	2.00	0.00	16.40	2.80	89.72	0.27	0.00	0.10	0.01	0.08	-	-	475.0	577.5
Average	**6.50**	**21.67**	**17.27**	**4.40**	**3.00**	**0.00**	**15.73**	**2.83**	**85.72**	**0.76**	**0.07**	**0.15**	**0.02**	**0.14**	**0.35**	**1.35**	**410.00**	**571.67**
Alluvial meadow soil, deep (profile 5)																		
Ah 0-30	6.10	36.60	29.80	6.80	5.90	0.00	27.50	3.20	83.88	1.52	0.19	0.16	0.03	0.20	1.18	5.80	270.0	570.0
A1 30-55	6.00	37.40	30.80	6.60	5.60	0.00	28.70	3.40	85.80	1.15	0.17	0.12	0.03	0.14	1.42	4.78	260.0	580.0
C1 55-105	6.00	36.70	29.70	7.00	5.60	0.00	28.00	3.10	84.74	0.68	0.09	0.07	0.02	0.11	1.29	3.27	740.0	675.0
C2 105-155	6.00	35.00	27.60	7.40	5.80	0.00	26.00	3.00	82.86	0.35	0.00	0.14	0.00	0.10	-	-	550.0	750.0
Average	**6.03**	**36.43**	**29.48**	**6.95**	**5.73**	**0.00**	**27.55**	**3.18**	**84.32**	**0.93**	**0.11**	**0.12**	**0.02**	**0.14**	**0.97**	**3.46**	**455.00**	**643.75**
Strongly leached Smolnitsa, super deep (profile 6)																		
A' 0-35	6.70	46.20	42.00	4.20	3.40	0.00	38.00	4.80	92.70	2.15	0.32	0.23	0.04	0.21	1.39	3.63	560.0	607.5
A'' 35-90	6.70	46.00	41.90	4.10	3.30	0.00	37.60	4.90	92.40	1.52	0.25	0.19	0.03	0.13	1.32	3.34	420.0	595.0
A''' 90-165	6.75	45.60	43.50	2.10	1.70	0.00	34.60	9.30	96.30	0.87	0.15	0.07	0.02	0.10	2.14	3.35	480.0	565.0
Average	**6.72**	**45.93**	**42.47**	**3.47**	**2.80**	**0.00**	**36.73**	**6.33**	**93.80**	**1.51**	**0.24**	**0.16**	**0.03**	**0.15**	**1.62**	**3.44**	**486.67**	**589.17**

Conclusions

Main alteration of pedo-chemical characteristics of studied urban soils are result of positive and negative transformation of their matrix. Positive changes are mostly related with organic matrix and intensive processes of humus-formation and accumulation. Main factors that favour accumulation of organic carbon in studied soils are high content of silt and clay fractions which are typically humus fractions since they contain high amount of humus and humino-mineral complexes; organic clays, smolnitsas, comprising in the parent materials of some soils (because they are rich in organic carbon), as well as the stability of humus acids and their low mobility. Stability of humic acids is related with their dense heterocyclic structure and high nitrogen enrichment. Recently formed humus is also well humificated and rich in highly condensed humic acids. For this reason, organic colloids are predominantly mature, persistent and slightly active. Simultaneously, in acidic soil horizons even a slight increase of FA content enhances the pH dependence on their content.

Positive changes of the mineral matrix are derived from mineral colloids and slow transformation of biotite into vermiculite – this process may reduce the soil hydrolytic acidity. Mineral colloids predominantly determine the sorption capacity and acidic complexes in studied soils. Negative changes of the mineral matrix are provoked from:

Acid destruction of clay minerals occurring as a consequence of the naturally occurring soil-forming and weathering processes of low intensity and associated processes of slight dispersion and disintegration of the mineral matrix;

Increase of exchangeable hydrogen content above the exchangeable magnesium levels up to the second abundant exchange ion after calcium although the H-destabilizing role itself is difficult to distinguish.

Anthrogenically induced changes, where they can be identified, can increase mineral N content and fluxes and may influence the existing acid-base status of soils due to the input of neutral, alkaline (urea, ammonia) or acidifying agents (water soluble compounds of CO_2, NO_2) present in the ground troposphere of the Sofia city.

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