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Géoscience

Sciences de la Planète

Laurent Jeanneau, Ophélie Fovet, Mikaël Faucheux, Gérard Gruau,
Marine Liotaud, Marie-Claire Pierret, Solenn Cotel, Jérôme Molénat,
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Volume 356 (2024), p. 157-175

Online since: 19 November 2024

https://doi.org/10.5802/crgeos.272

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www.centre-mersenne.org — e-ISSN : 1778-7025

Comptes Rendus. Géoscience — Sciences de la Planète
2024, Vol. 356, p. 157-175
https://doi.org/10.5802/crgeos.272

Research article

Compositional changes of dissolved organic matter during high flow events in headwater catchments along a gradient of climate and land use

Laurent Jeanneau [*,a], Ophélie Fovet [b], Mikaël Faucheux [b], Gérard Gruau [a], Marine Liotaud [a], Marie-Claire Pierret [c], Solenn Cotel [c], Jérôme Molénat [d], Manon Lagacherie [d], Céline Dessert [e] and Anne Probst [f]

[a] Univ Rennes, CNRS, Géosciences Rennes, UMR 6118, F-35000 Rennes, France

[b] UMR SAS, INRAE, Institut Agro, 35000 Rennes, France

[c] Université de Strasbourg, CNRS, EOST, ENGEES ITES UMR 7063, F-67000 Strasbourg, France

[d] UMR LISAH, Univ. Montpellier, INRAE, IRD, Institut Agro, Montpellier, France

[e] Université de Paris, Institut de Physique du Globe de Paris, CNRS, F-75005 Paris, France

[f] Centre de Recherche sur la Biodiversité et l'Environnement (CRBE), Université de Toulouse, CNRS, IRD, Toulouse INP, Université Toulouse 3 – Paul Sabatier (UT3), Toulouse, France

E-mail: laurent.jeanneau@univ-rennes1.fr (L. Jeanneau)

Abstract. High flow events in headwater catchments are associated with changes in the dissolved organic matter (DOM) composition. The aim of this work was to determine whether these changes are characteristic of headwater catchments and similar to what has been observed in other catchments. The evolution of the DOM composition during flood events was studied for five catchments covering a range of climatic, soil and land use contexts. The DOM composition was analyzed by thermochemolysis coupled with gas chromatography and mass spectrometry, making it possible to perform a joint analysis of several biomolecule families, monitor the proportion of compounds derived from plant inputs (%VEG) and study the lignin composition through the C/V ratio. The %VEG increased for all flood events studied. As this parameter is linked to the aromaticity of DOM, these increases are in line with worldwide observations. However, observations of increases in DOM aromaticity during floods in tropical and arctic zones are few and contradictory. This observation seems to be a general feature of temperate climates. This increase in aromaticity was accompanied by an increase in the C/V ratio for all rainfall-related flood events, indicating the mobilization of less biodegraded dissolved lignins than during base flows. These observations are in line with those made in the United States of America and could be characteristic of headwater catchments.

Keywords. Dissolved organic matter (DOM), Flood events, Molecular composition, Lignin, Headwater catchments, Climate gradient.

Funding. Research infrastructure OZCAR.

Manuscript received 5 July 2024, revised 6 September 2024, accepted 23 September 2024.

* Corresponding author

ISSN (electronic): 1778-7025

1. Introduction

High flow events are hot moments for the transfer of dissolved organic matter (DOM) at the soil-stream interface, accounting for over 80% of annual fluxes in forested and cultivated catchments [Dalzell et al., 2007, Raymond and Saiers, 2010]. These events are characterized by a change in the geometry of the water circulation, with an increase in the proportion of surface and subsurface flows compared to deep flows [Boyer et al., 1996, McGlynn and McDonnell, 2003]. These shallow flows connect the organic-rich surface horizons to streams, exporting terrestrial organic matter, resulting not only in an increase in dissolved organic carbon (DOC) but also in DOM aromaticity.

This modification of DOM composition during high flow events has been observed using different analytical techniques including spectroscopic analyses, chemical biomarkers and high-resolution mass spectrometry [Baek et al., 2019, Fellman et al., 2020, Hernes et al., 2008, Vidon et al., 2008, Wagner et al., 2019]. Moreover, it has been recorded for streams in arctic [Coch et al., 2019], subarctic [Fellman et al., 2020], temperate [Hernes et al., 2008, Jeanneau et al., 2015, Vaughan et al., 2019, Vidon et al., 2008], subtropical [Baek et al., 2019] and tropical [Osburn et al., 2018] climates. However, exceptions to this general behavior have been described for high flow events generated by rainfall in arctic [Coch et al., 2019] and tropical [Osburn et al., 2018] catchments and by snowmelt [Rose et al., 2023].

Among aromatic compounds found in stream DOM, dissolved lignins are terrestrial biomarkers. They contain varying proportions of vanillyl (V), syringyl (S) and cinnamyl (C) phenols, depending on the plant precursors [Hedges and Mann, 1979]. As C phenols are more sensitive to biodegradation than V phenols, lignin diagenesis modifies its composition inducing a decrease in the C/V ratio [Opsahl and Benner, 1995]. In headwater catchments where the homogeneity of the plant precursors can be assumed, the molecular composition of dissolved lignins can be used as a biodegradation proxy. During high flow events, the composition of dissolved lignins was modified with an increase in the C/V ratio, which has been interpreted as the export of less biodegraded lignins [Dalzell et al., 2007, Hernes et al., 2008, Jeanneau et al., 2015, Ward et al., 2012]. Since lignins that are less biodegraded correspond to compounds that are less lysed and oxidized, high flow events would therefore be a hot moment for the export of terrestrial DOM characterized by an increase in aromaticity, mean molecular weight and hydrophobicity. As these less biodegraded dissolved lignins were not observed in soil solutions during base flow periods [Jeanneau et al., 2015], several mechanisms have been proposed to explain their solubilization during rainfall events including litter lixiviation, surface erosion and subsurface erosion [Denis et al., 2017, Hernes et al., 2017b].

It is possible to determine whether the temporal variations in the DOM composition observed during high flow events in headwater catchments are universal and characteristic of low order catchments, or specific to the climatic, soil or land-use context of each catchment, by comparing streams across climate, substrate type and land use gradients. The French research infrastructure OZCAR, dedicated to the investigation of the critical zone [Gaillardet et al., 2018], provides an interesting tool for this purpose, insofar as it brings together five headwater catchments ranging from mountainous to lowland contexts, from forestry to intensive agriculture contexts, and from temperate oceanic to tropical climates via Mediterranean and mountain climates.

DOM exported at the outlet of these five catchments was sampled during base flow and storm flow events, with samples taken during the three main phases of each event (rising limb, peak flow and falling limb). The DOM composition was analyzed by thermally assisted hydrolysis and methylation coupled to gas chromatography and mass spectrometry (THM-GC-MS). This technique can simultaneously analyze the various biopolymers in soil organic matter and DOM in the same analytical conditions. Its relevance to the analysis of river DOM has been emphasized in the early 2000s [Frazier et al., 2003, van Heemst et al., 2000] and this technique is used to investigate the fate of DOM in soils and at the soil-stream interface [Gandois et al., 2019, Jeanneau et al., 2014, 2015, Kaal et al., 2017, 2020, Monard et al., 2020]. The modifications of the molecular composition of DOM during high flow events highlighted similar temporal variations along the investigated gradients with the specific case of snowmelt. For all catchments and for all events, the proportion of aromatic biomarkers increased and their distribution changed during high flow events.

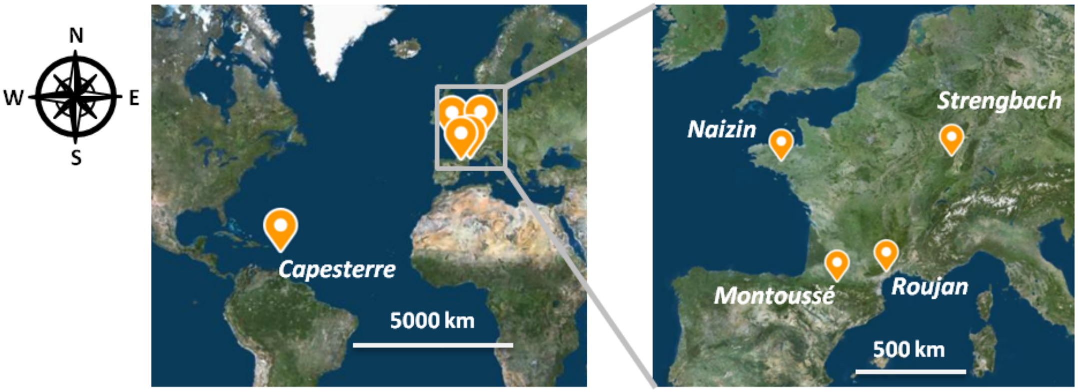

Figure 1. Location for the five investigated catchments.

2. Material and methods

2.1. *Description of the catchments and sampling*

The five sampling sites belong to the French Critical Zone research infrastructure OZCAR [Gaillardet et al., 2018]. Four are localized in metropolitan France and one is found on Guadeloupe Island in the Caribbean archipelago (Figure 1). The Kervidy-Naizin catchment, a 4.9 km^2 lowland catchment located in central Brittany in western France, is a part of a long-term monitoring research program undertaken by the AgrHys observatory aimed at understanding the impact of agricultural intensification and climate change on hydrologic processes and water quality [Fovet et al., 2018]. More than 70% of the catchment surface is occupied by crops and meadows and the main agricultural activity is intensive pig farming. The climate is temperate oceanic with a mean annual temperature and precipitation (1993–2011) of 10.7 °C and 814 mm, respectively. Rainfall events rarely exceed 20 mm per day, and 80% of rainfall events have an intensity of less than 4 mm per hour. The stream is ephemeral and often does not flow from the end of August to October due to the small volume of water stored in the bedrock. The high flow period generally lasts from December to April with a mean discharge (2000–2013) of 58 L/s, with maximum discharges in February and March with a mean storm discharge (2000–2013) of 303 L/s. The catchment topography is gentle, with hillslope gradients of less than 5% and elevations ranging from 93 to 135 m above sea level. The soil depth ranges from 0.5 to 1.5 m with soils classified as silty loams, specifically Stagnic fluvisols developed from alluvial material and Brioverian schist. The aquifer in the catchment consists of unconsolidated weathered bedrock, underlain by a locally fractured but generally impermeable unmodified bedrock. Five water samples were sampled on December 18, 2013 and seven between March 9 and March 11, 2016. The water samples were chosen to include baseflow conditions, the rising limb, the peak flow and the falling limb of the hydrographs. These events were characterized by 24 and 28 mm of rain and by a maximum discharge of 338 and 492 L/s, respectively. One water sample was taken under a base flow condition on December 3, 2013 (mean daily discharge: 14 L/s).

The Capesterre catchment (16°04′N, 61°36′W) is located on Basse-Terre Island, the volcanic part of the Guadeloupe archipelago in the French West Indies. This catchment is monitored by the OBSERA observatory dedicated to the study of weathering and erosion processes under tropical climatic conditions. The Capesterre River drains a 16.6 km^2 catchment, ranging from 200 to 1342 m in altitude, located in the primary tropical rainforest of the Guadeloupe National Park. It is underlain by andesitic rocks and covered with thin Andosol, related to the steep slopes of the young volcanic rocks (higher than 49%). The average C/N ratio of the soil is 11.4 ± 1.4 [Lloret et al., 2016]. It is characterized by a wet tropical climate, with a mean annual temperature around 23 °C and with 75% humidity. The Capesterre catchment receives 4000 mm/yr of rainfall on average. The climate is characterized by two seasons: the dry season from approximately January to June and the cyclonic wet season from July to December (60 to 90% of the average annual precipitation). During the wet season, hurricanes and tropical depressions produce intense individual rainfall events, which play a major role in the erosion of soils and weathering products [Allemand et al., 2014, Dessert et al., 2015]. Flood events have occurred throughout the years, but mostly during the wet season. Consequently, the river is in flood during 9.9% of the year (discharge > 3.5 m^3/s), and in extreme flood during 0.1% of the year (discharge > 32.5 m^3/s). Lloret et al. [2013] have shown that the export of organic carbon occurs essentially during floods and extreme floods, representing 54.5% of the annual DOC flux and 85% of the annual POC flux. One event was sampled on September 14, 2018 characterized by 32 mm of rain and by a maximum discharge of 24.8 m^3/s. One water sample was taken before the event, one at the beginning of the rising limb, four during the maximum discharge, one during the falling limb and one three days after the event.

The Roujan catchment is a 0.92 km^2 catchment located in the south of France and is part of the OMERE observatory [Molénat et al., 2018]. The long-term observations implemented in the catchment are dedicated to understanding the impacts of agricultural and land management on mass fluxes (water, sediments, pesticides, etc.) in Mediterranean cultivated headwater catchments. The climate is Mediterranean, characterized by an annual amount of rainfall of 645 mm (mean = 25 years), that is unevenly distributed throughout the year. Major rainfalls occur in spring and autumn. The mean maximum temperature is approximately 15 °C in January and 30 °C in July/August. The catchment presents a typical Mediterranean hydrological response, with annual stream runoff depending mainly on the annual rainfall and with the occurrence of extreme runoff events (maximum annual specific runoff of 520 mm). The elevation ranges between 75 and 125 m a.s.l., and the slope ranges from 2 to 20%. The substratum of the catchment is comprised mainly of Miocene marine deposits. A calcareous loose sandstone with centimetric laminations and intercalations of loamy clay materials is covered by lacustrine limestone, which constitutes the bedrock of the catchment. The soil along the hillslopes is developed directly over and from Miocene deposits and is representative of the main Mediterranean soils. The soil is calcareous silty, depending on the nature of the deposits and on the position within the slope. Temporary and permanent shallow groundwaters are present along the hillslopes and in the bottom lands. The deep loamy clay marine deposit (between 4 and 7 m deep) constitutes the lower bed of the shallow groundwater. More than 80% of the catchment area is used for agriculture. The steep slope areas of the catchment are landscaped with man-made terraces. The gentle slopes are covered mostly by vineyards, with some orchards in the bottom lands. The remaining parts are covered by shrubs and low trees. There are more than 10 km of ditches in Roujan around the vineyard fields. These anthropogenic features highly impact the hydrological behavior of the catchment. Five water samples were collected at the outlet in October and November 2018, four of them during storm flow, the fifth one during a base flow of 0.5 L/s. Due to technical constraints in this catchment, the storm samples are integrative and therefore it was not possible to differentiate between the different phases of the hydrographs. The high flow events were triggered by cumulative rainfall amounts of 48, 50, 16 and 33 mm, chronologically. The peaks of the stream flow were 34, 371, 110 and 216 L/s.

The Strengbach catchment is part of the OHGE observatory. It is a small (0.8 km^2), steep-slope (mean average 27%), middle-mountain (elevation ranging between 883 m and 1146 m) catchment located in eastern France in the Vosges massif (France). For almost 35 years, meteorological and hydrological data were monitored continuously. Research performed at this catchment, focused on the evaluation of water and soil resources in relation to climatic changes and anthropogenic forcing such as forest management [Cotel et al., 2020] or acid rain [Pierret et al., 2019]. The catchment bedrock is a Ca-poor granite. The soils belong to the brown acidic to ochreous podzolic series and are generally approximately 1 m thick. The whole catchment consists of commercially managed forest composed of 80% spruces and 20% beeches. The climate is temperate oceanic mountainous. Between 1987 and 2016, the mean annual temperature was 6 °C, and the mean annual precipitation was 1385 mm, with 19% snow on average. The mean annual runoff was 809 mm, corresponding to a mean discharge of 21 $L{\cdot}s^{-1}$. The Strengbach stream is perennial, with the highest water fluxes occurring during the snowmelt period and low discharge during the summer season. The hydrological response of the Strengbach catchment to rainfall varies according to the pre-event hydrological conditions and the rainy event characteristics. The response to rainfall is usually rapid and short, except during snowmelt events during which the hydrological response may be delayed and long-lasting. Quick-flow peaks are due to saturation excess overland flows originating from a saturated area located near the Strengbach outlet and delayed-flow peaks may be attributed to lateral subsurface flows coming from the hillslopes in the upper part of the site. Three events were sampled at the outlet of the catchment to include baseflow conditions, the rising limb of the hydrogaph, the peak flow and the falling limb of the hydrograph. Two summer events on July 20, 2018 (21 mm of rain in 20 min; 5 samples) and September 18, 2018 (22 mm of rain in 110 min; 6 samples) were quick-flow events due to thunderstorms in low-water conditions. The third sampled (6 samples) event on March 16, 2019 was a delayed-flow event due to snowmelt. The peaks of the stream flow were 162, 90 and 150 L/s.

The Montoussé catchment at Auradé (3.28 km^2) is located in southwestern France. It has been the subject of experimental research and long-term environmental observations since 1985 to investigate the influence of agricultural activities on water, soil, sediment and aquatic ecosystem quality, and more specifically on soil chemical and mechanical erosion, water and carbon fluxes and the transfer of pollutants (nitrogen, metals and pesticides) [Perrin et al., 2008, Ponnou-Delaffon et al., 2020]. The elevation ranges between 172 and 276 m a.s.l., and the average slope is 9% (maximum slope 29%). The geological substratum is an impermeable Miocene molassic substratum composed of a mixture of sands, clays, limestones and calcareous sediments. The soils are mainly calcareous and composed of silts and smectite-type clays, which have a high potential for water retention [Gandois et al., 2011]. Tillage and water erosion have shaped very shallow soils at the top of the hills (20–50 cm) and deeper colluvial soils, which can reach more than 2.5 m downslope. In terms of land use, 90% of the Montoussé catchment is mainly cultivated with an annual rotation of wheat and sunflower. The climate is an oceanic type climate with a mean annual air temperature and rainfall of 13.9 °C and 621 mm, respectively, calculated for the last 32 years. Rainfall events rarely exceed 20 mm per day and occur in May, June and January; their intensity does not depend on a particular period of the year. The mean annual stream discharge (1985–2018) is 17.2 ± 8.7 L/s [Ponnou-Delaffon et al., 2020]. The high flow period lasts from December to April and the major flood events generally occur in May (mean = 83 mm), while the low water flow period is from July to October. It is rare that the stream dries up [Brunet et al., 2011]. Flash floods (few hours) are frequent with variable discharge (mean discharge 226 ± 401 L/s, maximum 1580 ± 3527 L/s). Because the molassic substratum is impermeable and the slopes are steep, the stream discharge is mostly supplied by surface and subsurface runoff during flash flood events [Roussiez et al., 2013]. Three water samples were sampled in this catchment; two during a storm event in April 2018 (04/09/2018; 04/10/2018) and one in baseflow conditions after the event (04/20/2018) with corresponding discharges of 435, 231 and 19.4 L/s (first discharge peak, beginning of falling limb of the second peak, recession post-event, respectively). This double event was characterized by 20 and 12.5 mm of rain and by a maximum discharge of 435 and 714 L/s (first and second peak, respectively).

3. Chemical analyses

3.1. *Dissolved organic carbon*

Stream samples were filtrated at 0.7 µm (glass fiber filters, Sartorius, Germany) and stored in a fridge before the DOC analyses. DOC concentrations were determined using a Shimadzu TOC-5050A total carbon analyzer by differentiating between total and inorganic C. The samples from the Capesterre, Naizin and Strengbach catchments were analyzed at Géosciences Rennes in Rennes, the samples from the Montoussé catchment were analyzed at ECOLAB in Toulouse and the samples from the Roujan catchment were analyzed at Hydrosciences Montpellier in Montpellier. The precision of the measurements is estimated to be <±5% based on the repeated analyses of the sample and standard solutions.

3.2. *Molecular analyses*

A known volume (from 100 to 500 ml according to the DOC concentration) of filtrated river water was freeze-dried for molecular analysis. The mass of the lyophilisate was weighed with a precision balance. A mixture consisting of a known mass (from 1 to 6 mg according to the OC content) of lyophilisate, 5 mg of tetramethylammonium hydroxide (TMAH) and 10 μL of a solution of d9-hydrocinnamic acid at 25 ppm in MeOH (internal standard) is introduced in a reactor and placed in a vertical micro-furnace pyrolyser PZ-2020D (Frontier Laboratories). THM-GC-MS analysis was performed at 400 °C during 1 min. The gases produced are injected directly into a GC-2010 (Shimadzu, Japan) equipped with a SLB 5MS capillarity column (60 m, 0.25 mm i.d., 0.25 μm film thickness) with a split mode (between 10 and 15). The temperature of the transfer line was 321 °C, and the temperature of the injection port was 310 °C. The oven temperature starts at 50 °C (held for 2 min) and rises to 150 °C at 15 °C/min, then rises from 150 °C to 310 °C (held for 14 min) at 3 °C/min. Helium was used as a carrier gas with a flow rate of 1.0 mL/min. After separation by GC, the compounds were detected by a mass spectrometer QP2010+ MS (Shimadzu, Japan) operating in the full-scan mode for m/z values comprised between 50 and 600. The transfer line was at 280 °C and molecules were ionized by electron impact using an energy of 70 eV, and an ionization source temperature set at 200 °C. Molecules are identified by comparing their full-scan mass spectra with the library provided by the National Institute of Sciences and Technology (NIST) and research articles [Nierop et al., 2005]. The use of TMAH means that carboxylic acids are analyzed in the form of their methyl esters, and alcohols in the form of their methyl ethers.

Using the appropriate m/z for each compound, peak areas were integrated and corrected by a mass spectra factor (Table S1) which corresponds to the reciprocal of the proportion of the fragment used for integration and the entire fragmentogram of the NIST library. The identified compounds were classified into three categories: small organic acids (SOA), lignins and tannins (PHE) and fatty acids (FA). The proportion of each compound class was calculated by dividing the sum of the areas of the compounds in this class by the sum of the peak areas of all analyzed compounds and expressed as a percentage. Among the PHE markers, the ratio of coumaric to vanillic units (C/V) was used to trace the degradation state of lignin and calculated as the sum of the coumaric and ferulic acids divided by the sum of vanillaldehyde, acetovanillone and vanillic acid. It is possible to differentiate between plant and microbial biomarkers for FA. High molecular weight FA ($>C_{19:0}$) are from a plant origin while low molecular weight FA ($<C_{19:0}$) come from a microbial origin, with the exception of $C_{16:0}$ and $C_{18:0}$ which can derive from both [Frostegård et al., 1993, Zelles, 1999]. The proportion of plant-derived markers among the analyzed compound or %VEG was calculated as per [Jeanneau et al., 2015], assuming that SOA were from a microbial origin. The analytical uncertainty was determined on an internal soil sample reference and ranged from 10 to 20%, expressed as a relative SD, depending on target compounds and ratios.

4. Results

The list of target compounds and their concentration in ng/mg of lyophilisate are given in Table S1. The number of identified target compounds ranged from 21 (Roujan catchment, base flow conditions) to 57 (Strengbach catchment, March 15, 2019) (47 ± 9; average ± SD). On average, for all samples, the small organic acids (SOA) were dominated by succinic acid (26 ± 12% of SOA), benzoic acid (17 ± 12% of SOA) and nonanoic acid (15 ± 9% of SOA). The fatty acids (FA) were dominated by hexadecanoic acid (36 ± 9% of FA) and the phenolic compounds (PHE) were dominated by 3,4-dimethoxybenzoic acid (26 ± 12% of PHE) and 4-methoxybenzoic acid (14 ± 7% of PHE).

The DOC concentrations and molecular ratios are summarized in Table 1. For the Naizin catchment, the sampled events were characterized by rainfall amounts (>20 mm) and peak discharge values (>330 L/s) higher than the averaged values recorded for this catchment, classifying them as extreme events (Figure 2A, B). For both events, DOC increased sharply compared to the base flow conditions with the highest increase (8-fold) and DOC concentration (24.4 mg/L) recorded for the peak flow sample from the December 18, 2013 event. DOC decreased after peak discharge. The proportion of plant-derived biomarkers among the target compounds, %VEG, calculated from the molecular analyses ranged from 12 to 66%. The lowest values were recorded during base flow conditions while the highest values were recorded during peak flow (December 2013) and the early falling limb (March 2016). The lignin compositional ratio, C/V, ranged

Table 1. DOC and DOM molecular proxies in base-flow and high-flow conditions on the five investigated catchments

Sampling date/hour	Type	DOC*	%VEG	C/V	Sampling date/hour	Type	DOC*	%VEG	C/V
Montoussé catchment					**Naizin catchment**				
9/4/18 21:00	*P*	7.6	48	0.14	09/03/2016 02:31	*R*	8.9	46	0.23
10/4/18 13:00	*F*	6.3	43	0.07	09/03/2016 05:31	*R*	13.3	55	0.28
20/4/18 10:15	*B*	2.8	20	0.00	09/03/2016 07:01	*P*	13.0	63	0.29
					09/03/2016 08:31	*F*	12.0	66	0.36
Roujan catchment					09/03/2016 11:31	*F*	9.8	59	0.44
15/10/2018 06:49–14:40	*E*	8.2	32	0.71	10/03/2016 15:45	*B*	5.9	24	0.00
31/10/2018 01:59–14:37	*E1*	6.9	25	0.65	11/03/2016 16:25	*B*	3.8	12	0.00
31/10/2018 14:37–22:58	*E2*	5.3	25	0.30					
09/11/2018 04:51–22:24	*E*	26.2	23	0.65	**Strengbach catchment**				
26/11/18 10:00	*B*	4.5	5	0.00	20/07/2018 08:01	*B*	2.9	29	0.10
					20/07/2018 14:01	*P*	7.5	52	0.20
Capesterre catchment					20/07/2018 14:21	*P*	7.3	49	0.18
12/09/2018 09:50	*B*	0.8	4	0.07	20/07/2018 15:07	*F*	6.2	48	0.13
13/09/2018 09:50	*R*	2.7	32	0.15	20/07/2018 16:21	*F*	4.8	51	0.10
13/09/2018 17:50	*P1*	3.9	51	0.12					
13/09/2018 23:50	*P2*	3.1	38	0.07	18/09/2018 08:01	*B*	2.5	24	0.06
14/09/2018 05:50	*R3*	2.7	39	0.12	18/09/2018 15:05	*R*	7.9	56	0.28
14/09/2018 07:50	*P3*	2.8	47	0.12	18/09/2018 15:29	*P*	10.2	61	0.19
14/09/2018 17:50	*F*	1.8	24	0.14	18/09/2018 15:53	*F*	9.9	57	0.13
18/09/2018 12:55	*B*	0.7	11	0.11	18/09/2018 17:05	*F*	7.9	54	0.12
					19/09/2018 00:00	*B*	5.1	49	0.12
Naizin catchment									
03/12/2013	*B*	2.9	13	0.08	14/03/2019	*B*	2.0	25	0.14
18/12/13 19:11	*R*	8.0	20	0.17	15/03/2019	*R*	3.9	52	0.07
18/12/13 21:11	*R*	15.8	36	0.40	16/03/2019	*P*	2.8	24	0.07
18/12/13 23:11	*P*	24.4	49	0.57	17/03/2019	*F*	2.5	32	0.06
19/12/13 3:11	*F*	18.7	34	0.64	19/03/2019	*F*	1.8	26	0.10
19/12/13 5:11	*F*	19.4	40	0.62	02/04/2019	*B*	1.9	32	0.15

R: rising limb, P: peak flow, F: falling limb, B: baseflow, E: entire event.

* DOC in mg/L.

from 0.00 to 0.64. This ratio increased during the rising limb, the peak flow and the beginning of the falling limb to reach its highest values during the falling limb.

For the Capesterre catchment, the sampled event was characterized by high rainfalls and high discharges (>3.5 m^3/s) related to this catchment, classifying them as a flood event for this location. This event induced an increase in DOC from 0.8 to 3.9 mg/L (Figure 2C), which was in the range of previous DOC measurements [Lloret et al., 2013]. This highest value was recorded during the first peak discharge. The %VEG increased linearly with a discharge increase from 4 to 51%, resulting in the

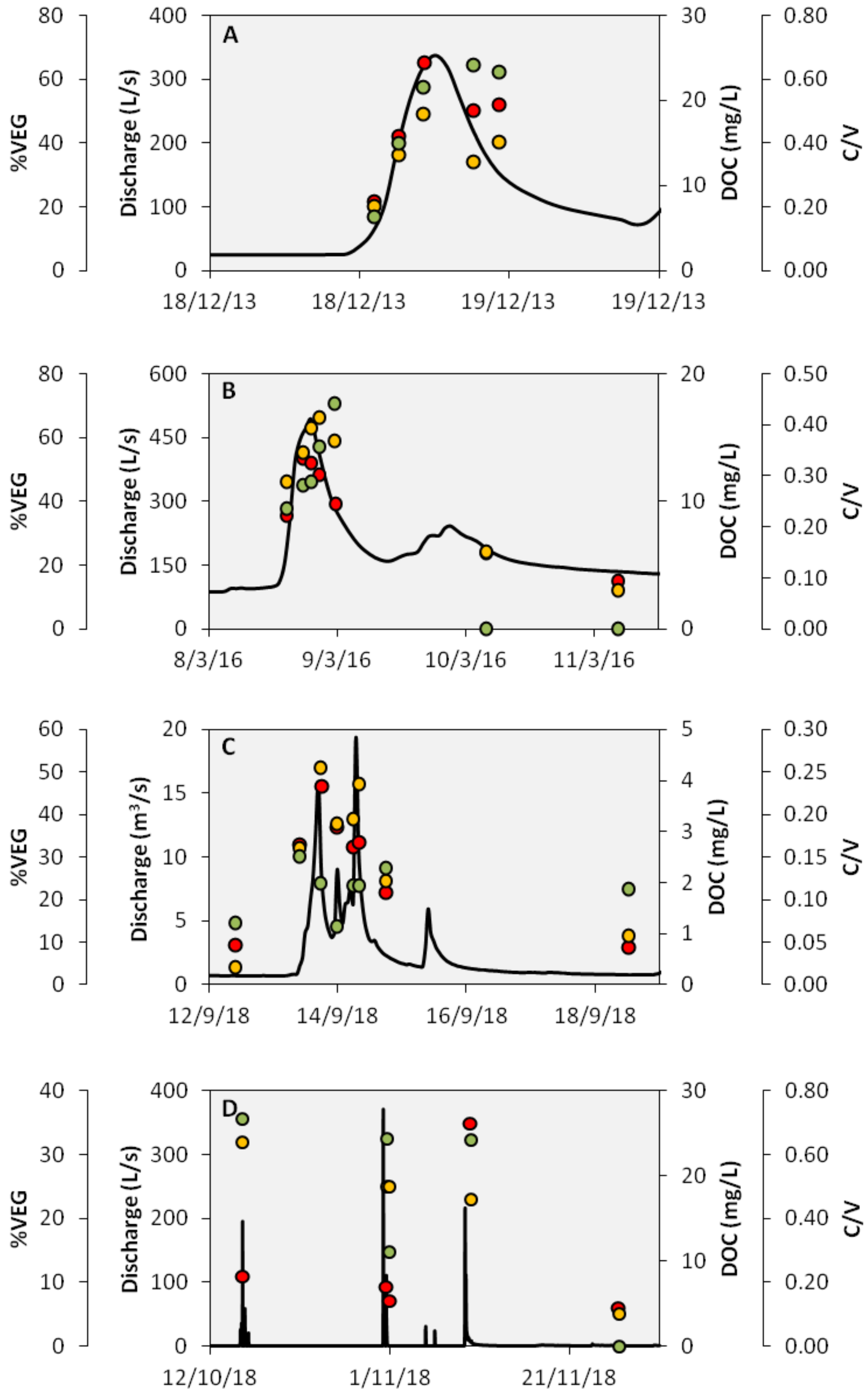

Figure 2. Evolution of the concentration of DOC (red circles) and the composition of dissolved organic matter (%VEG: gold circles and C/V: green circles) in the Naizin (A/B), Capesterre (C) and Roujan (D) catchments. (Continued on next page.)

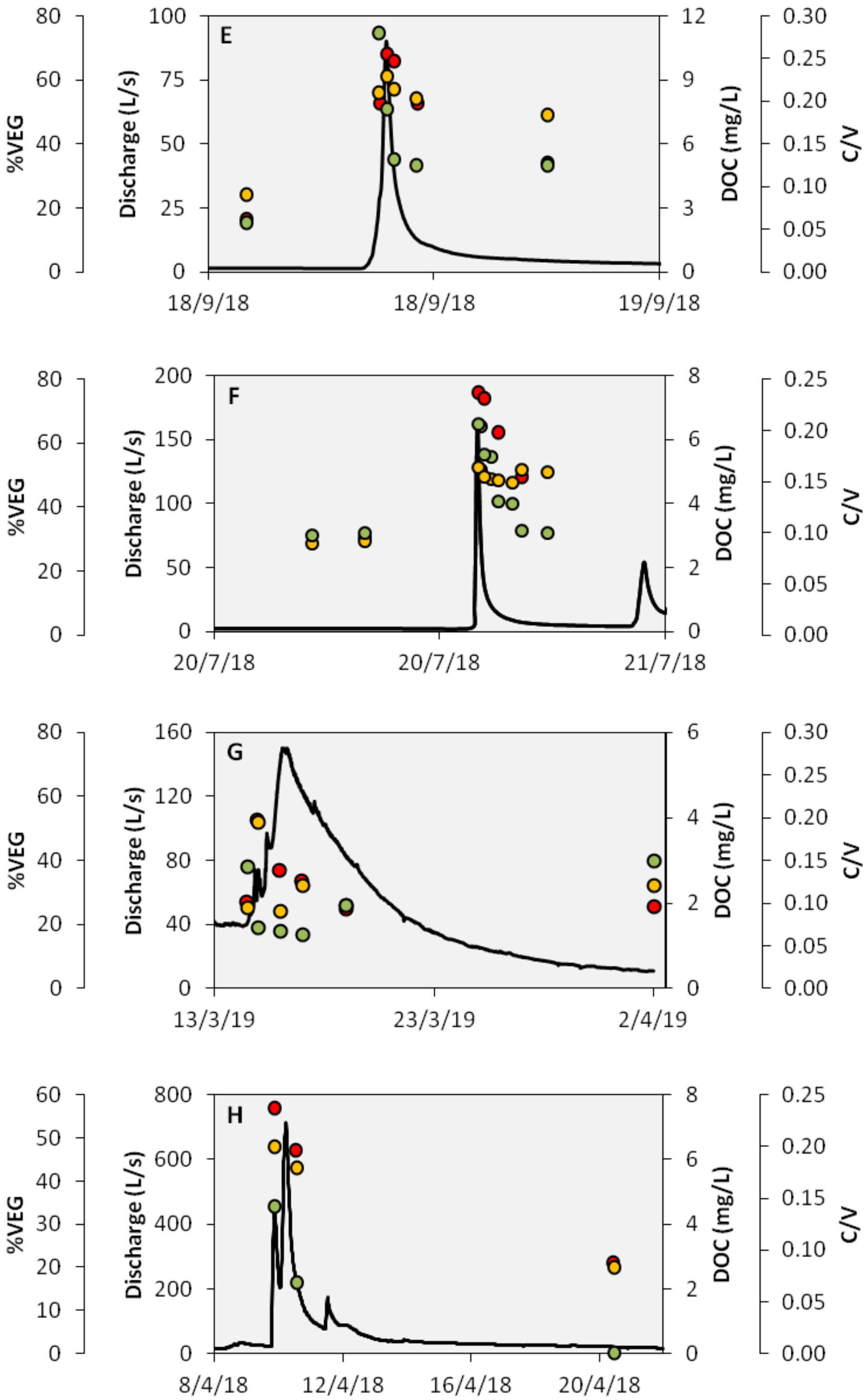

Figure 2 (cont.). Evolution of the concentration of DOC (red circles) and the composition of dissolved organic matter (%VEG: gold circles and C/V: green circles) in the Strengbach (E/F/G) and Montoussé (H) catchments.

absence of hysteresis (Figure 4E). The C/V ranged from 0.07 to 0.15. It increased during the rising limb of the first and third peaks and remained higher than the pre-event value even after the return to base flow conditions.

For the Roujan catchment, the four sampled events were characterized by moderate rainfall and discharge values, as compared to average values calculated for this catchment (Figure 2D). The rainfall events induced an increase in DOC up to 26.2 mg/L for the event on November 09, 2018, but also a 5-fold increase in %VEG on average and an increase in C/V from 0.00 during base flow to 0.30–0.71 (maximum value of 0.71 recorder during the storm event on October 15, 2018).

For the Strengbach catchment, the sampled events were characterized by three different precipitation dynamics related to this catchment: the first one corresponds to a short-term rainfall event (20 min) with high precipitation intensity (flood event on July 20, 2018), the second one is a quite short rainfall event (110 min) with medium precipitation intensity (flood of September 18, 2018) and the third one is a long rainfall (15 days) event with low precipitation intensity (flood event on March 16, 2019), the flow of which is due to a combination of rain and snowmelt. Each event was characterized by an increase in DOC but this increase was smaller for the winter event (March 2019) than for the summer events (July and September 2018). The temporal variation of the %VEG was quite variable depending on the events. During the summer events, the %VEG increased during the rising limb to reach its maximum at peak flow and then either remained stable or decreased slowly (Figure 2E, F). During the winter event, only the DOM sampled during the rising limb of the storm was characterized by a high %VEG; all samples collected during other storm flow conditions (i.e. peak flow and falling limb) showed a %VEG similar to the value found during base flow conditions (Figure 2G). In this catchment, the C/V ratio ranged from 0.06 to 0.28 (Table 1). During the summer events, this ratio increased with the discharge, reached its maximum at peak discharge (July 2018) or during the rising limb (September 2018), and then decreased rapidly during the falling limbs. During the winter event, the C/V ratio decreased from 0.14 to 0.06 and recovered a base flow value at the end of the event.

For the Montoussé catchment, the sampled event was characterized by moderate rainfall and discharge as compared to average values for this catchment. The rainfall event induced an increase in DOC, %VEG and C/V, with maximum values observed during peak flow conditions (Table 1, Figure 2H).

5. Discussions

5.1. *Are molecular results representative of the entire DOM compartment during storms?*

During storms, one of the main characteristics of DOM export is the increase in DOC concentration. The suitability of THM-GC-MS to provide representative information on the composition and origin of DOM during storms was determined by searching for correlations between the results at the scale of the entire DOM compartment (DOC concentration) and the results acquired at the molecular scale (sum of the concentrations of the target compounds including SOA, FA and PHE). The fairly good correlation between the two scales of investigation (r^2 = 0.66, $p < 0.001$; Figure 3) emphasized that the results of THM-GC-MS can be considered as characteristic of the DOM compartment. This type of correlation between these scales of investigation has already been described for qualitative results acquired at the DOM scale using different spectroscopic analysis (UV and fluorescence spectrometry) and different types of molecular results (biomarker analysis and high-resolution mass spectrometry) [Gandois et al., 2019, Hernes et al., 2013, Jeanneau et al., 2014, Zhou et al., 2020]. To our knowledge, this is the first time that this type of correlation is described using quantitative biomarker results.

Behind this correlation calculated with the data from the five catchments, it seems that the slope of the linear regression is catchment-dependent. It was calculated for three catchments (Capesterre, Naizin and Strengbach) for which the number of data was sufficient. The slope was 15, 21 and 31 μg of the target compounds per mg of organic carbon for the Naizin (r^2 = 0.5, $p < 0.01$), Capesterre (r^2 = 0.7, $p < 0.01$) and Strengbach (r^2 = 0.6, $p < 0.001$) catchments, respectively. This difference may be due to the geological contexts. The mineralogy of the sample may impact the yield of the THM reaction [Faure et al., 2006,

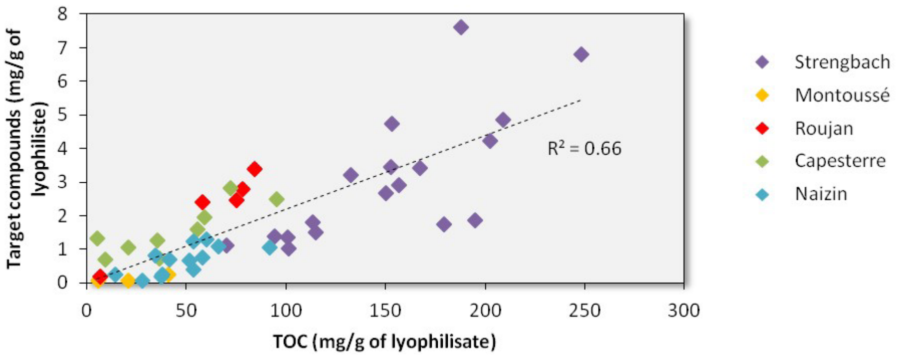

Figure 3. Relationship between the bulk scale of DOM (X-axis, concentration in OC in the lyophilisates) and the molecular scale (Y-axis, sum of the concentrations of target compounds). The regression line was calculated on the entire dataset.

Williams et al., 2019]. Mineral species whose thermal decomposition produces oxygen may oxidize organic compounds occurring in the sample [Lewis et al., 2015]. These correlations confirm that the compounds analyzed are ubiquitous compounds, whose sum varies with the size of the DOM compartment taken as a whole. Even if all the compounds analyzed represent less than 3% of the total DOC, the fact that their total abundance co-varies with the DOC content suggests that proportional variations between families of compounds very likely reflect significant differences in the nature and origin of the DOM compartment.

5.2. *How general are the modifications of the composition of DOM during high discharges?*

The proportion of plant-derived markers (%VEG) increased during high discharge events for all events along the investigated pedoclimates. Most of the plant-derived markers (98 ± 3%, mean ± SD) produced by the THM of DOM are phenols and benzoic acids coming from tannins and lignins. The remaining plant markers are composed of FA with more than 20 C atoms. These compounds are almost absent from DOM, whereas they occur in soil organic matter [Denis et al., 2017]. Since phenols and benzoic acids are the only aromatic molecules among the target compounds, this increase in %VEG corresponds to an increase in the proportion of aromatic compounds. Consequently, this is in accordance with the observation of a storm-induced modification of the spectroscopic properties of DOM [Broder et al., 2017, Hood et al., 2006] and with the results obtained by FT-ICR-MS [Wagner et al., 2019, Zhou et al., 2020] and lignin biomarker analyses [Eckard et al., 2017, Hernes et al., 2008] that have evidenced the same increase in the proportion of aromatic compounds among DOM during high discharge events for catchments under temperate climate. However, the opposite trend, with a decrease in the aromaticity, has been described for two storm events at the Capesterre catchment [Lloret et al., 2011] and for large storms in a tropical catchment in Costa Rica [Sánchez-Murillo et al., 2019]. Moreover, still in Costa Rica, the increase in DOM aromaticity has been recorded for one headwater catchment but not for an adjacent one, which has been attributed to different groundwater contributions [Osburn et al., 2018]. Consequently, and except for tropical catchments, taking into account the different pedoclimatic, geological and land use parameters which define the four analyzed temperate headwater catchments, this increase in the aromaticity of DOM during high discharges seems to be a general feature.

Not only does the %VEG and aromaticity increase during high discharge events but the composition of lignins changed as well. This was evidenced by the increase in the C/V ratio that was recorded for all events apart from the snowmelt event at the Strengbach catchment. In base flow conditions, this ratio was lower than 0.1 and was 0 for some samples since ferulic acid and coumaric

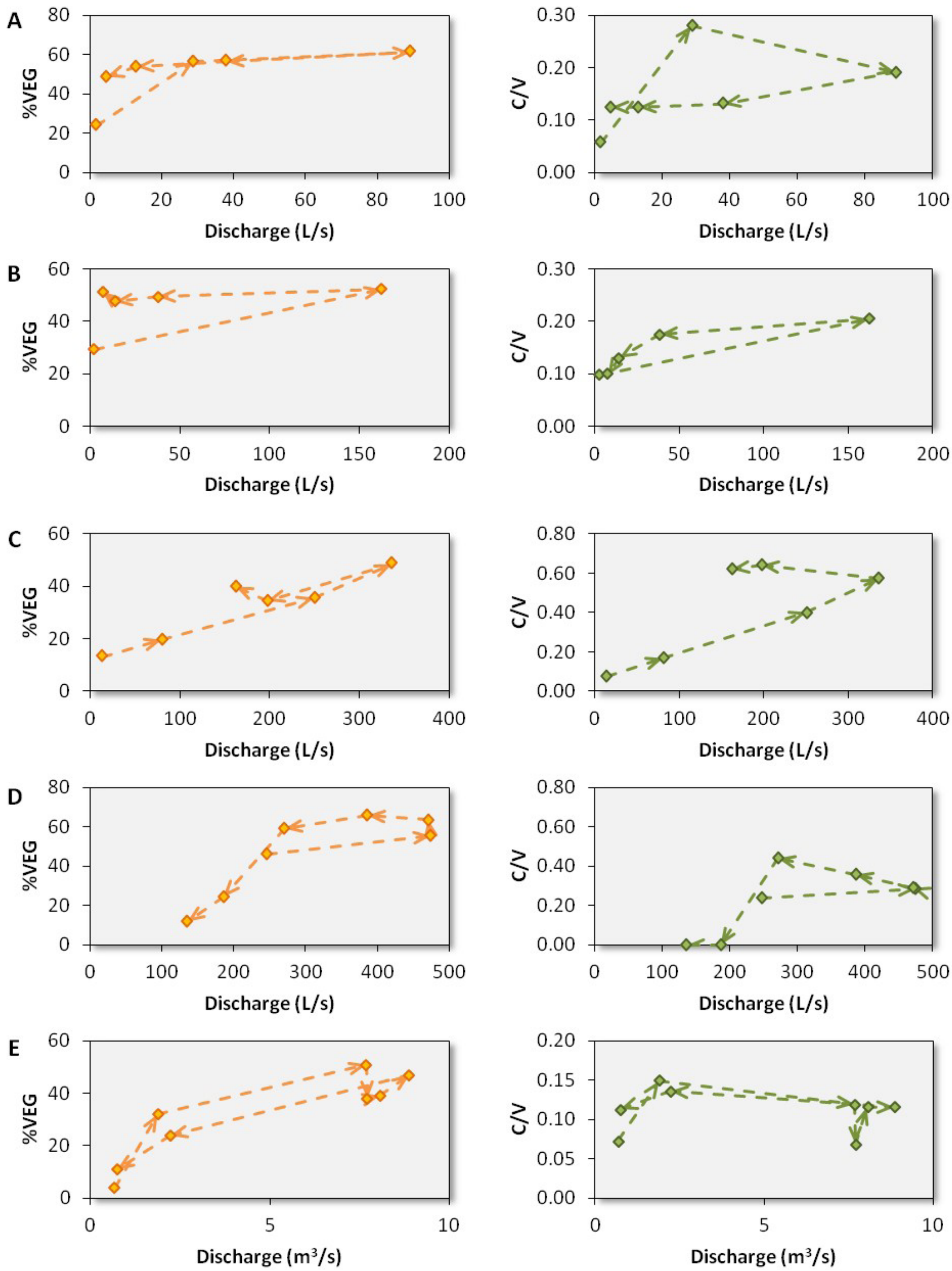

Figure 4. Relationships between discharge and compositional ratio (%VEG: gold diamonds and C/V: green diamonds) in the Strengbach catchment for the July 2018 (A) and September 2018 (B) events, in the Naizin catchment for the December 2013 (C) and March 2016 (D) events and in the Capesterre (E) catchment.

acid, the “C” compounds, were not detected. The maximum values changed from one catchment to another and ranged from 0.14 (Montoussé) to 0.71 (Roujan). The C/V ratio changes with the vegetal precursor [Hedges and Mann, 1979] and, for a given plant origin, is also a biodegradation proxy since C compounds are biodegraded faster than V compounds [Opsahl and Benner, 1995]. The inter-catchment differences observed for the maximum values are therefore probably due to differences in the composition of the vegetation. Moreover, by assuming uniform vegetation in these small headwater catchments, the increase in the C/V ratio during rain events could be due to the transfer of less biodegraded lignins. These increases in the C/V ratio during rain events are in accordance with previous investigations in the Naizin catchment [Denis et al., 2017, Jeanneau et al., 2015] and in three catchments in the USA [Dalzell et al., 2007, Eckard et al., 2017, Hernes et al., 2008, Ward et al., 2012]. However, there is no evidence for a statistically significant relationship with specific discharge for two tropical headwater catchments in Puerto Rico [Hernes et al., 2017a]. Consequently, although it was observed under eight different pedoclimates, more data on more catchments are necessary to determine if the increase in the C/V ratio during rain events can be considered as a general observation.

5.3. *Snowmelt as a shift from a general behavior?*

During the snowmelt event at the Strengbach catchment, the increase in DOC and %VEG was observed for only one sample during the rising limb of the hydrograph and the C/V decreased during the event. This was different from observations made for the other investigated high flow events induced by rainfall. It was even opposite with regards to the modification of the C/V ratio. The observation of an increase in DOC associated with an increase in aromaticity and in lignin biodegradation was in accordance with the export of DOM during a snowmelt in an upland forest in Vermont, USA [Sebestyen et al., 2008]. In this North-American catchment, the highest streamflow during snowmelt has been shown to exhibit the highest DOC concentrations but also the highest proportion of hydrophobic organic acids (HOA) and the lowest δ^{13}C-DOC. The HOA fraction has been characterized by high aromaticity [Wu et al., 2020] and a decrease in δ^{13}C has been associated with a higher amount of biodegraded OM [Kalbitz et al., 2003]. However, this contrasts with the observations from three catchments in the USA [Burns et al., 2016, Inamdar et al., 2011, Rose et al., 2023] where the export of aromatic rich DOM, monitored with the HIX fluorescence index, has continued even during the falling limb of the hydrographs. The increase in the aromaticity of DOM has been attributed to a shift in the water flow pathway from deep groundwater sources to increased contributions of infiltration and a lateral export of soil water during the early phase of snowmelt driven events resulting in the mobilization of aromatic-rich DOM from organic-rich surface horizons [Burd et al., 2018, Burns et al., 2016, Rose et al., 2023]. In the Strengbach catchment, the aromatic-rich DOM exported during the highest discharges was characterized by a lower C/V ratio, i.e. a higher amount of biodegraded dissolved lignins. This biodegradation may have occurred during soil thawing prior to the establishment of the connection between the surface horizons and the river and the export of DOM from the surface horizons. This may be due to microbial degradation, as the presence of active biomass has been demonstrated in temperate ecosystems under snow cover [Rindt et al., 2023] with a preponderance of fungal biomass [Zhang et al., 2014] that is known to biodegrade lignins [Haider and Trojanowski, 1975].

5.4. *What are the DOM transfer pathways during high discharge events?*

The modification of the DOM composition during rainfall has been attributed to the shift from aromatic-poor DOM coming from deep groundwater to aromatic-rich DOM mobilized from the surface horizons [Maurice et al., 2002, McGlynn and McDonnell, 2003]. Three sources have been suggested for the mobilization of aromatic-rich DOM characterized by an increasing C/V ratio: litter lixiviation, surface runoff and sub-surface runoff [Denis et al., 2017, Hernes et al., 2017b].

The shape (slope, rotational direction and size) of the relationship between the discharge and molecular proxy may provide valuable information about the source, timing and relative contributions of terrestrial DOM to rivers [Butturini et al., 2008]. Clockwise hysteresis is often associated with vicinal sources, while anticlockwise hysteresis indicates distant DOM sources or slow-flow pathways [Pellerin et al., 2011]. Among the present results, considering the number of samples and their distribution on the hydrographs, three catchments (Strengbach, Capesterre and Naizin) can be used to investigate this hysteretic character of the DOM composition.

For the Strengbach catchment, for both summer events, the %VEG increased with the discharge and remained high during the decrease, which could be interpreted as an anticlockwise hysteresis (Figure 4A, B). For these two events, the C/V ratio followed different patterns. For the July 2018 event, after an increase with the discharge, it decreased less rapidly than the discharge during the falling limb of the hydrograph, which could be interpreted as an absence of hysteresis or a light anticlockwise hysteresis. Conversely, for the September 2018 event, the C/V ratio reached its highest value before the peak of discharge and decreased quickly from the peak flow, resulting in a pattern that could be interpreted as a clockwise hysteresis. For the Naizin catchment, both events follow different trends for the %VEG and similar trends for the C/V ratio (Figure 4C, D). For the December 2013 event, the %VEG was highly correlated with the discharge ($r^2 = 0.87$, $p < 0.001$), which could be interpreted as an absence of hysteresis. On the contrary, for the March 2016 event, the %VEG remained higher than 50% even after the draw down and recovered base flow values (lower than 25%) the day after the event. This pattern may be characteristic of an anticlockwise hysteresis. For both events, the C/V ratio increased with the discharge to reach its higher values after the peak and remained elevated during the falling limb of the hydrograph before recovering base flow values the day after the event. These patterns could be in agreement with an anticlockwise hysteresis. In the Capesterre catchment, the %VEG proxy was highly correlated with the discharge ($r^2 = 0.79$, $p < 0.005$), which could be interpreted as an absence of hysteresis. Lastly, the C/V ratio was not correlated to the discharge during the investigated event ($r^2 = 0.01$, $p = 0.77$) (Figure 4E).

These data highlight the inter- and intra-catchment diversity of the DOM composition *versus* discharge relationships, which is in accordance with the diversity of hysteresis shapes observed for three catchments in Vermont (USA) using submersible online UV Vis spectrometer probes and, more specifically, the spectral slope, as it is a proxy of the mean molecular weight of DOM [Vaughan et al., 2019]. Linear correlations and clockwise hystereses are characteristic of vicinal sources of fast-flow pathways such as runoff [Pellerin et al., 2011]. For the Capesterre catchment, soil erosion has been suggested as the main source of DOM during rain events using δ^{13}C-DOC [Lloret et al., 2016], which is in agreement with the linear correlation between %VEG and discharge. The anticlockwise hystereses defined by %VEG, as observed for the Strengbach and Naizin catchments, are in accordance with the observations at the Willow Slough catchment (California, USA) using SUVA at 254 nm and the lignins concentration [Eckard et al., 2017] and for nested catchments in Connecticut (USA) using FT-ICR-MS [Wagner et al., 2019]. At the Naizin catchment, this kind of anticlockwise hysteresis has already been observed for the molecular composition of DOM, including the %VEG and the C/V ratio [Jeanneau et al., 2015] and the shape of the hysteresis has been shown to be event-dependent. One assumption that has been put forth to explain this variability is the shift between two DOM transfer pathways activated during rain events: surface solubilization by runoff followed by sub-surface erosion through a mechanism of colloidal mobilization [Jeanneau et al., 2015]. This second mechanism has been shown to be driven by antecedent rainfall conditions [Denis et al., 2017]. The C/V ratio can be used as a biodegradation proxy for lignins, where a higher C/V ratio is associated with lignins that are less biodegraded. DOM with a high C/V ratio could then be associated with a high molecular weight. An anticlockwise hysteresis for the C/V ratio in the Naizin catchment could then be in accordance with the observations of DOM export from an agricultural catchment in Vermont (USA) characterized by the mobilization of high molecular weight DOM with an anticlockwise hysteresis as determined using the spectral slope ratio calculated on UV spectra [Vaughan et al., 2019].

These intra- and inter-variabilities of the relationships between the DOM composition and discharge have highlighted a variability in the proportion of DOM coming from the different transfer pathways. These proportions may be controlled at the catchment scale by antecedent moisture, rainfall characteristics, groundwater dynamics and land-use and, at a larger scale, by pedoclimatic conditions. To improve our understanding of the transfer of DOM at the soil-stream interface, researchers would need to acquire data integrating these drivers. However molecular analyses are expensive, time-consuming and have an important environmental impact. The correlations between spectral indices and molecular composition [Baek et al., 2019, Eckard et al., 2017, Wagner et al., 2019, Zhou et al., 2020] emphasize that in situ probes deployed in critical zone observatories are valuable tools to document this variability while avoiding these drawbacks of molecular analyses.

6. Conclusions

The general behavior of the modifications in the composition of DOM exported from five headwater catchments during high flow events was investigated across a pedo-climatic gradient. The composition of DOM was analyzed by THM-GC-MS through the evolution of two molecular proxies.

The %VEG is the proportion of plant-based markers among the target compounds, which can be considered here as an aromaticity proxy. All the investigated high flow events for this study were associated with an increase in the %VEG. This observation was in line with several observations throughout the world in headwater catchments using a large panel of analytical methods ranging from the most common UV spectroscopy to the most precise FT-ICR-MS. However, it was not systematically observed for high flow events induced by rainfall in arctic and tropical catchments and by snowmelt. Based on all these observations, it seems reasonable to conclude that the increase in DOM aromaticity exported in hydrographic networks during rainfalls is a common feature to all catchments under temperate climate, independently of their pedological, hydrological and land use contexts. More data are needed to understand the specific behavior of arctic and tropical catchments as well as events generated by snowmelt.

The second investigated proxy was the C/V characteristic of the lignin composition. High flow events induced by rainfall were all associated with an increase in the C/V ratio, which was interpreted as the mobilization of less biodegraded dissolved lignins. This present work increases the number of catchments where this increase in the C/V ratio during high flow events was observed from 4 to 8. This number is obviously too small to be able to conclude that this characteristic is general and shared across all catchments worldwide. Further work will need to be carried out that includes different pedoclimates as well as intra-variability to verify whether this is a common feature. The present study also highlights the specificity of high flow events induced by snowmelt under a temperate mountainous climate with a decrease in C/V. This observation may be due to biodegradation processes during the soil thawing prior to the establishment of the connection between the surface horizons and the stream and the export of DOM from the surface horizons. Further work is needed to investigate the biogeochemistry of soil DOM under a snowy blanket and during snowmelt.

The relationships between discharge and molecular proxies tend to highlight that the modifications in the DOM composition observed in the Capesterre (tropical) and Strengbach (temperate mountainous) catchments were induced by the mobilization of aromatic-rich DOM through surface runoff, while in the Naizin (temperate oceanic) catchment, they were due to a combination of surface runoff and subsurface circulation. The relative proportions of these two processes in DOM export is probably driven by a combination of topography, meteorology and seasonality.

Increasing DOM aromaticity while decreasing the biodegradation state of dissolved lignins would result in more hydrophobic DOM. Consequently, the export of this more hydrophobic DOM may be a hot moment for the mobilization of hydrophobic organic micropollutants and metallic pollutants. Understanding these exports is therefore a key issue for water quality. However, it is necessary to improve our understanding of the DOM transfer pathways at the soil-stream interface and their dependence on topographic and hydroclimatic parameters. The correlations between spectral indices and the molecular composition that are described in the literature emphasize that in situ probes deployed in critical zone observatories are valuable tools to document these points.

Declarations of interest

The authors do not work for, advise, own shares in, or receive funds from any organization that would benefit from this article, and have declared no affiliation other than their research organizations.

Acknowledgements

The authors would like to thank the research infrastructure OZCAR for its financial support and the technical staff of the different observatories and laboratories, whose energy and commitment make this work possible.

Supplementary data

Supporting information for this article is available on the journal's website under https://doi.org/10.5802/crgeos.272 or from the author.

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