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RESEARCH ARTICLE **OJER0302001-404**

ESTIMATION OF DISSOLVED ORGANIC CARBON IN RIVER FLOWS AND IDENTIFICATION OF THE RELATIONSHIPS BETWEEN PEAT HUMIC FRACTIONS AND PHYSICOCHEMICAL QUALITIES

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ABSTRACT

Peatlands are wetlands that contain higher amounts of carbon, some of which is often released with water in dissolved form, especially when land use change occurs. However, peatland carbon is mostly stabilized in humic fractions where it forms complexes with metallic elements. This study sought to measure the levels of dissolved organic carbon (DOC) in rivers and analyze the link between physicochemical parameters and humic fractions along the Buhandanda and Lushala peat profiles. Inductively-Coupled Plasma Optical Emission Spectrometry, chemical fractionation followed by sulfochromic oxidation, and dosing by indirect chemical oxidation were used to determine major geochemical elements (MGE), humic fractions (HS), and DOC, respectively. Average MGE concentrations were 4.1±1.4, 3.6±0.5, 2.8±0.6, 1.8±0.7, 1.1±0.4, 0.3±0.1, 0.1±0.0, 0.5±0.3, 0.1±0.0, 0.03±0.0, 0.03±0.0 and 1.9±0.9, 3.6±0.8, 2.5±0.6, 2.0±0.5, 1.1±0.4, 0.3±0.0, 0.09±0.01, 0.18±0.1, 0.06±0.04, 0,02±0.0 for Ca, Fe, Si, Al, S, Ti, K, Mg, Mn, Na for Lushala and Buhandanda, respectively. Fulvic acid (FA) fractions were constantly higher than humic acid (HA) from 0 to 80 cm and lower beyond on Buhandanda peaty profile. FA was also higher than HA for Lushala peat except for depths 20, 90, 140, and 200 cm. Humin (HU) was the highest fraction on the two peatlands. Humification index (HI) and degree of transformation (DT) of HS had values of the same order of magnitude (from 0.32 to 2.43). No association was found between physicochemical properties and HS, except for FA and Fe, Ca, S, Mg, Mn, Se on Lushala peat. DOC showed a downward trend from entry to exit of peatlands. The two sites were not statistically different. Mountainous peat can contain high levels of MGE and loses a tiny fraction of its carbon with runoff waters.

Keywords: *Carbon, Fractionation, Geochemistry, Peat, River.*

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INTRODUCTION

Soil fertility in tropical Africa is cited as one of the major factors underlying low agricultural yields (Mutonkole, 2013). However, fertile soils, already scarce, are under increased pressure from generally poor populations (Bekunda et *al*., 2010). Thereby, conventional land use and management practices decrease organic matter (OM) quantity and quality (Tavares and Nahas, 2014; Ukalska-jaruga et *al.,* 2019), which plays a critical role in soil's fertility (Souza et *al.*, 2019). A study demonstrated the link between the dynamic change of chemical fractions of OM and the tillage (González et *al*., 2003). Indeed, the authors observed the loss of soil buffer capacity, drop in water retention, and nutrient low availability for plants after consecutive ploughings. These soil properties are known to be provided by OM. Thus, the carbon around which these chemical fractions are formed contains valuable information for the development and evaluation of sustainable agricultural practices. For peatlands already converted into cultivated land, it is necessary to choose agricultural practices compatible with environmentally sustainable management (Ukalska-Jaruga et *al.,* 2019).

In the Democratic Republic of Congo (DRC), several mountain peatlands are cultivated to meet the challenges of poverty and lack of fertile land. To facilitate the cultivation of these peatlands, smallholders carry out deforestation and build networks of drainage canals (Kabony 2012). This situation is the basis of peat deposition disruption and the increase in carbon exports out of peaty systems (Hirano et *al.* 2012). Currently, no information is reported on the form and amount of carbon exported from the cultivated and drained mountainous peatlands in Congo. With the recent discovery of the largest tropical peatland straddling the two Congo, some works (Dargie et *al*. 2017, Dargie et *al.* 2019; Biddulph et *al*. 2021) have however focused on the extent, the reserve of carbon, or even the risks to which peatlands are exposed. With the growing concern about the sustainable management of peatlands in the context of climate change, it is essential to assess the carbon rate exported by waters and to understand its behavior through different humic fractions of OM. Furthermore, soil organic carbon (SOC), which is a major component of OM, contains humic (HS) and non-humic (NHS) substances characterized by different turnover times and physicochemical properties (Ukalska-Jaruga et *al.* 2019). HS is considered to be more stable than NHS in soil because they form complexes with metals and hydrophobic chemicals (Wijesinghe et *al.*, 2020). Thus, peat chemical fractionation is essential to identify the mobility and reactivity of SOC in the context of land use change (Gosch et *al.* 2019). In addition, carbon losses occur in the dissolved form by leaching due to biodegradation and photochemistry/photooxidation (Reyes and Crisosto, 2016). Carbon losses, often with CO_2 emission, can shift the carbon balance of peatlands from the sink to the source (Marshall et *al.* 2021).

Until now, there is not any published study that brings back the relationship between peat soil conditions, OM accumulation, and humic fractions for Buhandanda and Lushala sites. The lack of data is particularly observed on the effect of soil physicochemical properties, and natural plant communities on the OM quantity and quality. This study hypothesizes that: (1) The OM fractional composition depends on local conditions but also land management practices; (2) the low-weight compounds molecular, such as FA, are used as trace element vectors in the soil solution, while the compounds of high-weight molecular, as HA, function like "well" for the polyvalent cations; (3) peatlands serve as a source of DOC to the downstream hydrological system. The results of this study will be useful for anticipating measures for the restoration and sustainable management of cultivated tropical peatlands.

This study aims to investigate the carbon displacement and its proportion in different mountain peat humic fractions of Buhandanda and Lushala. The objectives are (1) to split humic fractions and evaluate their quantities; (2) to examine the relationships between physicochemical properties and humic fractions using principal component analysis (PCA) (3) to determine DOC concentration of river waters upstream and downstream of Buhandanda and Lushala peatlands.

MATERIALS AND METHODS

STUDY AREA

The study was carried out in two mountainous peatlands in Kabare territory, south Kivu province, Democratic Republic of Congo (DRC), with GPS (Garmin GPSMAP 78, precision< 10 m (33 pi) of 2 16' 17.3" S; 28 49' 32.1" E and 2 14' 44.9" S; 28 48' 28.6" E, measuring 1,607 and 1,679 m above the sea level for Buhandanda and Lushala, respectively. Three to 4 decades earlier, both sites experienced degradation of their peat through deforestation and the construction of drainage canals. This has been the cause of increased OM decomposition to the detriment of productivity. This potentially releases more carbon from these sites. Two climatic types are observed in the region: the equatorial climate (Cw) with a dry season hardly exceeding 1 month and the tropical type (Aw) with a dry season of up to 3 months (Kottek et *al.*, 2006). The average annual temperature is 18.5 °C, with a minimum of 17.1 °C and a maximum of 20.2 °C between 2017 and 2020 (Metelsat, unpublished). Mean annual precipitation is 129.5 mm during the same period. Between 1,500–1,700 m altitude, the mesophilic forest was widespread but has disappeared today and been replaced by subsistence agriculture. The partial water supply, since another part comes from rainfall, is the work of the Tshongoloka, Kalehe, Kanamukongo, and Kalengo, Lottery rivers for Buhandanda and Lushala, respectively.

The physicochemical properties of Buhandanda and Lushala peats (Table 1), obtained in a previous study in the press, were used to examine the relationships with peat humic fractions. Data were obtained as follows:

Assays were performed on 1 cm thick sub-samples extracted from three short cores (70 cm) per site, at 2 cm intervals for the upper 15 cm and 5 cm intervals for the remainder. For long cores (200 cm), sub-samples of the same thickness (1 cm) were extracted at 10 cm intervals. Sorting was necessary to verify the peat nature of the sites because no study demonstrating it was found. This choice was also made to reduce the cost of analyses.

The potentiometric measurement of pH was carried out in peat/H_2O and peat/KCl suspensions at the ratio of 1:5 at room temperature (Mulaji 2011). To do this, 10 g of peat collected at 5 depths (10-20, 20-40, 50-60, 70-80, and 90-100 cm) were first dried at 105°C for 7 hours, then sieved and stirred in an Erlenmeyer flask containing 50 mL of water/KCl (1M) for 2 hours. The pH measurement was made on the supernatant after having rested for 30 min, using the FiveEasy F20-Standard Kit Benchtop pH Meter - Mettler Toledo. Total nitrogen (TN) and organic carbon (OC) were determined according to Belyea and Warner (1996) using a Shimadzu TOC-VCSH Total Organic Carbon Analyzer. Bulk density and water content were performed on the sub-samples after drying at 105°C according to

Chambers et *al*., (2011). For determining the loss of ignition and ash contents, samples were burned at 550 °C according to Könönen *et al.*, (2015). Two peat slices 1 cm thick each were centrifuged together for 10 min at 3,500 rpm in a 0.2 µm Teflon filter to collect pore water. Nitrate (NO_3^-) concentrations were measured in the extracted porewater by colorimetry according to Tréguer and Le Core (1975). Additional samples of porewater obtained by the above-described procedure were used for the determination of phosphate (PO_4^{-3}) concentration according to Grasshoff (1983). Two peat samples of 10 g each were collected at 0-5, 5-10, 10-20, 30-50, and 80-100 cm depth, one of which was dried at 105°C and the other kept moist to mix it with 200 mL of an aqueous solution based on Calgon detergent. The samples were alternately agitated, washed with HCl (2%), sieved, and evaporated to determine the fiber content according to Sneddon et *al*., (1970). The results of these procedures are presented in Table 1.

Table 1: Physicochemical properties of Buhandanda and Lushala peats

		pH Kcl	pH H_2O	[NO3] (mgL^{-1})	[PO4] (mgL^{-1})	[N] (%)	[C] (%)	[C/N]	BD (gcm^{-3})	H (%)	Fiber (%)	Ce (%)
B	E10-20	3.41	3.55	0.87	0.018	2.51	47.68	19.59	0.32	70.08	48	24.89
	E20-40	3.21	3.5	0.38	0.004	2.39	48.72	21.61	0.26	74.76	39.75	17.73
	E50-60	3.64	4.09	0.38	0.011	2.22	47.89	22.29	0.182	81.31	32.75	12.12
	E70-80	3.38	3.69	0.27	0.006	3.13	46.32	16.14	0.12	86.19	29.5	15.92
	E90-100	3.07	3.12	0.16	0.003	2.53	46.53	18.45	0.13	85.85	9.75	18.49
L	E10-20	5.04	5.26	0.93	0.008	1.62	26.68	16.99	0.27	75.24	45.25	36.72
	E20-40	4.96	5.11	30.04	0.066	2.27	36.35	17.61	0.21	80.27	38.5	24.9
	E50-60	5.11	5.2	89.57	0.006	1.89	31.69	16.81	0.14	85.07	36.25	30.32
	E70-80	4.37	4.51	0	0.004	1.76	31.27	19.25	0.14	85.21	26	24.29
	E90-100	3.1	3.17	0	0.002	2.12	33.47	16.51	0.17	83.15	8.5	39.7

Legend: B: Buhandanda, L: Lushala, pHKcl: pH in Kcl, pHH_2O: pH in water, [NO3]: nitrate, [PO4]: phosphate, BD: bulk density, [N]: nitrogen, [C]: carbon, H: humidity, Ce: ash, [C/N]: carbon-nitrogen quotient.

SOIL SAMPLE COLLECTION

Peat cores were collected during the rainy season over two campaigns (from 12th August to 20th September 2017 and from 17th February to 15th April 2018) using a Russian peat sampler (50 cm × 5 cm × 2.25 cm, Hydrobio model), following the method described in Kabony (2012). Indeed, the sampler was inserted face open in the peat to 50 cm depth corresponding to the collector blade and turned (360°), using the handle, in the direction of watch needles. Once done, the sampler is turned this time in the opposite direction to safely sample the peat. The collected peat is immediately placed on pieces of PVC (50 cm x 5 cm x 2.5 cm) and threaded with plastic film. The sampler is each time reintroduced into the same hole to collect the next 50 cm according to the same procedure up to a depth of 200 cm. the short cores were also collected by the same procedure but with a sampler not adapted for high depths. The carrots were then kept at 4°C and cut into different slices for analysis. During the first campaign, seven and six cores of ~70 cm in depth were collected. Two (200) cm long cores were collected for each site during the second campaign. The location of collecting points was determined by accessibility, proximity to an irrigation canal, and the refusal by smallholders to use their plots. Cores were placed in the cooler box at 4°C for conservation up to analysis. The geographical locations of sampling points were recorded using a GPS (Figure 1).

The water samples for dissolved organic carbon analysis were taken using sterile glass bottles (500 mL) per site, then stored at 4°C. The samples were taken at the entrances and exits of the rivers crossing the peat bogs. For Buhandanda, only Kalehe and Tshomgoloka were considered because Kanamukongo was not in the area of interest.

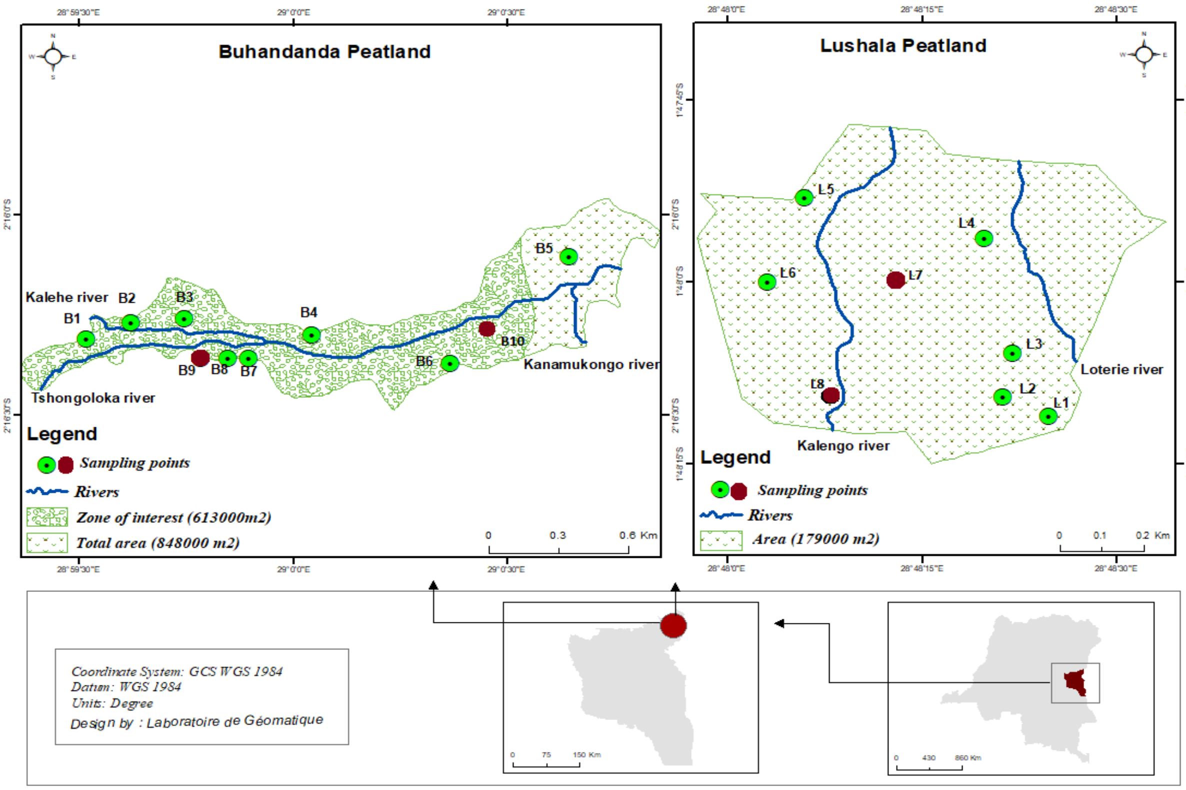


Figure 1: Location of sampling points in the research area 2018

PEAT ANALYSIS

One gram of peat collected successively at depths 1-10, 20-40, 50-60, and 90-100 cm on the Buhandanda and Lushala sites was dried at 105°C and then calcined for 4 hours at 550°C. The recovered ashes were acidified with 2% ultrapure nitric acid (HNO3) to determine major and trace metal elements by using Inductively-Coupled Plasma Optical Emission Spectrometry (Thermo iCAP 6200 Duo ICP-OES) (Gosch et *al*.,2019). The analyzes were performed in 3 replications

SOC was determined by sulfochromic oxidation of OC followed by titration of the excess $K_2Cr_2O_7$ with $FeSO_4(NH_4)_2SO_4{\cdot}6H_2O$ (Swift, 1996). To do this, 0.5 g of fine peat samples, collected on a 200 cm core at 10 cm intervals, were air-dried and mixed with 10 mL^{-1} of 0.1 mole L^{-1} of NaOH, stirred for 1 hour at 120 revolutions per minute then centrifuged at 3,000 revolutions for 20 minutes. The assessments of HS composition, comprising HA, FA, and HU, were carried out according to Mendonça and Matos (2005). The analyzes were performed in 3 replications. Additionally, the humification index (HI=HA/FA) and degree of HS transformation (DT=HA+FA)/HU) were calculated.

Water samples were initially filtered through a 0.45µm membrane filter (Thermo Scientific Polysulfone filter) to obtain dissolved C fraction (Gosch et *al.*,2019). DOC is determined by indirect chemical oxidation with the use of the O.I. Analytical©, model 1010 1.1 (in 3 replications).

DATA ANALYSES

The Kolmogorov–Smirnov (K-S) test was used to determine whether the sample was normally distributed. In addition, the coefficient of variation was used to measure the magnitude of character variation along the peat profile (Trigalet et *al.*, 2017). Basic statistical parameters (mean, standard deviation) were analyzed to explore the differences between the two sites. All statistical tests and mean comparisons were carried out at a 5% confidence level (Furukawa et *al.*,2005). Then, Statistica Version 12.0 software was used.

Principal component analysis was used to explore variations in peat properties and their relationships to site and depth (Könönen et *al*., 2015). Graphs were performed with OriginLab 21b software.

RESULTS

MAJOR GEOCHEMICAL ELEMENTS

Major geochemical elements' contents along the peat profile did not show a clear tendency except for Mg and Ti whose variations posted an increasing tendency with depth on Lushala. The concentrations of Ca, Fe, Si, Al, S, Mg, Ti, K, Mn and Na ranged from 2.0 to 5.1 and 0.8 to 3.1, 1.8 to 3.2 and 1.8 to 3.3, 0.09 to 0.1 and 0.07 to 0.1, 0.5 to 0.9 and 0.04 to 0.27, 0.06 to 0.1 and 0.02 to 0.1, 0.02 to 0.04 and 0.01 to 0.02, 0.9 to 2.7 and 1.5 to 2.8, 2.8 to 4.1 and 2.9 to 4.4, 0.6 to 2.7 and 0.5 to 1.4, 0.5. and 0.2 to 0.4 at Lushala and Buhandanda sites, respectively (Figures 2 to 11). The Ca, Si, K, Mg, Mn, and Na concentrations of Lushala peat were higher than those of Buhandanda unlike the Al concentration which was higher on Buhandanda. Fe, S, and Ti concentrations were however the same at both sites. No statistically significant difference (p=0.58) was found between the two sites despite relatively high levels of Ca, Fe, and Si on Lushala.

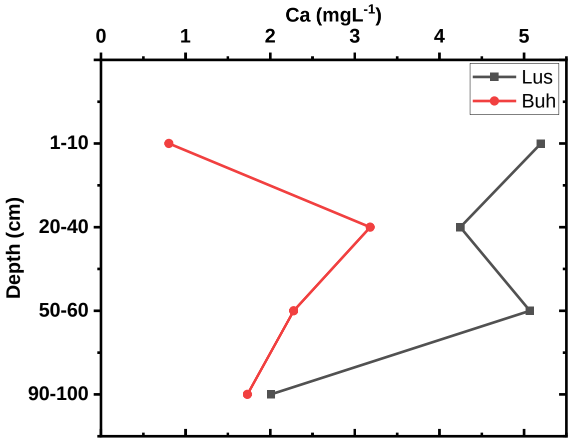


Figure 2: Calcium (Ca) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

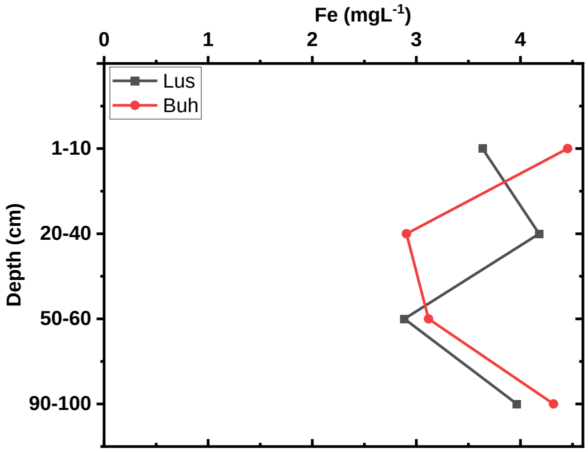


Figure 3: Iron (Fe) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

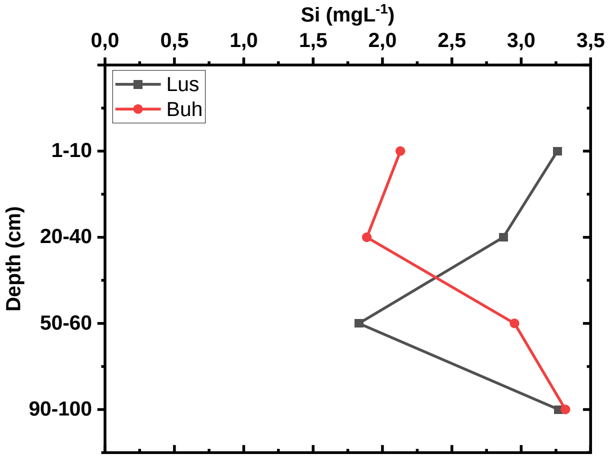


Figure 4: Silicium (Si) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles Lus: Lushala and Buh: Buhandanda 2018

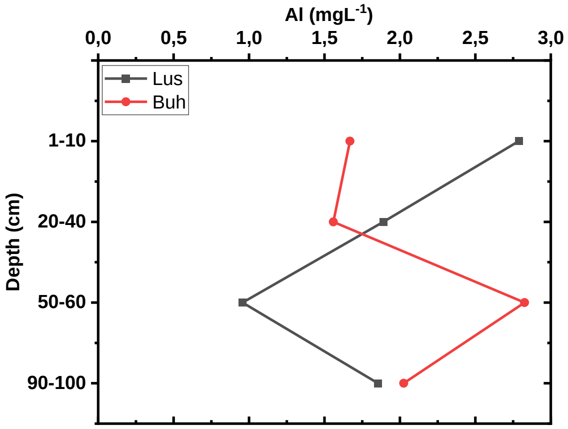


Figure 5: Aluminium (Al) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

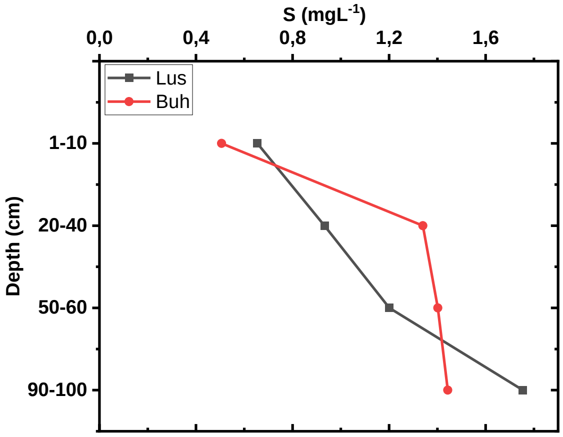


Figure 6: Sulfur (S) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

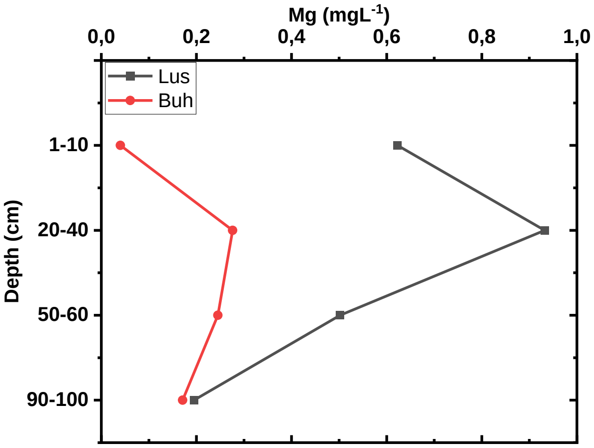


Figure 7: Magnesium (Mg) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

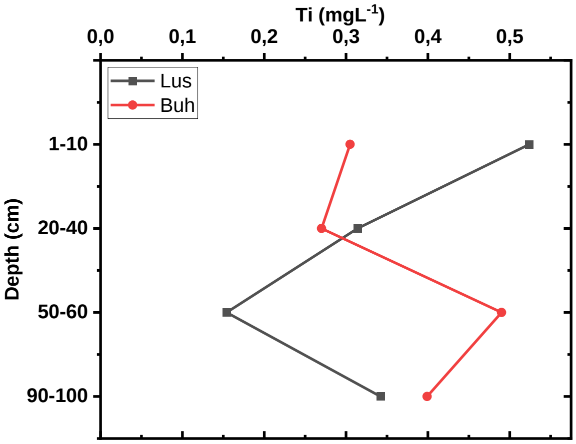


Figure 8: Titane (Ti) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda, respectively 2018

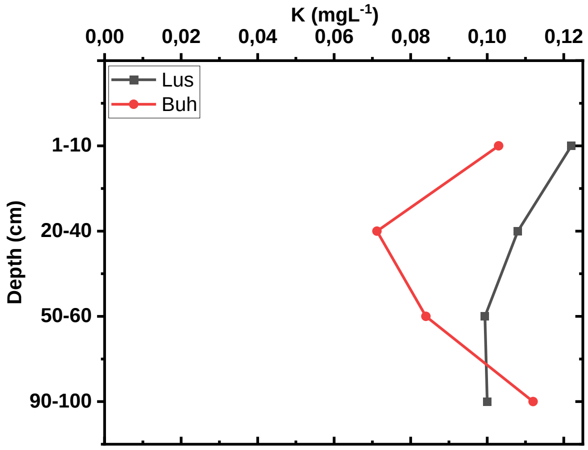


Figure 9: Potassium (K) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

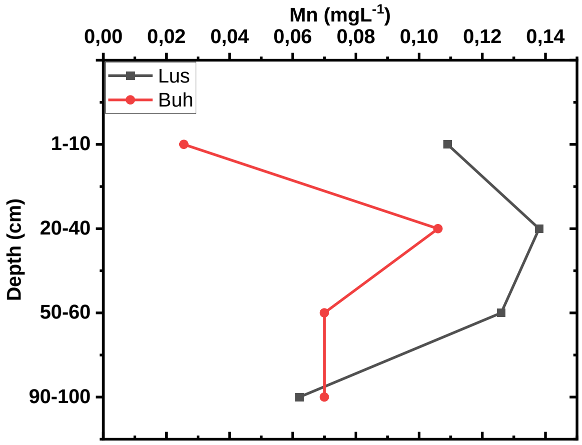


Figure 10: Manganese (Mn) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

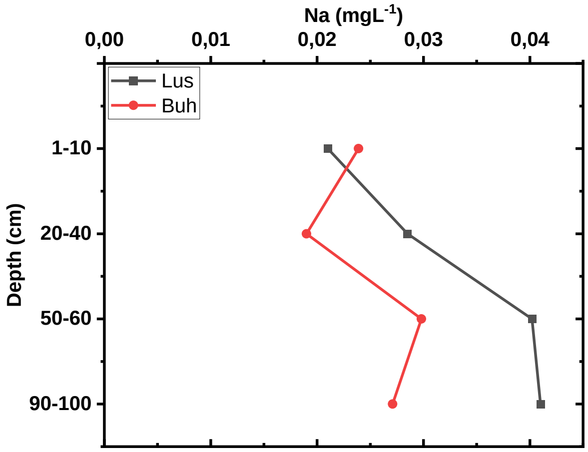


Figure 11: Sodium (Na) concentrations in mgL^{-1} along the Lushala and Buhandanda peat profiles. Lus: Lushala and Buh: Buhandanda 2018

FULVIC ACID, HUMIC ACID, AND HUMIN FRACTIONS

Between 0 and 80 cm from Buhandanda's peat profile, FA fractions were constantly more abundant than HA fractions. Reversed was the case for depths less than 80 cm with less abundant FA fractions and more HA. Similar results were noted on the Lushala peat profile where FA fractions were more abundant than those of HA except for the depths of 20, 90, 140, and 200 cm. Concretely, FA fractions varied from 0.82 to 4.29% at Buhandanda and 1.44 to 3.95% at Lushala (Figure 12).

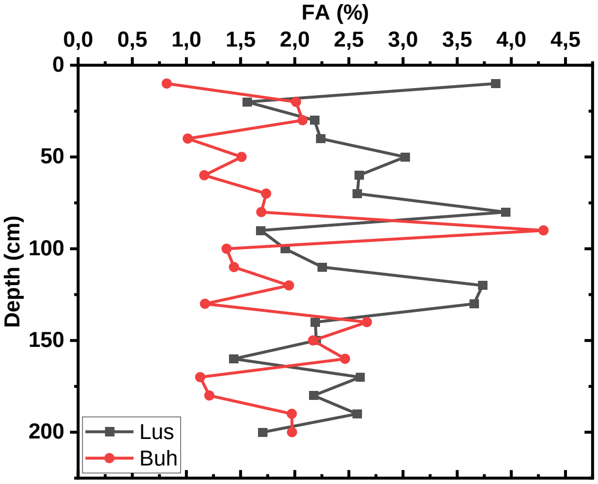


Figure 12: Fulvic acid fractions (FA) in % for Lushala (Lus) and Buhandanda (Buh) peat profiles 2018

Whereas the percentages of HA varied from 0.48 to 5.84% and 0.51 to 3.38%, on Buhandanda and Lushala respectively (Figure 13). FA and HA average rates were 1.79±0.77 and 2.51±1.32% for Buhandanda and 2.50±0.76 and 1.92±0.79% for Lushala.

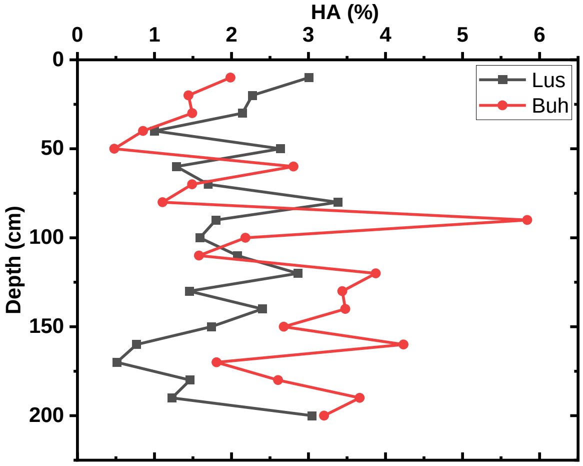


Figure 13: Humic acid fractions (HA) in (%) for Lushala (Lus) and Buhandanda (Buh) peat profiles 2018

HU fraction revealed more raised rates compared with the two preceding fractions on the two sites (Figure 14). Thus, the HU fraction varied from 2.70 to 8.30% and 3.28 to 11.32%, respectively on Buhandanda and Lushala. High values have been observed in the first 100 cm of Lushala peat and up to 150 cm for that of Buhandanda. Average HU rates were 4.36±1.44 and 5.51±1.88% for Buhandanda and Lushala, respectively. All fractions followed the general tendency HU > FA > HA and HU > HA > FA for Lushala and Buhandanda, respectively. Therefore, these intermittent variations of FA and HA fractions along the peat profile explain somewhat the dynamics of organic carbon including its stability.

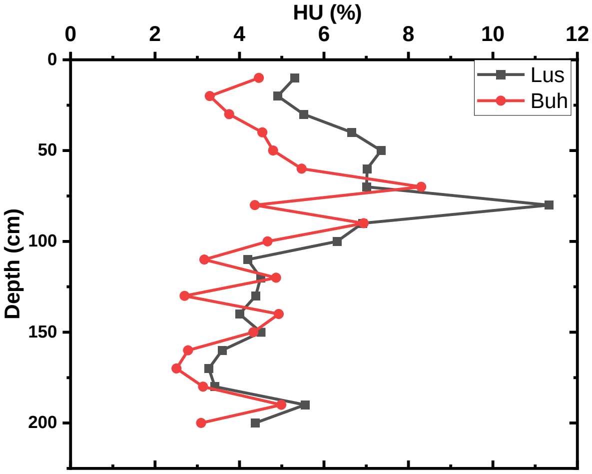


Figure 14: Humine fractions (HU) in (%) for Lushala (Lus) and Buhandanda (Buh) peat profiles 2018

The humic index varied from 0.32 to 2.43 and 0.19 to 1.79 on Buhandanda and Lushala, respectively. The average HI was 1.47±0.66 and 0.80±0.36 for Buhandanda and Lushala, respectively (Figure 15). The low to very low HI values were recorded in the section from 0 to 80 cm along the Buhandanda peaty profile, whereas high values were it in the second part of the profile (from 90 to 200 cm), except for depths 20 and 30 cm.

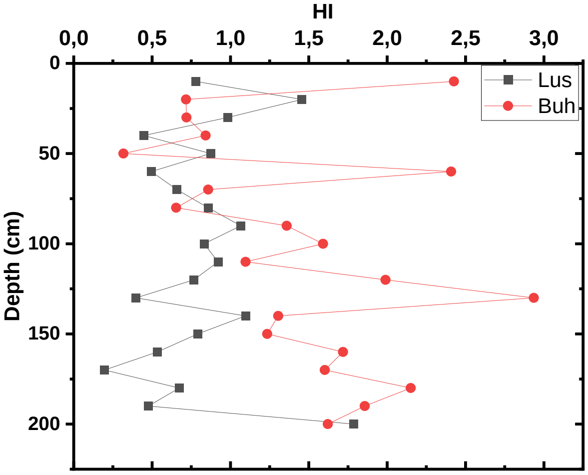


Figure 15: Humic index (HI) at Lushala (Lus) and Buhandanda (Buh) peat profiles 2018

However, DT varied from 0.39 to 2.41 and 0.49 to 1.46 on Buhandanda and Lushala, respectively. Average DT was 1.06±0.49 and 0.85±0.28 for Buhandanda and Lushala, respectively (Figure 16). These values are almost of the same order of magnitude as those observed for the HI for the two study sites.

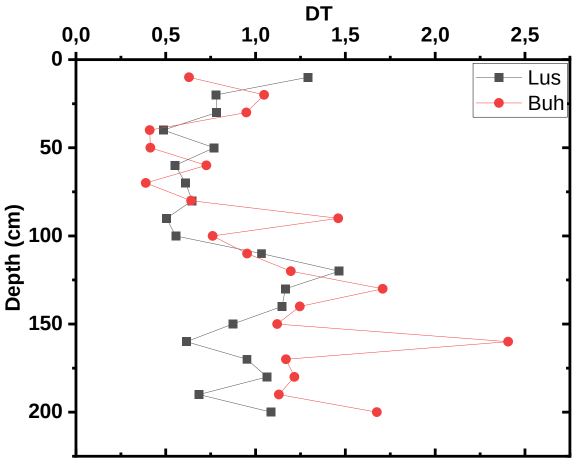


Figure 16: Degree of Transformation (DT) at Lushala (Lus) and Buhandanda (Buh) peat profiles 2018

Of all the fractions and indices of OM, only the FA fraction was significantly different, the others were not statistically different between the two sites (Figures 17 to 19).

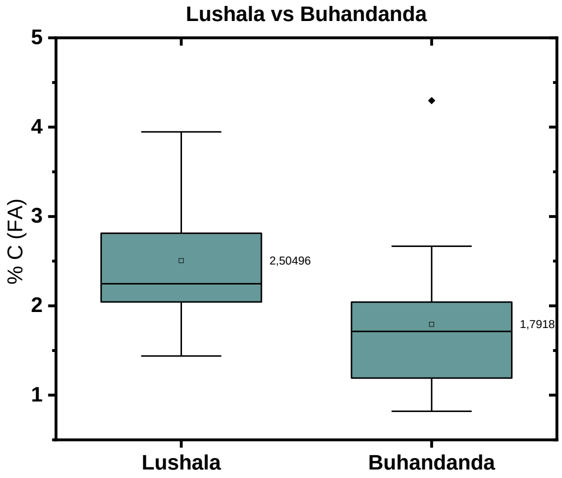


Figure 17: Mean comparison of FA fraction in C percentage between Lushala and Buhandanda peatlands 2018

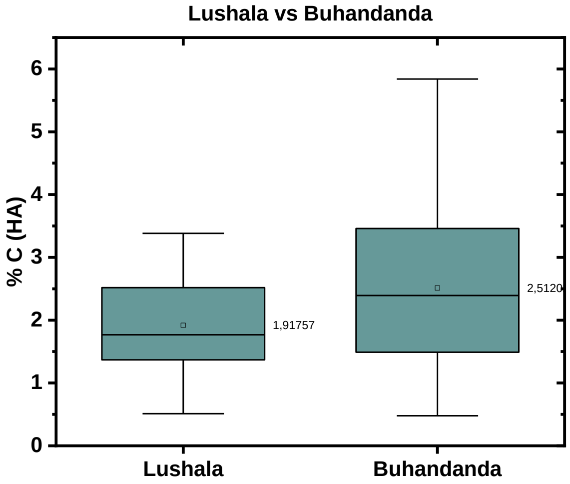


Figure 18: Mean comparison of HA fraction in C percentage between Lushala and Buhandanda peatlands 2018

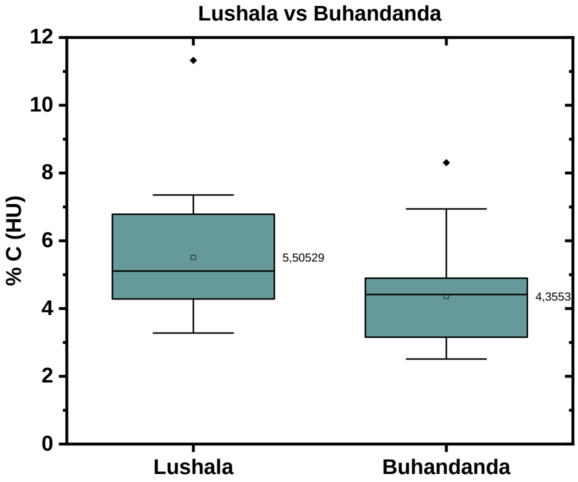


Figure 19: Mean comparison of HU fraction in C percentage between Lushala and Buhandanda peatlands 2018

PRINCIPAL COMPONENT ANALYSIS

Two principal components were detected in Lushala and explained 40.2% (PC1) and 36.3% (PC2) of the variation (Figure 20). PC1 showed a relatively weak negative correlation with HA, C, BD, H, O, Si, and fibers, and underscores the effect of asphyxiating conditions on carbon status in the peatland. PC2 showed a relatively weak negative association with FA, Fe, Ca, S, Mg, Mn, Ce and HI, and reveals the higher affinity of the FA moiety for heavy metal cations.

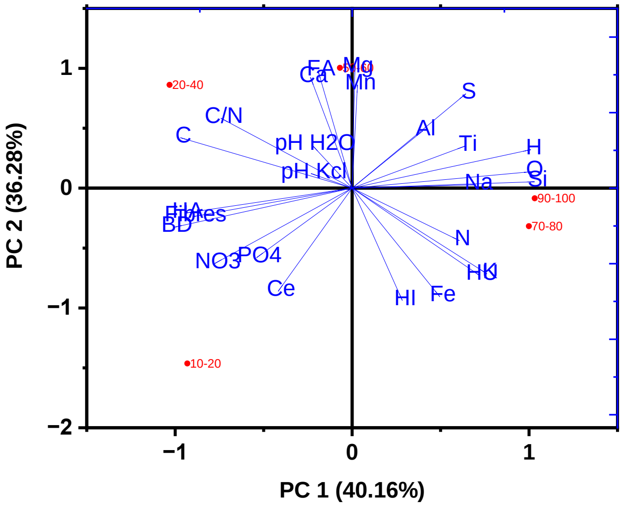
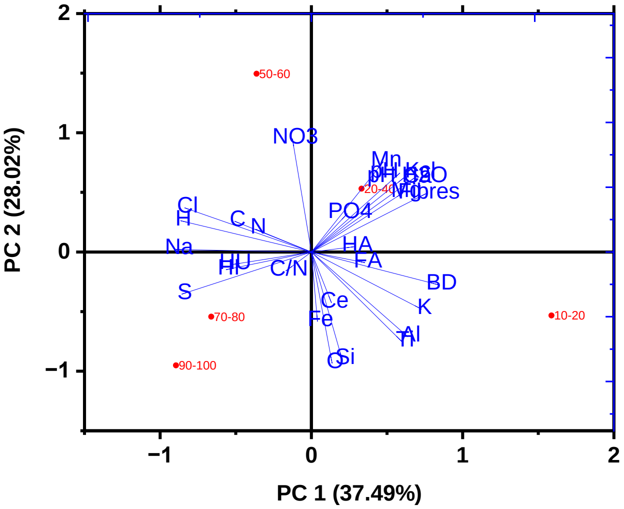


Figure 20: Correlation between physicochemical properties and humic fractions of Lushala. PC1: first component, PC2: second component, HA: humic acid, FA: fulvic acid, HU: humin, pH$_{KC}$l: pH to KCl, pH$_{H2O}$: pH to water, NO3: nitrate, PO4: phosphate, N: nitrogen, C: carbon, C/N: carbon-nitrogen quotient, BD: bulk density, H: humidity, O: oxygen, Ca: calcium, Fe: iron, Si: silicon, S: sulphur, Mg: magnesium, Ti: titane, K: potassium, Mn: manganese, Cl: chlorine, Na: sodium, Ce: ash, HI: humification index, red values: peat depth 2018

On Buhandanda, three main components (37.5%, 28%, and 21.3%) were detected in the PCA. The correlations were negatively weak for the components (CP1 and CP2); however, they underline both the action of the physical characteristics of peat on the availability of nutrients along the profile and the effect of tillage on the future of peat and the minerals' release. The importance of C/N quotient in the humification process of OM has been noted in a more or less positive association (CP3) (Figure 21).



Figures 21: Correlation between physicochemical properties and humic fractions of Buhandanda. PC1: first component, PC2: second component, HA: humic acid, FA: fulvic acid, HU: humin, pH$_{KC}$l: pH to KCl, pH$_{H2O}$: pH to water, NO3: nitrate, PO4: phosphate, N: nitrogen, C: carbon, C/N: carbon-nitrogen quotient, BD: bulk density, H: humidity, O: oxygen, Ca: calcium, Fe: iron, Si: silicon, S: sulphur, Mg: magnesium, Ti: titane, K: potassium, Mn: manganese, Cl: chlorine, Na: sodium, Ce: ash, HI: humification index, red values: peat depth 2018

Consequently, a lack of sufficiently strong correlations of the principal components with the various variables was observed in the two sites' PCAs. However, they have been both weak and negative, making it impossible to highlight the ability of the humic fractions to form complexes with heavy metals and trace elements. The relationship affects the fate of C and plays an important role in its general mobility (Könönen et *al.*, 2015). The negative correlations in the present study could be due to the weakness of data, the lack of sufficient replications, the use of samples collected at different depths, and/or having been subjected to different retention periods. However, to determine the nature and concentration of metal elements associated with OM fractions, an OM fractionation followed by an individual chemical analysis of each fraction is the best avenue.

DISSOLVED ORGANIC CARBON CONCENTRATION

Dissolved organic carbon concentration was higher at the entry and lower at the exit of peatlands. DOC concentrations were 11.2±0.1 mgL^{-1} and 7.1±0.0 mgL^{-1} at two Buhandanda entries (E1/B, E2/B) to drop to 0.42±0.0 mgL^{-1} at the exit (S/B) of the system (Figure 22).

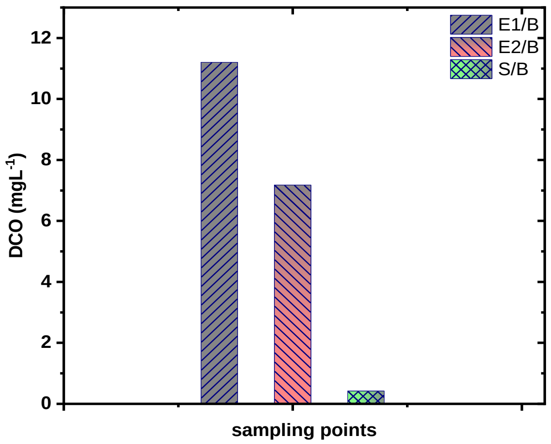


Figure 22: DOC concentration (mgL^{-1}) on Buhandanda. E1/B, E2/B, and S/B are sampling points 2018

The same tendency was observed on Lushala where DOC concentrations were evaluated to 9.8±0.3 mgL^{-1} and 5.9±0.1 mgL^{-1} for two entrance points (E1/L, E2/L) towards the peaty system and 1.3±0.1 mgL^{-1} and 2.3±0.1 mgL^{-1} at its two exit points (S1/L, S2/L) (Figure 23).

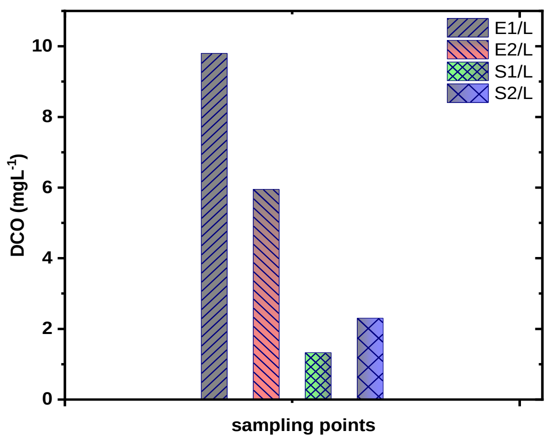


Figure 23: DOC concentration (mgL^{-1}) on Lushala. E1/L, E2/L, S1/L, and S2/L are sampling points 2018

The DOC concentration drop appeared very significant on each river between the entry and the exit of peatlands. The drop reached rates exceeding 1000% (±17X and 27X) on Buhandanda, whereas it was of the order of a hundred percentages (±2,5X and 7,5X) on Lushala peat bog, remaining nevertheless high.

DISCUSSION

MAJOR GEOCHEMICAL ELEMENTS

Mountainous peatlands can have high levels of MGE and at the same time maintain their respective proportions despite previous environmental phenomena, such as volcanic eruptions. The most abundant elements (Fe, Ca, Si, S, Al) are used for characterizing soil's geochemical and mineralogical nature (Savichev et *al*. 2019). The major elements, characteristic of studied sites, have higher contents than the reference peat materials except for Al which had an almost similar rate (Yaya et *al* 2004). The reference peat materials, mentioned here, have been certified from the pooling of several validated methods of tropical peat sample preparation from different laboratories to simplify the comparison and interpretation of the results and to increase the assurance of quality (Yaya et *al* 2004). However, the high content of sesquioxide in tropical environments would justify the high levels of Fe and Al. Concentrations of the same amplitude have been observed on tropical peatlands of Banyuasin Regency in South Sumatra (Sutejo et *al*. 2017), those of Sarawak (Andriesse 1988) and finally in ombrotrophic and minerotrophic peatlands of Amazonian flooded plains (Lähteenoja et *al* 2009). In contrast, the rates in the present study are higher than those in organic soils from Dunderdalen transect and Skilvika profile (Ziolek et *al* 2017) or Wizna in Poland (Kyziol 2002).

The land management type as fires, repeated removal of biomass, plowing, use of fertilizers (Könönen et *al.*, 2015) and soil properties (Fe (Al, Mn) oxides), pH and redox conditions would also reduce this bioavailability for plants (Wijayawardena et *al.*, 2016; Gosch et *al*., 2019). However, soils could have a natural deficiency in certain chemical elements: major (N, P, K), secondary (Ca, Mg, S), and minor (Fe, Cu, Mn, B, Mo, and Zn). This is the case with calcareous soils which have Fe deficiency for plants (Olk et *al.*, 2019). If the deficiency is severe, agricultural production could be impacted by reducing yields.

Moreover, the sum of exchangeable bases (Ca, Mg, K, Na) was twice as high on Lushala than on Buhandanda, Ca being the major constituent of mineral composition. The decreasing order of Ca, Mg, K, and Na in which the basic cations are classified reflects not only the decreasing energy of absorption at the surface of minerals (stronger as the valences increase and the radius of the cation decreases), but also the increasing mobility of ions (Duchaufour and Souchier 1983). Given the capacity of heavy metals to form complexes with HS (Olk et *al* 2019), the Mg/Ca quotient can make it possible to identify their origin depending on whether the dominant complexed form comes from litter (Duchaufour and Souchier 1983). The complexes thus formed prevent the absorption of nutrients by the plants leading in most cases to the loss of crop yield.

FULVIC ACID, HUMIC ACID, AND HUMIN FRACTIONS

A change in proportions between FA and HA observed at two sites could be explained by local factors, such as pH, type of OM (Sun et *al.*, 2012; Tan, 2014), microbial activity (Tavares and Nahas, 2014), or peat age (Hodgkins et *al.*, 2018). Indeed, humic fractions' (HA and FA) reactions in soil are controlled by pH except for the HU which is almost insensitive to any pH value. As an illustration, the HA fraction can have 1/1.4 times more acidic dissociation behavior at pH 4 than at pH 7 (Terashima et *al.*, 2004). Organic matter, when it is recalcitrant, can favor the progressive accumulation of non-humic fractions in the soil (Silva et *al.*, 2016). High FA amounts are justified because they are polymerized first during the initial phase of full maturation or later during incomplete maturation of HS. Other forms of FA would come from the destabilization of humification processes and mineralization intensification by cultural practices (Sun et *al*., 2012; Ndzelu et *al.*, 2020). Thus, more FA fraction is important (>AH) this implies greater C mobility and low humification rates (Błonska and Lasota, 2017).

Ukalska-Jaruga et *al.* (2019) observed almost similar trends (i.e., AF>AH rates) on arable and grassland soils with lower HS contents for arable sites. With higher humic fractions than those of our study, Becher et *al*. (2022) on the contrary found HA fractions more abundant than FA in all peat profiles. Inappropriate agricultural practices accelerate OM mineralization and change from FA to HA abundance or inversely (Ukalska-Jaruga et *al*., 2019). Humic fractions' distribution along the peat profile could result from the illuviation of clay/colloid (Torres-Sallan et *al.*, 2017). It is also in this way that the labile fractions of carbon in the soil accumulate (Ribeirinho et *al*. 2019). In conclusion, the status of OM is dynamic and varies according to environmental characteristics, composition, and tillage (Grzyb et *al*., 2020). An adjustment of the values of these factors makes it possible to determine the speed and the direction of the organic residues' mineralization.

High carbon density in peat soils relates tightly to its high proportion in individual HS fractions. However, the observed rates might appear low compared to those found by Valladares et *al* (2007), Murage and Voroney (2007) or Wijesinghe et *al* (2020) for peat soils. They were in the range of crop soils amended with organic manures (Xian-yung et *al.,* 2014; Hou et *al.*, 2014; Silva et *al.*, 2016; Ukalska-Jaruga et *al.*, 2019; Souza et *al.,* 2019). Low humic fraction rates could also be explained by chemical alterations that occurred during alkali extraction, leading to an undervaluation of these HS fractions (Olk et *al.,* 2019). HS study has proven to be a robust approach to resolving environmental issues and developing meaningful paths for mitigation steps.

Humification index

The relationship between HA and FA expressed by the humification index indicates the quality of organic material that could enhance soil physical properties and improve plant growth. Low values of HA/FA quotient as reported here are often associated with higher soil moisture, which may suggest increased carbon mobility in soils (Souza et *al*., 2019). Additionally, HI values >1 indicated that HA fraction persisted longer in soil and has a higher polymerization degree (Valladares et *al*., 2007), as was the case in Buhandanda. For sandy soils in tropical regions, this quotient could be higher, due to solubility and selective loss of organic compounds with higher solubility (Silva et *al.*, 2016). An understanding of the establishment peat history at the study sites, including the process of their transformation into agricultural sites, can provide insight into the role played by agricultural practices in the mineralization and humification of sites OM. However, it should be remembered that lower humification in agricultural soil increases the risk of soil depletion through gradual nutrient loss and, in the context of peatlands, through increased greenhouse gas emissions. Moreover, soil management practices consisting of turning the soil periodically and preventing the regrowth of natural vegetation further increase these risks. Accordingly, Sun et *al*. (2012) found a decrease in HI from 2.05 in uncultivated soil to 1.38 in cultivated soil for 200 years, indicating a lower humification degree in cultivated soils. The high annual average temperatures predicted over the next decades would favor greater humidification of tropical and subtropical peat, with the selective removal of carbohydrates and the accumulation of the aromatic compound leading to a highly recalcitrant residual peat (Hodgkins et *al*., 2018), therefore at a higher HI. If no thought is given to recovering Buhandanda and Lushala sites, the way is set for the loss of services provided by peatlands.

Transformation degree

Lower DT Lushala values indicated a predominance of insoluble fractions, while higher DT quotients in Buhandanda indicated a lower humification intensity. The insoluble fractions are generally characterized by a predominance of aromatic compounds to the detriment of carbohydrates. This translates more concretely to the stability of organic carbon which remains predominant in the humin fractions with beneficial effects on the local, regional and global environment, including on the climate. The C/N quotient of organic soils is often exploited to discuss the degree of HS biological transformation (Wijesinghe et *al*. 2020). A study discovered that a low C/N quotient favored higher HI and DT in organic soils compared to conventional soils (Marinari et *al*. 2007). These results suggest that in histosols with higher natural fertility, the transformation of OM would promote FA production, as is the case in the present study. In other words, the higher OM content resulted in a decrease in DT, hence a higher potential for subsidence (Valladares et *al*., 2007). In conclusion, investigations must continue for understanding the humic fractions' behavior in a degraded peat environment.

DISSOLVED ORGANIC CARBON

The high DOC concentrations observed at peat bog entrances could come from the constant input of OM derived from fresh and easily decomposable materials. On the production perimeter, on the other hand, the DOC release is low due to the low yield of plant productivity. However, DOC concentration and composition are linked to land management and crop residues quality (Silveira, 2005). The decrease in DOC concentrations along the hydrological continuum is explained by the existence of a probable link between its retention and the level of hydraulic connectivity between the water table and peatland rivers/canals. When there is a drop in the height of the water table (a few millimeters or centimeters per day), it is often accompanied by an increase in the residence time of water potentially loaded with DOC. An additional reduction may take place through DOC adsorption by clay minerals and large ash fractions (Kabony, 2012). Conversely, changes in water table level would positively affect the *in situ* DOC production at depth (i.e. in anaerobiosis) (Guan et *al.*, 2021). However, DOC release from peat is limited by its accumulation in pore water inherent in carbon mineralization (Blodeau et *al*., 2004). A study devoted to multiannual variation analysis of the DOC concentration in the Joaquin delta, revealed different behaviors depending on the rise or fall in the water quantity (Fuji et *al*., 1998). Indeed, the aforementioned authors found considerable amounts of DOC (up to 128 mgL^{-1}) in the peat interstitial waters, but which decreased (up to 2 mgL^{-1}) after intentional irrigation. Furthermore, DOC could undergo biodegradation and photochemistry/photo-oxidation with CO_2 emission (Reyes and Crisosto, 2016), as it can be bioreactive in the long term (Soares et *al.*, 2019).

Due to its high sensitivity to changes in soil moisture, ambient temperature, and plant species, DOC has a rapid turnover (Kaiser and Kalbitz, 2012) compared to HS. This renewal is more rapid in agricultural systems depending on the land use model applied (Strosser, 2010). Thus, Rita et *al*. (2011) considered the use of organic fertilizer at extremely high rates and containing a highly labile substrate directly affects the DOC content in proportion to the varying degrees of degradation and solubility of its organic components. After plowing, this more labile fraction of soil OM could elute to deep soil horizons and/or adsorb clay particles on the surface (Corvasce et *al*., 2006). However, DOC losses are strongly related to microbial activity only when the soil's ability to stabilize soluble carbon is low (Silveira, 2005). Due to its varying molecular weight and polarity, DOC is of considerable practical interest as it could serve as a sensitive indicator of changes in the soil ecosystem (Marshall et *al.*, 2021), especially with its ability to complex different types of pollutants (Reyes and Crisosto, 2016). The low DOC exports out of peat systems contribute to maintaining low carbon exchanges with the external environment. However, it is essential to quantify losses and retained fractions on a time scale to draw the consequences of current soil management and to propose sustainable management practices.

CONCLUSION

Humic fractions were determined from Lushala and Buhandanda peat cores to assess the status of OM and their relationships with peat physicochemical properties. The humic fractions contained carbon rates globally low because of the chemical alterations that would occur during alkali extraction (Olk et *al.*, 2019). Nevertheless, the HS study is a robust approach to resolving environmental issues and developing adapted mitigation measures. The relationships between HS and the physicochemical properties of peat were not very clear at the two sites except FA with some metals on Lushala. A determination of minerals distribution in each fraction would provide a real status of this OM. Dissolved organic carbon content declined from upstream to downstream favored by internal and external factors. To understand the DOC behavior along watercourses, it is necessary to assess its concentration at intermediate points.

CONFLICT OF INTEREST

The authors declare that we have no conflict of interest as authors.

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