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Linking variability in soil solution dissolved organic carbon to climate, soil type, and vegetation type

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Key Points:

- Soil DOC concentration is higher under coniferous forests than under broadleaves
- N, Fe and Al are important factors for DOC concentration variability in forests

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Abstract Lateral transport of carbon plays an important role in linking the carbon cycles of terrestrial and aquatic ecosystems. There is, however, a lack of information on the factors controlling one of the main C sources of this lateral flux, i.e., the concentration of dissolved organic carbon (DOC) in soil solution across large spatial scales and under different soil, vegetation, and climate conditions. We compiled a database on DOC in soil solution down to 80 cm and analyzed it with the aim, first, to quantify the differences in DOC concentrations among terrestrial ecosystems, climate zones, soil, and vegetation types at global scale and second, to identify potential determinants of the site-to-site variability of DOC concentration in soil solution across European broadleaved and coniferous forests. We found that DOC concentrations were 75% lower in mineral than in organic soil, and temperate sites showed higher DOC concentrations than boreal and tropical sites. The majority of the variation ($R^2 = 0.67–0.99$) in DOC concentrations in mineral European forest soils correlates with NH_4^+, C/N, Al, and Fe as the most important predictors. Overall, our results show that the magnitude (23% lower in broadleaved than in coniferous forests) and the controlling factors of DOC in soil solution differ between forest types, with site productivity being more important in broadleaved forests and water balance in coniferous stands.

1. Introduction

Lateral transport of carbon is an important process linking terrestrial and aquatic ecosystems. The global transport of carbon from rivers to the ocean is about 0.8 Pg C yr^{-1} [*Regnier et al.*, 2013], of which approximately 20% is riverine dissolved organic carbon (DOC) flux into coastal oceans [*Dai et al.*, 2012]. While losses and transformations of DOC in inland waters, that is, outgassing as CO_2 and CH_4 emissions or burial in sediments, are well reported [*Battin et al.*, 2009; *Ciais et al.*, 2008; *Cole et al.*, 2007; *Nilsson et al.*, 2008], little is known about DOC transformations in soil solution across different ecosystems. Such information is, however, essential to understand processes controlling DOC leaching from soils in order to link terrestrial DOC fluxes to those in aquifers and rivers [*Kindler et al.*, 2011].

The amount of DOC in soil solution is the balance of *inputs* and *outputs* of organic carbon to the soil water. DOC inputs to soil solution originate from biological decomposition, throughfall or litter leaching, root exudates [*Bolan et al.*, 2011], and from deposition of soot and dust [*Schulze et al.*, 2011]. The DOC outputs from soil solution are due to further mineralization and gaseous loss to the atmosphere, and to leaching into river headwaters [*Bolan et al.*, 2011; *Kalbitz et al.*, 2000]. However, DOC may also interact with the soil matrix and can be adsorbed or desorbed depending on the soil conditions: Fe, Al, and clay content, total organic carbon, cation exchange capacity (CEC), and pH [*Kaiser et al.*, 1996; *Kothawala et al.*, 2009]. These factors governing DOC removal from soils can be allocated to three groups: biological control over the net DOC production and decomposition, edaphic control over the net DOC sorption, and hydrological control over drainage and lateral export from the ecosystem.

The relative importance of these three groups of processes varies across sites. There is evidence that soil DOC concentrations are influenced by vegetation type. Larger DOC concentrations in coniferous than in broadleaved stands have been reported [*Currie et al*., 1996; *Fröberg et al*., 2011]. This difference is particularly pronounced in the forest floor organic layers, due to variations in humus type and organic matter composition among forest types [*Borken et al*., 2011]. Tree species may also affect the size and quality of soil DOC [*Lu et al*., 2012]. On the other hand, DOC export from peatland and forest soils has been shown to be dominated by extreme rainfall events [*Dinsmore et al*., 2013; *Xu et al*., 2012], which are expected to become larger and more frequent globally [*Intergovernmental Panel on Climate Change* (*IPCC*), 2012].

A growing number of studies focus on the controlling factors of variability in soil DOC concentrations at local, regional, or national scale [*Borken et al*., 2011; *Buckingham et al*., 2008b; *van den Berg et al*., 2012], but much less information is available on effects of vegetation type, climate, and soil properties on DOC variability at larger, continental to global scale. Two studies that address the larger-scale variation in DOC include *Michalzik et al*. [2001], who presented a review on controls of DOC fluxes and concentrations across 42 temperate forests, and *Kindler et al*. [2011], who investigated variability in DOC concentration and fluxes across 12 European sites of different land use type. Both studies concluded that leaching of DOC from subsoils is controlled by retention in B horizons of the mineral soils [*Kindler et al*., 2011; *Michalzik et al*., 2001]. However, while *Kindler et al*. [2011] found a close correlation between soil C/N ratio and DOC leaching from mineral topsoils, *Michalzik et al*. [2001] found no correlations between DOC leaching from litter layers and C/N. Hence, given the importance of DOC fluxes in the global carbon cycle, it is essential to analyze controlling factors of DOC concentrations and fluxes at larger scales with more complete data sets that cover different soil and vegetation types and various climate conditions.

To this aim we gathered data from the literature and from existing ecosystem monitoring networks (with a focus on European data) and compiled a database of DOC concentrations in soil solution and some key ancillary information. The database was analyzed to (1) quantify the differences in soil solution DOC among near-natural terrestrial ecosystems, climate zones, soils, and vegetation types at the global scale and (2) identify potential determinants of the site-to-site variability of DOC concentration in soil solution across European forests, differentiating between coniferous and broadleaved forests.

2. Material and Methods

2.1. Database Description

2.1.1. DOC Concentrations in the Soil Solution

A database was designed to compile measurements of DOC concentrations in soil solution in different ecosystems around the world. The data were collected by means of two different approaches: (1) for published literature, figures were scanned using the free software Engauge Digitizer 4.1, tables were copied, or the first author of the study was contacted to share the original data; and (2) we contacted the leaders of comprehensive networks such as the International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests) (http://icp-forests.net/) and the UK Environmental Change Network (ECN) (http://www.ecn.ac.uk/).

In total, there were 281 Level II plots from ICP Forests with available data on DOC in soil solution from the litter layer down to 80 cm deep, distributed over 20 different countries and ranging from Italy to Northern Finland. In addition to soil solution chemistry, also throughfall, litterfall, atmospheric deposition, and ground vegetation data are collected on a regular basis. The ICP Forests soil solution samples used for this analysis were collected between 1995 and 2008, with the majority sampled fortnightly. Soil solution was collected at different depths starting at 0 cm, defined as the interface between the organic layer and underlying mineral soil. Normally, lysimeters were installed at (at least) three depths: 0–20 cm, 20–40 cm, and 40–80 cm [*Nieminen*, 2011]. Full details of the ICP Forests sampling protocols can be found at http://icp-forests.net/page/icp-forests-manual.

These ICP Forests network data were complemented with observations from 75 independent sites taken from the literature and nine terrestrial sites (three grasslands, one forest, and five peatlands) from ECN. For the latter, data on soil solution, soil properties, vegetation, and meteorology were collected and analyzed by the network members.

Table 1. Overview of the Data Contained in the Database

Data Source	# of Sites	# of Depths Per Site				Sites Per Ecosystem Type		
							Nonforest	
		1	2	3	>3	Forest	Organic	Mineral
ICP Forests[a] data set	281	66	61	68	86	281	0	0
ECN network[b]	9	-	9	-	-	1	2	6
Literature, site PIs[c], and researchers	75	26	22	20	7	29	27	20

[a] International Cooperative Programme on Assessment and Monitoring of Air Pollution Effects on Forests.
[b] UK Environmental Change Network.
[c] PI: principal investigator.

Soil solution in ECN terrestrial sites was collected fortnightly by using samplers in the A horizon and B horizon. Details of the ECN protocols can be found at http://www.ecn.ac.uk/measurements/terrestrial.

The final database thus contained information from 365 sites (311 of which are forests and 80% are located in Europe; Tables 1 and S1 and Figure S1 in the supporting information), with all soil solution DOC observations measured between 1988 and 2012. All the soil solutions were sampled in situ by using lysimeters or piezometers. Lysimeters are typically used in unsaturated soils, while piezometers are used where superficial water tables are present, for instance, in peatland soils. In most sites with unsaturated soils, zero-tension lysimeters are installed under the O horizon and tension lysimeters installed at depth in the mineral soil are used in combination [*Kolka et al*., 2008]. Although comparative studies have shown larger DOC concentrations measured by zero-tension than by tension lysimeters [*Buckingham et al*., 2008a], when doing a cross-site comparison, no systematic differences between these techniques were found, because the effect of lysimeter type seems to be site specific [*Nieminen et al*., 2013]. For more information regarding the uncertainties in data collection see Appendix S1.

2.1.2. Ancillary Data

Additional site information on soil properties, vegetation, climate, annual water balance, and other soil solution parameters were also stored in the database.

2.1.2.1. Soil Properties

Soil properties, such as texture, bulk density, pH, total organic carbon and nitrogen content, C/N ratio, exchangeable and extractable elements (such as Fe, Al, or Mg), CEC, and base saturation, as well as information on soil type according to the World Reference Base for Soil Resources classification, were added to the database whenever available. A detailed list of variables, with descriptions and units can be found in Table S2. In the ICP Forests program this set of soil parameters was measured separately for the surface organic layer and for different depths in the mineral soil. A distinction was made between water-saturated (H) and unsaturated (O) organic layers, according to the Food and Agriculture Organization definition [*Cools and de Vos*, 2010]. The mineral layer was sampled at fixed depth layers (0–10 cm, 10–20 cm, 20–40 cm, and 40–80 cm). The ICP data network soil layer stratification was applied to all sites to harmonize the data set. For aggregation of sites according to their acidity, soils were classified using pH ($CaCl_2$) as “very acid” (<4.2), “intermediate” (4.2–5), “well buffered” (5–6.2), and “basic” (>6.2). In addition to DOC concentrations, other soil solution chemical parameters, such as ammonium (NH_4^+), nitrate (NO_3^-), total dissolved iron (Fe), aluminum (Al), and sulphate (SO_4^{2-}) concentrations, were often available.

2.1.2.2. Vegetation-Related Variables

A first classification of the data was made based on forest and nonforest ecosystems. In the nonforest sites, we further distinguished between mineral and organic soils, with the latter being mainly peatland sites. Within the forests, only one site was on organic soil; thus, no grouping into forests with mineral and organic soils was possible. Instead, this single site with forest on organic soils was excluded in order to prevent it biasing the analyses. We split forests into two forest types, i.e., coniferous and broadleaved (evergreen and deciduous) forests. Based on the dominant and codominant tree species, a litter decomposability class (1–5 from fast to slow litter decomposition rate) was assigned for the forested sites, according to *den Ouden et al*. [2010]. Monthly normalized difference vegetation index (NDVI) from 1982 to 2010 was extracted from the NDVI3g Global Inventory Modeling and Mapping Studies data set with a 4 km resolution [*Pinzon et al*., 2005]. Moreover, monthly gross primary production and latent heat or evapotranspiration (ET) were extracted from a global data set derived from upscaled eddy covariance data [*Jung et al*., 2011] for the period from January 1990 to December 2008 at 0.5° spatial resolution.

Table 2. Distribution of Sites Across Soil Types, Vegetation Types, and Latitude Zone[a]

	Forest			Nonforest Mineral			Nonforest Organic		
	B	Tem	Tro	B	Tem	Tro	B	Tem	Tro
Acrisol	-	-	-/2	-	-	-	-	-	-
Andosol	-	1/3	-/2	-	1	1	-	-	-
Arenosol	10/1	42/9	-	-	-	-	-	-	-
Cambisol	3/-	28/28	-	-	5	-	-	-	-
Ferralsol	-	-	-/5	-	-	2	-	-	-
Gleysol	-	3/8	-	-	1	-	-	-	-
Histosol	-	1/-	-	-	-	-	-	28	-
Leptosol	2/-	2/1	-	-	1	-	-	-	-
Luvisol	-	11/15	-	-	2	-	-	-	-
Podzol	22/1	58/11	-	1	2	-	-	1	-
Regosol	4/-	8/2	-	-	-	-	-	-	-
Others[b]	-	7/14	1/-	-	1	-	-	-	-
No data	2/-	7/7	1/2	-	9	-	-	-	-

[a] B: boreal; Tem: temperate; Tro: tropical. Double values presented for forests are (# coniferous/# broadleaved).

[b] "Others" category includes the following soil types (number of sites in brackets for each soil type): Albeluvisol (1), Alisol (4), Anthrosol (3), Calcisol (1), Fluvisol (1), Lixisol (1), Planosol (1), Stagnosol (5), Umbrisol (5), and Vertisol (1).

2.1.2.3. Climate and Water Balance Variables

When available, measured mean annual and monthly precipitation, evapotranspiration, drainage, and air temperature were added to the database. Due to inconsistencies and gaps in these measurements, in particular for precipitation and air temperature, monthly precipitation was also extracted for all sites for the period January 1990 to December 2008 from the Global Precipitation Climatology Centre data set at a resolution of 0.5° [*Rudolf et al.*, 2010]. Further, monthly air temperature at a height of 2 m, soil temperature, and volumetric soil water content in three soil layers (0–0.07 m, 0.07–0.28 m, and 0.28–1 m) were extracted from the European Centre for Medium-Range Weather Forecasts (ECMWF) Re-Analysis Interim data set for the period 1990 to 2008. This data set was obtained from the ECMWF Data Server. The resolution of these data was 0.75°. Climate class for each site was determined via the Köppen-Geiger climate classification system [*Kottek et al.*, 2006].

2.2. Preprocessing and Statistical Analysis

The data analysis focused on the potential controlling factors on site-to-site variability of DOC concentrations in soil solution. In order to relate the DOC concentrations with the set of drivers (Table S2), the median DOC concentration per site and per depth interval (organic layer, topsoil (0–20 cm), intermediate layer (20–40 cm), and subsoil (40–80 cm)) was taken to avoid the influence of outliers. First, we used bootstrapping to test for statistical differences among ecosystem types including all sites (Table 2). Histosols are organic soils and behave differently from mineral soils that represent the bulk of the sites in this data set. We therefore excluded Histosols from further comparison among forest types, pH classes, soil types, climate zones, and latitude ranges. Second, we selected a subset of 83 Level II plots from the ICP Forests program based on the availability of all necessary predictor variables and used forward stepwise linear regression analysis [*Hocking*, 1976] to identify the most significant multivariate relationship between DOC concentrations and the predictor variables. Plots included in the 83 Level II sites subset are broadleaved deciduous and coniferous forests in the temperate and boreal zones (marked in bold in Table S1). Models with the highest explained variance (R^2) and the minimum root-mean-square error (RMSE) were selected. Colinearity was checked with the variation inflation factor, and corrected Akaike's information criterion was used to assess overfitting. The data were split into broadleaved and coniferous sites based on results from previous studies [*Fröberg et al.*, 2011; *Lu et al.*, 2012; *Vestgarden et al.*, 2010] that indicate a difference in magnitude of DOC concentrations between vegetation types. For more information regarding the preparation of the data set and the statistical analysis, see Appendix S1.

3. Results

3.1. Variation in DOC Concentration Across Ecosystem Types, Soil Types, and Climate Zones

3.1.1. Effect of Ecosystem Type

DOC concentrations were higher for nonforest sites located on organic soils than for forest and nonforest sites on mineral soils ($P < 0.05$, Figure 1a and Table S3). DOC concentrations substantially decreased with

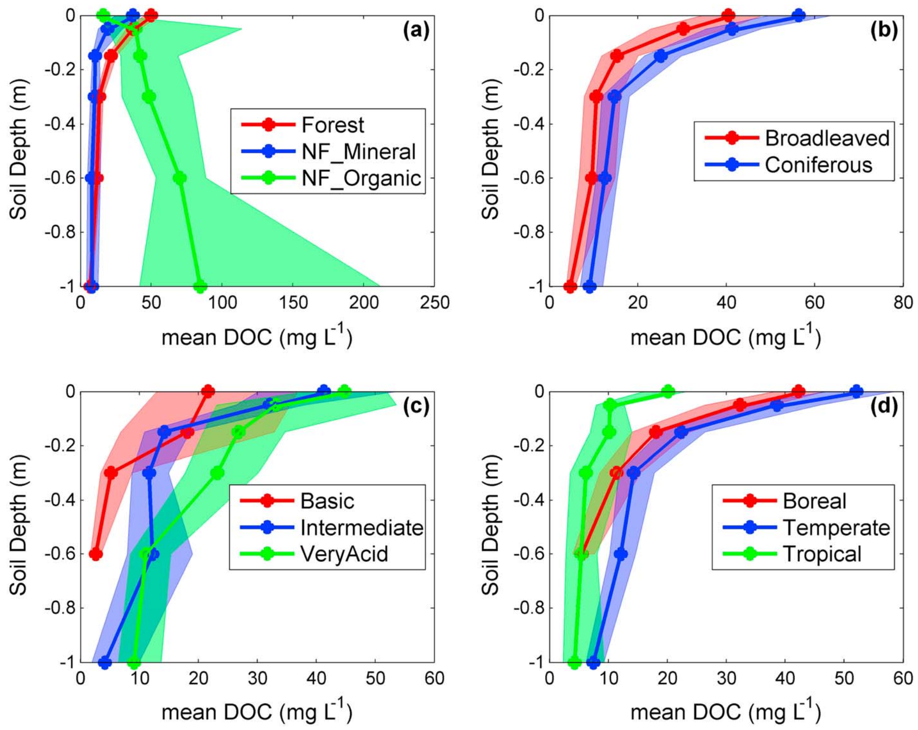

Figure 1. DOC profiles for (a) ecosystem type (NF: nonforest), (b) forest type, (c) pH classes with basic (>6.2), intermediate (5–4.2), and very acid (<4.2), and (d) latitude classification with boreal (>60°), temperate (35°–60°), and tropical (<35°). Solid lines represent the bootstrapped line and shaded areas the bootstrapped 95% confidence interval. Points are placed in the midpoint of the depth interval.

increasing depth in forests (Figure 1b), while in organic soils (mainly peat) the opposite was observed (Figure 1a). Nonforest sites with mineral soils also exhibited decreasing DOC concentrations with increasing depth, albeit with lower DOC concentrations in the surface layer than in forest soils (Figure 1a). On average, broadleaved forests exhibited lower DOC concentrations than coniferous forests (23% lower, broadleaved DOC mean = 13 mg/L, 95% CI = 11–17, *n* = 111; coniferous DOC mean = 17 mg/L, 95% CI = 15–19, *n* = 219, Figure 1b), while the vertical distribution of DOC did not differ between coniferous and broadleaved forests (Figure 1b).

3.1.2. Effect of Soil Type

Among all soil types, Histosols (organic peatland soils) showed the largest DOC concentrations (Figure 2), with significant differences compared to other soil types from the 20 to 40 cm layer downward (Table S3). The lowest DOC concentrations generally occurred in Andosols (volcanic soils) (Figure 2 and Table S3). Podzols, Arenosols, and Regosols showed intermediate DOC concentrations. We further observed that DOC concentrations were generally larger in very acid soils (pH($CaCl_2$) < 4.2) than in more basic soils, especially in the subsoil layers between 20 and 80 cm (Figure 1c).

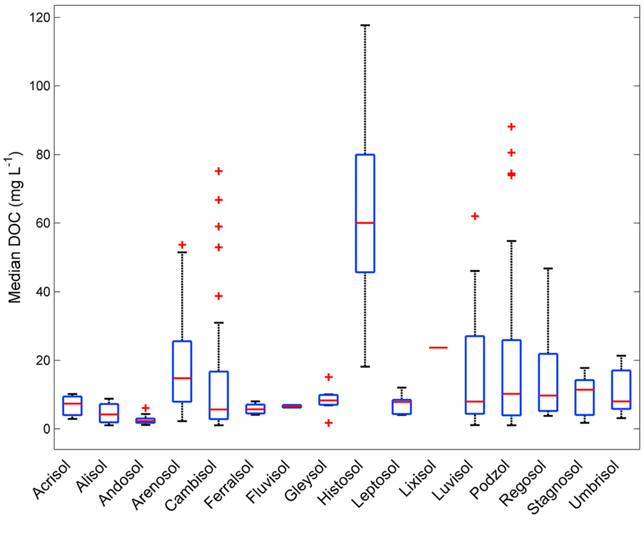

Figure 2. Median, 25th percentile, 75th percentile, and range in DOC concentrations averaged (depth weighted) over the soil profile, by soil type. Outliers are shown as crosses.

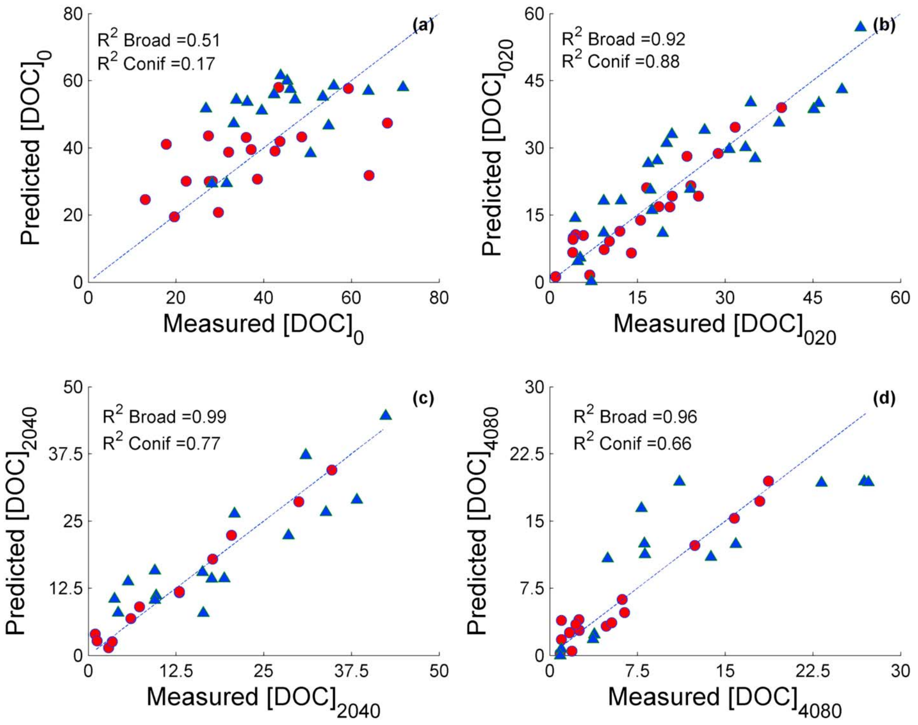

Figure 3. Predicted versus measured dissolved organic carbon (DOC) concentrations (mg L^{-1}) in soil solution in different soil depth intervals: (a) organic layer (0 cm), (b) topsoil (0–20 cm), (c) intermediate layer (20–40 cm), and (d) subsoil (40–80 cm). Predicted values have been calculated using stepwise linear regression. Circles represent the model for broadleaved (Broad) forests and triangles the model for coniferous (Conif) forests. The 1:1 line is shown. See Table 3 for additional information on the statistics.

3.1.3. Effect of Climate

DOC concentrations at lower latitudes (<35°) were significantly lower than in temperate regions (35°–60°) for all depths, except for the deepest layer ($P < 0.05$, Figure 1d). Boreal (for simplicity here defined as sites located above a latitude of 60°N) and temperate sites showed similar DOC concentrations in soil solution in the upper soil layers but not in the subsoil (40–80 cm), where DOC concentrations for the boreal sites were significantly lower ($P < 0.05$, Figure 1d).

3.2. Site-to-Site Variability of DOC Concentration in Broadleaved and Coniferous Forests Across Europe

Because coniferous forest soils exhibited larger DOC concentrations than broadleaved forests (see section 3.1) we separated both forest types for our model analysis of the controlling variables in the ICP Forests data set. The stepwise linear models produced for both forest types were successful in attributing the variation in DOC concentrations in the mineral soil layers to their possible drivers (Figure 3 and Table 3). For both forest types, only the model for DOC in the organic layer showed a poor fit (Figure 3a), although it was still statistically significant ($P < 0.05$) for broadleaved forests (Table 3). At all depths, models for broadleaved forests showed a better fit than the models for coniferous forests. Overall, nitrogen-related variables (NH_4^+ in soil solution and C/N), as well as Fe and Al, were most often selected as important drivers of variation in DOC concentrations across the sites (Figure 4 and Table 3). The coefficients of the stepwise regressions are given in Table S4.

Different predictor variables were retained in the models explaining DOC concentrations across sites in the organic layer for broadleaved compared to coniferous forests. Vegetation characteristics, such as summer NDVI (a proxy of leaf production) and litter decomposability, were better correlated with the DOC concentrations under broadleaf than under conifer forests. In coniferous forests, on the other hand, DOC was strongly correlated to water balance-related variables (Figure 4 and Table 3).

DOC concentrations under conifer surface litter layers correlated negatively to drainage in summer, while DOC concentrations under broadleaf forest litter layers correlated best with C/N ratio of the

Table 3. Dependent Variable and Final Predictor Variables, Number of Sites, R^2, RMSE, and *P* Value for Each Model[a]

	Coniferous					Broadleaved				
Dependent Variable	Predictor Variables	# of Sites	R^2	RMSE	*P* value	Predictor Variables	# of Sites	R^2	RMSE	*P* value
Median DOC_0	Drainage summer (0.17)	21	0.17	20.44	0.06	C/N (0.27), LitterDecomp (0.25)	20	0.51	13.5	0.002
Median $DOC_{0–20}$	NH_4 in SS (0.18), ExchAl (0.17), avgDrainage (0.09), C/N (0.08), pH (0.07), ST (0.04), Fe in SS (0.02), Sand (0.017)	30	0.88	7.24	<0.0001	NH_4 in SS (0.25), Fe in SS (0.1), ExchAl (0.03), NDVI summer (0.03), avgET (0.02)	23	0.92	4.52	<0.0001
Median $DOC_{20–40}$	Fe in SS (0.25), Al in SS (0.13), Sand (0.09)	16	0.77	6.63	0.0003	NH_4 in SS (0.63), ET summer (0.065), avgPrec (0.02), C/N (0.003)	14	0.99	1.9	<0.0001
Median $DOC_{40–80}$	Prec in summer (0.6), NH_4 in SS (0.2)	14	0.67	5.78	0.0028	C/N (0.07), ExchFe (0.06), avgET (0.05), Temp autumn (0.05), LitterDecomp (0.03)	16	0.96	1.6	<0.0001

[a] The predictor variables are listed in order of relative importance in the model, and the partial R^2 (a measurement of the marginal contribution of one explanatory variable when all others are already included in the model) for each variable in the model is between parentheses. (SS = soil solution, LitterDecomp = categorical variable for litter decomposability based on site species, ET = evapotranspiration, Prec = precipitation, Temp = air temperature, and ST = soil temperature).

forest floor and with litter decomposability (Figure 4). However, these models explained only 17% and 51% of the site-to-site variability in DOC concentrations in the organic layer for coniferous and broadleaved sites, respectively (Table 3).

The models for DOC concentrations in the upper layer of the mineral soil (0–20 cm) captured 88% (conifers) and 92% (broadleaf forests) of site-to-site variability (Table 3). For both coniferous and broadleaved models, NH_4^+ concentration in soil solution, together with exchangeable Al, was the most important variable explaining variability in DOC concentrations in the upper layer of the mineral soil. While NH_4^+ was positively correlated with DOC, exchangeable Al was negatively correlated. C/N ratio also appeared important at coniferous sites, while Fe in soil solution was relevant in broadleaved forests. DOC in the intermediate soil layer (20–40 cm) was mainly positively related to soil solution variables, with ammonium concentration in soil solution having the highest partial R^2 in the model for broadleaved forests and Al and Fe concentrations in soil solution being more important in coniferous forests. The best explanatory variables in models for DOC concentrations in subsoil (40–80 cm) differed strongly between broadleaved and coniferous models (Table 3). Nevertheless, in the case of broadleaved forests, selected variables exhibited only very low partial R^2 (Table 3). In coniferous forests, mean precipitation in summer was the most important variable with a high partial R^2, and a model including precipitation in summer and NH_4^+ in soil solution explained 67% of the site-to-site variation in DOC at 40–80 cm depth in these forests (Figure 3d).

4. Discussion

4.1. Differences Across Ecosystem, Climate, and Soil Type

In total, 365 sites are included in this database, located primarily in the humid temperate zone, and with especially tropical sites being underrepresented ($n = 13$). Mediterranean and (semi)arid sites were absent from the database. Although this is to be expected due to low potential for DOC production under these climate conditions, it hampers putting these fluxes into a global perspective. Furthermore, organic soils are scarce (29 organic soils with nonwoody vegetation) compared to forests on mineral soils (311 forests). Only one forest was on organic soil. The first part of the analysis focuses on generalities across ecosystem types, climates, and soil types, but due to the different sample size between soil types and vegetation cover (Table 2), discussions relying on this stratification will necessary confound the effects of soil and vegetation. Although this may appear as a shortcoming in the database, the spatial distribution of the sites correctly reflects our current knowledge basis. The second part of our analysis focuses on temperate and boreal forests only.

4.1.1. Effect of Ecosystem Type

Overall, we observed higher DOC concentrations in peatland soils than in mineral soils, and within ecosystems on mineral soils, higher concentrations (at least in the upper soil layers) in forests than in other vegetation types

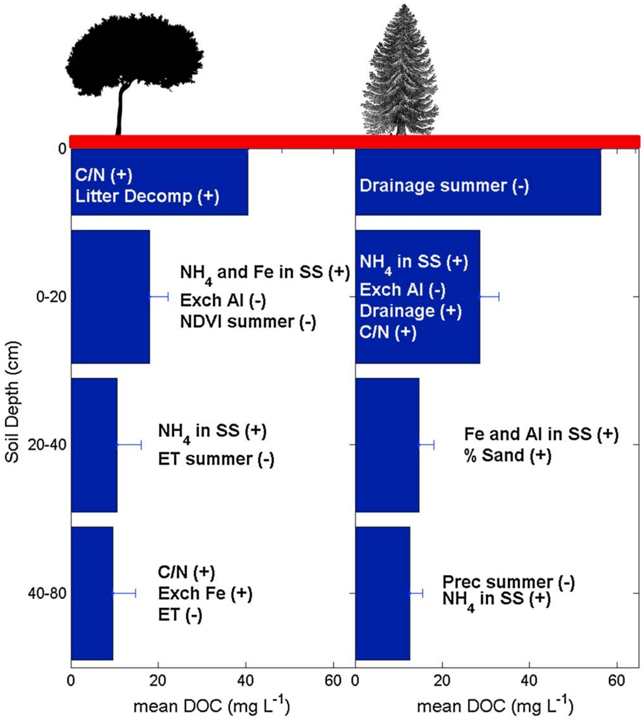

Figure 4. Most important explanatory variables selected for the stepwise regression models. Linear models fitted for broadleaved (left) and coniferous (right) separated for four different layers (0 cm, 0–20 cm, 20–40 cm, and 40–80 cm). The sign of the relationship is shown between parentheses. Mean DOC concentrations are based on all data. Most important explanatory variables are based only on European data.

(Figure 1). However, our database contained only 26 nonforest ecosystems on mineral soils (compared to >300 forests), and no data for forests on organic soils, indicating that care needs to be taken when generalizing these differences.

The mean DOC concentrations recorded in our database (Figures 1 and 2 and Table S3) are in the range reported in the literature. For example, we found an average DOC concentration of 50 mg L^{-1} (5th and 95th bootstrap confidence intervals: 45–56 mg L^{-1}) in the forest organic layers and a mean DOC concentration of 12 mg L^{-1} (5th and 95th confidence intervals: 10–14 mg L^{-1}) in the subsoil (40–80 cm). In their review, *Michalzik et al.* [2001] reported DOC concentrations in forest organic layers to range from 20 to 90 mg L^{-1} and from 2 to 30 mg L^{-1} in forest B horizons.

Our data compilation showed larger DOC concentrations for nonforest ecosystems on organic soils than for nonforest ecosystems on mineral soils (Figure 1 and Table S3). This difference in DOC concentrations was in line with the reported values of 26–75 mg L^{-1} for organic soils and 2–42 mg L^{-1} for nonforests mineral soils in the UK [*van den Berg et al.*, 2012]. The one exceptionally high concentration in our data set was observed for a cutover peatland undergoing restoration in New Zealand [*Moore and Clarkson*, 2007].

An early meta-analysis reported similar DOC concentrations for 42 broadleaved and coniferous forests, most of them temperate forests [*Michalzik et al.*, 2001]. These results were contradicted by other studies [*Currie et al.*, 1996; *Fröberg et al.*, 2011; *Kalbitz et al.*, 2000; *Khomutova et al.*, 2000] that, similar to our analysis, showed that DOC concentrations are on average lower in broadleaved forests than in coniferous forests. Including a larger number of forests and covering a wider range of soils and climates, we found a consistent difference in DOC concentrations between forest types. However, while the temperate zone contains similar number of broadleaved and coniferous forests, tropical forests only contain broadleaved and boreal forests that are mainly coniferous; thus, results should be carefully interpreted, as climate acts as a covariate. Nonetheless, restricting this analysis to the difference between conifers and deciduous forests in the temperate zone only, we can confirm the higher concentrations in the coniferous forests (Figure S2).

Concentration differences between upper soil layers in coniferous versus broadleaved forests have been attributed to the thicker litter layer in coniferous forests [*Fröberg et al.*, 2011; *Hansson et al.*, 2011], which in turn is caused by the slower decomposition rate of coniferous litter. It has been suggested that the thicker the litter layer, the longer the infiltrating water is in contact with the organic matter [*Borken et al.*, 2011], thereby increasing the probability for organic molecules to dissolve as DOC. The thickness of the litter layer is largely determined by the prevailing climatic conditions and the quality of the litter, which is dependent on tree species. Decomposition of higher quality (lower C/N ratio) litters, typical for broadleaved forests, results in higher rates of DOC production [*Cotrufo et al.*, 2013]. However, DOC production and microbial decomposition of litter are competing pathways, and because higher litter quality also stimulates microbial processing, proportionally less DOC remains in soil solution in broadleaved forests.

Overall, our data compilation thus confirms that since the review of *Michalzik et al*. [2001], the range of DOC concentrations in temperate forest ecosystems is well established. However, tropical forests and nonforest ecosystems, in general, are underrepresented in our database, so novel observations should preferentially focus on these ecosystems.

4.1.2. Effect of Soil Type

Not surprisingly, we found the highest DOC concentrations in Histosols (Figure 2), which are highly organic soils in which high water levels reduce mineralization rates [*Blodau*, 2002], such that incompletely decomposed plant material remains in the soil and acts as a source of DOC. On the contrary, we found the lowest DOC concentrations in Andosols. Andosols typically have a high content of soil organic matter (SOM), but this SOM is protected against decomposition through sorption to the volcanic minerals, resulting in stabilized SOM that does not take part in decomposition, yielding low DOC production [*Óskarsson et al*., 2004]. In general, the effect of soil type on the DOC concentrations is partly determined by soil texture and mineralogy [*Schwendenmann and Veldkamp*, 2005], which determines DOC sorption capacity and thus SOM stabilization potential.

We further observed that DOC concentrations in Histosols increased with increasing depth, which is opposite to most mineral soils. The depth profile of DOC concentrations in Histosols probably results from two mechanisms that reduce DOC consumption with increasing depth. First, decomposition rates and therefore DOC consumption may decrease with increasing depth following the increasingly anaerobic conditions in the deeper layers [*Moore and Dalva*, 2001; *Vicca et al*., 2009]. Second, the residence time of water increases with depth: in lower layers of Histosols, hydraulic conductivity is very low and, even though DOC production rates are also slow, this can lead to the buildup of DOC.

Our data compilation supports the idea that larger DOC concentrations are found in more acid soil solutions [e.g., *Clarke et al*., 2005; *Löfgren and Zetterberg*, 2011] (Figure 1c and Table S3). This relationship may be explained by the enhanced dissolution of organometal complexes at low pH [*Kalbitz et al*., 2000]. On the solubility of DOC, pH has a strong direct effect due to its acid-base properties [*Hruska et al*., 2003], and also an indirect effect through its impact on microbial activity (shifting between bacteria-dominated microbial community at high pH to fungi dominated at low pH), making it difficult to isolate the direct effect of pH on DOC concentrations.

4.1.3. Effect of Climate

The different climate zones reflect differences in temperature, precipitation, and nutrient availability. If we assume that no DOC is leached or adsorbed, the final DOC concentration in a soil solution is the outcome of two offsetting processes that both depend on climate, i.e., DOC production and DOC decomposition [*Kalbitz et al*., 2000]. It has been proven that the CO_2:DOC production ratio increases with warming, suggesting that although DOC production increases with temperature, its mineralization is even more temperature sensitive [*Moore et al*., 2008]. Accordingly, in the tropics high production is offset by high decomposition resulting in DOC concentrations below those observed in the temperate and boreal zones. Under boreal and artic conditions, both DOC production and decomposition are lower, but frozen conditions limit transport and dissolution of DOC by reducing the connectivity between soil organic matter and soil water [*Laudon et al*., 2012], resulting in slightly smaller DOC concentrations than in the temperate zone (Figure 1d).

In conclusion, the observed DOC concentration in a soil solution is the balance between DOC production and decomposition (largely driven by biological activity) and adsorption and desorption (largely determined by soil type). The four processes share a dependency on the climatic conditions. While we found a consistently higher DOC under coniferous forests than under broadleaved forests, the database heterogeneity complicates the separation of significant factors for different climates, and thus, the processes behind this vegetation effect remain largely hidden at global scale. For this reason, we conducted an analysis on a restricted data set, including only forests (both coniferous and deciduous) from the temperate and boreal zones, obtained from one network using standardized methodologies (the ICP Forests network). This allowed us to attribute the main controlling factors of DOC variability between forest types for the temperate and boreal zones.

4.2. Site-to-Site Variability in DOC Concentration Under Broadleaved and Coniferous Forests in Europe

The statistical models used here to predict the site-to-site variability of DOC in the mineral soil outperformed ($R^2 = 0.9$) those describing the variability of DOC in the organic layer ($R^2 = 0.5$ to 0.17). This was to be expected because the organic layer is more dynamic than the mineral layer, due to the former's more intense contact with the atmosphere and its higher dependence on abiotic processes, such as infiltration rates and moisture changes [*Michalzik and Matzner*, 1999; *Schulze et al*., 2011]. Therefore, the higher variability in DOC concentration in the organic layer across sites may largely be due to its higher temporal variability, which was not captured in the models. Moreover, we had fewer predictors available for the organic layer, and some important drivers, such as variability in throughfall inputs or type of herbaceous layer, are missing in the selected models for the organic layer.

4.2.1. Common Controlling Factors in European Forests

In the mineral soil solution, the site-to-site variability of DOC concentrations strongly correlated with nitrogen availability, especially to NH_4^+ in soil solution and to a lesser extent, soil C/N ratio, and aluminum- and iron-related soil variables (Table 3 and Figure 4). We observed that high DOC concentrations in soil solutions correlated with high NH_4^+ concentrations for both coniferous and broadleaved forests. Historical N deposition may have strengthened this relationship over Europe, because Level II plots of the ICP Forests program have often been located in areas with high N deposition [*Fischer et al*., 2007], particularly in the temperate zone. The addition of N has been reported to increase DOC leaching in some studies [*Bragazza et al*., 2006; *Findlay*, 2005; *Pregitzer et al*., 2004]. Although this has not always been observed in fertilization studies [*Evans et al*., 2008], it has been suggested that increased soil NH_4^+ results in incomplete degradation of lignin and lead to increased levels of soil phenolics and thus greater production of DOC [*Pregitzer et al*., 2004].

Our analysis confirmed that sites with low soil C/N ratios tend to exhibit low DOC at both regional [*Kindler et al*., 2011; *van den Berg et al*., 2012] and global scales [*Aitkenhead and McDowell*, 2000]. Different mechanisms influencing both inputs and outputs of DOC may contribute to this. On the one hand, low C/N litter was suggested to increase microbial carbon use efficiency and decrease SOM decomposition [*Cotrufo et al*., 2013; *Schimel and Weintraub*, 2003], which could thus decrease DOC production from SOM as well as promote the complete microbial assimilation of DOC. This idea was confirmed also by *Janssens et al* [2010], who found that N deposition leads to a change in microbial community and reduces decomposition rates. On the other hand, when N is limiting, trees typically allocate relatively more carbon belowground, in the form of root exudates or root symbionts, [*Vicca et al*., 2012] and a part of this extra C can end up in the soil solution [*Moorhead and Sinsabaugh*, 2006], resulting in higher DOC inputs at sites with higher C/N ratios.

Exchangeable Al and dissolved Fe and Al were also found to be important for explaining DOC variability across European forest sites (Table 3). In soils with high contents of exchangeable Al, less DOC was found in the top mineral soil solution in both broadleaved and coniferous stands. This relationship can be explained by the promoting effect of Al^{3+} on the sorption of SOM to clay minerals [e.g., *Theng*, 1976]. Elevated concentrations of dissolved Al^{3+} also promote the flocculation of DOC-metal complexes [*Nierop et al*., 2002]. In part, the relationship between exchangeable Al and DOC concentrations is probably caused by a covariation with pH: Large contents of exchangeable Al occur at $pH < 4.5$, and the solubility of SOM strongly decreases with pH [*You et al*., 1999]. Moreover, sorption of DOC to mineral soil horizons showed a maximum at pH values around 4 [*Ussiri and Johnson*, 2004] due to the balance between increasing positive charge of Fe- and Al-(hydr)oxides with decreasing pH and increasing protonation of DOC. The positive correlation between dissolved Fe and DOC concentrations we found from our data set was also reported for a Swiss forest catchment [*Hagedorn et al*., 2000]. Their analysis revealed that the dissolution of Fe-(hydr)oxides under reducing conditions increases not only dissolved Fe concentrations but also DOC concentrations as a consequence of the diminished sorptive retention of DOC. Overall, soil properties, particularly pH and sorption capacity of the subsoil, influence DOC concentrations in soil solution, independently of the standing forest type.

Sorption of DOC derived from topsoils leads to a stabilization of the retained DOC against mineralization and may contribute to accumulation of organic C in subsoils [*Kalbitz et al*., 2005]. Unfortunately, repeated soil samplings, which could verify an accumulation of C, have been carried out mainly for agricultural soils and almost exclusively for topsoils [e.g., *Bellamy et al*., 2005]. Significant increases of organic carbon stocks in the B horizon of a beech forest suggest that DOC sorption contributes to the buildup of Soil Organic Carbon (SOC) stocks also in forest soils [*Schrumpf et al*., 2014]. Therefore, DOC sorption plays an important role in soil C sequestration, with the amount of carbon that is retained in subsoils being determined by the subsoils available sorption capacity [*Kindler et al*., 2011].

4.2.2. Difference in Controlling Factors Between Broadleaved and Coniferous Forests

The difference between coniferous and broadleaved forests may be related either to a characteristic inherent to the forest type or it may be related to covarying factors. For example, conifers, especially pines, are more often located on sandy soils and in cold climates, where DOC concentration is primarily determined by the water balance, as drainage and precipitation, and the physicochemical characteristics of the soil, such as texture. The transport of DOC in sandy soils was reported to be dominated by the flow regime and macropore transport [*Kalbitz et al.*, 2000], because fast water movement might reduce adsorption and microbial processing of DOC [*Don and Schulze*, 2008; *Kaiser and Kalbitz*, 2012]. Accordingly, we hypothesize that differences in soil texture between coniferous and broadleaved forests may have contributed to the observed difference in the importance of precipitation and drainage in the models of DOC concentration (Table 3). Under this hypothesis, conifer trees, particularly pines, are associated with more sandy soils (which have lower water holding capacity), whereas broadleaved trees are associated with more silt and clay soils.

However, this separation between growth strategies is imperfect. Among the conifers, for example, pines are normally planted on soils with higher sand content, at lower altitudes and warmer conditions than spruces [*Barnes et al.*, 1998]. To better test this hypothesis, future studies examining the differences in factors controlling spatial variability should be performed at genus or even species level.

Broadleaved forests, on the other hand, generally grow more on fine-textured soils that are more fertile. These conditions stimulate also decomposition rates—often reflected in higher soil respiration [*Raich and Tufekcioglu*, 2000; *Wang et al.*, 2006]—owing to the importance of biotic factors in the models of DOC concentration, which may in turn be responsible for the lower DOC concentrations in broadleaved forests.

The difference in DOC concentration in soil solution among forest types should be kept in mind when modeling DOC production, transport, and decomposition at large scales and for different ecosystem types. These results suggest that different model formulations will be needed to develop models of DOC production and transport for the different plant functional types.

5. Conclusions

We present a database that substantially extends the scope of previous studies on the variability of DOC concentrations in soil solution. Using this database, we found that on average DOC concentrations were 75% lower in mineral than in organic soil and that temperate sites showed higher DOC concentrations than boreal and tropical sites. Further, DOC concentrations in soil solution were 23% lower in broadleaved sites than in coniferous forests. Overall, N availability, as indicated by C/N and NH_4^+ in soil solution, played a key role for the site-to-site variability of DOC in European forests, possibly by controlling microbial activity. Al and Fe are also important determinants of DOC site-to-site variability, reflecting pH controls on DOC concentrations. Biotic factors (litter decomposability or NDVI) become more important in explaining DOC in broadleaved forests, whereas water balance (drainage or precipitation) is more important in coniferous sites. We hypothesize that broadleaved sites are commonly more fertile and productive and exhibit higher SOM mineralization rates, resulting in smaller DOC concentrations measured in soil solution.

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