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SPATIAL AND TEMPORAL PATTERN OF SOIL pH AND Eh AND THEIR IMPACT ON SOLUTE IRON CONTENT IN A WETLAND (TRANSDANUBIA, HUNGARY)

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Abstract
Land mosaics have direct and indirect influence on chemical reaction and redox condition of soils. The present paper deals with the relationship between some environmental factors (such as soil and vegetation patterns, micro-relief, water regime, temperature and incident solar radiation) and the pH, Eh of soils and solute iron in a headwater wetland in Transdanubia, Hungary. Measurements have been taken in four different patches and along their boundaries: sedge (*Carex vulpina, Carex riparia*, three patches and two species), horsetail (*Equisetum arvense*), common nettle (*Urtica dioica*). The spatial pattern of the studied parameters are influenced by the water regime, micro-topography, climatic conditions and by direct and indirect effects of vegetation. The indirect effect can be the shading, which has influence on soil temperature and on the incident solar radiation (PAR). Root respiration and excretion of organic acids appear as direct effects.. There have been measured individual pH and Eh characteristic in the studied patches. Soil Eh, pH and solute iron have shown seasonal dynamics. Higher redox potentials (increasingly oxidative conditions) and higher pH values were measured between late autumn and early spring. The increasing physiological activity of plants causes lower pH and Eh and it leads to higher spatial differences. Although temperature is an essential determining factor for Eh and pH, but our results suggest it rather has indirect effects through plants on wetlands.

Keywords: geoecology, wetland, pH, Eh, iron

1. Introduction

Studying of the relationship between land mosaics and different kinds of ecological processes is an actual task for geoecology (Csató and Mezősi, 2003). One of the aspects of this key task is the characterisation of the macro- and microelement budget of land mosaics. Several publications have been available about geoecology of these elements until recently (Farsang and M. Tóth, 2003, Gambrell, 1994, Szabó et al. 2007, Szabó and Posta, 2008, Szalai 1998). Element flows among ecotopes are controlled by several abiotic and biotic factors. The most important abiotic factors can be the mineral properties (Németh et al. 2005, Sipos et al. 2005, Sipos et al. 2008, Szabó 2006), the chemical reaction (Impelliteritteri, 2005, Szabó and Szabó, 2006.) and the spatial ad temporal dynamics of redox conditions (Wiessner et al. 2005, Szalai 2008). These environmental agents have an affect on chemical status of solute microelements as well (Zih-Perényi and Lásztity 2005, Zih-Perényi et al. 2008). Some of abiotic environmental factors, as soil pH and Eh are strongly influenced by biotic environmental factors (Ascar et al. 2008). Several studies (Gambrell, 1994, Guo et al. 1998) have reported on the influence of microbial activities on soil pH and Eh, claiming that the role of higher plants (and their pattern) has less importance. The pattern ecotopes has an influence on soil erosion driven element flow, as well (Madarász et al. 2003, Farsang and Barta, 2004, Kertész et al. 2004).

The present paper focuses on spatial and temporal (seasonal and daily) patterns of soil pH and Eh and their impact on dynamics of iron in soil solution with a reference to mosaics of ecotopes. It has been supposed that vegetation pattern has a direct and indirect influence upon the temporal dynamics and spatial pattern of pH and Eh. The most important indirect effect is shading, which has an influence upon soil temperature, and reduces the incident radiation on the surface of herbaceous vegetation. The vegetation directly models soil pH and Eh through the activity of roots. The spatial and seasonal variations of soil Eh and pH may change solute macro- and microelement content, so they can be a key component in the budget of these elements. To verify our working hypothesis a geochemically homogeneous study area (Szalai and Németh, 2008) was selected. We supposed, that the photosynthetically active radiation (PAR, λ= 400-700 nm) could be an adequate indicator to clarify the role of higher plants in pH, Eh and solute iron dynamics.

2. Materials and methods

Study area was marked out in Tolna Hills, in a headwater valley extending in north to south direction. The studied ecotopes are located on the valley floor (Fig. 1). The valley floor is continuously fed by a small stream. Water discharge of the studied streams were determined by spillovers, which are located 300 m away from the studied area. Ecotopes were determined on the basis of homogeneous vegetation (and soil) patches (Keveiné, 2003). In our case all ecotopes were characterised by gleysols. However topography and oak and oak-conifer woodland of valley slopes shorten the duration of direct incident radiation onto all the ecotopes, therefore all the studied spatial units have individual daily and seasonal incident solar radiation characteristics. There are two kinds of ecotopes on the valley floor:

A. *Ecotopes with herbaceous vegetation*

1. *Carex vulpina* dominated sedgy meadow (crx0)
2. *Carex riparia* dominated sedgy meadow (mown) (crx1)
3. *Carex riparia* dominated sedgy meadow (crx2)
4. *Equisetum arvense* dominated patch (equ2)

B. Shaded ecotopes

5. *Acer campestre* and *Equisetum arvense* dominated patches (equ3)
6. *Acer campestre* and *Urtica dioica* dominated patches (urt3)
7. *Alnus glutinosa* dominated patch (aln4)

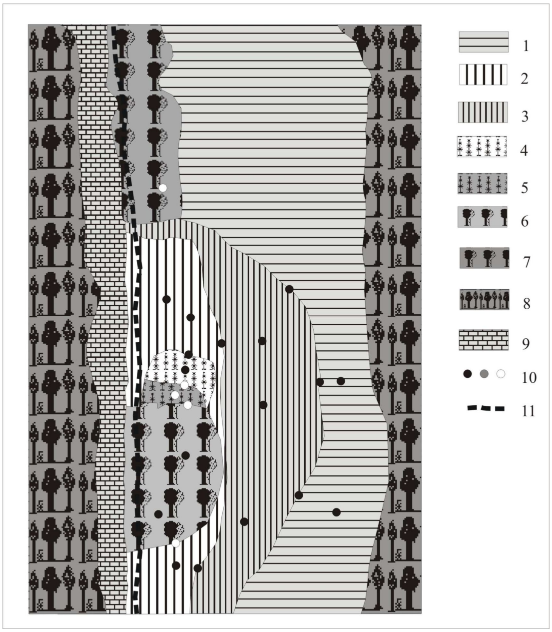

Fig. 1. Map of ecotopes (patches): 1 - Crx0, 2. Crx2, 3 - Crx1, 4. -Equ2, 5 - Equ3, 6 - Urt3, 7 - Aln4, 8 -Oak wood, 9 - macadam road, 10 - measuring points, 11 - stream

Two-three measuring and sampling points were applied for each ecotope. Each point of measurement included 3 measuring holes (d=0.9 cm, depth=15 cm) for the Eh, for the pH probes and for sampling. Testo Type 04 pH electrodes (with thermometer) were appied for pH measurement. The pH calibration was carried out in each hours. The applied pH probes have allowed continuous thermal correction. Applied probes have tested in our laboratory by pH 7.00 and by pH 10 buffer solutions in 25°C. 20 pcs Type 04 probes have recorded 24.9°C and 2 pcs probe measured 24.8°C compared with reference thermometer (TESTO 01: 25.0°C). Type 04 probes recorded pH 6.92-7.01 in pH 7.00 and they recorded pH 9.87-10.05 in pH 10.00, before calibrations. Type 04 probes have measured values in pH 6.98-7.04 and pH 9.98-10.03 ranges after calibrations. Eh conditions were recorded by Testo Type 06 electrodes. Redox probes were tested in laboratory by Ag/AgCl redox standard solution (+358 mV) in 25°C: applied probes recorded values in +352-+365 mV range. The Eh and pH probes were red out by TESTO 230. Soil pH was also measured in laboratory, on the basis of “International A method” (Buzás, 1988). Photo-synthetically active radiation (PAR, λ= 400-700 nm) was determined by Skye 200 quantum interceptor. PAR measurements were carried on upon the ground surface and on the surface of vegetation in the open ecotopes, and threy were performed upon the ground surface and on the surface of herbaceous vegetation in the shaded (woody) ecotopes.

Soil organic carbon (SOC) were measured by Tekmar Dohrmann Apollo 9000N N-DIR spectrometer. Clay fraction of soils were determined Fritsch Analysette Microtech A22 laser diffraction analyser. Clay minerals of soils were determined by X-Ray diffraction analyser (Philips PW1710), in Geochemical Research Institute of Hungarian Academy of Sciences. Aluminium and iron content of soils were measured by X-Ray Fluorescense Spectrometer (Atomika Extra IIA) in the Department of Inorganic and Analytical Chemistry, Eötvös Loránd University. Samples for solute iron content of soils were taken by vacuum pump and were conserved in pH 2 by cc. nitric acid. Solute iron was measured by Merck SQ118 VIS spectrophotometer and Zeiss AS30 atomic absorption spectrophotometer.

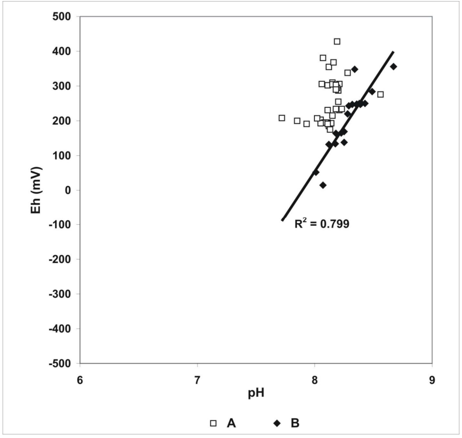

Fig. 2. Scatter of Eh and pH small freshwater bodies. A - “distrophic like” stream Q<0.001 m^3/s, B – stream Q<0.01 m^3/s

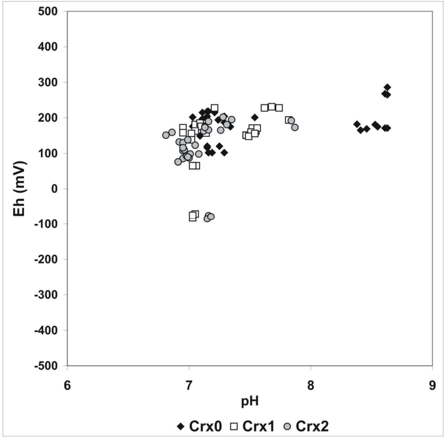

Fig. 3. Eh-pH scatter of sedge patches

Table 1. Geochemical parameters of soils of studied ecotopes

	Clay fraction (%)	Clay minerals* (%)	Quartz* (%)	SOC (%)	$CaCO_3$ (%)	Al (mg kg^{-1})	Fe (mg kg^{-1})
Crx 0	19,3	14	67	2,15	7,3	10060	14600
Crx 1	19,1	19	55	2,48	6,5	11010	16150
Crx 2	19,8	19	55	2,49	6,1	11060	16240
Equ 2	20,2	19	55	2,26	5,5	7510	11200
Equ 3	29,5	na	na	1,86	5,5	7200	11250
Urt 3	29,8	19	70	1,83	5,5	7790	11530
Aln 4	29,4	17	na	1,87	5,1	7850	11520

Clay fraction: d<2µm; * in clay faction; nd = no data

Table 2. Diurnal changes of soil temperature in three studied ecotopes (10 cm) and PAR (at surface of herbaceous vegetation), on 15. June, 2006.

	Crx 2		**Equ 2**		**Equ 3**	
T (h)	**t (^{o}C)**	**PAR (μmol m^{-2} s^{-1})**	**t (^{o}C)**	**PAR (μmol m^{-2} s^{-1})**	**t (^{o}C)**	**PAR (μmol m^{-2} s^{-1})**
2:00	15.5	0.0	15.6	0.0	14.2	0.0
3:00	15.4	0.0	15.5	0.0	14.2	0.0
4:00	15.4	0.2	15.5	0.2	14.1	0.0
5:00	15.3	5.1	15.5	5.0	14.1	0.5
6:00	15.3	34.0	15.5	33.3	14.0	0.9
7:00	15.1	762	15.4	760	14.0	18
8:00	14.9	995	15.3	993	14.0	102
9:00	14.9	1210	15.3	1210	14.1	151
10:00	14.8	1451	15.2	1451	14.2	165
11:00	14.9	1594	15.2	1594	14.2	165
12:00	15.0	1611	15.2	1611	14.1	105
13:00	15.1	1621	15.2	1621	14.1	102
14:00	15.1	1470	15.2	1465	14.0	108
15:00	15.3	1459	15.4	1455	14.3	98
16:00	15.4	1480	15.6	1472	14.4	91
17:00	15.2	970	15.4	980	14.5	58
18:00	14.7	258	15.0	250	14.5	39
19:00	14.9	13.1	15.0	12.5	14.5	1.1
20:00	14.7	4.9	14.9	4.3	14.4	1.1
21:00	14.6	0.0	14.9	0.0	14.4	0.0
22:00	14.6	0.0	14.8	0.0	14.4	0.0

3. Results and discussion

There is linear correlation between reduction-oxidation status and chemical reaction in a “pure abiotic system”. These kinds of systems were represented by small open freshwater with different discharge. The linear correlation between these parameters was observed during winter half-year (October-April) in the $Q=0.01$ m^3/s stream. while this correlation was not linear in case of smaller ($Q<0.001$ m^3/s) “distrophic-like” stream (Fig. 2). There is no correlation between pH and Eh in waterlogged soils. the values of sampling sites compose patches in the Eh-pH scatter. These patches belong to individual ecotopes. Location and shape of these patches depend on several environmental factors. The most important ones are the chemical parameters, microbial activity and temperature characteristics of soils (Stein et al. 2007). Topography and vegetation pattern have an indirect affect through shading (by reducing incident radiation and eradiation). The individual patches of vegetation patterns in Eh-pH scatter are based on changing soil biological activities and varied soil temperature characteristics of these units. as well. Some ecotopes are characterised by more than one patch. This exfoliation of patches is resulted by temporary reductive soil environment. We observed this kind of temporary low Eh values in Crx1 and Crx2 ecotopes and it was caused by root activity of Carex riparia. In contrast to heterogeneity of physiological activities, homogeneity of geochemical parameters (Table 1) has resulted overlaps (Fig. 3).

The soil temperature and incident solar radiation also have shown spatial differences (Table 2). These differences assist to microclimate formation of ecotopes. The various microclimatical properties of ecotopes have essential role in spatial and temporal pattern of soil Eh and pH.

Diurnal oscillation of soil pH and Eh were the most significant between May and August with prevailing high (atmospheric) pressure (Fig. 4). While daily oscillation of soil pH was not significant in shaded ecotopes (Equ3. Urt3. Aln4), it changed by 0.8 pH per day in herbaceous land mosaics: the lowest fluctuation of chemical reaction was found in Equ2 (*Equisetum arvense*) and Crx0 (*Carex vulpina*). whereas the highest one was established in Crx2 (*Carex riparia*). The daily (and seasonal) changes of soil pH fairly correlate with PAR values at the surface of herbaceous vegetation. In the early morning soil pH starts to increase if PAR is higher than 5-10 μmol m^{-2} s^{-1}. This parameter starts to decrease after sunset if soil temperature also starts to decrease.

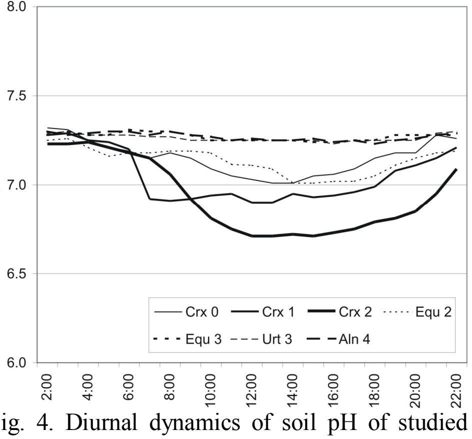

Fig. 4. Diurnal dynamics of soil pH of studied ecotopes on summer solstice

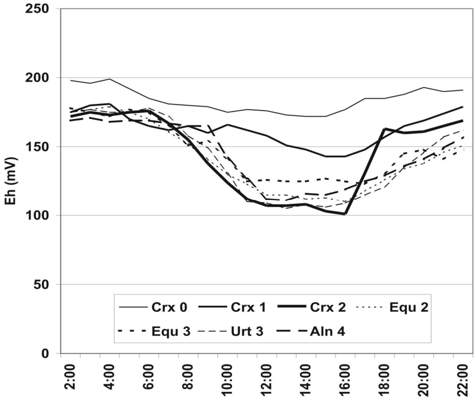

Fig. 5. Diurnal dynamics of soil Eh of studied ecotopes on summer solstice

In contrast to soil pH Eh values have shown diurnal oscillation in all studied ecotopes (Fig. 5). The amount of oscillation was similar in all studied ecotopes in summer solstice. We have found two exceptions: Crx1 and Crx2 ecotopes. where the open water surface has caused alterations. Diurnal changes of soil Eh also have correlated with PAR dynamics. Nikolausz et al. (2008) have also reported on diurnal fluctuation of redox conditions in soils. but them results shown the highest Eh during the highest incident radiaton. This paradox caused by different measurement techniques because they measured Eh on the rhizoplan, while our results have measured in the rhizosphere.

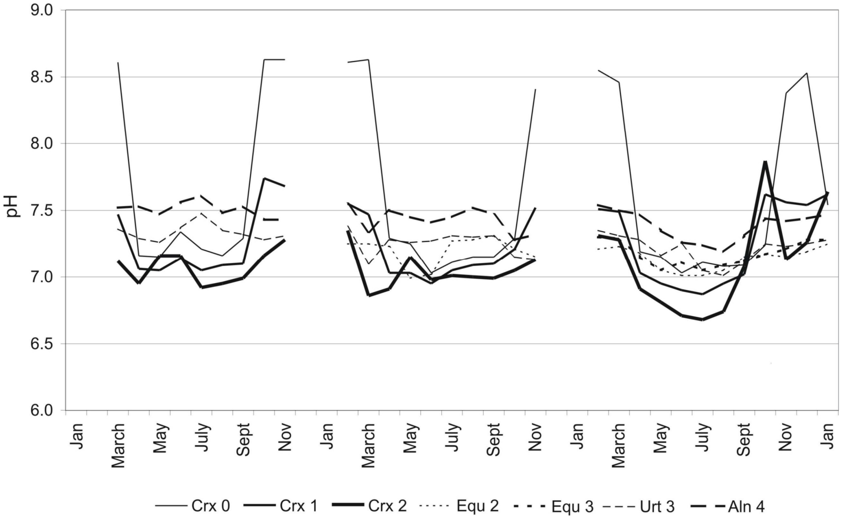

Fig. 6. Seasonal dynamics of soil pH of studied ecotopes (2004-2006)

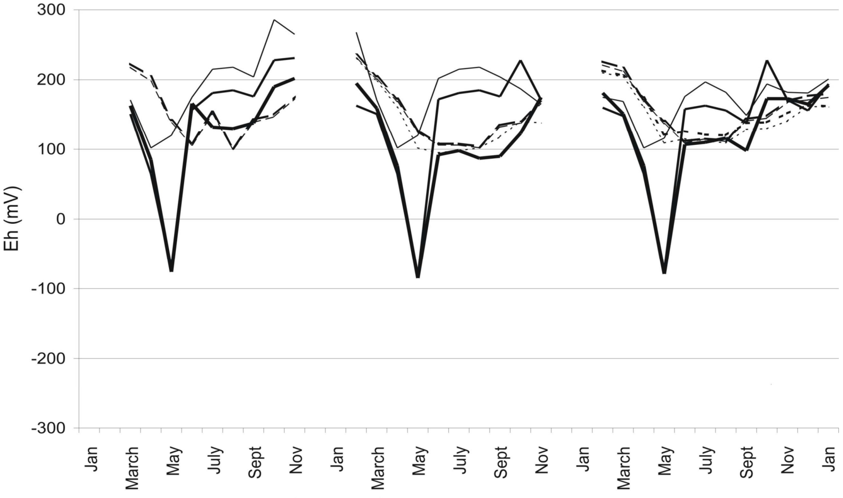

Fig. 7. Seasonal dynamics of soil Eh of studied ecotopes (2004-2006)

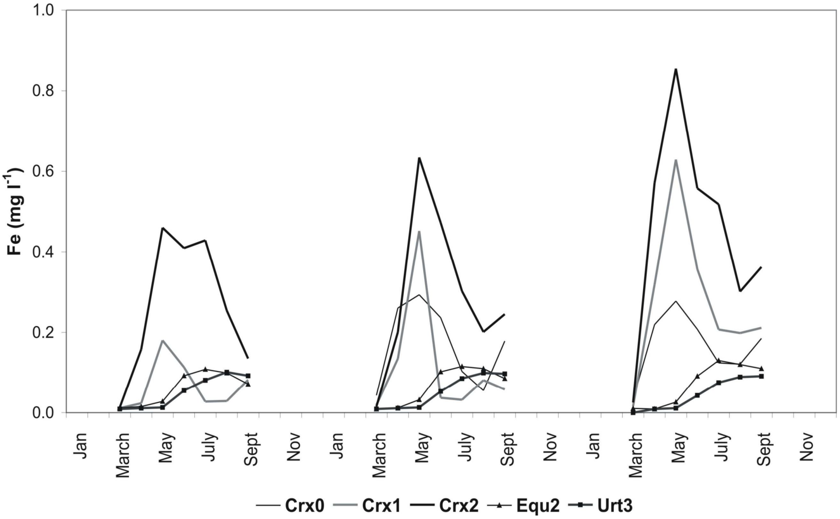

Fig. 8. Seasonal dynamics of soil solute iron of studied ecotopes (2004-2006)

Seasonal fluctuation of soil pH shows same pattern as soil temperature and incident solar radiation do (Fig. 6). Field measurement have resulted same soil pH as in the lab measurements during winter season (between November and March). Longer saturated conditions higher amount of soil organic matter (SOM) and the arboreal vegetation resulted slighty alkaline conditions. while the herbaceous vegetation with a lower amount of SOM coincided with higher soil pH in this period. This parameter usually has lower values during the growing season. Difference between January and December may reach 1.4 pH unit (Crx0). However the most striking changes were recorded in *Carex vulpina* ecotope. the lowest pH was measured in the soils of Crx2 ecotope. where the soil environment shifted to slightly acidic between May and September. It should be emphasised. that mowing of *Carex riparia* caused less seasonal changes in soil pH. This phenomenon suggests. that the differences in the physiological status of plants also can cause differences in soil chemical parameters.

Oxidation-reduction conditions of soils have seasonal dynamics similar to those found in soil pH (Fig. 7). Redox dynamics had similar characteristics in woody ecotopes and in horsetail dominated patches. There appeared differences among sedgy ecotopes. With regard to redox conditions small differences were found between studied land mosaics during winter months. Soil environment became increasingly reductive with rising soil temperature. The most relevant changes appeared in *Carex* dominated patches. where soil environment became extremely reductive compared with other spatial units. In this area *Carex riparia* created more reductive conditions than *Carex vulpina*. This phenomenon partly could be the result of worst aeration of Crx1 and Crx2 ecotopes. However these plants provide free O_2 in the rhizoplan – as a thin Fe(III) coat in the root surface confirms – permanent inundation and the high amount of exudated organic matter (Lambers et al. 1998) finally resulted reductive environment in the rhizosphere. The mowing also has an influence on soil Eh. because the soil environment became much more oxidative in Crx1 ecotope in the second half of growing season. This phenomenon may also depended on root exudation of organic matter.

Seasonal fluctuation of redox condition has lover magnitude in the all studied "non-sedgy" ecotopes. The seasonal change of Eh is not higher than 150 mV. We did not find significant differences between shaded and open ecotopes and between horsetail and nettle dominated patches.

Similar to seasonal dynamics of redox conditions and chemical reaction in studied gleysols. solute iron also showed seasonal fluctuation in the soils. Its concentrations have oscillated around low (0.01 mg l^{-1}) value in all ecotopes during winter period (Fig. 8). Highest iron concentrations could be found in Crx2 and Crx1 ecotopes. in May. The solute iron content in Crx0 ecotope also showed maximum in this period. but solute iron concentration was half of the Crx2. These high concentrations have coincided with the most reductive soil conditions as we expected. In the other studied ecotopes the highest iron concentrations were measured later. between July and September.. In these ecotopes the solute iron content of soils are less than in the Crx2. in turn there is no relevant differences in Eh and pH.

Although increasing temperature and decreasing pH also correlated with solute iron concentrations. the closest relationship was observed with soil Eh. as we expected. Since spatial and temporal pattern of studied environmental factors depends on ecotopes. Spatial and temporal fluctuation of solute iron content of gleysols also depends on land mosaics.

4. Conclusions

Recorded fluctuations of both soil Eh and pH have abiotic as well as biotic origin. as it was established in several papers (Nebauer et al. 2008; Weiss et al. 2005). Differences in water regime is one of the most important abiotic factors for the Eh and pH variations across different ecotopes. Some rainfall simulation experiments also testify to this (Szűcs et al. 2006). Our results suggest. that diurnal dynamics of these parameters have weaker oscillations than it was measured in lab scale experiments (Callie et al. 2003; Nikolausz et al. 2008; Wiessner et al. 2005).

Daily oscillation of soil pH and Eh is negligible during the winter season. Further these parameter values increase during the growing season then they decline again at late autumn.

Chemical reaction and soil redox conditions also show specific spatial pattern resulting from some landscape elements such as from topography and vegetation. Topography makes only indirect impact on the studied parameters modifying incident radiation. soil temperature and water regime. Vegetation exerts both direct and indirect influence on soil properties. Vegetation affects soil chemical parameters by shading (incident solar radiation. soil temperature). Direct influence of vegetation on these parameters manifests itself through the physiological activities of plants.

The importance of root activity of higher plants were indicated by the correlation between PAR and daily dynamics of soil Eh and pH. On the basis of diurnal dynamics of soil temperature and PAR it is presumed that the root activity has major importance on the dynamics of these parameters in the first half (morning time) of the day.

Just like effecting factors of iron mobility have spatial pattern and seasonal dynamics. the solute form of iron element also show seasonal dynamics and spatial distribution across the ecotopes. These variations proved to be relevant during growing season. when spatial differences could reach 60-fold values.

Solute iron is higher in *Carex riparia* dominated patches than in other non-sedgy patches in case of similar redox condition. during summertime. This phenomenon probably based on slow oxidation of ferro-iron.

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