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Depth function of manganese (Mn) concentration in soil solutions: Hydropedological translocation of trace elements in stratified soils

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Abstract

Periglacial cover beds are an important trigger of slope-water paths in sloped terrain of the mid-latitudes. Most hydropedological studies focus on the quantitative analysis about the interrelation between subsurface layering and runoff processes at the slope scale. In this research we emphasis on a qualitative environmental geochemical analysis of trace elements and dissolved organic carbon in a small forest hydrological study area in the central parts of the subdued mountains of Germany (Location: KrofdorferForst, +50° 41' 3.69", +8° 38' 38.87"). The main objective is to assess the effect of lithological discontinuities of stratified soils within the depth functions of trace elements concentration in soil solutions (soil water and its dissolved and mobile fraction in a vertical distribution). Lorz (2008) show that depth functions of manganese (Mn) are characterized by strong pedogenic dynamics, analysing a shortened sequential extraction of solid soil material. We investigated the hypothesis that lithological discontinuities act like aquicludes. Therefore we expect abrupt changes within the depth function of manganese as a result of such water-blocking effect (= geochemical barriers) as a consequence of mobilization under wet soil conditions. In a preliminary case study we sampled soil solutions from three different plots within a 400m-toposequence. We use in situ trench installed suction lysimeters with ceramic tips (Irrometer Soil Solution Access Tube) to extract soil water samples each 20 cm from top- (10 cm) to subsoil (110 cm). For geochemical element analysis we use an inductively coupled plasma mass spectrometry (ICP-MS). The results: A clear character of abrupt changes within the depth function could be illustrated for most of the plots. For example, at the upper slope plot a contrast of the depth function is from 1013 ppb mean concentration at 50 cm profile depth to 290 ppb mean concentration at 70 cm profile depth (17 month sampling period). To conclude, these results demonstrate that hydrochemical quality and translocation processes of soil solutions determining an interrelation between subsurface layering and run off processes - respectively could be seen as an environmental consequence of it.

Keywords: Pedohydrology, trace elements, periglacial cover beds, hillslope hydrology, geochemical barriers

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Introduction

Runoff generations in low mountain ranges in Europe are strongly influenced by lateral fluxes of soil water caused by periglacial cover beds (Chifflard et al., 2008, Chifflard et al., 2010, Gurtz et al., 2003, Moldenhauer et al., 2013). The latter represents the parent material for the soil formation in the low mountain ranges and typically consists of the lower basal layer (LB), the intermediate layer (LI) and the upper layer (LU) (Kleber

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and Terhorst, 2013, Semmel and Terhorst, 2010).Whereas the LU has a good infiltration capacity the LB acts as a lithological discontinuity in terms of Lorz et al. (2011) due to its higher bulk density as well as its higher skeleton content. This skeleton is aligned parallel to the slope inclination, thus the vertical percolating water is deflected more or less in a lateral direction. Although several studies emphasise the importance of stratified soils for preferential subsurface water flow (Moldenhauer et al., 2013), there is still a lack in experimental based knowledge of specific flow pathways and residence times of soil water in stratified soils (Weiler and McDonell 2006).These uncertainties are an essential reason why in hydrological research the stratification of soils and hereby especially cover beds is not really taken into account as a major trigger of slope water paths. By contrast in soil science the Substrate-Oriented-Soil-Evolution-Model (Lorz et al., 2011) underlines the importance of stratified soils and lithological discontinuities (LD) as a key element controlling ecological processes and depth functions of soil properties like acidification parameters or trace elements (Lorz and Phillips, 2006). LD act as geochemical barriers (Perelman, 1977) or migration barriers (Ostaszewska, 2010) since the LD are not a result of pedological processes consequently in this case the depth distribution of chemical soil properties is not a result of soil formation. Whereas (Lorz and Phillips, 2006) have assessed the depth distribution of e.g. trace elements in the soil matrix (vertical distribution of nonmobile fraction) at the point scale, Fiedler et al. (2002) showed a typical depth distribution for manganese (Mn) in the soil pore water depending on lithological discontinuities in stratified soils along a hillslope catena (SW-Germany) and underline that these depth functions indicate zones of preferential transport. Nevertheless, there is still a missing link of investigations at different scales regarding the impacts of the geochemical barriers and the pronounced depth distributions on the chemical composition of the subsurface runoff and consequently the hillslope runoff. In this preliminary study we focus on manganese (Mn) depth functions on the plot or pedon scale and various plot samples within a toposequence to analyse translocation of manganese at the hillslope scale. Manganese is an essential trace element and micronutrient for organisms. The bioavailability is an important ecosystem function. That is why we (first) focus on such element to study interactions between terrestrial and water ecosystems.

Material and Methods

The research and sampling design is based on a multi-scale approach (Reiss and Chifflard, 2014) combining experimental research at the point and hillslope scale in a small forested catchment (0.241 km^2) characterized by cover beds in Central-Germanycalled *KrofdorferForst*(Location: +50° 41' 3.69", +8° 38' 38.87"; Figure 1).

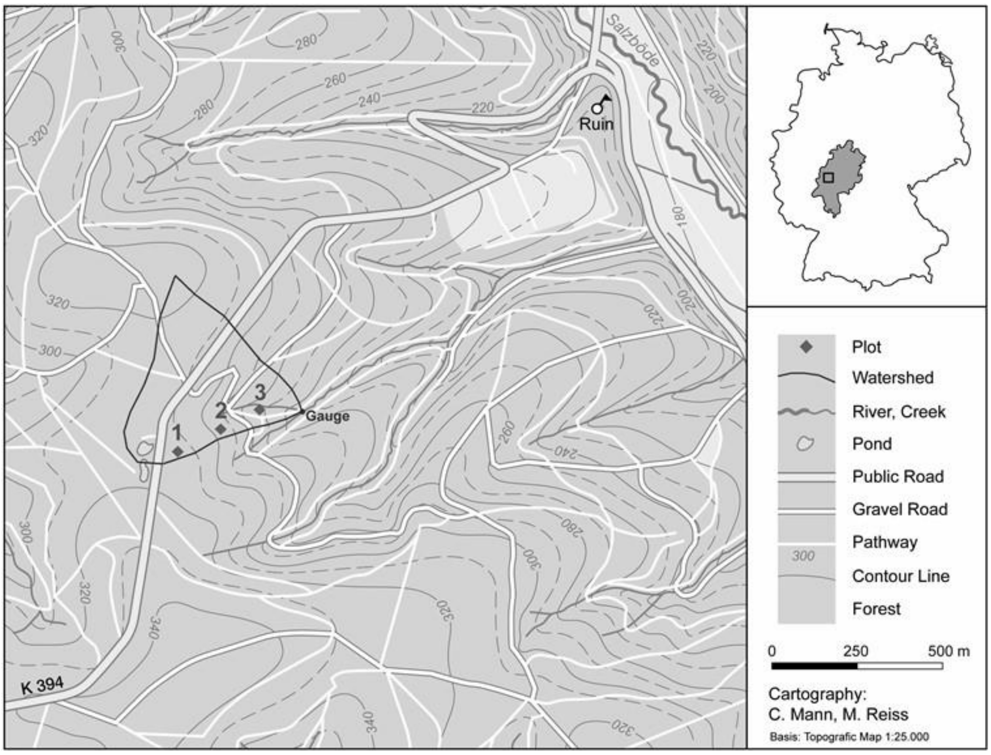

Figure 1: Study Area KrofdorferForst in Germany. Sampling Plots: 1) Upper Slope Plot 2) Middle Slope Plot 3) Foot Slope Plot.

The catchment is devoid of any riparian zone and is characterized by hillslopes that issue directly into the receiving creek. This enables us to assume that the runoff in the creek serves as hillslope runoff without influence of riparian zone mixing.The study area is totally covered by beech forest. Annual mean air temperature is 9.4 degree Celsius (48.9° F). Annual mean precipitation is about 650 mm.Base materials for soil genesis is greywacke and clay shale from Devonian deposits. Most common soil types are Cambisols (brown soils), Luvisols (*Parabraunerde*) and Gleysols. For detailed site description see Schumann et al. (2010). Lithological discontinuities were characterised by using the Germanmanual of soil mapping (BGR, 2005) and a handheld penetrometer for sampling soil compaction in kg/cm^2(bulk density) (Amacher and O'Neill, 2004). Soil water samples captured by soil solution access tubes (Grossmann and Udluft 1991, Weihenmüller et al. 2007) installed in different depths (from 10 cm depth to 110 cm depth in 20 cm steps) regarding lithological discontinuities.We installed the suction cups horizontal from a soil profile trench. The in-situ soil solution extraction runs in the discontinuous operation mode (manual hand pump for negative pressure), water collection is performed during selected short-time intervals, especially before, during and after rain fall events. We use Soil Solution Access Tubes (SSAT) by the Irrometer Company with a butyrate (transparent plastic) body and a ceramic tip for a good documentation of manganese and other trace metal concentrations (Weihenmüller et al. 2007).The samples (evacuation of soil solutions) were taken to precipitation events, i.e. before, during and after an event from October 2012 till February 2014. For this purpose a new scheme of rules for in-situ sampling of soil solutions in Germany has been considered (DWA, 2008). Soil solutions were filtered with 0.7µm Whatman (registered trademark of GE Healthcare) glass fibrefilters in the laboratory (method of microfiltration; Du Laing 2010) for sample preparation regarding the EPA Method 1311(EPA, 1993). The chemical concentrations were analysed with an ICP-MS (inductively coupled plasma mass spectrometry) by ThermoFisher Scientific Incorporation. In addition to the element manganese following trace metal elements were analysed: arsenic (As), cadmium (Cd), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), selenium (Se) and zinc (Zn).

Results and Discussion

Soil Types, Lithological Discontinuities and Basic Parameter

Soil types are mainly StagnicLuvisols, at the foot slope with colluvial coverage and in the subsoil with transitional features to a Gleysol (Table 1) (cf. Zakosek, 1971).

Table 1. Soil Types and Soil Compaction of the Sample Plots. LD: Lithological discontinuity.

Plot	Soil Type	LD
1 – Upper Slope Plot	StagnicLuvisol	at 60 cm profile depth
2 – Middle Slope Plot	StagnicLuvisol	at 60 cm profile depth
3 – Foot Slope Plot	StagnicLuvisol with colluvial coverage	at 80 cm profile depth

Lithological discontinuities are located at 60 cm at the upper and middle slope plot as well as at 80 cm at the foot slope plot characterised by abrupt soil compaction(mean increasing of 1.0 kg/cm^2 bulk density) and specific sedimentaryproperties like occurrence and orientation of clasts longitudinal axes parallel to the slopein the upper layer (Kleber et al., 2013).The mean acidity in soil solutions is pH 7.9 (Min.: pH 7.7, Max.: pH 8.8) without any abrupt changes of the depth function for all sampling plots. The same finding applies to the electrical conductivity (EC). No contrast within the depth function, the mean value is 0.314 mS/cm (Min: 0.203 mS/cm, Max: 0.548 mS/cm). For our results regarding cumulative parameters like pH and EC we can say that there are no proxies to characterise lithological discontinuities in depth functions of soil solutions. This finding is in contradiction to the results of Lorz and Phillips (2006) who has demonstrated significant abrupt changes in depth function for soil pore water extractions from the soil matrix. This leads us to the motivation that in future we have to analyse soil solution (mobile liquid phase of soil water) and soil pore water extraction (nonmobilesolid phase of soil water) in comparison.

Manganese Concentration in Soil Solutions at the Plot Scale

Upper Slope Plot

The manganese concentration at the upper slope plot is constantly increasing from the 10 cm to the 50 cm measurement point and is abrupt decreasing at the 70 cm measurement point of the vertical soil profile (Table 2, Figure 2).

Table 2. Manganese concentration of the upper slope plot and depth function. Double line: Lithological Discontinuity.

Upper Slope Plot	Mean Mn [ppb]	Min. Mn [ppb]	Max. Mn [ppb]
10 cm	272	40	385
30 cm	821	433	4501
50 cm	1013	474	1634
70 cm	290	123	744
90 cm	349	136	1074

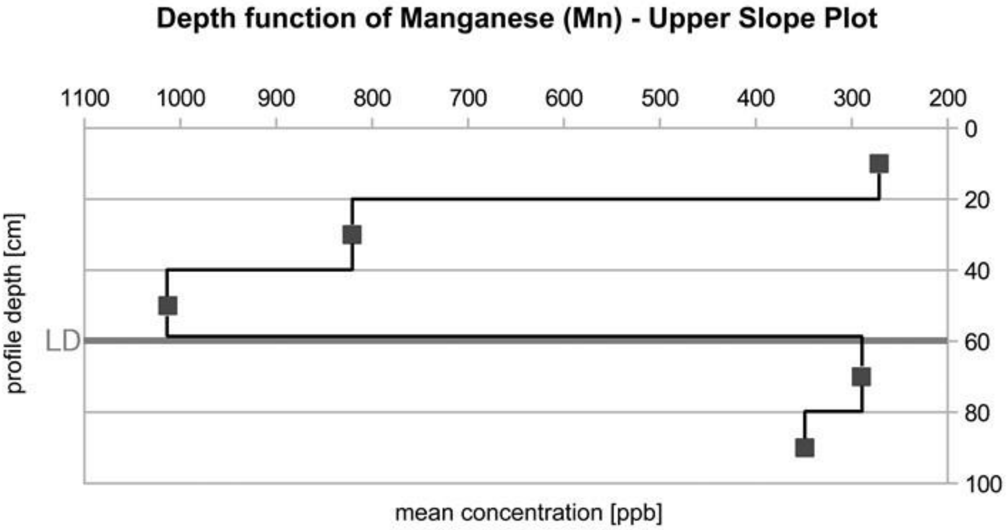

Figure 2. Depth function of manganese (Mn) of the upper slope plot. LD: Lithological Discontinuity

The lithological discontinuity at 60 cm depth led to a clearly and distinctive change of manganese concentration within the soil solution. After Lorz et al. (2011) the depth function of the manganese concentration within the mobile fraction can be characterised as a simple contrast. The depth function could be considered for the mean value of manganese concentration and is also remarkable for the extreme values of the minimum and maximum manganese concentrations. The influence of an abrupt changing pH value within the soil matrix is to be excluded, because the pH value is relative constant within its depth function (about pH [KCl] 3.7 to 4.2 from top soil to subsoil) (Führer, 1990). For the upper slope plot the mean values of the manganese concentration is in general in a normal range, regarding that water soluble Mn^{2+} is “normally” in a range of 20 ppb to 1000 ppb (Finck, 2007). Therefore, the concentration above the lithological discontinuity tend to exceed the normal range (see also maximum value), so that we identify a geochemical or migration barrier caused by a stratified soil profile at the plot scale. This means, we can ascertain a pedo-ecological consequence of lithological discontinuities with the meaning of Lorz and Phillips (2006).

Middle Slope Plot

The concentration of dissolved manganese at the middle slope plot is rapidly decreasing in the topsoil and is characterised by constant low concentration in the subsoil (Table 3, Figure 3).

Table 3. Manganese concentration of the middle slope plot and depth function. Double line: Lithological Discontinuity.

Middle Slope Plot	Mean Mn [ppb]	Min. Mn [ppb]	Max. Mn [ppb]
10 cm	3932	2313	8348
30 cm	737	429	2396
50 cm	148	115	437
70 cm	110	45	593
90 cm	180	82	1727

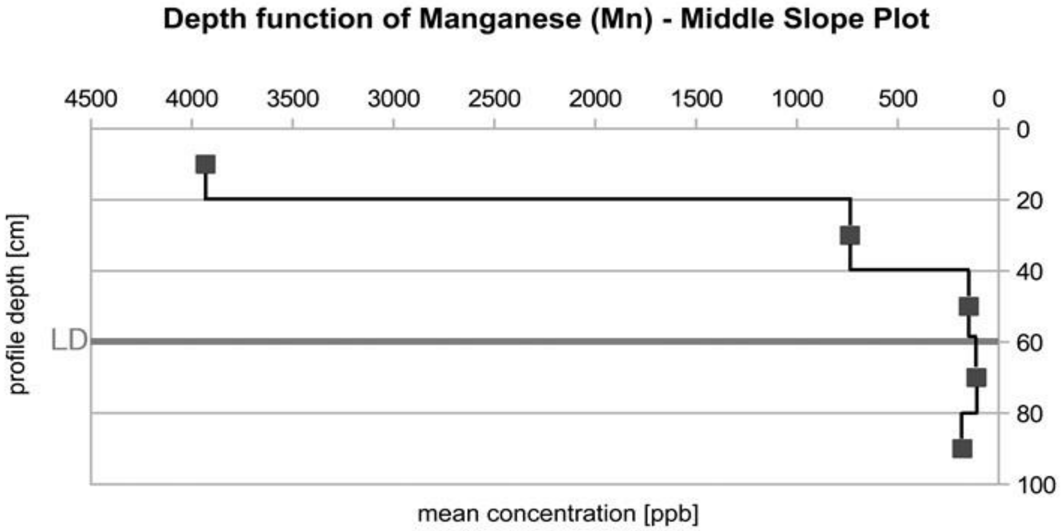

Figure 3. Depth function of manganese (Mn) of the middle slope plot. LD: Lithological Discontinuity.

The conspicuously high values of the manganese concentrations in the topsoil require a special interpretation, because of its disproportionate supply of water soluble manganese and bioavailability in the root zone. The assumption is that the microbial decomposition and thus the availability of dissolved manganese are higher as compared to the other two investigated slope plots.Perhaps there is a context to the fact that the slope inclination is lower and forms a higher litter / humus layer and therefore a potential source of manganese (Fiedler et al., 2002). Scherer (2003) showed that in forest ecosystems with low slope inclination the manganese concentration of the humus layer is much higher than in forest sites with higher slope inclination. To detect the source of manganese more detailed, we start to analyse interflow within the humus layer in the future, because in our investigation of precipitation and depression storage water we see no source for manganese input. Furthermore, the results lead to the conclusion that there is no vertical soluble transport of manganese and accumulation in the subsoil. Although no geochemical barrier can be seen by a lithological discontinuity, it should be noted that dissolved manganese is transported laterally, preferentially in the topsoil or is consumed by plants. The latter seems more plausible, because there is no accumulation in the foot slope plot detectable. Especially Führer (1990) shows a very low manganese concentration of sediment transport in the brook discharge at the gauging station. No relevant output from the terrestrial to the aquatic ecosystem might be assumed regarding sediment bound manganese concentrations. In further research we analyse event based DOC and dissolved trace elements content of the brook discharge to characterise possible dynamic changes of matter concentration and to test the lateral soluble transport hypotheses of manganese translocation in soil. Further research is also needed to analyse manganese concentration in plants to test these hypotheses, too.

Foot Slope Plot

The manganese concentration of the foot slope plot shows a heterogeneous trend within its depth function (Table 4, Figure 4). However, the depth function shows a clear and simple contrast of the manganese concentrationin conjunction with the lithological discontinuity.

Table 4. Manganese concentration of the foot slope plot and depth function. Double line: Lithological Discontinuity.

Foot Slope Plot	Mean Mn [ppb]	Min. Mn [ppb]	Max. Mn [ppb]
10 cm	149	96	548
30 cm	99	64	717
50 cm	146	28	255
70 cm	229	146	661
90 cm	84	44	323
110 cm	547	87	1529

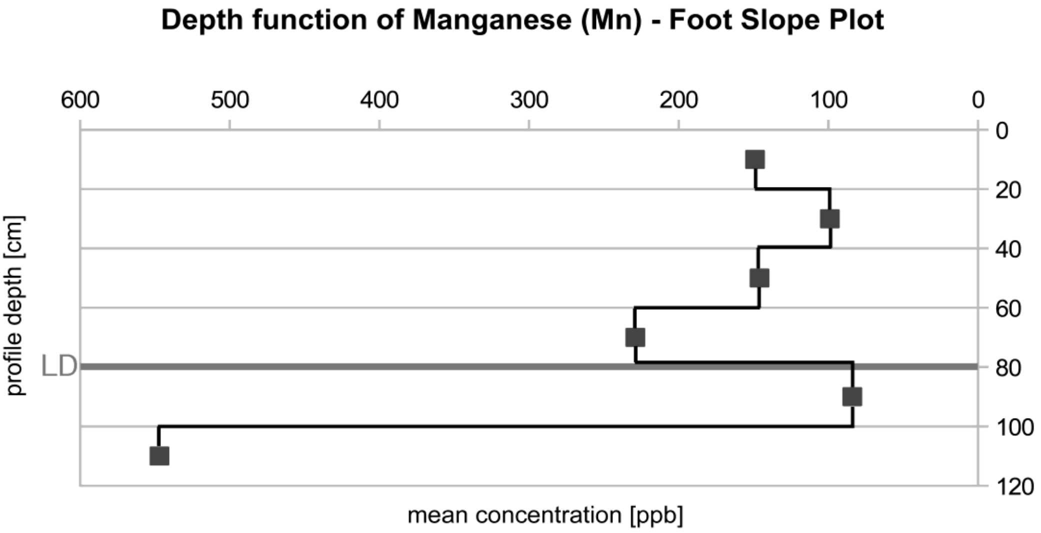

Figure 4. Depth function of manganese (Mn) of the foot slope plot. LD: Lithological Discontinuity.

The detection of a geochemical or migration barrier is similar to the upper slope plot, especially in view of the extreme values with the same clearly and distinctive change of manganese concentration within the soil solution. However, regarding the normal range of dissolved manganese concentration, there is no exceed of mean and extreme values of the concentration above the lithological discontinuity. But we see a pedo-ecological influence on the depth function of dissolved manganese caused by a stratified soil. To what extent the marked increase in manganese concentration is to be interpreted in 110cm depth is the more interesting question, because here an exceeding of the maximum value is obvious.Here we suppose a blended or a higher influence of ascending pore water from the gleyed subsoil horizon, because the lower parts of the subsoil represents a transition to the gley soil of the adjacent spring, where groundwater occurs to the surface.

Manganese Concentration in Soil Solutions and associated trace metals

A number of trace metals like iron (Fe), copper (Cu), nickel (Ni) and zinc (Zn) accumulate in manganese oxides relative to the concentration of these trace elements (Gilkes, McKenzie 1988). We analysed the concentration of these associated metals in the soil solution to characterise possible higher amounts of these elements at geochemical barriers (lithological discontinuities) and to quantify the relevance of manganese associated trace metals. The results are shown in Table 5.

The results of trace element concentrations for the upper slope plot showing no relevant abrupt changes within the depth function for Fe, Ni, Cu and Zn. These associated elements probably do not accumulate in Mn oxides. This result is astonishing, because of the relative high amount of manganese at the lithological discontinuity (see Table 2 and Figure 2). The same finding of no contrast depth function for the associated trace elements must be made for the middle slope plot, with the exception of Ni. The nickel depth function is characterised by an abrupt change of the Ni concentration at the lithological discontinuity. This same result for nickel is to be noted for the foot slope plot and for iron. Fe and Ni showing a simple contrast within their depth function caused by the lithological discontinuity and the function as a geochemical barrier at the foot slope plot. The missing simple contrasts of copper, zinc and partial of iron and nickel within their depth function are perhaps an expression of their forming of complexes with organic ligands (Norvell, 1988).

Table 5. Title. USP: upper slope plot; MSP: middle slope plot; FSP: foot slope plot. Double line: Lithological Discontinuity.

Profile depth	Fe [ppb]	Ni [ppb]	Cu [ppb]	Zn [ppb]
Upperslopeplot				
USP 10 cm	6	6	5	20
USP 30 cm	13	17	6	28
USP 50 cm	11	11	7	20
USP 70 cm	21	18	5	22
USP 90 cm	19	17	4	9
Middle slope plot				
MSP 10 cm	6	19	45	114
MSP 30 cm	14	19	29	57
MSP 50 cm	2	23	4	53
MSP 70 cm	4	11	6	70
MSP 90 cm	1	7	2	96
Foot slopeplot				
FSP 10 cm	7	8	3	-
FSP 30 cm	13	25	10	51
FSP 50 cm	1	13	3	16
FSP 70 cm	30	27	1	27
FSP 90 cm	3	6	4	33
FSP 110 cm	7	10	9	77

Manganese Concentration in Soil Solutions at the Hillslope Scale

We analysed the translocation of the manganese concentration in comparison of the results of the mean value of the same depth plot within a toposequence of the upper, middle and foot slope plot. Thereby, it is possible to characterise translocation for each depth of the soil profile from 10cm, 30cm, 50cm, 70cm to 90cm (Table 6).

Table 6. Manganese Concentration within a toposequence of the upper, middle and foot slope plot.

Profile depth	Upper Slope Plot Mn ppb	Middle Slope Plot Mn ppb	Foot Slope Plot Mn ppb	Trend (from upper slope to foot slope plot)	R^2
10cm	272	3932	149	Decreasing	0.00
30cm	821	737	99	Decreasing	0.84
50cm	1013	148	146	Decreasing	0.75
70cm	290	110	229	Decreasing	0.11
90cm	349	180	84	Decreasing	0.98

The results in Table 6 showing a decreasing in the translocation of manganese concentration of the soil solutions from the upper slope plot to the foot slope plotfor all profile depths. However, there is a difference in the correlation of the trend regarding the R^2 value as the coefficient of determination (using a statistical linear R^2 model). For the 30cm plot, 50cm plot and 90cm plot the results showing a strong significance for the decreasing trend in manganese concentration within the toposequence. For the 10cm and 70cm plot we haven´t found such a strong significance for the decreasing trend. Nevertheless, it is to assume that there is no accumulation of mobile manganese concentration in soil solutions from the upper slope plot to the foot slope plot. The results can be characterised for the topsoil and the subsoil equally.

Conclusion

Manganese is a very suitable trace element to analyze depth functions in soil solutions in soil profiles at the plot scale and therefore to characterize pedo-ecological consequences of lithological discontinuities as geochemical barriers.Manganese (Mn^{2+}) is found mainly as a useful parameter when certain factors such as the depth function of the acidity (pH) show no significant contrast in the soil depth profile. This means simple in-situ measurements during the field work are not sufficient for meaningful analyzes of pedo-ecological consequences of lithological discontinuities regarding soil solutions and their micro nutrient content. Otherwise, the laboratory analysis meansa significantly higher workload and related costs.Even though the results to date resulting from a preliminary study,the concentration of some manganese associated trace elements, especially for iron (Fe) and nickel (Ni) in the soil solution can be characterized as depth functionswith a simple contrast in the vertical soil profile at the plot scale. These results do not correspond for copper (Cu) and zinc (Zn). The results at the hillslope scale, combining the sampling plots within a toposequence showing a decreasing translocation trend of manganese concentration from the upper to the foot slope.There is to consider that these findings based on a short time sampling period of 17 month, including a very long and dry summer season in 2013 for the central German low mountain ranges. More and additional research is needed to determine existing trends and to find possible new trends.The importance of manganese binding to soil organic matter offers an essential thematic linkage to the previously missing investigation of the carbon budget in the study area, especially to analyze the DOC budget at the interface of terrestrial and aquatic systems within forest and other land use pattern.

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