Data on the elemental composition (mobile fractions and total content) of soils in catena at the SE Valdai Hills, Russia

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Abstract. This study presents a dataset on seasonal soils sampling from September 2016 to May 2018 in the southern part of the Central Forest Reserve (SE Valdai Hills) within a catena with Endocalcaric Albic Glossic Stagnic Profondic Retisols (Cutanic, Loamic) and Albic Gleyic Histic Retisols (Cutanic, Loamic) under coniferous-deciduous forest (Tilia cordata, Picea abies, Acer platanoides) on loess-like loams underlain by carbonate moraine deposits. 152 soil samples were taken to define total concentration of 67 chemical elements (ChEs), content of three mobile fractions (exchangeable, bound within organo-mineral complexes, bound with Fe and Mn hydroxides) of 69 ChEs and content of residual fraction, including macro elements (Al, Ca, Fe, K, Mg, Mn, Na, P, Ti, S, Si), heavy metals (Ba, Co, Cr, Cu, Ni, Pb, Rb, Sr, Th, U, V, Zn), trace elements (Ag, As, B, Be, Bi, Br, Cd, Cs, Ge, Hf, Li, Mo, Nb, Pd, Sb, Sc, Se, Sn, Ta, Te, Tl, W, Zr) and rare earth elements (Ce, Er, Eu, Gd, La, Lu, Nd, Pr, Sm, Tb, Tm, Dy, Ho, Y, Yb). We measured pH-value, total organic carbon content (TOC), seven particle-size classes (<1, 5-1, 10-5, 50-10, 250-50, 500-250, 1000-500 μm), and basicity from carbonates. The dataset is available from Mendeley Data (http://dx.doi.org/10.17632/r29psg69z7.1, Enchilik et al., 2020) and will be further updated.

Keywords. Potentially toxic elements, taiga, landscape geochemistry, specially protected natural territories, etalon ecosystems, ecosystem monitoring

1 Introduction

The assessment of background state of landscapes, being basically provided in biosphere reserves, takes a special place in international programmes on the environment by UNESCO and UNEP. The analysis of geochemical structure of landscapes at different levels is an important part of background monitoring. Nowadays, the basic method is catenary. It is founded on detection of typical objects and studies of chemical compounds allocation in its components. The parameters on radial and lateral allocation of elements in different parts of landscape are assessed on the example of model catenas which include the most spread elementary landscapes and its linkings.
2 Study object

In the Central Forest State Natural Biosphere Reserve (fig.1), the most common parent rocks are loess loams underlain by carbonate Valdai glaciation moraine deposits at the depth of 90-190 cm (Karavanova & Malinina, 2007, 2009, Puzachenko et al., 2006). Studied catena is located in the southern part of the reserve on the interfluve gentle slope (<2°) with southeast exposure (fig.2, table 1) covered by, covered by coniferous-deciduous plant communities that grow in summit (1) and middle slope (2) positions and southern taiga coniferous forests that grow in the waterlogged footslope positions (3,4). GPS coordinates of soil pits are: (1) N56°27'48.7'' E32°57'45'”, (2) N56°27'47.5''E32°56'15.4’’, (3) N56°27'47.1'' E32°56'19.8’’, (4) N56°27'48.0'' E32°56'21.1’’.

Catena was chosen in the south part of reserved core alongside the transect 91/92 for monitoring of structure, dynamics and functioning of reference south taiga ecosystem monitoring systems (Puzachenko et al., 2013; Puzachenko et al., 2006). The following changes are traced along the studied catena. Well drained summit position is a place where substances enter the ground basically from the atmosphere with wet and dry precipitation and migrate down the slope. Drainage weakens in upper footslope position and accumulation prevails. Drainage is generally affected by climatic and geological-geomorphological factors: rainfall and permeability respectively. Low permeability of parent rocks is characteristic for the territory of the reserve (Puzachenko et al., 2006) resulted in waterlogged conditions at the lower footslope position (soil profile 4) and a temporary watercourse, preferably after heavy rains. As a result, soil-moisture increases down the catena followed by the change in plant communities.

Summit (1) catena landscape is well drained that led to formation of Endocalcaric Albic Glossic Stagnic Profondic Retisols (Cutanic, Loamic) with horizons (photos of soil pits are shown in fig.3): Oi- Oe- Oa– Ah– Esc– BE– 2Bwk– 2BClk—2Csk(l) (Barham et al., 2006; IUSS Working Group WRB, 2014) under Tilia cordata+ Picea abies with Acer platanoides and Ulmus glabra - Corylus avellana - Oxalis acetosella plant community (Stellaria holostea, Anemone nemorosa, Lamium galeobdolon, Oxalis acetosella, Pteridium aquilinum, Aegopodium podagraria).

Albic Glossic Stagnic Profondic Retisols (Cutanic, Humic/ Ochric, Loamic) with horizons: Oi- Oe- Oa– Ah– AhE– Escl– BEscl– Bwsc– 2Bwsc(l)– 2Csk(l) under Picea abies+Tilia cordata+Acer platanoides - Corylus avellana – grass- plant community has developed on convex upper slope (2). Tilia cordata is the most frequent specie among broadleaf, Corylus avellana L dominates in undergrowth. Ground cover is represented by nemoral species (Hepatica nobilis, Galium odoratum, Lámium galeóbdolon, Ásarum europaéum, Pulmonária obscúra), Pteridium aquilínum L, Equisétum sylváticum and Oxalis acetosélla L.

Upper footslope (3) is occupied by Picea abies with Tilia cordata and Acer platanoides - Vaccinium myrtillus - Sphagnum on Albic Gleyic Histic Retisols (Cutanic, Loamic) with horizons: Hi-He-Ha-El–Etosc–Bwg–2Bwg–2Cgk. Grass-shrub layer is dominantly represented by Vaccinium myrtillus. Sphagnum sp takes place too.

Waterlogged conditions on lower footslope (4) characterize by temporary watercourse with weakly expressed relief. There is located Picea abies with Salix caprea, Tilia cordátá and Acer platanoides - Sphagnum with Oxalis acetosella plant
community on Albic Gleyic Histic Profondic Retisols (Cutaonic, Loamic) with horizons: Hi- He- Ha- Etoscl– BEtoscl– B–2Bg– 2Crk.

3 Methods and results

3.1 Sampling

Samples were taken during spring (May 2018), middle summer (June 2017), middle (September 2016) and late (November 2017) autumn from the middle of each soil horizon, from the 4 pits (Fig. 2) in all seasons of the catena studied. Also, samples from the A and B horizons were collected in 9 replicates around pits no 1, 2, and 4 in June. Samples of forest litter were taken in autumn. Altogether, 152 soil samples were collected.

3.2 Physical and chemical properties measurement

In all samples, pH value was measured in suspension (static conditions) using a pH-meter "Expert-pH" (Russia) at the Faculty of Geography of Lomonosov Moscow State University. Total organic carbon (TOC) content was determined in 120 samples using titrimetric method with phenylanthranilic acid (Reeuwijk, 2002). The particle-size distribution in soils was analyzed using laser diffraction technique and an ‘Analizeter 22’ equipment (Germany). Samples for the particle-size distribution analysis were pre-treated with 4% Na4P2O7. The Russian system of particle-size classes was used: G1 – clay (<1 μm), G2 – very fine silt (5–1), G3 – medium silt (10–5), G4 – coarse silt (50–10), G5 – fine sand (250–50), G6 – medium sand (500–250). All studied soils are loamy (containing >10% of <0.01 μm sized matter) with well-defined textural differentiation. Eluvial material is rich of silt fractions while clay fractions content is maximal in argic horizon and parent material. The content of clay fraction is also higher in parent material of middle-taiga landscapes of Karelia (Lukina et al., 2019).

3.3 Chemical composition measurement

Soil suspensions of NH4Ac, NH4Ac+1% EDTA, 1M HNO3 were used for mobile fraction extraction from soil subsample (soil:solution ratio of 1:5) by incubation for 18 hours. Mobile fractions (Vodyanitskii et al., 2020) F1 (exchangeable), F2 (bound within organo-mineral complexes), F3 (bound with Fe and Mn hydroxides) ChEs fraction were obtained with the use of the following reagents: F1 - with NH4Ac (ammonium acetate buffer) and the soil:solution ratio of 1:5, F2 - with 1% EDTA (ethylenediaminetetraacetic acid) and the soil:solution ratio of 1:5 and F3 - with 1M HNO3 and the soil:solution ratio of 1:10 by incubation for 18 hours. The residual fraction (F4) was determined by the difference between the total content of elements (F5) and the content of mobile forms (F1+F2+F3). Total content of chemical elements (ChEs) and mobile fractions was measured at the All-Russian Scientific-research Institute of Mineral Resources named after N.M. Fedorovsky using an
Elan-6100 ICP-MS System (Inductively Coupled Plasma Mass Spectrometer by PerkinElmer Inc., USA) and an Optima-4300 DV ICP-AES System (Inductively Coupled Plasma Atomic Emission Spectrometer by PerkinElmer Inc., USA).

The content of elements is close to the average for Retisols of Eurasia (Semenkov et al., 2016) and agricultural soils of Northern Europe, which were formed on moraine deposits and parent material of Scandinavia (Reimann et al., 2018). The content of Cr, Cu, Fe, Ni and Sr is located on the lower edge of the average for Retisols of Eurasia while the content of Mn, Pb and Zn - on the higher edge of the average. The lowest content of Fe was found in umbric horizon of soils of summit and upper slope landscapes due to high pH.

4 Description of dataset and data availability

Statistical analysis was carried out using software package 'Statistica' and Microsoft Office Excel. Descriptive statistics of soil properties and ChEs distribution (mean, maximum, minimum, standard deviation, etc.) represented in table 2 (table S1). This dataset is available from Mendeley Data at http://dx.doi.org/10.17632/r29psg69z7.1 (Enchilik et al., 2020). Descriptive statistics also characterized soil properties and ChEs distribution for nine replicates of horizons A and B within each landscape position (table S3).

The significance of seasonal changes for soil proxies was assessed using Mann-Whitney U-test (table 3, table S2). Vertical distribution was characterized using R coefficient (Kasimov, Perelman, 1992) calculated as a ratio between the level of elements in soil horizons to the level of elements in parent material (table S4). Spatial distribution was characterized using L coefficient (Kasimov, Perelman, 1992) calculated as a relation between the level of elements in soil horizons of catena's landscapes (upper slope, footslope) to the level of elements in soil horizons of the summit position (table S5). Significance of lateral differences was assessed using Sign Test, marked tests are significant at p<0.05 (table S6). Spearman's correlation analysis was used to calculate correlations between ChEs forms content and soil proxies. The differences were considered significant at p<0.05, p<0.01, p<0.001 (table S7.1, table S7.2). The calculations of relative error for elemental composition of soil and pure extraction solutions (of NH4Ac, NH4Ac+1% EDTA, 1M HNO3) were provided as well (table S8).

5 Conclusion

The soils of etalon south-taiga catena were studied to define conditions of migration, content, vertical and spatial allocation of total content and three mobile forms of its compounds: exchangeable ChEs fraction, bound within organo-mineral complexes ChEs fraction, bound with Fe and Mn hydroxides ChEs fraction as well as mobility of these metals.

Obtaining of fundamental knowledges on differentiation of metals in the soils of south-taiga catena is necessary to assess migration and accumulation of elements in natural and technogenic landscapes.

Reported data of the total content and mobile fractions of chemical elements in the soils of the natural landscapes might be considered as a part of the monitoring of etalon state of south-taiga landscapes, which now is generally provided in biosphere reserves. Data could be used by other researchers for understanding distribution of different compounds in soil catena in
soils of southern taiga forests. Data is applicable for the assessment of contamination level of the elements with potential toxicity. Data will help legislators to create health risk management plans. Elaborated data could be used for accurate identification of the sources of pollution and its migration routes as well as for more effective conservation and remediation of anthropogenically affected soils of southern taiga regions.

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Conflict of interest. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Supplementary data. The supplement related to this article is available online at Mendeley Data (doi:10.17632/r29psg69z7.1, Enchilik, et al., 2020).

References

Barham, P., Begg, E., Foote, S., Henderson, J., Jansen, P., Pert, H., Scott, J., Wong, A., & Woolner, D. Guidelines for soil description Fourth edition. In food and agriculture organization of the united nations, Rome, 109p., 2006.

Enchilik P.; Semenkov I. “Descriptive statistics of soil properties, ChE total concentrations and mobile fractions (mg/kg) in Retisols”, Mendeley Data, V1, doi: 10.17632/r29psg69z7.1, 2020.

IUSS Working Group WRB. World reference base for soil resources 2014. International soil classification system for naming soils and creating legends for soil maps. In World Soil Resources Reports No. 106. https://doi.org/10.1017/S0014479706394902, 2014.

Karavanova, E. I., & Malinina, M. S. Spatial and temporal variation in the elemental composition of soil solution from gleyic peaty-podzolic soils. Eurasian Soil Science, Vol. 40, p. 830–838 https://doi.org/10.1134/S1064229307080042, 2007.

Karavanova E.I., Malinina M.S. Spatial Differentiation of the Chemical Composition of Solid and Liquid Phases in the Main Soil Types of the Central Forest State Natural Biospheric Reserve. Eurasian Soil Science, Vol. 42, Is. 7, - p. 725-737, 2009.

Kasimov, N.S., Perelman, A.I., The geochemistry of soils. Eurasian Soil Sci. Vol. 24, 59–76, 1992.

Lukina, N. V., Orlova, M. A., Bakhet, O. N., Tikhonova, E. V., Tebenkova, D. N., Kasakova, A. I., Kryshen, A. M., Gornov, A. V., Smirnov, V. E., Shashkov, M. P., Ershov, V. V., & Kayazeva, S. V. The Influence of Vegetation on the Forest Soil Properties in the Republic of Karelia. Eurasian Soil Science, Vol. 52 Is. 7, 793-807, https://doi.org/10.1134/S1064229319050077, 2019.

Puzachenko, Y. G., Kozlov, D. N., Siunova, E. V., & Sankovskii, A. G. Assessment of the reserves of organic matter in the world’s soils: Methodology and results. Eurasian Soil Science. Vol. 39, pages1284–1296 https://doi.org/10.1134/E1114229306120027, 2006.

Puzachenko, Y., Sandlersey, R., Sankovski, A. Methods of evaluating thermodynamic properties of landscape cover using multispectral reflected radiation measurements by the landsat satellite. Entropy. Vol. 15 Is. 9 :3970-3982 https://doi.org/10.3390/e15093970, 2013.

Reeuwijk, L. Procedures for soil analysis. In Technical paper. Wageningen : International Soil Reference and Information Centre, The
Netherlands, 101p., 2002.

Reimann, C., Fabian, K., Birke, M., Filzmoser, P., Demetriades, A., Négrel, P., Oorts, K., Matschullat, J., de Caritat, P., Albanese, S., Anderson, M., Baritz, R., Batista, M. J., Bel-Ian, A., Cicchella, D., De Vivo, B., De Vos, W., Dinelli, E., Duriš, M., … Sadeghi, M. GEMAS: Establishing geochemical background and threshold for 53 chemical elements in European agricultural soil. *Applied Geochemistry*. https://doi.org/10.1016/j.apgeochem.2017.01.021, 2018.

Semenkov, I. N., Kasimov, N. S., Terskaya, E. V. Lateral distribution of metal forms in tundra, taiga and forest steppe catenae of the east European plain. *Vestnik Moskovskogo Universiteta, Seriya 5: Geografiya*, 29-39, 2016.

Vodyanitskii, Y., Minkina, T., & Zamulina, I. Methodological aspects in the analysis of the content of mobile compounds of heavy metals in hydromorphic soils. *Applied Geochemistry*, 113, https://doi.org/10.1016/j.apgeochem.2019.104493, 2020
Captions for Figures

Figure 1. A - Key area location and a satellite image of Central Forest State Natural Biosphere Reserve (yellow line – protected area of the reserve and red line – core area) © Google Maps 2019.

Figure 2. Positions (hereinafter in the figures and tables): S – summit (interfluve); US – middle slope; FS – footslope. 1 – 4 Location of the soil profiles: 1 – Endocalcaric Albic Glossic Stagnic Profondic Retisols (Cutanic, Loamic), 2 – Albic Glossic Stagnic Profondic Retisols (Cutanic, Humic/Ochric, Loamic), 3 – Albic Gleyic Histic Retisols (Cutanic, Loamic), 4 – Albic Gleyic Histic Profondic Retisols (Cutanic, Loamic). Soil horizons and materials: H – Histic, O – Folic and forest litter, A – Umbric, E – albic, B – argic, C – parent material; I – boundary between loess like loams and underlying carbonate moraine deposits; II – upper boundary of effervescence with 10% HCl; III – groundwater level.

Figure 3. Photos of soil pits. Pit locations are shown in Fig. 2.

Tables

Table 1 Morphological properties of Retisol.

| Soil | Horizon | Depth, cm | Color | Mansell | Structure |
|------|---------|-----------|-------|---------|-----------|
| Oa   | surface | Uniform, dark brown | 10YR 4/5 | Structureless |
| OAh  | 2-6     | Uniform, dark reddish brown | 2.5YR 6/6 | Structureless |
| E    | 20-30   | Uniform, whitish grey | 10YR 6/4 | Platy |
|      |         | Dark brown vertically oriented stripes of humic material | 10YR 6/6 | |
| BE   | 45-55   | Brown background | 7.5YR 6/6 | Platy |
|      |         | whitish grey stripes | 10YR 7/4 | |
|      |         | dark brown spots | 7.5YR 2.5/1 | |
| 2Bwk | 70-90   | Reddish brown | 7.5YR 6/6 | Prism-like |
|      |         | background clarified areas | 10YR 6/4 | |
| 2BClk| 110-130 | Reddish brown | 7.5YR 6/6 | Prism-like |
## Albic Glossic Stagnic Profondic Retisol (Cutanic, Humic/ Ochric, Loamic)

| Level | Horizon | Color | Texture | Soil Description |
|-------|---------|-------|---------|------------------|
| Oa    | surface| Uniform, dark brown | 10YR 4/5 | Structureless |
| OAh   | 2.5-4  | Uniform, dark grey   | 7.5YR 3/1 | Structureless |
| Ah    | 5-10   | Uniform, dark grey   | 7.5YR 3/1 | Granular |
| AhE   | 12-18  | Light brown background with whitish grey stripes | 7.5YR 4/4 | Platy |

## Albic Gleyic Histic Retisols (Cutanic, Loamic)

| Level | Horizon | Color | Texture | Soil Description |
|-------|---------|-------|---------|------------------|
| Escl  | 30-40   | Uniform, whitish grey | 10YR 7/4 | Platy |
| BEscl | 52-62   | Brown background light brown stripes | 7.5YR 5/6 | Platy |
| Bescl | 75-85   | Light whitish brown with bluish-grey stripes | 10YR 5/8 | Platy |
| Bwsc  | 104-114 | Reddish brown background | 5YR 5/6 | Prism-like |
| CBwsc | 140-150 | Uniform, reddish brown | 5YR 5/6 | Granular weakly structure |
| Ha    | surface| Uniform, dark brown | 5YR 2.5/1 | Structureless |
| Ah    | 9-14   | Dark reddish brown background | 2.5Y 2.5/1 | Structureless |
| AhEt1 | 17-20  | Light-gray background with light whitish brown areas | 10YR 4/1 | Prism-like |
| Etosc | 25-35  | Bluish-gray background light whitish brown areas | 2.5Y 7/4 | Prism-like |
| Bwg   | 48-58  | Light brown background | 5Y 6/2 | Massive, platy |
| Ha    | 0-8    | Uniform, dark brown | 10YR 2/2 | Structureless |
| HaE   | 8-12   | Light-gray background dark brown stripes | 2.5Y 6/2 | Massive |
| Etoscl| 17-23  | Bluish-gray background reddish brown spots | 10YR 5/6 | Massive |

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| Soil Type | Color Range | Background Color and Hue | Spots Color and Hue | Structure |
|-----------|-------------|--------------------------|--------------------|-----------|
| Etoscl    | 28-35       | Bluish-gray background   | reddish brown spots| Massive, platy |
|           |             | 10YR 6/3                 |                    | 7.5YR 3/4 |
|           |             | 10YR 5/6                 |                    | 10YR 6/3 |
| Betoscl   | 39-45       | Bluish-gray background   | reddish brown spots| Massive, platy |
|           |             | 10YR 6/4                 |                    | 7.5YR 7/5 |
| Bg        | 60-90       | Light brown background   | bluish-gray stripes| 7.5YR 5/6 |
|           |             |                         |                    | 7.5YR 6/4 |
| 2Crk      | 110-120     | Bluish-gray tint reddish brown spots | 10YR 5/8 | Structureless |
|           |             |                         |                    | 7.5YR 5/8 |

Table 2. Descriptive statistics datasets

| Dataset                                               | Purpose                                                                 |
|-------------------------------------------------------|-------------------------------------------------------------------------|
| Season/Month (all horizons, all landscape positions)  | for all landscape positions and all soil horizons in certain season (May, June, September or November). |
| Landscape position (all seasons, all horizons)        | for all study seasons and all soil horizons within a certain landscape position (summit, upper slope or upper and lower footslope). |
| Horizon (all seasons, all landscape positions)         | for all study seasons and all landscape positions in certain soil horizon (A, El, B, C). |
| Season/Month, landscape position (all horizons)        | for all soil horizons in certain season within certain landscape position. |
| Season/Month, soil horizon (all landscape positions)   | for all landscape positions in certain season and soil horizon.         |
| Landscape position, soil horizon (all seasons)         | for all seasons within certain landscape position and in certain soil horizon. |
Table 3. Significance of seasonal changes

| Month  | Changes |
|--------|---------|
| June   | Increases: Ti Nb Zr <0.001 Zr 0.02 Th <0.001 V <0.001 Na Nb 0.002 Ba Bi <0.001 V 0.004 Na <0.001 Ba Bi Mg Se <0.001 |
|        | Statistically insignificant difference |
|        | Decreases: W Na <0.001 Mo <0.001 Al Na <0.001 Ti 0.01 W 0.04 Fe <0.001 |
| September | Increases: V <0.001 Sn 0.001 |
|        | Statistically insignificant difference |
|        | Decreases: Na 0.005 K <0.001 K <0.001 |
| May    | Increases: Nb, Cd, Mo |
|        | Statistically insignificant difference |
|        | Decreases: |

Table 3. Significance of seasonal changes

| Month  | Changes |
|--------|---------|
| November | Increases: F1, F2, F3, F4, F5 |
| June    | Increases: F1, F2, F3, F4, F5 |
| September | Increases: F1, F2, F3, F4, F5 |
| December | Increases: F1, F2, F3, F4, F5 |
