



Tracing sources of dissolved organic matter along the terrestrial-aquatic continuum in the Ore Mountains, Germany

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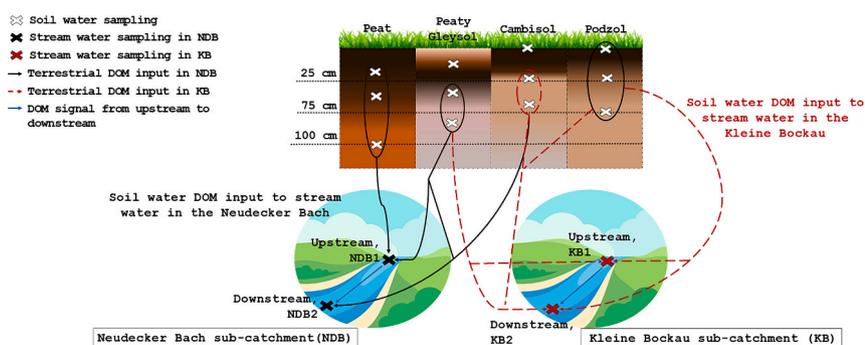
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HIGHLIGHTS

- Chemical signature was used to identify sources of DOM in stream water.
- Solid organic matter samples were of limited use for source identification.
- Peats contributed hardly to downstream DOM.
- Peaty Gleysol signals still detectable downstream the source location.
- Mineral soil horizons exerted the strongest overall control on stream DOM.

GRAPHICAL ABSTRACT



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ABSTRACT

There is growing concern about the rising levels of dissolved organic matter (DOM) in surface waters across the Northern hemisphere. However, only limited research has been conducted to unveil its precise origin. Compositional changes along terrestrial-aquatic pathways can help determine the terrestrial sources of DOM in streams. Stream water, soil water and soil horizons were sampled at four sites representing typical settings within a forested catchment in the Ore Mountains (Erzgebirge, Germany) from winter 2020 to spring 2022. The samples were analyzed using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS). The resulting data were successfully subjected to semi-automatic processing of the molecular composition of DOM, reaching a percentage of identified peaks up to 98 %. Principal component analysis (PCA) and cluster analyses were carried out to identify distinct differences between DOM from the potential sources and in the streams. According to the PCA, organic soil horizons, soil water, and stream water samples could be clearly distinguished. Cluster analysis

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revealed that soil water DOM at all depths of Peats and deeper horizons of the Peaty Gleysols contributed the most to DOM in the stream section dominated by organic soils. In areas dominated by mineral soils, stream DOM resembled the DOM from the deeper mineral horizons of Cambisols and Podzols. Overall, our results suggested that most of the DOM exported from the catchment was derived from deeper mineral soil horizons, with little contribution of DOM derived from organic soils. Therefore, DOM fingerprint analysis of in-situ soil water proved to be a promising approach for tracing back the main sources of stream water DOM.

1. Introduction

Dissolved organic matter (DOM) is ubiquitous in terrestrial and aquatic environments, occurring in throughfall, soil water, groundwater, and surface waters (Aitkenhead-Peterson et al., 2003). It is of high ecological relevance due to its complex role in carbon and nutrient cycling and food webs across the terrestrial–aquatic continuum (Li et al., 2020; Gu et al., 2020; Burns et al., 2016). It is a blend of diverse organic substances, varying in chemical structure, molecular weight, reactivity, and bioavailability (Zhao et al., 2022^a; Kothawala et al., 2021; Mentges et al., 2017). As DOM travels from terrestrial to aquatic environments, it is transformed by microbial degradation processes as well as retention and leaching processes (Danczak et al., 2021; Herzsprung et al., 2020; Bouwman et al., 2013). These alterations result in DOM compositions characteristic of individual ecosystem compartments, such as stream or soil water. During base flow, DOM is primarily exported to stream water from deep mineral soils (Yang et al., 2015; Wiegner et al., 2009), while topsoil and organic layers contribute more to DOM export during storm events (Denis et al., 2017; Broder et al., 2016). The distinct variations in DOM composition among these compartments, thus, offer a unique opportunity for identifying the sources of DOM in headwater streams (da Silva et al., 2021; Fovet et al., 2020; Broder et al., 2017; Rasilo et al., 2015).

Source identification has become increasingly important in the last decades because of continuously rising concentrations of dissolved organic carbon (DOC) in surface waters of Europe and North America (e.g., Toming et al., 2020; Monteith et al., 2023). Recent prognoses suggest that the trend of rising DOC concentrations in surface water will increase in response to global perturbations of the biogeochemical cycles of carbon and other elements (Havas et al., 2023). This will affect the supply of drinking water, as the associated browning is not only an aesthetic issue, but also potentially interferes with the required hygienic measures, e.g., chlorination or ozonation (Anderson et al., 2023; Ledesma et al., 2012). Due to the seriousness of the issue, the available literature has been dedicated to pinpointing the reasons behind the observed rise in DOM, ranging from anthropogenic acidification recovery and reduction in ionic strength (Lawrence and Roy, 2021; Hruška et al., 2009) to the impact of climate change (Xenopoulos et al., 2021; Kritzberg et al., 2020; Škerlep et al., 2020). However, many studies are predominantly focused on elucidating mechanisms solely within aquatic environments, thus missing to elucidate the potential role of terrestrial settings as sources of DOM in stream water (Carstea et al., 2020; Song et al., 2019; Cincotta et al., 2019; Fasching et al., 2016; Wong and Williams, 2010). Tracing the compositional DOM fingerprint along the terrestrial–aquatic continuum could help to determine potential terrestrial DOM sources (Kaal et al., 2022). Identification of sources can help to develop improved mitigation and prevention strategies allowing for managing DOM at the catchment level.

Characterization of DOM can be achieved by employing different analytical methods, such as fluorescence spectroscopy (Niloy et al., 2022; Ge et al., 2021; Wang et al., 2020; Broder et al., 2017), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS, Xu et al., 2020; Liu et al., 2020), and pyrolysis-gas chromatography coupled with mass spectrometry (Py-GC/MS, Kaal et al., 2017; Lu et al., 2003). All techniques are capable of providing information on the DOM composition, but they have certain limitations: Fluorescence spectroscopy reveals only basic compound classes typically not directly linked to

specific chemical moieties, while only ionizable compounds can be analyzed by FT-ICR-MS. Py-GC/MS, is another powerful and well-established method that offers insights into the molecular composition of natural organic matter based on the structure of the molecules. It provides information based on specific marker compounds, while being less affected by different matrices (Yang et al., 2022; Park and Snyder, 2018; Kaal et al., 2017; Kisand et al., 2013; Seelen et al., 2005), as compared to FT-ICR-MS (Zhang et al., 2020). During analysis, the pyrolytic process breaks down the molecules into small fragments, i.e., pyrolysates, which can be later traced back to the original macromolecule. Separation of the fragments produced throughout the analysis is facilitated by gas chromatography. Each pyrolysate can be identified and quantified by mass spectrometry based on the fragments' unique mass-to-charge ratios (m/z). The large amounts of fragments, however, made manual identification of pyrolysates a laborious and time-consuming process, especially when a substantial number of samples needs to be analyzed. Therefore, much effort has been put into developing more straightforward methods of assigning pyrolysates. In result, several software applications such as OpenChrom (Steinmetz et al., 2020) and AMDIS (Li et al., 2019; Smits et al., 2016), as well as codes (Chen et al., 2018; Smits et al., 2016) have been established allowing an automated processing of Py-GC/MS data.

The main objective of the present research was to identify the most important sources of stream water DOM in the catchment of a drinking water reservoir Sosa, in the Ore Mountains (Germany). The catchment consists of two sub-catchments with different proportions of organic soils (peats and peaty Gleysols) and mineral soils (mainly Cambisols and Podzols). We hypothesized that 1) the stream water would be strongly influenced by the adjacent soil, with the streams in their upper reach being more influenced by the peat than the lower reach streams, and 2) deeper mineral horizons would control downstream stream water DOM due to greater coverage of Cambisol and Podzol in the downstream area. The unique experimental setup allowed for linking potential sources of DOM along the entire terrestrial–aquatic continuum, from leachates of organic soil horizons, soil solutions at different depths of the mineral soil, as well as water in different parts of the streams draining the catchment. Source identification was based on analyzing DOM compositional fingerprints in each compartment using Py-GC/MS. A semi-automatic routine was used to process the raw Py-GC/MS data. To enable compound identification, the semi-automatic pipeline relied on the National Institute of Standards and Technology (NIST) Mass Spectral Search 2.0 and specific packages of Rstudio.

2. Materials and methods

2.1. Study sites

The study was carried out in the catchment area of the Sosa drinking water reservoir located in the Ore Mountains (Erzgebirge, Germany) (Fig. 1). The Sosa catchment is characterized by a mean annual temperature of 7.7 °C and mean annual precipitation of 1133 mm in the lower parts of the catchment. The vegetation within the catchment area is dominated by Norway spruce (*Picea abies*). In some of the Norway spruce stands, European beech (*Fagus sylvatica*) and Silver fir (*Abies alba*) saplings have been planted in recent years. There are few beech (*Fagus sylvatica*) stands and Black alder (*Alnus glutinosa*) can be found along the stream margins.

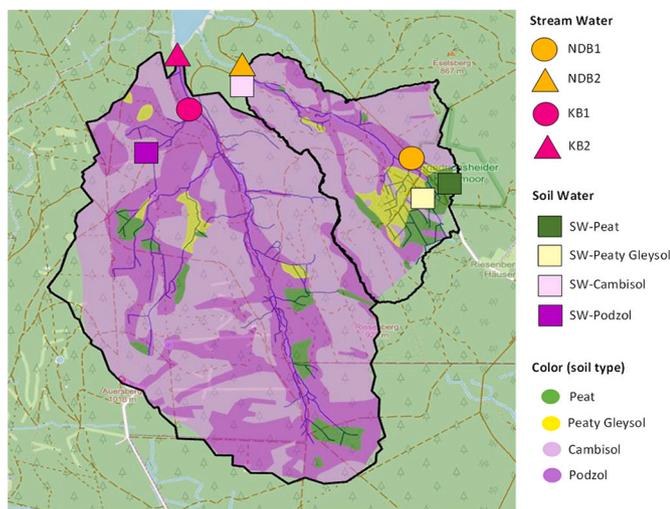


Fig. 1. Map of headwaters of the Sosa catchment, located in the Ore Mountains, with the two sub-catchments Neudecker Bach (NDB; sub-catchment on the right-hand side, more influenced by peats and peaty Gleysols) and Kleine Bockau (KB; sub-catchment on the left-hand side, dominated by mineral soils). The sampling sites for stream water, indicated by circles (upstream) and triangles (downstream), and labeled NDB1, NDB2, KB1, and KB2; for soil and soil water (SW) sampling site, the four prevalent soils in the catchment area are indicated by the squares (SW-Peat, SW-Peaty Gleysol, SW-Cambisol, SW-Podzol). The color scheme on the map illustrates the soil type distribution along the catchment area, being Peat represented by green, Peaty Gleysol by light yellow, Cambisol by lilac, and Podzol by purple.

Within the Sosa watershed (50°28'N 12°39'E), two sub-catchments with different characteristics were selected, Neudecker Bach (NDB) and Kleine Bockau (KB). The two sub-catchments are underlain by monzogranite/phyllite bedrock and comprise mainly mineral soils, i.e. Cambisols and Podzols. The Neudecker Bach sub-catchment is richer in peat and peaty Gleysols than the Kleine Bockau sub-catchment (Fig. 1). The organic soils cover approximately 27 % of the NDB1 area (green color, Fig. 1) and 9 % of NDB2 (yellow color, Fig. 1). Within the Kleine Bockau sub-catchment, both soil sampling sites, KB1 and KB2, are covered by 4 % of peat and peaty Gleysols.

In total, four small streams were studied using V notch weirs; two are located within the KB sub-catchment (dominated by mineral soils, KB1 and KB2) and two are within NDB (richer in organic soils, NDB1 and NDB2). Their average discharge is given in Table 1. The sizes of the four sub-catchments are 0.36, 1.48, 0.32 and 4.80 km² for NDB1, NDB2, KB1, and KB2, respectively. Additionally, we established continuous soil water (SW) monitoring systems in the stream water sampling sites, i.e., at four different sites representative of the potential terrestrial DOM sources. The sampling site “SW-Peat” is adjacent to the weir in NDB1 (Fig. 1) and represents a shallow, partly drained peat bog with a peat layer of up to 8 m. Its uppermost layer (20 cm) shows clear indications of enhanced oxidative peat decomposition. The sampling site “SW-Peaty Gleysol” is also close to weir NDB1 (Fig. 1) and the soil has been classified as Histic Gleysol (WRB, 2014). It likely represents the remainder of a former shallow peat. Both sampling sites representing organic-rich

Table 1

Average discharge (L s⁻¹) at each of the two positions of the Neudecker Bach stream (i.e., NDB1, upstream, and NDB2, downstream) and the Kleine Bockau stream (i.e., KB1, upstream, and KB2, downstream) during different seasons.

	NDB1	NDB2	KB1	KB2
Winter	5.22	25.37	11.75	113.16
Spring	2.57	16.03	8.72	97.97
Summer	2.52	7.86	4.19	121.92
Fall	1.48	7.57	3.39	43.17

soils, Peats and Peaty Gleysols, are located in the NDB sub-catchment. The sampling site “SW-Cambisol” is close to weir NDB2 (downstream area of the NDB sub-catchment, Fig. 1) and represents an important soil type in both sub-catchments. The sampling site “SW-Podzol” is close to weir KB1 (Fig. 1) and represents another important soil type in both sub-catchments of the Sosa watershed. More information and descriptions about the soil types and their specific horizon, pH, TOC, C/N ratio and soil texture are found in the supplementary material, Table S1 and Fig. S1.

At all soil sites, five plots were established to monitor soil water. At each of the five plots, suction plates were installed for collecting soil water underneath the uppermost organic horizon of the peat (depth 1, i.e. D1) as well as beneath the forest floor at SW-Cambisol and SW-Podzol (i.e., D1). In addition, suction cups were installed in the upper (depth 2, i.e. D2) and deeper (depth 3, i.e. D3) subsoil: at 50 and 100 cm depth for SW-Peat; at 45 and 80 cm depth for SW-Peaty Gleysol; at 25 and 65 cm depth for SW-Cambisol; at 25 and 75 cm depth for SW-Podzol. The suction cups' depth was decided according to soil horizons (see Table S1). Suction plates and cups were made of borosilicate glass (pore size approximately 1 μm) to prevent adsorption of DOM. A continuous vacuum of 300 mbar was applied to all suction devices and the collected soil water was sampled biweekly.

2.2. Sampling and sample preparation

The organic soil layers of the soil water (SW) monitoring sites were repeatedly sampled from winter 2020/2021 to spring 2022. Samples of the different organic horizons of the forest floor at SW-Cambisol and SW-Podzol and of the uppermost peat horizons at SW-Peat and SW-Peaty Gleysol were taken at five different locations near the five soil water monitoring plots and then combined to give a composite sample per horizon and site.

Soil and stream water were collected from winter 2020/2021 to spring 2022, excluding spring 2021 due to technical reasons. Water from the four streams was sampled biweekly throughout the sampling period, whereas soil and soil water samples were not collected during the winter of 2020/2021 due to frost and snow cover. Depending on the volume of the composite soil water samples obtained per sampling, composite samples from two or three consecutive samplings had to be combined to provide enough volume to carry out all required analyses.

The stream water samples from NDB1, NDB2, KB1, and KB2 were filtered through 0.45-μm membrane filters (cellulose nitrate; Sartorius Stedim Biotech GmbH, Germany) and frozen. Soil water samples were filtered directly through the suction plates/cups, and thus no additional filtration was necessary prior to the analysis.

2.3. Soil water and stream water analyses

All solution samples obtained throughout the period from Winter 2020/21 to Spring 2022 were analyzed for dissolved organic carbon (DOC), total nitrogen (TNb), nitrate, and ammonium. Concentrations of DOC and TN were measured using a Vario TOC cube (Elementar Analysensysteme GmbH, Langensfeld, Germany) with an error of ±0.25 and ± 0.015 mg.L⁻¹ for DOC and TNb, respectively. Before injection, the samples were acidified with HCl 37 % (Merck KGaA, Germany) to pH 1.8–2.0, then 2.5 mL were injected and exposed to catalytic combustion with O₂ at 850 °C. The released CO₂ was analyzed by an IR detector, and the released N by a chemiluminescence detector (Horiba APNA-370). Ammonium-N and nitrate-N + nitrite-N were measured according to the ISO/DIS 15923-1:2013 using an AQ400 Discrete Analyzer (SEAL Analytical, Norderstedt, Germany), with an error of ±0.015 and ± 0.005 mg N.L⁻¹ for nitrate-N and ammonium-N, respectively. Dissolved organic nitrogen (DON) was calculated by subtracting the sum of ammonium-N and nitrate-N + nitrite-N from the TNb.

2.4. Pyrolysis gas chromatography/mass spectrometry

In total, 45, 46, and 14 stream water, soil water, and solid samples of the organic horizons, respectively, were analyzed by pyrolysis gas chromatography/mass spectrometry (Py-GC/MS). Prior to the analysis, stream water and soil water samples were freeze-dried, and then finely ground. Solid samples of the organic horizons were air-dried, milled, and finely ground. Finally, they were placed in a desiccator until analysis. Samples of 700 µg of freeze-dried materials were pyrolyzed at 600 °C for 6 s using a Multi-Shot Pyrolyzer EGA/PY-3030D (Frontier Laboratories Ltd.; Fukushima, Japan). Prior to pyrolysis, 2 µL of a solution of either 37, 66, or 81 µg.L⁻¹ of androstane (Sigma-Aldrich, St. Louis, MO, USA) was added to the samples as an internal standard. That allowed identifying whether the pyrolysis was accomplished properly. The pyrolytic compounds released from the samples were transferred into the gas chromatograph (7890B GC, Agilent Technologies, Inc.; Santa Clara, CA, USA) by split injection (split ratio 1:20) with a helium flow of 1 mL min⁻¹ and an inlet temperature of 250 °C. Volatiles were separated using a Zebron ZB-5 ms column (30 m length, 0.25 mm inner diameter, 0.25 µm film thickness) with helium as carrier gas and an initial temperature of 50 °C, which was increased to 300 °C at a rate of 7 °C min⁻¹, and then held at 300 °C for 10 min. The GC was interfaced directly to a mass spectrometer detector (MDS), Agilent 5977 MSD, with electron ionization of 70 eV and a mass detection range of 50–600 m/z.

Aiming to achieve consistent results regarding peak identification and area quantification, the process was automated according to Chen et al. (2018). This approach prioritizes the optimization of efficiency, reliability, and the maximization of automation capabilities for data processing, allowing for rapidly analyzing the robust and complex Py-GC/MS data:

1. Py-GC/MS data was converted into a “.CSV” format using the open source software OpenChrom (<https://www.openchrom.net>). The “.CSV” data was used as the input data in the automated pipeline built in RStudio Desktop version 4.2.2.
2. All the compounds were automatically identified through NIST Mass Spectral Search 2.0 by comparing the peak mass spectra with those in the National Institute of Standards and Technology (NIST) Mass Spectral Library (2014) through NIST Mass Spectral Search 2.2 Software. Compound identification by NIST Mass Spectral Search 2.2 provided information about the compounds' chemical name, Chemical Abstracts Service Registry Number (CASRN), formula, molecular weight, and Simplified Molecular Input Line Entry System (SMILES) as well as major fragment ions.
3. A compound list was compiled comprising all identified compounds in order to perform the statistical analyses.
4. All the identified pyrolysates were assigned to a specific compound class according to their molecular structure, i.e., atoms, rings, aromatic rings, and functional groups, also to perform statistical analysis. The classification of compound classes (i.e. criteria applied) is shown in Table 2.

2.5. Data analysis

Boxplots were generated using RStudio Desktop version 4.2.2 to illustrate the distribution of DOC concentrations and DOC:DON ratios at the different soil water and stream water sampling sites, encompassing different seasons. As the data was not normally distributed, the Kruskal-Wallis test, was applied to assess the statistical significance of the interactions among the mean ranks of three or more independent groups. The Steel-Dwass test was used to perform pairwise comparisons. The null hypothesis for both tests was set as “there is no significant difference between any pair of group means” and a confidence level of 95 % was considered. The tests were performed using JMP® 17 software.

Principal Component Analysis (PCA) was performed on the data obtained from the automated pipeline, encompassing both identified

Table 2

Compound groups and their classification according to pre-established criteria.

Compound class	Acronym	Equation/criteria for compound class assignment
Aromatic hydrocarbons	ArH	Hydrocarbons containing an aromatic ring
Carbohydrates	Carb	C-, H-, and O-containing compounds only
Lignin-derived compounds	LgC	Organic compounds with aromatic ring(s), hydroxyl and ether groups
Nitrogen-containing compounds	Ntg	Pyrolysate with nitrogen atoms
Polyaromatic hydrocarbons	PAH	Hydrocarbons containing more than one aromatic ring
Phenolic compounds	PhC	Organic compounds with aromatic ring(s) and hydroxyl groups
Saturated hydrocarbons	SaH	Products containing only C and H atoms, which fit the equation: $C \times 2 + 2 = H + \text{number of rings} \times 2$
Unsaturated hydrocarbons	UnSaH	Pyrolysis-derived compounds that did not fit the SaH equation above and are comprised of exclusively carbon and hydrogen

compounds and compound groups. Incorporating compound groups alongside with individual compounds in the PCA analysis was crucial for enhancing the interpretability of the plots. The larger the explained variance, the more representative the principal component (PC) was of the total variance. The extent of each principal component present in each observation is defined as scores, while loadings represent how much each variable, i.e., compound, contributes to the given principal component. RStudio Desktop version 4.2.2 was used to carry out the PCA analysis, and the packages applied were FactoMineR (Lê et al., 2008) and factoextra (Kassambara and Mundt, 2020; for PCA visualization).

Hierarchical clustering of principle components and enhanced dendrogram visualization were performed using FactoMineR package from RStudio Desktop version 4.2.2 to support the information obtained by PCA analysis and improve the clarity of discriminating and identifying sources of stream water DOM. All identified compounds were taken into consideration for the analysis.

3. Results

3.1. Dissolved organic carbon and nitrogen along the terrestrial-aquatic continuum

In order to gain first insights into DOM transport within the catchment, we continuously tracked the DOC concentrations, (Fig. 2) and DOC:DON ratios (Fig. 3) in different soil compartments and at different stream positions.

Highest DOC concentrations were found in the soil waters of the organic horizons at all sites (Fig. 2), with greater variability in the forest floor of SW-Cambisol and SW-Podzol (Fig. 2B, 20 up to 170 mg L⁻¹) than in the peat layer of SW-Peat and the organic layer of SW-Peaty Gleysol (Fig. 2A, 1 up to 100 mg L⁻¹). The DOC concentrations in mineral soil of SW-Peaty Gleysol (Fig. 2B) decreased with depth, whereas the DOC concentrations in the peat increased along the depth (Fig. 2A). At SW-Cambisol and SW-Podzol, DOC concentrations decreased from the forest floor (Depth 1) to the upper (Depth 2, Fig. 2B) and deeper mineral soil (Depth 3) at both sites. For SW-Podzol, the decrease from the forest floor to the upper mineral soil was small compared (from 124.47 mg L⁻¹ to 57.97 mg L⁻¹, Table S3) to the drop in DOC concentration of SW-Cambisol (from 72.44 mg L⁻¹ to 6.07 mg L⁻¹, Table S3). Overall, the DOC concentrations in the mineral soil of SW-Cambisol were lower than those of SW-Podzol (Table S3). Seasonal effects were observed in the organic horizons, with higher DOC concentrations during fall and summer for all studied sites. Seasonal variations in mineral soil horizons were less strong.

The average DOC concentrations in stream water of the Kleine

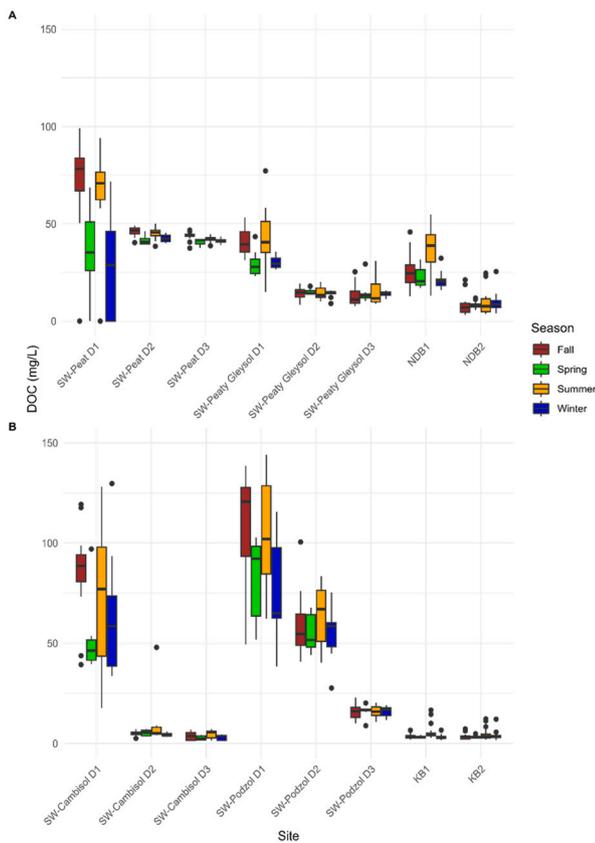


Fig. 2. Boxplot of the DOC concentrations across different seasons in the two streams as well as in the related soil waters (SW) at different soil depths (D1 = depth 1; D2 = depth 2; and D3 = depth 3), A) soil water from peats (SW-Peat) and peaty Gleysols (SW-Peaty Gleysol), and stream water of Neudecker Bach (NDB1 and NDB2, up- and downstream, respectively), and B) soil water from Cambisols (SW-Cambisol) and Podzols (SW-Podzol), and stream water of the Kleine Bockau (KB1 and KB2, up- and downstream, respectively).

Bockau sub-catchment (KB1 and KB2, up- and downstream, respectively) were comparable to the concentrations found in the upper and deepest mineral soil water of Cambisols (Fig. 2B, Table S3). The DOC concentrations in Neudecker Bach were higher, since the sub-catchment is characterized by larger areas with peats and peaty Gleysols than those in the Kleine Bockau sub-catchment, which is strongly dominated by mineral soils. In the upper segments of Neudecker Bach (NDB1, Fig. 1), the average DOC concentration was between the concentrations found at SW-Peat and SW-Peaty Gleysol (Fig. 2A). However, when considering no differentiation with depth, DOC concentrations at NDB1 were significantly different from those at SW-Peat and SW-Peaty Gleysol (Table S4). No conclusion could be drawn regarding the primary contributors to the DOM at NDB1. However, two scenarios are plausible: 1) both sources contributed significantly to upstream Neudecker Bach DOM, resulting in a distinct DOM fingerprint, or 2) NDB1 may receive DOM from additional sources that are not considered in this study. The DOC concentrations dropped from the up- to downstream position at Neudecker Bach (from 26.34 to 9.05 mg l⁻¹, Table S3 and Fig. 2A), which could indicate 1) dilution of the signal found upstream (NDB1) or 2) contributions from SW-Cambisol (Table S4).

Soil water of SW-Peat and SW-Peaty Gleysol showed higher DOC:DON ratios, ranging from 23.77 to 39.92, than soil waters in mineral soils (from 7.69 to 29.29). High variability of the DOC:DON ratios were detected at SW-Peat and SW-Peaty Gleysol during the summer, whereas these ratios did not vary much during the winter. Different depth trends of DOC:DON ratios occurred at SW-Cambisol and SW-Podzol. For SW-Cambisol (Fig. 3B), DOC:DON ratios decreased from the organic layer

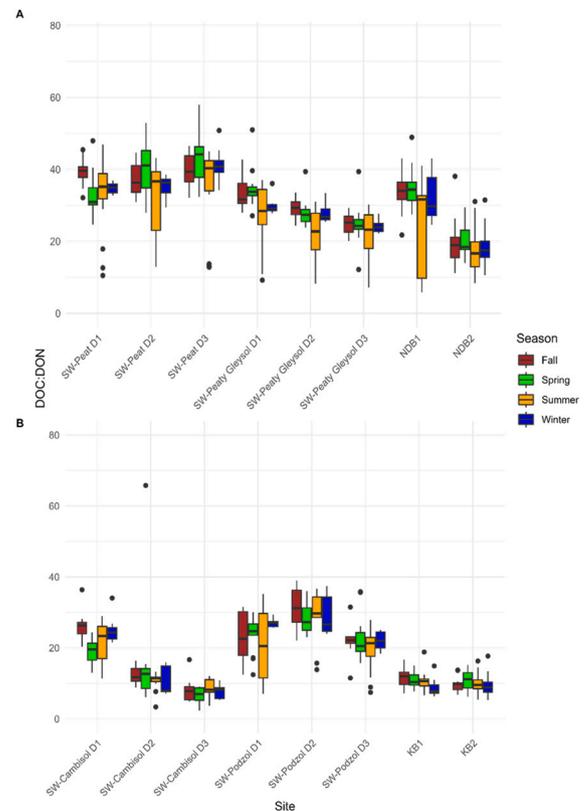


Fig. 3. Boxplot of the DOC:DON ratio across different seasons in the two streams as well as in the related soil waters (SW) at different soil depths (D1 = depth 1; D2 = depth 2; and D3 = depth 3), A) soil water from peats (SW-Peat) and peaty Gleysols (SW-Peaty Gleysol), and stream water of Neudecker Bach (NDB1 and NDB2, up- and downstream, respectively), and B) soil water from Cambisols (SW-Cambisol) and Podzols (SW-Podzol), and stream water of the Kleine Bockau (KB1 and KB2, up- and downstream, respectively).

to the upper mineral soil horizon and slightly further down into the deeper mineral soil (22.94, 12.14 and 7.69, respectively). For SW-Podzol, the DOC:DON ratios increased from the forest floor (depth 1, 23.71) to the upper mineral soil (depth 2, 31.03), and then decreased towards the third depth (D3, 21.04). Generally, DOC:DON ratios in the mineral soil horizons were lower for SW-Cambisol than SW-Podzol (Fig. 3B and Table S3).

Stream water DOC:DON ratio upstream of the Neudecker Bach (NDB1) reflected the ratios found at all depths at SW-Peat and depth 1 and 2 at SW-Peaty Gleysol (Fig. 3A, Table S3), whereas the ratios found downstream (NDB2) were closely related to those in the deepest mineral horizon at SW-Peaty Gleysol (depth 3, Fig. 3A). Nonetheless, both NDB1 and NDB2 were significantly different from all sources considered in this study (Table S6). In the sub-catchments of the Kleine Bockau, stream water DOC:DON ratios at KB1 and KB2 (up- and downstream, respectively) were similar to those of the mineral soil horizons at SW-Cambisol (depth 2 and 3, Fig. 3B, Tables S3 and S5).

3.2. Characterization of the potential DOM sources for stream water DOM

The number of identified compounds ranged from 150 to 254 depending on sample type, i.e. solid organic soil horizons, soil water and stream water, as well as environmental conditions, i.e. seasonal variations (Table S2). The method's accuracy in detecting the peaks resulted in a varying percentage of successfully identified peaks across different types of samples. Specifically, when analyzing stream water samples, the percentage of identified peaks ranged from 74 % to 96 %. For solid

organic soil horizon samples, the range was between 88 % and 96 %, while for soil water samples, it was within the range of 80 % to 98 %. A total of 176 compounds were accounted in this study and all these compounds were automatically assigned into one compound group described in Table 2. When analyzing the percentage of identified compound groups for each sample and site, differences in DOM composition were easily detectable (Table S6).

A principal component analysis (PCA) was carried out to highlight the differences in organic matter (OM) composition across sites and depths (Fig. 4). The first two principal components, PC1 and PC2, captured around 30 % of the total variance of the data (Fig. 4). PC1 was instrumental in distinguishing the solid samples of organic soil horizons from solution samples, highlighting the distinctiveness of their OM composition, whereas PC2 can be used to distinguish soil water from stream water, and to differentiate those samples according to their sites. Soil water and stream water had a very similar DOM composition (samples overlap), with some stream water samples (bottom left, Fig. 4) comprising mainly saturated and unsaturated hydrocarbons (SaH and UnSaH, respectively). DOM composition of the solid samples was very different when compared to the DOM composition found in soil water and stream water samples. The differences were due to the strong presence of lignin compounds (LgC) and carbohydrates (Carb).

Solid samples of organic horizons of Peats and Peaty Gleysols, Table S6, exhibited compositions differing from those from mineral sites (Cambisols and Podzols). This disparity was primarily due to lower percentages of lignin-derived compounds in Peat and Peaty Gleysols samples (around 7 %) than in samples from the mineral sites (around 20 %). In turn, the samples from Peat and Peaty Gleysols had higher percentages of carbohydrates (60 % vs. 45 % in mineral sites). The samples from the Peats had less N-containing compounds and more unsaturated hydrocarbons than samples from the other three sites. Additionally, a sphagnum-derived compound, *p*-hydroxybiphenyl (Schellekens et al., 2015), was found in the samples from the Peat and Peaty Gleysol sites.

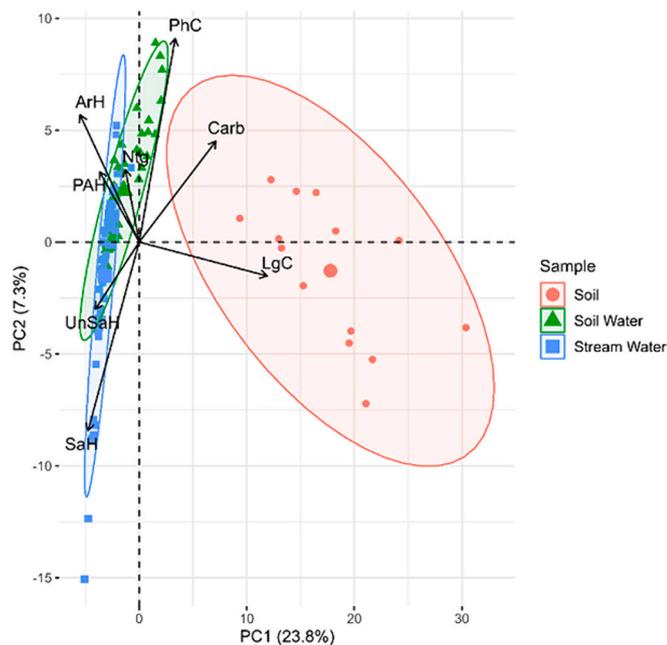


Fig. 4. Results of the principal component analysis (PCA) of the processed pyrolysis data to disclose the DOM composition for soil, soil water and stream water samples from year 2021 and 2022. ArH = Aromatic hydrocarbon, PAH = Polyaromatic hydrocarbon, SaH = Saturated hydrocarbons, Carb = Carbohydrate, Ntg = Nitrogen-containing compounds, UnSaH = Unsaturated hydrocarbons, LgC = Lignin-derived compound. The black dots indicate the direction and extent of the contribution of each variable to the corresponding principal component.

Solid forest floor material from Cambisol had the highest contents of lignin and phenolic compounds, while the forest floor samples from the Podzol site had high N-containing compounds and aromatic and saturated hydrocarbon content (Table S6). The forest floor samples from Cambisol and Podzol sites exclusively featured significant amounts of compounds related to Norway spruce, such as 4-vinylguaiacol, eugenol, and eugenol acetate (Table S2, Arias et al., 2010; Choi et al., 2001).

The DOM composition in soil water was depth-dependent for all the sampling sites, particularly at depths 2 and 3 (Table S6). Deeper horizons of SW-Peat (depths 2 and 3, Table S6) were characterized by high levels of carbohydrates, phenolic compounds (constituting up to about 70 % of the detectable matter), and aromatic hydrocarbons. Soil water DOM of SW-Peaty Gleysol exhibited a similar trend but with fewer phenolic compounds and carbohydrates, and higher contributions of N-containing compounds, aromatic, and unsaturated hydrocarbons. DOM of mineral soil horizons (depth 2 and 3, SW-Cambisol and SW-Podzol) was mainly composed of N-containing compounds and carbohydrates, with higher abundances at SW-Cambisol. DOM of SW-Podzol was characterized by high levels of aromatic compounds (29 %). Lignin compounds decreased with soil depth at all sites, persisting exclusively in deeper soil water of SW-Peat. The percentage of N-containing compounds at SW-Cambisol and SW-Podzol remained relatively stable with depth, whereas a significant drop was observed at SW-Peat and SW-Peaty Gleysol.

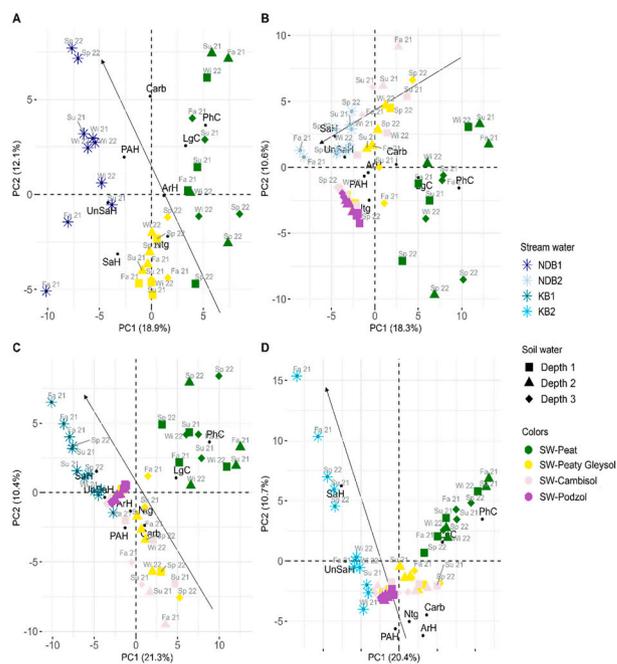


Fig. 5. Results of the principal component analysis (PCA) of processed pyrolysis data to disclose the main DOM sources for all the four stream sampling sites A) NDB1 (Neudecker Bach sub-catchment, upstream), B) NDB2 (Neudecker Bach sub-catchment, downstream), C) KB1 (Kleine Bockau sub-catchment, upstream), and D) KB2 (Kleine Bockau sub-catchment, downstream). Wi 21 = winter 2021, Su 21 = summer 2021, Fa 21 = fall 2021, Wi 22 = winter from year 2021/2022, Sp 22 = spring 2022. ArH = aromatic hydrocarbons, PAH = polyaromatic hydrocarbons, SaH = saturated hydrocarbons, Carb = carbohydrates, Ntg = Nitrogen-containing compounds, UnSaH = unsaturated hydrocarbons, LgC = Lignin-derived compounds. The black dots indicate the direction and extent of the contribution of each variable to the corresponding principal component. The black arrows are an interpretation of the changes in DOM composition along the continuum from terrestrial to aquatic systems according to the PCA.

3.3. Identification of DOM sources in stream water using PCA of Py-GC/MS data

Four different PCA were performed, Fig. 5A to 5D, to identify differences in composition among the four sampling sites for stream water and their potential DOM sources, i.e., soil water DOM potentially contributing to the DOM in the streams. PC1 and PC2 explained from 18.3 up to 21.3 % and from 10.4 up to 12.1 %, respectively, of the total variance in the post-processed Py-GC/MS data (Fig. 5). Plotting the scores of PC1 against PC2, revealed the potential sources of DOM in stream water at the four different sites (Fig. 5A to 5D). Differentiation of stream water and soil water was accomplished by PC1, whereas PC2 disclosed the changes in the composition of soil water DOM with increasing soil depth.

Soil water analysis revealed distinct DOM compositions. Soil water from SW-Peat exhibited the most unique DOM composition among the sites, while DOM of SW-Podzol formed a clustered group, indicating less variation (Fig. 5B to 5D). The DOM of SW-Peat (depth 1, Table S6), had a significant contribution of N-containing compounds (34 %, compared to 17 % in soil water DOM at mineral sites). Differences were also observed between soil water DOM from SW-Peat and SW-Peaty Gleysol, with the former having more lignin-derived and phenolic compounds, and the latter being richer in aliphatic and aromatic hydrocarbons. DOM of SW-Podzol was characterized by richness in carbohydrates and higher levels of unsaturated hydrocarbons (6.5 %) as compared to other samples (1.6–3 %).

Based on the location of SW-Peat and SW-Peaty Gleysol combined with the local hydrology, stream water of the upper reach of the Neudecker Bach (NDB1, Fig. 1) could be influenced by soil water from both peats and peaty Gleysols. The results from the PCA analysis revealed that the DOM fingerprint of NDB1 stream water was more similar to that of SW-Peaty Gleysol rather than to that of SW-Peat, especially during summer and winter (Fig. 5A).

The DOM composition downstream the Neudecker Bach (NDB2; 1.5 km downstream of NDB1) could be potentially affected by upstream soil and stream water (i.e., NDB1 stream water, soil water of peats and peaty Gleysols) but also by the surrounding mineral soils, i.e. soil water from Cambisols and Podzols (Fig. 1). Stream water samples were differentiated from soil water samples as well as the respective stream and soil waters according to site (Fig. 5B) along PC1. It became evident that the DOM composition of SW-Peat differed significantly from those of the other soils and did not affect the downstream water of the Neudecker Bach (NDB2). Instead, DOM from the upper and deeper mineral soil horizons of SW-Cambisol and SW-Podzol strongly influenced stream water of NDB2, with seemingly larger contributions of DOM from mineral horizons of Cambisols. No seasonal patterns were found in the PCA analysis for the stream water DOM of NDB2.

The sub-catchment of the Kleine Bockau is mainly composed of mineral soils with minor areas with peats and peaty Gleysols, thus all soil water sampling sites were taken into consideration as potential for both stream sampling sites, i.e., KB1 and KB2. A clear differentiation of soil water DOM composition between the peat and the other sites was accomplished (Fig. 5C), highlighting the missing influence of peat-derived DOM already in upstream Kleine Bockau (black arrow). Notably, DOM of SW-Peaty Gleysol had a composition resembling more that of SW-Cambisol and SW-Podzol, even when including the DOM from the uppermost organic horizons than that of DOM at SW-Peat. DOM from Podzols had a higher degree of uniformity in terms of its composition throughout seasons and along soil depth than DOM at the other sites. DOM from all depths of Cambisols strongly contributed to stream water DOM of upstream Kleine Bockau (sampling point KB1) in spring, while in winter, contributions were mainly from the upper and deeper mineral horizons (Fig. 5C). DOM from Podzols heavily influenced DOM in the KB1 stream water throughout the year. In addition, DOM from mineral horizons of Cambisols contributed strongly to stream water DOM during fall.

Stream water DOM of KB2 (downstream Kleine Bockau) was closely related to Podzol DOM from all depths (Fig. 5D). DOM of Cambisols and peaty Gleysols contributed about equally to KB2 stream water DOM, with signals of DOM from Cambisols being mainly those indicative of DOM of deep mineral horizons (depths 2 and 3), while those of peaty Gleysols were from the topsoil (depth 1).

In summary, soil water of peats had little to no influence on the export of DOM from the Sosa catchment, since the DOM patterns of downstream Neudecker Bach (NDB2) and in the entire Kleine Bockau sub-catchment (KB1 and KB2) was closely linked to those of DOM derived from mineral soil sites, with Cambisol soil water DOM being most important for NDB2 and Podzol soil water DOM for KB1 and KB2.

4. Discussion

4.1. Signature of the potential DOM sources

The analysis of the identified compounds (Table S2) revealed a clear difference in the number of compounds uniquely identified in soil water samples ($n = 7$) compared to solid organic soil horizon samples ($n = 37$) and stream water samples ($n = 42$). Half of the identified compounds, approximately ($n = 90$), were found in soil water and stream water and/or solid organic soil horizon samples. This observation implies a significant overlap in the composition of organic compounds among soil, soil water, and stream water, indicating potential sources of shared compounds or transfer pathways between these environmental compartments, particularly between soil water and stream water (Hutchins et al., 2017; Denis et al., 2017).

Examining specific compound groups, a clear discrimination between solid and aqueous samples was achieved mainly due to the presence of lignin-derived compounds and carbohydrates in the solid samples (Fig. 4). In stream water samples, the compound groups (i.e. lignin, aromatic and polyaromatic hydrocarbons, aliphatic compounds, carbohydrates, and N-containing compounds) also provided insights into the composition of DOM and its origin. Elevated concentrations of aromatic and lignin compounds in stream water suggested a stronger influence from organic-rich horizons, e.g. topsoil and forest floor (Nebbioso and Piccolo, 2013; Kalbitz et al., 2007). Conversely, higher amounts of microbially-derived carbohydrates, N-containing compounds, and lower quantities of lignin-derived compounds may indicate the mineral soils as sources, particularly during dry weather conditions, i.e., when base flow prevails (Denis et al., 2017; Marín-Spiotta et al., 2014; Singh et al., 2014).

Lignin-derived compounds (LgC) were mostly found in solid organic soil horizon samples (Table S6 and Fig. 4), indicating that such compounds were not released to deeper soil water (depth 2 and 3) and further to the stream water without undergoing intensive microbial processing. Also, in other mountainous regions, insignificant amounts or no lignin-derived compounds were observed in water-extractable organic matter of peat and Podzols (Kaal et al., 2020). Therefore, these compounds were not suitable as indicators of DOM source in stream water in the studied catchment. The presence of phenol and methyl-phenols in the samples provided insights into the complex nature of lignin degradation and the multiple pathways by which these compounds could be formed, even during pyrolysis (Kawamoto, 2017). These compounds were present in all tested compartments and were particularly present in samples from peats and peaty Gleysols (Fig. 5 and Table S6). Phenolic compounds were found in great proportions up- and downstream water of the Neudecker Bach (NDB1, NDB2), (Table S6), ranging from 10 to 18 % at NDB1 and from 4 to 17 % at NDB2. In contrast, up- and downstream waters of the Kleine Bockau (KB1, KB2; sub-catchment with little influence by organic soils, i.e., peats and peaty Gleysols) had smaller amounts of phenolic compounds, ranging from 1 up to 11 %. This aligns with findings from other studies that emphasized the prevalence of phenolic compounds in peaty environments (Yule et al., 2018; Hodgkins et al., 2018). It also indicated the little effect of

peats on stream water DOM in the Kleine Bockau sub-catchment with its low coverage of organic soils.

All stream water samples, particularly during fall, were rich in saturated hydrocarbons (ranging from 18 to 68 %), whereas such hydrocarbons were hardly detectable in soil water samples (Table S6). Despite extensive research efforts, the sources of the higher proportions of saturated hydrocarbons in stream waters than soil waters remain largely unresolved, which may point to in-stream production of these compounds (Mangal et al., 2020; Seifert et al., 2016). Similarly to saturated hydrocarbons, polyaromatic hydrocarbons (PAH) occurred preferentially in stream water samples, implying possible natural or anthropogenic origins within aquatic ecosystems (Grmasha et al., 2023).

While solid organic materials are the ultimate source materials of DOM, their compositional signature proved unsuitable for the identification of sources of stream water DOM. The composition of solid organic matter even lacked resemblance to the composition of soil water DOM (Fig. 4 and A3). This agrees with a study conducted wherein through a PCA analysis differentiation of stream water and soil samples according to their differential composition of organic matter was accomplished (Garcia et al., 2018). Consequently, the observed dissimilarity between solid and aqueous samples suggests strong transformation of organic matter during degradation and reactive transport within the soil (Zhao et al., 2022^b; Hobbey and Wilson, 2016; Kaiser and Kalbitz, 2012). Successful identification of DOM sources in a catchment cannot be achieved by analyses of soil samples only, it also requires collecting and analyzing soil water.

4.2. Identification of changes in sources of stream water DOM along the terrestrial-aquatic continuum

Cluster analysis was carried out to visualize the contribution of the different sources to stream waters (Fig. 6). It underlined the previous results indicating no direct influence of solid soil materials to stream DOM (Fig. 6, node 3). Therefore, this section will focus exclusively on unraveling the role and magnitude of contributions of soil waters to pinpoint the sources of stream water DOM.

4.2.1. Role of peat for stream water DOM

Soil water DOM from peaty Gleysols was the key contributor to the DOM composition in the upstream water of Neudecker Bach, i.e. NDB1 (black arrow, Fig. 5A). Concentrations of DOC and DOC:DON ratios in SW-Peat samples were overall greater than the values relative to the NDB1 stream water, indicating that inputs from SW-Peat potentially made minimal contributions to the DOM of NDB1 (Fig. 2 and Fig. 3). The majority of the Py-GC/MS signals in the stream water at NDB1 originated from deeper mineral horizons of peaty Gleysols (depths 2 and 3; Fig. 6, nodes 2 and 8), with very little influence of DOM from the topsoil. The difference between the DOC concentrations and DOC:DON ratios in the deeper mineral layers of peaty Gleysols and the concentrations/ratios observed in NDB1 stream water could be due to the contribution of peat-derived DOM (from all sampling depths), resulting in higher DOC concentrations and DOC:DON ratios in stream water. The strong influence of soil water from peaty Gleysols and the little contribution from peats indicated the importance of the immediate vicinity (Fig. 1) for the potential DOM source and its contribution to stream water DOM (Zhang et al., 2022; Ledesma et al., 2018). Peats, while covering large areas of the upper part of the Neudecker Bach sub-catchment, are located further away from the upper reach of Neudecker Bach (NDB1). Consequently, due to longer subsurface flow paths, soil water of both topsoil and deeper horizons of peats did not contribute much to the DOM of the NDB1 stream. According to Austnes et al., (2010), topsoil peat horizons may become important during storm events, although not delivering high concentrations due to dilution. Another study by Broder et al. (2017) also confirmed that during wet periods, peatland DOM (protein-like) was exported to stream water, although decreasing the overall concentration due to dilution, changing its composition. No direct

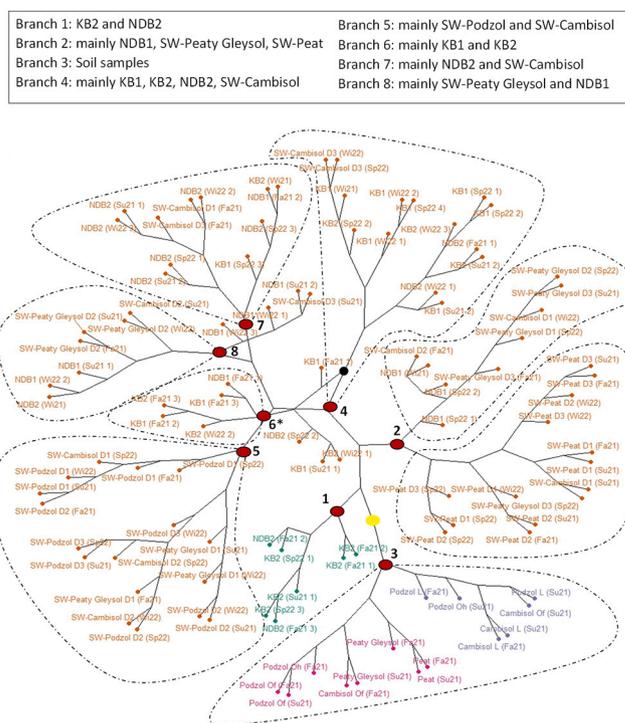


Fig. 6. Cluster dendrogram for all the samples analyzed in this study. NDB1 = upstream water of Neudecker Bach, mainly draining areas dominated by peats and peaty Gleysols, NDB2 = downstream water of Neudecker Bach, with additional influence of mineral soils, i.e. Cambisols and Podzols, KB1 = upstream water of Kleine Bockau, mostly draining areas with Cambisols and Podzols, KB2 = downstream water of Kleine Bockau, strongly influenced by mineral soils, i.e. Cambisols and Podzols. SW-Peat = soil water of peat, SW-Peaty Gleysol = soil water of peaty Gleysol, SW-Cambisol = soil water of Cambisol, SW-Podzol = soil water of Podzol. D1 = upmost soil layer (right below the organic layer), D2 = second soil depth, D3 = third soil depth. Wi21 = winter 2020/2021, Su21 = summer 2021, Fa21 = fall 2021, Wi22 = winter 2021/2022 and Sp22 = spring 2022. The yellow dot represents the main separation between samples, whereas the red dots (numbered branches) and dash-dot contours are given to support the dendrogram visualization and interpretation. 6* = node six is one branch inside of node 4 (black dot).

influence of the different seasons interfering in DOM source for the NDB sub-catchment was observed.

Despite a distance of only 1.5 km, a significant shift in DOM composition between the up- and downstream sampling sites along Neudecker Bach (NDB1 and NDB2, respectively) was observed. Lynch et al. (2019) also noticed changes in DOM composition along the streams. The decrease in DOC:DON ratios (Fig. 3B) could indicate a possible shift from more plant-derived to more microbial-derived DOM. This is in line with the idea of negligible contribution of peats, reduced influence of peaty Gleysols, and increasing contributions of DOM from mineral soil horizons of Cambisols and Podzols to stream water DOM (Fig. 5B) due to the neighboring soil (Fig. 1). Dilution by soil water from mineral soils resulted in attenuated signatures of peaty-derived DOM downstream Neudecker Bach. Considering the potentially low microbial degradability of peat-derived DOM (Kalbitz et al., 2003), we assume that in-stream degradation played a minor role in the downstream decrease in signatures of peat-derived DOM. Despite dilution, stream water at NDB2 still had distinct signatures of DOM derived from peaty Gleysols (in particular from depth 2; Fig. 6, nodes 4 and 7; Table S6).

Almost no contribution of SW-peat DOM was detectable by Py-GC/MS analyses (Fig. 5C and D) in the stream water of Kleine Bockau, which was corroborated by the lower DOC concentrations and DOC:DON ratios at both the up- and downstream sampling sites (KB1 and KB2, respectively). This can be attributed to two factors: 1) the

prevalence of mineral soils in the Kleine Bockau sub-catchment, and 2) the distance (≈ 1.0 km) between peat areas and the two stream water sampling points (Fig. 1). The latter could support the dilution (Bernal et al., 2018) or retention of peat-derived DOM along subsurface flow paths (Pearce et al., 2023). Upstream water of Kleine Bockau (KB1) and, to a lesser extent, downstream water (KB2), was partly influenced by DOM derived from deeper soil horizons of peaty Gleysols (depths 2 and 3), as illustrated in Fig. 5C and D, and Fig. 6 (nodes 4 and 6).

In summary, soil water DOM of peaty Gleysols contributed to stream water DOM in the Kleine Bockau sub-catchment, even though peaty Gleysols covered just around 4 % of the area. Similarly, soil water DOM from deeper horizons of peaty Gleysol contributed to the observed patterns in DOM composition of the Neudecker Bach, even 1.5 km downstream of the source area.

4.2.2. Role of the forest floor for stream water DOM

Forest floor soil water of Cambisols was not identified by Py-GC/MS analyses as a direct source of DOM in any stream water (Fig. 6). Considering all the samples of SW-Cambisol at depth 1, only two samples were identified within node 4 (encompassing nodes 5, 6*, 7, and 8, Fig. 6), where the majority of the NDB2, KB1, and KB2 samples are clustered. This observation suggests that the forest floor DOM of the SW-Cambisol had little influence on the DOM signature of the downstream waters of Neudecker Bach (NDB2) and the up- and downstream waters of Kleine Bockau (KB1 and KB2). A high flow event could be the cause of such particular DOM input from the forest floor of Cambisols, in which precipitation and consequently higher water levels would leach the DOM from the forest floor into the stream water (Singh et al., 2014). This finding is in accordance with the higher DOC concentrations of the Cambisol forest floors compared to those DOC concentrations of stream waters (Fig. 2A and B). Previous studies, including McDowell (2023), McDowell and Likens (1988), and Qualls and Haines (1991), reported similar observations, noting that DOC in stream water often reflects concentrations in soil water of deep mineral horizons rather than forest floors or riverbanks. Also, the differing DOC:DON ratios in forest floor solutions and stream waters suggest that there was little to no direct input of DOM derived from Cambisol forest floors into stream water (Fig. 3A and B).

The potential export of forest floor DOM from Podzols to streams throughout all seasons is corroborated by the clustering of all Podzols' samples at node 5 in Fig. 6. Although all SW-Podzol samples are clustered in node 5, node 5 is within node 4, along with nodes 8 and 7. Thus, export of Podzol forest floor DOM is possible. Part of the forest floor-derived DOM could potentially pass through the mineral soil and enter the stream water, although its influence seems not as significant as the contribution of DOM from deeper mineral horizons. This is line with the lower DOC concentrations and DOC:DON ratios (Fig. 2B and 3B) in the stream waters. Seemingly, the mobility of DOM within Podzols (McDowell and Likens, 1988) is an important factor on the transfer of terrestrial DOM into the streams in the Sosa catchment. This suggests that much of the retention capacity of the Podzol B horizons is already exhausted in response to in the high DOM concentrations entering the mineral soil from the forest floor (Fig. 2B) (Buurman and Jongmans, 2005). Other possible explanations for the observed contribution of forest floors to stream water DOM could be direct lateral transport or remobilization and translocation of forest floor-derived DOM that was previously retained in the Podzol B or C horizons (Kaiser and Kalbitz, 2012).

4.2.3. Role of mineral soil horizons for stream water DOM

As already mentioned in the above sections, the DOM in downstream waters of Neudecker Bach (NDB2) and both up- and downstream waters of Kleine Bockau (KB1 and KB2) featured compositional signatures closely resembling those of DOM in soil water derived from the mineral horizons. Stream water DOM at NDB2 was strongly affected by DOM from the lower mineral layers of Cambisols (Fig. 6, node 7), the

dominant soil in the vicinity of NDB2. The contribution of low-DOM soil water from Cambisols resulted in a reduction of DOC concentrations and DOC:DON ratios at NDB2 when compared to NDB1 (Fig. 2A and 3A). Soil water from Cambisols, particularly from depth 3 contributed to stream water DOM at NDB2, including saturated, aromatic, poly-aromatic hydrocarbons, carbohydrates, and phenolic compounds (Table S6). The contribution of soil water from Podzols was less than that of soil water from Cambisols (Fig. 5B and Fig. 6, nodes 7 and 4), without a clear distinction regarding the dominant soil depth of the Podzols (see section 4.2.2).

In the Kleine Bockau sub-catchment (primarily covered by Cambisols and Podzols, with small areas with peats and peaty Gleysols), stream waters had lower DOC concentrations and DOC:DON ratios than those in the Neudecker Bach sub-catchment. Despite the prevalence of Podzols in the surroundings of KB1 (Fig. 1), upstream waters of Kleine Bockau had similar DOC concentrations and DOC:DON ratios to soil waters of the uppermost mineral horizon of the Cambisols. This influence of Cambisol soil waters was supported by the Py-GC/MS results presented in Fig. 5C and Fig. 6 (nodes 4 and 6), with a composition of DOM from deeper mineral horizons of Cambisols (depth 3) matching the composition of stream water DOM at KB1. However, there was also contribution of DOM from Podzols, as all soil water samples from the Podzol overlapped with some KB1 samples (Fig. 5C). With the clustering of DOM signatures of SW-Podzol, no clear identification of which soil depth contributed the most to the export of Podzol-derived DOM to streams (see section 4.2.2). This means that some direct input of DOM from Podzol forest floors cannot be excluded. Overall, stream water DOM of Kleine Bockau mainly originated from inputs of water from deeper mineral horizons of the surrounding soils (i.e., Podzols and Cambisols). These results are in agreement with recent studies in Sweden, which highlights the impact of mineral soils in the surrounding area on DOC input into stream water (Singh et al., 2021; Fork et al., 2020). The idea of the surrounding soil controlling the stream water DOM was also supported by the similar DOM signatures (Fig. 6, node 6 and 4) as well as the similar DOC concentrations and DOC:DON ratios (Fig. 2B and 3B) at the two stream water sampling sites (KB1 and KB2) within the Kleine Bockau sub-catchments. Both sampling sites are surrounded by a fairly similar mosaic of Cambisols and Podzols. Nonetheless, the specific soil water source impacting the stream waters remains uncertain: although lower DOC concentrations and DOC:DON ratios in both streams suggested that Cambisols may be the dominant influence, the PCA analysis (Fig. 5D) indicated a closer resemblance between the chemical signatures of the stream water samples and the soil water samples from Podzols.

Despite the clear evidence of soil water controlling the composition of stream DOM, it is imperative to acknowledge the intrinsic capacities of streams for endogenous processes, including internal modification, consumption, and autochthonous generation of DOM (Pearce et al., 2023), as indicated by compounds exclusively occurring in stream water samples. Consequently, the DOM composition in a given stream cannot be exclusively attributed to the influx of soil water, as it undergoes dynamic transformations within the aquatic environment. Analysis of the DOM composition of soil water from the major soil types within the catchments is, nevertheless, a powerful tool to achieve successful source identification.

5. Conclusion

The composition of stream water DOM revealed by Py-GC/MS analyses resembled much more soil water DOM than soil organic matter itself, suggesting that soil water was the primary contributor to stream water DOM. Identification of similar and dissimilar compositional signatures was achieved using PCA in combination with cluster analysis. Peaty Gleysols affected upstream DOM in the Neudecker Bach sub-catchment, where peats and peaty Gleysols dominate. Downstream, the signatures of DOM derived from Peaty Gleysols became weaker while contributions of DOM of soil waters from mineral soils increased.

We assume this is due 1) the adjacent areas dominated by mineral soils, such as Cambisols, providing most water to streams, and 2) peats and peaty Gleysols recently cover only small portions of the Sosa catchment area, especially downstream. However, peaty Gleysols, representing remnants of peats degraded upon draining, contributed high DOM loads to the stream. Forest floor soil water of Cambisols had little effect on stream DOM. This suggests strong retention, especially in the deeper mineral soil horizons, and therefore not entering streams. In contrast, DOM from forest floors of Podzols contributed to the up- and downstream DOM of the Kleine Bockau (KB1 and KB2), either due to lateral transport or after the passage of the mineral soils with exhausted retention capacity. The findings unequivocally demonstrate that the majority of DOM in streams within the Sosa catchment is due to the input of soil waters from deeper mineral horizons of Cambisols and Podzols. Thus, it is essential to collect and analyze soil water samples from the predominant soil types to effectively pinpoint the sources of DOM in a catchment.

CRedit authorship contribution statement

Livia V.C. Charamba: Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Tobias Houska:** Writing – review & editing, Supervision, Conceptualization. **Klaus Kaiser:** Writing – review & editing, Supervision, Conceptualization. **Klaus-Holger Knorr:** Writing – review & editing. **Stephan Krüger:** Conceptualization. **Tobias Krause:** Methodology. **Huan Chen:** Writing – review & editing, Methodology. **Pavel Krám:** Writing – review & editing. **Jakub Hruška:** Writing – review & editing, Conceptualization. **Karsten Kalbitz:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2024.173807>.

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