Soil Forming Processes as Revealed by Soil Water Chemistry in an Alfisol and in an Inceptisol, Denmark

Lotte Marcussen

Abstract

Soil water chemistry in two soils, developed in loamy and in sandy materials, has been studied to reveal how the different profile developments are reflected in the soil solutions. Weathering conditions and current soil forming processes were identified by examining the chemistry of infiltrating soil water from selected soil horizons within the profiles. Tension lysimeters were used to collect the soil water. The two different soil types were clearly recognized by the degree of mineral dissolution as reflected in the soil solutions. In the sandy soil, iron and aluminium in solution were found deep in the profile indicating an advanced podzolization, which has possibly reached a stage of decline. In the loamy soil these metals were seen in solution only in the uppermost part of the profile. Brunification (brown soil formation) was the most pronounced process revealed by soil solutions, but podzolization in an early stage was also reflected.

Keywords

Soil water chemistry, soil weathering, soil formation.

Lotte Marcussen: Institute of Geography, University of Copenhagen, Øster Voldgade 10,1350 Copenhagen K.

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Soil forming processes are generally explained on the physical and chemical properties of the soil solid phase. Interpretation of soil solutions has been used as another aproach by e.g. Ugolini et al. (1977), Zabowski & Ugolini (1992), Vedy & Bruckert (1982), Driscoll et al. (1985), Litaor (1992) and Pecher (1994). Soil solutions reflect which proton donors are important in the mineral dissolution and which conjugate bases are responsible for the translocation of metals, processes described by e.g. Ugolini & Sletten (1991). Depending on the proton donors, the weathering will be more or less intense. The presence of strong chelating organic acids may lead to congruent dissolution with all elements of the dissolved mineral staying in solution. All elements will be leached, leaving no residues as secondary minerals. If weak acids like carbonic acid are prevailing, incongruent dissolution will dominate and some elements will remain in situ, forming secondary minerals such as iron and aluminium (hydr)oxides.

Certain soil forming processes or stage of profile development can be recognized by more or less distinct variations in soil solution compositions within a soil profile (solution profiles). Models of such variations have been proposed by Ugolini et al. (1987) and Ugolini et al.(1990), in which studies podzolization and brunification (brown soil formation) are related to the type of proton donors present in the soil water within a profile. According to these models, the podzolization process is characterized by a predominance of congruent dissolution in the upper part of the profile, where organic acids are present in solution. Iron and aluminium are mobilized in the A horizons and subsequently precipitated together with organic anions mainly in the B horizons. In the brunification process, incongruent dissolution is prevalent in all horizons. The dissolved organic anions, iron and aluminium from the A horizons are not translocated to the B horizons but are retained in the uppermost part of the profile.

In this paper the solution profiles of an eluviated loamy soil and a podzolized sandy soil are presented, and the soil formation processes as reflected in the soil solutions are related to the models described above.

Study area and soil profiles

The investigations were carried out in a beech and maple forest stand in Frederiksdal Forest, which is located in the

Table 1: Descriptions of soil profiles.

Profile L		
O	3-0	Litter
Ah	0-12	Brownish black (7.5YR 3/2) moist; sandy loam; weak granular; very friable; few stones; abrupt wavy boundary.
AE1*	12-33	Dark brown (10YR 3/4) moist; sandy loam; weak granular; very friable; few stones; abrupt wavy boundary.
AE2*	33-48	Pale yellowish brown (10YR 5/4) moist; sandy loam; weak granular; very friable; few stones; clear smooth boundary.
Btg	48-80	Pale yellowish brown (10YR 5/3) moist; common mottles; sandy clay loam with tongues of sandy loam cutting the horizon; strong coarse angular blocky; firm; few stones; gradual smooth boundary.
Bt	80-119	Brown (10YR 4/4) moist: few mottles around tongues; sandy clay loam; strong coarse angular blocky; firm; few stones; clear smooth boundary.
Ck	119-	Pale yellowish brown (10YR 5/4) wet; sandy loam; moderate very coarse angular blocky; sticky; few stones; calcareous.
Profile S		
O	2-0	Litter
Ah	0-10	Brownish black (10YR 3/2) moist; loamy sand; very weak crumb; very friable; few stones; abrupt wavy boundary.
E	10-18	Greyish yellow black (10YR 5/2) moist; loamy sand; very weak crumb; very friable; few stones; clear wavy boundary.
Bs1	18-23	Pale reddish brown (5YR 4/4) moist; loamy sand; weak crumb; very friable; few stones; clear wavy boundary.
Bs2	23-42	Yellowish brown (10YR 5/8) moist; loamy sand; weak crumb; very friable; few stones; clear wavy boundary.
BC	42-59	Yellowish brown (10YR 5/6) moist; sand; weak crumb; very friable; clear wavy boundary.
C	59-89	Bright yellowish brown (10YR 6/6) moist; sand; weak crumb; friable; abrupt smooth boundary.

* Horizon symbols are based on the textural characteristics (eluviation).

eastern part of Denmark, 15 km north west of Copenhagen (55°47' N, 12° 27' E). The landscape was formed during the Late Weichselian deglaciation. In the study area a small outcrop of loamy till is surrounded by sandy glaciofluvial deposits and the sloping terrain has a gradient of 5 - 10 %. The forest stand covers the till as well as the glaciofluvial deposits in the investigation area, which has not been cleared within the last 250 years at least.

The mean annual precipitation (1961-90) in the region is about 600 mm (DMI 1995) and is evenly distributed throughout the year with a little maximum during the summer and the autumn. Calculated on a monthly basis, the mean precipitation exceeds the mean potential evapotranspiration from September to March. The annual mean temperature is 7.6°C and the mean monthly temperature ranges from 16.0°C in August to -0.7°C in January (1961-90, Roskilde research station)(Jensen & Sørensen 1995).

Two soil profiles were investigated, one developed in the loamy till (Profile L) and the other in the sandy glaciofluvial deposit (Profile S). Soil profiles were described according to FAO (1977), descriptions given in table 1. Profile L is moderately well drained and roots reach about 120 cm into the soil. Profile S is somewhat excessively drained with roots reaching a depth of about 110 cm. Profile L is classified as an Aquic Glossudalf and profile S is classified as a Typic Dystrochrept according to Soil Taxonomy (Soil Survey Staff 1990).

Materials and methods

In both soil profiles, tension lysimeters were installed from the profile wall in the lower boundary of selected horizons. Suction cups were placed in the Ah, AE1, AE2 and Btg horizons of the loamy soil profile and in the Ah, E, Bs2 and C horizons of the sandy soil profile. The results from one set of suction cups (one per horizon) are presented in this paper. The cylindrical lysimeter cups were made of teflon, the tubes of polyethylene and the collection bottles of glass. Before installation, the lysimeter cups were rinsed with hydrocloric acid followed by deionized water.

Using an automatic pump, the soil water was sampled continuously and by a nearly constant vacuum throughout the sampling period. A vacuum of 0.10 bar was applied in the sand profile in order to collect infiltrating water. In the loamy profile the vacuum was maintained at 0.20 bar to obtain sufficient sample volumes within the sampling period, and still having a sample presumably representing the infiltrating water. The sampling lasted about 5 weeks (one sampling) and was carried out in February/March, when the soils had a water content near field capacity.

Throughfall was collected in two bulk samplers placed 1.5 m above ground in the immediate vicinity of each profile site. The samplers consisted of a funnel connected to a bottle made of polyethylene. The funnel was covered with a nylon net. The sampling took place in February during a period of 3 weeks.

pH and alkalinity were measured in unfiltered soil solutions. pH was determined potentiometrically with a combination electrode (Metrohm, 6.0233.100). From the given pH values in the solutions, it was assumed that only bicarbonate contributed to the alkalinity. Alkalinity was determined in 50 ml sample volume by titrating with HCl to an endpoint of pH ~ 4.5. The excact value was calculated on the basis of the approximate total alkalinity and the initial pH value (Dansk Standard 1977). Immediately after these analyses, the sample was filtered through a 0.45 μm filter (Satorius, Minisart NML), and two subsamples were preserved with HNO_3 and CH_3OH respectively. The first subsample was analysed for Ca, Mg, Fe and Al by atomic absorption spectrophotometry and Na and K by flame emission photometry (Perkin Elmer, model 3110). The second subsample was analysed for Cl, NO_3 and SO_4 by ion chromatography (Metrohm Ion Chromatograph, model 690) with a SUPER SEP column (6.1009.000) and an eluent of phtalic acid. The negative deficit in the charge balance of the measured ions was assumed to represent organic anions.

Fine earth (< 2 mm) was used in the following analyses. The texture was determined by sieving and by the Andreasen pipette method. Organic matter was calculated from the content of organic carbon, determined by combustion and IR-measurement in a LECO apparatus, model CR12. The organic carbon was assumed to make up 58 % of the organic matter. pH was determined potentiometrically in a 1:2.5 soil/water extraction. Fe and Al were extracted by sodium phyrophosphate (pp), acid ammonium oxalate (ao) and dithionite citrate (dc) and measured by atomic absorption spectrophotometry (Analytical Methods Manual 1984).

The amounts of dissolved Fe and Al in the ao extraction depends on the extraction time. According to thermodynamics, most soil iron oxides should be dissolved by oxalate, but because of the slow dissolution rate of well crystallized iron oxides, oxalate can be used in fractionation of iron oxides, taking the extraction time into account (Borggaard 1990). Besides, dc dissolves only finely divided hematite and goethite, while sand - sized grains of these minerals are attacked only slightly (Analytical Methods Manual 1984). These uncertainties concerning the determination of Fe and Al fractions may explain when values of ao - extracted Fe and Al exceed the amounts of Fe and Al extracted by dc.

Results and discussion

Profile L has a texture distribution caused by eluviation (Table 1 & 2). Bleached tongues of sandy loam have formed in the illuvial B horizons of sandy clay loam marking an advanced stage of development. Profile S consists of a more homogeneous material of mainly loamy sand. Alternating flow conditions during the sedimentation have resulted in a slightly varied texture within the parent material.

Both soils have a high content of organic matter in the Ah horizons and together with the presence of a litter layer it indicates a low decomposition rate. From the low pH, the biological activity is expected to be limited, and both soils may be characterized by having a little diversified microflora with fungi being important in the decomposition of organic material.

The amount of secondary iron and aluminium compounds in the loamy soil is somewhat larger than in the sandy soil (Table 2). Organically bound aluminium makes all the secondary aluminium compounds while iron is found as both organically bounded iron and amorphous and crystalline iron oxides. In profile L iron reaches maximum values in the AE1 horizon and in the B horizons with organically bound iron dominating in the AE1 horizon. In this horizon iron probably originates mainly from leaching, as suggested by the ratios of iron oxides and clay content (Table 2). Except for the AE1 horizon, the calculated ratios are less mutual divergent than the variations of iron oxides within the profile. These ratios also indicate that the maximum of iron oxides in the lower horizons comes from mechanical transport of colloids and that translocation of iron on soluble form is less important in this part of the profile.

Podzolization in the upper part of the profile has caused the specific distribution of iron and aluminium with local maxima in the AE1 and AE2 horizon respectively. Such

Table 2: Analyses of the two soil profiles.

Profile/ Horizon	Texture 0-2 (µm)	2-50	50-125	125-500	500-2000	Bulk density (g/cm³)	OM (%)	pH	Fe 1) dc (%)	ao	pp	Al 1) dc (%)	ao	pp	Fe_{oxid} 2)	Fe_{oxid}/clay
L Ah	10	31	17	34	8	1.06	7.4	4.4	0.26	0.26	0.21	0.06	0.06	0.06	0.05	0.005
AE1	8	27	20	37	8	1.14	2.5	4.4	0.41	0.52	0.29	0.10	0.12	0.12	0.12	0.015
AE2	10	27	20	35	8	1.47	1.0	4.6	0.28	0.28	0.18	0.14	0.17	0.19	0.10	0.010
Btg	22	26	15	31	6	1.65	0.3	4.9	0.50	0.30	0.15	0.09	0.11	0.14	0.35	0.016
Bt	24	20	16	34	6	1.71	0.4	5.3	0.57	0.29	0.12	0.07	0.09	0.09	0.45	0.019
Ck	18	20	16	38	8	1.78	0.0	8.4	0.31	0.05	0.01	0.03	0.03	0.02	0.30	0.017
S Ah	5	11	15	62	7	0.86	9.9	4.2	0.10	0.07	0.07	0.04	0.04	0.04	0.03	0.006
E	3	12	18	60	7	1.17	2.0	4.1	0.10	0.05	0.05	0.02	0.03	0.02	0.05	0.017
Bs1	4	10	15	64	7	-	2.3	4.2	0.44	0.59	0.35	0.09	0.09	0.10	0.09	0.023
Bs2	5	11	15	62	7	1.39	1.8	4.2	0.43	0.53	0.32	0.09	0.09	0.10	0.11	0.022
Bs2/BC	-	-	-	-	-	-	-	-	0.27	0.31	0.19	0.14	0.16	0.16	0.08	-
BC	3	6	8	73	10	-	0.7	4.6	0.11	0.08	0.06	0.11	0.15	0.11	0.05	0.017
C	2	5	9	70	14	1.44	0.3	4.6	0.09	0.04	0.03	0.07	0.11	0.07	0.06	0.030

1) dc: dithionite citrate, ao: ammonium oxalate, pp: pyrophosphate
2) Fe(dc) - Fe(pp).

displacements have been found at other locations in podzols developed beneath deciduous forest (Madsen 1984).

In profile S podzolization has also resulted in a displacement of iron and aluminium maxima. High amounts of iron are found in the Bs1 and Bs2 horizons while the highest aluminium content is seen in the boundary of the Bs2 and BC horizons and in the BC horizon. Organically bound iron makes a relatively large proportion of the secondary iron compounds, and aluminium is found almost exclusively as organic aluminium compounds.

Soil solution composition and dissolution processes

The soil solutions of the profiles are dominated by organic anions, iron and aluminium in the upper horizons. In the lower parts of the profiles, the concentration of these elements is reduced and bicarbonate (alkalinity) appears (Figure 1).

In profile L, the simultaneous decrease of organic anions, iron and aluminium and final disappearence under the Btg horizon suggest that organometal complexes are involved in the translocation of metals (Figure 2).

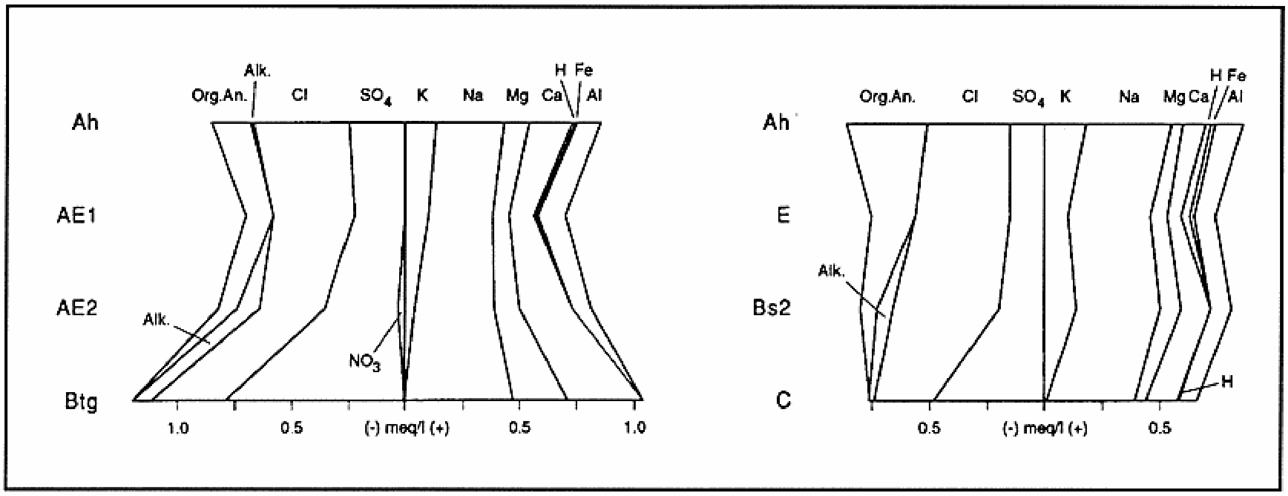

Figure 1: Soil solution compositions in profile L (left) and profile S (right).

Investigations of soil solutions have shown that such complexes can be of major importance in dissolving iron and aluminium in upper horizons, see e.g. Vedy & Bruckert (1982), Driscoll et al. (1985), Mulder & Breemen (1987) and Berggren (1990). Dahlgren & Ugolini (1989) have found that organically complexed aluminium can make up 73-100 % of aluminium in solution in the infiltrating soil water from Oa, E and Bhs horizons. Studies of gravitational water from the A1 horizon of a podzol have shown that 54% of the aluminium content and 73% of the iron content were in the form of stable complexes, including organometal complexes (Vedy & Bruckert 1982).

Iron was almost exclusively found in the A horizons. It was mobilized in the Ah horizon and subsequently retained in the AE1 and AE2 horizons in agreement with the maximum of secondary iron compounds in the AE1 horizon. Precipitation of some released iron may still take place in the Ah horizon, which has a high content of organically bound iron in the solid phase. The insignificant translocation of soluble iron from the AE2 horizon underlines that the pronounced enrichment with secondary iron compounds in the B horizons originates from particle migration.

The presence of secondary iron compounds in all horizons indicates that incongruent dissolution is prevailing throughout the profile. However, the translocation of dissolved iron together with the maximum of organically bound iron and the local maximum of iron oxides in the AE1 horizon show that congruent dissolution has become important in the weathering processes in the uppermost part of the profile.

Further, the mobilization of aluminium in both the Ah and AE1 horizon indicates a more complete mineral dissolution in the upper profile. The attenuation of aluminium and organic anions in the AE2 horizon coincides with a maximum content of aluminium in the solid phase. The remaining aluminium in solution precipitates combined with organic anions in the Btg horizon, below which there is no translocation, and the underlying horizons have a low content of secondary aluminium compounds.

Clayey soils are not necessarily susceptible to podzolization even when they are acid. If the A horizon contains sufficient iron and aluminium, soluble organic compounds will precipitate and hence be immobilized in the A horizon rather than in the B horizon. Of particular importance is aluminium, which is easily available as the dominant adsorbed cation in clayey acid soils (Petersen 1976). Using the organic complex concept in explaining podzolization, retention of dissolved organometal complexes in the A horizons of profile L is probably due to a relatively large proportion of iron and aluminium in the clayey soil, leading to a rapid saturation of organic anions with metals and subsequently precipitation.

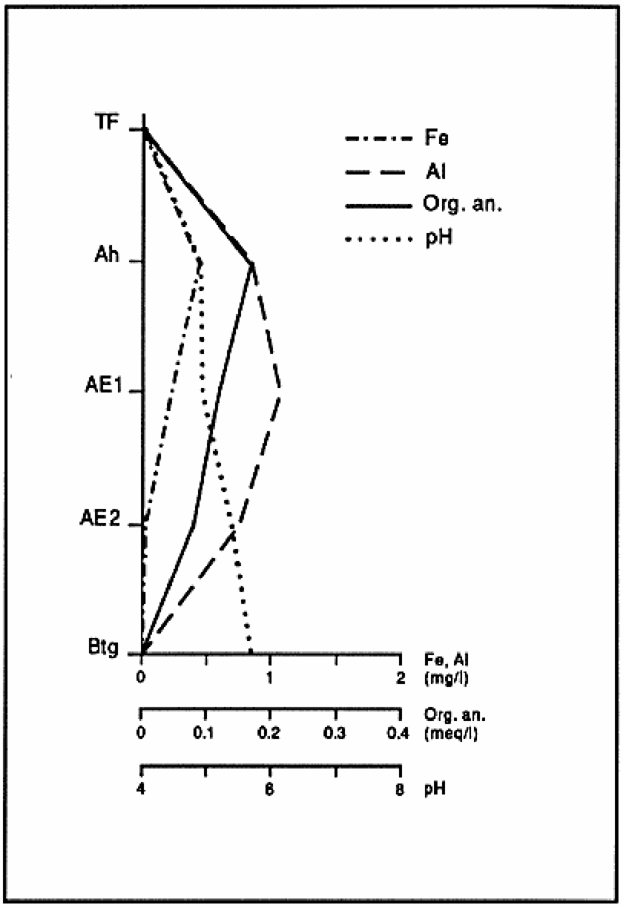

Figure 2: Organic anions, Fe, Al and pH in throughfall (TF) and in soil solutions from profile L.

Nevertheless, the translocation of iron and aluminium in the uppermost part of the profile with differentiation of the A horizons reflects podzolization at an early stage. In time, the upper eluviated part of the profile will likely develop into a podzol.

The reduced content of organic anions, the increasing pH and the appearence of bicarbonate even in the AE2 horizon (Figure 1 & 2) indicate a change of protondonors in favour of weak acids participating in the dissolution processes. The weathering in the Btg horizon and below is governed widely by carbonic acid, which is not able to keep iron and

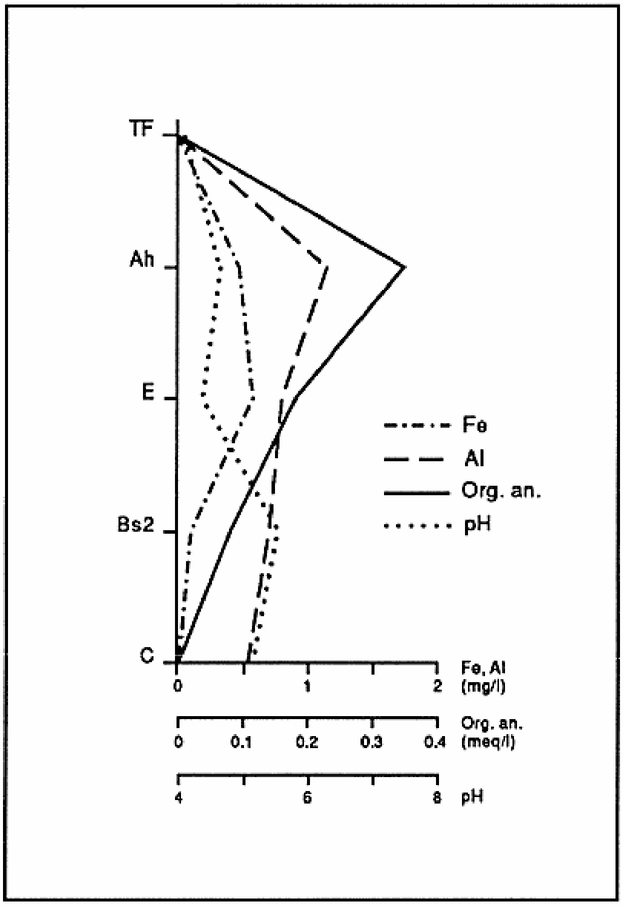

Figure 3: Organic anions, Fe, Al and pH in throughfall (TF) and in soil solutions from profile S.

aluminium in solution. Mono- and divalent cations are leached from the lower horizons while iron and aluminium are absent in the solutions. Weathering in situ leaves a residue of iron and aluminium oxides in the lower part of the profile.

In profile S, dissolved organic anions, iron and aluminium are seen even in the lower part of the profile (Figure 1 & 3). The translocation probably includes organometal complexes as discussed above. Iron is leached to the B horizons, where it is pecipitated as organically bound iron and iron oxides. The mobilization of iron in both A horizons together with the small amounts of secondary iron compounds in these horizons suggest that congruent dissolution is dominating in the A horizons.

Aluminium is mobilized in the Ah horizon and is found in solution through the whole profile. The lack of mobilization in the E horizon may be explained by a minimum content of aluminium in this leached horizon. If congruent dissolution has been dominating in the upper part of the profile during a long time, it has possibly caused a depletion of primary and secondary aluminium bearing minerals. Dissolved aluminium is retained in the B horizons, where enrichment in the solid phase is seen as organically bound aluminium. The major accumulation of secondary aluminium compounds appears in the Bs2/BC and BC horizons reflecting that leaching continues deep in the profile.

Weathering in the B horizons is less intense as indicated by a reduced concentration of organic anions, an increasing amount of bicarbonate and a minor content of iron in the solutions from the Bs2 horizon. Incongruent dissolution probably prevales here, but aluminium, however, is still leached from the C horizon due to a relatively low pH.

Other studies of soil solution profiles have shown the presence of two distinct compartments which are characterized by different dissolution processes, see e.g. Vedy & Bruckert 1982, Ugolini et al. 1982 and Ugolini et al. 1987. In the upper biopedolocical compartment, organic acids play a major role in the weathering processes and leaching of soluble organics and metal cations (iron and aluminium) takes place. Soluble organics and metals are accumulated in the illuvial B horizon which makes the transitional zone to the lower geochemical compartment, in which pH rises and carbonic acid becomes important as a weathering agent. The weathering is less intense and leaching of metals is reduced (Ugolini et al. 1987). Such differentiations are recognized in profile L, in which the AE2 and Btg horizons seperate two distinct compartments. In profile S, the (Bs1 and) Bs2 makes the transitional zone between the two compartments even though the division is less marked than in profile L.

Rates of iron accumulation

The average accumulation rate of iron translocated in a dissolved form has been estimated on the assumption that soil forming processes in the two profiles have operated for 11 000 years. The content of iron oxides (dc - pp, table 2) in the C horizons is taken as a rough estimate of weathering in situ. Subtracted this value, the remaining percent of secondary iron compounds in the horizons mentioned below is counted as coming from translocated dissolved iron. Infiltration is calculated from the difference between mean precipitation and mean potential evaporation (1961-90, Roskilde research station) on a monthly basis, which gives about 190 mm.

The translocated iron in the AE1 horizon of profile L then makes 0.11%. With a horizon depth of 21 cm and a bulk density of 1.14 g/cm^3, the total accumulation of translocated iron corresponds to about 260 g Fe/m^2 AE1 horizon, which yields an average accumulation of 0.02 g Fe/m^2 per year. Comparison of soil solutions entering and leaving the AE1 horizon shows a retention of 0.22 mg Fe/l percolating water (Figure 2). With an annual amount of about 190 mm of infiltrating water, the AE1 horizon will be added 0.04 g Fe/m^2 per year. These very rough calculations suggest that the current translocation of dissolved iron in the upper part of the profile is more pronounced than the previous transport, agreeing with an incipient stage of podzolization.

In profile S, the amount of translocated iron to the Bs1 and the Bs2 horizons has been 0.38% and 0.37% respectively (Table 2). This makes about 1240 g Fe/m^2 in all (assuming that the two horizons have the same bulk density, see table 2), giving an average historical accumulation of translocated iron of 0.11 g Fe/m^2 per year. Today the accumulation is 0.46 mg Fe/l percolating water (Figure 3), making 0.09 g Fe/m^2 per year. The results suggest that the present accumulation of leached iron in the B horizons does not exceed the earlier average rates of accumulation. An intensity maximum has possibly been reached in the podzolization process, which may be explained by a depletion of iron bearing minerals in the A horizons.

Summary and conclusion

Soil solutions from profile L reveal an effective mineral dissolution only in the uppermost part of the profile. The immobilization of organic anions together with dissolved iron and aluminium in the A horizons and the restricted translocation of iron to the B horizons correspond with the patterns described by the brunification model. However, the translocation in the uppermost part of the profile with differentiation of the A horizons reflects podzolization at an early stage. The present pedogenesis as revealed by soil solution compositions lies between the models of brunification and podzolization.

In profile S the presence of organic acids leads to congruent dissolution in all the upper part of the soil from which metalorganic complexes are leached. The soil formation may have reached a stage where redissolution of secondary metal compounds in the A horizons contributes to the content of iron and aluminium in solution. In general, the mobilization of iron and aluminium in the A horizons and subsequently retention in the B horizons place the profile close to the model of podzolization. The current process has possibly decreased compared to the earlier intensity of podzolization.

Substantial changes in soil solutions from given horizons, spatial as well as temporal, have been observed by e.g. Zabowski & Ugolini (1990), Luxmoore et al. (1990), Koch & Matzner (1993) and Johnson (1995). Furthermore, collecting by tension lysimeters may give a heterogeneous sampling as a result of different retention and flow properties of the horizons (Cochran et al. 1970) and may influence the chemical composition of the soil water sample, see e.g. Zabowski & Sletten (1991), Creasey & Dreiss (1988) and Beier et al. (1989). Such factors should be kept in mind when interpretating soil solution profiles. In spite of these uncertainties, the presented solution profiles are in agreement with the distinct variations in secondary iron and aluminium compounds in the two soils. The solution profiles clearly reveal different weathering conditions in upper and lower horizons and reflect the pedogenese in the two soils. In these cases, the soil formation can be described very well by the models of brunification and podzolization.

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