Spatial and temporal variations of dissolved organic matter (DOM) dynamics in a disturbed *Sphagnum* peatland after hydrological restoration

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A: Aim of the study

Peatlands act as global sinks of atmospheric carbon (C). However, global change has been shown to affect dissolved organic matter (DOM) dynamics. Monitoring and characterization of dissolved organic matter, particularly using its fluorescent and optical properties, can be a relevant tool to understand ecosystem dynamics under changing environmental conditions. This study aims to **i) target differences between disturbed and reworked peatlands** and, **ii) to figure out efficient indices in order to assess functioning of peatlands.**

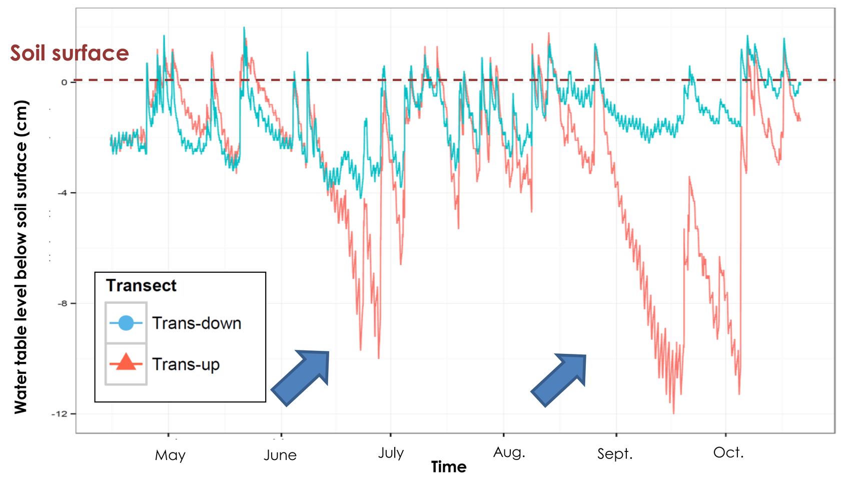

Fig.2: Fluctuations of water table since restoration

B: Study site

The investigated site was La Guette peatland (France, N 47°19'44", E 2°17'04", alt. 154m), which hydrological conditions are influenced by a road crossing over its former area. The road drain accelerates peat drying, thus favouring vascular plants settlement to the detriment of specific flora of peatlands (i.e. *Sphagnum spp*).

Hydrological restoration was undertaken in February 2014. It consisted in building thresholds to slow down drain runoff and to promote soil rewetting (see Fig. 1).

Since restoration work, most important water table drawdowns have been recorded on June and September 2014. Water table fluctuations are stronger in Trans-up than in Trans-down (6 cm vs 15 cm) (see Fig.2).

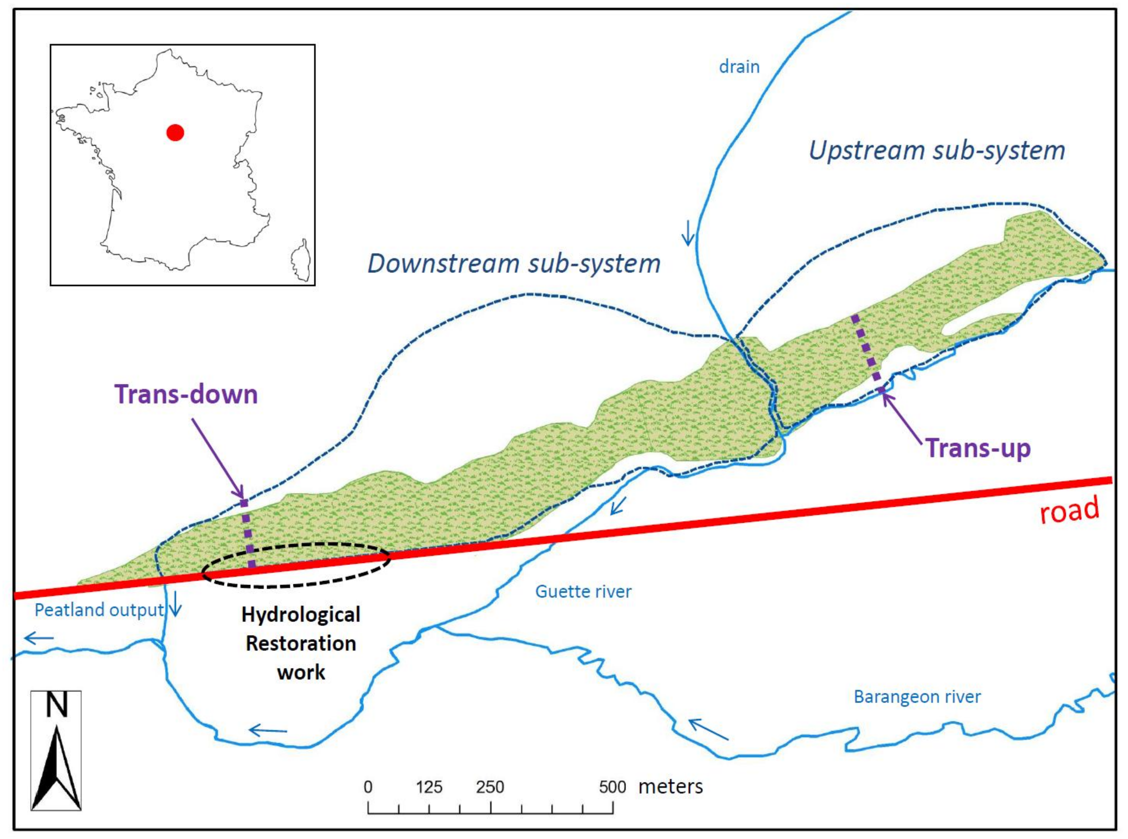

Fig. 1: Investigated site configuration

C: Sampling and analyses

Two transects of piezometers were settled in two independent hydrological sub-systems: Trans-up and Trans-down. Trans-down is supposed to be influenced by the hydrological restoration, while Trans-up is not. These transects cross the peatland and follow water flow direction.

Water was sampled in April, May, June, July, September and November 2014 in these piezometers and analysed by following techniques:

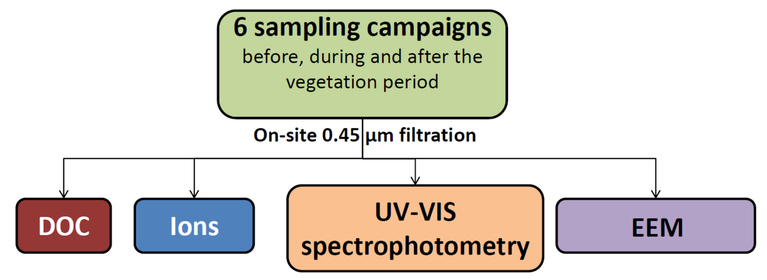

Fig. 3: Sampling and analyses

Absorbance was measured by UV-VIS spectrophotometer. Excitation–emission matrices (EEM) were undertaken to characterise fluorescent DOM (FDOM). PARAFAC algorithm was used to treat EEMs. Several indices were calculated from these analyses (see. Tab.1).

Parameter :	Technique :	Calculation :	Meaning :
SUVA 254	UV-VIS spectrophoto-meter	$\frac{Abs254}{[DOC]}$ x100	Degree of aromaticity of DOM
Aromaticity (%)		6.5 x SUVA + 3,6	
S(275-295) (nm^{-1})		$Slope_{Abs275\_Abs295}$	Negatively correlated with molecular weight of DOM
SR		$\frac{Slope_{Abs275\_Abs295}}{Slope_{Abs350\_Abs400}}$	
E2/E3		$\frac{Abs250}{Abs365}$	Negatively correlated with size of macromolecules
E4/E6		$\frac{Abs465}{Abs665}$	Negatively correlated with size of macromolecules, correlated with %C, % O, acidity and amount of COOH groups
HIX	Spectro-fluorometer	$\frac{L}{H}=\frac{Em(300:354)}{Em(435:480)}$ (λ_{Ex} =250 nm)	Increases with humification (C/H ratio), molecular mass and aromaticity
Ig/Ia		$\frac{Int\ \gamma}{Int\ \alpha}$	Contribution of protein-like material (microbial activity) in DOM
Ia'/Ia		$\frac{Int\ \alpha'}{Int\ \alpha}$	Contribution of recent and low humified material in DOM
Ca/Mg	Ion chromatography	$\frac{[Ca^{2+}]}{[Mg^{2+}]}$	Assess oligotrophy of peatland when compared to rain water reference

Tab. 1: Calculated parameters and indices and their meaning from literature

D: DOM Fluorescence

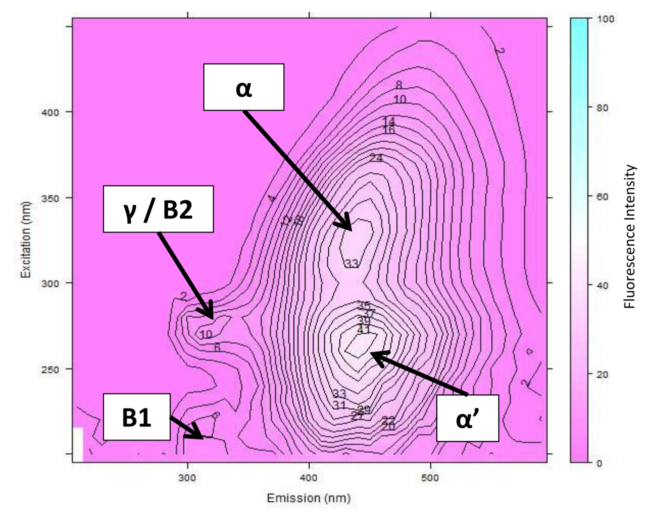

Fig. 4: Example of EEM from *La Guette* peat water

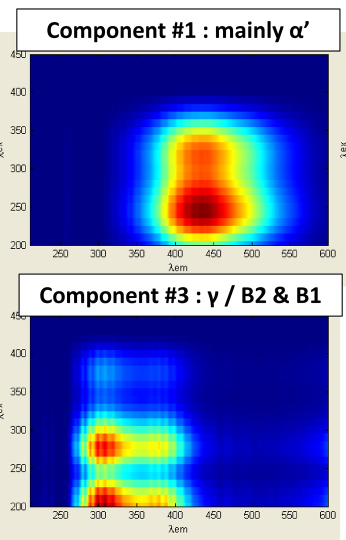

Fig. 5 : Results of PARAFAC decomposition on EEMs from La Guette peatland

Measured emission/excitation couples similar to those found in peat standards and references (International Humic Substances Society).
97% of EEMs are explained by following fluorophores:
- α (sub-humic material),
- α' (sub-humic + recent material),
- γ / B2 and B1 (protein-like).

E: Temporal variations

Amplitude of DOC concentrations and humification of DOM are globally more important in Trans-up than in Trans-down. SR shows that DOM would consist of smaller molecules in Trans-up than in Trans-down from September.

Aromaticity (calculated by $SUVA_{254}$) is not correlated with other indices, even these calculated from absorbance measurements. E2/E3 is correlated with SR only in Trans-down. E4/E6 is not correlated with SR although they are expected to be related to the same parameters in the literature (see Tab.1).

Contribution of less humified recent material and microbial degradation processes decrease until August and then increase during main water table drawdown. Humification falls also in September. These changes are stronger in Trans-up where drawdown is more important than in Trans-down showing higher reactivity of upstream system.

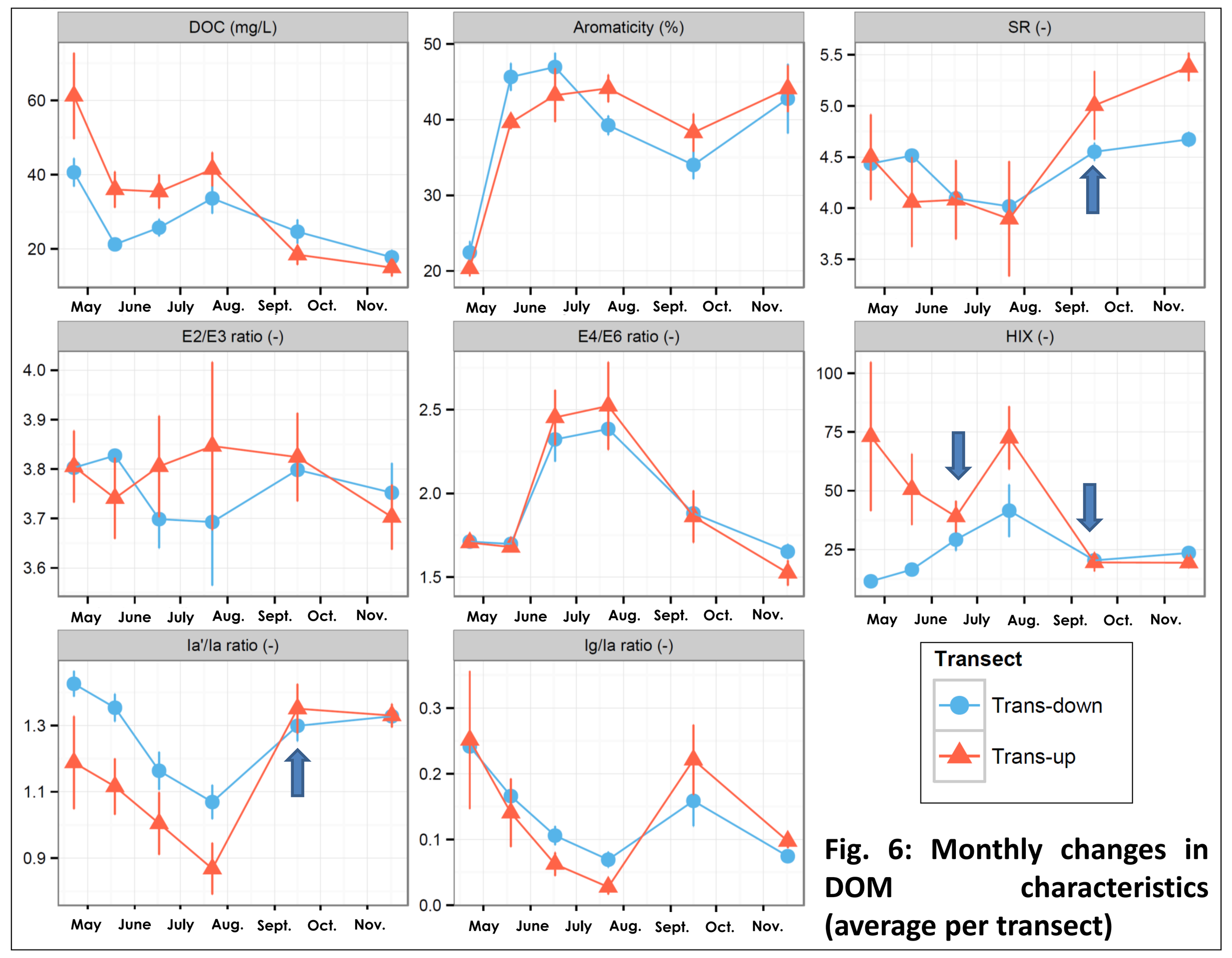

Fig. 6: Monthly changes in DOM characteristics (average per transect)

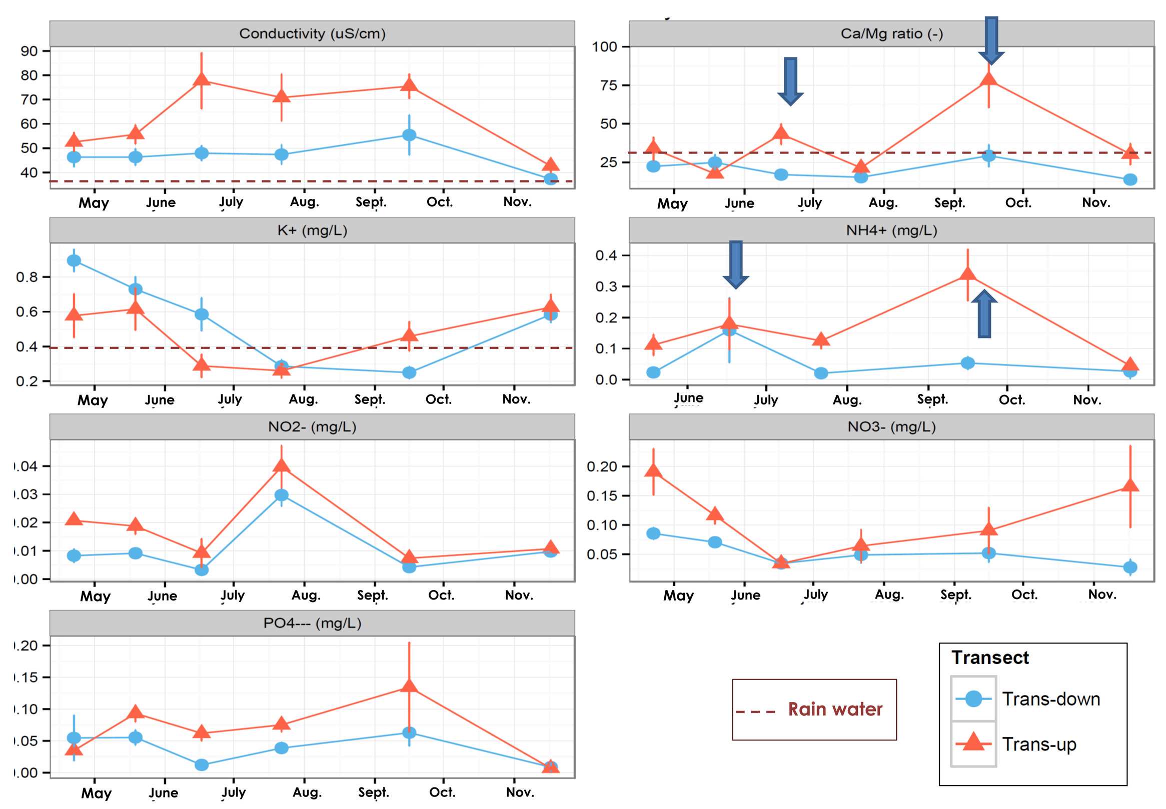

Fig. 7: Monthly changes in peatwater geochemistry (average per transect)

Conductivity and ionic concentrations show that Trans-down is globally more oligotrophic than Trans-up. In the latter, variations of Ca/Mg ratio, especially during main water table drawdowns (blue arrows), suggest that a new resource of water (potentially groundwater instead of rainwater) is solicited during main drawdowns in this system.

Concentrations of nitrogenous compounds, phosphate, and potassium in peat water, related to vascular plants, are higher in Trans-up during autumn. This can be related to more important decomposition processes of vegetal material and aerobic microbial activities (eg., nitrification, ammonification) than in Trans-down.

F: Spatial variations

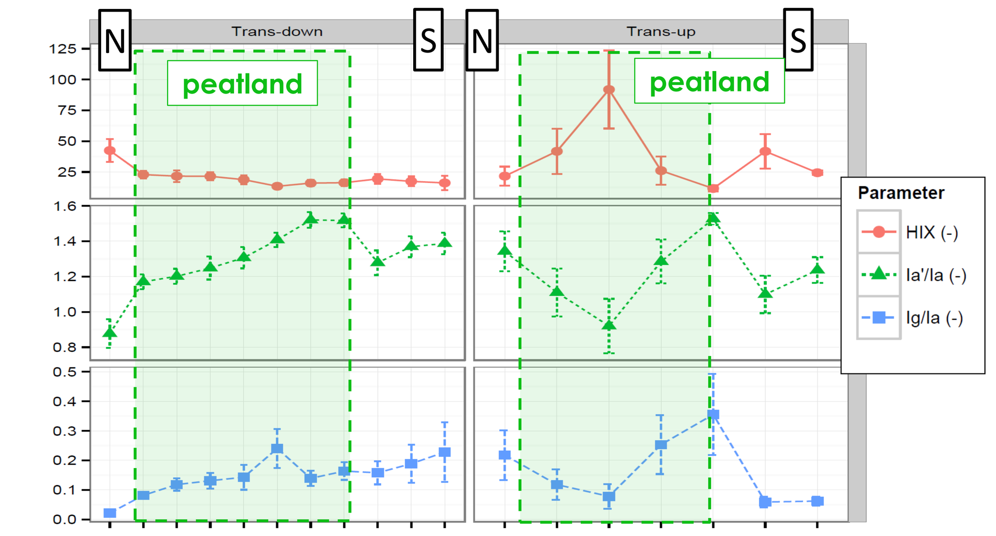

Fig. 8: Spatial variations in 3D fluorescence of DOM

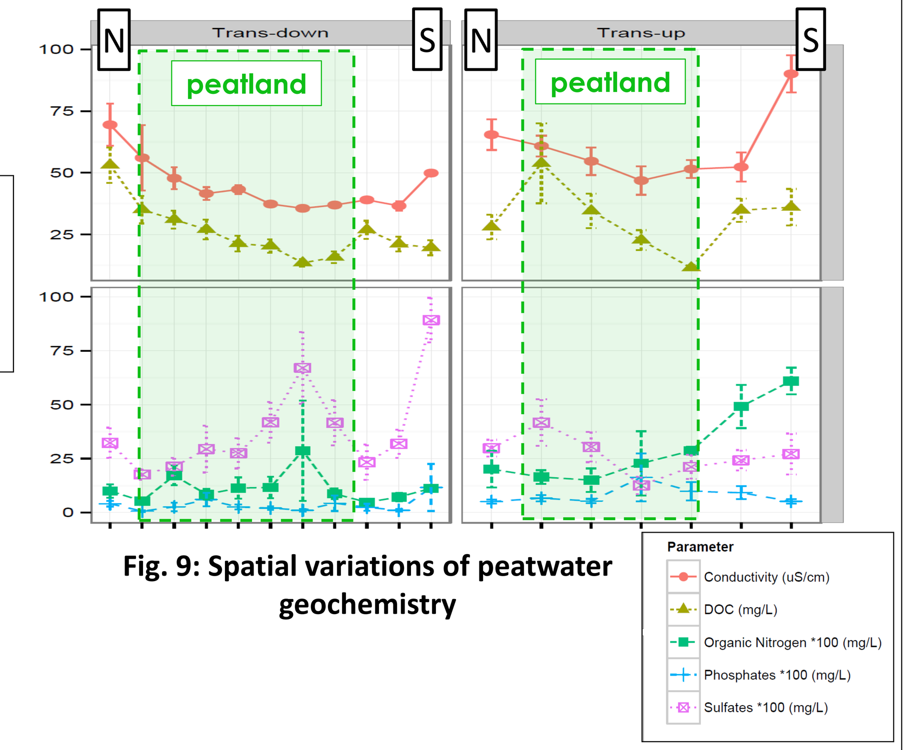

Fig. 9: Spatial variations of peatwater geochemistry

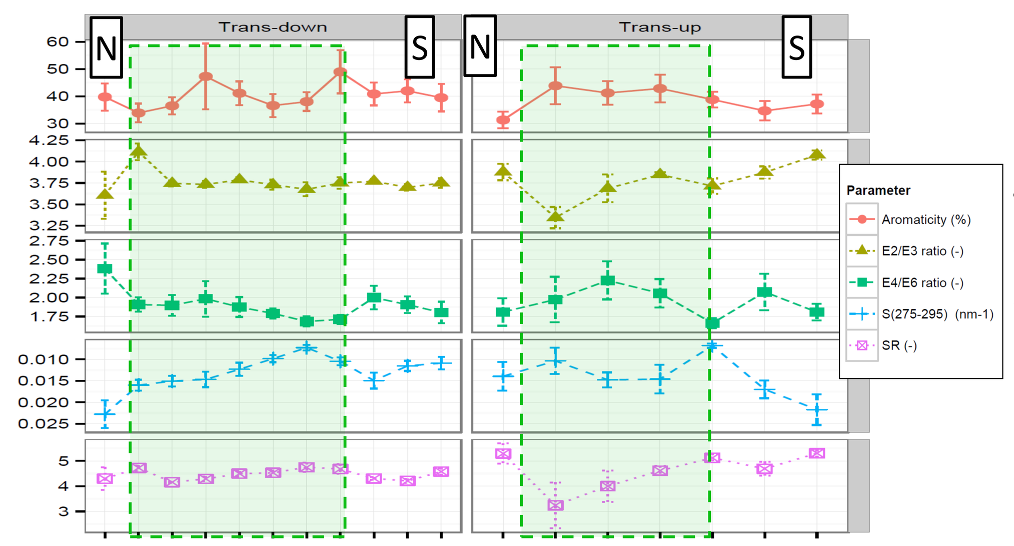

Fig. 10: Spatial variations in UV-VIS properties of DOM

E2/E3 is correlated with SR and so is E4/E6 with HIX. S(275-295), Ia'/Ia and DOC are correlated. However, HIX calculated from EEM, E2/E3 and aromaticity (%) calculated by $SUVA_{254}$ are not correlated although they are expected to be.

In both sub-systems, peat water looses DOC and conductivity while crossing the peatland following flow direction. Upstream and downstream systems seem to work as sinks of DOM. Changes in vegetation can be seen as breaks in gradients of several parameters (eg., DOC, Ia'/Ia). Nitrogenous compounds and sulfates show different patterns between the two systems. This suggests a spatial variation of microbial activity between two systems.

In Trans-down, contribution of recent and less humified material in DOM and microbial activity regularly increase while crossing peatland. Molecular weights are quite constant.

In Trans-up, humification degree, part of recent material, contribution of microbial activity and molecular weights show wider spatial variations than in Trans-down.

G: Conclusions

This study emphasizes the following points :

1- There are differences between reworked and non-reworked systems in terms of DOM composition and peat water geochemistry. Both systems seem to work as DOM sinks. Nevertheless, downstream system, influenced by hydrological restoration work, is more stable seasonally and spatially in terms of geochemistry and DOM properties than upstream system. Further sampling campaigns and analyses should however be proceeded in order to confirm the impact of hydrological work.

2- Indices calculated from fluorescence and other optical properties of DOM could be interesting tools in order to monitor spatial and temporal changes in DOM composition in peatlands, especially HIX and ratios of fluorophore intensities. However, they must be carefully chosen and interpreted, especially those calculated from absorbance measurements such as aromaticity inferred from $SUVA_{254}$. Spatial heterogeneity of DOM composition also should be taken into account.

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