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Composition and reactivity of DOC in forest floor soil solutions in relation to tree species and soil type

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Abstract. Metal coordinating properties of DOC (dissolved organic carbon), and hence its influence on heavy metal release and mineral weathering, depend on the composition and properties of DOC. Tree species produce litter with different chemical composition and degradability, and these differences might influence the composition and reactivity of DOC in soil solutions. Accordingly, analysis of composition and reactivity of DOC in soil solution samples collected by centrifugation from 16 forest soil O horizons from the four tree species beech (*Fagus sylvatica* L.), oak (*Quercus robur* L.), grand fir (*Abies grandis* Lindl.), and Norway spruce (*Picea abies* (L.) Karst.) on two clayey and two sandy soils were carried out. The composition and properties of DOC were determined by capillary zone electrophoresis, acid-base titration, Cu ion titration, total elemental analysis, IR and UV spectroscopy, and metal release assays. Concentrations of DOC ranged from 20 to 163 mM with pH ranging from 4.6 to 7.3. Norway spruce produced the highest DOC concentration, and the lowest pH. Carbon in low-molecular-weight aliphatic carboxylic acids (LACA) accounted for less than 6% of DOC with formic and acetic acids as the most abundant LACAs. The DOC was cation exchanged and proton saturated to obtain comparable forms of DOC. Titratable carboxylic acid and phenolic groups were in the range 51 to 82 and 20 to 64 mmol·mol^{-1} C, respectively, with fewer phenolic groups in grand fir DOC as the only significant difference. Infrared spectra of freeze-dried DOC samples suggest low contents of aromatic C in the DOC especially from grand fir stands. Stability constants, log K of Cu-DOC complexes, determined by Cu ion titration of DOC samples with fitting of the data to a two-site binding model, were in the range 5.63 to 6.21 for the strong binding sites and 3.58 to 4.10 for the weak sites, but with no significant effects of tree species or site. Freeze-dried DOC samples were found to consist of 41 to 45% C, 38 to 49% O, 4.4 to 5.4% H and 1.2 to 2.0% N and C/N ratios in the range 26 to 42. Reactivity of DOC in terms of release rates of Cd, Cu and Fe cations from a soil sample (flow cell experiments) showed no significant differences among DOC samples from different tree species and soil types. Apparently, only minor differences occur in chemical composition and reactivity of equivalent concentrations of DOC in forest floor soil solutions irrespective of origin, i.e. four tree species and two soil types. Soil solution pH and the concentration of

DOC produced by various tree species are the critical parameters when distinguishing among tree species in relation to heavy metal release and mineral weathering.

Introduction

Afforestation of intensively cultivated soils in water catchment areas is initiated in several European countries to protect high quality drinking water. Changing land use from agriculture to forest implies major changes in soil chemical properties as regular liming and fertilization cease, and less biomass is exported from the system. Within a few decades after afforestation nutrient cations are leached from the upper mineral soil layers and often a decrease in pH by 1 or 2 units can be observed (Jug et al. 1999; Strobel et al. 1999; Vejre et al. 1999).

Commercially important tree species used in afforestation in northern temperate regions, include beech (*Fagus sylvatica* L.), oak (*Quercus robur* L.), grand fir (*Abies grandis* Lindl.), and Norway spruce (*Picea abies* (L.) Karst.). Generally, coniferous trees accumulate more C in the O horizons (forest floor) as compared to deciduous trees (Vesterdal & Raulund-Rasmussen 1998), but little is known about the impact of tree species on chemical composition and reactivity of DOC in soil solutions, and the environmental consequences of planting either deciduous or coniferous species in large-scale afforestation programs. Soil solution DOC from O horizons represents the raw DOC in soil, as it has not been fractionated and transformed through sorption and microbial degradation processes in the mineral soil. However, information is scarce on DOC in soil solutions collected from organic soil horizons by centrifugation (Raulund-Rasmussen et al. 1998), whereas numerous investigations have fractionated and characterised fulvic and humic substances extracted from SOM (soil organic matter) (Cronan & Aiken 1985; Herbert & Bertsch 1995; Dai et al. 1996; Gaffney et al. 1996). Aquatic DOC isolated from freshwater environments have been characterised as well, and it appears that aquatic DOC from different sources are similar and allow some unified chemical properties of aquatic humic substances to be incorporated in chemical speciation models such as WHAM (Tipping 1994).

Soil solution DOC comprises a large number of compounds ranging from low-molecular-weight aliphatic carboxylic acids (LACA) to macromolecular fulvic and humic acids (Hue et al. 1986; Pohlman & McColl 1988; Herbert & Bertsch 1995; Strobel et al. 1999). Sub-millimolar concentrations of monocarboxylic acids such as formic, acetic and propionic acids, and the di/trivalent malic, succinic and citric acids are found in soil solutions from

O horizons, but generally the total C in LACA (LACA-C) constitutes less than 10% of DOC (Hees et al. 1996; Strobel et al. 1999). Nevertheless, the chelating di/trivalent LACAs in addition to fulvic acids may play an important role in weathering of soil minerals and release of metal cations through adsorption – desorption reactions at mineral surfaces. In-solution complexation of metal cations, e.g. Al and Fe increases the total concentration in the soil solution, and complexation of DOC to mineral surface cations might enhance and accelerate dissolution and weathering of minerals (Lundström & Öhman 1990; Drever 1994; Kelly et al. 1998; Raulund-Rasmussen et al. 1998; Strobel et al. 2001).

Heavy metal cations in soils respond differently to changes in pH and the presence of organic ligands. Adsorption and desorption of elements like Cd are strongly affected by pH, but not by DOC, while other elements such as Cu are strongly affected by complexation to the organic compounds but less affected by changes in pH (Berggren 1989; Strobel et al. 2001). Consequently, even moderate acidification will increase the solubility of Cd, Ni and Zn and cause increasing concentrations of these heavy metal cations in the soil solution at decreasing pH levels. These elements are mainly present as uncomplexed cations in the soil solution and weak interactions with the soil solid phase enhances leaching in periods with percolating soil water (Berggren 1989; Bergkvist et al. 1989). In contrast, other heavy metal cations such as Cu and Pb form strong complexes with solid and dissolved organic compounds, and they are strongly sorbed onto soil mineral surfaces (Berggren 1989; Bergkvist et al. 1989). Cadmium and Cu are representatives of the two different chemical categories of heavy metals found in forest soils with relative toxicity to organisms decreasing in the order $\mathrm{Cd} > \mathrm{Cu} > \mathrm{Pb} \gg \mathrm{Zn}$ (Tyler et al. 1989).

This work focused on tree species and soil type influence on the chemical composition and reactivity of soil solution DOC from forest floor O horizons. Sixteen soil solution DOCs collected under beech, oak, grand fir and Norway spruce at four sites were characterised by various titrimetric and spectroscopic techniques, and the corresponding reactivity of DOC was determined by measuring release rates of selected metal cations from a soil sample in flow cell experiments. Relationships between chemical properties and reactivity of DOC are discussed with emphasis on effects of tree species on initial release of metal cations.

Materials and methods

Site descriptions

Four Danish sites, two clayey and two sandy soils developed on till from the Weichsel Glaciation, were selected within a tree species trial (Table 1). All sites are level and the soil appeared uniform within each of the four sampling areas. The tree species trial comprising 0.5 ha stands (plots) of various tree species in monoculture was established in 1964 on former farmland (Vesterdal & Raulund-Rasmussen 1998).

Soil solutions

In March 1998, the forest floor O horizon was sampled in stands of beech (*Fagus sylvatica* L.), oak (*Quercus robur* L.), grand fir (*Abies grandis* Lindl.), and Norway spruce (*Picea abies* (L.) Karst.) at the four sites (16 samples). From a total area of 5 to 10 m^2 in each stand, about 25 L of the total O horizon was sampled and kept cold (0–10 °C) in black polyethylene bags until isolation of the soil solution. Approximately 1 L of soil solution was isolated from each of the naturally moist O horizon samples by centrifugation at 4000 g for 30 minutes and passed through a filter paper (S&S 289^3) and a Durapore® membrane filter type 0.45 μm HVLP. The DOC was cation exchanged and proton saturated by passing successively through three cation exchange columns; 2.5 × 50 cm of Dowex 50W-X8 cation exchange resin (mesh 16–40) at a flow rate of 13 $mL \cdot min^{-1}$ (Strobel et al. 2001). The protonated DOC solutions (pH 2–3) were stored at 4 °C to minimise decomposition and precipitation of DOC.

Analyses of DOC

Solution concentrations of DOC were determined with a total organic C analyser (Shimadzu TOC-500). Concentrations of metal cations were determined by ICP–AES (Perkin Elmer Optima 3000XL, AS90) in aliquots of the DOC solutions sampled before and after cation exchange, and the total content of Cd and Cu was determined by graphite furnace AAS (GFAAS) (Perkin Elmer 5100, Zeeman 5100). Inorganic anions and LACAs were determined by capillary zone electrophoresis (Westergaard et al. 1998; Strobel et al. 1999). The absorbances at 465 and 665 nm (E_4/E_6 ratios) were recorded by a Shimadzu UV-1601 spectrophotometer in 20 mM DOC solutions with pH adjusted to 4.0 with NaOH (Chen et al. 1977).

The contents of carboxylic acid and phenolic groups in the proton saturated DOC solutions were determined by titration of 25.0 mL DOC solution

Table 1. Parent material, mean annual temperature and precipitation, and soil classification of the four sites where forest floor O horizon material were collected

Site	UTM coordinates	Parent material	Temperature[1] (°C)	Precipitation[2] (mm)	Soil Taxonomy[3]	World Reference Base[4]	FAO-Unesco[5]
Christianssæde	32UPF52207262	Calcareous clayey till	8.4	614	Fine-loamy, mixed, mesic Mollic Hapludalf	Cutanic Luvisol	Haplic Luvisol
Løvenholm	32VNH94415819	Sandy till	7.7	630	Sandy, mixed, mesic Entic Haplumbrept	Arenic Umbrisol	Umbric Regosol
Stenholtsvang	33UUC34830457	Clayey till	7.7	642	Coarse-loamy, mixed, mesic Oxyaquic Hapludalf	Cutanic Luvisol	Haplic Luvisol
Tisted Nørskov	32VNH62249443	Sandy till	7.2	681	Sandy, mixed, mesic Entic Haplumbrept	Arenic Umbrisol	Umbric Regosol

[1] Laursen et al. (1999); [2] Frich et al. (1997); [3] Soil Survey Staff (1997); [4] ISSS-ISRIC-FAO (1998); [5] FAO-Unesco (1990).

in 10 mM NaCl background electrolyte in two replicates. Aliquots of DOC solution were flushed with argon before and throughout titrations to prevent interferences from CO_2. The titrations were performed with a Metrohm 665 dosimat with 0.02 mL of 0.05 M NaOH added every 30 seconds and pH recorded potentiometrically. The titratable acidity of DOC was calculated using Eqn. (1) (David & Vance 1991; Strobel et al. 2001).

$$A^- = \frac{C_{\mathrm{NaOH}} - [\mathrm{OH}^-] - C_{\mathrm{anions}}}{C_{\mathrm{DOC}}} \tag{1}$$

where A^- denotes the titratable acidity of DOC ($\mathrm{mol \cdot mol^{-1}}$ C), C_{NaOH} ($\mathrm{mol \cdot L^{-1}}$) the total concentration of NaOH added, $[\mathrm{OH}^-]$ ($\mathrm{mol \cdot L^{-1}}$) the hydroxide ion concentration, C_{anions} ($\mathrm{mol \cdot L^{-1}}$) the concentration of inorganic anions in the DOC solution, i.e. Cl^-, NO_3^-, SO_4^{2-} and $H_2PO_4^-$, and C_{DOC} (mol $\mathrm{C \cdot L^{-1}}$) the concentration of DOC in the 25 mL solution titrated. The total number of carboxylic acid groups was calculated as titratable acidity of DOC up to pH 7.0. The content of phenolic groups was calculated as titratable acidity between pH 7.0 and 11.0 (David & Vance 1991; Strobel et al. 2001).

The stability constants of Cu-DOC complexes were determined for each of the 16 DOC samples. Solutions with 2.5 mM DOC, 0.1 M KNO_3 and 0.012 M MES (2-[N-Morpholino]ethanesulphonic acid) buffer adjusted to pH 5.3 were titrated with 10 mM $Cu(NO_3)_2$ at 25 °C. Copper activity was recorded potentiometrically by a Cu ion selective electrode (Radiometer ISE25Cu) and Ag/AgCl reference electrode (Radiometer REF251) that was calibrated by standard solutions with Cu^{2+} in IDA (iminodiacetic acid) at pH 5.3 (Sauvé et al. 1995). Concentrations of Cu^{2+} were derived from activities by means of the Davies equation, and the content of Cu bound to DOC calculated by difference: $[\mathrm{Cu\text{-}DOC}] = [\mathrm{Cu}^{2+}]_{\mathrm{added}} - [\mathrm{Cu}^{2+}]_{\mathrm{measured}}$. Conditional stability constants, K_1 and K_2, and number of binding sites, n_1 and n_2, were calculated by fitting a two-site binding model (Eqn. (2)) to the titration data obtained until Cu^{2+} occupied 10 to 20% of titratable binding sites in DOC.

$$[\mathrm{Cu} - \mathrm{DOC}] = \frac{n_1 \cdot K_1 \cdot [\mathrm{Cu}^{2+}]}{1 + K_1 \cdot [\mathrm{Cu}^{2+}]} + \frac{n_2 \cdot K_2 \cdot [\mathrm{Cu}^{2+}]}{1 + K_2 \cdot [\mathrm{Cu}^{2+}]} \tag{2}$$

Samples of 100 mL of the DOC solutions were freeze-dried for characterization by infrared spectroscopy and total CHN analysis. Fourier Transform Infrared Spectroscopy (FT-IR) spectra were run on KBr pellets containing 1 mg proton saturated DOC using a Perkin Elmer System 2000 FT-IR spectrometer that accumulated 20 scans. The elemental composition (C, H, N) of the freeze-dried DOC samples was determined in duplicates by a Perkin Elmer 2400 CHN Elemental Analyzer.

Table 2. Selected soil properties of the Ap horizon of the intensively cultivated arable soil at Christianssæde that was used for metal ion release experiments

Parameter	Unit	Ap horizon[1]
Clay	%	20 ± 2
Silt	%	14 ± 2
Fine sand	%	40 ± 3
Coarse sand	%	26 ± 3
pH_{H2O}		6.5 ± 0.1
Carbon	$g{\cdot}kg^{-1}$	12.0 ± 0.2
N_{total}	$g{\cdot}kg^{-1}$	0.98 ± 0.05
Cd_{total} [2]	$\mu mol{\cdot}kg^{-1}$	4.9 ± 0.1
Cu_{total} [2]	$\mu mol{\cdot}kg^{-1}$	118 ± 2
Al_{ox}	$mmol{\cdot}kg^{-1}$	120 ± 6
Fe_{ox}	$mmol{\cdot}kg^{-1}$	20 ± 1
Al [3]	$cmol_c{\cdot}kg^{-1}$	0.84 ± 0.04
Ca [3]	$cmol_c{\cdot}kg^{-1}$	11.6 ± 0.6
Mg [3]	$cmol_c{\cdot}kg^{-1}$	0.55 ± 0.03
K [3]	$cmol_c{\cdot}kg^{-1}$	0.15 ± 0.02
Na [3]	$cmol_c{\cdot}kg^{-1}$	0.07 ± 0.01

[1] Average value ± standard deviation.
[2] Aqua regia extraction.
[3] Exchangeable cation.

Statistical analysis of soil solution contents and chemical composition of DOC was performed as two factor analysis (species and site) with SAS proc ANOVA and correlation analysis with SAS proc Corr (SAS 1996).

Release experiments

The Ap horizon from an intensively cultivated soil was used as a test soil for determining the release of Cd, Cu and Fe in the initial period after afforestation (Table 2). The soil is a sandy clay loam from Christianssæde in Lolland (southeastern Denmark) and developed on calcareous clayey till from the Weichsel Glaciation (Strobel et al. 2001). The cultivated soil is adjacent to one of the forested plots used for DOC sampling, and classified as fine-loamy, mixed, mesic Typic Hapludalf (Soil Survey Staff 1997), Haplic Luvisol (FAO-Unesco 1990) and Cutanic Luvisol (ISSS-ISRIC-FAO 1998).

The kinetics of metal cation release from 5.0 g soil was investigated in completely mixed flow cells (Strobel et al. 2001). Influent DOC solution was continuously pumped through the flow cells at a flow rate of 1.7 mL·hr^{-1} applied by a peristaltic pump (Alitea-XV, Stockholm). Effluent was collected in polypropylene vials and four of every five vials contained 0.2 mL of 2.5 M ultra pure HNO_3 to prevent metal cation adsorption to the vials and to preserve the samples until analysis. Every fifth vial was used for determination of pH and DOC, and the acidified vials for metal cation analysis (Strobel et al. 2001).

Influent solutions were prepared by dilution of the proton saturated DOC solution to 5.0 mM DOC and adjusted to pH 4.0 with NaOH. A solution without DOC and pH adjusted to 4.0 with nitric acid was prepared for reference release experiments. The effluent concentrations of Cd and Cu were determined by GFAAS, and concentrations of Al, Ca, Fe, Mg and K were determined by ICP-AES and accumulated release vs. time diagrams plotted. Release rates were derived by linear regression of these curves (SAS 1996; Strobel et al. 2001).

Results

Soil solution

The concentration of DOC in centrifuged soil solutions from the forest floor O horizon under the four tree species shows large variation (Figure 1). In the soil solutions from Norway spruce concentrations ranged from 79 to 163 mm, whereas DOC concentrations under beech, oak and grand fir were found in an even wider range from 20 to 143 mM. The soil solution pH was lower under Norway spruce and in a narrow range from 4.6 to 5.2 as compared to pH from 5.4 to 6.8 under beech. Grand fir and oak produced soil solutions with pH in a wider range from 4.8 to 7.3.

The concentrations of Cd were in the range 5 to 45 nM with the highest concentrations found at low soil solution pH (Table 3). The concentration of Cu was in the range 0.1 to 1.4 μM without any clear correlation with pH, but grand fir solutions were all low in Cu. The concentrations of Al and Fe showed no distinct differences among tree species or sites.

The concentration of $H_2PO_4^-$ was at least twice as high in the soil solutions from Norway spruce as compared to the other tree species at all sites, and SO_4^{2-} concentrations were much higher under coniferous than under deciduous species (Table 4). At the two clayey sites (Christianssæde, Stenholtsvang), the concentrations of NO_3^- were highest under grand fir and Norway spruce, whereas for the two sandy sites there were no clear differences among tree species.

Table 3. Chemical composition of the DOC solutions before and after (bold) cation exchange

Sites	Tree species	Cd	Cu	Al	Ca	Fe	K	Mg	Na	DOC	pH
		nM		μM						mM	
Christianssæde	Norway spruce	45	1081	99	3187	33	1004	753	1740	150	4.55
		–	**42**	**34**	**4.5**	**12.6**	**6.2**	**2.0**	**8.7**	**137**	**2.37**
	Grand fir	18	309	84	1864	18	387	456	702	55	4.78
		–	**15**	**14**	**2.8**	**5.5**	**4.8**	**1.6**	**7.1**	**43**	**2.64**
	Beech	8	306	44	1082	22	305	302	203	20	6.28
		–	**32**	**15**	**2.6**	**9.1**	**4.6**	**2.3**	**6.5**	**17**	**2.76**
	Oak	25	1350	128	3046	40	1092	1346	898	143	4.88
		–	**57**	**48**	**2.7**	**14.9**	**5.9**	**2.8**	**8.0**	**124**	**2.48**
Løvenholm	Norway spruce	30	716	119	4261	36	1846	1069	1315	163	4.99
		–	**34**	**35**	**3.2**	**11.1**	**7.4**	**2.3**	**9.5**	**147**	**2.34**
	Grand fir	10	261	144	2883	12	886	725	1328	54	5.05
		–	**54**	**18**	**2.8**	**2.7**	**6.7**	**1.5**	**9.4**	**45**	**2.35**
	Beech	15	845	117	2968	27	1171	904	556	123	5.35
		–	**26**	**40**	**3.3**	**7.2**	**5.70**	**1.9**	**8.0**	**107**	**2.48**
	Oak	6	135	40	507	11	509	420	626	26	4.78
		–	**26**	**14**	**3.3**	**2.9**	**4.3**	**1.4**	**6.7**	**23**	**2.85**
Stenholtsvang	Norway spruce	25	615	78	2490	26	906	521	896	90	5.07
		–	**48**	**37**	**3.7**	**17.8**	**7.1**	**4.0**	**7.3**	**76**	**2.61**
	Grand fir	5	374	135	3352	16	1132	562	532	70	7.33
		–	**20**	**43**	**3.1**	**5.3**	**4.8**	**2.8**	**6.6**	**52**	**2.76**
	Beech	10	394	48	1399	21	410	605	343	45	6.81
		–	**51**	**37**	**3.6**	**15.5**	**6.8**	**4.6**	**6.4**	**40**	**2.84**
	Oak	17	790	176	1206	77	627	594	352	53	5.70
		–	**53**	**119**	**3.2**	**40.7**	**14.8**	**12.2**	**6.9**	**45**	**2.81**
Tisted Nørskov	Norway spruce	16	335	51	2058	14	551	504	952	79	5.16
		–	**19**	**22**	**2.6**	**6.3**	**5.1**	**1.5**	**7.8**	**64**	**2.54**
	Grand fir	8	219	163	1966	13	772	524	1147	39	6.37
		–	**16**	**28**	**2.8**	**4.6**	**4.8**	**1.7**	**7.0**	**38**	**2.66**
	Beech	14	661	169	3290	38	778	1137	908	96	5.79
		–	**42**	**48**	**3.8**	**9.6**	**5.6**	**2.4**	**7.7**	**89**	**2.56**
	Oak	13	637	54	2745	13	720	949	849	57	6.93
		–	**33**	**17**	**3.0**	**4.2**	**4.7**	**1.9**	**6.9**	**49**	**2.69**
LSD		11	537	89	1829	28	631	541	487	70	1.07

– Below detection limit.

Table 4. Content of aliphatic carboxylic acids and inorganic anions in the DOC solutions collected by centrifugation of forest floor O horizon material

Sites	Tree species	Oxalic	Malonic	Malic	Succinic	Citric	Formic	Acetic	Propionic	Butyric	Valeric	Phosphate	Chloride	Sulphate	Nitrate
		μM										mM			
Christianssæde	Norway spruce	–	5	5	7	5	289	238	–	–	–	0.28	0.70	0.98	0.22
	Grand fir	41	–	2	3	4	98	262	81	–	–	0.08	0.39	0.92	0.23
	Beech	–	–	–	–	–	–	–	–	–	–	0.06	0.15	0.09	0.08
	Oak	–	6	3	–	1	126	869	–	–	–	0.09	0.43	0.03	0.13
Løvenholm	Norway spruce	54	18	33	26	19	415	1267	403	–	–	0.49	0.54	1.56	0.32
	Grand fir	30	7	7	5	–	199	443	31	83	295	0.13	0.49	0.24	0.28
	Beech	1	5	7	4	2	127	1664	326	98	15	0.18	0.39	0.01	0.29
	Oak	–	–	–	–	–	–	–	–	–	–	0.22	0.38	0.61	0.19
Stenholtsvang	Norway spruce	8	7	25	12	19	275	665	249	30	22	0.38	0.42	0.28	0.19
	Grand fir	–	–	–	1	4	–	–	–	–	–	0.02	0.32	–	0.20
	Beech	–	4	4	1	3	67	93	15	–	–	0.15	0.19	0.04	0.07
	Oak	–	–	3	–	3	–	–	–	–	–	0.12	0.30	–	0.08
Tisted Nørskov	Norway spruce	19	11	14	4	6	206	167	70	21	5	0.18	0.49	0.95	0.23
	Grand fir	40	3	9	–	6	124	–	16	–	–	0.06	0.58	0.21	0.27
	Beech	–	–	–	3	–	–	–	–	–	–	0.06	0.40	0.02	0.22
	Oak	–	2	3	3	1	18	–	–	–	–	0.10	0.42	0.09	0.18

Standard deviation for organic and inorganic anions is 10–25%.
– Below detection limit.

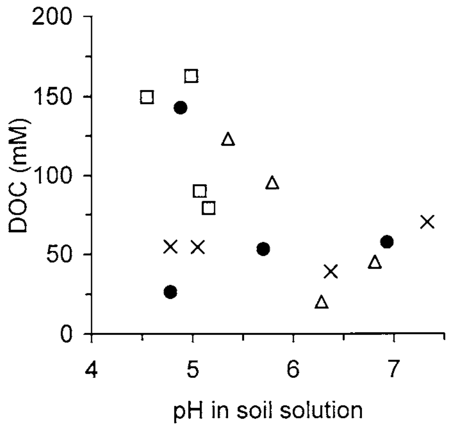

Figure 1. The concentration of DOC versus pH in soil solutions isolated from the forest floor under △ beech, ● oak, × grand fir and □ Norway spruce at four sites in Denmark.

The content of LACA in soil solutions was dominated by acetic, formic, and to some extent propionic acids with concentrations up to 1.7 mM (Table 4). There was a clear tendency towards higher concentrations of monocarboxylic acids at low pH (Figure 2(a)). The concentration of dicarboxylic acids was higher under coniferous as compared to deciduous species, and except for oxalic acid, the concentrations were higher under Norway spruce as compared to grand fir within each site (Table 4). Calculations showed that LACA-C constitutes less than 6% of DOC. The amounts of LACA–C are poorly correlated with DOC in the soil solutions (Figure 2(b)).

Composition of DOC

The absorbance at 465 and 665 nm was determined for the proton saturated DOC solutions, and the resulting E_4/E_6 ratios were in the range 12 to 27 (Table 5). The E_4/E_6 ratio was significantly higher ($p < 0.01$) for Norway spruce at all sites, whereas only minor differences were found for the other tree species. The DOC from Løvenholm and Christianssæde had the highest E_4/E_6 ratios when comparing sites, while DOC from Stenholtsvang had significantly lowest ($p < 0.05$) ratios.

The number of titratable carboxylic acid groups in the DOC solutions were in the range of 51 to 82 mmol·mol^{-1} C for most DOC solutions, but two extreme values of 129 and 142 mmol·mol^{-1} C were observed for grand fir and beech, respectively (Table 5). The contents of phenolic groups were roughly 50% of the carboxylic acid groups and contributed to the total titratable acidity with 20 to 64 mmol·mol^{-1} C. The four grand fir DOC solutions had the lowest contents of phenolic groups in the range 20 to 35 mmol·mol^{-1}

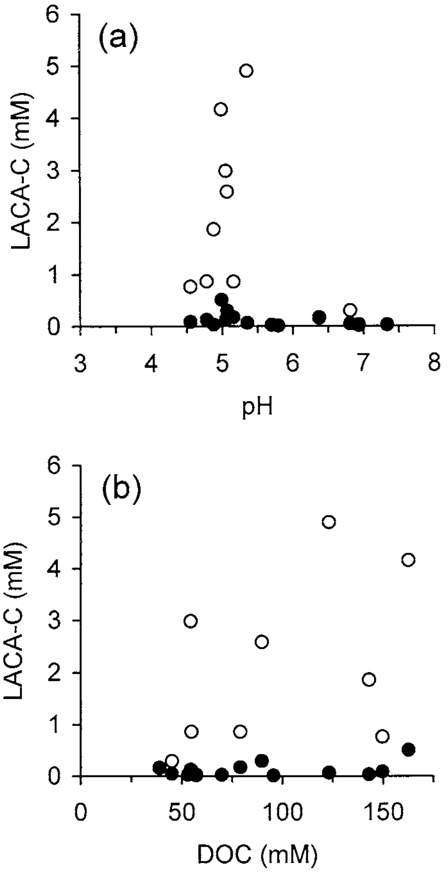

Figure 2. Soil solution LACA-C versus pH (a) and DOC (b) in soil solutions from the forest floor underneath four tree species at four sites in Denmark. Carbon in monocarboxylic acids (○) and di/tricarboxylic acids (●).

C. All other tree species had values above 40 mmol·mol^{-1} C with the exception of the Løvenholm Norway spruce DOC that contained 32 mmol·mol^{-1} C. The elemental composition of DOC revealed only minor variations among tree species, as the freeze-dried DOC consisted of 41 to 45% C, 38 to 49% O, and 4.4 to 5.4% H (Table 5). Accordingly, the C/O and C/H molar ratios were within rather narrow ranges, i.e. 1.12 to 1.46 for C/O ratio and 0.67 to 0.82 for the C/H ratio. The content of N was in the range 1.2 to 2.0%, and the C/N molar ratios were in the range 26 to 42 with only 3 values higher than 35.

Table 5. Elemental composition of the DOC isolated from the forest floor O horizon underneath four tree species at four sites in Denmark

Sites	Tree species	C[1]	O[2]	H[1]	N[1]	C/O	C/H	C/N	E_4/E_6 ratio[3]	COOH[4]	Ar-OH[5]
		Weight %				Molar ratio				mmol·mol^{-1} C	
Christianssæde	Norway spruce	45.2	44.4	4.6	1.5	1.36	0.82	34	22	66	41
	Grand fir	42.3	41.4	5.1	1.3	1.36	0.70	38	19	51	29
	Beech	40.8	48.5	4.4	1.6	1.12	0.77	30	19	142	64
	Oak	44.3	48.8	4.7	1.2	1.21	0.79	42	20	80	48
Løvenholm	Norway spruce	44.8	42.7	4.8	1.8	1.40	0.78	29	27	67	32
	Grand fir	41.3	47.1	4.7	1.8	1.17	0.73	27	21	129	35
	Beech	43.5	48.2	4.8	1.9	1.20	0.75	27	20	83	41
	Oak	41.3	37.7	4.6	1.2	1.46	0.75	39	18	58	48
Stenholtsvang	Norway spruce	44.6	44.4	4.9	1.8	1.34	0.76	30	20	73	42
	Grand fir	43.5	47.9	5.4	1.6	1.21	0.67	32	14	68	21
	Beech	42.9	48.3	4.7	1.5	1.18	0.76	33	16	78	50
	Oak	42.8	48.8	4.8	1.5	1.17	0.74	33	12	74	46
Tisted Nørskov	Norway spruce	43.6	42.5	4.8	1.5	1.37	0.76	35	21	57	45
	Grand fir	42.6	45.1	5.2	1.6	1.26	0.69	32	17	77	30
	Beech	44.0	48.3	4.8	1.6	1.21	0.76	33	17	81	44
	Oak	42.9	47.3	4.8	2.0	1.21	0.74	26	17	78	51
LSD		1.9	5.1	0.3	0.4	0.14	0.03	7	2	42	11

[1] Standard deviation for total element analysis is 1% for C and 5% for H and N.

[2] %O calculated by difference (100 – (%C + %H + %N + %Cl + $\%SO_4$ + $\%NO_3$ + $\%PO_4$)).

[3] Standard deviation is ± 1.

[4] COOH is titratable carboxylic acid groups.

[5] Ar-OH is titratable phenolic groups.

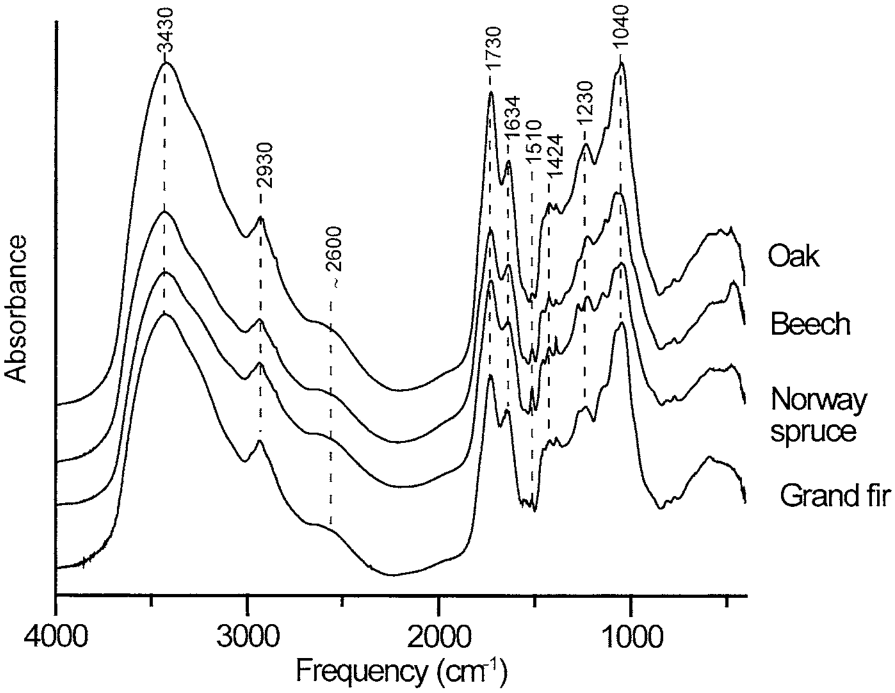

Figure 3. Selected FTIR spectra of the proton saturated and freeze-dried DOC from soil solution under beech, oak, grand fir and Norway spruce at Stenholtsvang.

Infrared spectra of freeze-dried DOC samples

Infrared (IR) spectra were obtained for proton saturated and freeze-dried DOC samples from soil solution under beech, oak, grand fir and Norway spruce. Generally, all the IR spectra were similar with strong absorbances in the regions 3500 to 2500, 1750 to 1600 and 1450 to 1000 cm^{-1} as shown for DOC from Stenholtsvang (Figure 3). A number of pronounced absorption bands at 3430, 2930, 1730, 1634, 1510, 1424, 1230 and 1040 cm^{-1} were observed for all DOC samples with minor differences in the intensity of the absorbance among samples. The absorption band at 1510 cm^{-1} was strongest for Norway spruce and weakest for grand fir at all sites. The absorbance at 1230 cm^{-1} was strongest for oak and beech, whereas the absorbance at 1384 cm^{-1} was clearly stronger for grand fir and Norway spruce at Christianssæde, Løvenholm and Tisted Nørskov.

Table 6. Conditional stability constants (log K) and number of sites (n) for Cu-DOC complexation derived from a two-site model

Sites	Tree species	n_1[1]	n_2	log K_1[2]	log K_2
		mmol·mol^{-1} C		M^{-1}	
Christianssæde	Norway spruce	5.52	58.8	6.05	4.00
	Grand fir	4.92	105.0	5.63	3.60
	Beech	5.44	72.0	5.77	3.87
	Oak	5.68	65.6	5.89	3.92
Løvenholm	Norway spruce	5.84	79.2	6.01	3.83
	Grand fir	3.72	59.2	5.86	3.87
	Beech	4.76	48.4	6.03	4.05
	Oak	5.28	56.0	5.87	3.94
Stenholtsvang	Norway spruce	4.56	57.6	5.97	3.96
	Grand fir	4.88	98.4	5.64	3.58
	Beech	4.00	49.2	5.88	3.96
	Oak	5.80	96.4	5.64	3.66
Tisted Nørskov	Norway spruce	6.12	67.6	5.70	3.74
	Grand fir	4.84	100.0	5.80	3.63
	Beech	4.12	55.6	5.83	3.93
	Oak	4.84	47.6	6.21	4.10

[1] n_1 is the number of strong binding sites and n_2 is the number of weak binding sites in two-site model.

[2] log K_1 is apparent stability constant for strong binding sites and log K_2 is apparent stability constant for weak binding sites in two-site model.

All equation fits had $r^2 > 0.999$.

Stability constants of Cu-DOC complexes

Fitting a two-site binding model to Cu titration data for each of the 16 DOC samples produced conditional stability constants of Cu-DOC complexes. This model estimates a small number of strong binding sites n_1 with conditional stability constant K_1, and approximately 10 times more of the weaker binding sites n_2 with conditional stability constant K_2 as presented in Table 6. All values of K_1 are two orders of magnitude higher than K_2 values, and variations among sites and tree species are small for both stability constants and number of sites estimated. However, K_2 values were significantly ($p < 0.05$) lower for grand fir as compared to beech and oak at the four sites, and though insignificant, K_1 was lowest for grand fir DOC as well. No significant differences in stability constants were found among sites, but the trend was higher values for DOC from the two sandy sites as compared to the two clayey sites.

Release of metal cations in flow cell experiments

The effect of DOC on cation release from an Ap horizon soil sample from Christianssæde was studied by using the 16 DOC solutions in flow cell experiments. Influent solutions with 5.0 mM DOC and pH 4.0 produced effluent solutions with DOC of 3.1 to 4.3 mM and pH in the range 5 to 7 when steady state was established (Table 7).

Approximately 1% of total Cd in the soil was released in experiments running for one week, and the accumulated release of Cd was higher with DOC from oak and Norway spruce compared to beech and grand fir (Figure 4(a)). Approximately 2.5% of total Cu was released in experiments with DOC from Norway spruce and a little less for DOC from the other tree species (Figure 4(b)). All DOC samples released about twice as much Cu as compared to the reference experiment without DOC added.

Release rates were calculated by linear regression (Proc GLM) of the accumulated release versus time data for all experiments (SAS 1996). Data for the first 24 hrs showing faster release than for the subsequent period were omitted in the regression analysis, and the release rates listed are for the period 24 to 150 hours with steady state conditions, i.e. the period where almost no change in pH, concentration of DOC and release rates of cations was observed (Table 7). The release rates of Cd were low and within a narrow range for all DOC samples, and no significant trends in differences among tree species or sites were observed. The release rates of Cu appeared in a wider range with a weak tendency to higher rates in experiments with effluent pH near 7 compared with those with pH near 5. However, the Cu release rates appeared unaffected by the origin of the DOC.

The greatest effect of DOC in this investigation was observed for the release of Fe as virtually no Fe was released in experiments without DOC (Figure 4(c)). Accumulated release of Fe was curvilinear with declining release rate versus time observed for beech and oak, whereas for grand fir the release rate increased slightly after four days.

Correlation analysis of cation release rates

Correlation analysis for metal cation release rates and stability constants for Cu-DOC complexation was performed with Proc Corr in SAS (1996). Copper release rates were significantly correlated ($p < 0.05$) with Cu-DOC stability constants, i.e. positively correlation with log K_1 and negatively correlation with log K_2 (Table 8). Cadmium and Fe release rates were positively correlated, and Fe release rates were negatively correlated with log K_2 similar to Cu.

Table 7. Experimental conditions and release rates for Cd, Cu and Fe in release kinetics experiments

Site	Tree species	$\mathrm{pH}_{\mathrm{eff}}$[1]	$\mathrm{DOC}_{\mathrm{eff}}$[2] mM	Cd rate[3] $\mathrm{amol \cdot g^{-1} \cdot s^{-1}}$	Cu rate[3] $\mathrm{fmol \cdot g^{-1} \cdot s^{-1}}$	Fe rate[3] $\mathrm{fmol \cdot g^{-1} \cdot s^{-1}}$
Christianssæde	Norway spruce	5.5	3.8	25.3 ± 1.4	1.42 ± 0.01	243 ± 13
	Grand fir	6.4	3.1	8.4 ± 14.3	2.71 ± 0.22	187 ± 25
	Beech	–[5]	–	–	–	–
	Oak	5.6	3.5	17.3 ± 3.5	1.70 ± 0.77	62 ± 5
Løvenholm	Norway spruce	6.1	4.2	–	0.69 ± 0.54	180 ± 35
	Grand fir	7.0	3.1	3.2 ± 8.5	1.67 ± 0.39	117 ± 51
	Beech	5.2	4.0	10.0 ± 2.6	1.05 ± 0.16	47 ± 9
	Oak	5.5	3.2	13.2 ± 2.6	1.13 ± 0.13	43 ± 5
Stenholtsvang	Norway spruce	6.2	3.5	4.8 ± 6.4	1.48 ± 0.63	162 ± 11
	Grand fir	6.2	3.4	41.4 ± 3.2	2.25 ± 0.12	349 ± 26
	Beech	5.4	3.7	3.4 ± 1.9	0.85 ± 0.11	45 ± 13
	Oak	5.1	4.3	54.1 ± 4.4	1.98 ± 0.47	268 ± 18
Tisted Nørskov	Norway spruce	5.1	4.3	38.5 ± 1.8	1.09 ± 0.45	243 ± 12
	Grand fir	6.0	4.2	18.2 ± 2.7	0.91 ± 0.19	226 ± 28
	Beech	5.0	4.1	42.7 ± 4.4	1.46 ± 0.43	201 ± 19
	Oak	5.0	3.5	11.4 ± 3.3	0.83 ± 0.13	69 ± 19
Reference[4]	no DOC	6.9	0.2	5.1 ± 1.1	0.75 ± 0.18	4 ± 2

[1] $\mathrm{pH}_{\mathrm{eff}}$ denotes pH in the effluent solution at steady state conditions in the flow cell.

[2] $\mathrm{DOC}_{\mathrm{eff}}$ denotes the DOC concentration in the effluent solution at steady state in the flow cell.

[3] Release rate calculated as slope of accumulated release data ± standard deviation.

[4] Reference experiment without DOC in the influent.

[5] – Denotes data missing.

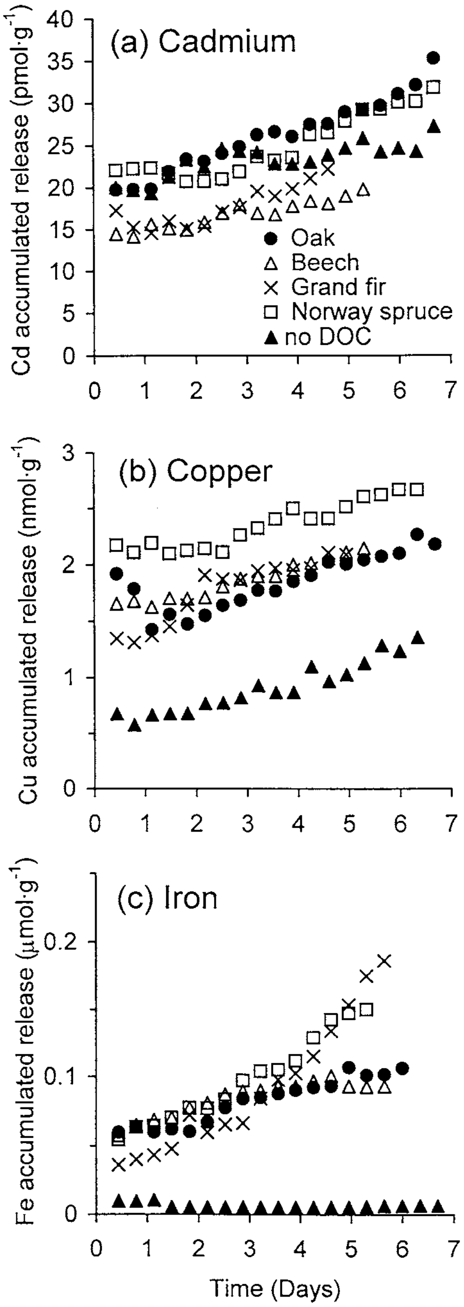

Figure 4. Accumulated release of metal cations from the Ap horizon from Christianssæde in flow cell experiments with DOC from four tree species (average for DOC from four sites). Influent solutions consisted of 5.0 mM DOC with pH 4.0 or a reference solution at the same pH but without DOC added.

Table 8. Correlation matrix with Pearson correlation coefficients and p values (italic) for steady state pH and concentration of DOC, and release rates of metal cations

	pH	DOC	log K_1[1]	log K_2[1]	Cd rate[2]	Cu rate
DOC	–0.524					
	0.037					
log K_1	–0.211	0.019				
	0.434	*0.943*				
log K_2	–0.380	–0.106	0.860			
	0.147	*0.696*	*<0.001*			
Cd rate	–0.433	0.604	–0.507	–0.450		
	0.122	*0.022*	*0.064*	*0.107*		
Cu rate	0.385	–0.444	0.659	–0.563	0.258	
	0.156	*0.097*	*0.008*	*0.029*	*0.372*	
Fe rate	0.129	0.414	–0.457	–0.670	0.731	0.437
	0.635	*0.111*	*0.075*	*0.005*	*0.003*	*0.103*

[1] K_1 and K_2 are apparent stability constants at strong and weak binding sites estimated with a two-site binding model.
[2] Cadmium release rates in flow cell experiments.

Discussion

Soil solution composition

The concentration of DOC in soil solutions from beech, oak, grand fir and Norway spruce was significantly negatively correlated ($p < 0.05$) with pH in the range of 4.5 to 7.3 (Figure 1). Christianssæde and Løvenholm had higher concentrations of DOC than Tisted Nørskov and Stenholtsvang, and pH in soil solutions at Stenholtsvang was significantly higher ($p < 0.05$) than at Christianssæde and Løvenholm (Table 3). Cronan and Aiken (1985) and Ross and Barlett (1996) found highly significant negative correlations between DOC concentration and pH in sandy soils, and the negative correlation seems applicable to several tree species at both sandy and clayey soils. At all sites, Norway spruce produced the highest concentrations of DOC, and Norway spruce caused significantly lower ($p < 0.05$) pH in soil solutions than beech (Table 3).

Christianssæde and Løvenholm have somewhat higher concentrations of Ca, Mg, K, H_2PO_4 and NO_3 in soil solutions (Table 3 & 4), and hence probably increased production of litter and DOC (Vesterdal & Raulund-Rasmussen 1998).

Monocarboxylic acids were the most abundant of identified LACAs found in the soil solutions (Table 4), whereas concentrations of di/tricarboxylic acids were lower for all tree species with concentrations up to about 50 μM as often found in forest soils (Hue et al. 1986; Hees et al. 1996; Strobel et al. 1999). The relatively high concentrations of formic and acetic acids found in O horizon soil solutions are most likely metabolites from microbial decomposition of litter (Küsel & Drake 1999). The LACA-C constituted only a minor fraction of DOC (Figure 2), and the major part of DOC remains unidentified compounds, including the operationally defined fulvic and humic acids (Hees et al. 1996; Strobel et al. 1999). The content of LACA and fraction of LACA-C found in soil solutions varied considerably, but no clear differences among tree species and sites could be determined.

Composition of DOC

The composition of freeze-dried DOC (Table 5) was similar to the hydrophilic acids and fulvic acids isolated from forest floor soil solution by Vance and David (1991) and Kalbitz et al. (1999). With increasing concentration of DOC the relative C content increased with highly significant correlation ($p < 0.001$). The C content was significantly higher ($p < 0.05$) for Norway spruce compared to grand fir. Grand fir had the highest H contents ($p < 0.05$), and the lowest C/H ratios ($p < 0.05$) of all tree species. The slightly lower contents of O in DOC under Norway spruce might indicate lower degree of humification (Stevenson 1994). The content of O was significantly positive correlated ($p < 0.05$) to the number of titratable carboxylic acid groups, but not to titratable phenolic groups.

The C/N ratios (26–42) for soil solution DOC showed no significant differences among tree species or between the clayey and sandy soils (Table 5). The C/N ratios were almost equivalent to C/N ratios calculated for the SOM in a previous investigation (Vesterdal & Raulund-Rasmussen 1998). According to that investigation SOM from grand fir at the two clayey sites had remarkably higher C/N ratios than the other species, whereas a corresponding difference was not observed in C/N ratios of DOC in the present investigation. Differences in SOM in O horizons seem not to have caused differences in C/N ratios in DOC at the four sites investigated, and indicate that litter decomposition in grand fir stands follows reaction pathways similar to those in other stands despite the higher C/N ratios in SOM.

The E_4/E_6 ratios were slightly higher in DOC from Norway spruce at all sites, but the differences were within the variation among sites (Table 5). These E_4/E_6 ratios were two to three times higher than reported for hydrophilic and hydrophobic acids fractionated from forest floor leachates (Vance & David 1991) and water extracts of forest floor litter (Gressel et al. 1995). However, E_4/E_6 ratios of 16 to 18 were obtained for extracted soil fulvic acids by Baes and Bloom (1990) and for aquifer DOC by Christensen et al. (1998). The higher E_4/E_6 ratios in soil solution DOC may indicate structural differences such as less hydroxy- and carboxy-substituted aromatic moieties (Baes & Bloom 1990) and smaller molecular size (Gressel et al. 1995). Infrared spectra for the proton saturated DOC samples were quite similar for the four tree species (Figure 3). The strong absorption around 3430 cm^{-1} is assigned to O-H stretching vibrations in OH groups, especially phenolic and alcoholic groups. The absorption band at 2930 cm^{-1} is ascribed to aliphatic and methyl C-H stretching, and the weak absorbance around 2600 cm^{-1} indicates strong H-bonded OH in undissociated carboxylic acid groups (Candler et al. 1989; Vance & David 1991). The absorption band at 1730 cm^{-1} is due to C = O stretching vibrations in undissociated carboxylic acid groups, and the band at 1634 cm^{-1} is partly due to dissociated carboxylic acid groups (Candler et al. 1989; Gu et al. 1995). The absorption band at 1510 cm^{-1} is assigned to aromatic C = C bonds (Vance & David 1991; Gressel et al. 1995; Gu et al. 1995), and absorption at 1424 cm^{-1} is probably due to O-H bending vibrations in carboxylic acid and alcoholic groups or C-O stretching in phenolic OH groups (Vance & David 1991; Gressel et al. 1995). The absorption at 1230 cm^{-1} is assigned to C-O stretching vibrations and O-H bending deformations in undissociated carboxylic acid groups (Vance & David 1991; Gressel et al. 1995), and the absorption at 1040 cm^{-1} is due to C-O and C-C stretching vibrations in carbohydrates (Candler et al. 1989; Gu et al. 1995). The principal differences in the infrared spectra for the tree species were the higher intensity of the absorption band at 1510 cm^{-1} and hence more aromatic moieties in soil solution DOC under Norway spruce. Grand fir DOC had the lowest absorption intensity at 1510 cm^{-1} at all sites, and in connection with the low number of titratable phenolic groups in DOC found for grand fir (Table 5), this implies that DOC from grand fir stands contained less aromatic moieties and less phenolic groups as compared to beech, oak and Norway spruce. The higher signal at 1230 cm^{-1} for beech and oak indicates more O stretching and bending in carboxylic acid groups, which agreed with slightly higher O contents in DOC from beech and oak. The absorbance band at 1384 cm^{-1} observed for DOC from grand fir and Norway spruce at Christianssæde, Løvenholm and Tisted Nørskov was assigned to NO_3^- (Candler et al. 1989). This is in good agreement with the higher concentrations of NO_3^- found in soil solutions under the two coniferous species as compared to the two deciduous species (Table 4).

Reactivity of DOC

The relative numbers of titratable carboxylic acid and phenolic groups in DOC samples are within the range reported for DOC in soil solutions from deciduous and coniferous trees (Cronan & Aiken 1985; Vance & David 1991; Martin et al. 1998). Titratable acidity of DOC is similar to that of fulvic acids, whereas the larger humic acid molecules contain fewer functional groups (Martin et al. 1998). The relative number of titratable phenolic groups and the estimated K_2 values are significantly ($p < 0.05$) lower in grand fir DOC (Table 6) as compared to the two deciduous species and with intermediate values for Norway spruce. The K_1 values are lowest for grand fir but no correlations were found between stability constants and the number of titratable carboxylic acid groups (Table 5). The values of log K_1 near 6 and log K_2 near 4 (Table 6) for Cu–DOC complexation are in good agreement with corresponding constant for strong and weak binding sites for Cu-fulvic acid complexation (Stevenson 1994).

The effect of DOC on cation releases from the test soil in flow cell experiments is almost the same for all 16 DOC solutions in this investigation, and average values for each tree species are shown in Figure 4. Cadmium and Cu exemplify release reactions of trace elements, and reactivity of DOC in weathering processes is shown by Fe release. Cadmium belongs to a group of elements with strongly decreasing adsorption with decreasing pH, but is not influenced by DOC (Berggren 1989; Strobel et al. 2001). Release rates of Cd vary within one order of magnitude with the median value obtained in the reference experiments without DOC (Table 7). No influence of DOC is observed and as pH is above 5 in all experiments, the low release rates of Cd are in good agreement with previous findings (Strobel et al. 2001). Copper belongs to a group of elements with strong interactions with DOC in the pH range 4 to 7 (Berggren 1989; Bergkvist et al. 1989; Strobel et al. 2001).

Release of Cu increased in all experiments with DOC as compared to experiments without DOC, and releases caused by DOC from Norway spruce are slightly higher than for the other species. The differences in accumulated release are due to faster release in the initial 12 hours whereas in the subsequent period the calculated release rates are almost the same for all DOC, and the average release rates of Cu in experiments with DOC are only slightly higher than in reference experiment without DOC added (Figure 4(b)). In a previous paper (Strobel et al. 2001) it was shown that DOC had no effect on Cu release rates at pH 5, whereas DOC enhanced Cu release rates when pH increased from pH 5 to 7. Therefore, only minor increases in release rates caused by DOC are expected as steady state pH is in the range 5 to 6 in most of the experiments in this work. Release rates of Cu were significantly correlated ($p < 0.05$) to log K_1 and log K_2 (Table 8).

However, the positive correlation for strong binding sites and negative correlation for weak binding sites might indicate that the influence of DOC on Cu release includes several mechanisms, e.g. in-solution complexation of Cu^{2+} and complexation of cations at the mineral surfaces as discussed by Strobel et al. (2001). Apparently, the reactivity of DOC in terms of enhancing trace element release in soil is not dependent on the origin of DOC, and the effect of DOC on metal release is limited to a group of strongly complexing elements such as Cu and Fe(III).

Accordingly, accumulated release of Fe was greatly influenced by DOC, irrespective of its origin, and most of the calculated release rates are 50 to 100 times higher as compared to the reference experiment without DOC (Figure 4(c)). The DOC from coniferous trees seems to increase release rates of Fe more than DOC from deciduous species at pH 5 to 7, but those differences are insignificant due to the considerable variations in release rates within tree species and sites. The release rates of Fe increased more rapidly with DOC than other common cations in soils, as also found in a previous investigation (Raulund-Rasmussen et al. 1998).

Conclusions

The concentration of DOC in soil solutions under four tree species at four sites varied in the range 20 to 163 mM with highest concentrations under Norway spruce at all four sites as compared to beech, oak and grand fir. The content of LACA was dominated by formic, acetic and to some extent propionic acids in concentration up to 1.7 mM, whereas the di/tricarboxylic acids were found in concentrations up to 54 μM. The concentrations of LACAs were highest in soil solutions under Norway spruce for most di/tricarboxylic acids, but oxalic acid was higher under grand fir at two sites. The concentrations of $H_2PO_4^-$ and SO_4^{2-} were much higher under coniferous species at all sites, and at the two clayey sites NO_3^- was higher under coniferous species. The composition and chemical properties of soil solution DOC from Norway spruce seem to contain a little more aromatic moieties and fewer titratable carboxylic acid groups compared to grand fir, beech and oak. Grand fir DOC had significantly fewer titratable phenolic groups. The total elemental composition, the number of titratable carboxylic acid and phenolic groups, and the conditional stability constants for Cu-DOC complexes were in good agreement with values reported for soil solution fulvic acids. Release rates of Cu and Fe from soil in flow cell experiments increased with 5 mM DOC solutions, irrespective of origin of DOC, whereas the release rate of Cd was not affected by DOC. Therefore, the concentration of DOC and pH in soil solutions are major parameters controlling metal cation release in soil.

The concentration of DOC and pH varies between soil solutions, but the composition, chemical properties and reactivity of DOC were not influenced by tree species or soil type.

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References

Baes AU & Bloom PR (1990) Fulvic acid ultraviolet–visible spectra: Influence of solvent and pH. Soil Sci. Soc. Am. J. 54: 1248–1254

Berggren D (1989) Speciation of aluminum, cadmium, copper, and lead in humic soil solutions – a comparison of the ion exchange column procedure and equilibrium dialysis. Intern. J. Environ. Anal. Chem. 35: 1–15

Bergkvist B, Folkeson L & Berggren D (1989) Fluxes of Cu, Zn, Pb, Cd, Cr, and Ni in temperate forest ecosystems. Water Air Soil Pollut. 47: 217–286

Candler R, Zech W & Alt HG (1989) A comparison of water soluble organic substances in acid soils under beech and spruce in NE-Bavaria. Z. Pflanzenernähr. Bodenk. 152: 61–65

Chen Y, Senesi N & Schnitzer M (1977) Information provided on humic substances by E_4/E_6 ratios. Soil Sci. Soc. Am. J. 41: 352–358

Christensen JB, Tipping E, Kinniburgh DG, Grøn C & Christensen TH (1998) Proton binding by groundwater fulvic acids of different age, origins, and structure modeled with the Model V and NICA-Donnan model. Environ. Sci. Technol. 32: 3346–3355

Cronan CS & Aiken GR (1985) Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York. Geochim. Cosmochim. Acta 49: 1697–1705

Dai KH, David MB & Vance GF (1996) Characterization of solid and dissolved organic carbon in a spruce-fir Spodosol. Biogeochemistry 35: 339–365

David MB & Vance GF (1991) Chemical character and origin of organic acids in streams and seepage lakes of Central Maine. Biogeochemistry 12: 17–41

Drever JI (1994) The effect of land plants on weathering rates of silicate minerals. Geochim. Cosmochim. Acta 58: 2325–2332

FAO-Unesco (1990) Soil map of the world. Revised Legend. World Soil Resources Report 60. FAO, Rome, 119 pp

Frich P, Rosenørn S, Madsen H & Jensen JJ (1997) Observed precipitation in Denmark, 1961–1990. Technical report no. 97-8, Danish Meteorological Institute, Copenhagen

Gaffney JS, Marley NA & Clark SB (eds) (1996) Humic and fulvic acids. Isolation, structure, and environmental role. ACS symposium series 651. American Chemical Society, Washington

Gressel N, McGrath AE, McColl JG & Powers RF (1995) Spectroscopy of aqueous extracts of forest litter. I: Suitability of methods. Soil Sci. Soc. Am. J. 59: 1715–1723

Gu B, Schmitt J, Chen Z, Liang L & McCarthy JF (1995) Adsorption and desorption of different organic matter fractions on iron oxide. Geochim. Cosmochim. Acta 59: 219–229

Hees PAW van, Andersson AMT & Lundström US (1996) Separation of organic low molecular weight aluminium complexes in soil solution by liquid chromatography. Chemosphere 33: 1951–1966

Herbert BE & Bertsch PM (1995) Characterization of dissolved and colloidal organic matter in soil solution: A review. In: McFee WW & Kelly JM (eds) (pp 63–88). Carbon Forms and Functions in Forest Soils. Soil Science Society of America, Madison

Hue NV, Craddock GR & Adams F (1986) Effect of organic acids on aluminium toxicity in subsoils. Soil Sci. Soc. Am. J. 50: 28–34

ISSS-ISRIC-FAO (1998) World Reference Base for soil resources. World Soil Resources Report 84. In: Deckers JA, Spaargaren OC, Nachtergaele FO, Oldeman LR & Brinkman R (Eds) International Society of Soil Science (ISSS), International Soil Reference and Information Centre (ISRIC) and Food and Agricultural Organization of the United Nations (FAO), Rome, 88 pp

Jug A, Makeschin F, Rehfuess KE & Hofmann-Schielle C (1999) Short-rotation plantations of balsam poplars, aspen and willows on former arable land in the Federal Republic of Germany. III. Soil ecological effects. For. Ecol. Manage. 121: 85–99

Kalbitz K, Geyer W & Geyer S (1999) Spectroscopic properties of dissolved humic substances – a reflection of land use history in a fen area. Biogeochemistry 47: 219–238

Kelly EF, Chadwick OA & Hilinski TE (1998) The effect of plants on mineral weathering. Biogeochemistry 42: 21–53

Küsel K & Drake HL (1999) Microbial trunover of low molecular weight organic acids during leaf litter decomposition. Soil Biol. Biochem. 31: 107–118

Laursen EV, Thomsen RS & Cappelen J (1999) Observed air temperature, humidity, pressure, cloud cover and weather in Denmark – with climatological standard normals, 1961–1990. Technical report no. 99-5, Danish Meteorological Institute, Copenhagen

Lundström U & Öhman L-O (1990) Dissolution of feldspars in the presence of natural, organic solutes. J. Soil Sci. 41: 359–369

Martin D, Srivastava PC, Ghosh D & Zech W (1998) Characteristics of humic substances in cultivated and natural forest soils of Sikkim. Geoderma 84: 345–362

Pohlman AA & McColl JG (1988) Soluble organics from forest litter and their role in metal dissolution. Soil Sci. Soc. Am. J. 52: 265–271

Raulund-Rasmussen K, Borggaard OK, Hansen HCB & Olsson M (1998) Effect of natural organic soil solutes on weathering rates of soil minerals. Eur. J. Soil Sci. 49: 397–406

Ross DS & Barlett RJ (1996) Field extracted Spodosol solutions and soils: Aluminium, organic carbon and pH interrelationships. Soil Sci. Soc. Am. J. 60: 589–595

SAS (1996) SAS (r) Proprietary Software Release 6.12 TS050, SAS Institute, Cary

Sauvé S, McBride MB & Hendershot WH (1995) Ion-selective electrode measurements of copper(II) activity in contaminated soils. Arch. Environ. Contam. Toxicol. 29: 373–379

Soil Survey Staff (1997) Keys to soil taxonomy. 7th Edition. Pocahontas Press, Blackburg

Stevenson FJ (1994) Humus chemistry: genesis, composition and reactions. Wiley, New York

Strobel BW, Bernhoft I & Borggaard OK (1999) Low-molecular-weight aliphatic carboxylic acids in soil solutions under different vegetations determined by capillary zone electrophoresis. Plant Soil 212: 115–121

Strobel BW, Hansen HCB, Borggaard OK, Andersen MK & Raulund-Rasmussen K (2001) Cadmium and copper release kinetics in relation to afforestation of cultivated soils. Geochim. Cosmochim. Acta 65: 1233–1242

Tipping E (1994) WHAM – a chemical equilibrium model and computer code for waters, sediments, and soils incorporating a discrete site/electrostatic model of ion-binding by humic substances. Computers Geosci. 20: 973–1023

Tyler G, Påhlssson AMB, Bengtsson G, Bååth E & Tranvik L (1989) Heavy-metal ecology of terrestrial plants, microorganisms and invertebrates. Water Air Soil Pollut. 47: 189–215

Vance GF & David MB (1991) Chemical characteristics and acidity of soluble organic substances from a northern hardwood forest floor, central Maine, USA. Geochim. Cosmochim. Acta 55: 3611–3625

Vejre H, Madsen M, Marott T, Olsen T & Zlateva T (1999) Evaluation of soil acidification vulnerability in afforestation areas. In: Landscape Ecology, The Science and the Action, 5th World Congress IALE, pp 155–156

Vesterdal L & Raulund-Rasmussen K (1998) Forest floor chemistry under seven tree species along a soil fertility gradient. Can. J. For. Res. 28: 1636–1647

Westergaard B, Hansen HCB & Borggaard OK (1998) Determination of anions in soil solutions by capillary zone electrophoresis. Analyst 123: 721–724