Water Quality From High Mountain Peatlands: Spring of Campo Belo River, Itatiaia -Brazil

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Abstract

Peatlands are a transitional environment between terrestrial and aquatic ecosystems that provide essential hydrological, ecological, and biogeochemical functions. Peatlands have been recognized as important environmental matrices in the storage of organic carbon and water. However, little is known in the literature about the influence of peatlands on the quality of surface water. Therefore, this study aims to evaluate the water quality from peatlands in the spring of the Rio Campo Belo, in Itatiaia National Park, Itatiaia-Brazil. The spring water quality from peat profiles was based on the determinations of the temperature, dissolved oxygen (DO), electrical conductivity, pH, turbidity, dissolved organic carbon (DOC), total organic carbon (TOC), silica, ions, and trace elements (Al, Sb, As, Cd, Co, Cu, Cr, Sn, Fe, Mn, Mo, Ni, V, Ga, Rb, Sr, and Zn) on spring water and peat core samples. The highest DO values observed in the spring waters that leachate water and may be related to the lower water temperature, as well as the movement of water. The DOC values were relatively low suggesting no difference between the spring water and the water leached (1.6 and 1.7 mg l⁻¹, respectively). Higher values of ions and trace elements in the leaching water from core peat demonstrate a greater contribution of the peatland to the concentration of these ions in spring water. An increase in TOC peatland did not cause an increase in pH, however, the removal of organic matter promoted an increase in pH.

1. Introduction

Peatlands are soil formed by organic sediment derived from the fungal and bacterial degradation of plant biopolymers (Hatcher and Spiker 1988), being a transitional environment between terrestrial and aquatic ecosystems that provide essential hydrological, ecological, and biogeochemical functions (Fraser et al. 2001; Joosten and Clarke 2002; Chapman et al. 2003; Mitra et al. 2005; Krueger et al. 2015). It is estimated that 4.2% of Earth's land surface is covered by peatland (about 4 million km²) (Yu 2012). About 75–80% of peatlands are located in boreal and sub-arctic regions and only 10–15% in tropical regions (Lappalainen 1996). There are approximately 612,000 ha or 0.07% of peatlands in Brazil (Bispo et al. 2015). Peatlands have recognized importance in the storage of organic carbon. Lourençato et al. (2017) observed that in the last century the tropical peatlands stocked above 200 tons ha⁻¹ of carbon, these values were higher than values obtained in temperate and boreal regions.

The peatlands have a lower bulk density and higher porosity, lower hydraulic conductivity, nutrients, and minerals that are bound to organic matter due to their high cation exchange capacity. These properties are crucial for the peatland to have a high capacity to retain water (Mitsch and Gosselink 2000). Estimated that 10% of the planet's fresh water is stored in peatlands (Mitra et al. 2005; Limpens et al. 2008; Bragazza et al. 2013). Peatlands water plays a fundamental role in the biogeochemical cycling of these ecosystems. Therefore, they have a crucial role in drinking water catchments, and the preservation of this ecosystem is crucial for water security now and in the future. The waters that aim to public supply and originate from peatlands without anthropogenic disturbances have good quality and low levels of nutrients and contaminants, requiring only a direct treatment for the supply. However, peatlands without having suffered some kind of anthropogenic interference become increasingly rare (Hájek et al. 2020).
The chemistry of the peatland water is dependent on the chemistry of the source. Minerogenic peatland processes more water and inorganic constituents dissolved than an ombrogenic peatland. In minerotrophic peatlands, the source of inorganic elements is the deposition and nutrients from waters originating from mineral soils. The water inputs to peatland may be very different in different mires, in different parts of an individual mire, and at different times of the year. The water balance of a minerogenic peatland is formed by the difference between inputs and outputs. Inputs include precipitation directly to the peatland, surface runoff from mineral soil, and groundwater recharge from mineral soil, while outputs include evapotranspiration, and the net infiltration losses to mineral soil (Sallantaus 1988). Several studies have evaluated the human impact and climate change in these environments (Lourençato et al. 2017; Da Silva et al. 2013; Xing et al. 2015; Wang et al. 2014), but studies that assess the quality of the water formed in tropical peatland are scarce.

In this sense, the present study aims to evaluate the quality of peat water in the spring of the Rio Campo Belo, in the Itatiaia National Park, Rio de Janeiro - Brazil. For this, the physical-chemical parameters (pH, temperature, oxy-reducing potential, electrical conductivity), the concentration of major ions, organic matter, and trace elements present in the springs were determined.

2. Experimental

2.1. Study area

The study was carried out at the head of the Campo Belo river, in the Itatiaia National Park (INP), Itatiaia municipally, Rio de Janeiro state - Brazil. The Campo Belo River basin has approximately 60 km² and extends from the slopes of the Itatiaia plateau (2400–2600m altitude) to the left bank of the Paraíba do Sul River (~ 400m), being responsible for the water supply of the Itatiaia city with approximately 30 thousand inhabitants. Three samples were collected: Springwater, peat core – 24 cm, and peat core – 17 cm (22°22'39.85" S 44°41'36.91" W, altitude 2419 m).

From the geological point of view, the Highlands are constituted by a very strong and rugged topography with bare rock surfaces, suspended valleys with a large predominance of kaolinite, with fresh alkaline rocks, covered by mafic material (Miano 2000). The SiO₂/Al₂O₃ ratio is marked and the Fe content is low.

The rocks present in INP, belong to four lithostratigraphic and geochronological groups: 1) Paleoproterozoic crystalline basement, 2) neocretaceous alkaline rocks of the Itatiaia, Passa Quatro e Morro Redondo massifs, 3) tertiary sedimentary rocks of the Resende Basin and 4) quaternary unconsolidated sediments. (Ribeiro et al. 2002; ICMBIO 2013; Ribeiro et al. 2007; Penalva 1963).

On the plateau, the average annual temperature is 11.4 ºC, with January being the hottest month with an average of 13.6 ºC; July is the coldest month with an average of 8.2 ºC. (Furtado et al. 2001). Annual rainfall is 2500 mm (Nimer 1979; ICMBIO 2013).

2.2. Materials and Methods
The peat core with 24 cm was sectioned with a 1 cm resolution to determine the chemical composition of the peat and analyze the correlation between the pH variation and the organic matter and aluminum variation. Peat core of 17 cm was air-dried, inside the transparent PVC tube, is coupled at one end to an ultrapure deionized water source with controlled flow, and the other end to an outlet for percolated water collection.

At the site, with a multiparametric probe, the following parameters were measured: temperature, dissolved oxygen (DO), electrical conductivity (EC), and hydrogen potential (pH). In the laboratory, dissolved organic carbon (DOC) was measured for the spring water sample and the water sample resulting from the leaching column, together with the analysis of the same physical-chemical parameters. Besides that, the ions analysis Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4^{2-}\), F\(^-\) e NO\(_3^{-}\), were performed on the filtered samples (0.45 µm cellulose acetate filter) and without previous dilution by ion chromatography and turbidity was measured using a portable turbidimeter.

The trace element analysis (Al, Sb, As, Cd, Co, Cu, Cr, Sn, Fe, Mn, Mo, Ni, V, Ga, Rb, Sr, Zn) was performed using a mass spectrometer of inductively coupled plasma - ICP-MS, method (Method 6020a) recommended by the American Environmental Protection Agency - EPA of the USA. For this, a sample of 15 ml was filtered and the pH adjusted to the range below 2.0, with the addition of 200 µL of pure nitric acid. Also, rhodium was used as an internal standard, with 0.3 mL of the standard with a concentration of 500 ppb being added to each sample.

Silica (H\(_4\)SiO\(_4\)) was determined using the colorimetric method, with specific reagents, calibration standards, and wavelengths, following the methodology of Grasshoff et al. (1983). To determine the dissolved organic carbon, a sample was filtered on an acetate/cellulose membrane and analyzed by the Total Organic Carbon Analyzer - TOC-V equipment. The total organic matter (TOC) of the peat layers was determined by the muffle method. Following the EMBRAPA methodology (2006), soil solutions were prepared according to the analytical reagents, to extract the active, exchangeable, and potential acidity. The results were analyzed using Pearson's correlation test, performed in the IBM SPSS Statistics software, between the variation of pH and analyte concentrations in the profile of twenty-four centimeters of soil.

3. Results And Discussion

3.1 Chemical-physical characterization of spring and leachate water of the peatland

The physicochemical parameters (conductivity, pH, Eh, temperature, dissolved oxygen, turbidity, and dissolved organic carbon) were determined in the spring and leachate water samples taken from the head of the Campo Belo river and the leaching column, and the results are presented in Table 1 below.
Table 1
Physical-chemical parameters of spring and leachate waters from Campo Belo River.

| Water samples | Temp. | DO | Turbidity | pH  | EC  | Eh  | DOC  |
|---------------|-------|----|-----------|-----|-----|-----|------|
|               | ºC    | mg L\(^{-1}\) | UNT       |     | µS cm\(^{-1}\) | mV   | mg L\(^{-1}\) |
| Leachate      | 18.6  | 2.4 | 0.3       | 4.9 | 9.0 | 8.4 | 1.7  |
| Spring        | 12.3  | 4.6 | 0.2       | 4.8 | 8.0 | 7.4 | 1.6  |

Dissolved oxygen (DO) is one of the most important parameters for the water quality evaluation in surface water (Brooks et al. 1997). It is an important oxidizing agent, controlled by several factors. Since the solubility is proportional to the partial pressure of O\(_2\), it can be inferred that at a given temperature the solubility of oxygen in water decreases with increasing altitude. In addition to the altitude, the solubility of gases in water decreases with rising temperatures (Fiorucci and Filho 2005; Yvon-Durocher et al. 2010). Diffusion from the atmosphere at the stream surface exchange is increased with the moving of the stream water, increasing the DO of the water (O'Driscoll et al. 2016). Thus, the highest DO values observed in the spring waters in the present study may be related to the lower water temperature, as well as the movement of water, since the measurements were made in the field in the spring water, while leaching water measurements were performed in the laboratory.

Water samples collected in the spring and leachate from core showed similar values of turbidity (0.2 and 0.3 UNT respectively), which is well below the value acceptable by the CONAMA standard n° 357/2005 in natural water for supply (100 UNT) (Table 1). The low turbidity observed indicates a low amount of particulate matter in suspension in the collected waters. Also, the spring and leachate waters showed considerably low pH values (4.8 and 4.9 respectively), being classified as acidic.

Grabs et al. (2012) observed high total organic carbon (TOC) values in water from riparian organic soils (8–16 mg L\(^{-1}\)). According to the authors, organic riparian peat soils in forested areas exporting large amounts of TOC to water. However, the largest fraction of organic carbon present in peat waters is found as dissolved organic carbon (DOC). The DOC values observed in this study were relatively low and showed no difference between the spring water and the water leached from the core (1.6 and 1.7 mg L\(^{-1}\), respectively). The organic carbon obtained in the spring water comes from the peat leached DOC, since the DOC value of the spring water was similar to the DOC leached from peat core, in addition, the turbidity values indicate a low amount of particulate material. Fraser et al. (2001) observed a range of DOC concentration typical for peatland-associated waters from Mer Bleue in Ontario was 30–60 mg L\(^{-1}\). Leaching processes that occur in peatlands increase the dissolved organic carbon concentration in water, making it the main source of organic carbon in water (Vasander and Kettunen 2006).

Higher values of Na\(^{+}\), NH\(_4\)\(^{+}\), K\(^{+}\), Mg\(^{2+}\), F\(^{-}\), Cl\(^{-}\) and NO\(_3\)\(^{-}\) ions in the leaching water from core peat demonstrate a greater contribution of the peatland to the concentration of these ions in spring water, as shown in Table 2 and the Stiff diagrams represented in Fig. 1. Although the study area is an environment with very low anthropogenic influence, the values of NO\(_3\)\(^{-}\) observed in the leachate water are high (6.07
mg l⁻¹) being very close to the maximum contaminant level (MCL) of 10 mg L⁻¹ as recommended by the US EPA (2009). This high nitrate value may be related to the increase of 25% in wet atmospheric nitrogen deposition over the past decade has been observed (Jia et al. 2014). This increase has been disproportionate, as the wet deposition of nitrate has had a much higher increase than that of ammonium. This increase has induced soil acidification, aggravation of cation and nitrate leaching, and decreased microbial biomass (Liu et al. 2011; Huang et al. 2014; Gao et al. 2015; Liu et al. 2013).

Table 2
Ion concentrations of spring and leachate waters from Campo Belo River.

| Water samples | Cl⁻ | SO₄²⁻ | Br⁻ | F⁻ | NO₃⁻ | Na⁺ | NH₄⁺ | K⁺ | Ca²⁺ | Mg²⁺ | H₄SiO₄ |
|---------------|-----|-------|-----|----|------|-----|------|----|------|------|-------|
| Leachate      | 1.02| 0.04  | 0.09| 0.02| 6.07 | 5.04| 0.13 | 3.14| 0.91 | 1.34 | 14.6  |
| Spring        | 0.03| 0.06  | 0.11| 0.01| 0.02 | 1.10| 0.01 | 0.61| 1.41 | 0.25 | 13.4  |

Br⁻ is a conservative element and has a strong positive correlation with leaching (Kessavalou et al. 1996). However, leachate of the peat core showed lower values of Br⁻ than water collected in the spring. Maw and Kempton (1982) observed that peatland studies had higher values of Br than mineral soils, however the largest fraction of this Br was found in organic form. In contrast, Cl⁻, another conservative element and widely used for determining preferential flow paths (Jabro et al. 1994), was found in higher values in leached water, showing that this element present in spring water is related to the leaching of this element in the peat. The highest concentrations of SO₄²⁻, Br⁻ and Ca²⁺ in spring water indicate that there are other sources of this element.

The concentrations of silicic acid were 13.4 mg L⁻¹ for spring water and 14.6 in mg L⁻¹ for the leachate sample. As it is a region of intense leaching, with the presence of silicates in its mineral composition, values considered silicates in water are expected. These values are close to the values suggested by Lazzerin et al. (2014) the basic silica values of 9.8 for tropical aquifers. Under normal conditions, the predominant Si species occurs as orthosilicic acid (H₄SiO₄) and, more commonly, as metasilicic acid (H₂SiO₃) (Lazzerini 2014). The non-ionic colloidal form tends to predominate in surface water and water dispersed in soils, mainly in the presence of organic matter. Silica is from the geochemical weathering of minerals and its concentrations in the waters of the peatlands are indicative of the degree of miningotrophic influence of the peatlands (Shotyk 1988). In addition to Si, calcium is also an element of minerotrophic origin, therefore positively correlated with as a concentration of Si (Bendell - Young 2003)

The hydrogeochemical modeling performed using the PHREEQC 3.3.12 software indicates that gibbsite (Al(OH₃)) are sub saturated in both spring and leached samples, with average saturation indexes (SI) of – 0.96, however, modeling indicates the diaspore mineral (AlO(OH)) sub saturated only in the spring samples, with SI of – 0.07, as shown in Table 3.
Table 3
Saturation indexes of the main minerals modeled in spring and leachate waters from Campo Belo River.

| ID          | Cuprous ferrite | Diaspore | Gibbsite |
|-------------|-----------------|----------|----------|
| Leachate water | 3.31            | -0.07    | -1.47    |
| Springwater  | 4.07            | 0.90     | -0.46    |

Copper and iron are leaving the solution through the precipitation of cuprous ferrite (CuFeO$_2$) in the two samples. Leachate water sample has a favorable condition for the dissolution of the diaspore mineral and spring water sample has a favorable condition for the dissolution of the gibbsite mineral. In the study area, the high concentrations of aluminized minerals, the oxidizing environment, and the low pH value may explain the occurrence of gibbsite and diaspore dissolved in water. Gibbsite and diaspore are minerals formed by intense weathering in a region of aluminosilicate minerals. The presence of aluminum minerals dissolved in water is an indication of the presence of aluminum in the monomeric form Al$^{3+}$, responsible for the acid hydrolysis of water.

Regarding trace metals, it was observed that the concentration in the leached water from the peat was higher than the levels of the spring water, once again indicating the influence of the peat in the chemical composition of the spring water, as can be seen in Table 4. The exception was for Fe, Cu, Rb, Sr, and Ba, which had higher concentrations in the spring water. Gandois et al. (2019) observed in Black rivers draining peatlands a high concentration of Al, Fe, Pb, As, Ni, and Cd and a significant association between DOC, Fe, As, Cd and Zn in the dissolved and fine colloid fraction, while Al is associated to Pb and Ni and present in a higher proportion in the coarse colloidal fraction. Thus, peatland presents itself as a significant source of these elements for surface waters, especially when they are in a state of degradation.
Table 4
Trace element concentrations of spring and leachate waters from Campo Belo River.

|          | Leachate | Spring |
|----------|----------|--------|
| µg L$^{-1}$ |          |        |
| Al       | 80.28    | 22.04  |
| V        | 0.072    | 0.040  |
| Mn       | 61.60    | 0.184  |
| Fe       | 1.050    | 47.00  |
| Co       | 1.078    | 1.006  |
| Ni       | 3.632    | 0.330  |
| Cu       | 0.118    | 1.344  |
| Ga       | 0.252    | 0.092  |
| As       | 0.928    | 0.158  |
| Rb       | 0.134    | 0.346  |
| Sr       | 0.750    | 1.618  |
| Y        | 0.244    | 0.200  |
| Mo       | 0.618    | 0.086  |
| Cd       | 0.482    | 0.100  |
| Sn       | 1.910    | 0.230  |
| Ba       | 0.134    | 1.402  |
| La       | 0.246    | 0.018  |
| Ce       | 0.480    | 0.820  |
| Pr       | 0.144    | 0.010  |
| $^{143}$Nd | 0.022    | 0.016  |
| $^{149}$Sm | 0.006    | 0.002  |
| $^{156}$Gd | 0.042    | 0.010  |
| $^{161}$Dy | 0.002    | 0.004  |

3.2 Chemical-physical characterization of peatland
First, the peat was classified as Sapric or Black Peat, according to the methodology proposed by Von Post (1924), in which the peat material is subjected to compression analysis between the fingers and evaluated according to the resulting texture and coloring. The material had a muddy texture and strong decomposition.

The total organic carbon (TOC) content fluctuates considerably in the first five centimeters of the soil, with a peak of 48% of TOC at 4 cm in depth, as can be seen in Fig. 2. After 10 cm of depth, the TOC content stabilizes, with a value of about 20% TOC. Lourençato et al. (2016) in a study carried out in another peatland in the same region, observed at 15.5 cm of depth (corresponding to 1950s) a TOC content of 16.37%, while TOC content at lower depths had 9.54% of carbon. The authors associated this variation with the major period of industrial development in Brazil, a period that also coincides with the exponential increase in global emissions of carbon.

Organic matter is a source of $\text{H}_3\text{O}^+$ protons that tend to acidify soils. Such acidification reflects more strongly in the extractable acidity values than in the soil pH. Especially when there is a great variation in the organic carbon content, the variation in the active acidity (pH) is smaller and, sometimes, there is no dependence relationship between organic C and $\text{H}_3\text{O}^+$ concentration in the soil solution (Tibau 1984).

Although the increase in TOC in the peatland did not cause an increase in pH (Fig. 2), when removing organic matter, through calcination, the pH rises on average by 0.8 units. The contribution of organic matter to the acidity of the soil occurs through organic acids (fulvic and humic) and the complexation of bases (Charman 2002). After the calcination of the organic matter, the clay minerals that were complexed are released. In an acidic environment, the mineral dissolves, releasing hydroxyl groups, present in the interlayer in the mineral. Along with this process, there is also the release of the silicate ion, which in solution promotes the basic hydrolysis of water (Alcarde 1992). Rinaldi et al. (2019) observed that the pH of Pondok soar, Tanjung Puting National Park varied between 3.7–5.2 (very acid to acid) with an average pH of 4.5 (acid) and associated with no differences. The pH of different litters of only one level of decomposition of organic matter. The chemical characteristics of tropical peatlands are determined by mineral content, thickness, type of mineral, not substrate (based on turf), and or degree of decomposition of turf (Sani 2011).

The statistical analysis of the results using the Pearson test showed that it showed that there is no correlation between the variation in the concentration of organic matter and the variation in pH in the soil column. However positive results were found when analyzing the pH and aluminum concentration data, as illustrated on the graphic of Fig. 3, a positive Pearson correlation (0.45 to significant non-level 0.05), indicate that the increase in pH follows the same behavior of increase in the concentration of aluminum. Aluminum forms part of a range of reactions in a single solution, being present in various forms, it is dissolved in a watery solution, in the form of simple minerals or complex elements, or even adsorbed on organic matter, forming chelates through metal-binding or clay mineral adsorption. Also, it is important to note that, regardless of all the aluminum conditions in the studied system, the variation in its concentration interferes correlatively with the variation in pH.
3.3 Anthropogenic Influence on water peat quality

Atmospheric components are potentially important contaminants of peatlands (Gorham et al. 1991; Shotyk 1988). Airborne $\text{SO}_4^{2-}$ and $\text{NO}_3^-$ from anthropogenic and natural sources might decrease the pH of peatlands and if they are not assimilated or used in biogeochemical reactions, they may replace a portion of the natural organic acidity. Bourbonniere (2009) attributed the variation of water chemistry peatlands $\text{SO}_4^{2-}$, Mn and Ni, pH (atmospheric deposition), however factors like anion, the base cations, pH, alkalinity which are of mineral influence or buffering capacity, in addition to DOC influence, metals like Al, Fe and other trace metals which are dependent on both sources.

Moore (1987) observed that DOC levels were not affected by disturbance and, peatland, meanwhile the increased runoff following drainage causes an increase in organic loading on the receiving system. The increase in DOC in the water can lead to acidification or buffering the pH its pH, affecting metal cycling, in addition to erasing primary productivity through light attenuation or a reduction of phosphorus and iron availability in water (Urban et al. 1989).

With global warming, peatlands are expected to become drier with lower water tables under a warmer climate (Roulet et al. 1992). These changes will result in shifts in microbial activity and nutrient cycling, altering the entire ecosystem functioning of these areas (Macrae et al. 2013). Also, changing the level of the water table in the peatlands can cause the peatlands to lose their function as a carbon sink, becoming a $\text{CO}_2$ emitter into the atmosphere (Lourençato et al. 2016), and consequently increase nutrient export to waters (De Mars et al. 1996).

Although peatland is highlighted as a carbon sink and trace metals, nutrient cycling and storage, and water source for supplying many cities, few policies have been developed to preserve these environments. As can be seen in this study, these environments have great spatial differences and these differences influence water quality. However, few studies have been carried out in order to understand the differences between these environments, mainly in tropical peatlands. In addition, these environments have suffered strong anthropic interferences and further studies are needed so that these interferences can be better understood and mitigated if necessary so that these environments do not lose their ecosystem functions.

Conclusion

Several studies have shown that peat bogs are ecosystems, which when they are not impacted by anthropogenic influences, are important sinks of carbon and trace metals present in the atmosphere. In addition to the importance of carbon cycling, peatlands are also important water source regulators. Many cities have been supplied with water from peat bogs, and when these are not impacted by their water, they have good quality for human consumption, just needing a simple treatment for the supply. However, few studies have been carried out in tropical regions in order to evaluate waters from peatlands.
Through this study, it was possible to understand the chemical parameters of the peat that affect the water quality of the source of the Campo Belo river. The lithological formation gives the spring water specific hydrochemical characteristics. The leaching column experiment demonstrated that there is a great contribution of the soil to the physicochemical characteristics of the water, mainly the acidity, either by the mineral contribution of ions or by the contribution of organic matter.

Hydrogeochemical modeling showed that there is aluminum dissolved in water, in monomeric form (Al\(^{+3}\)), which suggests the occurrence of acid hydrolysis of water. Pearson's analysis indicated that there is a correlation between the variation of aluminum in the soil and the variation of pH. These two results corroborate the conclusion that the acidity of the spring water is governed by the availability of aluminum in the soil.

Besides, many of the parameters that determine the chemical characteristics of peat water can be strongly affected by anthropogenic influences. Although the study area is located in a preservation area, some changes can already be observed, such as nitrate. In this sense, more studies are necessary for policies to be developed with the intuition to preserve these ecosystems.

**Declarations**

**Declaration of interests**

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

☒ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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