Biogeochemical features of soil formation without parent rock in natural conditions and in an urban environment

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Abstract. The aim of the present study is to establish the biogeochemical characteristics of the primary soil formation, separately for natural conditions (protected areas) and urban environment (with incoming technogenic aerosols) for pedogenesis models when there is no parent rock ("upward soil growth"). This makes it possible to assess the contribution of the still poorly studied pedogenesis factors that can form the specific geochemical features of the material composition of soils non-inherited from the parent rock, and without the involvement of biogenic bottom-up migration of elements. We have studied two contrasting regions to perform a comparative analysis of pedogenesis conditions. We have compared embryonic soils on megalithic gabbro-diabase blocks in a 17^{th} century defence wall located on the territory of a natural reserve, 1 km away from the Black Sea coast (ecologically clean area) and a 45-year solid bitumen cover between a thermal power plant and a busy railway (an industrial zone in the central part of the city). In the natural reserve, the average dust deposition rate was 0.82 $\mu m\ yr^{-1}$ (0.082 mm / 100 yr) due to stardust, atmospheric aerosols and biogenic processes of pedogenesis. The mineral part of soils, which had formed on the solid bitumen in 45 years in the city's industrial zone, differs from the soil developed in 320-350 years without the involvement of the parent rock in the protected area by higher content of V (9 times) and Cr (2 times), as well as CaO, SiO_2 and Pb. In the industrial zone of the city, emission dust mostly contributes to the accumulation of V, Cr and Cu in comparison with the pedogenesis conditions in the ecologically clean area, where the rate of solid-phase soil matter accumulation is twice lower due to background aerosols and biogenic factors.

1. Introduction

The emergence of the soil as a vertically structured natural historical body depends primarily on the frontal advance of humus strata deeper into the parent rock with increase of soil age. According to the proposed model [1], the soil aggregate consists of quartz crystals and oriented clays, and it is stabilized through quartz-clay links strengthened by organic polymers. Non-aggregated elementary soil particles can be detected when micro-aggregates < 1 mm are observed with a microscope under reflected light [2]. The proportion of elementary soil particles varies from 10-15% (arable soils) to 23% (virgin soils) [3]. Humic substances, silt and cations (Ca, Al, Fe) connect together primary mineral particles, which results in formation of soil unit [4]. A typical model of soil formation in time on fresh parent rocks in autonomous landscape and geochemical positions can be characterised as a complex of interrelated pedogenic processes, such as biogeochemical transformation of zeolite (lithogenic component), accumulation of humic substances, formation of organic and mineral complexes followed by consolidation of pedogenesis products in the form of para-genetic association of genetic horizons ("downward soil growth").

Under the current bioclimatic conditions, the rate of soil humus horizon formation on newly exposed parent rocks in automorphic conditions ("downward soil growth") can vary from 0.11 mm yr^{-1} (steppe) to 3–4 mm yr^{-1} (forest-steppe) [5]. When pedogenesis develops on any dense unstratified rocks (basalts, granites, diabases), an unusual scenario is observed - soil formation precedes weathering process. This scenario is diametrically opposed to the situation when the biotic factor plays a minimal role in soil formation as shown in the soil development study on the ice-free areas in the Transantarctic Mountains [6]. Thus, we can see several pedogenesis scenarios different from the widespread type of soil formation. When analysing this development model, a significantly smaller role is played by factors, which in some situations can cause supply of substances gradually assimilated with pedogenic complex. A quantitative assessment of the combined effect made by these factors and their description are poorly known, and the problem is becoming urgent due to the influence produced by anthropogenic activities on the soil cover.

The soil is characterised by interpenetration and close connection between living and non-living matter, which made it possible for V.I. Vernadsky to consider this natural and historical body to be a bioinert system. The usual course of pedogenesis is characterised by mutually opposite processes in automorphic soils such as bottom-up biogenic migration of chemical elements, on the one hand, and physico-chemical elemental migration in aqueous solutions (leaching), which is directed downward [7]. However, by studying soils on dense weathering-resistant rocks, we can evaluate the contribution made by the processes that define only substance supply. These sources can include cosmic dust, chemical elements with atmospheric precipitation, including salts impulverised from the seawater area (within the breeze circulation coverage), decomposition products of plant litter of above-ground and surface layers, including mineral microbiomorphs. The space continuously sends to the Earth's atmosphere flows of material particles, in particular, cosmic dust (particles ranging from 0.001 μm to tens-hundreds μm) [8]. Various observational data [9] has shown that the amount of cosmic dust entering the atmosphere is within from 0.25-14 to 106 $t{\cdot}yr^{-1}$. And the arrival of Stardust on Earth is not constant, since the flux of meteorite and smaller-sized objects has varied over the recent geologic past [10]. A review of estimated average annual inflow of extra-terrestrial material into the Earth's atmosphere obtained using different methods [11] also includes field studies, which show the range of values (in $kilotons{\cdot}yr^{-1}$) from 2.0 ± 0.6 (measured with a Lidar) to 10 ± 2 (results of the study of Greenland ice). The role of Earth's dust is much more clearly represented by the research results for the effects made by deserts on adjacent territories. In particular, it was previously shown [12] that aeolian dust even in the natural conditions is an important source of trace elements, nutrients, and biological material. Anthropogenic dust emission is of both impact and trans-boundary character in industrial and urban landscapes. As Hooper [13] believes, due to human activity, at least a doubling in dust emissions has occurred during the past ~ 250 years.

2. Materials and Methods

The studied objects included embryonic soil without parent rock and two uneven-aged soils in an ecologically clean area (the South Coast of Crimea (SCC)), as well as embryonic soil in the city's industrial zone (table 1).

The Ayu-Dag dom-shaped mountain (571 m) is a magmatic diapir of the Middle Jurassic. The study site was located on the northern slope of the Ayu-Dag Mountain (table 1, site 2). The study area climate is favourable for pedogenesis; it belongs to the subtropical sub-Mediterranean type (the average annual temperature is 13 °C, the length of the frost-free period is 247 days, the average temperature in January is +3.5 °C, the average amount of precipitation average precipitation is 635 mm per year) [14]. The distance to the Black Sea coast is 1010 m; therefore, during the breeze period (April-September) it is possible that salts can geochemically migrate (impulverised) to the land. The upper defence wall is composed of megalithic gabbro-diabase blocks. Its surface is covered with a layer of mosses with some fallen leaves from oak (*Quercus pubescens*) and hornbeam trees (*Carpinus orientalis*), with their crowns partially hanging over the defence wall. The mineral layer has been formed under the cover of bryophytes (*Bryophyta*), and is densely penetrated by their root-like outgrowths (rhizoids), on a diabase not affected by weathering. Using the soil classification the mineral part of the Embryozem under the moss cover (table 1, site 2) by the amount of particles <0.01 mm (17.16%) can be considered as sandy loam. The chemical composition of this substrate is characterised by a high content of the Corg (9.23%), but a low content of the carbonate (Ca0 is 2.84%). According to historical data [15], there are the ruins of Christian temples of the 14–16th centuries here, which are supported by the author's data on humus horizon thickness of the soils in the area of ruins adjacent to the defence wall, which made it possible, using the specified method of pedogenetic chronology [5], to determine that human activities in relation to this monument had ceased within the range of 320 to 350 years. Cambisols has been studied in automorphic position between two treated stone blocks. It was formed on crushed stone with an underlying slab (table 1, site 3). By morphological structure (Ah (moss layer 4 cm thick), A horizon is 48 mm, A+AB is 83.4 mm), this is a newly formed soil, which structurally belongs to sandy loam (particle content <0.01 mm is 28%). It is characterised by a high degree of organic matter enrichment (Corg content is 6.93%) and mobile phosphorus (1.48 mg kg^{-1}), low $CaCO_3$ content (1.54%) with moderately acidic reaction of the soil solution (pH (H_2O) is 4.75). A brown red soil on limestone eluvium has been studied in the representational section of the Nature Reserve "Cape Martjan" (table 1, site 1). The soil has been forming since the beginning of Holocene (11550 years ago) or even earlier, as the Sub-Mediterranean climate was continuously illustrative of the SCC since Neocene. The soil is under cover of *Quercus pubescens* and *Carpinus orientalis*, with junipers (*Juniperus excels, J. oxycedrus*) and a developed grass layer. The upper part of horizon A with Corg content 3.8% has a reddish colour (5YR 4/4) typical for *terra rossa.* The top layer (0-6 cm) from horizon A was used to compare with the newly formed soil. It has a color of 5YR 3/2 (dry), the content of Corg is 9.0%, $CaCO_3$ is 2.09%, mobile phosphorus is 0.11 mg kg^{-1}, is defined as an silty loam (fraction of particles <0.01 mm is 34.8%).

Table 1. Objects of study.

No Site	Coordinates	Area	Object of study
1	44°30'34.7" N 34°14'53.8" E	Cape Martjan, nature reserve	Protected calcaric Cambisols (Holocene)
2	44°33'39.0" N 34°20'03.3" E	Ayu-Dag, the upper defensive wall	Embryonic soil on gabbro-diabase
3	44°33'44.8" N 34°19'48.3" E	Ayu-Dag, ring-shaped strengthening	Newly formed soil on crushed stone
4	50°36'2" N 36°36'55" E	Belgorod, industrial zone	Embryonic soil on asphalt

The meteorological data for Belgorod station describes the city climate as moderately continental (the average annual temperature is 6.5 ° , the length of the frost-free period is 230 days, the average temperature in January is -8 , the mean annual precipitation is 595 mm) [16-17]. The Embryozem on solid bitumen with underneath sandy fraction in the industrial zone of the Belgorod city (table 1, site 4) was covered by leafy moss (*Dicranum*) 10-12 mm thick. The mass of mosses was 4.13 t ha^{-1}. The second biological agent is represented by fallen leaves from *Tilia cordata* and *Morus nigra* growing in the nearest vicinity of the site.

The mineral part of the embryonic soils was separated from the topsoil by distilled water flotation using a Fritsch sieve column. The particle size distribution was determined with the use of laser light scattering particle size analyser Analysette 22 MicroTec (Fritsch GmbH). Soil colour were described using the Munsell-System [18]. Concentration of macro and microelements within the soils were determined by technique of measuring metals mass fraction and oxides in powder samples using the wavelength-dispersion X-ray fluorescence spectrometer (Spectroscan Max-GV). Chemical analyses of soils included the following standard procedures [19]: the *C*org content by titrimetric version of Tyurin's method with oxidation in a thermostat at T = 140°C; CO_2 in carbonates by acidometry; pH

(H_2O) by potentiometric method (pH meter Sartorius Basic Meter PB–11); the available P_2O_5 (mg・kg^{-1}) by Machigin's method (spectrophotometer UNICO–1200).

3. Results and Discussion

As shown earlier, based on the results of studying different-aged soils at archaeological sites under the SCC conditions [20], the average rate of formation of the humus horizon thickness at parent rock over 100–400 years is 6.6 mm / 100 years. In the absence of the parent rock, the rate of dust deposition caused by atmospheric input and other above-mentioned factors of pedogenesis can be estimated as 0.0078-0.0086 t ha^{-1} yr^{-1}, or on average 0.082 mm / 100 yr. In comparison, these estimates are 2.7 times higher than, for example, the rates obtained on basalt in semi-arid regions in north Queensland, Australia (0.03 mm / 100 yr) [21], which is obviously associated with more favourable climate at SCC. In addition, we would like to note that seacoast soils are formed under special hydrothermal conditions, which is due to breeze circulation as well as impulverisation of sea water salts and their fallout with precipitation totalling 15-17 g m^{-2} [22]. Based on the rate of accumulation due to atmospheric aerosols and biogenic processes of pedogenesis in the protected area, we can say that this contribution is only 1.7% of the rate of embryonic soils formation under man-made environmental impact. It is promising to use soil elemental composition to analyse the particular pedogenesis results since it is determined by their mineralogical and grain size compositions [23]. As the comparison of millennial and centennial soils (sites 1 and 2) shows, the accumulation of such chemical elements of life as Si, Al, K, Ca, and some essential trace elements (Ni and Cu) in horizon A depends on the duration of pedogenesis and the active involvement of higher plants in this process under the Sub-Mediterranean conditions. These particular features are partially confirmed when comparing the Holocene soil with tercentenary soil within forest environment (sites 1 and 3) in terms of macroelements accumulation in horizon A (Ca and K), and trace elements (Cu and Ni). The soils that had parent rock and were involved in soil formation using litter and root secretions of higher plants (sites 1 and 3) accumulated in horizon A consisting of main essential elements (Si, Al, Fe, Mn, Ca, K, P) such as Si, Al, Fe and K (over three centuries of pedogenesis) and Si, Al, K and Ca (over the entire Holocene) more significantly than under the conditions of pedogenesis without parent rock site 2). Plant litter and its decomposition products form fixed composition of soil solutions, which largely determines the transfer of soil organic matter and heavy metals [24]. Mineral microbiomorphs (calcite, siliceous, ferriferous and other) [25] are accumulated in the soil because of phytomass transformation of growing plants, and the share of microscopic opal plant stones can reach 97 % (of the total) in the upper layers (0-3 (6) cm) of soils [26].

Table 2 shows the results 22 chemical parameters, both for natural site 1 and industrial site 2 soil samples.

The material composition of igneous rock-based Embryozem in the sea coastal zone is geochemically richer as compared to Urbanozem. Thus, the ratio of oxides and element concentrations at site 2 to site 4 (table 2) ranged from highest to lowest as follows: MnO >Sr > Ni >Na_2O >P_2O_5 >Co > Rb > TiO2 > Fe > MgO > CaO > Ba > Zn > K2O > Al_2O_3 > Pb > As. These particular features can be explained both by specific influences from lithogenic and climatic factor and by longer (seven fold) duration of pedogenesis at site 2 since from the above row only Mn, P, Fe, Ca, K and Al can be classified as a biological accumulation element. The mineral particles and ions coming with rainwater flowing down from the roof of one of the buildings of the Belgorod gas turbine power plant and thermal power plant (TPP) because the registered sites were under the roof canopy. A potential source of technogenic influence is the dust produced by the railway. The registered site is located between the TPP building and 14 railway tracks, including the nearest track at a distance of 14 m, while the closest actively used track is only 38 m away. In addition, there is also background industrial dust in the urban industrial zone. Fine suspended particles with aerodynamic diameter <10 μm (PM10) and <2.5 μm (PM2.5) are considered one of the most dangerous types of air pollutants in the urban environment. As shown by the impact assessments of the Belgorod Cement Plant [27], most particles >10 μm fall on the underlying surface at a distance of up to 0.5 km from emission sources, while the content of suspended particles ranges from 41.5% to 49.8% for fractions 2.5-10 μm and <2.5 μm respectively at a distance of 4 km from emission high sources. The embryonic soil on asphalt under the canopy of mosses (*Dicranum*) had a mineral mass of 23.03 t ha^{-1}, including fine earth (particles ≤ 1 mm) of 20.33 t ha^{-1}. Over 45 years, the average annual rate of soil formation was 0.49 t ha^{-1}, while under the same bioclimatic conditions for the same period of time, the rate of soil formation on loams can reach 24.1 t ha^{-1} per year. In the urban environment, the content of heavy metals in the Embryozem (table 2, site 4) exceeds the maximum permissible concentrations established by the state soil standard for six elements (excess are given in brackets): Pb (6.4), Zn (3.7), Cr (2.2), As (1.6), Cu (1.5) and Co (1.3). Dust emission in the urban industrial zone mostly contributes to the accumulation of V, Cr and Cu as shown by Embryozems comparison with site 4 and site 2.

Table 2. Comparison of the content of macro- and trace elements in the Embryonic soil of the protected area (site 1) and the industrial zone of the city (site 2).

Indicators	Site 1	Site 2	Site 3	Site 4
Layers (mm)	0-60	0-4	0-83	0-2
Soil colour (dry)	5 YR 3/1.5	–	10 YR 6/3	10 YR 4/2
SiO_2 (%)	27.07	5.60	47.16	60.52
Al_2O_3 (%)	11.57	5.92	14.52	3.91
CaO (%)	4.35	2.84	0.88	1.18
Fe (%)	3.35	3.47	5.05	1.14
K_2O (%)	1.59	1.00	1.05	0.53
MgO (%)	1.08	1.19	1.59	0.43
TiO_2 (%)	0.95	0.96	1.44	0.30
Na_2O (%)	0.84	1.77	1.68	0.43
P_2O_5 (%)	0.20	0.67	0.20	0.17
Ba (ppm)	400.75	479.74	351.87	229.65
Zr (ppm)	149.70	86.17	211.98	159.96
Zn (ppm)	127.14	355.56	183.63	183.39
V (ppm)	101.27	89.64	164.58	1555.96
Sr (ppm)	95.63	363.69	150.37	44.01
Cr (ppm)	92.79	91.49	98.99	216.64
Rb (ppm)	87.02	55.41	74.79	16.37
Cu (ppm)	67.50	14.95	41.95	29.51
Ni (ppm)	61.21	47.24	54.32	9.34
Pb (ppm)	27.53	95.84	54.78	63.82
Co (ppm)	22.23	40.82	34.08	10.56
As (ppm)	9.34	12.85	10.03	9.66
MnO (ppm)	0.15	0.34	0.21	0.03

Initial pedogenesis soils located in the anthropogenic impact zone differs from the protected area soils (table 2, sites 4 and 3) by higher content of V (more than 9 times), Cr (more than 2 times), as well as CaO, SiO_2, Pb and a lower content of elements and oxides (concentration ratio <0.75), which can be represented as an increasing series: MnO < Ni < TiO_2< Fe < Na_2O < MgO, Al_2O_3 < Sr < Co < K_2O < Ba < Cu < Zr. An analysis of this row shows that such heavy metals as Ni, Co, Ba and Cu did not accumulate in 45 years in the industrial zone in concentrations, which would exceed the background level (soils in an ecologically clean area). However, it should be noted that Sub-

Mediterranean Cambisols, especially in the area affected by ancient intrusive magmatism, is characterised by high content of Ni, Co, and Cu.

4. Conclusion

Lead, zinc, chromium, arsenic, copper and cobalt are the most dangerous heavy metals, which can accumulate over four decades in concentrations exceeding the maximum permitted limits for soils in the urban industrial zone. Based on the rate of accumulation of the mineral part of the embryonic soil in the protected area due to stardust, atmospheric aerosols and the predominant involvement of lower plants in pedogenesis (0.82 $\mu m\ yr^{-1}$), we can say that this contribution is only 1.7% of the rate of embryonic soils formation under anthropogenic impact. Higher content of such essential elements as Si, Al, Fe, K and Ca was observed in horizon A of the soils formed on parent rock with the involvement of higher plants in soil formation than in the conditions of pedogenesis without parent rock.

References

[1] Emerson W W 1959 *J. of Soil Sci.* **10(2)** 235
[2] Bulygin S Yu and Komarova T D 1990 *Pochvovedenie* **6** 135
[3] Bulygin S Yu and Lisetskiy F N 1992 *Eurasian Soil Sci.* **24(3)** 59
[4] Shein E and Milanovskiy E 2014 *Biogeosystem Techniq* **2** 182
[5] Lisetskii F N 2016 *Eurasian Soil Sci.* **49(8)** 846
[6] Bockheim J G 1990 *Geoderma* **47** 59
[7] Fedor L and Oleg C 2014 *Adv. Environ. Biol.* **8(4)** 996
[8] Ermakov V I 2009 *Bull. RAS: Physics* **73** 416
[9] Parkin D W and Tilles D 1968 *Science* **159** 936
[10] Zolensky M 2006 *Meteorit. and the early solar system II* **943** 869
[11] Ogurtsov M G and Raspopov O M 2011 *Geomagn. Aeron* **51(2)** 275
[12] Dastrup D B 2018 *Atmos. Environ* **193** 251
[13] Hooper J and Marx S 2018 *Glob. Planet. Change* **169** 70
[14] Korsakova S, Attri S D, Rathore L S and Sivakumar M V K 2011 *Challenges and Opportunities in Agrometeorology* (Berlin, Heidelberg: Springer) 385–396
[15] Firsov L V 1990 *Isary: Essays on the history of medieval fortresses on the southern coast of Crimea* (Novosibirsk: Science. Siberian Branch)
[16] Petin A N 2014 *Adv. Environ. Biol.* **8** 544
[17] Lebedeva M G 2015 *Nauch. Ved. Belgorod. Gos. Univ., Ser. Estestv. Nauki* **9** 160
[18] Munsell A 1994 *Munsell Soil Color Charts. Revised Edition* (New York: Gretag Macbeth New Windsor)
[19] Arinushkina E V 1970 *Manual for the Chemical Analysis of Soils* (Moscow: University Press)
[20] Lisetskii F 2019 *Geosciences* **9(6)** 266
[21] Pillans B 1997 *Geoderma* **80** 117
[22] Zolotun V P 1974 Formation of soils in the South Ukraine over the Last 50–45 centuries. *Extended Abstract of Doctoral Dissertation (Agric.)* (Kiev) 74
[23] Lisetskii F N et al 2016 *Contemp. Probl. Ecol.* **9(3)** 366
[24] Kalinitchenko V P 2021 *Environ. Res.* **194** 110605
[25] Piperno D R 1989 *Rev. Palaeobot. Palynol.* **61** 147
[26] Golyeva A and Svirida N 2017 *Quat. Int.* **434** 51
[27] Lisetskii F and Borovlev A 2019 *AAQR* **19** 504