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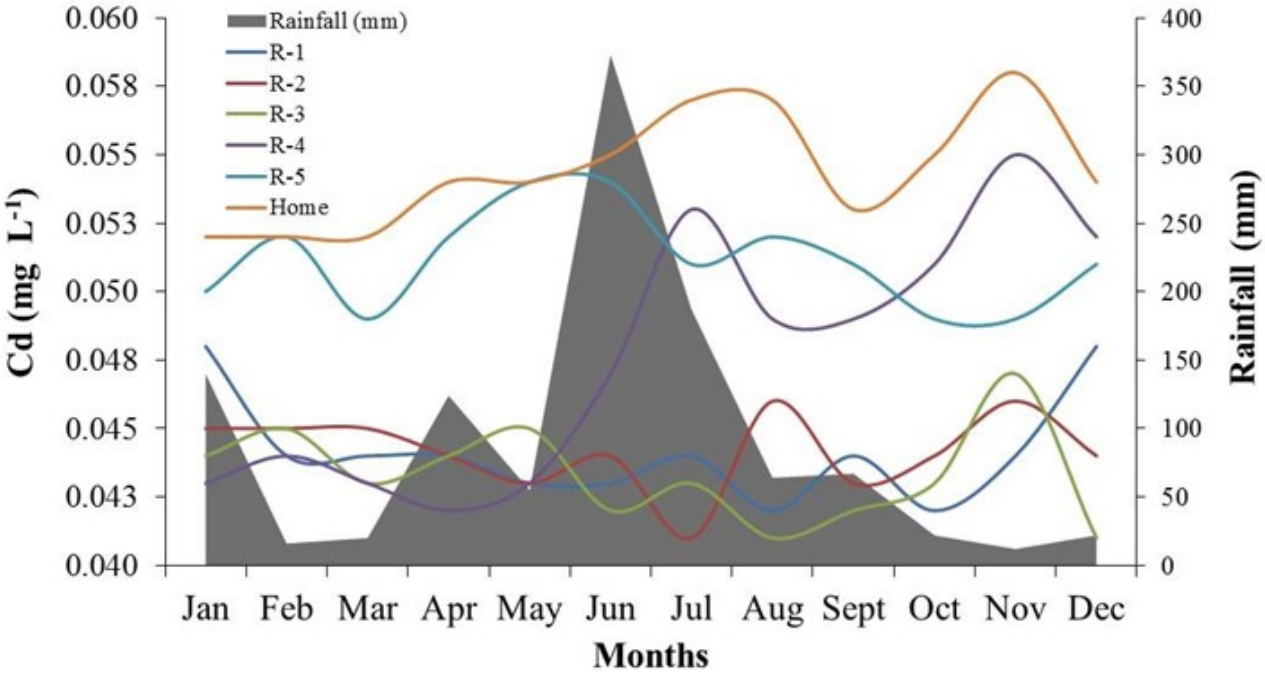

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Heavy metals in waters used for human consumption and crop irrigation

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ABSTRACT

The consumption of contaminated water is a major source of heavy metal contamination in humans and animals. This study therefore aimed to assess Cd, Cu, Mn, Ni, Pb, and Zn levels in water used for human and animal consumption and vegetable crop irrigation in Camocim de São Félix, Pernambuco, Brazil. Water samples were collected on the studied farms from an artesian well and reservoirs used for human and animal consumption as well as for crop irrigation. The results showed that concentrations of Cd (> 0.001 mg L^{-1}), Ni (> 0.025 mg L^{-1}) and Pb (> 0.01 mg L^{-1}) were above the maximum allowable limits established under Brazilian law, indicating the need for a preventive monitoring program and immediate intervention initiatives aimed at the sources of contamination. The results demonstrate the need to quantify heavy metal content in vegetable crops, since their contamination by irrigation water may make them harmful to human health. Rainfall has a seasonal effect on heavy metal concentrations in water, showing a significant effect on Pb levels, whereas Cd and Ni content was less dependent on seasonal variation.

Keywords: agrochemicals, cadmium, diffuse pollution, lead, trace elements.

Metais pesados em águas utilizadas para consumo humano e irrigação de culturas

RESUMO

O consumo de águas contaminadas representa uma das principais vias de contaminação humana e animal por metais pesados. Neste sentido, o objetivo deste trabalho foi determinar as concentrações de Cd, Cu, Mn, Ni, Pb e Zn em águas utilizadas para consumo humano e animal

e na irrigação de hortaliças no município de Camocim de São Félix (PE). Nas propriedades agrícolas, as amostras de água analisadas foram coletadas de poço artesiano e de reservatórios destinados ao consumo humano, animal e irrigação das lavouras. Os resultados demonstraram que as águas analisadas no presente estudo apresentaram concentrações de Cd (> 0,001 mg L^{-1}), Ni (> 0,025 mg L^{-1}) e Pb (> 0,01 mg L^{-1}) superiores aos teores máximos permitidos indicados pela legislação brasileira, sinalizando a necessidade de um programa de monitoramento preventivo e ações de intervenção imediata das fontes de contaminação. Os resultados indicam a necessidade de quantificação das concentrações de metais pesados nas hortaliças, visto que contaminadas pelas águas de irrigação podem ser uma fonte nociva à saúde humana. A precipitação pluviométrica tem influência sobre a variação sazonal dos teores dos metais nas águas, com maior efeito na concentração de Pb e influência moderada nas concentrações de Cd e Ni.

Palavras-chave: agroquímicos, cádmio, chumbo, elementos-traço, poluição difusa.

1. INTRODUCTION

Heavy metals can affect crop development and compromise the health of humans and animals by contaminating the food chain (Lee et al., 2006; Amin et al., 2013). In aquatic ecosystems, metals can occur naturally or be introduced by human activity. Natural occurrence is through atmospheric deposition and rainfall, or the release and transport of heavy metals from sediment or soil, in the case of soil erosion (Bezerra et al., 2014). Anthropogenic sources include raw sewage in urban areas and the discharge of industrial effluents and agricultural waste that widely contaminate basin areas (Gomes and Sato, 2011).

Agriculture is one of the most important sources of heavy metal pollution of bodies of water, largely through fertilizers (Cd, Cr, Pb, Zn) and pesticides (Cu, Pb, Mn, Zn) (Mendes et al., 2006, Silva et al., 2016). In this respect, although agrochemicals are a decisive factor in increasing yields, they can also cause heavy metal contamination (Mendes et al., 2010). For example, fertilizers made from phosphate rocks can increase levels of heavy metals such as Cd, Cu, Mn, Ni, Pb and Zn in the soil (Freitas et al., 2009).

In order to protect human health and ecosystems, monitoring agencies have established maximum allowable limits for heavy metals in water (CETESB, 2005; CONAMA, 2005). A study of water samples from the Caetés watershed in Paty de Alferes, Rio de Janeiro (RJ), found Mn, Cd and Pb levels higher than the allowable limits stipulated by the National Environmental Council (CONAMA, 2005), attributed to atmospheric deposition and agricultural activities (fertilizers and agrochemicals) (Ramalho et al., 2000). Cunha Filho et al. (2014) analyzed crop irrigation water for the heavy metals Fe, Mn, Zn, Cu, Pb, Cd and Cr and found that only Fe content (0.908 mg L^{-1}) exceeded the allowable limit of 0.3 mg. L^{-1} (CONAMA, 2005).

In Pernambuco state, vegetable cultivation is concentrated in municipalities in the rural region, particularly Camocim de São Félix, where vegetable farming is the main economic activity. However, farmers in this area have used fertilizers without following technical criteria for at least 30 years, causing N and P contamination and eutrophication of water used for irrigation as well as human and animal consumption (Silva et al., 2001).

In this context, the present study measured levels of the heavy metals Cd, Cu, Mn, Ni, Pb and Zn in water used to irrigate vegetable crops and for human and animal consumption, in the municipality of Camocim de São Félix (PE), and compared them to the maximum allowable limits for these elements. Additionally, seasonal variations in water levels of these metals due to rainfall were also assessed.

2. MATERIAL AND METHODS

The study was conducted in vegetable farming areas in the municipality of Camocim de São Félix, located in the southern rural region of Pernambuco state, in the Brejo Pernambucano microregion. Annual rainfall in the area is between 900 and 1300 mm and altitudes range from 600 to 1000 m.

Water samples were taken from small dams in five vegetable farming areas along the slope. Samples were collected *in loco* and based on information obtained by the rural farmers and the Pernambuco Agronomic Institute (IPA). Each area had its own reservoir (R-1, R-2, R-3, R-4 and R-5), from which samples were taken of water used for crop irrigation as well as for human and animal consumption. Samples were also collected directly from a residential water source (artesian well). The reservoirs and residential well were georeferenced and the coordinates are shown in Table 1.

The areas containing the reservoirs are farmed using similar agricultural management systems, and exhibit an average 33% slope and consecutive annual vegetable crops. The farmers in this region use preventive and corrective irrigation and fertilizer/pesticide application during the different crops cycles. In this study, 200 mL of water was collected from the reservoirs each month, in addition to samples of the water used for human consumption, over a 12-month period (January to December 2010).

Table 1. Altitude, geographic coordinates and area of the bodies of water studied.

Reservations:	Altitude (m)	Coordinates	Body of water (m^2)
[a]R-1	643	S 8°22’34.5” and W 35°45’59.4”*	7600
R-2	640	S 8°22’37.0” and W 35°46’02.5”	8100
R-3	646	S 8°20’39.3” and W 35°45’04.9”	5250
R-4	656	S 8°20’36.7” and W 35°45’00.2”	5950
R-5	665	S 8°20’49.9” and W 35°44’58.1”	6300
Home[b]	699	S 8°21’50.2” and W 35°45’44.2”	---

[a]R = reservoir; [b] = artesian well. *data on altitude, coordinates and the bodies of water were obtained using a Garmin eTREX VISTA HCx GPS device.

Collections were performed between the 5th and the 8th of each month (January to December 2010) at different points of the reservoirs, avoiding areas with murky water or suspended material. At the residence, water was collected from a water outlet on the artesian well. An average of five subsamples were collected to form a 200 mL sample. The containers used for sampling were previously immersed in acidic solution (3% HCl) for 24 hours.

The samples were immediately acidified with dilute nitric acid, at 1 mL of HNO_3 for every 100 mL of sample. Once sealed, the flasks were kept in coolers and transported to the laboratory. On the same day they were collected, the samples were filtered in the laboratory using slow-filtering qualitative filter paper to prevent the release of low levels of the elements from the particulate material into the solution and stored in a refrigerator at 4°C. Concentrations of Cd, Cu, Mn, Ni, Pb were determined by flame atomic absorption spectrometry (Perkin Elmer AAnalyst 800), with detection limits for Cd (0.002), Cu (0.005), Mn (0.05), Ni (0.002), Pb (0.003) and Zn (0.002). For quality control purposes, samples of multielement standard solutions (spikes) were used, prepared based on 1000 mg L^{-1} standards (TITRISOL®, Merck), with concentration equal to the central point of the calibration curve of the device, for each chemical element.

The results were compared to the parameters established by Resolution 357 (CONAMA, 2005), which addresses the classification of bodies of water and their relevant environmental guidelines, as well as conditions and standards for effluent discharge. The resolution also

stipulates quality parameters for water for human and animal consumption, as well as irrigation of vegetables consumed raw and/or fruit that grows close to the ground and is eaten raw without removing the peel.

Monthly rainfall data for 2010 and the previous 10 years in the municipality of Camocim de São Félix were obtained from the Pernambuco Institute of Technology (Figure 1), to determine whether rainfall influenced heavy metal levels in the water analyzed (ITEP and LAMEPE, 2010).

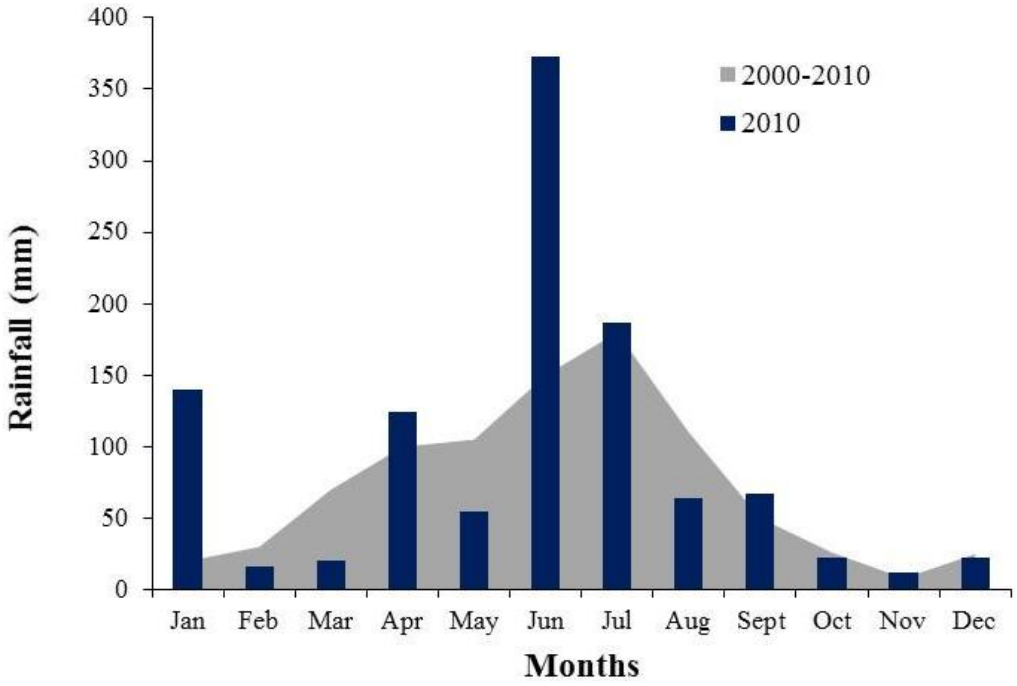

Figure 1. Mean monthly rainfall (January to December 2010) and historic mean in the municipality of Camocim de São Félix-PE. Source: Data provided by ITEP/LAMEPE, Camocim de São Félix Weather Station; * monthly rainfall in 2010 and 10-year average.

3. RESULTS AND DISCUSSION

No Cu, Mn or Zn was detected in water from the reservoirs and artesian well studied. These results are similar to those reported by Sobral et al. (2007), who recorded Cu, Mn and Zn levels below the detection limit in water from the Cabedelo River (Rio Cabedelo), in the Mangabeira industrial district of João Pessoa (Paraíba state - PB).

Cd levels in the water samples varied from 0.041 to 0.058 mg L^{-1} (Table 2 and Figure 2), with all samples found to be above the established standard (CONAMA, 2005) of 0.001 mg L^{-1}, indicating contamination of these water sources; a similar situation was reported by Paty do Alferes (RJ) (Ramalho et al., 2000) in Barra do Choça (Bahia state - BA). Cd is highly toxic and can cause poisoning when ingested in water or food (McGrath et al., 2006). The element is carcinogenic and can occur in agriculture through the use of pesticides and fertilizers (Sharma et al., 2007; Manzini et al., 2010).

Cd contamination in the water samples may be due to excessive use of phosphate fertilizers (Nacke et al., 2013; Gonçalves Júnior. et al., 2014; Benson et al., 2014; Balkhair and Ashraf, 2016). Around 60% of the Cd in triple superphosphate comes from phosphate rock. Bizarro et al. (2008) found Cd in the acidified P sources single and triple superphosphate, ranging from 2 to 13 and 3 to 33 mg kg^{-1}, respectively. These values are relatively low; however, intensive

farming using agrochemicals (fertilizers and pesticides) can increase heavy metal concentrations in the soil-water-plant system, especially in the case of elements poorly retained by the soil and easily lost to leaching (Singh and Agrawal, 2008; Freitas et al., 2009; Silva et al., 2016).

Table 2. Heavy metals in water samples from five reservoirs and an artesian well used to irrigate vegetable crops and for human and animal consumption in the municipality of Camocim de São Félix-PE.

	Months												
Areas	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sept	Oct	Nov	Dec	Mean
	[b]Cd mg L^{-1}												
[a]R-1	0.05	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
R-2	0.05	0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.05	0.04	0.04
R-3	0.04	0.05	0.04	0.04	0.05	0.04	0.04	0.04	0.04	0.04	0.05	0.04	0.04
R-4	0.04	0.04	0.04	0.04	0.04	0.05	0.05	0.05	0.05	0.05	0.06	0.05	0.05
R-5	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Home	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.05	0.06	0.06	0.05	0.05
CONAMA Nº 357/05*	0.001												
	[c]Ni mg L^{-1}												
R-1	1.95	2.18	2.14	2.47	2.73	2.59	2.57	2.48	2.51	2.7	2.41	2.07	2.4
R-2	2.26	2	1.87	2.02	2.23	2.09	2.35	2.23	2.32	2.44	2.43	2.06	2.19
R-3	2.45	2.58	2.22	2.44	2.19	2.14	2.62	2.57	2.33	2.57	2.17	1.85	2.34
R-4	2.67	1.97	2.3	2.58	2.38	2.46	2.72	2.96	2.56	2.5	2.69	2.62	2.53
R-5	2.78	2.25	2.45	2.47	2.55	2.89	2.62	2.61	2.9	2.75	2.75	2.52	2.63
Home	2.32	2.71	2.53	2.58	2.49	2.95	2.88	2.9	3.17	3.28	3.31	3.25	2.86
CONAMA Nº 357/05*	0.025												
	[d]Pb mg L^{-1}												
R-1	<Ld[e]	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	0	<Ld
R-2	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	0	<Ld
R-3	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	<Ld	0	<Ld
R-4	0.08	0.04	0.06	0.11	0.1	0.1	0.12	0.1	0.12	0.13	0.12	0.09	0.1
R-5	0.11	0.15	0.16	0.16	0.18	0.19	0.19	0.18	0.04	0.08	0.09	0.12	0.14
Home	0.08	0.12	0.09	0.09	0.08	0.05	0.08	0.05	0.07	0.07	0.07	0.06	0.08
CONAMA Nº 357/05*	0.01												

[a]R= reservoir; [b]Cd= cadmium; [c]Ni= nickel; [d]Pb=lead; [e]Ld= not detected.

There were no changes in Cd content as a function of varying monthly rainfall, and only a slight increase in some of the reservoirs after periods of intense rainfall, possibly due to large amounts of sediment carried by erosion or more intense percolation of the element in the soil.

Ni levels in the water samples ranged from 1.85 to 3.31 mg L^{-1}, at least 70 times higher than the established maximum allowable limit of 0.025 mg L^{-1} (Figure 3) (CONAMA, 2005), indicating significant nickel contamination of the bodies of water studied. This may also partially explain the decline in Ni in the cultivated areas, given its greater movement in the soil, which may favor leaching, leading to Ni contamination of the groundwater and, consequently, dammed water, exacerbated by evaporation. The rise in Ni levels after intense rainfall (January and June) may indicate the introduction of the metal along with sediment carried by erosion.

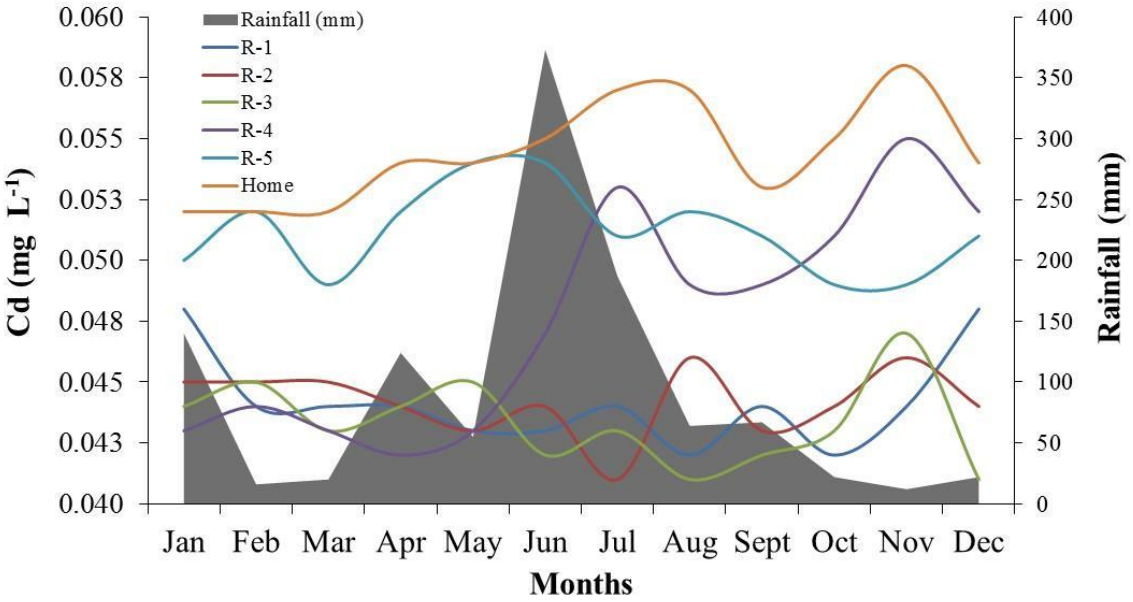

Figure 2. Influence of rainfall on the seasonal variation in cadmium (Cd) concentration in water samples from five reservoirs (R) and an artesian well (home) used to irrigate vegetable crops and for human and animal consumption in the municipality of Camocim de São Félix-PE.

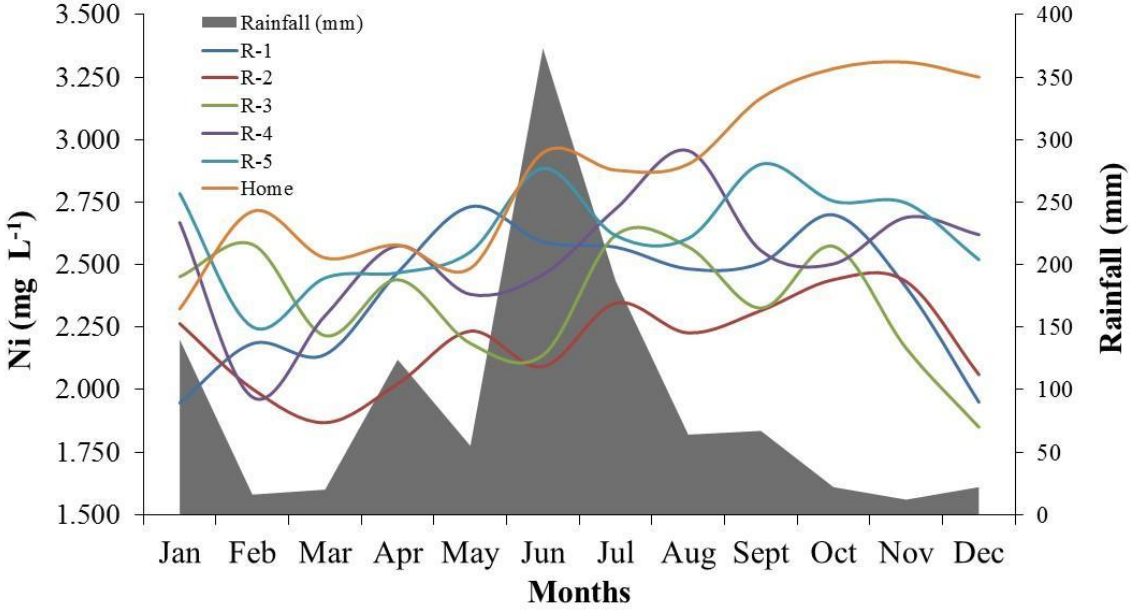

Figure 3. Influence of rainfall on the seasonal variation in nickel (Ni) concentration in water samples from five reservoirs (R) and an artesian well (home) used to irrigate vegetable crops and for human and animal consumption in the municipality of Camocim de São Félix-PE.

Pb content varied between 0.051 and 0.144 mg L^{-1} and was not detected in water from reservoirs R-1, R-2 or R-3 (Figure 4). Ramalho et al. (2000) studied heavy metal contamination in the Paty do Alferes watershed (RJ) and also found Pb levels higher than the maximum allowable limit. The values recorded in our study were higher than the established standard of 0.01 mg L^{-1}, with R-5 exhibiting the highest Pb content. This reservoir supplies farming area AC5, which displayed the highest soil heavy metal levels, possibly due to the use of agrochemicals and the irrigation water itself (Vieira, 2011).

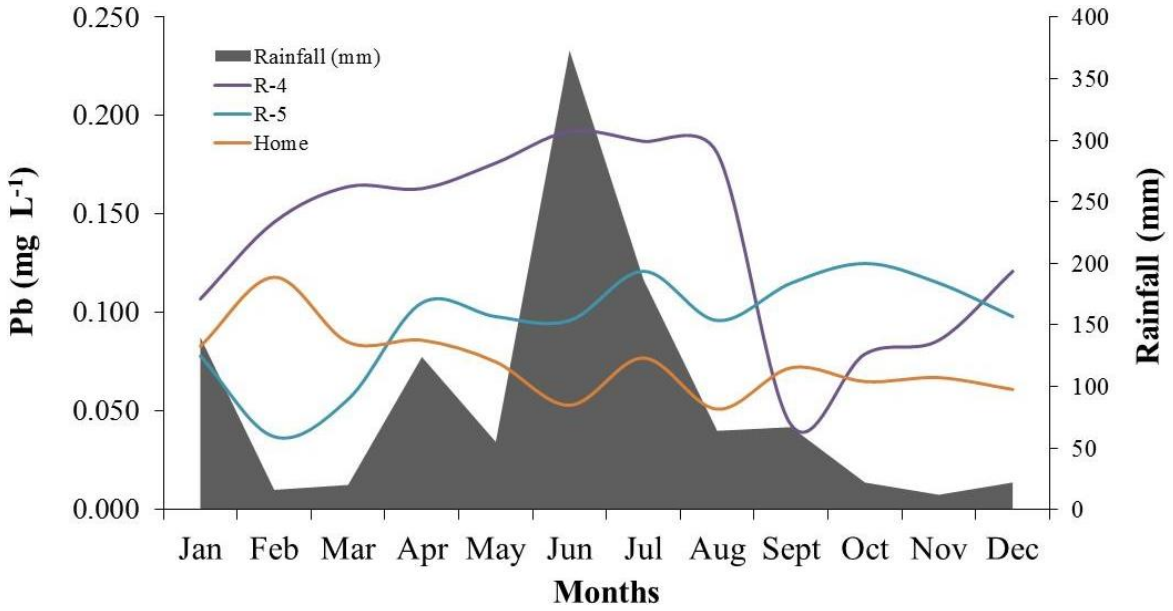

Figure 4. Influence of rainfall on the seasonal variation in lead (Pb) concentration in water samples from five reservoirs (R) and an artesian well (home) used to irrigate vegetable crops and for human and animal consumption in the municipality of Camocim de São Félix-PE.
* No Pb was detected in reservoirs R-1, R-2 and R-3.

As such, given its low mobility in the soil, it is suggested that this metal is transported primarily by erosion and concentrates in the reservoir water; since this water is used for irrigation, the element returns to the soil and risks contaminating the vegetables grown on the site.

It is important to underscore that Pb content in the water consumed in the city, which is drawn from the subsoil (well) and distributed to homes without prior analysis or treatment, ranged from 0.051 to 0.086 mg L^{-1}, that is, far higher than the limit stipulated by CONAMA (2005). Most Pb enters the human body through the respiratory and gastrointestinal tracts; once absorbed, it can be found in the blood and soft tissue and mineralized in bone (ATSDR, 2012). Pb can affect almost all the body's organs and systems, but the nervous system is the most sensitive, in both adults and children; the effect of the element is cumulative and causes chronic lead poisoning (CETESB, 2009).

The influence of rainfall on Pb levels declined in the months following the heaviest precipitation, suggesting a possible dilution effect, since Pb concentration rose again when rainfall was low and remained stable during those months.

In Brazil, there is almost no control over Pb pollution sources due to the lack of information on the actual exposure of the population (Neves et al., 2009). Thus, further research is needed in order to support public health authorities in initiatives to control environmental damage. The case of the municipality of Camocim de São Félix is an example of this scenario. The data in this study demonstrate the urgent need for additional studies on the issue, as well as environmental education measures and technical assistance, in order to reduce heavy metal contamination, thereby ensuring food security and water quality.

4. CONCLUSIONS

The water analyzed in the present study exhibited higher Cd, Ni and Pb levels than the maximum allowable limits under Brazilian legislation, indicating the need for a preventive monitoring program and immediate intervention initiatives aimed at the sources of contamination.

The results demonstrate the need to quantify heavy metal content in vegetable crops, since their contamination by irrigation water may make them harmful to human health.

Rainfall influences the seasonal variation in heavy metal levels in water, exhibiting a greater effect on Pb concentration and a moderate influence on Cd and Ni.

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Critical evaluation of the factors affecting *Escherichia coli* environmental decay for outfall plume models

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ABSTRACT

The *Escherichia coli* T_{90} parameter is widely employed in outfall plume hydrodynamic models. Although there is a great deal of academic literature estimating T_{90}, no standard methodology has been validated so far. Estimation of die-off rates should consider many other biological, chemical and physical processes. Over the last three decades, while a great deal of new knowledge about microbial biology and ecology has become available, it has not been fully incorporated into the overall research. Consequently, hydrodynamic models of sewage plumes lack consistency with environmental dynamics and frequently do not fully reproduce processes. This article scrutinized the relevant works that could improve T_{90} assessment using the most robust and realistic approaches. The most important related literature since the 1990s was considered, together with earlier relevant works. The research focused on techniques and methodologies, especially their ecologic and cellular biology aspects. A brief discussion of the methods applied to evaluate the T_{90} of bacteria examined aspects like representativeness of incubation, incubation scale, measurement procedures and models' representations of bacterial decay. The factors affecting population decay, such as solar radiation, salinity and interaction with solids, were considered in the light of the very large literature registry. Finally, biological aspects affecting decay, like predation and genetic resistance, were also analyzed. The resulting updated understanding of T_{90} may contribute to better managerial procedures that could improve water quality in freshwater and coastal systems, and consequently improve human health outcomes.

Keywords: bacteria, environmental decay, water quality.

Avaliação crítica dos fatores que influenciam o decaimento de *Escherichia coli* para modelagem de plumas de emissários submarinos

RESUMO

O parâmetro T_{90} de *Escherichia coli* é muito empregado na modelagem hidrodinâmica de plumas de emissários submarinos. Apesar da extensa literatura disponível que aplica T_{90} em

modelos hidrodinâmicos, não existe uma padronização metodológica para sua avaliação que seja validada até hoje. Além das taxas de decaimento, muitos outros processos biológicos, químicos e físicos deveriam ser considerados nas modelagens hidrodinâmicas. Nas últimas três décadas, embora um extenso conhecimento sobre biologia e ecologia microbiana tenha sido desenvolvido, pouco deste conhecimento foi incorporado às aplicações. Consequentemente, os modelos de plumas de esgotos não lograram reproduzir de maneira fiel os processos ambientais. No presente artigo, os trabalhos relevantes que poderiam melhorar a determinação do T_{90}, sob abordagens mais robustas e realistas foram revisados. A literatura mais relevante desde os anos 1990 foi considerada, juntamente com alguns trabalhos relevantes mais antigos. A pesquisa focou em técnicas e metodologias de avaliação de aspectos ecológicos e de biologia celular. Uma breve discussão dos métodos aplicados à avaliação do T_{90} examinou aspectos como a representatividade das incubações, escala dos experimentos de incubação e procedimentos de medição, com ênfase em modelos de decaimento bacteriano. Os fatores que afetam o decaimento bacteriano como radiação solar, salinidade e interação com sólidos foram considerados à luz do extenso registro da literatura. Finalmente, aspectos biológicos que afetam o decaimento como predação e resistência genética foram analisados. O entendimento atualizado resultante da pesquisa com T_{90} pode contribuir para o desenvolvimento de procedimentos de gestão que podem melhorar a qualidade da água em sistemas costeiros e continentais, dando soluções para problemas de saúde em populações humanas.

Palavras-chave: bactéria, decaimento ambiental, *Escherichia coli*, qualidade de água.

1. INTRODUCTION

One of the most widely used and cost-effective destinations for the disposal of large amounts of domestic sewage is marine outfalls, especially in coastal areas (Yang et al. 2000). Despite its popularity, this method constitutes a population health risk because bacteria can remain alive for a long time (Alkan, 1999; van Elsas et al., 2011). In fact, previous studies have shown that coliforms from domestic sewage, including the pathogenic *Escherichia coli* strains, can survive for long periods of time (Omar 2010) as Viable But Not Cultivable (VBNC) organisms, retaining their enteropathogenicity (Lothigius et al., 2010, Pommepuy, et al. 1996a; van Elsas et al., 2011). The pathogenic *E. coli*, however, is not the only danger present in domestic sewage. In fact, in the present study, we regarded it principally as an indicator of overall pollution risk (de Brauwere et al. 2014b). The management of that risk starts long before the outfall step, because the construction of a waste management technique requires hydrodynamic modeling that can assess the environmental impacts on the surrounding ecosystems (Fernández, 2011, Yang et al., 2000).

Finite element, finite differences, and other transport numeric models are adequate tools that enable the forecasting of results of a process before it happens (Feitosa et al., 2013a; Fernández, 2011; Rodrigues et al., 2011). On the other hand, the model must be fed with consistent local parameters (Ozcan, 2002) and rates (Chan et al., 2015) that yield realistic estimations. In outfall modeling, one of the important parameters of the environmental conditions is the time required for 90% of the *E. coli* to die-off (*E. coli* T_{90}), and several researchers throughout the world have come up with values for this parameter (Table 1) under various conditions (Chan et al., 2015; Feitosa et al., 2013a; Jozić et al., 2014; Rozen, 2001; Yang et al., 2000).

Table 1. *E. coli* die-off values (T_{90}) obtained from the literature.

Location	T_{90} ranges	Specific conditions	Authors
Laboratory, with samples collected from Taiwan, China	1.67 – 3.17 hours	In the presence of predators, sea water during daytime and night respectively	(Yang et al., 2000)
Various	1.9 – 46.4 hours	Various locations, reviewing the data of various authors	(Feitosa et al., 2013a)
Laboratory	0.31 – 190 hours	Experiments with two *E. coli* ATCC strains under solar radiation or in the dark	(Jozić et al., 2014)
Hong Kong	10.8 - 42.3 hours	Daylight *in situ* experiments	(Chan et al. 2015)
New Zealand	100 -135 hours dark 3.3 – 20.3 hours under sunlight	outdoor experimental open-top chambers light and dark conditions	(Sinton et al., 2002)

Research on *E. coli* T_{90} has found values ranging from 2 hours to many days, under both light and dark conditions (Chan et al., 2015; Craig et al., 2004; Jozić et al., 2014; Lothigius et al., 2010; Zhang et al. 2015). The large variation is the result of the varying conditions under which these studies were carried out (Alkan et al., 1995; Berney et al., 2006; Craig et al., 2002; 2004; Lothigius et al., 2010; Moriñigo et al., 1990; Rozen, 2001). Thus, as already noted by Alkan et al. (1995) in the 1990s, it is still not fully understood even now how the varying factors act on *E coli* T_{90} or how intensely they act.

This study reviewed the current knowledge about the factors affecting the T_{90} of *E. coli*, summarizing the ways in which studies have been carried out, and analyzing their methodological design in order to suggest new paths for improvements. Available literature about marine *E. coli* from the last 30 years were surveyed, and the most significant studies beyond this period as well. A particular focus was addressing the methods and parameters employed in these studies, the resulting decay models, and the obtained data. Other factors that could influence T_{90} were also discussed.

2. ADEQUACY OF *E. COLI* PARAMETERS FOR OUTFALL-PLUME MODELING

The study of the *E. coli* T_{90} of outfall plumes started with the premise that this organism is a reliable indicator of the presence of domestic sewage (Craig et al., 2004), and has been used in several contaminant models, becoming almost a standard. Recently, more attention has been focused on *E. coli* T_{90}, as a result of increasing water pollution, antibiotic resistance, and enterophatogenicity in the environment (Araujo et al., 2016; Carneiro et al., 2015; Fernández-Delgado and Suárez 2009; Griffith et al., 2016; Nataro and Kaper, 1998; Omar, 2010; Pommepuy et al., 1996b; USEPA, 2009). Notwithstanding this, it is important to highlight that although there is a relationship between *E. coli* bacterial counts and sewage, no relationship has currently been established between *E. coli* counts and pathogenic bacteria (Carneiro et al., 2015; Omar, 2010). Thus, whether to consider *E. coli* a sewage pollution bioindicator (a Fecal Indicator Bacteria (FIB)) or simply a pathogen to be monitored has not yet been determined. Before that determination can be made, its population dynamics in the environment need to be better understood. For this purpose, the academic community should increase research on *E. coli* T_{90}, trying to balance the best tools for scientific study with practical management of environmental systems. This important discussion must be pursued (Bucci et al., 2011; Craig

et al. 2004; Nataro and Kaper 1998; Omar, 2010; Pommepuy et al., 1996b; van Elsas et al., 2011).

Although *E. coli* have been broadly used in modeling, other microorganisms and molecular markers have been studied as alternative indicators. In most studies, *Enterococcus sp*. seems to present longer T_{90}s, but requires less accumulated radiation to decay. Coliform bacteria have shown lower T_{90} than coliphages, (*e.g.*, F-DNA phages, *Bacteroides fragilis* phages, F-RNA phages, *Clostridium perfringens*) and markers (*e.g.*, Enterococci 23S rRNA [ENT-23] and – *Escherichia coli* [EC-uidA]), in several types of matrices (Alkan et al., 1995; Brooks et al., 2015; Davies-Colley et al., 1994; Sinton et al., 1999; Zhang et al., 2015). On the other hand, Rippy et al. (2013) encountered larger *Enterococcus* decay rates (lower T_{90}) than *E. coli* in Huntington Beach, California, U.S.A. (using the enzymatic method). This apparent contradiction could be the result of the different methodological approaches to study the application of culture or enzymatic method to VBNC (Viable But Not Cultivable) bacteria, as will be further discussed in this article.

3. METHODS FOR EVALUATING *E. COLI* POPULATION DECAY

3.1. Decay factors

From the literature, one can observe two principal factors engendering bacterial population decay in the environment. The first is composed of physical processes that separate cells from one another: these are principally currents and tides, dilution, adsorption, sedimentation and resuspension (Alkan, 1999; de Brauwere et al., 2014a; Craig et al. 2004). Another factor affecting decay is biological. Biological decay can be led, modulated and minimized by solar radiation, turbidity (radiation attenuation), salinity, predation, temperature, pH, competition, growth under different nutrient conditions, and growth under the release of nutrients from dead cells (Alkan et al., 1995; Beardsley et al., 2003; Bucci et al., 2011; Carrillo et al., 1985; Chan et al., 2015; Davies-Colley et al., 1994, Jozić et al., 2014, Troussellier et al., 1998; van Elsas et al., 2011; Yang et al., 2000). Jozić et al. (2014) adds to that list variations at the gene level, which can improve bacterial resistance. The results of both physical and biological processes might explain the so-called biphasic decay. As stated by Bucci et al. (2011), biphasic decay is characterized by an early period with a higher apparent first-order constant decay rate, followed by a later period with a lower constant rate. Obviously, in the environment these two large decay phases act together, making decay studies even more complex and hard to simulate with first-order decay models (Figure 1).

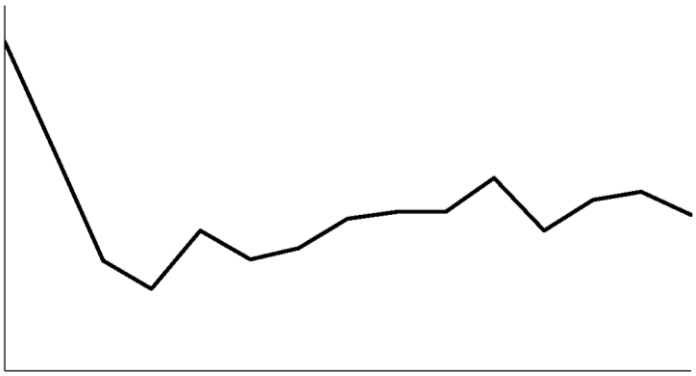

Figure 1. An example of the biphasic decay of *E. coli*. Inoculated in phosphate buffer solution (PBS). *Escherichia coli* K-12 MG1655 strain MV1973, which is a streptomycin resistant (adapted from Bucci et al., 2011).

3.2. Increasing Methodological robustness on assays

Biological, molecular and environmental factors act synergistically to alter the *E. coli* T_{90} (van Elsas et al., 2011), and this general frame cannot be assessed with simple experimental arrangements. Hence the T_{90} studies in seawater depend to a large extent upon the methodologies adopted (Rozen, 2001). An example of this dependency was given by Rhodes (1988), who studied *E. coli* survival in estuarine conditions, observing a less than one-log population decrease. In this case, inoculum with filtered water was maintained for 16 days in *in situ* diffusion chambers, while other *in situ* studies in chambers without water filtration showed T_{90} to be as little as 2-3 hours. Lee et al. (2011), investigated whether the decay rates for *E. coli* were similar to halophilic and non-halophilic bacterial pathogens. For this purpose, they used 6 different pore size filters, namely 250 µm (unfiltered), 0.7 µm (for cleaning nanoflagellates and ciliates) and 0.02 µm (for cleaning from any eventual predator). This design allowed the determination of the importance of protist bacterivory on bacterial decay in tropical coastal waters. According to these authors, *E. coli* is a poor indicator of halophilic pathogens, because they don't survive well in seawater. However, since these authors used culture methods, short survivorship might be a consequence of the non-cultivability. Sinton et al. (1999) carried out solar inactivation experiments in large chambers (300 L) in a so-called thermal jacket, 13,000 L in size, in order to improve the thermal homogenization of water. Besides sunlight assays, dark assays were carried out simultaneously, allowing the subtraction of the die-off results under dark conditions from those under sunlight conditions.

Presently, the advancement of molecular methods for strain detection and differentiation has led to a better understanding of the fates of, and changes in, microorganism communities in the environment (Kim and Wuertz, 2015; Korajkic et al., 2014). Omar (2010) looked for several gene targets, using PCR to encounter pathogenic and commensal *E. coli* in sewage effluents, and concluded that PCR has a large potential to be used for the monitoring of water samples for the presence of pathogenic *E. coli* without the need to culture the organisms. Zhang, He, and Yan (2015), using cultivation-independent qPCR quantification of 16S rRNA genes and Next-Generation Sequencing (NGS), were able to analyze a microbial community. Korajkic et al. (2014) evaluated the effects of ambient sunlight and biotic interactions on the decay of culture-based Fecal Indicator Bacteria (FIB), and compared them to the application of molecular markers with qPCR using 1) Entero1a to target the Enterococcal 23S rRNA gene; 2) GenBac3 to target the Bacteroidales 16S rRNA gene; 3) HF183 to target the Human-associated Bacteroidales 16S rRNA gene; and 4) HumM2 to target the Bacteroidales-like putative σ factor. These authors concluded that there was a strong correlation between molecular FIB and human-associated genetic markers, but no correlation between any molecular markers and cultured FIB. This may be due to the greater persistence of the genetic marker in the environment. It may be that molecular markers could be used to trace sewage pollution farther than could cultured FIB. The molecular approach, then, could bring a new conceptual frame, free of the former culture methods and the confounding physiologic stages or differential decay of strains.

3.3. Studies on VBNC (Viable But Not Cultivable) bacteria

The hostile situations encountered by enteric bacteria in seawater lead to loss of the ability to form colonies and to grow on media, sometimes remaining viable (VBNC state; Xu et al., (1982)). Enteric bacteria can survive for long periods in fresh or salty water, as Viable But Not Cultivable (VBNC) organisms, a capability that is important because it allows them to retain their infectious ability. *E. coli* die-off measurements can be influenced by the presence of VBNC which is not accounted for, leading to underestimation of health risk for the modeling of outfalls and allowing direct human contact in contaminated waters (Bonamano et al., 2015; Gonzalez et al., 1992; Lothigius et al., 2010; Oliver et al. 2005; Omar, 2010; Pommepuy et al. 1996b, Rozen, 2001). Pommepuy et al. (1996b) have already proposed that most (maybe all) *E.*

coli die-off attributed to sunlight could in fact be induction to the VBNC stage. Finally, an early study carried out by Gonzalez et al. (1992), using Rhodamine-stained bacteria (RSB), could straighten out this conceptual picture, enunciating that bacterial death should be understood as lysed bacteria that cannot grow on standard bacteriological media, cannot metabolize, and cannot infect other organisms. On the other hand, the VBNC, although injured, are active bacteria that have simply lost cultivability (Gonzalez et al., 1992, Lothigius et al., 2010). Thus, both Cultivable - Viable and VBNC bacteria are viviform cells and should also be counted in water-quality studies, monitoring and modeling (Omar, 2010).

Whenever studying VBNC bacteria, it is necessary to comprehend the differences in the counts obtained in various media. Generally, there are lower colony counts in more selective media like the Standard Levine BEM, and higher counts in less selective ones such as Nutrient Agar supplemented with sodium chloride (Gauthier et al, 1987; Pommepuy et al., 1996a). Even in less-selective media, up to 30% of the bacteria do not grow, because of the presence of VBNC (Taimur-Khan et al., 2010). Enzymatic assays, based on the detection of the enzymes β-galactosidase—characteristic of the Coliform group, and β-glucuronidase—characteristic of *E. coli*, can disclose the presence of cells even after they have lost their colony-forming capacity (Davies et al. 1995; Nataro and Kaper, 1998; Pommepuy et al., 1996a).

There are other techniques that produce reliable but differing results from cultures, like flow cytometry counts, and epifluorescence microscopy (Beardsley et al., 2003; Pommepuy et al., 1996b; Taimur-Khan et al. 2010; Troussellier et al., 1998), which are worth applying in decay studies. For example, Pommepuy et al., (1996b) evaluated *E. coli* decay in flasks and chambers. After 26 hours they obtained stable direct counts - from flasks - by epifluorescence microscopy plus acridine orange stain, while measurements on spread culture methods obtained no detectable count. Dark assays did not show significant decreases in culture measurements (as agreed by Troussellier et al. (1998). These results showed that solar radiation impacts culture counts, but not bacterial viability. All these findings demonstrate the effects of the chosen methodologies on the results, but also weakens solar radiation disinfection theory, and can reinforce the conclusions of Pommepuy et al., (1996b) that in many cases, the die-off attributed to natural sunlight may actually mean that cells become VBNC rather than experiencing a definitive die-off or cell death.

3.4. The scale of the studies

In order to assess *E. coli* T_{90}, researches have been employing an inoculum of bacteria accounting of 10^6-10^9 CFU/100 mL on assays, where decay is used for the establishment of mathematical expressions (Alkan, 1999; Alkan et al., 1995; Chan et al., 2015; Lothigius et al., 2010; Moriñigo et al.; 1990) These techniques are performed in microcosm- or mesocosm-scale experiments in the field or under laboratory conditions, but can also be carried out in field monitoring surveys. Rozen (2001) draws attention to the limitations of both field and laboratory experiments: the laboratory experiments cannot simulate the environmental complexity; field studies, used to validate laboratory results, yield site-specific data; and field monitoring surveys lack target population control: most of them ignore the previous growth history of the strains. The studies range from well-controlled systems, yielding superficial knowledge to complex systems in which processes cannot be adequately controlled, and hence may not produce valid results. Thus, to overcome these limitations, consideration of the appropriate scale is required, consistent with what can be expected. It should be understood that any experimental design can give only partial and imprecise information.

Laboratory microcosm-scale experiments have been widely employed and have attained significant improvements in T_{90} knowledge. After Carpenter (1996), this scale has been used to estimate the response of organisms — in terms of decay velocity, replicability and power

increment — to specific environmental conditions. Microcosm scales have been built with bottles, beakers, flasks or columns, equipped with lamps, under very controlled conditions (Carpenter, 1996; Craig et al. 2004; Jozić et al., 2014; Lothigius et al., 2010; Pommepuy et al., 1996b; Zhang et al., 2015). However, the microcosm treatments can significantly alter the features of communities and ecosystems. Microcosms, then, can be considered a very indirect way of learning about the ecology, but can yield misleading results concerning environmental processes (Beardsley et al., 2003; Carpenter, 1996; Davies-Colley et al., 1994).

Mesocosm is another form that can precede ecological assays. It can be structured as an experimental outdoor plot or as an "*in situ*" partially closed environment, with limited exchanges with its surroundings (Kampichler et al., 2001). Mesocosms differ from microcosms in their fundamental concepts. The arrangement of a mesocosm allows assay control, without the mentioned limitations and confounding factors from microcosms, and has been used by many authors (Davies et al., 1995; Forster and Schubert, 2001; Moriñigo et al., 1990; Pommepuy, et al., 1996b; Rhodes, 1988; 1990). However, mesocosms cannot provide full access to real aquatic ecosystems, promoting both bacterial species' selective growth and grazing, distorting the community structure (Beardsley et al., 2003). For example, Forster and Schubert (2001) used a robust 1-m^3 mesocosm to test the effects of enhanced and reduced ultraviolet radiation (UV) on the planktonic community. These authors encountered smaller zooplankton population densities (rotifers and Copepods) that increased rapidly to populations that were denser than those observed in the estuary, probably due to the absence of predators like fish and larger zooplankton. Therefore, in order to study *E. coli* T_{90} under near-real conditions, the mesocosm should comprise closed containers located in the real environment, avoiding loss of cells or mixing with environmental constituents, but still allowing fluxes. Some authors (Davies et al., 1995; Moriñigo et al., 1990; Pommepuy et al., 1996b; Rhodes, 1988) tried to solve these technical limitations using diffusion chambers (as modified by McFeters and Stuart (1972) with 0.2 µm polycarbonate membranes to interface with the environment. Other authors showed that dialysis bags (13 to 14 kDa pore-size) could attain still-better results (Beardsley et al., 2003; Korajkic et al., 2014). These chambers allow dissolved matter, but no cells, to pass through them.

3.5. Modeling

The literature includes several models that simulate *E. coli* T_{90} die-off in the laboratory and in environmental marine conditions. Alkan et al. (1995) constructed a model considering five influences: light (W m^{-2}), turbidity (absorbance), sewage load (%v/v), mixing (cm^2 s^{-1}) and temperature (ºC). However, multiple regressions explained only 76% of the cultivated *E. coli* die-off, and the authors concluded that the limited accuracy may be the result of the experimental conditions. Feitosa et al. (2013a) made a statistical evaluation of several models and recommended the one designed by Mancini (1978), which presented the most reliable result when compared to others. This model includes the decay rate (K) in the presence and absence of solar radiation, and combines the salinity and temperature actions. Feitosa et al. (2013b) coupled Mancini's decay equation in hydrodynamic models, and found strong correlations between fecal coliform concentrations and solar radiation levels. In addition, in order to attain better reliability, the modeling studies have been optimized in field surveys, which calibrated marine currents, tides, wind or added particulate matter, attached and free bacteria settling, and advection/diffusion variables. Several of these models can be examined in the literature (*e.g.*, Chan et al., 2015; Fernández, 2011). Chan et al., (2015) used the same environmental factors as Mancini's, resulting in good accuracy with field data. Rodrigues et al. (2011) coupled a three-dimensional hydrodynamic and fecal contamination model, and were able to represent the main patterns and trends observed in *E. coli* and fecal *Enterococcus* concentrations along a stream. Zhu et al. (2011) concluded that efflux from sand during high tide was responsible for the

concentrations of indicator microbes. Regardless of the success of these models, it must be taken into account that these results might be distorted by the modeling procedures and the chosen monitoring fecal indicators employed, which were limited by the physiologic state, as mentioned above.

4. FACTORS AFFECTING POPULATION DECAY

4.1. Solar radiation

A large number of studies have assessed the importance of solar radiation on *E. coli* T_{90} under natural conditions (*e.g.*, Hernroth et al., 2010; Herrig et al., 2015; Korajkic et al., 2013). Jozić et al. (2014) tested two different *E. coli* strains, from canine (ATCC 36218) and human (ATCC 8739) feces, and found strong and significant effects of solar radiation, reducing the T_{90} by 15- to 70-fold. These authors also observed that UV declined by around 9% to 2% per meter of depth with a proportional increase in T_{90}, principally at 320- to 360-nm wavelengths. This wavelength range was shown to have the highest impact on bacterial survival (Davies-Colley et al., 1994). Sinton et al. (1999) found that cultivable *E. coli* decayed 29 times faster under solar radiation than under dark conditions. Craig et al. (2004) assessed cultivable *E. coli* counts between 10 and 100 times smaller from seawater under sunlight than from bottom sediments, two days after a storm event. Considering these data, the T_{90} from oligotrophic areas should not be applied in eutrophic ones, where plankton and suspended solids reduce the lower wavelength of sunlight, principally UV-B (Rozen, 2001). Confirming this behavior, Alkan et al. (1995) observed the highest cultivable *E. coli* die-off when the sewage was diluted to 0.25% under 900 W/m^2, and the absorbance attained a rate of 0.04, its lowest assays value. Herrig et al. (2015) developed a model made for water-quality simulations in the Lahn River, resulting in a strong correlation between turbidity and fecal indicators, probably because of the reduced solar radiance in that area. Along these same lines, Craig et al. (2004) attributed differences between modeled and measured values of coliform die-off to varying turbidity after storm events. Thus, where irradiance is important, the turbidity factor is important also, and has been considered a dominant predictor for T_{90} on enteric bacteria and somatic coliphages (Hernroth et al., 2010; Herrig et al., 2015; Kay et al., 2005).

4.2. Salinity

Because salinity increases osmotic potential of the water, coliform bacteria are strongly affected. However, the effects of salinity is not only osmotic, but interacts with other parameters. Troussellier et al. (1998) highlighted the importance of the interactions of nutrient deprivation and salinity, while Sinton et al. (1999) observed that the solar radiation inactivation (making bacteria VBNC) increased when the salinity was high. These works agree with those of Yang et al. (2000). Lothigius et al. (2010), who, when working with enterotoxigenic *E. coli* during long-term incubation (up to 6 months), encountered a large difference (2 weeks) in cultivability between seawater and freshwater. Jozić et al. (2014) also obtained significantly different results, demonstrating that *E. coli* decay is linked to salinity, although this author used a narrow salinity range.

The pre-adaptation to high osmolarity would up-shift the cell resistance to seawater salinity, because during osmotic shock, a bacterial cell starts to accumulate osmoprotectant molecules (Gauthier et al., 1987, Rozen 2001). Confirming these results, de Brauwere et al. (2014a) measured strong *E. coli* decay in a river sector where salinity changes were pronounced. Other authors showed that salinity seems to synergistically influence *E. coli* decay, an effect that, along with other parameters, will be further discussed in following sections of this article.

4.3. Dilution

Dilution was indicated as one of the most important factors influencing *E. coli* decay in the Scheldt River and estuary (de Brauwere et al., 2014a). The effects of solar radiation, turbidity, salinity and predation are modified by dilution (Alkan et al., 1995; Yang et al., 2000). Yang et al. (2000), highlighted that dilution is important not only because it reduces the sewage concentration, but also because:

a) In seawater, the salinity of sewage increases, thereby increasing its deleterious influence over bacteria
b) Elevated concentrations of suspended solids increase turbidity, which reduces the penetration and action of solar radiation in sewage. Dilution restores the radiation penetration, increasing mortality of the bacteria.
c) Dilution causes predators to disperse in the sewage mixture, reducing predation pressure.

4.4. Temperature

Although temperature is often cited as an important factor for bacteria, it was excluded from the model of Herrig et al. (2015), because these authors considered that temperature depends on solar radiance. Jozić et al. (2014), carried out regression analyses and found no significant influence of temperature, even when interacting with salinity. Alkan et al. (1995) and Brooks et al. (2015) encountered no significant effect of temperature on the persistence of cultivable *E. coli* and *Enterococcus* sp. Thus, many authors have given little importance to the effect of temperature oscillations on T_{90} values (Alkan et al., 1995). On the other hand, Mackay (1985) pointed that high temperatures inactivate bacteria, and promote increased metabolism, which requires extra sources of nutrients.

Hernroth et al. (2010) encountered a better performance of ETEC (Entero-Toxigenic *E. coli*) cultivated at 8ºC compared to 18ºC, agreeing with Craig et al. (2004), who worked at 10ºC, 20ºC and 30ºC. It should be also considered that Rhodes (1988) evidenced significant effects of temperatures greater than 10ºC, on *E. coli* multiplication; the higher temperatures reduced its net die-off, in assays. Finally, Blaustein et al. (2013) reviewed 166 datasets on *E. coli* survival under dark conditions, and found an increasing trend of inactivation values following temperature increase. The role of temperature might be considered synergistically with nutritional aspects. In both cases, to manage systems or model water quality, it is very important to consider the local temperature conditions.

4.5. Nutrient availability

Nutritional availability seems to play a key role in the viability of *E. coli* in the environment. The existence of readily usable nutrients and the way the bacteria use them will determine the period the bacteria will remain viable (*e.g.*, Gauthier et al., 1987; Hernroth et al., 2010). The nutritional status works synergistically with other factors. For example, Hernroth et al., (2010) analyzed ETEC cultivated at 18ºC in highly nutritional water, and observed a significant positive effect on its cultivability, compared to cultivation in low-nutritional water. In fact, nutritional conditions could promote population increase (Rhodes, 1988). Besides, Carrillo et al. (1985) concluded that the primary regulator of densities of coliforms in the tropical environment is probably the nutrient concentration. However, under nutritional stress, *E. coli* can modulate its physiology to conserve energy or to use nutrients released from dying cells (Bucci et al., 2011). Knowledge of the nutritional requirements and their implications on research under laboratory conditions that use cultivated inoculum is relevant. However, nutritional mechanisms are also controlled by genetic modulations, which will be discussed in following sections.

4.6. Interactions with solids

The resuspension process is an emerging issue, and an important gap in bacterial environmental decay research, linking adsorption, desorption, viability and the infectivity capacity of *E. coli* bacteria (Korajkic et al., 2013; Steets and Holden, 2003; de Brauwere et al., 2014a). Using a sedimentation column, Alkan (1999) studied the relationship between particles and bacteria, observing that the concentration of clay particles, the shear rate, and the concentration of sewage, had significant roles in the removal of *E. coli* from the water column (up to 36%). Nevertheless, this removal was not linear, because although on the one hand the bacteria associate with the particles, sinking together, on the other hand, sewage particles compete with bacteria for adsorption sites on the particles. In his study, the principal removal of *E. coli* occurred through a shear rate of 25 s^{-1} at a concentration of 60 mg L^{-1} clay and 0.5% sewage content. The authors concluded that bacteria removal in the sea becomes significant when shear rates vary between 20 and 25 s^{-1} and with turbidities of up to 50 mg L^{-1}. Considering that many outfalls are modeled with an initial sewage dilution of 1% (1), the highest removal rate could take place in the mixing zones. It can be inferred that the removal of bacteria by solids will be important principally in restricted coastal areas with both high turbidity and high shear rates.

Another point to be considered is the relationship between *E. coli* and suspended solids associated with adsorption/desorption and precipitation/resuspension processes. Adsorption can occur dramatically in short intervals after storm events leading to the removal of bacteria from the water column. In sediments, bacteria are protected against ultraviolet radiation and present concentrations significantly different from those in the water column (Craig et al., 2004). de Brauwere et al. (2014a), used a mixed bacterial condition in the Scheldt River and Estuary model (free, attached and bottom-settled bacteria) and observed that bacteria presented different die-off rates, and that free-stage bacteria presented higher decay rates than adsorbed ones. These findings reproduced reality because they achieved good fitting (or agreement) with field data. On the bottom, the cells remain protected from solar radiation, but are exposed to competition from native microbiota and are subjected to the effects of other precipitated pollutants (like heavy metals). The temperature, biotic relations and nutritional conditions are also different. The newly settled layer formed by solids covers the former bacteria that might be still viable and available for a re-suspension process. Resuspended bacteria can be a long-term source of contamination for the water column, mainly after storm events, and they must be considered in management systems and water-quality models. And finally, adsorption processes' binding properties between the bacteria and particles are highly dependent on the size and composition of the particles. These features highlight the importance of considering regional sediment characteristics and dynamics before defining the methodology for any study of bacterial decay (Abessa et al., 2005; Craig et al., 2002; 2004; Crump, 1996). The presently available results reinforce the importance of outlining outfall plumes that avoid contamination of sandy beaches and bottom sediments.

4.7. Predation

Although several die-off models have omitted the predation of *E. coli*, some authors have highlighted its importance. Lothigius et al. (2010), using sterile water with no predation did not encounter any significant decay in cultivable ETEC from either seawater or freshwater until after 48 hours, in a laboratory microcosm. Bacterial decay began at that time. Davies et al. (1995) encountered an important impact of predation on fecal coliforms in beach sediments, and Rhodes (Rhodes, 1988; 1990) encountered a significant impact of natural microbiota on *E. coli* die-off in an estuarine microcosm. Korajkic et al. (2013) found that the magnitude of the decay was significantly greater in the water columns of both fresh and seawater, when

indigenous microbiota was present (natural assay). By contrast, when assays were performed using freshwater and cycloheximide – which aimed to eliminate protozoan predators – there were die-off rates approximately one order of magnitude lower than natural assay. Several authors have concluded that predation by protozoa – particularly, the nanoflagellates – is a significant biotic factor affecting bacterial development in natural environments (Beardsley et al., 2003; Gonzalez et al., 1992; Rozen, 2001). Crump (1996) consider rotifers and small ciliates as possible bacterial predators. This reinforces the above-mentioned results of Korajkic et al. (2013), which suggested that interactions with non-protozoan microbiota also affect *E. coli* survival.

Yang et al. (2000) studied the interactions between cultivable bacteria decay and three factors: salinity, light intensity and dilution (seawater/wastewater). In the absence of predation, light caused 90% of the decay rate. However, in the presence of predators, the light+salinity+dilution combination contributed to only 50% of the population decay rate. However, Korajkic et al. (2014) observed that *E. coli* did not seem impacted by indigenous microbiota in *in situ* Mississippi mesocosms. It was also observed that there was little *E.coli* increase after 120 hours under no indigenous microbiota, plus solar radiation assays.

In light of the above-described results, we can argue whether the practice of removing microbiota from sewage to carry out T_{90} decay experiments is appropriate. It is further important to consider that decay results from autoclaved sewage assays should account for the effects of lack of predation and possible changes in chemical compounds. An alternative method to autoclaving for comparison assays would be to use a 0.22-µm filter to exclude microbiota and produce sterile natural water samples (*e.g*., Abessa et al., 2005; Hernroth et al., 2010).

4.8. Resistance variations at the gene-expression level

Since researchers have drawn attention to environmental stress resistance, it has become important to consider the molecular mechanisms involved. Studies have identified that starvation induces cross-resistance to both osmotic and heat stress, and even a strong general resistance to environmental stressors. The overall response to stress is mediated by RpoS(σ) genes, which increases or decreases in specific culture growth rate. The RpoS(σ) transcription factor controls many genes involved in responses to several types of stresses, such as starvation, osmotic stress, acid shock, thermal shock, and oxidative damage, which can shift bacteria to a stationary phase (Berney et al., 2006; Jenkins et al., 1990; Rozen, 2001; Siegele, 1992; van Elsas et al., 2011). On the other hand, RpoS (σ) is regulated by ppGpp, the global genetic regulator in *E. coli* (Magnusson et al., 2005), through complex transcriptional switching (Sharma and Chatterji 2010). This leads bacteria to change their physiology or their phenotypes (Berney et al., 2006; van Elsas et al., 2011).

van Elsas et al. (2011) found that the availability of carbon substrates is probably the main critical factor that controls the persistence of *E. coli* in the environment, a result that is in agreement with ecological surveys (Carrillo et tal., 1985; Craig et al., 2004; Crump, 1996). Berney et al. (2006) observed that nutritional status directly affects the cell growth phase and the medium composition, conditions that in turn affect the expression of *E. coli* heat shock proteins (HSPs). These authors also observed that oxygen concentration in broth cultures declined as bacterial growth proceeded, leading to an eventual decrease in bacterial growth. It is therefore very important to precisely control (i.e., standardize) the growth rate, for which Berney et al. (2006) suggested an inoculum with a µ (Population growth) = 0 h^{-1} for stationary-phase cells.

Several *in situ* surveys concerning the sanitation quality of the environment have underlined the significance of gene expression. The *E. coli* T_{90} from raw sewage was shorter than that from waste stabilization ponds previously exposed to sunlight (Sinton et al., 1999), a difference that can be attributed to higher resistance of the latter. Jozić et al. (2014) found that

E. coli cultivated under stressful environmental conditions decay three times slower than their first generation taken directly from, and then isolated from, the sea. The authors concluded that there are varying mechanisms acting within the cell to provide environmental bacterial protection. The practical concerns of these findings are that gene expression can improve the differential survival of different strains under the same environmental conditions (Bucci et al., 2011; Zhang et al., 2015). Further genetic studies that may affect T_{90} should be carried out, looking for virulent and persistent strains. The understanding of these processes is important for both health and public safety reasons.

5. CONCLUSIONS

For the last three decades, much more bacteriological knowledge has been accumulated, yet gaps in bacterial decay modeling remain. The existence of a group of decay models providing a good representation of the sanitation quality of the environment, from several locations worldwide, is witness to the efforts spent on this kind of research. Apparently, these models work fine; but the question is "What are they modeling?" In this review, we saw that models are considering viable *E. coli* to be still cultivable, excluding viable but not cultivable (VBNC) cells.

UV radiation seems to be the most important factor inducing the VBNC state in *E. coli* bacteria. However, the most-applied methods for the evaluation of colimetry do not consider these viable cells, which is a major issue, considering that most results on colimetry are underestimated. VBNC cells cannot be cultivated *in vitro*, but they can be active in the environment.

The presence of turbidity in the water column may also affect the influence of UV radiation. Hence, it is expected that degraded eutrophicated environments will tend to display longer T_{90} periods, increasing health issues.

We have shown that salinity and dilution can affect decay, because osmotic pressure in saline systems may kill bacteria. However, slow dilution may promote a gradual decrease in salinity, that engenders increasing preadaptation to the new osmotic pressure, so that if the amount of sewage is too large, as in large outfalls, T_{90} may be severely increased. In this dilution process, temperature can also be modified; however, we have shown that *E. coli* is little affected by this parameter. And temperature may play a more important role when associated with variations in nutrient concentrations.

Because they are associated with suspended particles, bacteria can be removed from the water column through settling, and may find a suitable environment within the sediments, where nutrients are abundant, UV radiation hardly penetrates, and temperatures are more constant. Sediment may then function as a source of bacteria to the water column during resuspension processes, as during storm events.

Concerning the biological aspects, we discussed predation as a factor reducing T_{90} values, and showed that many researchers, mainly modelers, disagreed, claiming it to be irrelevant compared to other factors. Although a review of the literature showed that in many situations predation may be relevant, it has been excluded from the experiments because their water is autoclaved, killing any possible predator. Including predators in laboratory experiments is a difficult task because results become more complex and random; however, considering its importance, it should be more frequently considered.

Finally, we discussed some aspects of the genetics of *E. coli* in the environment, in the light of emerging tools. It was interesting to note inductions in the genetic expressions as a function of environmental stresses like starvation, and osmotic and thermal stress. These "induced" phenotype modifications may be marked in populations subjected to increasing

stress, and these populations may be developing environmental resistances. T_{90} values in these adapted bacteria are expected to be much longer than in bacteria coming out of outfalls

The knowledge of factors affecting *E. coli* allowed the development of new methodologies and new decay models that give more accurate and reliable information. With this new information, the researchers have been able to establish new management procedures that reduce the survival rates in the natural environment. Such procedures are important, because as coastal human populations continue to increase, bacterial loads are also increasing, despite sewage-treatment efforts.

As discussed throughout in this paper, there are many parameters that affect *E. coli* decay rates, many of them have been disclosed from field studies and many have been observed in *in vitro* experiments, both with clear limitations. Researchers should therefore consider associated field and *in vitro* experiments, considering that different locations may induce different behaviors of these important bacteria.

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Importance of adequate appropriation of physiographic information for concentration times determination

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ABSTRACT

Concentration time is an important parameter for drainage systems design and is closely related to the physiographic characteristics of a given hydrographic basin. Information from cartographic bases or images obtained by remote sensing, which present certain scales/resolutions, are often employed for the appropriation of concentration times. The present study sought to investigate the influence that the combination of different physiographic information, in different scales, and different calculation methods can produce in concentration times' values. The applied methodology included a concentration times appropriation methods survey, identification of methods compatible with the study area characteristics, physiographic variables appropriation from information plans at different scales and concentration times determination for different regions. The results show that there is an equivalence between Tulsa District and US Corps of Engineers methods, and that these methods produce higher concentration times estimates than those produced by the George Ribeiro method. For the study area, the maximum calculated relative error was 52%.

Keywords: concentration time, drainage, hydrology, scale, watershed.

Importância de adequada apropriação de informações fisiográficas para definição de tempos de concentração

RESUMO

O tempo de concentração representa um importante parâmetro para projetos de drenagem e está intimamente relacionado às características fisiográficas de uma determinada bacia hidrográfica. Para a apropriação de tempos de concentração, muitas vezes são utilizadas informações provenientes de bases cartográficas ou imagens obtidas por sensoriamento remoto, que apresentam determinadas escalas/resoluções. O presente estudo buscou investigar a influência que a combinação de diferentes registros fisiográficos, em diferentes escalas, e diferentes métodos de cálculo podem produzir nos valores dos tempos de concentração. A metodologia empregada consistiu no levantamento de métodos de apropriação de tempos de concentração, identificação dos métodos adequados às características da área de estudo, apropriação das variáveis fisiográficas a partir dos planos de informação em diferentes escalas

e determinação dos tempos de concentração para as diferentes regiões hidrográficas da área de estudo. Os resultados obtidos mostram que existe equivalência entre os métodos *Tulsa District* e *US Corps of Engineers*, e que esses métodos produzem tempos de concentração superiores aos produzidos pelo método de George Ribeiro, produzindo erro relativo com valor máximo de aproximadamente 52%.

Palavras-chave: bacia hidrográfica, drenagem, escala, hidrologia, tempo de concentração.

1. INTRODUCTION

Hydrological models are mathematical water systems behavior representations. Among hydrological models, there are the so-called "rainfall-runoff," which represent rainfall transformation processes and consequent flow propagation in a watershed (Fan and Collischonn, 2014).

The rainfall-runoff models are usually used for flow-data series complementation, hydrograph determination for engineering design, flood forecasting and basin land-use assessment (Ferraz et al., 1999). Shuster and Pappas (2010), Halwatura and Najim (2013), Silva et al. (2014), Walsh et al. (2014), Vinagre et al. (2015) and Cabral et al. (2017) illustrate different possible rainfall-runoff models' applications.

The concentration time parameter is necessary for determination of peak flow rates and hydrographs formatting by using rainfall-runoff models (Silveira, 2005; Farias Júnior and Botelho, 2011). Silveira (2005), however, observes that the determination of concentration times is a difficult task due to limited information about the applicability of some of the available empirical formulas.

Concentration times estimation can be done by two approaches: the direct, which uses hydrometeorological records or tracers; and the indirect, which uses previously established mathematical expressions for certain regions. Direct methods are widely utilized when hydrometeorological records with discretization intervals shorter than the concentration time or tracer data collected in field surveys are available (Farias Júnior and Botelho, 2011). In Brazil, however, the availability of information is scarce, especially for medium and small hydrographic basins. Therefore, for this type of regions, the alternative that is usually used for concentration time appropriation is the use of indirect methods.

Mata-Lima et al. (2007) divide the indirect methods formulations' characteristics into two groups: empirical and semi-empirical. According to the authors, the empirical formulations result from correlations and statistical treatment of physiographic variables observed in the field without considering the effect of changes in soil use and occupation, and generally do not require detailed input data. Semi-empirical formulations result from a similar process; however, they also consider the effects of changes in the land use and occupation dynamics and other variables that change over time.

For appropriation of physiographic variables considered in concentration time equations, the use of Geographic Information System (GIS) as a support tool is recurrent. Through GIS it is possible to manipulate digital information plans, available in different scales and resolutions, from which the physiographic variables can be obtained.

The cartographic representation of geographic elements, in paper or digital format, is only possible through using a representation scale. According to Fitz (2008) it is relevant to highlight the fact that when working with digital maps, the scale can easily be transformed to several values. This freedom causes concern about the actual scale represented in digital format. However, the author indicates the need for caution when working with this type of space representation, since the reality represented in a digital map is closely linked to the scale of the information plan that generated it and, therefore, can not assume precision higher than that for

the original scale.

The present study evaluated the influence of physiographic records scale in hydrographic basins' concentrations time determination. The study area is a medium-sized river basin located in the southwest portion of Espírito Santo state.

2. STUDY AREA

The study area consists of a medium-sized hydrographic basin, called Norte Braço Esquerdo River watershed, which presents an area of 333.52 km² and a perimeter of 111.71 km and is located in the southwest portion of Espírito Santo state (Caparaó region), Brazil, as can be observed in Figure 1. The watershed has as its main water course the Norte Braço Esquerdo River, an Itapemirim River tributary.

The region presents dry temperate climate, with an average annual rainfall of 1,371 mm, and relief ranging from strongly corrugated to hilly. The predominant soils are classified as Red Latosol and Dystrophic Yellow Latosol, degraded by extensive pastures, degraded crops abandonment, coffee plantations and new annual crops implementation, as well as roads construction and maintenance by using inadequate technologies (INCAPER, 2011).

The basin limits were obtained from the set of Level 5 Ottobacias, available in the Espírito Santo State Geospatial Bases Integrated System (GEOBASES).

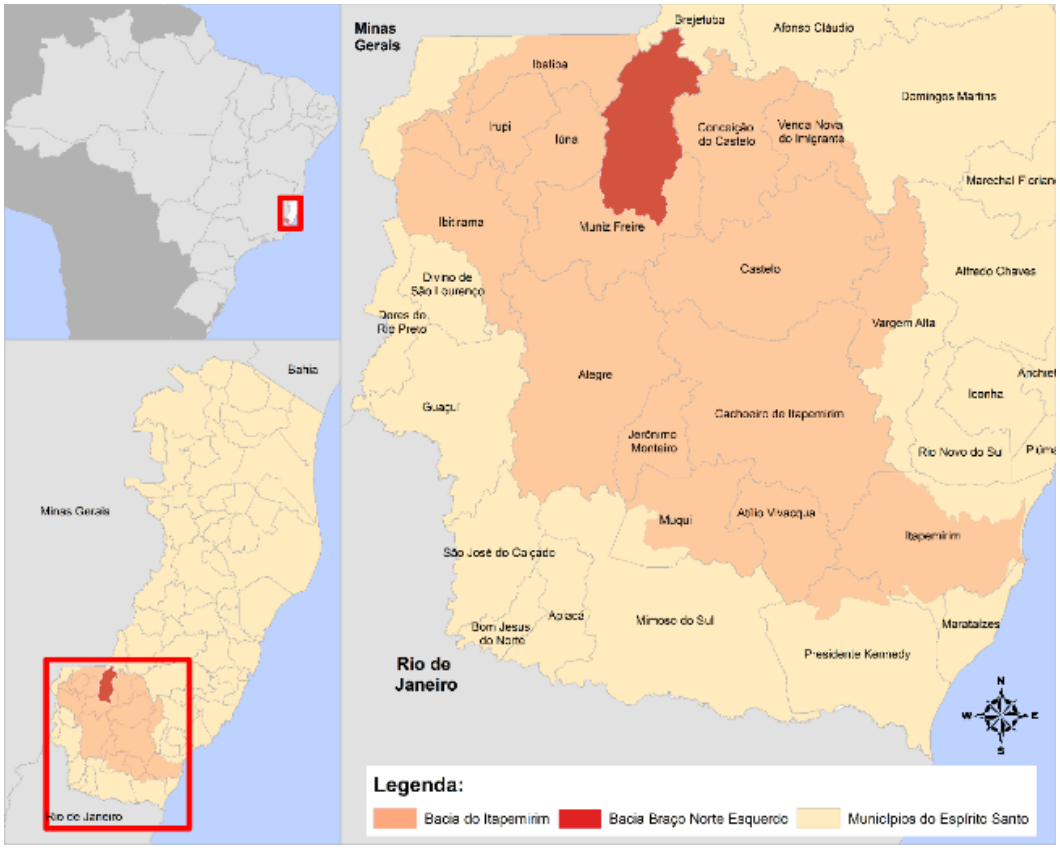

Figure 1. Braço Norte Esquerdo River basin location.

Aiming to make possible comparative analysis of different-sized basins' hydrological response, it was decided to adopt a study area of Level 6 subdivision Ottobacias, available in the GEOBASES database, which present limits compatible with those that are considered for Espírito Santo state water resources planning. In this way, the study area was divided into eight hydrographic basins, whose limits are presented in Figure 2.

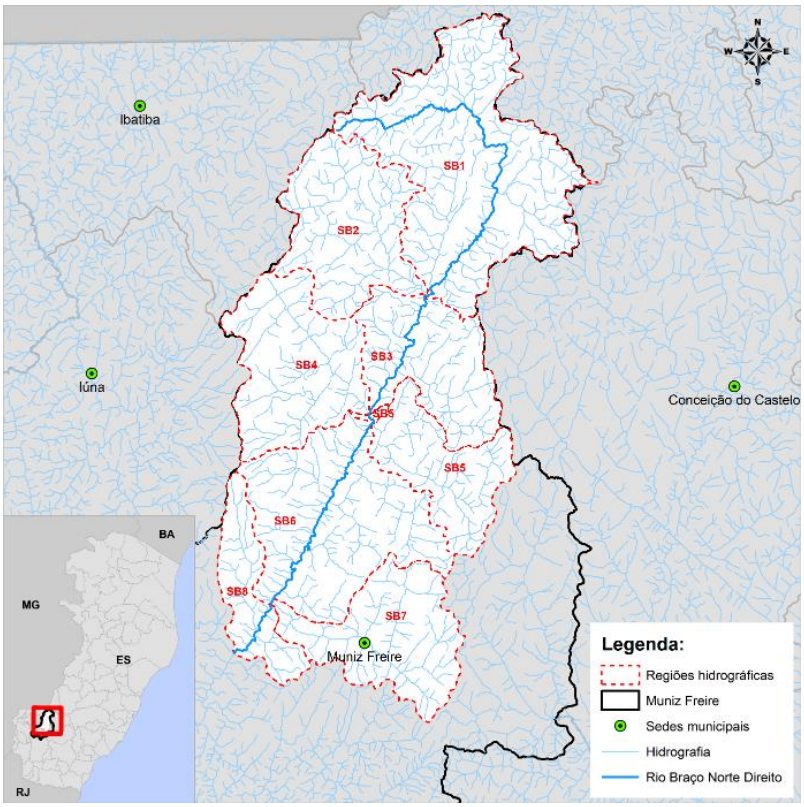

Figure 2. Braço Norte Esquerdo River basin subdivision.

3. METHODOLOGY

Two basic assumptions were established for implementing the used methodology different stages:

- Adoption of low-cost and easily reproduced methodologies, prioritizing the use of free computational tools whenever possible; and
- Use of public domain information, free of charge, provided by public institutions.

3.1. Databases selection

Physiographic characteristics, which represent the basin's physical characteristics, such as relief, drainage network, vegetation cover, soil and surface use and occupation, among others, are usually extracted from maps, aerial photographs and satellite images. It was decided to use data from digital cartographic bases. In this way, digital files containing information plans in raster or vector format (shapefile format) were manipulated through the Geographic Information System.

In this work, information plans related to relief, drainage network and land use and occupation were used to estimate concentration times. Information plans with dubious origin or low detail level (very small scales) were previously discarded and the other files were submitted to attributes consistency analysis and geometric features representation. This analysis involved information conferencing, file comparison, correction of topological faults and projection systems and coordinates transformations, aiming to work with the data in the same coordinate system and Datum (SIRGAS 2000).

Table 1 summarizes the databases selected for subsequent steps implementation.

Table 1. Data sources of physiographic information.

Subject	Geospatial data	Data type	Spatial resolution/scale	Source
Relief	Digital Elevation Model	Matrix	90 meters	Empresa Brasileira de Pesquisa Agropecuária (EMBRAPA)
	Digital Elevation Model	Matrix	30 meters	ASTER GEDEM
	Level Curves	Vector	1:50,000	GEOBASES
Drainage network	Drainage sections	Vector	1:50,000	GEOBASES
		Vector	1:250,000	Instituto Brasileiro de Geografia e Estatística (IBGE)
Use and occupation	Land use (2008-2010)	Vector	1:10,000	Instituto Estadual de Meio Ambiente e Recursos Hídricos do Espírito Santo (IEMA)

3.2. Concentration times appropriation methods selection

Existing hydrographic basins' concentration times appropriation methods identification was conducted through a current literature review.

For appropriation methods selection, all methods restrictions were compared with the study area type of occupation, area, slope and talveg length. In this selection stage, three possible outcomes were established:

• Applicable: when all hydrographic basins presented area, slope, talveg length and occupation type within the applicability range established by the concentration time determination method;

• Not applicable: when at least one of the hydrographic basins presented area, slope, talveg length and occupation type outside the applicability range established by concentration time determination method;

• Unidentified restriction: when there was no restriction on the use of the method identified in the revised literature.

4. RESULTS AND DISCUSSION

4.1. Physiographic information

The equations selected for estimating concentration times involve four variables: a) basin occupation type, b) basin area, c) slope, and d) talveg length. In the subsequent items the cited variables estimated values are presented, considering the different digital cartographic bases used.

4.1.1. Basin Occupation Type

Basin occupation type consists of information related to basin predominant land use and occupation, urban or rural. In order to determine the hydrographic basins' occupation types, the areas corresponding to each use class were surveyed by using land use and occupation information plans provided by IEMA in the 1: 10,000 scale. Table 2 was produced from this survey, which presents the percentages of areas associated with different types of land use and occupation.

Table 2 shows that for all hydrographic basins farming activities and forests predominate. The presence of built-up areas is practically negligible in most regions. Only in the SB7 basin do built-up areas occupy approximately 2%. Therefore, all the study area hydrographic basins were classified as rural.

Table 2. Percentage of area occupied by different land uses and occupation.

Land use and occupation	Hydrographic basins							
	SB1	**SB2**	**SB3**	**SB4**	**SB5**	**SB6**	**SB7**	**SB8**
Rock	1.95	1.87	5.89	5.72	5.61	5.74	10.10	2.20
Built area	0.05	0.00	0.49	0.00	0.00	0.28	1.91	0.00
Swamps	0.33	0.59	0.04	0.01	0.05	0.03	0.15	0.00
Agricultural crop – Banana	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Agricultural crop – Coffee	11.74	9.10	28.39	24.61	15.09	12.06	14.02	14.90
Agricultural crop – Coconuts	0.03	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Agricultural crop – Other permanent crops	0.63	1.13	0.51	0.52	0.16	0.14	0.42	0.13
Agricultural crop – Other temporary crops	7.10	2.60	1.67	0.82	1.11	0.53	1.03	0.96
Mining	0.05	0.00	0.04	0.00	0.04	0.00	0.00	0.00
Macega	16.28	11.35	11.39	6.76	10.00	8.15	6.58	5.31
Water	0.11	0.07	0.29	0.00	0.11	0.34	0.03	0.46
Native forest	22.18	16.85	8.90	25.57	9.66	16.32	17.09	26.76
Native forest - initial regeneration stage	5.17	7.16	3.35	8.79	3.88	6.21	7.58	7.87
Other	3.17	1.41	3.11	1.70	1.66	1.31	2.44	1.58
Pasture	22.93	31.02	32.32	20.50	50.77	47.00	37.26	38.30
Reforestation - Eucalyptus	5.73	14.79	2.47	4.30	1.59	1.20	0.78	1.29
Reforestation - Pinus	0.71	0.10	0.00	0.00	0.00	0.00	0.00	0.00
Uncovered Soil	1.82	1.96	1.14	0.61	0.27	0.67	0.61	0.19

4.1.2. Basin Area

The hydrographic basins areas were appropriated from the file containing the Level 6 Ottobacias watersheds limits, adopted for study area subdivision, as mentioned in the item "Study Area". From GIS files software manipulation, the regions areas were obtained by adopting Mercator Transversal Universal Projection System and SIRGAS Datum 2000. The areas values that resulted from the performed process are available in Table 3.

Table 3. Hydrographic regions' areas.

Hydrographic basin	Area (km²)
SB1	82.33
SB2	39.70
SB3	32.94
SB4	40.34
SB5	27.33
SB6	57.82
SB7	35.28
SB8	17.77

4.1.3. Talveg Length

The main hydrographic basins talveg lengths were appropriated by the sum of the stretches of the drainage network associated with the greatest length starting from the basins outlets. In order to characterize the drainage networks, information plans were used in the 1: 50,000 and 1: 250,000 scales. The talveg lengths obtained by information plans manipulation are shown in Table 4. The relative errors presented in this table were appropriated by comparison with the talveg lengths obtained from the larger scale (1: 50,000) information plans.

Table 4. Main talvegs hydrographic basins lengths.

Hydrographic region	Main Talveg	Talveg length (km)		Error	
		1:50.000	1:250.000	Absolute (km)	Relative (%)
SB1	Braço Norte Esquerdo River	21.64	20.55	1.0982	5.07
SB2	Estrondo Creek e do Mata-Pau Creek stretch	13.36	13.12	0.2426	1.82
SB3	Sossego and Braço Norte Esquerdo stretch	10.768	10.68	0.0752	0.70
SB4	Piaçu Creek or Cantagalo and Tombos Creek stretch	10.46	10.26	0.1944	1.86
SB5	São João Creek and Córrego Rico Creek stretch	11.33	11.38	0.0456	0.40
SB6	Mata do Barão Creek and Braço Norte Esquerdo stretch	17.93	17.85	0.0747	0.42
SB7	Águas Claras Creek and Ribeirão Vargem Grande stretch	13.49	12.06	1.4378	10.66
SB8	Seio de Abraão Creek and Trecho do Braço Norte Esquerdo stretch	10.07	9.91	0.1630	1.62

4.1.4. Declivity

Slope is a variable used in the application of different concentration time determination methods. Since most methods that present restrictions related to slope values employ the talveg mean slope to estimate concentration times, it was decided to use the talveg slope value as the standard criterion for formulas applicability analysis. In this context, the points coordinates corresponding to the headwater and outlet of the main watercourses of each sub-basin were taken into account, considering the drainage network layout available on the 1: 50,000 and 1: 250,000 scales information plans. Then, each main talveg head and outlet points altimetric dimensions were obtained, considering the different sources of information related to the relief. From the obtained altimetric dimensions, each of the main talvegs slope values was determined. The obtained dimensions and corresponding slope values are presented in Tables 5 (scale 1: 50,000) and 6 (scale 1: 250,000).

It is relevant to observe that the talveg slope is a physiographic characteristic that depends on two main factors: a) the drainage network or hydrography, which establishes the trajectory of the water courses and serves as basis for appropriating the talveg lengths; and b) the relief information, which provides information on altimetry. In this work, the information regarding the drainage network presents two different scales (1: 50,000 and 1: 250,000), and the information concerning the altimetric dimensions came from three different sources (level curves, 30-meter resolution DEM and 90-meter resolution DEM). In this way, each hydrographic basin presented six different possible slope values for the main talvegs.

4.2. Concentration times estimation methods

Indirect methods for concentration times determination were identified from a review of the literature. These methods were summarized by McCuen et al. (1984), Paiva and Paiva (2001), Pruski et al. (2004), DNIT (Brasil, 2005), Silveira (2005), Santos et al. (2009), Farias Junior and Botelho (2011), Grecco et al. (2012), Dhami and Pandey (2013) and Porto et al. (2014). The authors present, when available, information regarding each selected method's applicability and constraints. The variables basin occupation type (rural or urban), basin area,

slope and talveg length - which determine concentration times appropriation indirect methods selection - and their respective reference values are shown in Table 7.

Table 5. Main talvegs slopes obtained from hydrography on 1: 50,000 scale data source.

Hydrographic region	Headwater level (m)			Exudation level (m)			Slope (m/m)		
	DEM 30 m	DEM 90 m	DTM	DEM 30 m	DEM 90 m	DTM	DEM 30 m	DEM 90 m	DTM
SB1	1236	1275	1208.8	606	624	617.6	0.0291	0.0301	0.0273
SB2	1309	1371	1302.1	606	624	617.6	0.0526	0.0559	0.0512
SB3	1015	1049	1046.5	523	536	530.6	0.0457	0.0477	0.0480
SB4	1262	1250	1264.4	523	536	530.6	0.0707	0.0683	0.0702
SB5	990	1051	1016.7	487	508	491,2	0.0444	0.0479	0.0464
SB6	998	989	1000.5	405	419	399.9	0.0331	0.0318	0.0335
SB7	654	734	670.4	405	419	399.9	0.0185	0.0233	0.0200
SB8	1326	1352	1318.5	377	396	369.4	0.0942	0.0949	0.0943

Note: DEM - Digital Elevation Model; DTM - Digital Terrain Model.

Table 6. Main talvegs slopes obtained from hydrography on 1: 1:250,000 scale data source.

Hydrographic region	Headwater level (m)			Exudation level (m)			Slope (m/m)		
	DEM 30 m	DEM 90 m	DTM	DEM 30 m	DEM 90 m	DTM	DEM 30 m	DEM 90 m	DTM
SB1	1302	1333	1323.6	609	617	617.6	0.0337	0.0348	0.0344
SB2	1362	1377	1364.4	609	617	617.6	0.0574	0.0579	0.0569
SB3	1038	1066	1058.9	529	536	533.8	0.0476	0.0496	0.0492
SB4	1247	1261	1259.6	529	536	533.8	0.0699	0.0706	0.0707
SB5	1066	1100	1116.4	488	499	489.7	0.0508	0.0528	0.0551
SB6	994	979	997.6	405	417	399.9	0.0330	0.0315	0.0335
SB7	702	676	687.1	405	417	399.9	0.0246	0.0215	0.0238
SB8	1332	1352	1324.8	384	396	371.8	0.0957	0.0965	0.0962

Note: DEM - Digital Elevation Model; DTM - Digital Terrain Model.

4.3. Concentration times

As previously cited, concentration times calculation methods that exhibited in one or more study areas catchment area restrictions related to at least one criteria were considered unsuitable, and were disregarded as options for concentration times determination. Considering this perspective, Kirpich, California Culverts Practice, Federal Aviation Agency, Kinematic Wave, SCS Lag, Dooge, Ven Te Chow, Izzard, Arnell, Jhonstone, Tsuchiya, DNOS, Carter Lag equation for partially sewered, McCuen, IPH-II and Denver methods were not employed.

There were also disregarded methods that showed "Restriction unidentified" status for all criteria, as observed for the SCS - kinematic method, Giandotti, Pasini and Hathaway methodologies.

Among the remaining methods (Picking, Bransby-Williams, Riverside Country, US Corps of Engineers, Williams, Ventura, Putnam, Tulsa District and George Ribeiro), three were selected to estimate the study area's hydrographic basins' concentration times. The selected methods were George Ribeiro (method that proved to be applicable under all five criteria), Tulsa District (which showed to be applicable according to three of the four criteria) and US Corps of Engineers method (selected from the methods that were considered applicable under one of the analysis criteria and without use restrictions considering the other criteria).

Table 7. Criteria for application of concentration time appropriation methods.

Métodos	Occupation Type	Area (km²)	Declivity (%)	Talvegue Length (km)
Kirpich	Rural	< 0.50	3 – 10	< 10
California Culverts Practice	Rural	< 0.50	3 – 10	< 10
Federal Aviation Agency	Urban	–	–	0.015 – 0.030
Kinematics wave	Urban	Similar to Rational Method	–	–
SCS Lag	Rural	< 8	–	–
SCS – Kinematics Method	-	–	–	–
Dooge	Rural	140 – 930	–	–
Ven Te Chow	Rural	< 24.28	–	–
Picking	Rural	–	–	–
Izzard	Urban	–	< 4	< 0.02
Giandotti	-	–	–	–
Arnell	Urban	0.20 – 50	–	–
Bransby-Williams	Rural	–	–	–
Jhonstone	Rural	65 – 4,200	–	1–
Tsuchiya	Rural/Urban	0.001 – 0.002	–	–
Riverside Country	-	5 – 1,600	–	–
Pasini	-	–	–	–
DNOS	-	0.45	3 – 10	< 1.20
US Corps of Engineers	-	< 3,000	–	–
Carter Lag equation for Partially Sewered	Urban	< 20.70	< 0.50	< 11.26
Williams	-	< 129.50	–	–
Ventura	Rural	–	–	–
McCuen	Urban	0.40 – 16	< 4	< 10
IPH–II	Urban	2.50 – 137	–	–
Putnam	-	0.75 – 340	–	–
Tulsa District	-	1 – 1,300	0.08 – 18	1.60 – 96
Denver	-	< 13	Moderada	–
George Ribeiro	Rural	< 19,000	1 – 10	< 250
Hathaway	-	–	–	–

Source: Adapted from McCuen et al. (1984), Paiva e Paiva (2001), Pruski et al. (2004), DNIT (Brasil, 2005), Silveira (2005), Santos et al. (2009), Farias Junior e Botelho (2011), Grecco et al. (2012), Dhami and Pandey (2013) and Porto et al. (2014).

The concentration times obtained by using the three selected methods are assembled in Tables 8 and 9. Table 8 shows the values obtained by using the hydrographic information available for the 1: 50,000 scale information plans. Table 9, on the other hand, presents the values corresponding to the use of hydrography in 1: 250,000 scale information plans.

From simple inspection of Tables 8 and 9, it can be observed that the concentration times values for each hydrographic basin present variations that depend on the selected method for concentration time appropriation, the spatial resolution used to describe relief employed in the slope appropriation and drainage network scale. In both tables, it is possible to observe that the influence of the concentration time appropriation method is less significant for the SB1, SB2 and SB8 hydrographic basins. In all others, the comparison with the other methods adopted presents a difference greater than 10% in the estimated time of concentration.

Table 8. Concentration times (minutes) obtained from 1:50,000 scale hydrography.

Hydrographic region	Concentration time (min)								
	US Corps of Engineers			Tulsa District			George Ribeiro		
	DEM 30	DEM 90	DTM	DEM 30	DEM 90	DTM	DEM 30	DEM 90	DTM
SB1	372.65	371.62	378.63	377.54	376.47	383.76	350.99	350.94	351.08
SB2	219.76	219.25	222.05	238.60	238.03	241.15	218.49	218.44	218.52
SB3	237.05	230.41	238.91	252.67	245.40	254.70	167.63	167.61	167.60
SB4	187.08	185.75	188.91	210.26	208.74	212.37	170.70	170.73	170.71
SB5	218.00	216.25	217.43	232.46	230.54	231.84	176.70	176.65	176.67
SB6	375.46	378.30	379.34	370.35	373.23	374.28	284.72	284.76	284.71
SB7	277.60	272.87	278.32	321.90	316.27	322.77	215.57	215.37	215.50
SB8	178.04	177.20	177.12	178.73	177.86	177.78	163.25	163.24	163.25

Table 9. Concentration times (minutes) obtained from 1:250,000 scale hydrography.

Hydrographic region	Concentration time (min)								
	US Corps of Engineers			Tulsa District			George Ribeiro		
	DEM 30	DEM 90	DTM	DEM 30	DEM 90	DTM	DEM 30	DEM 90	DTM
SB1	359.31	356.15	363.41	372.68	369.32	377.06	332.98	332.94	332.96
SB2	217.10	215.72	218.94	238.74	237.18	240.81	214.45	214.45	214.46
SB3	234.81	226.20	235.81	250.12	240.71	251.22	166.44	166.41	166.42
SB4	183.71	181.50	185.01	208.35	205.79	209.87	167.54	167.53	167.53
SB5	216.46	213.09	215.40	231.37	227.67	230.20	177.32	177.29	177.26
SB6	371.81	371.06	374.37	369.17	368.40	371.77	283.54	283.59	283.52
SB7	257.04	251.62	257.40	310.14	303.43	310.59	192.38	192.48	192.40
SB8	175.24	174.03	174.31	176.97	175.72	176.01	160.60	160.59	160.59

In order to evaluate concentration time-value variations, a reference scenario was established, corresponding to the concentration times obtained from the information plans presenting larger scale or resolution and by the method applicable considering all criteria. This scenario was composed by the concentration time determined by the George Ribeiro method (method usually employed in urban drainage studies in Brazil), using 1:50,000 scale hydrography and digital terrain model appropriated from the 20-meter equidistant contours (sources with higher levels of detailing for hydrography and digital terrain model).

The concentration time percentage value variations in relation to the reference scenario are shown in Table 10.

The values presented in Table 10 indicate that the different concentration time method combinations (US Corps of Engineers. Tulsa District and George Ribeiro) used for hydrography description scale (1: 50,000 and 1: 250,000) and local relief description alternatives (DEM 30 m. DEM 90m and DTM) produced values that varied from approximately -11% (underestimation associated with SB7 when compared to the referential scenario, when using the George Ribeiro method and 1: 250,000 hydrography) and + 52% (overestimate for SB3, Tulsa District method and 1: 50,000 hydrography).

In addition, the following observations are considered relevant: a) the scale variation associated with hydrography produced percentage variations in concentration time values invariably lower than 11% (the greatest variations were estimated for SB7, when using the George Ribeiro method and 30m digital elevation model); and b) the change in the relief representation, retained the scale associated with hydrography and concentration time

estimation method, did not produce variations greater than 6%, regardless the analyzed combination; and c) the concentration time appropriation methods, maintaining relief and hydrography representation forms, produced maximum variations greater than 50% (variations estimated for SB7, when considering errors referring to Tulsa District and George Ribeiro methods).

Table 10. Percentage variations in relation to the referential scenario.

Hydrographic basin	Hydrography	Percentage Variations								
		US Corps of Engineers			*Tulsa District*			George Ribeiro		
		DEM 30 m	DEM 90 m	DTM	DEM 30 m	DEM 90 m	DTM	DEM 30 m	DEM 90 m	DTM
SB1	1:50.000	6.15	5.85	7.85	7.54	7.23	9.31	-0.03	-0.04	Reference Scenario
SB2		0.57	0.34	1.62	9.19	8.93	10.36	-0.01	-0.04	
SB3		41.44	37.47	42.55	50.76	46.42	51.97	0.02	0.00	
SB4		9.59	8.81	10.66	23.17	22.28	24.41	0.00	0.01	
SB5		23.39	22.40	23.07	31.58	30.49	31.23	0.02	-0.01	
SB6		31.88	32.88	33.24	30.08	31.09	31.46	0.01	0.02	
SB7		28.82	26.62	29.15	49.38	46.76	49.78	0.03	-0.06	
SB8		9.06	8.55	8.50	9.48	8.95	8.90	0.00	0.00	
SB1	1:250.000	2.34	1.44	3.51	6.15	5.20	7.40	-5.15	-5.17	-5.16
SB2		-0.65	-1.28	0.19	9.25	8.54	10.20	-1.86	-1.86	-1.86
SB3		40.10	34.96	40.70	49.24	43.62	49.89	-0.70	-0.71	-0.71
SB4		7.61	6.32	8.38	22.05	20.55	22.94	-1.86	-1.86	-1.86
SB5		22.52	20.62	21.92	30.96	28.87	30.30	0.37	0.35	0.33
SB6		30.60	30.33	31.49	29.67	29.40	30.58	-0.41	-0.39	-0.42
SB7		19.28	16.76	19.44	43.92	40.81	44.12	-10.73	10.68	-10.72
SB8		7.35	6.60	6.78	8.41	7.64	7.82	-1.63	-1.63	-1.63

5. CONCLUSIONS

The study identified concentration times appropriation methods applicable to the hydrographic basins that comprise part of the study area, considering soil occupation, area, length and slope of the main talveg characteristics. Among the identified methods, George Ribeiro, Tulsa District and US Corps of Engineers were considered more appropriate, in the order in which they were mentioned.

The estimated concentration times varied up to 11% considering the variables calculated from different information plans and varied up to 52% considering the variables calculated from different concentration times methods. It was also possible to conclude that there is equivalence between Tulsa District and US Corps of Engineers equations for the hydrographic study basin, and that change of information source related to relief and hydrography did not significantly affect the concentration times appropriation. The adequate concentration times values large importance for drainage systems design and the differences in results obtained by different models in this study shows the importance of field surveys for obtaining information that could contribute to model choice and calibration.

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Mobile transect for identification of intra-urban heat islands in Uberlandia, Brazil

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ABSTRACT

The "heat island" phenomenon is one of many serious problems caused by rapid urban growth. This study therefore sought to characterize and quantify heat islands in Uberlandia, to evaluate the seasonality of these islands (winter-summer) and to identify the effect of surface coverage on their intensity. To identify intra-urban heat islands in Uberlandia, air temperature data were collected in two seasons (winter and summer) using mobile and fixed transects seasons. Transition measurements were recorded automatically every 0.5 seconds using a car-mounted thermos-hygrometer moving at an average of 40 km h^{-1}. GPS was used to select approximately ten data points every 500 meters of each transect. Fixed weather stations measured air temperature at three sites in the region. Transect data analysis showed that the intra-urban heat islands were more intense in winter ($\Delta T = 2.2ºC$) than in summer ($\Delta T = 1.2ºC$) mainly because by reduction in atmospheric vapor in winter (dry season) and by higher rate of radiative cooling that is favored in permeable areas. The methodology used in the present study proved to be a quick and efficient way to carry out this type of monitoring.

Keywords: air temperature, urban heat island, winter.

Transecto móvel para identificação de ilha de calor intra-urbana em Uberlândia, Brasil

RESUMO

O fenômeno da ilha do calor é um dos muitos problemas graves causados pelo rápido crescimento urbano. Assim, os objetivos deste estudo foram: caracterizar e quantificar ilhas de calor em Uberlândia, avaliar a sazonalidade destas ilhas (inverno-verão) e identificar o efeito da cobertura superficial na intensidade das mesmas. Para identificar as ilhas de calor intra-urbanas em Uberlândia, os dados de temperatura do ar foram coletados em duas estações (inverno e verão) usando transectos móveis e estações climáticas fixas. As medidas de transição foram gravadas automaticamente a cada 0,5 segundos usando um termo-higrometro montado em carro movendo-se a uma média de 40 km h^{-1}. O GPS foi usado para selecionar aproximadamente dez pontos de dados a cada 500 metros de cada transecto. As estações

meteorológicas fixas mediram a temperatura do ar em três locais da região. A análise dos dados mostrou que as ilhas de calor intra-urbana em Uberlândia foram mais intensas no inverno ($\Delta T = 2,2^{o}C$) que no verão ($\Delta T = 1,2^{o}C$) devido principalmente à redução no vapor de água atmosférico no inverno (estação seca) e pela taxa de resfriamento radiativo maior nas áreas permeáveis. A metodologia utilizada no presente estudo mostrou ser uma maneira rápida e eficiente de realizar esse tipo de monitoramento.

Palavras-chave: ilha de calor urbano, inverno, temperatura do ar.

1. INTRODUCTION

The urban heat island (UHI) phenomenon is characterized by higher urban temperatures relative to those of surrounding rural areas (Oke, 1973) and can cause many serious problems. Several factors contribute to the formation of heat islands including diurnal absorption and storage of heat, thermal and calorific properties and nocturnal heat emissions of construction materials, anthropogenic emissions (vehicle and pedestrian traffic), reduced evapotranspiration caused by replacing natural surface coverage with asphalt and concrete surfaces and canalizing and covering rivers and streams, and reduced heat loss due to taller buildings that decrease wind speeds and block radiation (Erell and Williamson, 2007; Rizwan et al., 2008).

UHI have also been positively correlated with population size (Oke, 1973), which determines the level of heat produced directly by people or indirectly by buildings (Rizwan et al., 2008). Urban Heat islands may also be directly related to temporary causes such as a stationary cyclones, low wind speeds, and limited cloud cover (Oke, 1973).

Not only do heat islands cause discomfort, especially in tropical cities, they also increase energy consumption, ozone levels (lower troposphere), respiratory illness and death (Rizwan et al., 2008). Furthermore, increasing urban temperatures have contributed to climate change.

Temperature differences between urban and rural areas determine the intensity of UHIs (Oke, 1973). Urban Heat island intensity ($\Delta T_{u\text{-}r}$) is an important indicator of the degree of urbanization (Rizwan et al., 2008). It tends to be higher at night, lower or even negative during the day (Oke 1973) and seasonal (Jonsson, 2004; Yokobori and Ohta, 2009) given the rapid radiative cooling in rural areas due to favorable atmospheric conditions.

The methodologies used to determine $\Delta T_{u\text{-}r}$ involve collecting meteorological data from static-automated stations, mobile transects and by atmospheric microwave emissions in urban and rural areas (Hedquist and Brazel 2006). However, there is increasing use of remote sensing data for this study. It can be determined more accurately by using horizontally scaled sites (10^2 - 10^4 m), collecting data close to the ground (1-2 m) and by measuring for days, months or years (Stewart, 2011).

According to Hedquist and Brazel (2006), mobile transects are especially useful when climatological data is limited and when automated-fixed stations are too sparse for accurate representation of urban and rural atmospheres. Fixed networks are also more expensive and subject to vandalism (Erell and Williamson, 2007). However, mobile transects are always suspect as to what they spatially represent along or adjacent to the transect routes (Hedquist and Brazel, 2006).

Although the UHI has been widely documented in much of the world, there are still few studies in medium-sized Brazilian cities. Therefore, our main objective was to verify if mobile transect methodology is efficient in the characterization of urban heat islands in Uberlandia, seeking to achieve the following specific objectives: a) to characterize and quantify the heat islands in Uberlandia, b) to evaluate heat island seasonality (winter-summer) and c) to identify the effect of surface coverage on heat island intensity.

2. MATERIALS AND METHODS

2.1. Experiment area

Uberlandia is located in the southeast of Minas Gerais state (18°55'23" S and 48°17'19" W). The city covers 4,115 km² and has a 219 km perimeter. The economy of Uberlandia is diverse; however, wholesale distribution is especially strong given the strategic location of the city.

The climate of Uberlandia is classified as tropical climate with dry winter Aw (Köppen) with dry winters and rainy summers dominated by inter-tropical and polar systems.

Natural vegetation (Cerrado – the Brazilian savannah, forest, hydromorphic fields, lowland fields and hydrophilic fields) covers 17.7% of the municipality of Uberlandia whereas urban areas cover 4.6%. Excluding the largest metropolitan centers, Uberlandia is one of the most populous regions in the country. According to the last census the city had 604,013 inhabitants (97.2% urban, 2.8% rural). In addition, the population of the city grew at 1.8% between 2000 and 2010, whereas the populations of the surrounding region and state grew at 1.5% and 0.9%, respectively. The city comprises distinct socioeconomic regions (Figure 1). Most upper-class neighborhoods, recreation clubs and private universities are concentrated in the southern sector. Lower-class neighborhoods comprise the western and eastern regions, and the airport and industrial district are located in the northern region. The downtown is home to stores, banks, a bus station and interspersed residential areas. The altitude of the municipality ranges from 750 to 900 m and the city is crossed by the Uberabinha River from east to west. Streams in downtown Uberlandia have been channelized. Consequently, flooding is frequent during heavy summer rainfall.

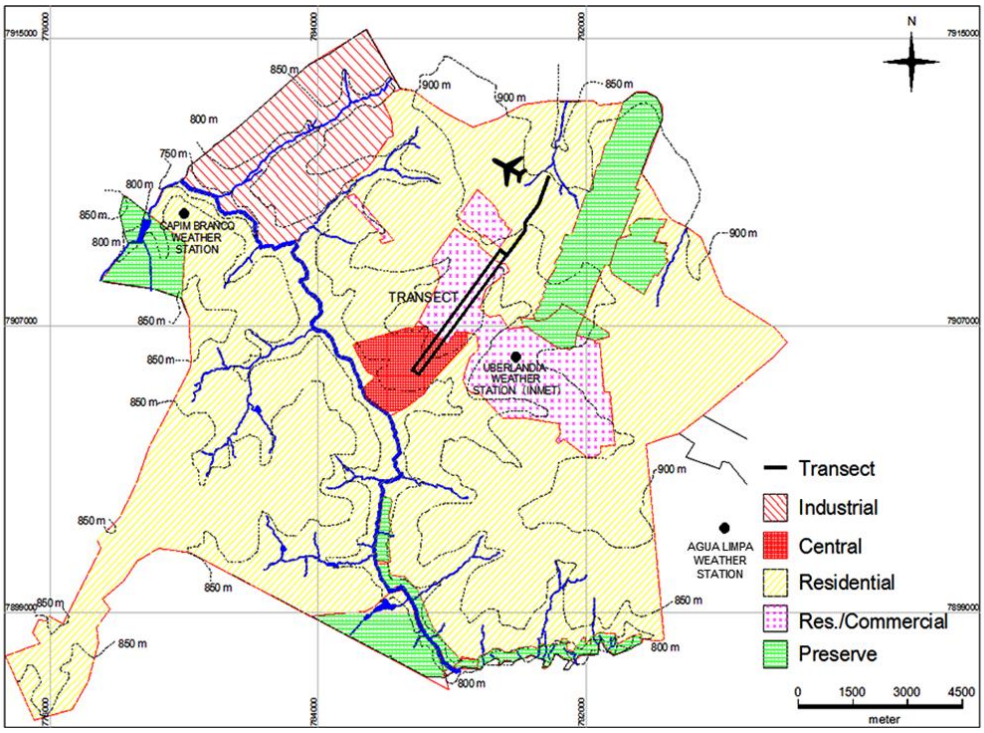

Figure 1. Characterization of urban land use and the mobile transect route.

2.2. Meteorological data collection

Temperature was measured along a straight transect from the periphery of the city to the center to evaluate how urban land use in Uberlandia influences air temperature. Mobile transects were first used to study urban temperature conditions by Oke (1981). Since then, studies have employed this technique (Hedquist and Brazel, 2006; Stewart, 2011).

The city urban area is large (135 km²) and mobile transects across its entire area are difficult because of large traffic volumes and long time-sampling issues. Thus, the route was chosen based on topography and soil cover diversity (Figure 1). Heat islands are well-defined at evening hours (Amorim et al., 2015). Thus, measurements were taken at 20h (local time) on the 15th, 20th and 21st of August, 2012 (winter) and on the 26th, 27th and 28th of February, 2013 (summer). Wind speeds during the transect were 0.6 to 1.4 and 0.0 to 1.0 m s^{-1}, during winter and summer, respectively.

Air temperature was measured with a thermo-hygrometer (mod.HMP 45°C, Vaisala, accuracy: ±0.4ºC, range: -24~38°C e ± 2% between 0~ 90%) coupled to an automatic datalogger (mod. CR10X, Campbell Scientific) programmed to take readings every 0.5 s and store one on average per second. Before taking the temperature measurements, the average temperature readings from the sensor were checked against the temperatures measured by an automated weather station belonging to the National Meteorological Institute (INMET) located near downtown Uberlandia at the Geography Institute of the Federal University of Uberlandia (18º54'66" S, 48º15'00" W, 869 m above sea level).

The thermo-hygrometer was housed in a meteorological structure located 1.5 m above the ground and lateral to and 30 cm above the vehicle roof. To avoid interference from heat emissions, only measurements taken at speeds greater than 40 km h^{-1} were considered (similar to a study by Wong and Yu, 2005). Time and geographic coordinates were recorded (Etrex portable GPS – Garmin) at the same time as the meteorological measurements and used to discard data points when the vehicle was stopped (e.g. stoplights).

Traversing the route (6.5 km) took approximately 30 min. Air temperature and humidity were measured on both outbound and return routes to make a more accurate temporal adjustment of nocturnal cooling rates over the area. Additionally, an adiabatic gradient (-0.65ºC /100 m) was used to adjust the temperature data to compensate for altitude-related temperature differences along the route. After data collection, averages were calculated for every 500 m of the transect. Differences in air temperature (ΔT) and absolute humidity were then calculated relative to corresponding values in the city center.

The terms intra-urban heat island (IUHI) and intra-urban heat intensity ($\Delta T_{urb\text{-}sub}$) were used because the transect had little contact with rural areas and to avoid a debate over whether this transect was large enough to properly assess the UHI. These terms were also used by Erell and Williamson (2007) and Yokobori and Ohta (2009).

In addition to transect measurements, hourly air temperature observations were made on the days of the transects using an INMET weather station located in an urban area 2.5 km from the city center. Two other weather stations were used (Mod. Vantage Pro2 Plus, Davis), accurate to ±0.5°C (-40~ 65.5°C) for air temperature and ±3% for relative humidity. One station was located in a suburban area (Capim Branco farm, 8 km from the city center) and the other in a rural area (Agua limpa, 21 km from the city center) of Uberlandia. Before the experiment, readings from these weather stations were checked against data from a National Institute of Meteorology (INMET) weather station.

2.3. Land cover classification

Similar to Yokobori and Ohta (2009) aerial photographs were used to classify the land cover conditions in a swath extending 150 m to either side of the transect. These aerial photographs were geometrically corrected to UTM Zone 22, Datum WGS84. A GIS computer program (Envi 4.8, ITT Corporation) was used to identify objects in the images using object segmentation and classification techniques. Segmentation involves subdividing an image into segments or neighboring pixel groups with similar attributes such as reflectance, texture and color. Segmentation usually comprises three steps: (1) defining the segmentation scale (Scale

Level), (2) merging the segments (Merge Level) and (3) classifying. Five classes were used in this study: roads and parking lots, buildings, green areas (trees and shrubs), bare soil and undefined areas. Scale and merging were empirically determined to be 90 and 95, respectively.

Figure 2 shows the percentages of each class along the transect. Construction (buildings, roads and parking lots) covered most of the area (70.6%). Nevertheless, construction diminished significantly 5.0 km from the city center where it was replaced by bare soil and grassy vegetation. With these images, the percentage of impermeable areas was also determined.

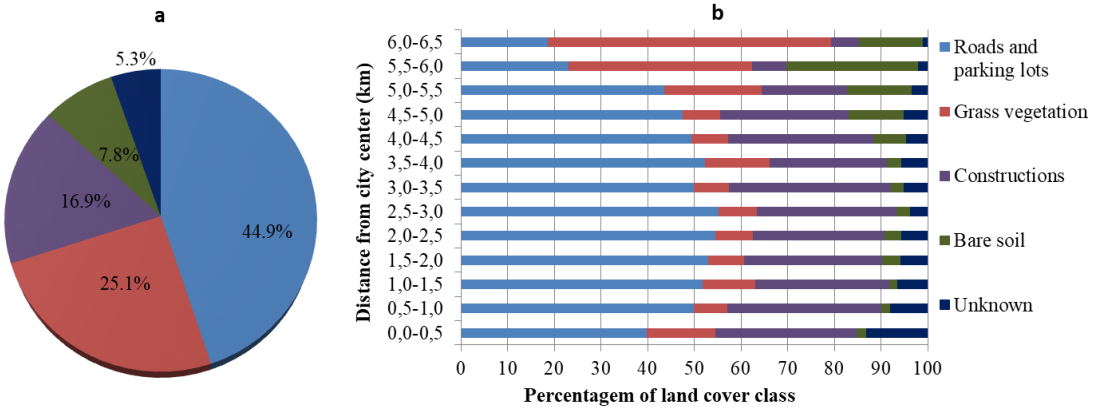

Figure 2. Average percentages of each class land cover: (a) total and (b) along the transect.

3. RESULTS AND DISCUSSION

Figure 3 shows the mean air temperature and absolute humidity along the transect (from the center of the city) in summer and winter on the three evaluation days of each season. Our methodology showed that IUHI existed in both winter and summer, even though there was no characteristic air temperature "spike" at the center point, as suggested by Oke (1973). The intra-urban heat island intensity ($\Delta T_{urb\text{-}sub}$) was 2.2°C in the winter and 1.2°C in the summer on the days studied. Most cities investigated in tropical regions showed higher IUHI in the dry season (Jonsson, 2004). In Campina Grande, Silva et al. (2010) found that high $\Delta T_{urb\text{-}sub}$ was observed during the representative month of the dry season. They are most frequent during the dry season when it is likely that low rural thermal admittance of dry soils combines with relatively low air moisture to cause rapid cooling rates at the rural site throughout the night.

The influence of urban development on humidity has been studied much less intensively than UHI phenomenon. Humidity can be measured by different forms (i.e., dew air point temperature, water vapor pressure, relative humidity). In this paper, absolute humidity was chosen because it is possible to quantify the mass of water present in the air. Hedquist and Brazel (2006), in Phoenix, found higher dew air temperature points in rural areas in summer because of evapotranspiration from irrigated rural areas. In our study, there was minimal humidity variability along the transect but mean values for absolute humidity in summer were about triple that of those observed in winter because of the rainy season.

With respect to observed air temperature differences among fixed weather stations (Figure 4), they were greater at night and in winter, especially from 19h to 23h and minimum diurnally. During the day, the low evapotranspiration in rural areas due to the low soil moisture reduced evaporative cooling. In summer, the differences were lower but persisted even during the day. The lowest air temperature values were recorded at Agua Limpa (rural) followed by Capim Branco and INMET. Also note that during the summer Agua Limpa station presented the lowest temperature values throughout the day. The INMET (urban) station only shows higher values at night (summer).

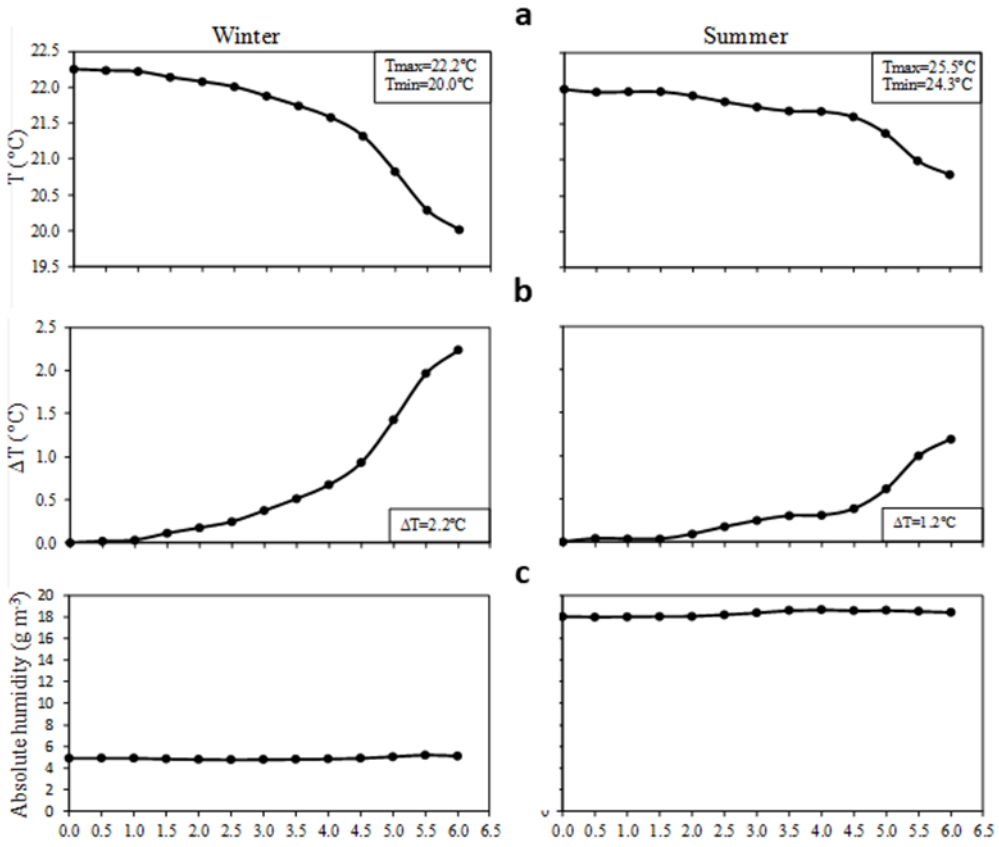

Figure 3. a) Average temperature (T), b) Air temperature variation (ΔT), c) Absolute humidity at every 500 meters, starting from the city center (winter, 2012 and summer, 2013) in Uberlandia, Brazil. Each point represents the average of 30 measurements.

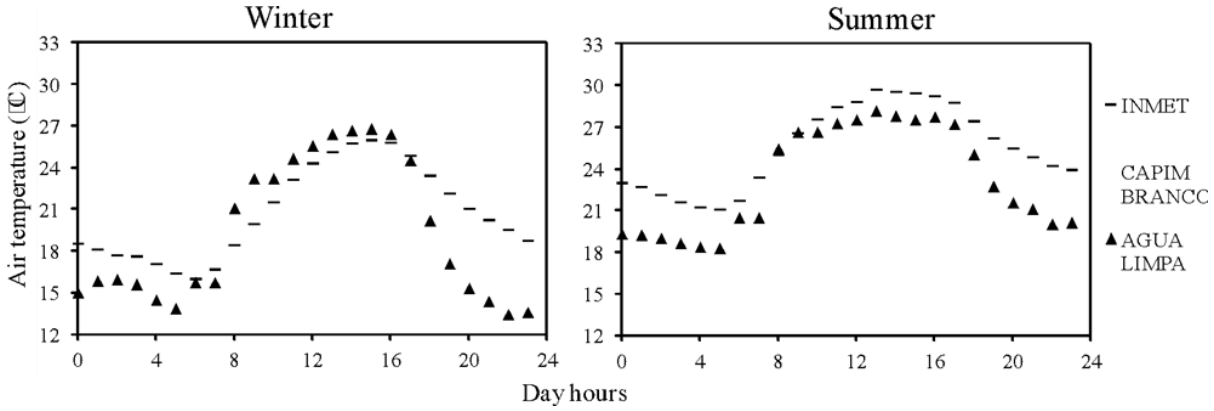

Figure 4. Hourly air temperature between fixed weather stations: urban (INMET), suburban (Capim Branco) and rural (Agua limpa) in summer and winter in Uberlandia, Minas Gerais. Each point represents the average of 36 measurements.

In winter, during daytime hours (8 to 16h), the air temperature was similar between the stations although the INMET station had slightly lower values. At night, the drop in air temperature was high at Agua limpa station and a little less for Capim Branco station. Thus, in winter and at night, the air temperatures differences are enlarged. By the time the transect was made (20h), the intensity $\Delta T_{urb\text{-}rur}$ were 5.8°C and 3.5°C for winter and summer, respectively. However, considering only INMET and Capim Branco stations (i.e., intra-urban area), $\Delta T_{urb\text{-}sub}$ were 1.9°C and 1.0°C (winter and summer, respectively), which was close to that observed with

the mobile transect. Although $\Delta T_{urb\text{-}sub}$ were higher in winter, they were also present both day and night in the summer. Higher urban air temperatures in the summer occurring with higher absolute air humidity inevitably aggravate thermal discomfort (Silva et al., 2010).

In the transect on the days evaluated (Figure 1a), both summer and winter air temperatures at 20h decrease gradually from the city center to 4.5 km and more drastically thereafter. This matches with surface cover changes (Figure 2) from impermeable (e.g., buildings, roads, parking lots) to permeable (e.g., vegetation and bare soil). This suggests that land use is crucial in determining urban climate. The correlation between the percentage of impermeable area and air temperature was linear (Figure 5). Despite greater data dispersion in winter, regression was more sensitive as indicated by the greater angular coefficient and lower linear coefficient.

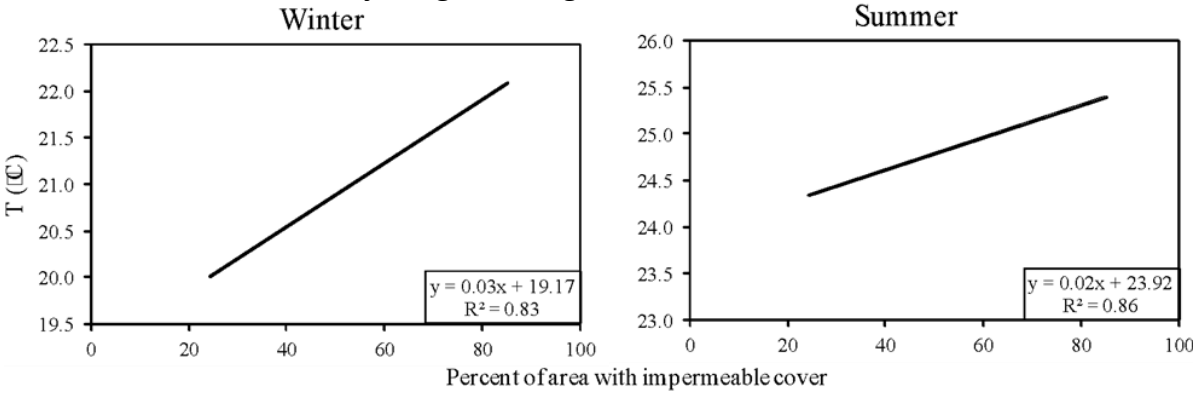

Figure 5. Relationship between the percentage of impermeable cover land and the average air temperature during transect measurements. Each point represents the average of 30 measurements.

Many studies have shown the influence of surface cover type on environmental temperature variation (Jonsson, 2004; Yokobori and Ohta, 2009; Hart and Sailor, 2009). During the day, impermeable areas absorb great amounts of solar radiation. Additionally, these areas do not allow evaporation, which causes surface temperatures to rise leading to greater sensible heat emissions and infrared radiation to the adjacent air layer. This in turn causes air temperatures in the urban center to rise during the day and night (Asaeda and Ca, 2000). The water in a permeable surface acts as a thermal regulator (Hart and Sailor, 2009). When the water content of the permeable layer is sufficiently high, almost three-fourths of solar radiation can be eliminated through the latent heat of evaporation. Hart and Sailor (2009) also report that state that surface cover is the most important characteristic differentiating warmer regions from cooler ones and emphasize the impact of parks and green areas on urban temperature variation.

Sun et al. (2009) states that increasing vegetated areas in urban settings minimizes the effect of heat islands. However, urban vegetative cover is generally declining globally, inevitably intensifying UHI effects. Uberlandia is a mid-sized city with just 6.6 m^2 of green space per inhabitant, which is well below the recommended 15 m^2 per inhabitant (Toledo et al., 2009). Thus, constant and systematic temperature monitoring is necessary throughout the urban area to identify areas with critical temperatures and propose mitigating measures.

In addition to increasing permeable space, trees could also be planted in the streets, which could cool the air via evapotranspiration, filter pollution and provide shade. The benefits provided by trees can be even greater if they are planted around buildings. Hoyano (1988), for example, showed reductions of up to 20°C on shaded walls.

Other solutions might include adding lighter-colored pigment to pavement or using porous pavement that allows water infiltration and evaporation. Light colors can increase the reflectance of pavement by 30% thereby reducing the surface temperature and limiting the heat dissipated to the surrounding environment. Asaeda and Ca (2000), in Japan, observed that maximum mid-day temperatures of porous pavement were similar to those of vegetated soil and almost 10 ºC less than the temperature of asphalt pavement. Porous pavement can also

improve water drainage and reduce flood risk. Nevertheless, additional studies are needed to evaluate the durability and economic viability of these materials.

Regardless, municipalities must monitor heat intensity in order to evaluate urban environmental quality and to determine the effectiveness of mitigating measures. For this, it is important to plan multiple transects on a year round basis.

4. CONCLUSIONS

The thermal analysis of the city of Uberlandia via mobile transect showed that: (1) the methodology used in the study proved to be a quick and efficient way of conducting this type of monitoring, as it could be applied quickly and was relatively economical in several cities of the country where climatic data are limited; (2) night air temperatures increase proportionally with the percentage of soil covered by buildings, which characterizes the heat islands in urban centers; (3) the analysis of the transect data of the evaluated days showed that the urban heat islands were more intense in winter ($\Delta T = 2{,}2ºC$) than in summer ($\Delta T = 1{,}2ºC$) because of the reduction of the atmospheric vapor in winter (dry season) and because of the higher rate of radiative cooling that occurs in permeable areas, that is, in the areas without construction, thus characterizing the effect of surface coverage on heat islands.

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Water quality of springs in areas under different land uses in the southern highlands of Santa Catarina

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ABSTRACT

This study sought to characterize the conditions of springs used for domestic consumption and to analyze their water quality. The springs are situated in catchment areas (drainage areas) with different soil uses in rural properties of the southern plateau of Santa Catarina, Brazil. To this end, 56 springs used to supply rural properties were selected in the counties of Lages, Otacílio Costa, São José do Cerrito, Painel, and Bocaina do Sul. The water catchment area of the springs were described in detail with regard to topography, management, forest, protection, fences, channels to contain runoff, and macroscopic aspects of water. In addition, the water was analyzed for total and fecal coliforms, pH, dissolved oxygen, electrical conductivity, temperature, clarity, and nitrate and total phenol contents. The samplings for water analysis were performed in compliance with Standard Methods for Examination of Water and Wastewater (APHA). The above parameters were evaluated under the following soil uses in the drainage areas: native forest, native grassland, planted pine forest, and cropland. Data were analyzed by comparison of means by the Student's t test ($p < 0.05$). More than 80% of the springs were found to be contaminated with fecal coliforms. The main risk factors for microbiological contamination in the region are extensive cattle ranching and the lack of adequate protection of the springs in most properties, with emphasis on the catchment areas of native grassland and native forest. Springs in pine forest areas have the lowest mean pH and the highest phenol content.

Keywords: contamination of water sources, drainage areas, spring protection.

Qualidade da água de fontes em diferentes usos do solo no Planalto Sul Catarinense

RESUMO

O objetivo deste trabalho foi caracterizar as condições das nascentes para consumo doméstico e analisar a qualidade da água destas, situadas em áreas de contribuição (microbacias), em diferentes usos do solo em propriedades rurais do planalto sul de Santa Catarina, Brasil. Para isso foram selecionadas 56 fontes utilizadas para o abastecimento

doméstico em propriedades rurais nos municípios de: Lages, Otacílio Costa, São José do Cerrito, Painel e Bocaina do Sul. Foi realizada a caracterização detalhada da área de contribuição às fontes quanto à topografia, manejo adotado, floresta, proteção, cercas e valas de contenção de enxurradas e aspectos macroscópicos da água. Além disso, realizou-se análise da água para coliformes totais e fecais, pH, oxigênio dissolvido, condutividade elétrica, temperatura, limpidez, nitrato e fenóis totais. As amostragens para análise seguiram as normas do Standard Methods for Examination of Water and Wastewater (APHA). Os parâmetros foram avaliados nos seguintes usos do solo nas áreas de contribuição da fonte: floresta nativa, campo nativo, reflorestamento de pinus e lavoura. Os dados foram analisados por comparação de médias pelo teste T-Student ($p<0,05$). Mais de 80% das fontes estão contaminadas por coliformes fecais. Os principais fatores de risco de contaminação microbiológica são a presença da pecuária extensiva e ausência de proteção das fontes na maioria das propriedades, com destaque para as áreas de contribuição com campo nativo e floresta nativa. Nas áreas com pinus a água das fontes tem a menor média de pH e maior teor de fenóis.

Palavras-chave: área de drenagem, contaminação de fontes de água, proteção de nascentes.

1. INTRODUCTION

The availability of water, aside from playing an essential role in production, fulfills social and environmental functions. Water is fundamental for the maintenance of life and has multiple uses, including that of human drinking water. The function of water in natural cycles ensures the ecological balance. Shortages of safe, clean drinking water are a major cause of illness and death in developing countries (Boutilier et al., 2014).

The importance of water was anchored in Resolution no. 64/292 of the United Nations General Assembly, by which clean and safe water and sanitation are acknowledged as human rights. The access to good-quality water is a precondition for food and nutritional security (SAN). The World Health Organization (WHO) and the United Nations Children's Fund (UNICEF) warn about the danger of not investing enough in clean water and sanitation, resulting in public spending to treat diseases transmitted by contaminated water in Brazil (Menezes et al., 2009).

Excessive water demand and the lack of sustainable management in the agricultural sector can compromise water resources quantitatively and qualitatively, reduce access to good-quality water for human consumption, and trigger social conflicts. Although the water demand for direct human consumption is not very representative (mean of 0.56% of the total consumption in the state of Santa Catarina) compared to the demand for livestock (accounting for 1.74%) and for agricultural activities (97.7%) (Conceição et al., 2013), the data from the Brazilian survey of sampled households (PNAD) showed severe inequality between urban and rural inhabitants in terms of access to water supply services. In Brazil, 66.6% of the rural households use wells or collect water directly from springs (FUNASA, 2014).

In the rural area of the highland region of Santa Catarina, residents are supplied with different water sources, e.g., from wells, springs, creeks, rivers, and artesian wells. These water sources are often used without any kind of protection or treatment, exposed to the most varied forms of contamination. The quality of water for domestic supply can be affected by pollution from different sources, such as domestic or industrial effluents, urban surface runoff, and agricultural activities (Bertoncini, 2008).

The consumption of poor-quality water can deter people from drinking enough to supply the vital necessities and may eventually compromise the health of the people. Biological contamination with total and fecal coliforms usually occurs due to the lack of physical

protection of the springs associated with inadequate use and management of their catchment areas, mainly in the vicinity of domestic animals (Stolf and Molz, 2017).

Land use and occupation are interference factors in surface water quality, and water quality management should be based on minimizing or mitigating environmental damage. In addition, local particularities such as topography, soil type, presence/absence of forests, soil management, and the presence of livestock and other domestic animals can increase the contamination risk of springs, influencing the biological, physical and chemical water properties, mainly the levels of nitrate and fecal coliforms (Barrington et al., 2013).

In intensive agricultural production systems, the need for agrochemical applications is high, raising nitrate levels in water. The nitrate anion is weakly retained in colloidal charges and tends to remain in solution. In the soil solution, the nitrate is prone to leaching and over time, its contents may increase in the water of springs or wells. High nitrate concentrations in the water are a potential cause of damage to human health and the environment (Jadoski et al., 2010).

The phenol concentration in spring water can also be influenced by the type of land use in the drainage area that supplies the source (Turtola et al., 2002). Phenols may be toxic to human health, aquatic organisms and to microorganisms that are part of aquatic systems.

The study of the water quality of springs is based on evaluations of macroscopic (surroundings and condition of the spring) and microscopic (laboratory water analysis) aspects. In this sense, this study sought to characterize the conditions of springs used for domestic consumption and to analyze the water quality under different land uses in rural regions in the southern highlands of Santa Catarina, Brasil.

2. MATERIAL AND METHODS

The study was carried out in the southern highland region of Santa Catarina in the counties of Lages, Otacílio Costa, São José do Cerrito, Painel and Bocaina do Sul. Rural properties with springs were selected based on indications of agents of technical assistance and rural extension (ATER) according to the following criteria: (a) springs used for human consumption; b) surrounded by different types of land use in the drainage areas, e.g., native forest, native grassland, cropland, and planted pine forest. These four types of land use are representative of the economic activities in the studied region; the native forest and native grassland areas are used for extensive livestock raising.

The study region is located in the sub-basins of Rio Caveiras and Rio Canoas. The soils of the region are derived from the Serra Geral mountain chain, characterized by effusive rocks, and are predominantly clayey (part of the counties of Lages, São José do Cerrito and Painel). Immediately below the Serra Geral, Botucatu Sandstone is found, which is the rocky matrix of the Guarani Aquifer. This formation has a narrow outcrop, giving rise to the characteristically sandy soil. The Rio do Rastro formation range also covers a large area of the region, e.g., in Lages, Bocaina do Sul and Otacílio Costa, creating soils of varied texture.

We considered the space between the water source where it is collected and the highest point upstream that contributes to the source as drainage areas. The drainage areas of the sources were classified according to their use and predominant vegetation cover.

Samples were collected from 56 springs for laboratory analysis between March and August 2016, according to the Standard Methods for Examination of Water and Wastewater (APHA, 2012). The samplings were carried out within an interval of at least three days after rainfall above 5 mm.

The points were characterized in detail according to the geological and topographic conditions, type of spring, form of catchment and geographical coordinates. The geological conditions, given by the predominant soil type, were evaluated macroscopically for clay or

sandy texture. The topographic condition was defined as flat, slight or steep slope. The type of spring was classified as surface spring when it emerged at the soil surface, and as well when the water was accessed by excavation. The form of water outflow and channeling was also evaluated, differentiating between water flow by gravity or motor pump.

The preservation of the spring surroundings was evaluated with regarding the type of vegetation, presence or signs of livestock, contamination sources, type of land use and management, and macroscopic aspects of the water conditions of the springs.

The type of vegetation in the surroundings of the spring was classified as present when the spring was shaded by tree canopies, or absent when the spring was exposed.

The material at the bottom of the reservoir was classified as rock, sand, sludge, or mud. The difference between sludge and mud was distinguished by the color, since gray to black colors indicate the presence of organic material, corresponding to sludge, while the material was classified as mud when it had the appearance of clay or sand originated from the banks of the spring. The water transparency/clarity was visually assessed for the level of light crystalline appearance and absence of residue.

The presence or absence of a physical protection of the springs was evaluated, and classified as present, weak or absent. The protection was considered present when the spring was fully protected from external contamination sources, e.g., source safely enclosed below the soil surface with piping of the water from the outlet directly to the consumption location; vegetation cover of the source location with native species; and protection against animal access and other contamination sources, or encased in closed and sealed concrete tubes or boxes to prevent the entry of insects, amphibians, or larger animals. Where failures in these structures of reservoir containment were detected, the protection was considered weak, and absent where the reservoir was dug directly into the soil without protection.

Fences were considered to be present when they protectively surrounded the drainage area of the spring against animal access; weak when they allowed sporadic access of animals and did not adequately enclose them; and absent when animals had free access to the spring. Containment embankments and channeling of runoff water were only taken into consideration when they were functionally effective.

The macroscopic aspects were evaluated with regard to the presence in the spring of aquatic vegetation and foam, for water color and transparency/clarity. This evaluation of the springs was performed as described by Felippe and Magalhães Junior (2013), by a simple and practical methodology with satisfactory results, with the objective of evaluating the conservation level of springs qualitatively and visually, based on the identification of negative environmental impacts. These assessments are supplementary to the laboratory analyses and contribute to a better understanding of the forms of environmental contamination.

Water samples were collected for analysis of microbiological parameters (total coliforms and *Escherichia coli*), and 100 mL was filled in sterile 250 mL polypropylene flasks, in compliance with the technical norms for storage and conservation, and stored until analysis. The material used for sampling was pre-purified with water and commercial liquid detergent and the equipment used for the microbiological analyses was sterilized in an autoclave.

Microbiological analyses were performed with the Readycult® kit Coliforms 100 (Merck). The kit consists of a culture medium that determines the presence or absence of coliform bacteria and *E. coli* in the sampled water. Immediately after sampling, one dose of the kit is added to each 100 ml water sample, followed by incubation at 36 ± 1°C for 24 ± 1 h. In the presence of coliform bacteria, the content of the sample changes from yellow to slightly greenish blue. Additionally, in the presence of *E. coli*, the medium emits bright blue fluorescence when subjected to ultraviolet (UV) light (wavelength 365 nm).

The following physic-chemical parameters were analyzed: pH, temperature, electrical conductivity, and nitrate and total phenol contents. The analyses of water pH, temperature and electrical conductivity were carried out in the field at sampling with a YSI multiparameter water quality probe. The nitrate (NO_3^-) levels were analyzed using the Spectroquant® Nitrattest Kit (Merck) and the readings were performed in a spectrophotometer Spectroquant® (Merck).

The data were tabulated and subjected to descriptive analysis, and the means of results for the different land use types were compared by the T test using Excel® software. To compare the water quality of the sources, under the four types of land use in the catchment areas, graphic models of the radial type were organized, in which each attribute is located in one of its radii with percentage values.

3. RESULTS AND DISCUSSION

Of the 56 water sources sampled, 18 were found in native forest, 19 in native grassland, 11 near crop fields and 8 in planted pine forest areas. In all agricultural areas, they were surrounded by small grassland or forest patches, usually with a radius of 2-10 m springs, i.e., insufficient to offset the predominant effects of the surrounding cropland on the spring catchment.

All evaluated springs had continuous flow and 90% were surface springs. Half of the springs had a lentic character, i.e., stagnant waters with renewal; 22% were lotic and the others were intermediate. A lentic character can considerably affect water quality due to the dynamics of accumulation of polluting elements, especially in areas under intensive agricultural management.

The slope was gentle at 54% of the locations; the water supply of 68% of the residences was actuated by gravity (Table 1) and that of the others by motor pumps.

The predominant soil near the springs was clayey in 93% of the drainage areas (Table 1). Only at four sampling sites (two in São José do Cerrito in areas of Botucatu sandstone outcrop and two in Bocaina do Sul) sandy soil was predominant.

Table 1. General properties of the environment of domestic water sources in rural properties of the southern highlands of Santa Catarina.

Spring type	Topography			Predominant soil type		Bottom of the reservoir				Water conduction
Superficial	Steep	Gentle	Plane	Clayey	Sandy	Rock	Mud[1]	Sand	Sludge[2]	Gravity
	%									
90	23	54	23	93	7	12	43	3	42	68

1 – fine material (clay/silt), with no visible presence of organic material; 2 - fine material with visible presence of organic material.

Regarding management of the areas surrounding springs, 84% were not enclosed with fences. In the springs located in pine forests and native grassland, respectively, 100 and 95% had no protective fences (Figure 1). Cattle or animal traces, such as trampling and feces, were observed at 64% of the springs. This occurrence was even more common at springs in native forest and native grassland areas, where bovines and other animals had free access to almost 100% of the springs.

Cattle trampling near springs forms mud and contributes to the silting of the reservoirs during flooding periods. This fact is aggravated by the formation of animal tracks leading to the springs that function as drainage channels, by which dung and contaminants are swept into the springs, while the soil near the springs is compacted. On the other hand, the presence of

animals around water springs affects the water quality and poses serious risks to human health. Contamination by animals may, for example, become a vehicle for contamination of pathogenic organisms, such as tuberculosis, brucellosis, foot-and-mouth disease, leptospirosis and parasites that can contaminate humans (Daker, 1976).

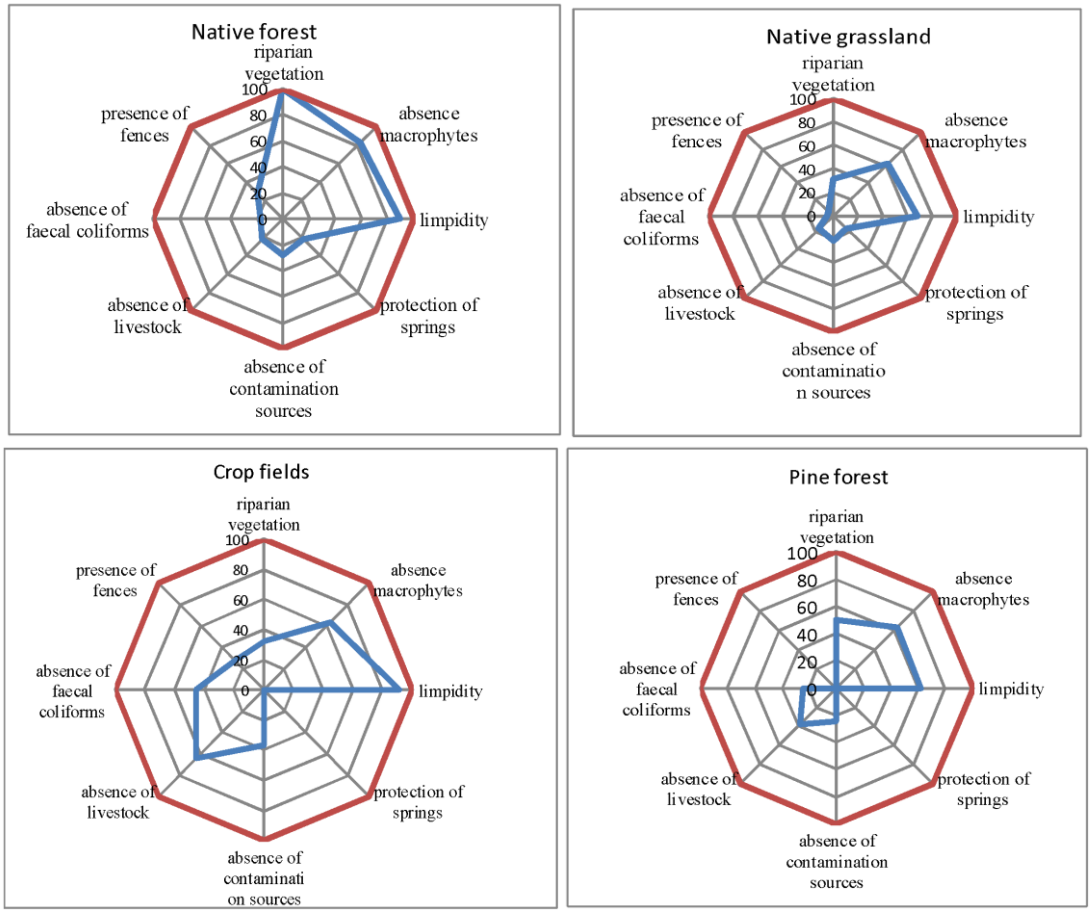

Figure 1. Radial plot of environmental and biological parameters in relation to land uses. The ideal situation is defined by the line circumscribing the entire plot area.

The riparian vegetation of springs in native forest areas had the highest level of conservation in an evaluation according to the minimum criteria established by Federal Law nº. 12.651/2012, known as the New Forest Code (Brasil, 2012). However, in most drainage areas, the presence of cattle and a high degree of degradation of the native forest were observed, with the exception of some difficult-access locations. The riparian area around most springs located in native grassland and cropland areas, if present at all, consisted of small tree groups restricted to the spring margin or scattered in the field, insufficient to represent an effective protection area.

Only 12% of the springs used for human consumption had sufficient protection to ensure potability. At 48% of the springs there was no protection or management of any kind. In these sites, the water was collected in a hollow, dug into the soil, forming a water puddle or pond, which is silted at flooding and contains algae, macrophytes, and organic material. Forty percent of the springs were encased in concrete boxes or tubes and covered with wood, asbestos cement or steel sheets, but were not safely protected against contamination.

The most common deficiencies observed in the spring sources protection were rotten covers, part of the reservoir outside the fenced area, use as watering place for animals, very

restricted enclosure, absence of embankments for water containment and diversion, contamination by runoff, and lack of maintenance.

The predominance of clayey soils on the banks contributed to the presence of mud at the base of 44% of the studied springs (Table 1). In the presence of animals, it was common to find dark sludge at the bottom of the reservoir, indicating organic matter from animal feces, which can promote the growth of phytoplankton and aquatic macrophytes. The presence of spongy or filamentous (mossy) materials was observed in the water of 28% of the springs, varying from brown to green, with foam. Water transparency and color can be indicators of several problems related to water quality. The lack of transparency/clarity (turbidity) and presence of color, as observed in 23% of the sampled springs, can be attributed mainly to suspended solid particles that interfere with light transmission in the medium. Turbidity can be caused by plankton, algae, organic debris, and other substances, such as zinc, iron precipitates, manganese compounds and sand resulting from natural erosion or domestic pollutants. Some alga species produce toxins in water resources that are harmful to animals and humans, for example the cyanobacteria *Microcystis*, which produces hepatotoxic microcystin (Azizullah et al., 2011).

Among the macroscopic parameters in different land uses, the native forest areas stood out with springs with less macrophyte (aquatic vegetation) growth, and more limpid and colorless water. These characteristics are mainly due to the lower light incidence within the forest and the higher water infiltration capacity in the soil. The worst situation was identified for springs located in native grassland and pine forest areas, in which the values of all analyzed parameters were unsatisfactory (Figure 1).

In the coliform analysis, total coliforms were detected in 95% of the spring sources, and fecal (thermotolerant) coliforms in 82%. The presence of fecal coliforms was detected in 83% of the springs located in native forests, in 95% of those in native grassland, 75% of those in pine forests, and in 55% of those in cropland (Figure 1). It is worth mentioning that the incidence of fecal coliforms in springs in cropland areas was low, coinciding with a lower cattle stocking rate. For rural areas with untreated water, these results are not new in the literature (Stolf and Molz, 2017). The greater amount of contaminated springs in native forest and native grassland was due to the higher concentration of animals at these locations. The presence of fecal coliforms is an indicator of contaminants from warm-blooded animals and represents risks of transmission of several infectious diseases (Brasil, 2011; CONAMA, 2005).

The water pH of the springs ranged from 5.46 to 9.84, with an overall mean of 6.28 (Table 2). Regulation Nº. 2,914 of the Ministry of Health recommends a pH in the range of 6.5 - 8.8 for drinking water, tolerating values between 6.0 and 9.0. Overall, 32% of the springs had a pH of less than 6.0. The mean pH of springs located in pine forests was 5.9, and 75% were beyond the acceptable range of the threshold determined by the regulation. Significant differences were observed between the pH of springs in pine forests compared to those in native grassland and native forests (Table 2). In a study of springs in the state of Minas Gerais, Barcellos et al. (2006) observed that 47% of the springs did not fit into the pH range of regulation nº. 2,914 of the Ministry of Health and resolution nº. 357 of CONAMA. The water pH of the springs may be influenced by the soil pH, which is in a range of 4.0 to 5.5, under the natural conditions of the southern highlands of Santa Catarina.

The overall mean dissolved oxygen (DO) of 5.76 (Table 2) was below the value of the CONAMA resolution no. 357 of 2005 (DO > 6.0 mg L^{-1}), by which only 36% of the springs fit in Water Class 1. There were no significant differences at 5% between the means of different land uses in the drainage areas (Table 2).

The mean electrical water conductivity (EC) was 40 µS cm^{-1} in the analyzed springs. This value falls within the range established for natural water bodies which, according to the FUNASA control manual of water quality ETAS, should have EC levels between 10 and 100 µS/cm (FUNASA, 2014).

Table 2. Physical-chemical water properties of springs, means and standard deviation (SD) according to land use in the drainage areas of springs.

	pH	DO ($mg.L^{-1}$)^{ns}	EC ($\mu S/cm$)^{ns}	T $^{o}C^{ns}$	Nitrate mg $L^{-1\ ns}$	Phenols ($mg.L^{-1}$)
Native forest	6.34 ± 0.46*[1]	5.76 ± 1.75	42 ± 0.014	15.9 ± 2.7	1.03 ± 0.68	0.021 ± 0.01*[3]
Native grassland	6.48 ± 1.14 *[2]	5.64 ± 1.99	37 ± 0.017	15.5 ± 2.2	0.84 ±0.97	0.027 ± 0.01
Cropland	6.09 ± 0.41	6.09 ± 2.23	45 ± 0.018	14.4 ± 4.5	0.54 ± 0.95	0.021 ±0.01 *[4]
Pine forest	5.91 ± 0.36*[1.2]	5.64 ± 1.4	38 ± 0.029	15.1 ± 2.2	1.11 ± 1.52	0.032 ± 0.01*[3. 4]
Overall mean	6.28 ± 0.76	5.76 ± 1.85	40 ± 0.018	15.4 ± 2.8	0.88 ± 0.98	0.025 ± 0.01

^{ns} no significant contrast. * 1 Differ from each other by the t test ($p < 0.01$) and; * 2, * 3 and * 4 Differ from each other by the t test ($p = 0.05$).

The water temperature of the springs ranged from 6 to 19ºC, with a mean of 15.5ºC ± 2.8. The variation in the atmospheric temperature observed in the days of sampling ranged from 6 to 22ºC. It is known that the water temperature of the springs can vary according to the climate variations throughout the year (Marmontel and Rodrigues, 2015). Although the presence of riparian forest may mitigate water temperature fluctuations caused by the variation in atmospheric temperature, the mean water temperatures of the springs under the studied land uses did not differ from each other at 5% probability.

The nitrate (NO_3^-) contents in the water were below the maximum permitted value (MPV) of 10 mg L^{-1} established by CONAMA resolution nº. 357 of 2005 and regulation nº. 2,914 of Ministry of Health/2011 (Brasil, 2011; CONAMA, 2005). The general content was 0.88 mg L^{-1} ± 0.98, with a minimum of <0.2 and maximum values of 4.2 mg L^{-1}. Under the different land uses in the spring catchment areas, the means did not differ from each other, ranging from 0.54 ± 0.95 to 1.11 ± 1.52 mg L^{-1} NO^{3-}.

Despite the presence of animals around most of the analyzed springs, the observed NO_3 levels indicate a reasonable presence of native forest and non-intensive management of agricultural and livestock areas, in particular upstream of the spring catchment areas. The presence of nitrogen in the water is usually a consequence of intensive fertilization. However, since the main crop was soybean, little or no N fertilizer was applied, and in addition, the data were collected in a fallow period of the soil.

The phenol content in the water exceeded the MPV of the CONAMA resolution nº. 357 of 2005, determining a limit of 0.003 mg L^{-1} (CONAMA, 2005). The overall mean was 0.025 mg L^{-1}, with a minimum of 0.008 and a maximum of 0.048 mg L^{-1} (Table 2).

Under the different land uses in the spring catchment area, the mean phenol contents were 0.027, 0.021, 0.021, and 0.032 mg L^{-1}, respectively, in the native grassland, native forest, cropland, and pine forest areas. The mean phenol contents in the springs in pine forests were significantly higher than the means of the native forest and cropland areas and did not differ from native grassland ($p < 0.05$) (Table 2). Although the phenol concentration in water may have different origins, in rural environments where industrial pollution is less likely, they may be a result of the degradation of organic residues added to the soil, or released directly from lignin and oxidative phenols that contribute to the formation of defensive barriers. In addition, in these environments, this fact may be related to the volume of pine needles that remain on the soil surface, and during decomposition release phenols that are carried into the water (Turtola et al., 2002).

It is worth emphasizing that the MPVs of the legislation are defined for water for urban consumption, in which the presence of phenols of industrial origin is more likely. However, in natural environments, less susceptible to the contamination of synthetic phenolic products, the main contamination sources may be the decomposition of organic residues and the type of vegetation cover in the catchment areas (Charrière et al., 1991).

4. CONCLUSIONS

More than 80% of the springs in southern highlands of Santa Catarina are contaminated with fecal coliforms and approximately half of these springs have a low content of dissolved oxygen, which may result from the high content of microorganisms.

The most contaminated spring sources with fecal coliforms were those where the catchment areas were occupied by native grassland and native forests, while in cropland areas where few cattle were present, contamination was lower.

The main risk factors for contamination of the springs in the region are the lack of protection of the springs and cattle ranching on most farms. These are more severe for the springs in the catchment areas used with native pasture, followed by the areas of native forest and planted pine.

The type of land use in the catchment areas also influences the pH and phenolic contents. Approximately half of the analyzed water sources present pH below the potability standards, while the phenol content exceeds the MPV established by current legislation. This fact is more pronounced for the water sources in pine forests.

The low water quality observed on the farms reinforces the importance of this type of study for the evaluation of health risks of the rural populations and of the environmental impact of human activities. Our results highlight the need for sustainable development plans aimed at the quality of life of rural populations and the need to raise public awareness and to inform the population regarding the need to preserve the quality of water resources on rural properties.

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Biogas originated from residual biomass in ecosystem services

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ABSTRACT

Human demand for the provisioning services of the ecosystem has been rising and shows the existence of trade-offs in their generation. Brazil is a great producer of agricultural commodities and animal protein, which generates a large amount of residual biomass throughout the production process, especially animal highly polluting waste concentrated in small areas. Ecosystems provide a wide range of services that are of fundamental importance to the well-being, health, subsistence and survival of human beings. The impacts of the waste generated by confined animals can degrade the ecosystem and reduce the services it can supply. Using waste to generate biogas does not require direct resources from the ecosystems to generate energy. In this context, it is an energy product classified as a provisioning service and, at the same time, an ecosystem regulating service, as it mitigates undesirable effects in the environment. The main goal of the classification of biogas as an ecosystem service is to explore its contributions to the ecosystem and to human well-being.

Keywords: ecosystem services, renewable energy, residual biomass.

Biogás oriundo da biomassa residual nos serviços ecossistêmicos

RESUMO

A demanda humana pelos serviços de provisão do ecossistema vem crescendo, e mostram a existência de trade-offs na sua geração. O Brasil é um grande produtor de commodities agrícolas e proteína animal, mas que gera um grande volume de biomassa residual ao longo do processo produtivo, com destaque para os dejetos de animais concentrados em pequenas áreas e com alto grau poluidor. Os ecossistemas fornecem uma gama de serviços que são de fundamental importância para o bem-estar, saúde, meios de subsistência e sobrevivência aos seres humanos. Os impactos da produção de animais confinados podem degradar o ecossistema e reduzir os serviços que o ecossistema pode fornecer. O aproveitamento dos dejetos para gerar biogás não utiliza recursos diretos dos serviços dos ecossistemas para gerar energia, e neste contexto é um produto energético classificado como um serviço de provisão e ao mesmo tempo um serviço ecossistêmico de regulação, na medida em que exerce a mitigação de efeitos indesejados no ambiente. A classificação do biogás nos serviços ecossistêmicos tem como finalidade principal abordar as contribuições ao ecossistema e para o bem-estar humano.

Palavras-chave: biomassa residual, energia renovável, serviços ecossistêmicos.

1. INTRODUCTION

Ecosystems provide a wide range of services that are of fundamental importance to the well-being, health, subsistence and survival of human beings. The impacts of the production of concentrated residues can degrade the ecosystem and reduce the services it can provide. Ecosystem services can be defined as the direct and indirect contributions of structures and functions of ecosystems, in combination with other factors of production, to human well-being (Burkhard et al., 2012).

Agricultural production interacts with the environment through use of resources and production of residues and through its volume and composition, which can contain high levels of organic matter, nutrients and microorganisms with potential for pollution of water, air and soil. The leaching of nutrients, especially nitrogen (N) and phosphorus (P), evaporation of ammonia (NH_3) and contamination by pathogens are some of the biggest threats (Holm-Nielsen et al., 2009). The volume of animal excrement is an environmental challenge due to its huge quantity and high risk of water and air pollution (Fernandez-Lopez et al., 2016; Oudart et al., 2015). The emission of NH_3, greenhouse gases and odors is a concern related to excrement disposal (Loyon, 2017) and, in addition, they are a source of pathogenic agents and nitrates (NO_3-) that may affect the surface waters and groundwaters (Millner et al., 2014).

With a growing demand for food production, agricultural production is increasingly causing impacts on the environment, with a larger scale of animal production in small spaces and more waste production, which represents a considerable threat of pollution leading to more pressure on the environment in these areas. This brings us to the challenge of integrating ecosystem services with the management of the residual biomass generated by confined animals. When managed improperly, this may adversely impact the environment.

Managing the environment requires us to understand how changes in demand, production and offer of products and energy affect ecosystem services. The products and services generated in an economy are associated with unavoidable environmental consequences, even non-intentional (Baumgärtner et al., 2001), and the environmental impacts may occur in different stages of the life cycles of these products and services (Tukker and Jansen, 2006). Therefore, it is important to understand the impact of animal waste on the environment and how it affects local ecosystem services. It is also important to understand its interactions and multiple effects, and to explore alternatives to reduce these impacts on the environment without compromising the delivery of other ecosystem services and risk generating trade-offs.

The use of biomass for energy production is one of the most promising alternative sources of sustainable and renewable energy (Cherubini and Strømman, 2011); its production and usage therefore assumes great economic and environmental importance. In comparison to other biofuels, biogas is versatile and flexible, and can be produced from different types of feedstock, like the ones provided by the agricultural sector and from other flows of organic residues from society in general. In the rural environment, the biggest resource is represented by waste of animals confined in production units, such as swine, birds and bovines.

Within the context of ecosystem services and with the intention of using renewable and sustainable energy, biogas is a practical approach to reduce the local energy deficit and mitigate problems of environmental contamination. Thus, biogas generated from animal waste can be considered an energy product with a provisioning service function and, at the same time, it functions as a regulating service because it mitigates undesirable effects in the environment. The goal of this paper is therefore to describe how biogas generated from of animal waste fits in the concept of ecosystem services of provision and regulation.

1.1. Residual biomass and biogas

Having a safe supply of energy is crucial for the well-being of people and the economy in the world (Olson-Hazboun et al., 2016). Biomass represents a renewable and abundant source

of energy and has the potential to become a global font of resources in the 21st century. The current energy supply depends on fossil sources, which are non-renewable and limited. Renewable energy sources are not subject to depletion and are beneficial to the environment. Reusing waste is a great opportunity to generate renewable energy in the form of biogas, as it represents an attractive trade-off in terms of reduction of the impact in the development and use of renewable energy.

It is likely that biomass, because it is a cleaner energy, will become an appealing option to reduce emissions of greenhouse gases (Junfeng and Runqing, 2003) The potential for reduction in the emission of greenhouse gases is one of the main benefits of the use of biomass in the production of energy and the use of biodigesters represents a unique platform for recycling nutrients, thus closing the cycles of important resources which, if not controlled adequately, may cause negative environmental impacts (Holm-Nielsen et al., 2009).

Sustainability is of fundamental importance in the use of biomass as feedstock for production of energy. Its use can promote a more-sustainable agriculture, since promoting sustainability in productive ecosystems can lead to synergy between production and maintenance of ecosystem services, resulting in the production of food, fibers and energy, given that agricultural productive systems are also a source of ecosystem services (Swinton et al., 2007).

Managing residues is a basic component of economic and environmental sustainability in the production of confined animals, especially in relation to waste. At the scale of the rural property, the most usual way of handling it is through use in the soil, which produces significant atmospheric emissions of greenhouse gases, consumes fossil energy resources and can result in the accumulation of nutrients in the soil (Aguirre-Villegas et al., 2014).

The amount of waste produced per year in Brazil corresponds to a considerable volume of residual biomass. Highlighting the production of waste from swine breeding, it is possible to include waste from broiler chickens, laying birds, milk cows and beef cattle, which totals 1,703,773,970 t $year^{-1}$ of waste (IPEA, 2012). In swine breeding the main problem is the volume and the characteristics of the waste, which is in liquid form and with high organic rate; with cattle, the biggest impact is the system of breeding (extensive or confined), because to generate biogas it is necessary to pick up the waste, which is only plausible in confined breeding. The waste produced by aviculture is of great volume and is usually concentrated in small areas.

Using the waste from these animals can promote a cleaner environment and provide energy as a product with economic potential. Treatment of residual biomass can be made through anaerobic digestion with the production of biogas (Qiao et al., 2011). Anaerobic digestion is a microbiological process in which organic matter is degraded in the absence of oxygen, which therefore decreases the organic load, resulting in biogas. In the specific case of animal waste, the stabilized suspension after anaerobic digestion, the digestate, can be used as a fertilizer and consists of essential nutrients for the growth of plants (Mata-Alvarez et al., 2000).

From the perspective of the production of biogas originated from residual biomass, agricultural production goes from a productive role to a multifunctional one, considered in a systemic approach capable of producing food and meeting the new needs of consumers, offering services like energy, landscape, tourism, etc. Energy production from residues represents this concept, in search of environmental balance in production activities; it integrates animal and energy production from renewable sources, and in the case of biogas, contributes to the treatment of potentially polluting residues.

1.2. Ecosystem services

The term “ecosystem services” describes the benefits we obtain from ecosystems. According to Costanza et al. (1997), goods from the ecosystem (like food) and services (like assimilation of residues) represent the benefits enjoyed by human populations, directly or

indirectly from the functions of the ecosystem. People benefit from ecosystem services which are, among others, nutrition, access to air and water, health, safety, leisure (Maes et al., 2016). The benefits from ecosystem services potentially influence several elements of human well-being, such as basic human necessities, economic necessities, environmental necessities and subjective happiness (Summers et al., 2012). Human well-being is incorporated into the concept and the definition of ecosystem services, as there are no services if human beings do not benefit from either the functions or the processes that generate them (Kandziora et al., 2013). Therefore, assuming human well-being strongly depends on services provided by well-functioning ecosystems, changes in the operation of any system may have direct and indirect effects on it.

Impact and human management strongly affect ecosystems, including their processes and functions (Gissi et al., 2016). Nowadays, the demands for ecosystem services created by human activity surpass what is available, which is the capacity of the ecosystems to mitigate pollutants and provide necessary natural goods, affecting the operation of ecosystem services (Steffen et al., 2015). Changes in human needs result in modifications of human demands. This reflects on the services provided by ecosystems, resulting in adverse consequences, as it is fundamental to ensure the provision of ecosystem services in quantity and quality and maintained at adequate levels. The challenge is to manage the trade-offs between immediate human needs and the maintenance of the capacity of the ecosystem to provide goods and services.

The basis definition of CICES (Common International Classification of Ecosystem Services) is that ecosystem services are the contributions of the ecosystems (natural or modified) that directly or indirectly affect human well-being; the goods and benefits from ecosystems are what people create or what derives from ecosystem services and can be referred to as “products” (Haines-Young and Potschin, 2013). According to CICES, ecosystem services are “final” because they are the results from ecosystems that most directly affect the well-being of people, giving the idea that services lead to changes in human well-being because of the benefit they generate. In the context of CICES, the classification is according to services, not benefits (Haines-Young and Potschin, 2013).

We depend on the provisioning of ecosystem services. However, continuous interference in the dynamics of ecosystems is altering all of these services. The use of indicators can provide information that help in the understanding and managing activities that potentially interfere in the ecosystems, such as the residues produced by confined animals. Thus, ecosystem services provide groups of indicators that include descriptive aspects and evaluation items (Reyers et al., 2010). The indicators also help in understanding more complex realities and, for this reason, are instruments of communication that assist in reducing the complexity of human-environmental systems (Kandziora et al. 2013).

2. MATERIALS AND METHODS

This article used CICES as a basis to classify the ecosystem services of biogas originated from residual biomass from the waste of confined animals. According to Haines-Young and Potschin (2013), CICES are organized within three main groups of services (regulating, provisioning and cultural services), including more detailed definitions and suggestions of potential indicators. The indicators may refer to actions that cause environmental changes, to the exposure of an environmental component to stress, to environmental conditions, to effects caused by certain impacts, or to social responses to environmental changes (Braband et al., 2003). The CICES classification was adopted because it provides a method to classify ecosystem services in a hierarchical structure, with each level providing a more detailed description of the ecosystem service being considered.

Provisioning services are related to the nutrition, materials and energy of living systems, including tangible products from the ecosystems that human beings use, which can be

commercialized and consumed or used directly (Haines-Young and Potschin, 2013). Regulating services are the ways in which living organisms can mediate or moderate the environment that affects human performance (Haines-Young and Potschin, 2013). These are services with less tangible benefits, resulting from ecosystems when abiotic and biotic factors are controlled and/or modified (Haines-Young and Potschin, 2010).

Cultural services are related to non-material and normally non-consumable aspects of the ecosystems that affect the physical and mental states of people (Haines-Young and Potschin, 2013), referring to intangible benefits that people receive from ecosystems in the form of non-material, spiritual, religious, inspiring and educational experiences (Kandziora et al., 2013).

There was also a proposal of potential indicators for the ecosystem services of biogas. That is, indicators were used to show the quantity and types of services specific to biogas, considering primarily a local scale in a rural property. An indicator for an ecosystem service is information that communicates the characteristics and tendencies of the ecosystem services, making it possible, for example, for those who propose policies to understand the conditions, tendencies and the rate of change in the ecosystem services (Layke et al., 2012).

The hierarchical structure of CICES also allows evaluations to be adapted to specific needs, at the same time allowing the possibility of comparisons, referring specifically to final results or products of the ecosystems. CICES uses the triple division consisting of provisioning services, regulating services and cultural services. To sum it up, provisioning services are related to materials, while regulating services relate to the intervention of aspects of the environment that affect the well-being of people, while cultural services include material and intellectual benefits.

3. RESULTS AND DISCUSSION

In order to mitigate climate change and increase energy safety, the search for renewable energy has been growing in the past years (McBride et al., 2011). However, the expansion of renewable energy can be considered controversial in terms of competition for land use and implies in trade-offs (Jackson, 2011), like intensification of use of land and competition with food production caused by the production of biofuels, leading to the need to systematically analyze advantages and disadvantages of renewable energy to find a better solution (Silveira et al., 2017).

Sustainability is of great importance to the production of energy and, for it to be considered sustainable, it must not compete with other chains of production, distribution or use of food. Land dedicated to the production of food should also not compete with the land used to produce energy (Arodudu et al., 2013). For this reason, in order not to represent a risk for food and environmental safety, the increase of production of renewable energy must involve a selection of feedstock like residual biomass, because biomass must not consume more carbon (C) from fossil fuels than it can remove (Whalen et al., 2017). In this sense, it is important to use biomass that does not compete with food production, but complements it in terms of ecosystem services and its contribution to human well-being (Bühring and Silveira, 2016).

As put by Hastik et al. (2015), the concept of ecosystem service seems to represent an appropriate approach to evaluate environmental matters associated with the expansion of the exploration of renewable energies like biogas. Most of the impacts on ecosystem services are determined by rising demand resulting in the intensified use of land, which does not happen with biogas originated from residual biomass, such as animal waste.

The energy of the biogas produced from residual biomass, which used to be considered worthless and having a pollutant organic load, does not raise the pressure on the usage of land and water. These systems of biogas production can make animal production more sustainable and avoid dilemmas between food and fuels, which occur with other biofuels, turning biogas

into a differentiated energy source. As it gives energy, biogas can be classified as a provisioning ecosystem service, according to Table 1; it can generate compensations by providing ecosystem services (energy) and its adoption can benefit the whole society, because it depends on the ecosystem services provided. When the feedstock is made of residues, one can understand that the production of biogas acts as a regulating service, according to Table 1, because it uses residual biomass that reduces the organic load of waste and the emission of greenhouse effect gases in the environment. This way, the impacts caused by residues of animal production can, according to Müller and Burkhard (2012), be understood as changes in the provisioning of goods and ecosystem services and in the socioeconomic system. Therefore, the use of these residues in the production of energy can elevate the status of biogas to ecosystem service.

Agricultural production systems can satisfy the growing demand for renewable energy providing adequate biomass for production of energy, in which high volumes of waste need to be managed in a sustainable way, optimizing the use of nutrients and energy potential, while at the same time minimizing negative impacts in the environment. The interest in energy derived from biomass is based on the premise that it can reduce external dependence on energy supply, develop a renewable base and also reduce greenhouse gas emissions, which contribute to climate change. Due to their growing importance, energy sources based in biomass have been included in CICES as provisioning ecosystem services.

The classification of biogas originated from residual biomass according to CICES and a proposal of potential indicators for biogas are shown in Tables 1 and 2.

Table 1. Classification of the ecosystem services of biogas originated from residual biomass presented in the section, division, group and class levels according to CICES.

Ecosystem service	Section	Division	Group	Class
Biogas	Provisioning	Energy	Source of energy from biomass	Resources based in animals
	Regulation and maintenance	Mediation by residues	Mediation by ecosystems	Filtration, capture, storage, accumulation by ecosystem Mediation of odors
		Maintenance of physical, chemical and biological conditions	Atmospheric Composition and climate regulation	Global climate regulation through reduction of concentration of greenhouse effect gases

The ecosystem services may be set as indicators if the goal is a relevant management communication about the recent, past or future conditions of human-environment systems (Müller and Burkhard, 2012). It is important to emphasize that the definitions and classifications of indicators, as well as ecosystem services, deeply depend on the characteristics of the investigated ecosystems and on the decision context in which they are applied (Fisher et al., 2009; Reyers et al., 2010). The classification of biogas originated from residual biomass in ecosystem services allows a general view of the potential services of the ecosystem that might be relevant in this context, especially those related to the production unit. It is important to note that it is a starting point to reflect upon functions, processes and subjacent structures and on how to reach sustainable management of the process of production of confined animals and the environment, especially locally and regionally.

Table 2. Proposal of indicators to represent biogas in the regulatory and provisioning ecosystem services.

	Definition	Potential indicator
Provisioning service		
Energy Provisioning	Generation of energy through treatment of waste by anaerobic digestion.	Availability of waste (m^3 $year^{-1}$) Production of biogas (m^3 $year^{-1}$) Energy per m^3 of waste (Toe, kWh, kCal)[a]
Regulating service		
Regulation of air quality	Capture of odors from waste stored through the treatment by anaerobic digestion	Perception of odor
Regulation of nutrients in the soil and water	Reduction of organic load and nutrients of waste after treatment through anaerobic digestion	Concentration of nutritious elements (C, N, P, K) in digestate
Regulation of global climate	Reduction in the emission of greenhouse effect gases	Carbon capture from emissions of CH_4, CO_2, N_2O (t C $year^{-1}$)

[a]Toe: Tonne of oil equivalent; kWh: Kilowatt hour; kCal: Kilocalories.

3.1. Biogas contributions to the ecosystem and human well-being

Biogas as a provisioning ecosystem service is considered an energy product, originated from the treatment of animal waste through anaerobic digestion, which can be used to generate electricity and heat or purified and used in the transportation sector. To exemplify the energetic use of the biogas considering the herd of pigs that has the potential to produce biogas, some estimates that show the importance of biogas for general human well-being were calculated, as well as the environmental benefits for the ecosystems. The number of pigs in Brazil in 2016 was 39.95 million head and the Southern region held 49.9% of this total (IBGE, 2015). The estimated production of excrement, the potential of biogas production and the reduction in the emissions of methane (CH_4)[1] through the anaerobic digestion regarding pigs from the southern region are found in Table 3.

Table 3. Estimate of the production potential of excrement, biogas and reduction in emissions of methane by pigs from the Southern region.

	Production of excrement (m^3 $year^{-1}$)	Production of biogas (m^3 $year^{-1}$)	Reduction in emissions (tCO_2e $year^{-1}$)
Southern Region	46,076,114	979,707,211	7,443,619

[1] Calculations on the estimate of production of excrement based on the production of 0.007 m3/day (Oliveira, 1993); and for the calculation of the estimates of biogas production and emissions of methane, the methodology established by the Intergovernmental Panel On Climate Change (IPCC) contained in the guidelines of UNFCCC (United Nations Framework Convention on Climate Change), and the reference value of the Guidelines for National Greenhouse Gas Inventories (IPCC, 2006) was used.

From the data contained in Table 3 and considering the energy equity of the cubic meter of biogas described by Barreira (2011), the energy equity of pigs from the Southern region was estimated. The biogas estimated in equity with gasoline (0.613 L of gasoline) would generate about 1,645,371 L per day, which would permit, for example, traveling about 23,035,194 km per day, considering a popular car (14 km L^{-1} of gasoline). It would be possible to replace cooking gas (liquefied petroleum gas) with biogas (0.454 L of cooking gas) which would generate 1,218 m^3 of gas per day. Comparing with electric energy (1.43 kWh) the biogas could meet the energy demand of 659,223 homes in the Southern region, considering the average consumption of 177.1 kWh of electric energy per month, according to the Empresa de Pesquisa Energética in 2016 (EPE, 2017).

As a regulating service, biogas is especially related to the reduction of the emission of greenhouse gases like CH_4, CO_2 (carbon dioxide) and N_2O (nitrous oxide), reduction of odors and organic load and of some nutrients present in the waste. The odors are an important loss to the environment for people who live near pig production units, affecting public health due to the diffusion of diseases and odors to the nearby population (Orzi et al., 2015). However, anaerobic digestion reduces the atmospheric emissions of methane and odorous compounds (Van Horn et al., 1994; Orzi et al., 2010).

The digestate, is usually a low dry matter product, rich in plant nutrients and can be recycled as a high quality organic soil fertiliser, if the content of heavy metals and organic pollutants makes it suitable for this. The use of digestate originated from the anaerobic digestion of animal waste, in relation to the use of waste in natura, reduces or eliminates completely the energy and economic costs of production of fertilizers. It makes exportation, redistribution and recycling of excess waste possible (Holm-Nielsen et al., 2009). The nutritional value of waste has been especially linked to the presence of N, P and K (potassium), but the need for nutrients depends on the soil and on the characteristics of the culture and the proportion of nutrients available in the waste or digestate may not be adequate, resulting in excess or lack of these nutrients (Aguirre-Villegas et al., 2014). The digestate presents high concentrations of N and P, as well as C and K (Appels et al., 2008; Schievano et al., 2009) and when applied to the soil improves fertility and increases the microbial community (Owamah et al., 2014).

In livestock production, N_2O, CH_4 and CO_2 are the most important contributors to global warming (Olesen et al.,2006), depending on how they are produced (solid, liquid) and managed (collection, storage, arrangement). Anaerobic digestion through biodigesters is a promising practice to mitigate the emission of greenhouse effect gases from the collected waste, with potential to decrease odor and loads of pathogenic bacteria of waste when compared to direct application in the soil without treatment (Montes et al., 2013) and, when used correctly, anaerobic digesters are a source of renewable energy in the form of biogas, which is from 60 to 80% CH_4, depending on the substrate and conditions of operation (Holm-Nielsen et al., 2009; Montes et al., 2013). Therefore, production of biogas is a mitigation strategy that has significant potential to capture and destroy most CH_4 from the waste and generate renewable energy, reducing emissions of greenhouse effect gases, NOx, hydrocarbons and particles (Montes et al., 2013).

Table 3 gives an example of the reduction of greenhouse gases emissions from the excrement. In this context, the reduction of the emission of greenhouse gases, such as methane, occurs by treating the excrement through anaerobic digestion in biodigesters and with biogas combustion, which is converted into CO_2, preventing, consequently, emissions of methane into the environment.

The generation of biogas from anaerobic digestion of biomass is a technology that can produce sustainable energy and also help in the management of waste. Thus, it has potential to assist in the transition of energy based in fossil fuels to renewable energy, especially because of the availability of residual biomass. It can also contribute to strategies of sustainable

development in rural areas. The capacity of biogas to decrease pollutant load through use of residues, regulate ecosystem service, and improve the efficiency of the energy supply infrastructure, like the provisioning ecosystem service, are arguments in favor of the development of biogas. For this reason, it is possible to say that the production of biogas has less trade-offs than other renewable sources, as trade-offs play a crucial role in the interpretation of sustainability of developments related to human well-being (Liu et al., 2015; Wu, 2013).

4. CONCLUSION

The environmental problems created by intensive systems of livestock production derive mainly from their local concentration, but also from the technology and the management system adopted. The high density of animals is always followed by the production of surplus excrement, which leads to pressures on the ecosystem and generates impacts on the environment, mainly through the volume and composition of the excrement when improperly discarded. In view of the lack of economic and environmental incentives to treat the excrement efficiently and to internalize the environmental costs, more excrement is produced than can be assimilated, which increases the risks associated with water-, soil- and air pollution. However, this waste constitutes a residual biomass available to generate energy, exported or used by the very own system of production or another system of the property, also using the digestate as a fertilizer. The use of residual biomass to produce biogas can be considered sustainable because it does not use direct resources from ecosystem services, and supplies regulating and provisioning services.

Besides the relevance for the understanding of the impacts of the decisions and actions about the environment, the understanding of biogas in the ecosystem services is interesting in order to understand how the environment is affected. In addition, the framework of the biogas in the ecosystem services systematically shows the contributions to the ecosystem and to the human well-being. These facts can help raise awareness of the political decision-makers and farmers regarding the importance of excrement treatment and the generation of renewable energy through biogas.

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Use of zeolite synthesized from coal ashl from Santa Catarina for removal of iron, manganese and methylene blue dye in water

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ABSTRACT

The fly ash of coal, generated in a thermoelectric plant, was used to synthesize zeolite by hydrothermal treatment with a sodium hydroxide solution. The zeolite synthesized was used as an adsorbent of metals (Fe and Mn) and of the methylene blue dye in water. The characterization of the zeolite showed that silicon oxide is the main compound in its composition, followed by aluminum, iron, sodium and calcium, which together correspond to more than 86% of its composition. These were used to investigate the kinetic parameters of adsorption and the isotherm of the metals and the methylene blue dye in aqueous solutions. Three kinetic models, pseudo-first order, pseudo-second order and intraparticle diffusion were used to predict adsorption rate constants. The adsorption kinetics of the dye and metals followed the pseudo-second order kinetics and reached equilibrium in 15 minutes with a 99% removal rate for metals, independently of the pH. The values of the diffusion constants (K_2) for iron in pH 5, 7 and 8 were 1.3158; 1.3881 e 0.6053 $mg.g^{-1}.min^{-1}$ and for manganese 1.2511; 1.5239 and 1.4336 $mg.g^{-1}.min^{-1}$, respectively. For methylene blue, the removal rate was 90% and the constant (K_2) value was 0.5437 $mg.g^{-1}.min^{-1}$. The studies showed the existence of different stages in the adsorption of the metals and the methylene blue dye in zeolite.

Keywords: coal ashes, water purification, zeolite.

Uso de zeólita sintetizada a partir de cinzas de carvão de Santa Catarina para remoção de ferro, manganês e o corante azul de metileno em água

RESUMO

As cinzas volantes de carvão, geradas em uma usina termelétrica, foram utilizadas para sintetizar zeólita por tratamento hidrotérmico com solução de hidróxido de sódio. A zeólita sintetizada foi utilizada como adsorvente de metais (Fe e Mn) e do corante azul de metileno em água. A caracterização da zeólita, mostrou que o óxido de silício é o principal composto na sua composição, seguido pelo alumínio, ferro, sódio e cálcio, que juntos correspondem a mais de 86% da sua composição. Estas foram utilizadas para investigar os parâmetros cinéticos de

adsorção e a isoterma dos metais e do corante azul de metileno em soluções aquosas. Três modelos cinéticos, pseudo-primeira ordem, pseudo-segunda ordem e difusão intrapartícula foram utilizados para prever as constantes da taxa de adsorção. A cinética de adsorção do corante e dos metais seguiram a cinética de pseudo-segundo ordem e, atingiram o equilíbrio em 15 minutos com uma taxa de remoção 99% para os metais, independentemente do pH. Os valores das constantes de difusão (K2) para o ferro em pH 5, 7 e 8 foram 1,3158; 1,3881 e 0,6053 $mg.g^{-1}.min^{-1}$ e para o manganês 1,2511; 1,5239 e 1,4336 $mg.g^{-1}.min^{-1}$, respectivamente. Para o azul de metileno a taxa de remoção foi de 90% e o valor da constante (K2) foi de 0,5437 $mg.g^{-1}.min^{-1}$. Os estudos também mostraram a existência de diferentes estágios na adsorção dos metais e do corante azul de metileno em zeólita.

Palavras-chave: cinzas de carvão, purificação de água, zeólita.

1. INTRODUCTION

Mineral coal is one of the more abundant and widely distributed fossil fuels in the world, with proven global reserves of almost 1000 billion tons. It is found in subsoil deposits and extracted by mining. Coal feeds most electricity production in several countries, like South Africa (93%), Poland (92%), China (79%), India (69%) and the United States (49%) (Bukhari et al., 2014).

In Brazil, the energy matrix results from several sources, and one of them is from mineral coal burning, which generates about 1.3 to 1.5% of the electric energy used in the country. This electricity generation through thermal electrical plants produces about 3 million tons of ashes yearly, which were composed of 65 to 85% fly ash and 15 to 35% heavy ash (Cardoso et al., 2015a). Around the world, about 500 million tons of fly ash and 100 million of heavy ash are generated by year (Cunico et al., 2009).

Ash disposal directly on the environment maximizes negative environmental impact (Yao et al., 2015). The main effort to minimize the impacts of the disposal of these residues in the environment must be a search for enlarging potentialities for their use (Itskos et al., 2015).

Only 30 to 35% of fly ash are used to produce pozzolanic cement, fertilizers and in paving (Hemalatha and Ramaswamy, 2017), while the heavy ash still does not have much commercial application. There are several studies to use ashes in other fields, like metal removal of industrial interest (Tang and Steenari, 2015), ceramic application (Luoa et al., 2017; Zhu et al., 2016), geopolymer production (Mehta and Siddique, 2017; Dassekpo et al., 2017) and in the synthesis of several zeolites (Ojumu et al., 2016; Cardoso et al., 2015b).

Mineral coal fly ashes are constituted basically of silica and alumina, and it is possible to change them into zeolite material after hydrothermal treatment in an alkaline medium (Lee et al., 2017; Fukasawa et al., 2017).

According to Ayele et al. (2016), zeolites are crystalline microporous materials, and during the second half of the 20th century and the early decades of the 21st century, they have been consolidated as important catalysts in processes in the oil refining, chemical and petrochemical industries (Rehan et al., 2017), as well as in environmental control (Nekhunguni et al., 2017; Wan et al., 2017).

Fly ash is an ideal precursor to zeolite production due to its composite similarity with volcanic materials, SiO_2 and Al_2O_3. Zeolite material is still characterized by high capacity for cation exchange and good adsorption, which enables several industrial uses in water and liquid effluent treatment. Therefore, they are an alternative to reduce environmental impacts due to their disposition in the environment (Visa, 2016). This broad spectrum of applications is related to the physical and chemical properties of these materials, which can be controlled during their preparation for a specific application (Abdelrasoul et al., 2017).

Activated coal has been widely used to remove contaminants from residual water due to its large surface area and excellent capacity for adsorption of these composites; however, the high cost has limited its usage (Simate et al., 2016; Mor et al., 2017). This fact aroused interest to develop other low cost products using the residue generated in coal thermal electrical plants (ashes) as raw material for the production of adsorbent (Attari et al., 2017). It is important to mention that rapid industrialization and urbanization has led to the contamination of sediments and water with metals and organic contaminants that created a pervasive problem worldwide. Major sources of contamination include agricultural, human and industrial activities, spills, drainage of mines and accidents.

Water and sediments containing these contaminants act as secondary sources of contamination, posing significant direct and indirect environmental risks through bioaccumulation in aquatic organisms and incorporation into aquatic food webs that may lead to human exposure (Knox, 2016). In this way, the quality of water can easily degraded by contaminants from anthropogenic activities and natural phenomena such as erosion and volcanic activity. Among common contaminants, metals and metalloids may pose significant risks to human life, living organisms and natural ecosystems because of their toxicity, persistence, and accumulation potential (Calugaru et al., 2018).

It is important that wastewater that contains metals, especially iron (Fe) and manganese (Mn), be treated properly for reuse applications or disposed of at the appropriate levels so as not to have an impact on public health. Iron, although not a toxic element, presents several problems for the public water supply. Besides conferring color and flavor to the water, it also causes the development of deposits in pipes and iron-bacteria, causing the biological contamination of the water. Unlike iron, manganese when inhaled may cause irritation, respiratory tract infection, and pneumonitis. Therefore, developing simple and cheap new technologies that enable the reduction of the pollution charge from water and industrial effluents (residual water) are strategic studies to ensure the continuation of these activities in industrial regions. Further, throwing contaminated wastewater in water chains reduces the photosynthetic activity and affects the natural balance of biota (Nimick et al., 2011).

Within this context, the main objective of the present work was to synthesize zeolite from coal ash and use it as an adsorbent in residual water treatment to remove metals (Fe and Mn) and methylene blue dye.

2. MATERIALS AND METHODS

2.1. Materials and reagents

The methylene blue dye and the sodium hydroxide (NaOH) used in this study were purchased with Vetec, purity ≥ 99%. All other reagents (analytical-reagent grade) were purchased from Merck. The iron chloride tetrahydrate ($FeCl_2.4H_2O$) and manganese chloride tetrahydrate ($MnCl_2.4H_2O$) were quantitatively dissolved in deionized water (Millipore Milli-Q system) for preparing solutions containing ions Mn^{+2} and Fe^{+2}.

2.2. Synthesis of zeolite

Synthetic zeolite was prepared from fly ashes retained in the bag filter, collected in the *Usina Termelétrica Carbonífera Jorge Lacerda*, which belongs to *Tractebel Energia/ENGIE*, located in *Capivari de Baixo* town, *Santa Catarina* state, Brazil.

Zeolite synthesis was performed in two types of reactor, semi-open and closed. A closed system reactor produced zeolite with morphological characteristics and appropriate chemical purity, which agrees a description in the literature (Bruno, 2008).

To perform the reaction, 30 g of ash were placed inside the reactor, and the NaOH (3.5 $mol.L^{-1}$) at 100°C mass variates (60 to 300 g) for 24 hours. After finishing the reaction, the

suspension was filtered and the residue was washed repeatedly with deionized water until achieving pH ~ 10. The residue was washed in a stove at 50°C for 12 h. It is important highlight that zeolites were obtained in several proportions of ash and alkaline solution of NaOH; 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:10. However, the relation 1:10 (m/m) presented the best chemical and morphological characteristics.

2.3. Characterization of ash and synthesized zeolite

To perform the oxide analysis, 300 mg of sample (ashes or zeolites) were dissolved in 2 mL HF (hydrofluoric acid, Merck), 3 mL HNO_3 (nitric acid, Merck) and 2 mL HCl (hydrochloric acid, Merck) concentrated for digestion in microwave (Provecto Analytical; model: DGT L00 PLUS) oven for 26 minutes. The digestion programming occurs in 5 steps: Step 1 (5 min, 180 W); Step 2 (5 min, 0 W); Step 3 (5 min, 340 W); Step 4 (5 min, 0 W); and Step 5 (6 min, 250 W).

After digestion was performed chemical composition analysis of coal ashes and/or zeolites were carried out using the method AOAC (1977) using an Atomic Absorption Spectrophotometer with a Graffiti oven (ETAAS), Model ZEEMAN 220, VARIAN.

Sulfur analysis was performed according to method 4500 SO_3^{2-} B described in *Standard Methods for the Examination of Water and Wastewater* (APHA, 2012).

2.4. Melting temperature analysis

For each ash sample, the following parameters were determined in relation to the melting temperature (°C): deformation point (d.p.), ballpoint (b.p.), hemisphere point (h.p.) and pour point (p.p.). To perform these determinations, a heating microscope with figure analysis and optical dilatometer Model EM201 (Hesse Instruments) were used, using the standard DIN 51730.

2.5. Adsorption studies

2.5.1. Adsorption of methylene blue dye

To perform the determination of dye concentration during the kinetic experiments, a calibration curve for the methylene blue was constructed. Initially, using 10 $mg.L^{-1}$ solutions, a wavelength scan of 300 to 800 nm was made to determine the wavelength of higher absorbance for methylene blue. The observed wavelength of greatest absorption was 650 nm. To determine the concentration of the dye solutions throughout the experiments, a calibration curve was constructed. For this, solutions were prepared in various concentrations (1 to 10 $mg.L^{-1}$), whose absorbances were measured in triplicate, and plotted as absorbances versus concentration. The correlation coefficient was (R^2) 0.99871.

The kinetic adsorption of methylene blue dye in batching system was carried out in triplicate. Aqueous solutions were prepared in concentrations of 10 $mg.L^{-1}$, pH 5 and environmental temperature 25 ± 2ºC. The pH was adjusted with hydrochloric acid solution 1 $mol.L^{-1}$. An aliquot of 100 mL of solution was added to 0.5 g adsorbent and the suspension was agitated at 60 rpm (magnetic stirrer) by time intervals from 0 to 50 min. At the end of each desired time period, 5 mL were removed and the solution was separated from the adsorbent by gravitational filtration (filter paper). A supernatant portion was analyzed by spectrophotometry, Model CARY 1G, Varian, at 650 nm.

The adsorption efficiency was calculated using Equation 1:

$$R = \frac{100(C_0 - C_f)}{C_0} \quad (1)$$

Where R is the adsorption efficiency (%), $C_0$is the initial concentration of methylene blue dye (mg L^{-1}) and Cf is the final concentration of dye in time t (mg L^{-1}).

The amount of dye adsorbed in the adsorbing stage was quantified according to Equation 2:

$$q_{(t)} = \frac{V(C_0 - C_{(t)})}{M} \quad (2)$$

Where C_0 is the initial concentration of methylene blue dye (mg.L^{-1}), C(t) is dye concentration in time t (mg.L^{-1}), V is the volume of dye solution (L) and M is the adsorbent mass (g).

2.5.2. Heavy metal adsorption

Kinetic adsorption of metals in batching system was performed in triplicate. Aqueous solutions of iron chloride II (tetrahydrate) and manganese chloride II (tetra hydrate) were prepared in concentrations of 22 mg.L^{-1} in different pHs of 5, 7 and 8, and environmental temperature of 25 ± 2ºC. These pH values were chosen because at pH below 5 solubilization of the metals occurs and with pH above 8 precipitation of the metals under study may occur. The solutions were adjusted to the desired pH using hydrochloric acid (0,1 mol.L^{-1}, standard) and sodium hydroxide (0.1 mol.L^{-1}, standard). Afterward, an aliquot of 100 mL of each solution was added to 0.25 g of adsorbent (zeolite) and the suspension was stirred at 60 rpm (Magnetic stirrer) for time intervals between 0 and 60 min. At the end of each desired time period, 5 mL were removed and the solution was separated from the adsorbent by gravitational filtration (filter paper). A supernatant portion was analyzed by spectrophotometry, using Spectroquant, Model Nova 60, Merck. The Fe (II) and Mn (II) were quantified in solutions using standard Merck kits. A standard Merck kit was used to assess iron content, determination of iron II, number 14770. To assess manganese, a Merck kit was used, determination of manganese II, number 14896. Equations 1 and 2 were used to evaluate adsorption efficiency and the concentration of metal adsorbed.

3. RESULTS AND DISCUSSION

3.1. Characterization of coal ash samples

Foremost, the chemical composition of 10 coal ash samples from the *Usina Jorge Lacerda, Tractebel Energia, ENGIE,* located in the city of *Capivari de Baixo, Santa Catarina* state, Brazil, was analyzed.

Physical, chemical and mineralogical characteristics of coal fly ash depends on several factors, such as composition of the coal they are made from (precursor), combustion conditions, type and efficiency of the emission control system and disposition methods used. Therefore, generalizing on the chemical composition of ashes or on their behavior in the environment is difficult. However, some characteristics are uniform for most ashes. Fly ashes are considered a ferrous aluminosilicate mineral, with Al, Si, Fe, Ca, K and Na as predominant elements.

Results obtained by chemical composition analysis of ash are shown on Table 1. According to the results presented, silicon oxide is a major composite of the analyzed samples, followed by aluminum, iron and potassium, which together correspond to 76% of the mass composition of ash samples.

Table 1. Results of the analysis of chemical composition of ashes in terms of oxides, determined by Atomic Absorption Spectrophotometry with Graffiti oven.

Values	SiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	K_2O (%)	CaO (%)	TiO_2 (%)	Na_2O (%)	MgO (%)	SO_3 (%)
Average	63.46	6.07	4.72	1.82	0.39	1.41	0.75	0.79	0.58
Maximum	66.98	11.32	5.10	2.65	0.87	1.76	0.84	0.29	0.82
Minimum	61.88	3.59	4.34	1.12	0.19	1.12	0.31	0.01	0.25
Standard deviation	3.28	2.30	0.28	0.24	0.25	0.26	0.18	0.07	0.18

Similar values were also observed in other works, like the one carried out by Fallavena et al. (2013), who analyzed coal from the south of Santa Catarina; Van Dyk et al. (2009), who analyzed the coal from South Africa; and Unuma et al. (1986), analyzing coal from the United States of America and in Canada. On the other hand, Song et al. (2009), working with Chinese coal, observed 28% calcium oxide in ash composition; Ozbayoğlu and Özbayoğlu (2006), studying the coal from Turkey, obtained ashes containing 49.62% iron oxide, 36.85% calcium oxide and 32.95% sulfur oxide, as the maximum values after analyzing several samples. From these results, it is possible to observe that the mining local of coal is fundamental for the chemical composition of ash, which will influence its melting temperature (fusibility).

Results obtained for the melting point analysis are presented in Table 2. The coal physical composition starts, on average, at 1285°C, when the deformation point is observed, and it extends until 1456°C, which is its melting point. There is one variable among the values of the melting point of ash that can be observed and, consequently, influences the physical behavior of different samples of the analyzed ash (melting temperature).

Table 2. Results obtained for analysis of melting point of ash.

Values	d.p. (°C)	b.p. (°C)	h.p. (°C)	p.p. (°C)
Average	1285	1376	1412	1456
Maximum	1292	1383	1432	1594
Minimum	1275	1363	1394	1433
Standard deviation	30	7.2	12.5	7.5

3.2. Synthesized zeolite characterization

Hydrothermal synthesis was carried out using two models of reactors, the semi-open system and the closed system. According to the data obtained, the semi-open system became unfeasible for the zeolite synthesis, because it presented low performance (50%), low purity content and a long time period, about 96 hours for the reaction to occur.

On the other hand, the closed reaction system showed more efficiency when compared with the semi-open system, with a performance over 90%, good purity degree and a reaction time of 24 hours.

In order to characterize the zeolite synthesized by the closed system, analysis of chemical compositions (oxides) were performed. Results showed that silicon oxide is the major composite in the analyzed samples, followed by aluminum, iron, sodium and calcium, that together correspond to over 86% of mass composition of zeolite samples. In lower concentrations, there are potassium, titanium sulfur and magnesium oxides and other composites in amounts lower than 4%.

In Table 3, the results obtained from the analysis of chemical composition of zeolites synthesized in a closed reactor are shown.

Table 3. Results of chemical composites of zeolites.

Oxides	SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	K_2O	TiO_2	SO_3	MgO
% in mass	59.91	7.96	8.72	5.03	5.01	3.31	1.60	1.26	1.07

Formation of zeolite can be observed during the synthesis process by means of the increase of concentration of some oxides from the ash, mainly by the increase of concentration of aluminum oxide.

According to the results obtained, there was an increase of aluminum and sodium oxides, when compared to the content of these oxides in fly ash. In fly ash, the average content of aluminum oxide was 6.07%, while sodium oxides attained 0.75%. In the synthesized zeolite, the aluminum concentration obtained was 7.96% and the sodium concentration was 5.01%. The melting point of synthesized zeolite was 1365^{o}C.

It is important to highlight that the composites responsible for the formation of zeolite before the hydrometric treatment are mainly amorphous SiO_2 and Al_2O_3. While all the analyzed coal ash samples presented similar percentages of mass for SiO_2 and Al_2O_3, the amount of these composites is probably different for each coal sample used for the formation of zeolites.

3.3. Kinetics of adsorption of metals

According to the data obtained, removal of iron and manganese by adsorbent was fast initially, but decreased gradually with time until 15 minutes (balance time). In order to evaluate the adsorption capacity in the balance time, studies were carried out for adsorption of Fe and Mn, with time from 0 to 15 minutes, pH 5, 7 and 8.

Figure 1 shows the influence of contact time for ion adsorption of Fe(II) and Mn(II) in zeolites, in solutions with pH 5, 7 and 8, with initial concentration of Fe(II) and Mn(II) equal to 22 mg.L^{-1}. It was possible to verify that the removal increases promptly during the initial stages and the adsorption rate decreases progressively until achieving the start of balance, around 5 minutes. In the first 3 minutes, Fe(II) removal achieved 77.9, 96.3 and 96.8% with pHs of 5, 7 and 8, respectively. After 10 minutes, removal reached 96, 99 and 99.34% with pHs of 5, 6 and 7, respectively, corresponding to an average increase of about 19% (pH 5); 3% (pH 7) and 2.6% (pH 8) regarding the first 3 minutes. Kinetics reaches balance in 15 minutes with average removal of 99%, regardless of pH. Similar results were observed for Mn (II), and, after 15 minutes, a removal of 88.9, 99.4 and 99.77% with pHs of 5, 7 and 8, respectively, was observed.

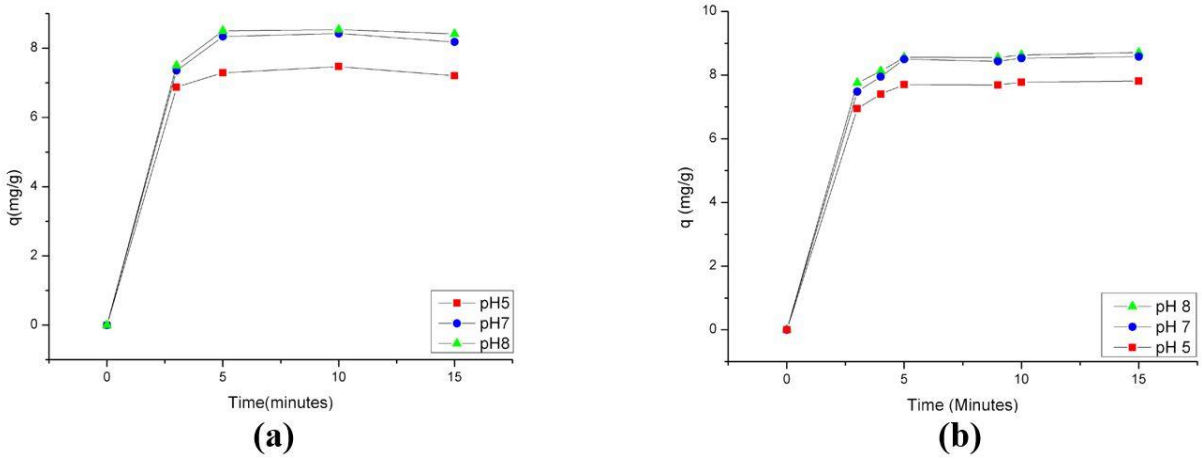

Figure 1. Results of adsorption of iron (**a**) and manganese (**b**) in zeolite in relation to time in different pH values.

This velocity of major removal at the start is due to the larger available surface of adsorbent. It is important to highlight that the contact time between adsorbate (Fe and Mn) and the adsorbent (zeolite) is very significant for the treatment of water and/or wastewater by adsorption. Fast removal of adsorbate and reaching the balance in a short time period indicates that the adsorbent is very efficient under the evaluated conditions.

Another significant datum is the occurrence of a simple and continuous shape of the curve until the saturation, what suggests a metal monolayer cover on the zeolite surface.

Comparing the results obtained for adsorption of iron and manganese ions in different pHs, we observed that the best results were obtained at basic pH (pH 8), regardless of the metal analyzed. Chemically, the basic pH provides metal adsorption, because in a basic medium metal can become rusty, and this facilitates interactions between the adsorbate (metal) and the adsorbent. At pH below 5, the solubilization of metals occurs, and at pH above 8 occurs the precipitation of the metals which hinders adsorption.

These results prove that under the conditions studied the use of active zeolite is a good adsorbent of water contaminants such as iron and manganese, since it is a strong cationic changer and promotes a good chemical interaction with the molecules of the adsorbate

Data still showed that kinetic studies are important to determine the balance time. The time is balanced when the amount of adsorbate that is being adsorbed by the adsorbent is in dynamic balance with the amount of adsorbate that is being desorbed. The time required to achieve the balance state reflects the maximum capacity of adsorbate by adsorbent under determined operational conditions.

Kinetic parameters are also important to evaluate the velocity of adsorption and are used to develop the kinetic models, and then understand what parameters influence the adsorption process. Several mathematical models in the literature describe the kinetics of adsorption. Among them, we can highlight the kinetics described by the models of pseudo-first-order, pseudo-second-order and intraparticle diffusion. The application of these models depends on the experimental data obtained.

Kinetic equation of pseudo-first-order is widely used to forecast the kinetics of adsorption of some elements/composites. In this model, velocity of adsorption can be determined by a velocity expression of pseudo-first-order by Lagergren (1898), for adsorption in a liquid-solid system based on the solid adsorption capacity. Lagergren presumed that the adsorbate velocity of removal, with time, is directly proportional to the difference in the concentration of saturation and the number of solid active sites. The Lagergren kinetic equation is the most used one for adsorption of an adsorbate of aqueous solution. Equation 3 gives the linear form of the pseudo-first-order:

$$\log_{10}(qe - q) = \log_{10} qe - \frac{k_1}{2{,}303} t \quad (3)$$

Where *qe* and *q* are amounts of metals adsorbed ($mg.g^{-1}$) in balance and in time t(min), respectively; k_1 is the constant of velocity of adsorption (min^{-1}). The constant k_1 can be calculated from the inclination of the straight of the graph log (*qe -q*) *vs* t.

The results obtained were also analyzed using the model of pseudo-second-order developed by Ho and colleagues (1996), in which the velocity of reaction depends on the solute adsorbed amount on the adsorbent surface and the amount adsorbed in balance. The linear model of pseudo-second-order is represented by the Equation 4:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{1}{qe} t \quad (4)$$

Where *qe* and *qt* are the amount metals (Fe and Mn) adsorbed (mg.g^{-1}) in balance and time t (min); k_2 is the constant of velocity of pseudo-second-order (mg.g^{-1}.min^{-1}). According to the data of the straight of the graph t/q versus t, the values of k_2 (g.mg^{-1}.min^{-1}) and *qe* (mg.g^{-1}) can be calculated. In contrast with the kinetic model of pseudo-first order, there is no need to know some previous parameters, because this model already forecasts the behavior on the complete adsorption period and it occurs according to an adsorption mechanism responsible by the velocity control stage.

Kinetic models previously described usually cannot describe the kinetic adsorption. Then, the intraparticle diffusion model can be used. According to Weber and Morris (1963), if the intraparticle diffusion is a determinant factor for velocity, the adsorbate removal varies according to the square root of time. Therefore, the intraparticle diffusion coefficient (k_{di}) is determined by Equation 5:

$$q_t = k_{di} t^{1/2} + C \quad (5)$$

Where *qt* is the adsorbed metal amount (mg.g^{-1}), t (min) is the stirring time and C (mg.g^{-1}) is a constant related to the diffusion strengthening.

According to Equation 5, values of k_{di} (mg.g^{-1}.min$^{-1/2}$) and C can be obtained by inclination and intersection of the graph curve q_t *vs* $t^{½}$, respectively. C values provide an idea about the thickness of the limit layer; in other words, the higher the C value, the higher the effect from the boundary (Dizge et al., 2008). There are studies showing that the graph can present multilinearity, which characterizes different adsorption stages: external mass transference followed by diffusion macro, meso and micro pore.

Tables 4 and 5 show the kinetic parameters of iron and manganese adsorption by synthesized zeolite, which were obtained by linear regression of curves for each model (Figures 2 and 3).

Table 4. Kinetic parameters for iron removal by zeolite.

Pseudo-first-order						
	pH	**Metal** (mg.L^{-1})	**K_1** (min^{-1})	**qe_{calc}** (mg.g^{-1})	**$qe_{exp.}$** (mg.g^{-1})	**R^2**
	5	22	1.2802	4.9946	7.0733	0.9522
	7	22	0.7738	6.3067	7.9253	0.9751
	8	22	0.7028	6.5690	8.2467	0.9753
Pseudo-second-order						
	pH	**Metal** (mg.L^{-1})	**K_2** (mg.g^{-1}.min^{-1})	**qe_{calc}** (mg.g^{-1})	**$qe_{exp.}$** (mg.g^{-1})	**R^2**
	5	22	1.3158	7.0621	7.0733	0.9999
	7	22	1.3881	7.9365	7.9253	0.9998
	8	22	0.6053	8.2508	8.2467	0.9999
Intraparticle diffusion							
pH	**Metal** (mg.L^{-1})	**K_{di1}** (mg.g^{-1}.t $^{-1//2}$)	**R_1^2**	**C_1**	**K_{di2}** (mg.g^{-1}.t $^{-1//2}$)	**R_2^2**	**C_2**
5	22	0.05514	0.92327	7.353508	0.05514	0.92327	8.81856
7	22	0.31535	0.61319	7.20586	0.0049	0.09338	7.9245
8	22	0.3428	0.6603	7.296	-0.0002	-0.0127	8.26204

Table 5. Kinetic parameters for manganese removal by zeolite.

Pseudo-first-order					
pH	**Metal** ($mg.L^{-1}$)	**K_1** (min^{-1})	**qe_{calc}** ($mg.g^{-1}$)	**$qe_{exp.}$** ($mg.g^{-1}$)	**R^2**
5	22	0.5327	4.5123	7.8120	0.9021
7	22	0.5161	4.6409	8.5800	0.8364
8	22	0.4645	4.5426	8.7093	0.8551
Pseudo-second-order					
pH	**Metal** ($mg.L^{-1}$)	**K_2** ($mg.g^{-1}.min^{-1}$)	**qe_{calc}** ($mg.g^{-1}$)	**$qe_{exp.}$** ($mg.g^{-1}$)	**R^2**
5	22	1.2511	7.8864	7.8120	0.9994
7	22	1.5239	8.6730	8.5800	0.9991
8	22	1.4336	8.7796	8.7093	0.9994
Intraparticle diffusion							
pH	**Metal** ($mg.L^{-1}$)	**K_{di1}** ($mg.g^{-1}.t^{-1/2}$)	**R_1^2**	**C_1**	**$K_{di\ 2}$** ($mg.g^{-1}.t^{-1/2}$)	**R_2^2**	**C_2**
5	22	1.49044	0.99701	4.34807	0.11601	0.83819	7.36975
7	22	2.01485	0.99642	3.9682	0.13678	0.85057	8.05818
8	22	1.58791	0.99684	4.98573	0.15766	0.9426	8.10394

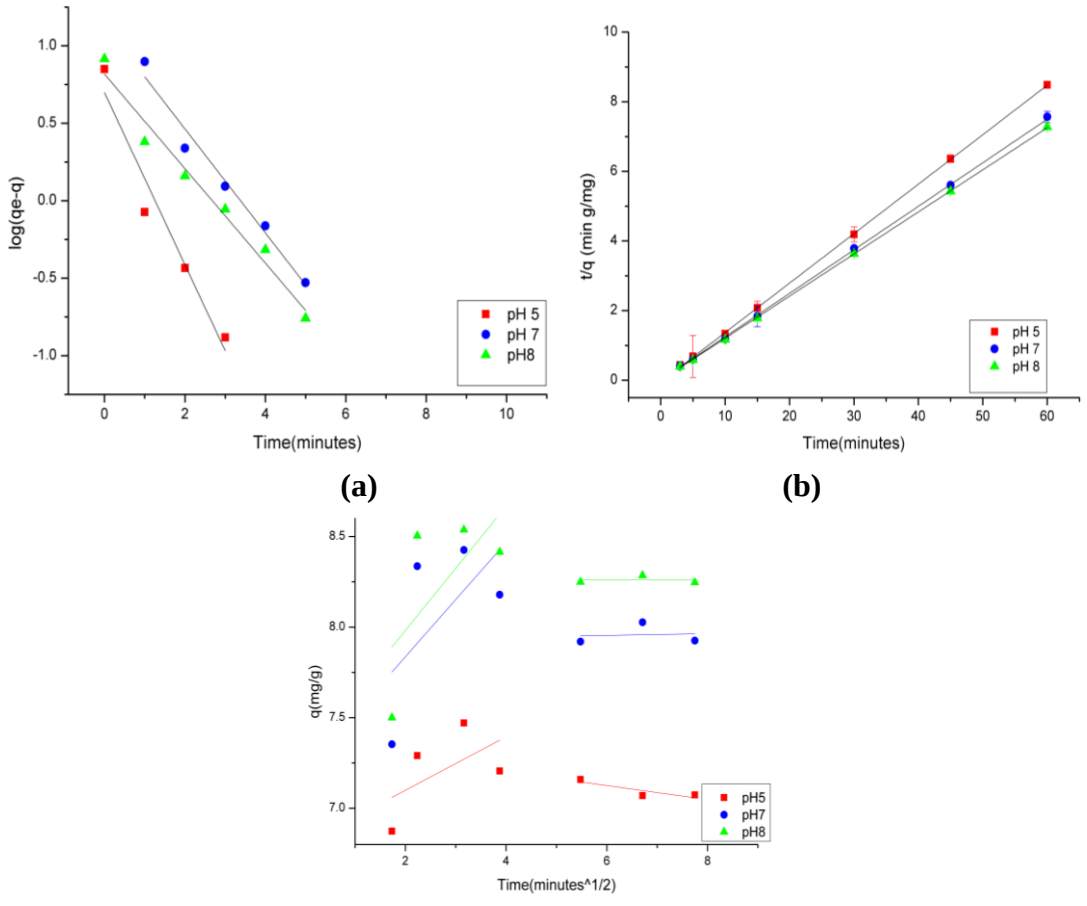

Figure 2. Kinetic models of ion adsorption of iron on zeolite: (a) pseudo-first-order; (b) pseudo-second-order; (c) Intraparticle diffusion.

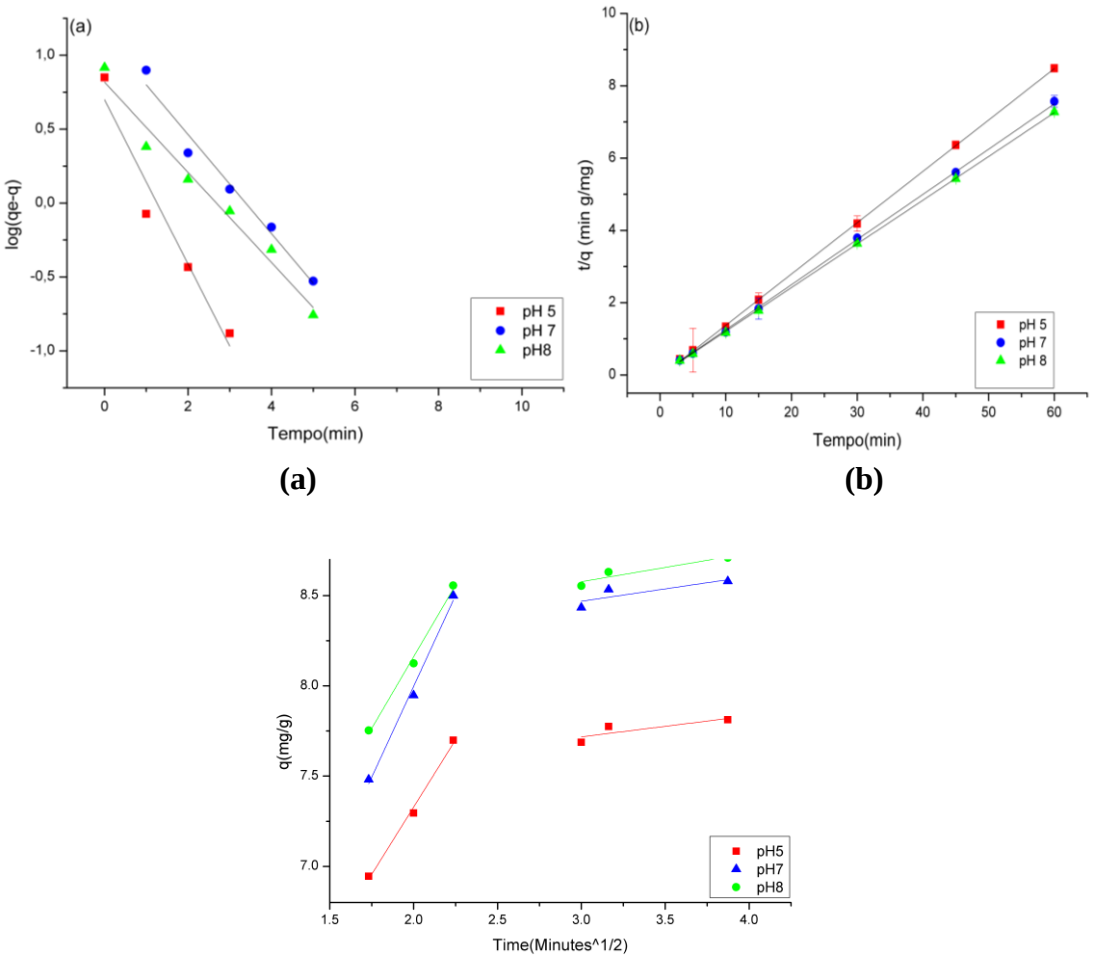

Figure 3. Kinetic models of ion adsorption of manganese on zeolite: (a) pseudo-first-order; (b) pseudo-second-order; (c) Intraparticle diffusion.

A quantitative evaluation of the models studied was performed by comparison of correlation coefficients (R2) and by calculated qe versus qe obtained experimentally.

When comparing data from Tables 4 and 5 with the correlation coefficient values calculated for Lagergren's pseudo-first-order and Ho's pseudo-second-order kinetic models, the values were higher than 0.9, which shows the applicability of both kinetic models. Tables 4 and 5 also show the kinetic parameters for each studied model.

Figures 2 and 3 show the experimental results obtained with Lagergren's and Ho's models and intraparticle diffusion. The results analyzed show that the pseudo-second-order model (by Ho) presented lower error when compared to Lagergren's (pseudo-first-order). Lagergren's model presented a theoretical value well below the experimental value, despite its good linear correlation (Tables 4 and 5). Further, when comparing the constant of velocity for both models, k2 (Ho's model) is about 2 times higher than k_1 (Lagergren's model), regardless of the pH and the metal (Fe and Mn) analyzed.

Still, the good concordance of theoretical results of Ho's model with experimental data is observed. It suggests the control of velocity must occur as an active or chemisorption mechanism.

In order to obtain information on the mechanisms that affect the kinetic adsorption, experimental results were applied to the intraparticle diffusion model proposed by Weber and Morris (1963).

Figures 2C and 3C show the diffusion model proposed by Weber and Morris (1963). According to this model, if intrapore diffusion is the stage that controls adsorption, then the graph *qt vs* $t^{1/2}$ will result in a straight line and its angular coefficient will correspond to the diffusion constant k_{di} ($mg.g^{-1}.min^{-1/2}$). In practice, the process is not simple, because it involves several straight segments in which each equation corresponds to an adsorption stage. The balance is reached when the adsorption capacity *q* ($mg.g^{-1}$) does not change over time and the line observed is horizontal. This model suggests that, if the first straight segment (adsorption initial stage) has a linear coefficient equal to zero (in other words, the straight segment cuts the origin), then intrapore diffusion controls the adsorption process. However, if the linear coefficient is different from zero, then the process that controls the adsorption might be an intrafilm diffusion, whose thickness is attributed to the linear coefficient in $mg.g^{-1}$.

Figure 2C shows the stages involved in Fe(II) adsorption on the zeolite adsorbent surface. For time interval 0-10 minutes, the linear coefficients were different from zero and the diffusion coefficients at pHs of 5, 6 and 7 were kdi = 0.055, 0.415 and 0.343 $mg.g^{-1}.t^{-1//2}$, respectively.

Similar results were obtained for Mn (II), as shown in Figure 3C. Diffusion coefficients at pHs of 5, 6 and 7 were kdif(I) = 1.490, 2.014 and 1.587 $mg.g^{-1}.t^{-1//2}$, respectively .

In stage II, both for Fe(II) and Mn(II), there is reduction of the diffusion constant until reaching balance. Tables 4 and 5 show the parameter values for the Stages I and II. Figures 2C and 3C show the time in which the change from one stage to another occurs along the adsorption process. According to the results, the Webber-Morris model does not allow easy knowledge what happens near t=0. It is therefore not possible to foresee whether intrapore diffusion predominates during the initial stages (previous to Stage I in the graph).

3.4. Adsorption kinetic of methylene blue dye

Data obtained from the calibration curve were used to evaluate the kinetics of dye removal. Removal was calculated through the difference between the initial and final methylene blue dye concentration in a determined time interval, using the zeolite as adsorbent. Data obtained are shown on Figure 4.

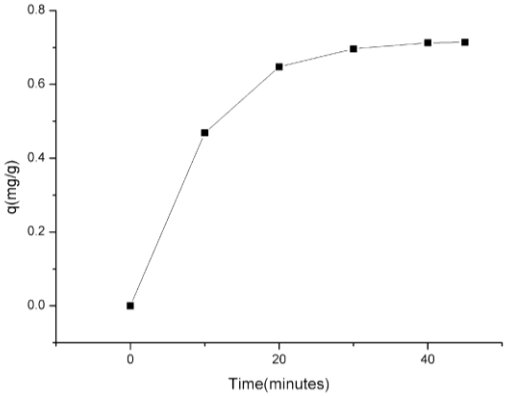

Figure 4. Results of kinetic adsorption of methylene blue in zeolite over time.

According to the results, it is possible to observe that the balance time was about 30 minutes and the adsorption efficiency average was above 90%. In addition, when the starting process occurred, the competition of methylene blue molecules by the active sites of adsorbent molecules was higher, and then, a higher concentration of dye was adsorbed in the first 10 minutes, near 50%. Data obtained from the adsorption process of methylene blue by zeolite were analyzed applying Lagergren's pseudo-first-order, Ho's pseudo-second-order kinetic models and the intraparticle diffusion model.

Figure 5 shows the results of the adsorption process of methylene blue in zeolites applying the kinetic models previously described. Kinetic parameters obtained by data treatment for the different models are shown on Table 6.

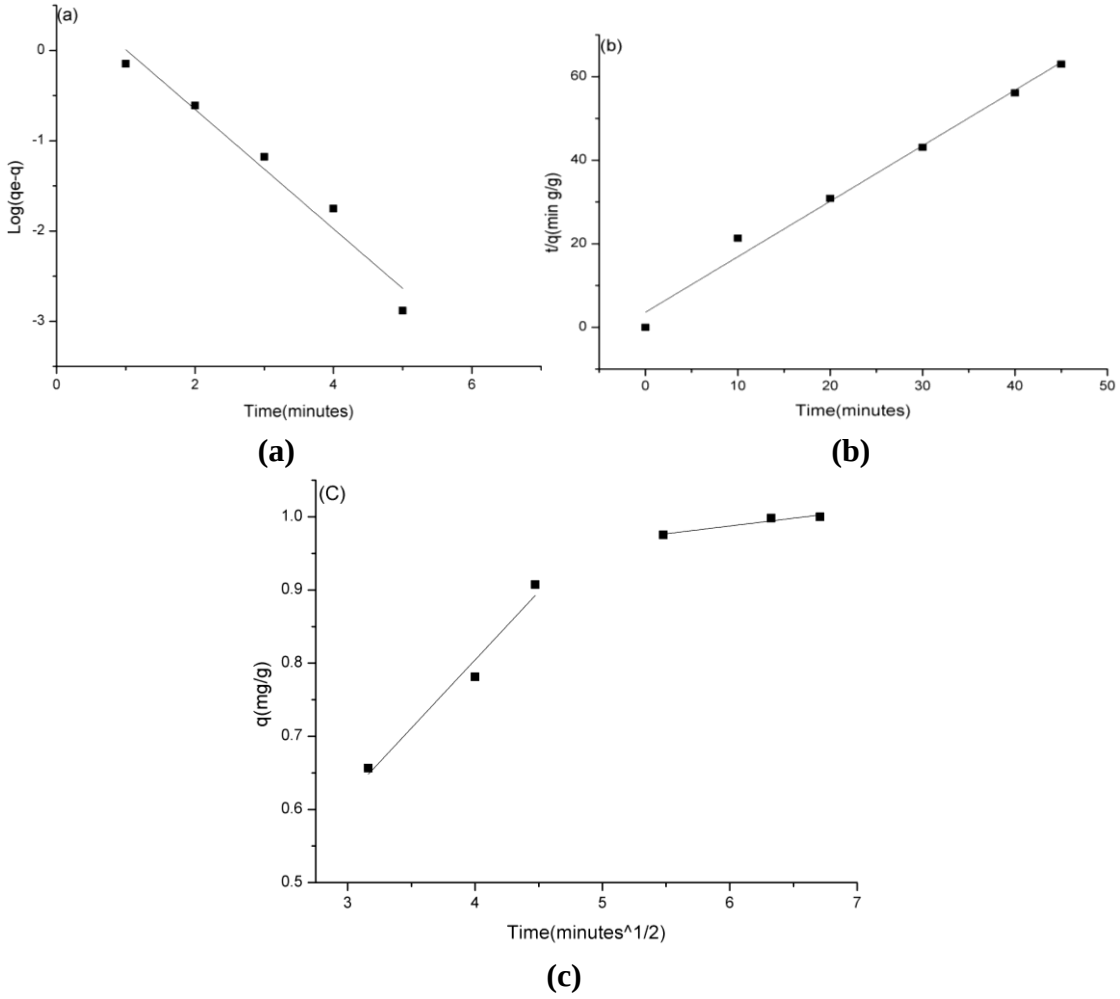

Figure 5. Kinetic models for adsorption of Methylene blue over zeolite: (a) pseudo-first-order; (b) pseudo-second-order; (c) intraparticle.

Table 6. Kinetic parameters for methylene blue removal by zeolite applying different kinetic models.

Pseudo-first-order						
	Dye ($mg.L^{-1}$)	**K_1** (min^{-1})	**qe_{calc}** ($mg.g^{-1}$)	**$qe_{exp.}$** ($mg.g^{-1}$)	**R^2**	
	22	0.15236	1.0205	0.7141	0.9659	
Pseudo-second-order						
	Dye ($mg.L^{-1}$)	**K_2** ($mg.g^{-1}.min^{-1}$)	**qe_{calc}** ($mg.g^{-1}$)	**$qe_{exp.}$** ($mg.g^{-1}$)	**R^2**	
	22	0.54370	0.7522	0.7141	0.9876	
Intraparticle diffusion						
Dye ($mg.L^{-1}$)	**$K_{di\ 1}$** ($mg.g^{-1}.t^{-1//2}$)	**R_1^2**	**C_1**	**K_{di2}** ($mg.g^{-1}.t^{-1//2}$)	**R_2^2**	**C_2**
22	0.1864	0.98681	0.0586	0.02129	0.97064	0.85977

By means of the analysis of the kinetic data, the application of kinetic models studied was observed, because the correlation coefficients (R^2) were higher than 0.9, regardless of the model studied. However, when comparing the constant velocity for the both models, k_2 (0.54370 $mg.g^{-1}.min^{-1}$) is about 4 times higher than k_1 (0.15236 min^{-1}). Besides, the pseudo-second-order model (by Ho) presented lower error when compared to the Lagergren one (pseudo-first-order). Lagergren's model presented a theoretical value (1.0205 $mg.g^{-1}$) above the experimental value (0.7141 $mg.g^{-1}$), despite the good linear correlation (Table 6). This indicates that the model which better adjusts to experimental data was Ho's model.

When analyzing data from the intraparticle diffusion graph, it is observed that the correlation coefficient was higher than 0.9 and the line did not pass by the origin, which indicates this stage is not decisive for adsorption velocity. Figure 5C shows the stages involved in the adsorption of methylene blue in zeolite. At a time interval of 0-20 minutes, the linear coefficient was different from zero, with a value equal to 0.0586. The diffusion coefficient for this stage was kdi = 0,1864 $mg.g^{-1}.t^{-1//2}$.

In Stage II, there was a constant reduction of diffusion from 0.1864 to 0.02129 $mg.g^{-1}.t^{-1//2}$ until balance was achieved.

Table 6 shows the values of parameters for Stages I and II. Figure 5C shows the time in which the change from one stage into another occurs along the adsorption process. The Webber-Morris model does not allow knowledge of what happens near t=0. It is therefore impossible to estimate whether intrapore diffusion predominates or not in initial stages (prior to the Stage I in the graph). Some kinetic studies on the adsorption of methylene blue in zeolite showed similar results. In other words, the process followed the velocity expression of pseudo-second-order. These studies used synthetic and natural zeolite clinoptilolite as adsorbent materials (Wang and Wu, 2006; Wang and Zhu, 2006; Wang et al. 2009).

4. CONCLUSIONS

Kinetic data showed that the adsorption of iron, manganese and dye increases faster during the initial stages and that the adsorption rate decreases progressively until achieving the beginning balance. Kinetic models reach equilibrium in 15 minutes, with a removal rate of 99% for iron and manganese and 90% of methylene blue dye.

Kinetic studies also showed that the model which better corroborates the experimental data is the pseudo-second-order model by Ho. Studies on intraparticle diffusion showed multilinearity, which characterizes the different stages of adsorption of metal and dye, like the external mass transference, followed by diffusion macro, meso and micropore.

Finally, the zeolite synthesized from mineral coal fly ash revealed potential to be used as an alternative material to remove metals such as Fe and Mn and dye from wastewater. Further, if the mineral coal fly ash is not appropriately discarded, as an adsorbent raw material they are a continuous source of pollution in the environment.

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The degradation of methylene blue dye by the strains of *Pleurotus* sp. with potential applications in bioremediation processes

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ABSTRACT

Fungi have a large capacity to produce enzymes that are capable of degrading compounds. In this regard, soluble dyes are often used as a means of evaluating and selecting strains with potential for biodegradation. This study verified the capacity of the strains of *Pleurotus* sp. in degrading methylene blue dye, in order to identify the strains with potential for the bioremediation. For this reason, a total of seven strains of *Pleurotus* sp. were grown in a potato liquid medium with the methylene blue dye at the concentrations of 0.02 g L^{-1} and 0.04 g L^{-1}. The results of the absorbances showed that all the isolates were visibly able to reduce the media staining following seven days of growth. However, a reduction of approximately 80% in the staining was observed for the strains named ERY, HI, and SB compared to the control. Thus, it was observed that these strains could be used in the color removal bioprocesses and in the biodegradation of pollutant compounds.

Keywords: absorbance, discoloration, fungi.

Degradação do corante azul de metileno por linhagens de *Pleurotus* sp. com potencial aplicação em processos de biorremediação

RESUMO

Os fungos têm uma grande capacidade para produzir enzimas que são capazes de degradar compostos. De acordo com esse fato, os corantes solúveis são frequentemente utilizados como maneira de avaliação e seleção de linhagens com potencial de biodegradação. O presente estudo verificou a capacidade de linhagens de *Pleurotus* sp. na degradação do corante azul de metileno, a fim de identificar linhagens com potencial para processos de biorremediação. Desse modo, um total de sete linhagens de *Pleurotus* sp. foram cultivadas em meio líquido de batata com o corante azul de metileno nas concentrações de 0,02 g L^{-1} e 0,04 g L^{-1}. Os resultados das absorvâncias mostraram que todos os isolados foram visivelmente capazes de reduzir a coloração do meio, após sete dias de crescimento fúngico. Observou-se ainda, uma redução de aproximadamente 80% na coloração para as linhagens denominadas ERY, HI e SB em comparação com o controle. Assim, foi possível constatar que essas linhagens podem ser

utilizadas em bioprocessos de remoção de cor e na biodegradação de compostos poluentes.

Palavras-chave: absorbância, descoloração, fungo.

1. INTRODUCTION

In the different cities of Brazil, environmental pollution is directly related to the disorderly growth of the urban population and the lack of basic sanitation. The improper dumping of toxic effluents into the rivers has left them with large deposits of toxic metals and other substances that are difficult to degrade. Due to this situation, there is a need to restore these ecosystems through planned interventions, rebuild their structures, and create conditions for restoring the natural ecological processes of each environment (Soares et al., 2011).

One of the alternatives to solving this problem is the use of bioremediation processes, which are treatments performed through the use of living organisms, efficient and adequate in the process of minimization or even in the complete elimination of pollutants in the impacted environment. Several organisms can be used as bioremediation agents in the environment, depending mainly on the presence of microorganisms capable of metabolizing the original molecules and the products of their degradation (Cajthaml, 2015).

The fungi are a group of promising microorganisms for studies and also for application as bioremediation agents since they present a series of economic, ecological, and potential characteristics to degrade recalcitrant compounds through their enzymatic systems (Atagana et al., 2006). Compared to other microorganisms, the use of the fungi in bioremediation processes is highly viable because they are able to rapidly adapt their metabolism to different sources of carbon to produce a large amount of intracellular and extracellular enzymes, responsible for the degradation, mineralization, and accumulation of the toxic materials (Kamida et al., 2005).

In addition to these factors, the fungi have a mode of growth that is chemostatically induced toward the source of organic carbon through the elongation and branching of hyphae, which allow the colonization of large areas. Thus, the superficial contacts with the contaminants are optimized, thereby increasing their bioavailability and consequently, their biodegradation (Przystaś et al., 2018).

Considering the characteristics presented by these organisms, studies in the area of biotechnology indicate that strains of *Pleurotus* sp. have a high potential as an agent in the recovery of environments contaminated by a variety of recalcitrant compounds (Zhuo et al., 2017). The fungi produce a high amount of mycelial mass and are considered good biosorbents due to the chemical composition of their cell walls and the mechanisms of their resistance to the conditions of environmental stress (Křesinová et al., 2018). The chemical composition of the cell walls of the fungi is responsible for attracting and retaining metals in the fungal biomass through the electrostatic interactions, a process known as biosorption (Gupta and Rastogi, 2009).

Due to the high degradative potential and the mechanisms of resistance under adverse environmental conditions, the use of the filamentous fungi and their metabolites has grown in recent years (Santana et al., 2016). In this regard, the use of the dyes, mainly methylene blue, as a selection method for identification of the lignolytic activity and the degradation capacity offers several benefits, including the development of simple, rapid, and quantitative spectrometric methods. Besides, dyes do not hinder the growth of organisms and their polymeric nature ensures that their degradation occurs extracellularly, at least in the initial stages (Pozdnyakova et al., 2018).

Therefore, this work verified the capacity of isolates of *Pleurotus* sp. in degrading methylene blue dye in order to identify some of the strains with potential for bioremediation processes.

2. MATERIALS AND METHODS

2.1. Isolation and maintenance of *Pleurotus* sp. strains

For the realization of the experiments, a total of seven strains of fungi belonging to the genus *Pleurotus* were analyzed. A total of four strains were obtained from the *in natura* species, commercialized in the supermarkets of Belo Horizonte-MG and were named P1, P2, P3, and P4. For the isolation of the fungal mycelia from these mushrooms, acquired in supermarkets, fragments were extracted from the inner parts of the fungi and were isolated in Petri dishes, containing the potato dextrose agar (PDA) medium, previously sterilized in an autoclave at 121°C for 20 min, followed by the addition of 50 μg mL^{-1} of ampicillin.

The other three strains, obtained from the Microorganisms Genetics Laboratory at the State University of Londrina, Londrina, PR, Brazil were identified as *Pleurotus eryngii* (ERY) and *Pleurotus ostreatus* (HI and SB).

The plates containing the strains of *Pleurotus* sp. were kept at 28°C until the medium surface was completely colonized by the fungal mycelia. Subsequently, all the strains were kept in a refrigerator at 4°C and were periodically tested for maintenance.

2.2. Growth of the fungi in the liquid medium

Potato dextrose (PD) liquid medium was used for the growth of the fungal strains. After preparation, an aliquot of 3 mL of the liquid culture medium was transferred into test tubes and autoclaved at 121°C for 20 min.

For each of the isolates of *Pleurotus* sp., a disk of 1 cm in diameter was removed from the mycelia growing in the solid medium and inoculated into test tubes, each containing 3 mL of the PD liquid medium. Subsequently, the test tubes containing the samples were incubated in a static incubator at 28°C for seven days.

2.3. Preparation of the culture medium containing the methylene blue dye

Using the PD culture medium, the experiments were performed by giving two treatments with the methylene blue dye at concentrations of 0.02 g L^{-1} and 0.04 g L^{-1}, chosen according to Babá et al. (2009). Also, the PD control medium was prepared without the addition of the dye.

The solutions were prepared in 250 mL Erlenmeyer flasks, followed by the distribution of 100 mL of the PD liquid medium and the addition of the methylene blue dye at the different concentrations of 0.02 g L^{-1} and 0.04 g L^{-1}. All the solutions were autoclaved at 121°C for 20 min. After sterilization, each Erlenmeyer flask received 3 mL of the liquid culture medium, previously inoculated with the seven strains of *Pleurotus* sp. prepared in the test tubes as described above. All the treatments were performed in triplicate.

After this procedure, the flasks were incubated in an orbital incubator at 110 rpm for seven days at 28°C.

2.4. Evaluation of mycelial growth

The growth of fungal biomass was evaluated by the filtration of the treatments, using a funnel and Whatman N1 filter papers, weighed initially. After the procedure, the filter papers with the mycelial mass from each of the isolates were kept in a static incubator at 60°C until a constant weight was reached. Subsequently, the fungal mycelia were measured in an analytical balance and their masses were expressed in grams.

2.5. Evaluation of the degradation of the methylene blue dye

The supernatants from each of the seven isolates were evaluated by reading their absorbances on a spectrophotometer at a wavelength of 520 nm. The absorbances of each of the final solutions inoculated with the fungal strains were compared to their respective initial solutions without the fungal inoculation, resulting in the percentage of degradation of the dye for each of the fungal isolates.

2.6. Statistical analysis

All the statistical analyses were performed using the SPSS software version 2.1. The statistical methods used were ANOVA, followed by Tukey's test at the 5% level of significance.

3. RESULTS AND DISCUSSION

It was observed that all of the isolates of *Pleurotus* sp. were able to grow at the different concentrations of the methylene blue dye (Figure 1).

The strains of *Pleurotus* sp. have the capacity to produce a significant amount of mycelial mass because of their efficiency, and being one of the most cultivated fungi, they have extensive applicability in biological processes. The fungi are able to grow in different media due to their ability to secrete enzymes to absorb the nutrients necessary for their development (Przystaś et al., 2018).

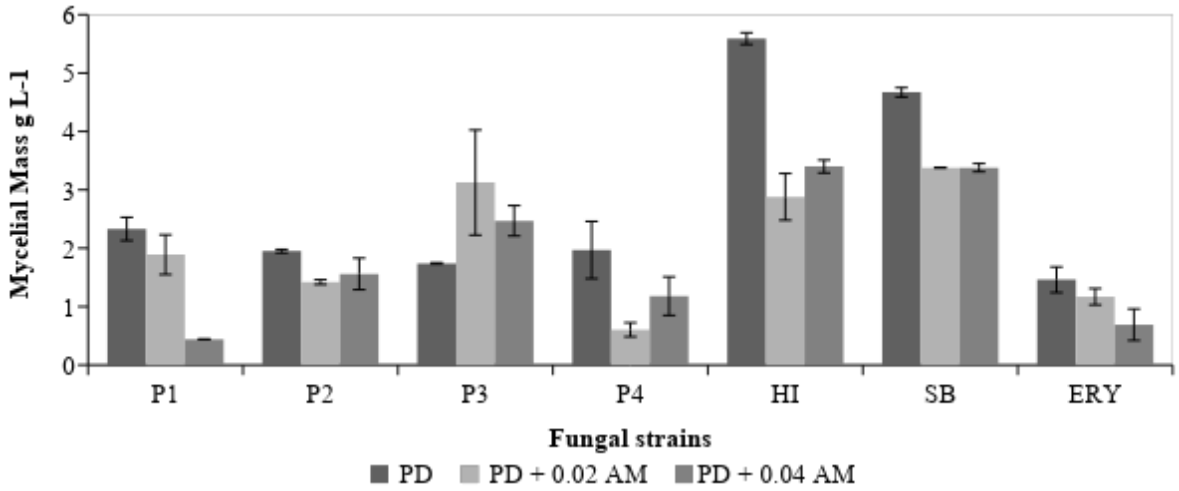

Figure 1. Mycelial mass production by the seven *Pleurotus* strains (P1, P2, P3, P4, HI, SB, ERY) after seven days of incubation at 28°C under agitation in the medium without the addition of methylene blue dye (PD); in the medium with the addition of 0.02 g L^{-1} of methylene blue (PD + 0.02 g L^{-1} AM); and in the medium with the addition of 0.04 gL^{-1} of methylene blue (PD + 0.04 g L^{-1} AM).

The analysis of the production of fungal mycelial mass (Figure 1) showed that, except for isolate P3, almost all the isolates in the solution with the PD medium were able to produce a higher mycelial mass compared to the other solutions. Such a good development of the isolates in the PD medium can be attributed to the fact that the medium was composed of only glucose and potato, thereby generating a high capacity of development for the strains and becoming ideal for their growth. However, the addition of the dye resulted in a lower development of the fungi due to their necessity of expending energy for the degradation of this compound (Confortin et al., 2008).

In the solution with the PD medium, only strain P3 presented the lowest mycelial mass average, compared to the other solutions. However, as shown by Tukey's test at the 5% level of probability in Table 1, this value did not differ significantly from the results of the P1, P2, P4, and ERY strains for this treatment.

Table 1. Production of Mycelial Mass (g L^{-1}) presented by *Pleurotus* strains (P1, P2, P3, P4, HI, SB, ERY) for the treatments in the medium without addition of the methylene blue (PD); in the medium with the addition of 0.02 g L^{-1} of methylene blue (PD + AM 0.02 g L^{-1}); and in the medium with the addition of 0.04 gL^{-1} of the methylene blue dye (PD + AM 0.04 g L^{-1}).

Treatments	Fungal Strains						
	P1	P2	P3	P4	HI	SB	ERY
PD	2.34 bA	1.95 bA	1.74 bB	1.97 bA	5.59 aA	4.68aA	1.46 bA
PD+AM 0.02 g L^{-1}	1.90 bA	1.42 bcA	3.13 aA	0.65 cB	2.89 aB	3.38aB	1.17 bcAB
PD+AM 0.04 g L^{-1}	0.44 dB	1.56 bcA	2.47abAB	1.19cdB	3.40 aB	2.61aC	0.69 cdB

Equal lowercase letters in the same row and upper case in the same column indicate averages with no statistical difference for Tukey's HSD^{ab} test at the 5% level of significance ($p < 0.05$).

Among the seven strains of *Pleurotus* sp., the isolates HI and SB presented more extensive mycelial mass averages for the treatment of the PD medium, reaching 5.59 g L^{-1} and 4.68 g L^{-1}, respectively. The same fungal strains, when grown at the different concentrations of methylene blue dye had a higher production of mycelial mass relative to the other strains and when compared to each other. The behavior of these two isolates presented mycelial mass averages without statistically significant differences, thereby indicating a good development of these two isolates in the treatments tested.

However, the analysis of the behavior of these strains in the solutions revealed that the strain HI showed a statistically equal growth between the two treatments with the methylene blue dye, indicating that regardless of the concentration the mass averages are statistically the same for this strain. That differed from the SB strain, presenting a distinct growth in the different treatments with its highest mycelial mass being found in the solution containing 0.02 g L^{-1} of the methylene blue dye.

The analysis of the mycelial growth of the strains in the treatment with 0.02 g L^{-1} and 0.04 g L^{-1} of the methylene blue dye showed that the isolate P3 did not present statistically significant differences with the isolates HI and SB and that only in the treatment with a higher concentration of the dye, strain P3 presented a mycelial mass average without any statistically significant difference from strain P2.

During the treatments with the methylene blue dye, the behavior of strain P3 showed that in the two concentrations of the dye, the growth was also statistically equal, indicating a good development of the strain in both the treatments. Table 2 shows that the lowest mass averages were found for fungal strains P1, P2, P4, and ERY in the treatments with 0.02 g L^{-1} and 0.04 g L^{-1} of the dye, and only isolate P1 presented a decline in growth between the two treatments with a statistically significant difference. Thus, among the fungal strains studied, isolates HI, SB, and P3 stood out in relation to the production of mycelial mass.

In our study, it was noticed that the mycelial growth of the strains varied with the increasing concentrations of the dye, showing that each strain presents a different behavior in relation to its growth, varying not only with the characteristics of the culture medium but also with the characteristics of the individual species.

The analysis of the absorbances, described in Figure 2 and Figure 3, demonstrated that all the isolates were visibly able to reduce the color of the medium following seven days of growth, thus corroborating with the results obtained by Babá et al. (2009). Through a visual analysis in that study, the color was observed to decrease when the PD culture medium containing the methylene blue dye was inoculated with an isolate of the fungus *Pleurotus ostreatus*.

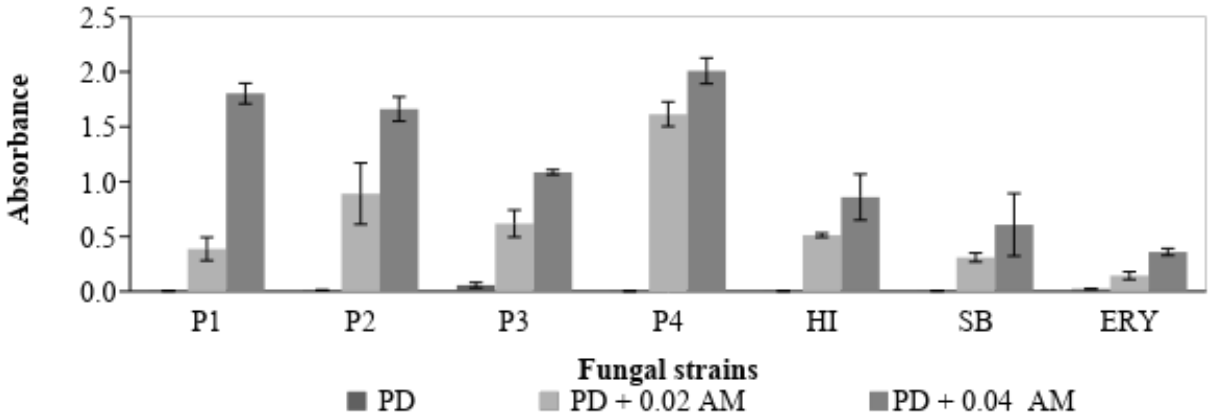

Figure 2. The absorbance of the solutions in which the *Pleurotus* strains (P1, P2, P3, P4, HI, SB, ERY) were cultivated. The medium without addition of methylene blue dye (PD), the medium with the addition of 0.02 g L^{-1} of methylene blue (PD + 0.02 AM) and the medium with the addition of 0.04 g L^{-1} of methylene blue (PD + 0.04 AM).

Figure 2 shows the results of the absorbances obtained for each treatment after the period of inoculation with the fungal strains. Comparing the absorbances of these treatments with their respective controls, it was possible to identify the reductions obtained for each of the solutions (Figure 3). However, only in the PD medium, the reduction in the color of the solution was not possible to verify because it was the control.

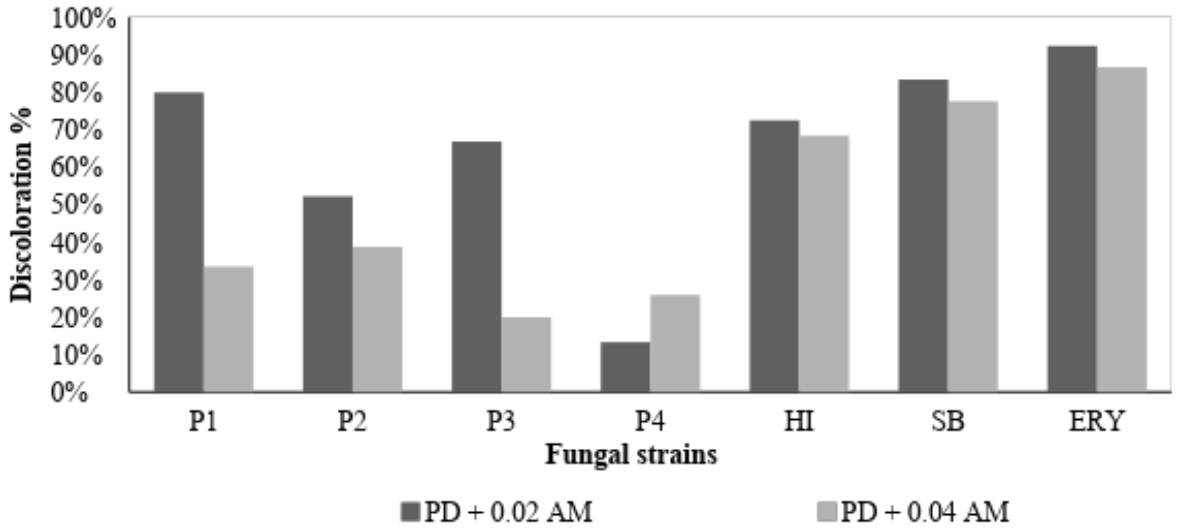

Figure 3. Percentage reduction of the absorbance of the initial solution in which the *Pleurotus* strains (P1, P2, P3, P4, HI, SB, ERY) were cultivated. The medium with the addition of 0.02 g L^{-1} of methylene blue (PD + 0.02 AM) and the medium with the addition of 0.04 g L^{-1} of methylene blue (Medium PD + 0.04 AM).

The values described in Figure 2 and Figure 3 indicated the decolorizing potential of the seven strains of *Pleurotus* sp. with reductions in the color of the methylene blue dye ranging between 13.3% to 92.3%. Figure 3 also shows that almost all the fungal isolates presented greater reductions in the absorbances of the solution at both concentrations, indicating that these fungi present the ability to degrade this dye at the lowest concentration with the greatest efficiency. Only strain P4 presented a different behavior, because it showed a higher percentage of reduction in the absorbance of the solution with the PD medium, containing 0.04 g L^{-1} of the methylene blue dye, indicating that in this way the metabolism of each fungal strain can develop a different capacity, in order to metabolize compounds.

Among all the fungal isolates, the ERY strain presented the best results with a 92.3% reduction in the absorbance for the treatment of the PD medium with 0.02 g L^{-1} of the methylene blue dye and a 86.7% reduction in the absorbance for the treatment of the PD medium with 0.04 g L^{-1} of the dye, compared to the treatments without fungal inoculation.

As shown in Table 2, the analysis of the treatment of the PD medium with 0.02 g L^{-1} of the methylene blue dye verified that the absorbance differences among the strains ERY, SB, HI, and P1 were not statistically significant, indicating that for this treatment they exhibit a similar efficiency in the removal of the color. On the other hand, it was also observed that in the PD + AM solution, containing 0.02 g L^{-1} of the dye, the strain P3 did not present statistically significant differences in relation to the strains SB and HI, thereby suggesting that this strain also shows a significant reduction in the color of this solution.

Table 2. The absorbance of the *Pleurotus* strains (P1, P2, P3, P4, HI, SB, ERY) for treatments in the medium without addition of the methylene blue dye (PD); in the medium with the addition of 0.02 g L^{-1} of methylene blue (PD + AM 0.02 g L^{-1}); and in the medium with the addition of 0.04 g L^{-1} of methylene blue (PD + AM 0.04 g L^{-1}).

Treatments	Fungal Strains						
	P1	P2	P3	P4	HI	SB	ERY
PD	0.01aA	0.01aA	0.06aA	0.003aA	0.004aA	0.01aA	0.02a A
PD+AM 0.02gL^{-1}	0.39baB	0.89cB	0.62bcB	1.62dB	0.51baB	0.31baB	0.14 a AB
PD+AM 0.04gL^{-1}	1.80dC	1.66dC	1.09cC	2.01dC	0.86bcC	0.61baC	0.36 aB

Equal lowercase letters in the same row and upper case in the same column indicate averages with no statistical differences for Tukey's HSD^{ab} test at the 5% level of significance ($p < 0.05$).

The analysis of the treatment with 0.04 g L^{-1} of methylene blue dye revealed that the strain ERY presented the lowest absorbance average and consequently, the highest reduction in the color between the treatments (Table 1). The strain ERY was the only isolate that did not present statistically significant differences between the two treatments to which it was subjected (Table 2). Some of the isolates were also seen to present a direct relationship between the growth of mycelial mass and the reduction in the absorbance, while the other isolates such as the strain ERY showed an inverse relationship.

The strains SB and HI showed statistical equality in the treatment with 0.04 g L^{-1} of the methylene blue dye with the performance of the strain SB being statistically equal to that of the strain ERY. When compared to the control treatments, the other strains showed high absorbance averages, thereby generating lower reductions in the color than these three strains.

For each isolate, the evaluation of the mean absorbances of the three treatments verified that the ERY, SB, and HI isolates presented reductions of over 60% in all the solutions. Thus, they were found to be most promising for the processes of bioremediation as they presented tolerance and efficiency in the removal of the color of methylene blue dye.

Rosolen et al. (2004) also carried out an evaluation of the capacity of the two strains *Pleurotus ostreatus* and *Pleurotus sajor-caju* in the degradation of the nine textile dyes, including Palanil Yellow 3G, Drimaren Yellow CL-R, Indanthren Yellow 5GF, Drimaren Red CL–5B, Indanthren Red FBB, Dispersol Red C–4G, Dispersol Blue C–2R, Drimaren Blue CL-R, and Indanthren Blue RCL. The authors verified that the above two strains were visibly able to discolor almost all the dyes, except Indanthren Red FBB, which presented a complex structure compared to the other dyes. The rate of degradation of the dyes in this work followed the growth rate of the fungi, indicating that the percentage of removal of the color was related to the capacity of the fungi to grow, differing from the present study, where it was verified that the strains such as ERY did not present such direct relationship.

In the same work carried out by Rosolen et al. (2004), the toxicity of an effluent containing these dyes was tested and it was verified that the effluent treated with both the fungal strains presented a lower toxicity, indicating the efficiency of the fungal strains of the genus *Pleurotus* in the processes of removal of color and toxicity.

The data of work carried out by Bettin et al. (2011) also corroborates the results found in the present study, where it was possible to verify a 15–70% discoloration of the dye Reactive Blue 220 when placed in contact with the crude enzyme extract of the fungal strain *Pleurotus sajor-caju*, suggesting that this strain presents a potential for the discoloration of textile dyes.

In another study by Bettin et al. (2011), the dye discoloration of chromophore groups such as anthraquinone, azo, and triphenylmethane during the growth of the *Pleurotus sajor-caju* strain PS–2001 was tested in Petri dishes and the discoloration of the dyes was verified visually, indicating that treatment with this fungal strain could be used in the biotechnological processes.

The fungi, belonging to the division Basidiomycetes are microorganisms with great capacities to biodegrade and mineralize diverse compounds, having the most varied structures. Among these compounds, the dyes represent a class of substances with complex chemical structures with the possibility of being broken into simpler molecules by the action of the extracellular enzymes produced by these fungi.

The fungi of the genus *Pleurotus* have a high capacity to produce enzymes, organic acids, and other metabolites that are capable of promoting the discoloration of the dyes and agroindustrial residues. Due to their lack of substrate specificity, these enzymes are also capable of degrading a variety of xenobiotics (Křesinová et al., 2018). Furthermore, the fungi of this genus differ in the degradation ability of these substances due to the qualitative and quantitative characteristics of their individual enzymes (Kamida et al., 2005).

In fact, fungi of the genus *Pleurotus* are known to be good producers of lignolytic enzymes, which are capable of oxidizing xenobiotic compounds as well as dyes, showing a correlation between the lignolytic enzymes and the discoloration of compounds (Vilar et al., 2018).

Corroborating these findings with the present work, we can highlight the capacity of the genus *Pleurotus* in bioremediation processes, thereby indicating the importance of the selection of isolates, since strains from the same genus or even the same species can behave in different ways against environmental degradation.

4. CONCLUSIONS

The analysis of the growth of fungal biomass showed that the seven strains of *Pleurotus* sp. tested in this study are able to grow under atypical conditions with different concentrations of the methylene blue dye, thereby indicating their potential to be used in bioremediation processes.

The results concerning the performance of the seven strains of *Pleurotus* sp. in the degradation of the methylene blue dye showed significant reductions in the absorbances of the solutions after the incubation period. The discoloration of both the culture media, with dye at concentrations of 0.02 g L^{-1} and 0.04 g L^{-1}, was successfully achieved by the strains of *Pleurotus* sp., designated as ERY, HI, and SB with a reduction of around 80% in the absorbance.

The tests showed that despite contributing to the discoloration of the solutions tested, the amount of biomass production is not a determining factor, since the strain ERY presented a lower production of mycelial mass but reached the highest values in reducing the color of the substrate containing the methylene blue dye.

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Efficacy of a solar still in destroying virus and indicator bacteria in water for human consumption

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ABSTRACT

Natural water distillation can destroy and/or inactivate microorganisms that are sensitive to heat and ultraviolet radiation (UV). This method is currently used to provide fresh water in ships and in the desalination of brackish water. For the development of this research, a pilot-scale solar still was built and installed in the southern region of Brazil, in order to assess its efficiency in water disinfection, which was based on the most probable number (MPN) of total coliforms and *Escherichia coli*, in addition to the DNA copy number of human adenovirus type 5 (HAdV-5) in raw, undistilled samples and in treated distilled water. Results showed that the distillation process removed 100% of total coliform and *Escherichia coli* and 4.5 log (99.997%) of HAdV-5, which meets the microbiological standards for drinking water according to national Brazilian regulations, as well as USEPA and HEALTH CANADA requirements.

Keywords: adenovirus, solar distillation, water disinfection.

Eficácia de um destilador solar na desinfecção de vírus e bactérias indicadoras em água destinada ao consumo humano

RESUMO

A destilação natural da água pode destruir e/ou inativar microorganismos que são sensíveis ao calor e a radiação ultravioleta (UV). Este método é utilizado, atualmente, para fornecer água potável em navios e para dessalinização de água salobra. Para o desenvolvimento desta pesquisa, um destilador solar em escala piloto foi construído e instalado na região sul do Brasil de forma a se verificar a eficiência do equipamento na desinfecção de água. A verificação de eficiência do equipamento foi baseada na determinação do número mais provável (NMP) de coliformes totais e *Escherichia coli* bem como no número de cópias de DNA do adenovírus humano tipo 5 (HAdV-5) em amostras de água antes e após a destilação. Os resultados demonstraram que houve 100% de remoção de coliformes totais e *E. coli* e 4,5 log (99,997%) de remoção de HAdV-5 após a destilação, o que está de acordo com o padrão microbiológico

de potabilidade determinado pela legislação brasileira, pela USEPA e pela HEALTH CANADA.

Palavras-chave: adenovírus, desinfecção de água, destilação solar.

1. INTRODUCTION

According to the World Health Organization (WHO), every year there are around 2.5 billion cases of diarrhea among children in the world. Most of these cases are associated with the consumption of contaminated water, and result in the death of nearly 750,000 children under the age of five (5) (WHO and UNICEF, 2013). In addition, a quarter to a half of the cases of diarrhea reported annually can be prevented by improving water, sanitation and hygiene (Clasen et al., 2015). These diseases are usually caused by enteric pathogens, namely those associated with the fecal-oral transmission route, which are shed in the feces of infected individuals and transmitted to others through the consumption of contaminated water. Further, water may also carry pathogens of non-fecal origin which are released into the environment by wounds (Prüss-Üstün et al., 2008).

The implementation of public water supply systems has ensured the delivery of safe drinking water to the population; however, there are very few water-quality monitoring programs relating to individual wells used by the rural population of Brazil. Thus, since many water sources commonly used in rural areas of the country, such as private wells, cisterns or reservoirs, are contaminated by pathogenic microorganisms, the risk of contamination by enteric pathogens in these locations is high. These contaminants must therefore be removed or inactivated in order to ensure the safety of these waters (Nogueira, 2003; Tchobanoglous et al., 2003; Alves et al., 2014).

Some of the bacteria responsible for causing diseases in humans are difficult to identify in water samples, due either to their presence in small amounts or to the cost and time needed to obtain results. Consequently, an indicator is usually used to test for the presence of pathogenic microorganisms, i.e., some sort of organism that can be quickly and easily found and which can indirectly indicate the presence of other organisms that are potentially disease-causing (Von Sperling, 2003; USEPA, 2006). Research for pathogens in waters intended for human consumption has for some time been restricted to assessing bacteria that serve as indicators for fecal contamination. The main reason for using coliform bacteria for this purpose is that it is released in large quantities through feces, 100 to 400 billion per day per person (Tchobanoglous et al., 2003). However, advances in concentration, detection and identification techniques of several types of viruses has enabled the assessment of viral contaminants in aquatic environments to be included within the framework of several studies (Wyn-Jones and Sellwood, 2001; Bosch et al., 2008; Fabres, et al., 2017).

It is known that viruses are the main cause of water-related diseases, and since the treatment techniques currently used do not ensure their complete removal or inactivation, they contaminate hydric resources on a large scale, becoming a serious health concern (Rodrigues et al., 2015). Although its role in transmitting diseases through water is less understood than those of bacteria and protozoa, it is known that the risk of viral infection is 10 to 10000 times greater (Bosch, 1998). Adenoviruses, in particular, are shed in high numbers in human feces and are also commonly found in sewers, polluted waters, water-harvesting sources for human consumption and even in drinking water around the world (Lee and Kim, 2002; Albinana-Gimenez et al., 2009; WHO, 2011). In addition to its host specificity, i.e., not having any particular animal source, its resistance to UV radiation is 60 times greater that of RNA viruses, making it possible to use these as a reliable indicator for systems that use UV radiation as

disinfecting agent (Davison, 2003; Lechevallier and Au, 2004; Fong and Lipp, 2005; USEPA, 2007; WHO, 2011; Wong et al., 2012).

This research therefore assessed the efficacy of a pilot-scale solar still in removing total coliform bacteria and *Escherichia coli*, along with its removal and/or inactivation of adenovirus. The solar still inlet water samples (raw water) came from three different sources: two natural waters (from rooftop runoff and a small stream) and one water sample that had been artificially contaminated in laboratory. As far as the authors are aware, this is the first study to evaluate the disinfection of adenovirus in water for human consumption using solar stills.

2. MATERIALS AND METHODS

2.1. Area of study

The pilot-scale solar still was installed in the city of Taquara, RS, located 72 km from the state capital, Porto Alegre, at 29º39'02" latitude south and 50º46'50" longitude west, with a maximum altitude of 600 meters above sea level. The minimum annual temperature in the city is 4ºC and the maximum is 37ºC, with an average of 23ºC, which makes it a mild climate (Taquara, 2013). The city is located on the middle sub-stretch of the Sinos River and is near to five rivers, namely Sinos, Padilha, Rio da Ilha, Paranhana and Rolante.

2.2. Pilot scale equipment

In this study, a symmetric double-slope solar still was built by the authors considering the geographic characteristics of the area where it was installed (Badran and Al-Hayek, 2004; Hashim et al., 2010; Saidur, 2011; Sharshir et al., 2016). With the aim of achieving greater productivity, the orientation of the chosen model was south-north, i.e., with the glass facing east-west (Figure 1), as studied by Abderachid and Abdenacer (2013).

With regard to the gradient of the cover (angle of inclination), Abdenacer and Nafila (2007) suggest this to be the same as the regional latitude of the installation location. Although for Rio Grande do Sul, Brazil this results in an average of 30º, in order to reduce the size of the equipment it was designed with a 25º inclination. The basin has an external dimension of 836 x 836 mm and an internal dimension of 800 x 800 with side walls of 120 mm in height, which results in an approximate central height of 306 mm (calculated using trigonometry) (Figure 1).

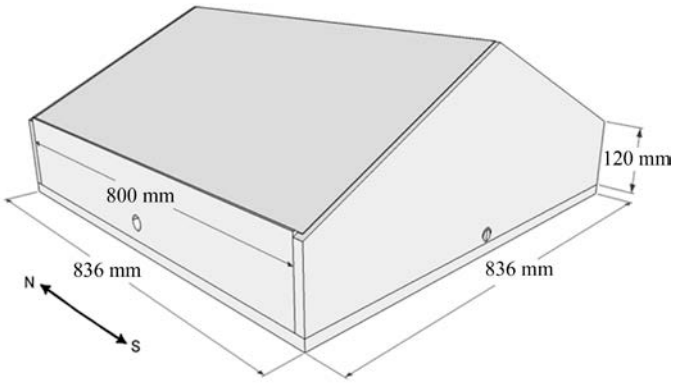

Figure 1. Isometric perspective of the pilot-scale solar still.

As shown in Figure 2, in order to provide support and rigidity to the structure, 18 mm thick MDF (medium-density fiberboard) was used due to the ease of working with this material, which also provides good thermal insulation. The basin had an inside area of 0.64 m^2 and was painted black in order to increase its rate of absorbance, as suggested by Badran (2007). The

impermeability of the internal side (base and walls) was accomplished using FRP (Fiber-reinforced plastic), commonly known as fiberglass, used in the construction of drinking water reservoirs, and for the cover a 4 mm glass plate was used.

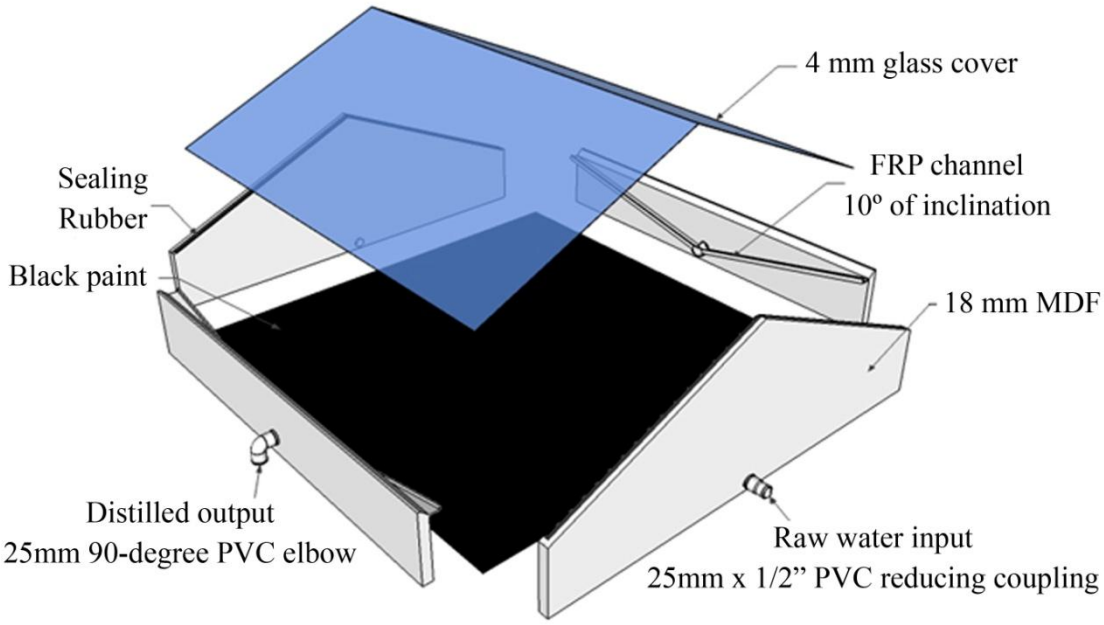

Figure 2. Exploded view of the solar still and materials description.

2.3. Disinfection efficacy

In order to assess the system's efficacy in disinfecting contaminated waters, total coliform bacteria, *Escherichia coli* and human adenovirus type 5 (HAdV-5) were used as indicators.

Prior to the start of each test, the equipment was washed using Extran® detergent and water from a public supply. Five liters of contaminated water were then placed in the raw water basin of the still, resulting in an initial 8 mm water depth. The tests were carried out from 8:00h to 15:00h, and the water distilled in the first hour was discarded in order to avoid possible contamination by the water used to wash the equipment. Afterwards, at 15:00h, a sample of distilled water relating to the period (9:00h to 15:00h) was collected for analyses (0.5L for viruses and 0.1L for coliform bacteria)

All samples tested were stored under refrigeration following collection and taken in Styrofoam boxes filled with ice to the Molecular Microbiology Laboratory of Feevale University, Brazil, where the experiments were carried out.

2.3.1. Removal of total coliform and Escherichia coli

The efficiency of removal of total coliform bacteria and *E. coli* was tested using the following samples:

- roof runoff of a rural residence, at coordinates 29º37'5.48" S and 50º46'28.55" O;
- water from a small stream collected on the same property (naturally contaminated);
- artificially contaminated water (inoculated in laboratory);

For the artificially contaminated samples, a bacterial culture using *Escherichia coli* ATCC 25922 grown *overnight* in *Tryptic Soy Broth* at 37°C was prepared. Then, 15 mL of this medium was added to 5 L of the rainwater.

All samples were tested for the presence of total coliform and *E. coli* using the Colilert® kit and following the manufacturer's methodology up to 24 hours following sampling (IDEXX, 2013).

2.3.2. Disinfection of HAdV-5

To evaluate the efficiency of the system in removing HAdV-5, a sample of roof runoff rainwater collected as stated earlier (previously tested negative for the virus under study) was contaminated in laboratory with a viral culture medium. Two 5-liter containers of water were contaminated with the same amount of HAdV-5; one was subjected to the solar still model and other remained as the control sample. After processing by the method of disinfection, both samples were subjected to the concentration process described below. Quantitation of genomic DNA copies in the control sample was considered the total quantity inoculated (2.53×10^{10} DNA copies L^{-1}), and was then compared to the treated sample. The removal efficiency was calculated based on the DNA copy number present in the sample, which were assayed by Real Time Polymerase Chain Reaction (qPCR) method.

Sample preparation

In order to artificially contaminate the raw water sample, the A549 cell line was used (A549 being epithelial cells derived from human lung carcinoma and permissive to most human adenoviruses). The culture was carried out in cell culture flasks (75 cm^2), using as growth medium a minimum essential medium (MEM) with Eagle salts supplemented with 5% fetal bovine serum (FBS) CULTILAB, 1% of antibiotics and fungicide (PSA Cultilab-penicillin G 100U/ml/100 g streptomycin sulfate/ml/0.25 g amphotericin B/ml).

Concentration

The water samples were concentrated using an adsorption-elution method previously described by Katayama et al. (2002) with some modifications. The following concentration protocol was used: with the aid of a vacuum pump, 0.5 L of water sample was filtered through an HA-type cellulose membrane with pores measuring 0.45 µm, provided with a negative charge (Millipore). This water had its pH previously adjusted to between 4.5 and 5.5, and $MgCl_2$ was added. The viral particles that by chance were present in the test samples were then adsorbed to the membrane. Next, 87.5 ml of a 0.5 mM of H_2SO_4 solution were filtered through the membrane decoupling major cations, followed by another 2.5 ml of 1 mMNaOH (pH 10.5 -10.8) solution, filtered through the same membrane. The resulting filtrate was placed in a tube containing 12.5 µL solution of 50 mM H_2SO_4 and 12.5 µL of TE 100X concentrated buffer.

DNA Extraction and qPCR

The viral genomes present in the samples were extracted through the RTP® DNA/RNA Virus Mini Kit (Invitek) extraction kit. After the extraction of viral genomes, the samples were subjected to amplification procedures of the genome target fragment in a preserved region of the hexon gene of the AdV (VTB2-HAdVCf 5'-GAGACGTACTTCAGCCTGAAT-3'and VTB2-HAdVCr 5'-GATGAACCGCAGCGTCAA-3'). The polymerase chain reactions (qPCR) in real time were carried out in an IQ5 Bio-Rad (Biorad, USA) thermo-cycler using the MyiQ™2 device Two-Colour Real-Time PCR Detection System with the iQ™5 optical system software, Version 2.1. We used the commercial Platinun® SYBR® Green qPCRSupermix-UDG (Invitrogen, USA) kit, following the manufacturer's recommended methodology. Each reaction was composed of a denaturation cycle at 95°C for 10 min., followed by 40 cycles, composed of one step at 95°C for 20 s, and a combined annealing/extension step at 55°C for 1 minute. The fluorescence data were collected during the annealing/extension step. After that, a denaturing curve was made to check the specificity of amplification products (melting step

between 55 and 95°C). Melting curve analysis was done using High Resolution Melting electrophoresis (HRM) to verify PCR product specificity, each viral specie has a specific temperature (HAdV-5; 86°C). For generating standard curves, 10-fold serial dilutions of standard controls (HAdV type 5) from 10^{-1} to 10^{-5} were prepared, starting at 4.55×10^{9} genome copies per reaction. Prototype viral strains from HAdV-5 were cultivated in A549. All standard controls and samples were run in duplicate in 96-well plates (MicroAmp Applied Biosystems). No template control (NTC) and negative control were used in each run to confirm that there was no contamination in the assay. Only the results from assays within the range of E=90–110%, slope in the range of 3.2-3.4 and R_2=0.98–0.99 were considered. All results were confirmed by checking the peaks obtained during the high resolution melting curve.

3. RESULTS AND DISCUSSION

The tests were carried out in October, when the monthly average daily global solar irradiation for the southeast Brazil is estimated in about 4.25 kWh/m²dia by the physical solar model BRASIL-SR (INPE, 2017).

3.1. Total coliform and *Escherichia coli* removal efficiency

The results obtained using total coliform and *Escherichia coli* as indicators for determining the efficacy of the solar still in disinfecting contaminated waters from natural sources and for a sample contaminated in the laboratory are shown in Table 1.

Table 1. Results of disinfection tests using total coliform bacteria and *Escherichia coli*.

Sampling	Total coliform bacteria (NMP/100mL)		*Escherichia coli* (NMP/100mL)	
	Raw	Distilled	Raw	Distilled
Roof runoff	>2419.6	<1	3	<1
Stream	>2419.6	<1	365.4	<1
Inoculated in laboratory	>24000	<1	>24000	<1

The temperature of the water inside the still reached 63.8ºC and 68.8ºC on the days when both the rainwater and the water from the small stream were tested, respectively. On the test day with laboratory-inoculated water, the temperature exceeded 70°C.

The number of total coliform and *E. coli* for all samples treated by the solar still were below the detection limit of the analytical method (<1 NMP / 100mL), i.e., the system showed 100% efficiency in reducing the number of these microorganisms. In addition, the use of water inoculated in laboratory with a high amount of *E. coli* and the roof runoff rainwater with near zero contamination demonstrates that regardless the degree of contamination of raw water the system is capable of providing treated water within the microbiological standards required by the Brazilian Ministry of Health Ordinance 2914/2011. In particular, these results are important when considering the roof runoff intended for potable purposes, since up-to-date studies demonstrate that the use of rainwater in houses may contribute to reduce the impacts of water shortages in drinking water distribution systems in southern Brazil (Lopes et al., 2016).

Other studies report the removal of 100% of total and fecal coliform; however, this did not occur in all samples tested by the authors. Balladin et al. (1999) found contamination by total coliform bacteria in all their treated water samples and claimed that this was probably due to airborne bacteria. Hanson et al. (2004) found contamination in 8% of their treated samples, in this case by fecal coliforms, and claimed that this may have occurred due to the formation of turbulence at the time of adding the raw water to the equipment, which caused tiny bubbles to project contaminated water onto the internal surface of the cover.

Several authors explain that the inactivation efficiency is related to the disinfecting power of UV radiation and visible light, which form part of the solar spectrum, and to the temperature the water reaches during the process, in addition to asserting that the synergistic effect of temperature and visible light occurs closer to 50°C (Acra et al., 1984; Wegeling et al., 1994; PROSAB, 2001). Thus, in cases where contamination of distilled water was found, it is important to know at what hour of the day these contaminations occurred, or, in cases where the determination of coliform was made in one single daily sample, what was the operating time schedule of the equipment. However, the authors reporting contamination do not present this data (Balladin et al., 1999; Hanson et al., 2004).

Therefore, because this study was conducted during the daytime period, i.e., with a higher incidence of radiation (9h00 to 15h00), it is important to carry out more tests in order to check that the microorganism reduction efficiency is maintained under less favorable conditions, such as the nighttime period or on rainy days, i.e., when there is little or no radiation. This necessity was made evident by the results found by Rijal and Fujioka (2001), who demonstrate that a disinfection system based on the synergistic effect of solar radiation and temperature, for the purpose of disinfecting drinking water, suffered reduced efficiency on cloudy days. Further, the factors mentioned by Balladin et al. (1999) and Hanson et al. (2004) as having influenced the microbiological quality of treated water in their studies highlight the need for adequate operation and maintenance of the equipment in order to avoid any future failures.

Overall, raw water quality (regardless of its source) does not seem to have influenced the efficiency of the pilot system, since the samples used are from sources that often have different physical, chemical and microbiological characteristics (Nascimento and Naime, 2009; Gikas and Tsihrintzis, 2012; Lee et al., 2012). Nevertheless, more studies are required, to include physical and chemical analyses of the samples, in order to obtain a more reliable result.

Despite the proven efficiency of solar distillation in the disinfection of water intended for human consumption, given the national legislation in relation to microbiological parameters, there is a deterrent to the exclusive use of the method when using surface water as the feed water for the distiller, given that Ordinance 2914/2011 of the Brazilian Ministry of Health states that in such cases filtration is mandatory (Brasil, 2011). However, with 100% removal of *E. coli* from water contaminated with more than 24000 MPN / 100 ml, the solar distillation technique is more efficient than slow filtration, which is suitable for *E. coli* values of up to 5000 MPN / 100mL (Di Bernardo et al., 1999; 2005). In addition, when using well water as a raw water source, maintaining a free residual chlorine content is required by law, that is, the addition of chlorine after solar distillation is required (Brasil, 2011).

3.2. Virus removal efficiency

A comparison between the DNA copy number of HAdV-5 present in the contaminated and treated samples is shown in the graph in Figure 3. Additionally, the red line indicates the delimitation of the minimum amount of removal / inactivation established by USEPA and Health Canada.

The artificially contaminated laboratory sample used to feed the solar still had 2.53×10^{10} DNA copies L^{-1}, which was reduced to 6.94×10^{5} in the sample treated by the system, representing a reduction of 4.5 log and thus complying with the USEPA and Health Canada standards (Canada, 2012; USEPA, 1989).

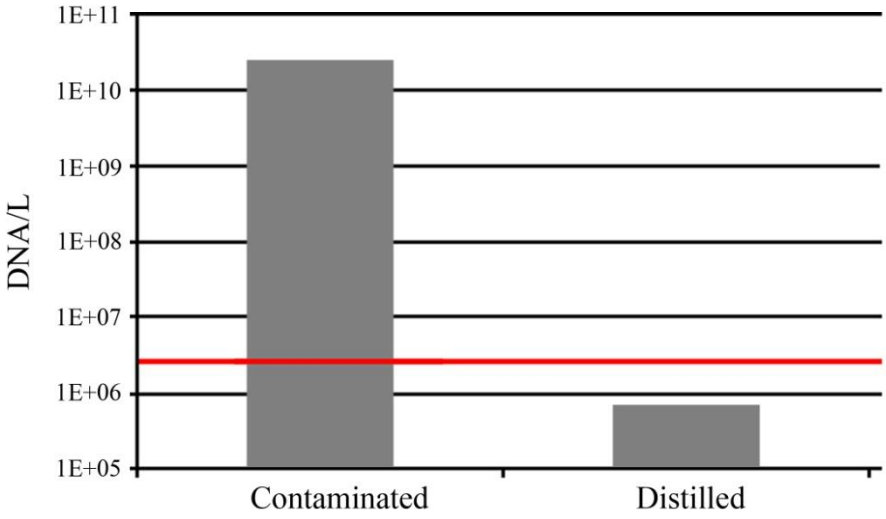

Figure 3. Results of DNA/L in contaminated and treated samples and USEPA and HEALTH CANADA disinfection standard.

This result represents the total number of genomic copies in the sample, i.e., originating from both virions as well as non-viable viral particles. However, high temperatures may damage the viral capsid or nucleic acids, preventing adsorption to the host cells or inactivating enzymes required for multiplication, causing the virus to lose its infection capacity, .i.e., the distillation process may have also inactivated the remaining viral load in the samples, which could be determined by plaque assay (Fong and Lipp, 2005). Using the pilot system of this study, on the removal/inactivation test day of HAdV-5 the raw water exceeded 70°C. It is therefore suggested that for future studies enzyme testing for viral integrity in the samples treated by the system be undertaken, in order to identify whether the DNA quantified by qPCR technique is associated to integral particles of HAdV or to free-viral DNA, whereby it is possible to find out whether these viruses are capable or not of infecting cells and possibly causing diseases (Albinana-Gimenez et al, 2009 ; Girones et al, 2010; Ruppach, 2014).

After temperature, UV irradiation is primarily responsible for the inactivation of viruses; however, despite their susceptibility to this aspect, viruses can be more resistant than bacteria, as evidenced by the results obtained. Furthermore, survival of the viruses in water environments may be significantly related to flagellate predators, extracellular protease, nuclease and other enzymes; therefore, it is convenient for studies on viruses inactivation using solar stills to be extended to other environmental water sources (Fong and Lipp, 2005)

The results obtained in this study show that the removal/inactivation efficiency of viruses by solar distillation is much greater than that of simple filtration and comparable to advanced treatment techniques, such as micro- and ultrafiltration membrane techniques (Madaeni et al., 1995; WHO, 2012). Currently, it is clear that multiple disinfection steps increase the reliability of a treatment system, i.e., a system comprising a single step of 4 logs inactivation/removal efficiency of a given pathogen is less reliable than one showing a two-step process with two logs each (Brasil, 2006; Ruppachi, 2014). Therefore, one factor that can be cited as a disadvantage when it comes to the use of solar distillation as a disinfection method regards its reliability, given that the process does not consist of multiple protection barriers, i.e., it needs only a simple failure to significantly compromise the quality of the water produced.

The development and improvement of inexpensive, alternative treatment technologies aimed at individual water supplies can lead to the reduction of contamination due to waterborne diseases, which, even with all current technological development, still occur in significant

numbers. Among the non-conventional alternatives currently available, solar water distillation is a prominent method and can meet the demand for treated water in developing countries, small communities and rural properties that do not have access to a public water supply.

4. CONCLUSION

The removal efficiency of total coliform and *Escherichia coli* in all tests carried out was 100%, regardless of the sample used to feed the system or its contamination level. This result is within drinking water's microbiological standards as established by the Brazilian Ministry of Health Ordinance 2914/2011. However, disinfection testing was not carried out neither during overnight periods, nor on rainy days. The removal of enteric viruses using HAdV-5 as an indicator was 4.5 log, which meets the USEPA and HEALTH CANADA regulations.

It is concluded that solar distillation is a simple, low-cost technique that is highly efficient in removing enteric pathogens from water intended for human consumption, with its efficacy comparable to more-expensive treatment methods. In addition, its use is recommended for rural properties or residential water-supply units that do not yet have access to a public drinking water supply. This will result in a significant reduction in contamination levels of waterborne diseases in these communities.

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Microclimate in understories of a mango orchard and a degraded area in the Eastern Amazon

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ABSTRACT

Changes in land use alter regional microclimate. This study compared the microclimate in understories of a mango orchard and a degraded area in the municipality of Salinópolis, in the northeast of the Brazilian State Pará, eastern Amazon. In both environments, the microclimate was monitored through collecting data on the following variables: maximum, minimum and average air temperature, air thermal amplitude and vapor pressure deficit. The microclimate was monitored daily during four seasons: early rainy season, late rainy season, early dry season and late dry season, between December 2015 and November 2016. Vegetation coverage was the most important factor to soften maximum and average air temperature in the understories. Lower values of meteorological variables were observed in the mango orchard understory, especially during late rainy season and late dry season, except for minimum air temperature, which was lower in the understory of the degraded area, especially during the late rainy season. The microclimate in the understory differed between both environments, and mango orchards may ameliorate the understory microclimate more efficiently than degraded areas; therefore, the mango orchard can be used as an alternative for the rehabilitation of degraded areas.

Keywords: air relative humidity, air temperature, thermal comfort.

Microclima em sub-bosque de pomar de mangueiras e de vegetação de área degradada na Amazônia Oriental

RESUMO

Modificações no uso da terra alteram o microclima regional. Este estudo teve como objetivo comparar o microclima em sub-bosque de um pomar de mangueiras e uma área degradada, no município de Salinópolis, nordeste do Estado do Pará, Amazônia Oriental, Brasil. O microclima no sub-bosque do pomar de mangueiras e no sub-bosque da área degradada foi monitorado por meio da temperatura máxima do ar, temperatura mínima do ar, temperatura média do ar, amplitude térmica, e déficit de pressão de vapor de água na atmosfera. O monitoramento do microclima no sub-bosque foi realizado diariamente durante quatro estações

distintas, denominadas início da estação chuvosa, estação chuvosa, estação de transição e estação menos chuvosa, no período de dezembro de 2015 a novembro de 2016. A cobertura vegetal foi fator determinante na atenuação das temperaturas máximas e médias do ar no sub-bosque. Os menores valores das variáveis meteorológicas foram obtidos no sub-bosque do pomar de mangueiras, principalmente, nas estações chuvosa e menos chuvosa, exceto a temperatura mínima do ar que foi menor no sub-bosque da área degradada, sobretudo, no início da estação chuvosa. Os microclimas no sub-bosque diferem entre os dois ambientes, e o pomar de mangueiras pode melhorar o microclima no sub-bosque quando comparado ao sub-bosque da área degradada; portanto, o pomar de mangueiras pode ser utilizado como alternativa para reabilitação de áreas degradadas.

Palavras-chave: conforto térmico, temperatura do ar, umidade relativa do ar.

1. INTRODUCTION

The occupation process of the Amazon, from the 1960s and 1970s, occurred along the highways where population growth occurred through intense migratory movement and the expropriation of land in the region. This process brought as the main problem deforestation that persists to the present day. As a consequence, the expansion of agriculture, livestock and logging, especially related to the length of the roads, the number of settled families and the indigenous lands (Becker, 2005).

The conversion of forested areas (greater roughness) into agricultural cultivation (e.g. grain crops), pasture or bare land (less roughness), decreased the turbulent exchange of heat in the boundary layer of this tropical region, and promoted reduction evapotranspiration, thereby increasing surface temperature (Perugini et al., 2017). It is clear that changes in land use may result in regional microclimate alterations.

The presence of trees reduces the average air temperature by 1.25ºC (Pinheiro et al., 2013), the maximum air temperature by 0.77ºC (Pezzopane et al., 2015), the air thermal amplitude by 2.40ºC, and the vapor pressure deficit of the understory by 0.34 kPa (Pezzopane et al., 2010). Therefore, planting trees may ameliorate understory microclimate (Pezzopane et al., 2010; 2015; Pinheiro et al., 2013), especially in degraded areas with a history of land use changes.

Tree species with desirable functional characteristics for the recovery of degraded areas (e.g. broad canopy and high tolerance to changes in soil moisture) may be obtained by using non-native trees for forest restoration (Chazdon et al., 2016). In such a context, one species may be used to restore at least one ecosystem function through understory microclimate amelioration.

The use of mango orchards (*Mangifera indica* L.) is an alternative for restoration of degraded areas. It is a tropical tree species, with a broad canopy and evergreen leaves, that can tolerate long dry periods and low-nutrient soils, and also has efficient nutrient absorption (Ganeshamurthy and Reddy, 2015). Additionally, mango trees produce fruit that is a source of nutrients, vitamins and dietary fiber (Kumar et al., 2015). In this scenario, mango trees may be used to provide ecosystem services for trapping (soil quality and food production), and regulation (climatic regulation) (Ganeshamurthy and Reddy, 2015; Kumar et al., 2015). In Brazil, the mango is the 7th most-produced fruit, and in 2015 the country produced 976,815 t of mango and harvested 64,305 ha, with yield of 15.19 t ha^{-1} (IBGE, 2015).

In this context, the hypothesis tested was that mango orchards are effective to ameliorate the understory microclimate in comparison with the understory of degraded areas. To test this hypothesis, this study compared understory microclimates in a mango orchard and a degraded area in the eastern Amazon.

2. MATERIALS AND METHODS

The study was conducted in the understories of two distinct environments: a mango orchard (MO) and an regenerating forest area (DA) separated by a linear distance of 1.5 km, where the vegetation of secondary forests predominates. Both areas are located in the municipality of Salinópolis, northeast of the Pará State, eastern Amazon, Brazil. The soil type in the area is Dystrophic Yellow Latosol (EMBRAPA, 2013). According to Köppen, local climate is Am subtype, tropical rainy with a short dry season (Alvares et al., 2013). Average air temperature and humidity are 27ºC and 82.5% in the region, respectively; average wind speed and insolation are 1.75 m s^{-1} e 2,100 h, respectively; while mean annual precipitation is 2,750 mm (Ramos et al., 2009). Figure 1 shows rainfall and the average air temperature above the canopy of mango trees and the climatological normal of Salinópolis according to Ramos et al. (2009).

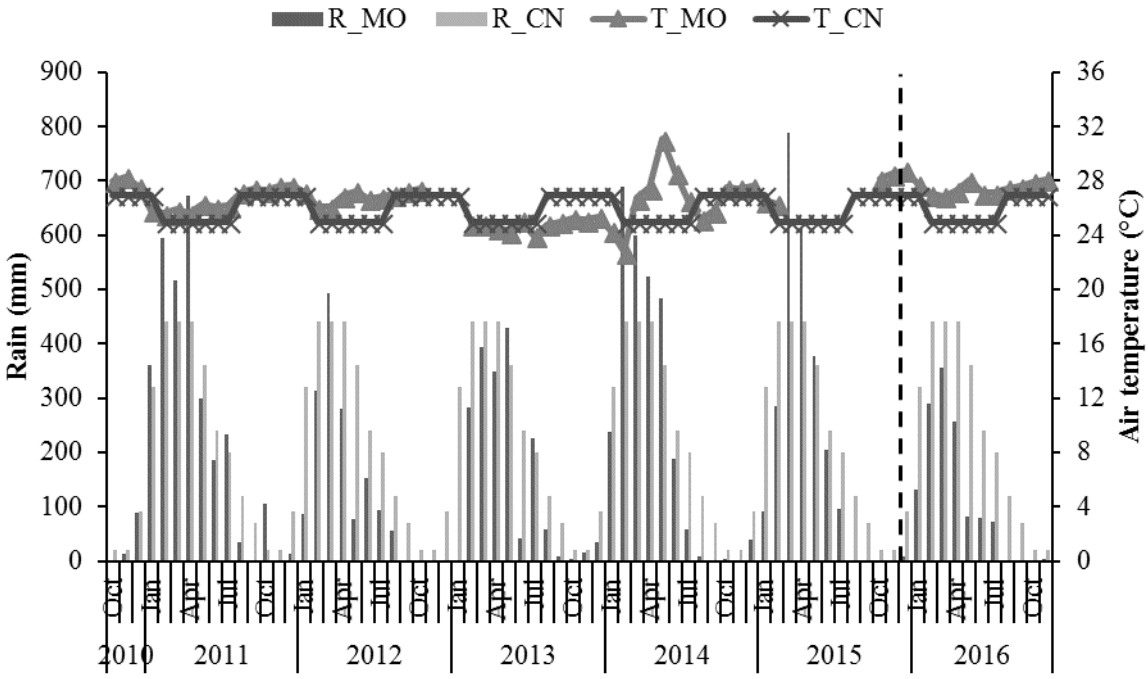

Figure 1. Rain (bar) and the average air temperature (lines) above the canopy of mango trees (October 2010 to November 2016) and the climatological normal (1961-1990) of Salinópolis, Pará. Highlight for the period of this study. R_MO: Rain in the mango orchard; R_CN: Rain in the climatological normal; T_MO: Average air temperature in the mango orchard; T_CN: Average air temperature in the climatological normal.

The Tommy Atkins mango variety (00°39'50.50" S, 47°17'04.10" W, height: 17 m) was planted between 1991 and 1993 in partnership with a culture of soursop (*Annona muricata* L.). Afterwards, the orchard was abandoned. From 2003, the cultural practices inherent to the culture were carried out, as well as the cleaning of the area by the burning of vegetation residues. This process extinguished the soursop plants. Currently, the orchard has a total area of 25 ha cultivated in a non-irrigated system, spaced 10 x 10 m (100 plants ha^{-1}), and the average height of the plants is 6.5 m. The average fruit yield in the orchard is 15.66 t ha^{-1} (Rodrigues et al., 2013). Before the implantation of the mango orchard, the vegetation of secondary forest predominated in the region.

The regenerating forest area (00°40'09.44" S, 47°17'47.58" W, height: 22 m) was used for the cultivation of cashew trees (*Anacardium occidentale* L.). In 2012, after productivity declined, the area was abandoned and a secondary forest was subsequently established in the

initial stages of succession, called "capoeirinha". Ecosystem services were lost in this area, with a reduction of physicochemical soil quality in comparison to the surrounding open ombrophylous forest with palms. The changes in land use through which this area passed have caused its degradation; therefore, this area was denominated as degraded area. The degraded area had high soil bulk density (1.82 g cm^{-3}), low total porosity (29%); and a small quantity of organic matter (10.21 g kg^{-1}), while in the forest the values were 1.74 g cm^{-3}; 32%; and 21.52 g kg^{-1}, 10-20 cm deep in the soil. Before the implantation of the cashew trees, secondary forest vegetation predominated in the region.

A 100 x 100 m plot was installed in each area, where data were collected on the understory microclimate from December 2015 to November 2016. A meteorological station was installed on the ground at the center of each plot. Thermohygrometers were installed 1.5 m above the ground to collect daily data of maximum, minimum and average air temperature, and air humidity. An HMP155A (Vaisala) thermohygrometer was used in the mango orchard, while in the degraded area the thermohygrometer used was part of an integrated Vantage Pro2 (Davis) meteorological station.

Rain data were collected daily with a TB4, Campbell Scientific pluviometer, installed at a height of 10.5 m above the mango trees' canopy. All sensors were connected to an automated data collection system (datalogger), which collected information every ten seconds. Every ten minutes, means were calculated and stored with total amount of data collected. In the mango orchard, a Campbell Scientific CR1000 datalogger was used, while in the degraded area, the datalogger was integrated into the meteorological station.

Using the data of air temperature and relative humidity, we obtained the air thermal amplitude and vapor pressure deficit. Air thermal amplitude was calculated from the difference between maximum air temperature and minimum air temperature. Vapor pressure deficit was calculated from the difference between saturated vapor pressure (Equation 1) and the actual vapor pressure, which was obtained from relative air humidity (Pereira et al., 2002). Vapor pressure deficit data was always collected between 10h00 and 15h00, because this is the period of the day with greatest atmospheric demand for water in the region.

$$es = 0.6108 * 10^{\frac{7.5*T}{237.3+T}} \quad (1)$$

where: es is the saturated vapor pressure (kPa) and T is the average air temperature (°C).

The microclimate was monitored between December 2015 and November 2016. This period was divided into four seasons: early rainy season (ERS – December 2015 to February 2016); late rainy season (LRS – March to May 2016); early dry season (EDS – June to August 2016); and late dry season (LDS – September to November 2016), according to the classification proposed by Moraes et al. (2015) for rainfall on Pará coast.

Sampling design was entirely randomized and investigated two treatments (understory in mango orchard and understory in degraded area) and four seasons (ERS, LRS, EDS e LDS). The number of replications varied according to season, that is, 91 days for ERS and LDS, and 92 days for EDS and LRS. To test for differences between treatments, meteorological variables were submitted to analysis of variance, and then the means were compared using a Student's T test, with 5% significance level. Statistical analyzes were performed using Systat software (Systat, version 12.02).

3. RESULTS AND DISCUSSION

Total rainfall between December 2015 and November 2016 was 1279.40 mm (Figure 2), which was lower than the mean annual rainfall levels in the region, 2750 mm (Ramos et al., 2009). Lower rainfall levels have been related to the occurrence of the El Niño ocean-atmosphere phenomenon (2015-2016).

The highest rainfall levels were registered during LRS (693.80 mm) and lowest levels were registered during LDS (4.20 mm) (Figure 2). In both cases, rainfall levels were lower than mean rainfall levels for each period of the year on the Pará coast, which are between 1200 and 1500 mm (LRS) and between 400 and 600 mm (LDS) (Moraes et al., 2015). During the early rainy season and early dry season, registered rainfall levels were 428.60 and 152.80 mm, respectively.

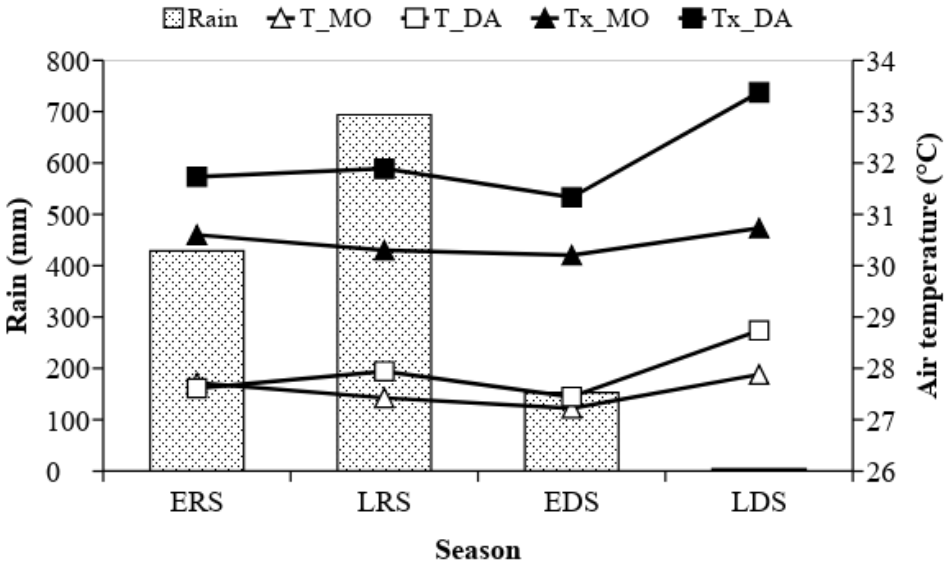

Figure 2. Rain (bars) above the mango trees canopy and air temperature (lines) in the understory of the studied environments, in four seasons, in Salinópolis, Pará. T_MO: Average air temperature in the mango orchard; T_DA: Average air temperature in the degraded area; Tx_MO: Maximum air temperature in the mango orchard; Tx_DA: Maximum air temperature in the degraded area; ERS: Early rainy season; LRS: Late rainy season; EDS: Early dry season; LDS: Late dry season.

Maximum air temperature differed between the understories of the mango orchard and the degraded area ($p<0.001$) (Table 1). The mango orchard reduced maximum temperature in the understory by an average of 1.63ºC in relation to the degraded area The greatest reduction in maximum air temperature in the understories between the mango orchard and the degraded area was observed during LDS (2.65ºC).

Reduction of maximum air temperature in understories has been observed in other studies, where the mean reduction was 0.77ºC in forest understories, in São Carlos, São Paulo State (Pezzopane et al., 2015) and 2.20ºC, in the understory of macadamia nut trees (*Macadamia integrifolia* Maiden & Betche), in São Mateus, Espírito Santo State (Pezzopane et al., 2010), in relation to other environments outside of the understory.

In the case of minimum air temperature in the understory, there was a difference between the areas only during ERS ($p=0.042$) (Table 1). Minimum air temperature in the understory was 0.16ºC lower in degraded area than in the mango orchard. Similar results were observed by Pezzopane et al. (2015), in São Carlos, São Paulo State, where minimum air temperature was 0.10ºC lower in the forest understory with less vegetative cover than the other. In areas with

less vegetation, minimum air temperature is usually lower, because having less vegetation facilitates the passage of longwave radiation (coming from Earth), leading to atmospheric cooling. This mainly occurs during the night, when the radiation balance is governed by longwave balance (Pereira et al., 2002).

Mean air temperature in the understory differed between the mango orchard and the degraded area only during LRS (p=0.041) and LDS (p<0.001) (Table 1). The mango orchard reduced mean air temperature in the understory by 0.37ºC in comparison to the degraded area. Similar results were observed in São Carlos, where average air temperature was reduced by 0.25ºC in the forest understory with more vegetation coverage in comparison with the other understory (Pezzopane et al., 2015). This was lower than the results found in Jussari, Bahia State, where the reduction of the average air temperature was 1.25°C in the understory of the forest areas and a shaded cacao crop (*Theobroma cacao* L.) (Pinheiro et al., 2013).

Table 1. Mean of the maximum, minimum and average temperatures, air temperature amplitude and vapor pressure deficit (mean ± standard deviation) in the understory of the studied environments, and analysis of variance, degrees of freedom of the residue, F, significance, and t test in four seasons of the year in Salinópolis, Pará.

Season	Environment		ANOVA	
	MO	DA	DF	F
		Maximum air temperature (°C)		
ERS	30.60 ± 0.67 A	31.73 ± 1.16 B	122	44.95***
LRS	30.30 ± 1.03 A	31.89 ± 0.45 B	107	38.95***
EDS	30.20 ± 0.43 A	31.33 ± 0.25 B	107	110.98***
LDS	30.73 ± 0.46 A	33.38 ± 0.38 B	101	366.30***
		Minimum air temperature (°C)		
ERS	25.62 ± 1.36 A	25.08 ± 1.17 B	122	4.22*
LRS	24.96 ± 1.25 A	25.01 ± 1.16 A	107	0.03^{ns}
EDS	24.49 ± 1.37 A	24.28 ± 1.03 A	107	0.38^{ns}
LDS	26.22 ± 0.54 A	26.28 ± 0.58 A	101	0.09^{ns}
		Average air temperature (°C)		
ERS	27.72 ± 0.89 A	27.61 ± 1.15 A	122	0.29^{ns}
LRS	27.43 ± 0.98 A	27.94 ± 0.69 B	107	4.29*
EDS	27.22 ± 0.67 A	27.45 ± 0.28 A	107	1.89^{ns}
LDS	27.88 ± 0.28 A	28.74 ± 0.24 B	101	103.47***
		Air thermal amplitude (°C)		
ERS	4.98 ± 1.00 A	6.65 ± 0.79 B	122	75.96***
LRS	5.34 ± 1.20 A	6.88 ± 1.21 B	107	23.48***
EDS	5.71 ± 1.47 A	7.05 ± 1.18 B	107	12.59**
LDS	4.51 ± 0.55 A	7.10 ± 0.53 B	101	236.32***
		Vapor pressure deficit (kPa)		
ERS	1.05 ± 0.31 A	1.05 ± 0.43 A	122	0.00^{ns}
LRS	0.86 ± 0.30 A	1.03 ± 0.19 B	107	4.92*
EDS	1.12 ± 0.13 A	1.22 ± 0.10 B	107	8.76**
LDS	1.30 ± 0.11 A	1.67 ± 0.14 B	101	120.06***

ANOVA: Analysis of variance; MO: Mango orchard; DA: Degraded area; DF: Degrees of freedom of the residue; ERS: Early rainy season; LRS: Late rainy season; EDS: Early dry season; LDS: Late dry season. The level of significance is indicated (*: p<0.05, **: p<0.01, ***: p<0.001, ns: not significant).

For air temperature in the understory, vegetation was the most important factor to soften

maximum and average air temperature (Figure 2). The influence of vegetative cover was greater during the diurnal period than during the nocturnal period, mainly in the late dry season, causing greater alteration in the maximum temperature than in the minimum (Figure 3), corroborating Pezzopane et al. (2010). Different intensities of tree cover systems influence the amelioration of microclimate as observed in this study; agreeing with the results obtained by Pinheiro et al. (2013) when the average air temperature in a forest understory area and a shaded cacao crop were compared.

Air thermal amplitude in the understory differed between the mango orchard and the degraded area ($p<0.001$) (Table 1). Smaller air thermal amplitude was observed in the understory of the mango orchard in comparison with that of the degraded area; air thermal amplitude was reduced on average by 1.78ºC. However, a greater reduction has already been observed during LDS (2.59ºC). The values of air thermal amplitude in the understory observed in our study (Table 1) were similar to those observed in other studies, varying on average between 0.72ºC and 2.40ºC (Pezzopane et al., 2010; 2015). Areas with vegetative cover act as thermal insulators, hampering the passage of heat brought by sunlight towards the ground, and reducing the variation in air thermal amplitude (Pereira et al., 2002).

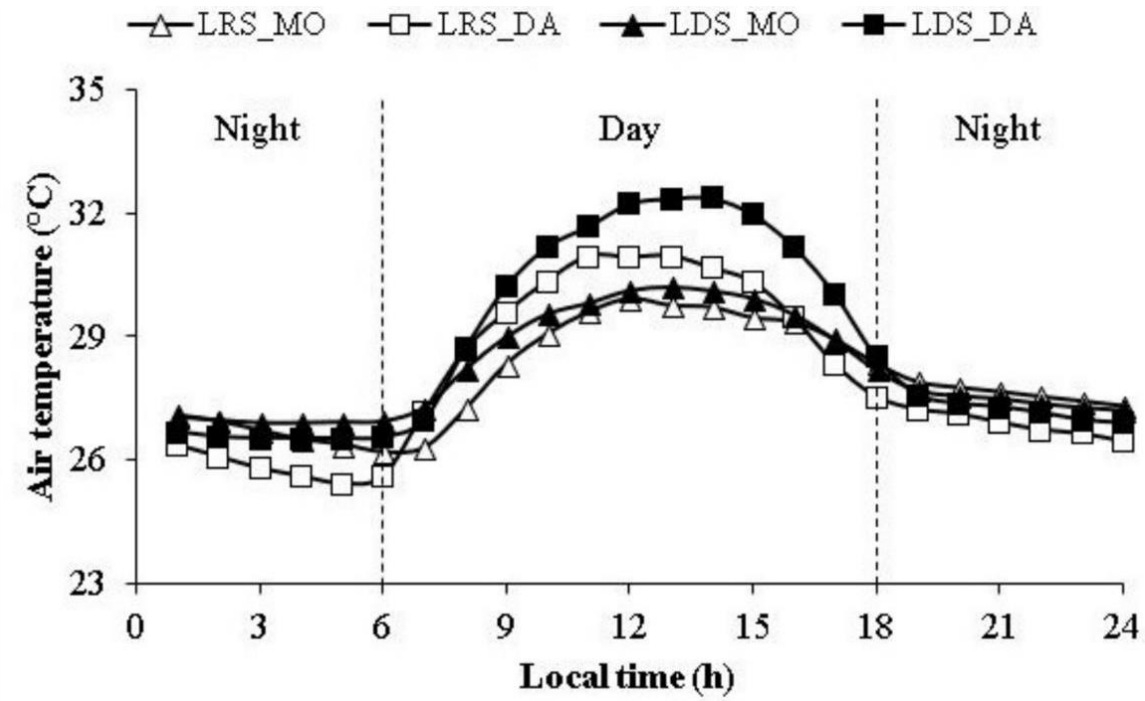

Figure 3. Average hourly average air temperature (T) in understories during the late rainy and the late dry season, in two environments, during daytime and night time, in Salinópolis, Pará. MO: Mango orchard; DA: Degraded area. LRS_MO: late rainy season in the mango orchard; LRS_DA: late rainy season in the degraded area; LDS_MO: late dry season in the mango orchard; LDS_DA: late dry season in the degraded area.

Variations in air temperature in the understory relates to the energy balance in the environment (Pereira et al., 2002). In the mango orchard, there is more vegetative cover than in the degraded area, and for that reason, the vegetation in the degraded area is not able to hamper the passage of solar radiation. Therefore, most of the radiation was probably converted into sensible heat, responsible for air warming, providing higher maximum and mean air temperatures, and higher thermal amplitude in the degraded area in comparison with the mango orchard. In this way, the mango orchard acts as a thermal insulator, providing greater thermal comfort in the understory, while in the degraded area, thermal insulation provided by the

vegetation is not so efficient. Because of this, the thermal discomfort in this environment is evident.

The vapor pressure deficit in the understory differed between both environments during LRS ($p=0.029$), EDS ($p=0.004$) and LDS ($p<0.001$) (Table 1). The vapor pressure deficit increased, on average, 0.16kPa in the understory of the degraded area compared to the understory of the mango orchard. The vapor pressure deficit presented higher values during LDS when compared to LRS in both environments (Figure 4), due to the higher demand of water from the atmosphere during LDS.

Lower values of vapor pressure deficit in mango orchard understory showed that, due to the greater aerodynamic resistance of the vegetation, the evaporating capacity of the air is reduced. The distribution of mango trees in the orchard creates a wind barrier. When this barrier is transposed, the wind enters the understory at a slower speed and with less power to affect the vapor pressure gradient between the evaporating surface and the air. Such a condition reduces the vapor pressure deficit in the understory of mango orchard, differing from what was observed in degraded area.

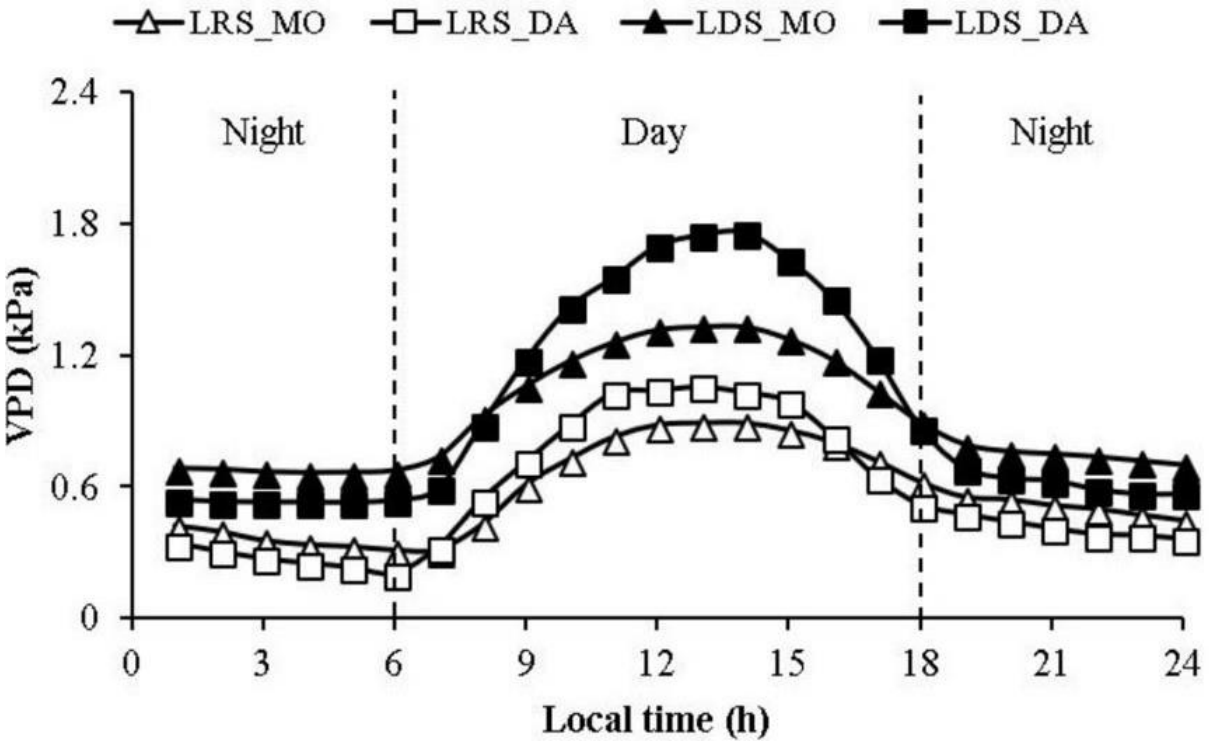

Figure 4. Demand average daily vapor pressure deficit (VPD) in the understory during the late rainy and late dry season, in two environments, during daytime and night time, in Salinópolis, Pará. MO: Mango orchard; DA: Degraded area. LRS_MO: late rainy season in the mango orchard; LRS_DA: late rainy season in the degraded area; LDS_MO: late dry season in the mango orchard; LDS_DA: late dry season in the degraded area.

Vapor pressure deficit in the understory observed in our study (Table 1) was in the range observed in other studies (0.34-1.38kPa) (Pezzopane et al., 2010; 2015). Afforestation promotes absorption of water vapor from the atmosphere in its understory, increasing air humidity, and providing thermal comfort. However, the excess water vapor in the atmosphere of the understory makes the environment uncomfortable.

4. CONCLUSIONS

The microclimates of the mango orchard understory and the degraded area understory differ, especially during the late dry season. The mango orchard ameliorates microclimate in the understory in comparison with the vegetation of the degraded area, mainly, due a reduction of maximum air temperature and air thermal amplitude, therefore providing the important ecosystem service of climate regulation. Mango tree orchards grown as rustic fruit trees and to soften the understory microclimate may be used as an alternative for the rehabilitation of degraded areas, since they provide ecosystem services, such as food production and climate control.

5. ACKNOWLEDGEMENTS

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Participatory guarantee system, equivalence and quality control in a comparative study on organic certifications systems in Europe and Brazil

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ABSTRACT

Although organic agriculture in Brazil targets mainly local consumers, there is growing demand for research related to commercializing this sector abroad. A study was done in Europe on the perception of entities related to this theme, specifically on Participatory Guarantee Systems (PGS), the feasibility of equivalence between the countries, and control procedures. An exploratory study was conducted through interviews with five organic certification bodies, two in Switzerland, three in Italy, and with a producer association in Italy. PGS is little known in Europe in general and it is suggested that it be better disseminated in the member countries. PGS has been evaluated positively for reducing certification costs and promoting benefits from a social aspect, but it can fail in organic compliance and in large scale production. There are significant differences that must be overcome in order to establish equivalence, such as the lack of homogeneity among European countries on control procedures, the existence of PGS in Brazilian legislation, lack of wild crop products in Europe, different conversion periods, and the requirement of a higher number of inspections in Brazil. Equivalence is seen as beneficial to both Europe and Brazil, and it would therefore be appropriate to promote its viability. The Brazilian law on organic agriculture is taken as very restrictive and complex.

Keywords: environmental sustainability, organic certification body, organic production systems.

Sistema de garantia participativa, equivalência e controle de qualidade em um estudo comparativo sobre sistemas de certificação orgânica na Europa e no Brasil

RESUMO

Embora a agricultura orgânica no Brasil atinja principalmente aos consumidores locais, há uma crescente demanda por pesquisas relacionadas à comercialização com o exterior neste setor. Uma pesquisa foi realizada na Europa sobre a percepção de entidades relacionadas a este tema, especificamente sobre Sistemas Participativos de Garantia (SPG), a viabilidade da

equivalência entre os países e os procedimentos de controle. Um estudo exploratório foi realizado através de entrevistas com cinco organismos de certificação orgânica, dois na Suíça, três na Itália e uma associação de produtores na Itália. O SPG é pouco conhecido na Europa em geral e é sugerido divulgar melhor nos países membros. O SPG foi avaliado positivamente para reduzir os custos de certificação e promover os benefícios de um aspecto social, mas pode falhar na conformidade orgânica e na produção em grande escala. Existem diferenças significativas para estabelecer equivalência, como a falta de homogeneidade entre os países europeus em procedimentos de controle, a existência de SPG na legislação brasileira, a falta de produtos do extrativismo vegetal na Europa, diferentes períodos de conversão e a exigência de um maior número de inspeções no Brasil. A equivalência foi considerada benéfica para ambos e seria apropriado fazer esforços para torná-la viável. A legislação brasileira sobre agricultura orgânica é considerada muito restritiva e complexa.

Palavras-chave: organismo de certificação orgânica, sistemas de produção orgânica, sustentabilidade ambiental.

1. INTRODUCTION

Due to the growing appreciation of products related to environmental sustainability, organic production systems have become increasingly more economically important in recent years. Global retail sales of organic food and beverages reached 81.6 billion dollars in 2015, a growth of about 10% over the previous year. Between 2000 and 2015, the market expanded nearly four times and such growth might still continue. North America and Europe consume the most organic products, about 90% of the total (Willer and Lernoud, 2017; Seufert et al., 2017). Specifically considering the economic dimension of organic production systems, resource constraints experienced by farmers regarding their production and commercialization are usually highlighted. Also, consumer need is often associated with product quality (Canavari and Olson, 2007). Consequently, providing a certification service becomes an important aspect of ensuring organic quality. Certification guarantees the confidence of those involved in the production system by making transparency in the system possible, just as with any other food system (Frewer et al., 2014). International audit certification plays a predominant role in production and organic trade. The basis of its operation is the periodic inspection on the rural property by an organic compliance body (ODC). Audit certification, also referred to as "third party", is based on the technical audit procedure. The audit can be broadly defined as a systematic procedure whereby an organization evaluates its practices and operations in order to ascertain conformity with certain pre-established criteria, and these criteria may be legal requirements. There is no universally accepted definition of the term “audit”, so the peculiarities of the activities to be audited must be observed. The addition of an audit procedure tends to raise the final cost of the organic product since it is run by a private organization that charges the certified operators for its services.

This has made it necessary to look for alternative systems for organic production systems certification, which has always given rise to discussion regarding its proper legal framework in each country. Regarding alternative organic certification systems in place of the audit system, several formal certification systems have been developed, such as internal control systems (ICS), which are mainly destined for export markets, full government certification, as used in Denmark, and participatory guarantee systems (PGS), aimed mainly at local markets. In terms of propagation, alternatives to third-party certification for compliance assessment are ICS and PGS, which were developed in parallel (Sacchi et al., 2015; Mikkelsen and Lundø, 2016; Nelson et al., 2015).

In Brazil, the legislation allows organic production systems two alternatives to the audit system, direct sales to the consumer, in which the certified product does not need to carry the organic seal and PGS, carried out by a Participatory Conformity Assessment Body (OPAC), certified and supervised by the Ministério da Agricultura, Pecuária e Alimentação - Ministry of Agriculture, Livestock and Food. The product certified by this system has the official national organic label (Brasil, 2012). PGS is a system based on the farmers' own ability to establish control and regulatory mechanisms in the organic production chain in order to comply with the general rules established by the national certification legislation. Thus, PGS does not necessarily depend on records and inspections to be carried out by a technician or external auditor in the production unit, as required by an audit procedure (Martinez, 2013).

The application of this system foresees that the ones involved assume a tacit and full commitment to the principles of organic production, as well as an active role in the supervision of all process levels. (Caldas et al., 2012; Home et al., 2017). However, PGS is not practiced in Europe due to the constraints of law. This is major problem in the organic certification of equivalence with Brazil, as organic quality control procedures differ between both. On the other hand, an increasing convergence between organic certification systems internationally is clear. Therefore, technical and conceptual procedures used in the control of organic quality in Brazil are becoming important, considering discussions to set criteria to establish equivalence for certification procedures with other countries. Taking into account only the case between Brazil and Europe, it is expected that approximation of the organic systems of quality certification might focus especially on the standardization of the main theoretical and regulatory frameworks; equivalence between the two systems would be a natural consequence of that approach.

This study explored the opinions of institutions in Europe, which operate with the certification of organic agriculture, and focused on topics such as PGS, equivalence of certification and organic quality control procedures. It also discusses practical applications of research in Brazil.

2. MATERIALS AND METHODS

Using a survey as a technical procedure, a study was carried out using a qualitative approach. Its results should be interpreted as exploratory, as further quantitative research is planned for the future. As a sampling design, two European countries were selected, Italy and Switzerland, which have different profiles, the first one belonging to the European Union and the second not. The institutions studied in Italy were: ProB.E.R. - Associazione Produttori Biologici e Biodinamici Emilia Romagna (Organic and Biodynamic Producers Association of the Region of Emilia-Romagna) and the ODCs IMC - Mediterranean Institute of Certification, ICEA – Istituto Certificazione Etica e Ambientale (Institute of Certification in Environmental Ethics), CCPB – Controllo e Certificazione (Control and Certification). In Switzerland the ODCs studied were: FiBL –Research Institute of Organic Agriculture and Bio-Inspecta. The study was conducted by obtaining data on the opinion of professionals appointed by those institutions. The selection of institutions was carried out by researchers from the Agrarian Science Department of the Agrarian College of the University of Bologna, Italy. A structured questionnaire was created for the interviews with ten questions, which were applied in the same way in six interviews in the form of monologue, with each interview lasting approximately one hour and a half. The research covered the following topics: European certification systems, laws and regulations, sanctions, incentives, packaging and labels, marketing and sales, participatory guarantee systems (PGS), control procedures and possibility of equivalence. For the present study, only the last 3 topics were considered the most relevant. Six English translations of documents were obtained, each of which was considered as a datum for a qualitative analysis,

which is an adaptation of the research model carried out by Molteni and Troilo (2003). The qualitative analysis used is considered adequate, and it is prevalent in publications related to the organic food market, including the issue of environmental certification (Dias et al., 2015). From the contents of each interview an individual interpretation of three selected topics was made, considering the context thereof and their integration in the European Union, Italy, Switzerland and Brazil. Data were collected from January to June 2013 in Bologna, Italy and Frick, Switzerland.

3. RESULTS AND DISCUSSION

The results consist of the notes made by the interviewers and are presented separately in the two sampling sites, namely Italy (Table 1) and Switzerland (Table 2). Each site is separated into 3 study topics (Participatory Guarantee System, Equivalences between the two systems of Organic Quality Control). As instituições ProB.E.R. (Organic and Biodynamic Producers Association of the Region of Emilia-Romagna), IMC (Mediterranean Institute of Certification), ICEA (Institute of Certification in Environmental and Ethics), CCPB (Control and Certification), FiBL (Research Institute of Organic Agriculture) and Bio-Inspecta will be referred to in the discussion respectively as ProBER, IMC, ICEA, CCPB, FiBL and Bio-Inspecta.

3.1. Considerations in Italy on Participatory Guarantee System (PGS)

The interviewees were unanimous in stating that PGS is beneficial for Brazil, and that its main advantage is to reduce the final cost of organic product, as long as inspection is done on a voluntary basis (Table 1). This point is worthy of note, since the assertion that PGS reduces costs is historically the main reason for its creation and implementation as guarantee of organic quality. This is consistent with the assertion from many authors who claim that this occurs in Brazil and foreign countries (Sacchi et al., 2011; Corsi, 2012; Dabbert et al., 2012; Home et al., 2017).

Thus, PGS may represent a way to also lower certification costs in Europe, especially for groups of small farmers' direct sales or short chain. In addition to lowering costs, the participatory certification system has the additional advantage of ensuring consumers organic quality while enabling small farmers to avoid the consequent difficulties of audit certification (Home, et al., 2017). Although PGS is known for reducing the final cost of organic certification, there have been efforts with audit certification that aim work around this problem through inter institutional cooperation. In Paraná state, for instance, Programa Paranaense de Certificação de Produtos Orgânicos (PPCPO) - Paranaense Program for the Certification of Organic Products - provides organic farmer certification free from charge by means of university outreach. The same involves state public universities, Instituto de Tecnologia do Paraná (TECPAR) - Paraná Technology Institute - and state government (Cavallet et al., 2013). Another point regarding PGS made by interviewees, mainly by the Institute of Certification of Environmental Ethics (ICEA), is that participatory certification creates confidence in the quality of the product, in addition to facilitating the creation of a marketplace. This position is important as most of the other respondents pointed out that PGS promotes an increased risk of non-compliance with organic quality.

On the other hand, ICEA and ProBER interviewees were in Brazil and experienced the field procedures of this system. This is possibly related to the fact that the ICEA interviewee also stated that PGS increases credibility in organic quality assurance. This may demonstrate that on-site verification of the application of PGS certification procedures by organic operators enhances the credibility of the quality assurance system.

Table 1. Points made by interviewees in Italy on the organic production system used in Brazil and Europe, addressing the topics of participatory certification, equivalence between the two systems, and the control of organic quality.

Topics	Main Points
Participatory Guarantee System (PGS)	-Decreases the certification cost and has greater civil participation -Creates confidence in product quality -Increase risk of non-compliance with organic quality -Promotes healthy relationship between social factors and the property -Has meaningful differences from the European system -Is considered as a self-certification -Does not allow large-scale production -Is suitable for Brazilian and Latin American reality -Is practically unknown in Europe
Equivalences between the two systems	-Define a strategy to overcome the differences between the two systems -Obtaining an agreement will depend on political efforts of both parties. -Favors that 95% of the inputs are the same in both systems -Equivalence is beneficial for both countries
Organic Quality Control	-All items are checked at least once a year -Control cost is high, but it is more efficient -Control efficiency is related to the technical assistance to producers -Intensity of inspections is made according to the level of risk -No homogeneity of procedures between control bodies -No uniformity of procedures between countries -Updating of knowledge for the auditors is done only once a year -Lack of training regarding the main risks -In general, there is lack of uniformity of procedures -Should take advantage of Brazilian experience with its new regulations

In addition, ICEA qualified participatory certification in a positive way, as it promotes the efficient use of the territory and social interaction among farmers. The advantage on social aspect attributed to PGS is consistent and well founded, as it promotes empowerment for groups of farmers who base their activities on lasting social processes, strengthening their connection with their local communities. This way, the combination of tradition and upward collaboration within social structures at a local level allows this type of certification to overcome its challenges and guarantee its future as an alternative system to audit certification (Home et al., 2017). On the other hand, the interviewees also raised some unfavorable points for PGS. For example, the IMC interviewee asserted that it does not allow the farmer to have an individual operator certificate in the organic sector because the certificate is issued to the institution to which he belongs. The ProBER observed the PGS' impossibility with the production of large quantities, which would be required for import and export. Finally, CCPB asserted that PGS is considered a self-certification and could fail as an organic quality guarantee, and the organic world market would hardly accept it as a certification system. Nevertheless, such points were not unanimous among the interviewees, as well as among some authors who claim that PGS could be convenient to Europe, suggesting that PGS illustrates an example of a certification system to improve the current organic certification systems in Europe (Dabbert et al., 2012).

3.2. Considerations in Italy on equivalence

ProBER., IMC had the majority opinion of the interviewed professionals, in that there are many problems that equivalence of certification systems for organic products between Brazil and Europe may engender (Table 1), but equivalence must be sought. According to the ProBER interviewee the equivalence between countries will only be achieved if they have the same control system and currently this does not occur. The main problem is the existence of PGS in Brazil, which is not included in European legislation. IMC interviewee stated that

"... international relations that could unite Brazil and Europe in an equivalence regime and facilitate trade between Brazil and Europe without requiring double certification", and also that "There are still conditions that make it difficult to recognize, and consequently there is a need to certify the product twice." This type of difficulty is due to the specific characteristics of the certifications of conformity for each country, as pointed out by Alves et al. (2012), It is neither simple nor quick to enact regulations to make the products subject to mandatory certification. Instead, it is a systematic process in which procedures require an appropriate legislative framework, as well as adequate technological infrastructure and cooperation from every party involved. In addition, the product certification process requires participation of different professionals in the organic production sector, which is one reason for the slowness of process. While there may be significant differences in the legislative framework, there is the fact that the European legislation led to the installation and development of the framework of an organic quality control system in Brazil. It follows that 95% of agricultural inputs are the same in both countries. This is a technically favorable feature of obtaining equivalence. The CCPB interviewee mentioned that it would not be difficult for equivalence to be achieved, when he used the expression "Therefore, I do not see great barriers to the fact that European and Brazilian legislation can be considered equivalent." The ICEA interviewee was the most optimistic about this issue and even stressed that the present research would be important for this.

This type of research can be very useful in order to reinforce the achievement of a treaty of possible equivalence between the European Union and Brazil. " He even volunteered to work personally with the ministries of agriculture and foreign affairs in Italy to request assistance for this cause. Therefore, the opinion was unanimous that it is important to establish the equivalence of organic certification between Brazil and Europe. While there are problems to be overcome, efforts should be made to accomplish it.

3.3. Considerations in Italy on the organic quality control system

Regarding the procedures of organic quality control, all of the interviewees had similar views regarding the technical aspects existing in Italy. The CCPB interviewee talked about it, saying that in Italy the control bodies (ODC) must be registered with the national accreditation body. After approval, the Ministry of Agriculture and Forestry delegates the supervision of the control of private bodies to the Inspection of Food Quality Control and to the 20 provincial governments and 2 autonomous governments. This report is consistent with Dabbert et al. (2012). In addition, the production, processing and distribution of the organic sector in Italy and Europe must be checked at least once a year. Thus, it is argued that the control cost is higher than in Brazil. On the other hand, these procedures are more effective for the control of organic quality (Table 1). In Italy, there is a need for an increasing number of assessments according to the risk of non-compliance, therefore inspections are on average 1.3 to 1.4 times a year. There are inspections at all levels within the production chain, from seed to sales. On the other hand, there is no checklist of equal items for all ODCs; each has its own list. This means that, in Italy, the technical inspection process in organic production units may vary from region to region, which is also observed by Genaro and Roselli (2008). This may be an indication that the European organic quality control system has problems with lack of harmonization of procedures among its countries. In Italy, professionals qualified to control organic quality can be from agronomy, agrarian sciences, cartography, agricultural engineering, biology, chemistry and natural sciences and must participate annually in technical updates. Thus, the CCPB interviewee states that risks with organic non-compliance are considered to be associated mainly with lack of harmonization of procedures, lack of inspectors´ professional preparation and lack of availability of minimally sufficient technical information. Also, as stated by ICEA and ProBER, it is important for Europe to work together with Brazil on their respective experiences in organic

quality control, since the Brazilian experience can help to make European legislation in this sector more appropriate and consistent. This would be convenient not only in terms of control procedures, but also in relation to the performance of public ODCs accreditation bodies. The IMC respondent further stated that the cost of organic quality control in Italy is higher, but considers it more complete and efficient. Thus, he pointed out that "Therefore, confronting the two control systems they do not have the same effectiveness, because in Europe the control is much more punctual compared to the control that is practiced in Brazil, where on the contrary the Internal Control System is applied". The author of the IMC has always referred to the participative system with the technical name of "Internal Control System", and affirms that the existence of the PGS in Brazil is the main item that makes it difficult for an approximation between the two countries regarding the harmonization of technical control procedures. The ICEA interviewee added something relevant when he said that "If it a dialogue for equivalence were to start, it would be very important to understand how it works, whether it is the activity of controlling the certification or the supervisory activity of the competent Brazilian public bodies." On the other hand, the ProBER interviewee, who said that he worked for more than 20 years with organic producers, did not highly value the effectiveness of the means of control for organic quality assurance, citing that "... because it is clear that if one wants to do an organic management in the easiest way, that is, he does day and night management with not allowed chemical control, for this farmer control does not suffice one inspection per year." He added that "Perhaps one inspection each month would not be enough". He also stressed that more important than the control system is the availability of technical assistance to the farmer, because " without adequate technical assistance it is better not to do organic farming." He also thinks that more important than the control system would be to know how the farmer thinks, the physical conditions of the location of his unit of production, and what are the unit's main problems. It should be noted here that this vision of the ProBER interviewer departs somewhat from conventional certification, where the control procedure is based on annual inspections, and reminds more the approach of participatory guarantee. One might even argue that it fits within the broader context of organic agriculture, which is the agroecological approach, as Cotrim and Dal Soglio (2016) argue.

3.4. Considerations in Switzerland on PGS

Responders from both institutions (FiBL and Bio-Inspecta) did not go as far on issues related to participatory certification as the responders in Italy did. However, it was also indicated that "this system is profitable for the Brazilian reality, but it is unlikely to be accepted in Europe in the near future" (Table 2). In addition, "it is suitable for the local market, but not for the export market. Retailers accept it, farmers want it and also some local consumers, but the big sales mechanisms do not, because they consider it to be a step backwards in relation to the credibility of organic quality". According to these notes, it is reasonable to assume that a large volume of sales of organic product is not important for Brazilian consumption. In Brazil, there are local and regional consumption chains, which do not include the large supermarket chains. Thus, the operators are not interested in a large amount of sales of these products, either for ideological reasons, or due to the structure of the system itself (Rover, 2011). However, there is a lack of product at the international level, so that one of the great challenges today for organic agriculture is increasing the supply of organic products. Therefore, large-scale production of these products is something that every producing country should consider, whether or not they are exporters (Willer and Lernoud, 2017). However, the responder from FiBL also mentioned that "in Europe PGS is not well known and its terms have not yet been discussed. So it probably will take a long time for it to be recognized in Europe as an organic certification system". They said that such difficulty increases, given that Europe usually takes more time to make decisions on the commercial sector. Due to this, it was suggested that efforts

be taken "to promote in Europe greater PGS dissemination practiced in Brazil". This suggestion is important for the Brazilian organic sector, insofar as this strategy could tackle other problems related to the acceptance of this system, such as the mistaken view that it will necessarily induce a lack of credibility in organic quality.

The responders in Italy also said that PGS could help the European organic certification system itself, since it is characterized by being constantly discussing its internal structure (Dabbert et al., 2012). A probable reason for lack of knowledge of PGS in Europe is due to the way in which other organic certification systems have emerged and continue to operate within it.

This aligns with Caldas et al. (2012), who studied the lack of successful implementation of PGS in the region of Andalusia, Spain and concluded that one of the reasons for this failure is the existence of audit certification, which is the only way to guarantee the organic quality for farmers interested in selling organic products. Therefore, unlike PGS, it is clear that organic production systems certification by audit is of great importance in the European context. However, this may fail to assess the social dimension. For example, Nowacki et al. (2009) tested the methodology in rural properties in Paraná state, Brazil, to test specific state legislation on compulsory environmental auditing.

Table 2. Points made in Switzerland on the organic production system used in Brazil and Europe, addressing the topics of participatory certification, equivalence between the two systems, and organic quality control.

Topics	Main Points
Participatory Guarantee System (PGS)	-Does not exist in European legislation for organic products -Contributes to discredit the organic certification seal -Will take a long time to be accepted in Europe -Makes it difficult to set equivalence with other countries -Impairs the export of Brazilian organic products -Is beneficial to Brazil and other Latin American countries
Equivalences between the two systems	-In Brazil the legislation is very detailed when compared to the European legislation -In Brazil, the legislation appears to show equivalence with other countries -Too much detail hinders the viability of equivalence with Europe -The existence of participatory certification is the main problem -Will be hampered by the slow pace of policy decisions in the European Community -Brazil is said to have very protectionist market policies -Certifiers can request individual recognition in Europe - It is suggested that Brazil set equivalence with countries which already have it with Europe -Seek equivalence with Latin American countries -Simplify the control system aiming at the establishment of equivalence - Current need for recertification is for both countries
Organic Quality Control	-Switzerland has a less-complex control system than Brazil -In Europe, there are both system modes (public and private) -In Denmark it is public, in Germany it is private and in Spain there are both -In Europe, the inspection is made by the country where they are headquartered -The control body must be accredited by the Ministry of Agriculture -Once accredited, they must report to the European Union -In Europe, the operator must be inspected at least once a year -In Brazil, the organic operator must be inspected at least twice a year -In Europe, there are two types of organic seal, one for the public and another for the private -In Europe, private seals are considered more reliable -In Europe, private seals are more detailed due to the requirements of the legislation -In Brazil, the control system is much more restrictive than in Europe

They observed that it proved quite sensitive regarding legal obligations and polluting potential, but it was not enough to assess the social dimensions of the agrarian environment, and was therefore an instrument geared to the legal environmental aspects. Thus, the verification of the conformity of a normative criterion through an audit may fail when it comes to the social aspects. This may be an indication that the audit procedure applied to organic production system may fail to verify criteria linked to what is socially fair, which is one of the three pillars of sustainability. This justifies the inclusion of PGS as this, as alternative to the certification system audit, may be more conducive to sustainability due to being more sensitive to the social dimensions of the agrarian environment.

3.5. Considerations in Switzerland on equivalence

Several points were raised in Switzerland on equivalence, including many already declared in Italy, especially with respect to meaningful differences between the two systems (Table 2). Differences such as: lack of standardization of procedures in Europe for organic certification in wild crop production, as well as the conversion period in Brazil, which is much more restrictive than in Europe. Another claim deals with how detailed Brazilian legislation is and the fact that the farmer must register all the inputs entering the farm. It was also pointed out that the technical regulations for organic quality control in Brazil have many secondary documents such as standards, technical guides and forms. This latest note is certainly related to third party organic certification, for on the other hand PGS in Brazil does not present itself as excessively bureaucratic in its structure. Nelson et al. (2015) emphasize that aspect of PGS, and also point that excessive bureaucracy in third party for certification can act as a barrier to small producers seeking to take part in the organic market. Therefore, the PGS simplified internal structure can help to reduce the problem of significant divergence between Brazil and Europe, as it considers the Brazilian model of organic certification too bureaucratic in general. To that end, Switzerland stated that Brazilian law on the organic sector appears to have been drawn up aimed at easy recognition and equivalence with several countries, because it is very detailed and presents itself as prepared to achieve equivalence with several markets. However, this situation makes it difficult for Brazil to import European organic products, as well as ingredients and processes. Therefore, excessive restriction in regulating the organic sector facilitates exports from Brazil to other countries, but that makes it difficult to import from Europe. It follows that the only way for a company in Europe to export some organic products to Brazil is to contract with a Brazilian certification body and recertify the entire procedure. For example, Switzerland exports chocolate and sugar products to Brazil, but it is mandatory to recertify them. The statement on the need to recertify European products to export them to Brazil is appropriate, when it is based on the regulatory framework COAGRE 11/2012 (Brasil, 2012). It establishes procedures for organic product registration, labeling and internalization. Also, in Italy it was mentioned that such regulatory framework reduced the possibility of trade between Europe and Brazil in the sector. In fact, a recertification procedure for organic products increases their final cost. In part, this may have the effect of limiting the development of the Brazilian domestic market for organic products due to the limitation of imports. At that point, the equivalence would be suitable for Brazil once it increased domestic trade of imported products at a lower cost due to eliminating the need to recertify. On the other hand, it was stated that equivalence would pave the way for the export of Brazilian organic products, mainly animal feed, since there is no such raw material in Europe. Another important issue pointed out in Switzerland was the conversion period. In Brazil, this is established by ODC and varies according to the type of agriculture, the previous use of the place of cultivation, and also considers the current ecological and social situation. However, a minimum period of 12 months of organic management is established for crop production of annual crops, 18 months for perennial crops, and at least 12 months of organic cultivation or settling are established for perennial pastures. In Europe, the conversion

period is not as detailed and, different from Brazilian law, it does not consider the social situation of rural property (Brasil, 2011; European Community, 2007). There are clear points where both systems differ. For example, in Europe, the conversion period cannot begin before the day on which the control body begins to register the production unit. In Brazil, this may be possible, since some official body, such as EMATER, for example, provides a document certifying that the farm already has all organic management conditions from certain dates before the initial registration. Still, it was observed that in order to obtain equivalence between Brazil and Europe there should be some meaningful political effort on both sides. Such an attitude has been important for the regulation of the organic sector, at least in Brazil, since the discussion of the relationship between organic agriculture and agroecology has always been in political dispute, since it defines principles, association criteria and even scientific legitimacy (Abreu et al., 2012). Finally, it was mentioned that any organic certification body in Brazil can apply for recognition particularly to Europe, whether inside or outside the country. For this, one must present their standards and control system to the registration body in the intended country, and the latter must check for conformity between both systems.

On the other hand, an important structural principle of PGS is that consumers should be included in the inspection process. For the present case, one of the biggest challenges regarding equivalence is how this can happen when physically they cannot reciprocally visit production units because of distance. It is observed that none of the interviewees of the 6 entities interviewed in this study (ProBER, IMC, ICEA, CCPB, FiBL and Bio-Inspecta) mentioned anything about this aspect. Possibly they did not because this kind of information would have been technically very specific and went unnoticed. Entities in Switzerland have probably not done so because they have been opposed to the PGS from the outset since the current European law for the sector does not allow it, so there would be no reason to dwell on technical details of the subject. It is also possible that, as the PGS is little known in Europe, the respondents did not have in mind the clear relation of this technical aspect to the question of equivalence. But it is considered opportune to make some speculation as to how this kind of problem could be solved or, at least mitigated, by assuming that the equivalence between the two countries had to be consolidated. As mentioned previously, the feasibility of on-site verification of the application of PGS certification procedures in Brazil by representatives of consumers in the organic sector in Europe could be a way forward. This is reinforced when one realizes that the ICEA interviewee who was in Brazil experienced the field procedures of this system and concomitantly stated that the PGS increases the credibility in the organic quality assurance. It is very likely that it would not be very different for consumers, or representatives of these. Another way that could be proposed to approach the distant consumer would be to use hierarchy management structures of a more general level within a given certification body. One example is the Ecovida network, one of the largest certifiers with PGS in Brazil. According to Martinez (2013), within the Ecovida network the farmers' associations are small, usually have between 5 and 10 members and decide how they want to make their system of meetings and visits. At a second level, by geographic area, what is defined in the network are the Regional Centers, which are composed of several producer associations, some technical assistance NGOs and some groups of consumers that meet periodically. The latter also establish their own methodology for conducting visits. From the Regional Core, an Ethics Board is formed, which will analyze the available information on farmers to decide whether or not to grant them the seal of the network. Thus, local consumers participating in the Regional Centers and the Ethics Council could be used as potential actors for European consumer engagement in the inspection procedures.

3.6. Considerations in Switzerland on the organic quality control system

With respect to the organic quality control system in Europe, the FiBL responder said that it is considered simple when compared to the Brazilian one, except in Germany where it is more complex (Table 2). There is a norm that regulates the control bodies for certifications in general, including organic production systems, and it establishes the operating requirements. There are basic requirements that are checked with annual inspection, according to the main rules that establish how the control should be done. As did the responders in Italy, they emphasized that two annual inspections are required in Brazil, which means "a significant difference to the European system where, in general, only one inspection is needed". The responders from FiBL said that in Europe there are two types of organic control systems, public or private, and some countries have only the private system and some have both. For example, Spain has both systems, Germany and Italy have only the private control system, and Denmark has only the public one. The case in Denmark stands out for the present study, in which organic quality assurance is part of a public certification system for food services including organic products in the menu, along with a sales volume monitoring system and a training of food service workers. Such importance increases as public agencies and institutions in Europe are considered to be quite influential in general by pointing to more appropriate ways of food consumption through government purchases (Mikkelsen and Lundø, 2016). As with the responders in Italy, regarding the supervision of organic quality control bodies, they said that it is public in every country and also accountable to each country internally. The accreditation body belongs to the ministry of agriculture, which records and decides whether to accept the private ODC or not. Once accepted, each ODC must report directly to the European Community. In this way, FiBL said that "the whole system has a simple structure, where basic requirements serve to guide organic quality control". There was an emphatic statement on the question of the organic product label from the Bio-Inspecta responder. For example, in organic products the European label has different laws for public and private control bodies. For private brands, the law is more restrictive and establishes the need to present more details about the products. As a result, consumers tend to rely more on private labels. Therefore, the more detailed the label, the more useful it will be in organic quality control as a whole. Thus, he said that "the private labels may contribute to greater control of organic quality". Regarding this subject, Zorn et al. (2012) said that for the private inspection bodies' supervision, it is necessary to guarantee an equal minimum level of control intensity in a competitive market environment, as in Europe. Finally, both responders pointed out emphatically that "Brazil has a very detailed and very restrictive legislative framework that guides the regulation of organic production systems". This may be true if the evolution of the regulatory system that has occurred in the country since its inception in the 1970s is observed, as described by Alves et al. (2012), as presented previously. However, over-regulation does not always align with the fundamental principles of organic agriculture. Darnhofer et al. (2010) studied organic agriculture in Europe focused on the production unit level related to compliance regulations. Although organic agriculture certainly has the potential to meet the expectations of organic food consumers, the authors have shown that some certified organic production units cannot. This is because their practices often comply with regulations, but not with the principles of organic agriculture. This trend has been called the "conventionalization" of organic agriculture. In addition, they argue that it is not enough to focus on structural changes to properly understand the dynamics within organic agriculture and its potential impact on the ability to meet the expectations of consumers and decision makers. Instead, it needs to assess whether the observed changes are or are not being met in accordance with the principles and values that are the foundation of organic agriculture. Thus, it can be assumed that over-regulation in Brazil may not make sense at all when related to the principles of organic agriculture. On the other hand, this statement values PGS, in which the theoretical basis is close to deregulation. This could be another argument in favor of the fact that the

approximation between the system of control of the organic production systems between Brazil and Europe could bring benefit to both, from the point of view of its constant improvement.

4. CONCLUSIONS

The participatory organic quality guarantee system (PGS) is seen in Europe as attractive because it reduces the final cost of the product and also promotes the social integration of local communities. However, there are unfavorable aspects, such as the fact that PGS is not feasible for large-scale production and that its procedures may incur an increased risk of organic non-compliance. However, the position that PGS creates a risk of organic non-compliance was not unanimous, since there were conflicting opinions, which suggest that PGS can create confidence in the quality of the product and also facilitate marketing. In Europe, PGS is not well understood and it would be important to develop a strategy to promote a better understanding of its benefits. This procedure could even assist the improvement of European legislation for this sector. The equivalence between both organic certification systems was considered economically beneficial for both countries. However, there are meaningful differences that make it potentially difficult to establish, such as lack of standardization of regulations among member countries and lack of organic certification for wild crop products in Europe. Also, in Brazil there are the existence of PGS, the existence of different conversion periods, greater number of inspections in the production unit, and excessive detailing of the legislation in the sector. In general, it is seen that Europe is aware of Brazilian reality regarding the context of social inclusion that involves organic production systems. This suggests that Brazilian organic products can be disseminated in Europe with more emphasis on being socially fair, economically viable and environmentally friendly.

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Environmental performance of a full-scale wastewater treatment plant applying Life Cycle Assessment

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ABSTRACT

Life Cycle Assessment (LCA) was applied to estimate and analyze the environmental impacts from the construction and operation phases of a full-scale wastewater treatment plant (WWTP) located in the municipality of Lauro de Freitas, Bahia, Brazil. The WWTP process consists of the association of an Upflow Anaerobic Sludge Blanket (UASB) reactor followed by four constructed wetlands (CWL) and a disinfection step. The functional unit was defined as one cubic meter of treated effluent during the useful life of this WWTP (20 years). The LCA was carried out using SimaPro® software and the Centre of Environmental Science (CML) assessment method. The environmental impacts during construction phase were mainly from the wooden forms for concrete and the use of reinforcing steel. During the operation phase, the chlorine used as effluent disinfectant caused the greatest impacts in the abiotic depletion and acidification categories. Macronutrient concentrations present in the treated effluent and the methane generated also caused significant environmental impacts during the WWTP's useful life. The results obtained highlight the importance of the application of a methodology like LCA to assist in decision-making with regard to the implementation, construction and operation of a WWTP.

Keywords: life cycle assessment, UASB reactor, wastewater treatment.

Desempenho ambiental de uma estação de tratamento de esgoto em escala real aplicando a Avaliação de Ciclo de Vida

RESUMO

A Avaliação de Ciclo de Vida (ACV) foi aplicada para quantificar e analisar os impactos ambientais oriundos da construção e operação de uma estação de tratamento de esgotos (ETE) localizada no município de Lauro de Freitas, Bahia, Brasil. O processo de tratamento consiste de um reator UASB seguido de quatro *wetlands* construídos e uma etapa final de desinfecção. A unidade funcional foi definida como um mero cúbico de esgoto tratado durante a vida útil da ETE (20 anos). A ACV foi realizada por meio da utilização do *software* SimaPro® e o método de avaliação de impactos escolhido foi o CML. As fôrmas confeccionadas com madeira tratada e o aço CA 50 apresentaram maior potencial de geração de impactos ambientais para a fase de

construção. Já na fase de operação, o uso do cloro como desinfetante resultou em maiores impactos nas categorias de depleção abiótica e acidificação. A presença de macronutrientes e a geração do gás metano, também, foram responsáveis por significativos impactos ambientais durante a vida útil da ETE. Os resultados demonstram a importância da aplicação de metodologia de avaliação de impactos ambientais como a ACV de modo a auxiliar na tomada de decisão para as fases de implantação, construção e operação dessas ETE.

Palavras-chave: avaliação de ciclo de vida, tratamento de esgotos, reator UASB.

1. INTRODUCTION

Wastewater treatment plants (WWTP) are designed to protect public health and minimize the environmental impacts of discharging untreated wastewater into natural aquatic systems. However, different WWTP have distinct performances and generate direct environmental impacts like any process that uses natural resources. Some WWTPs consume high amounts of energy, use chemicals and materials which have a high embodied energy (e.g. plastics), occupy large land areas, produce and release greenhouse gases and generate significant amounts of biological or chemical sludge (Corominas et al., 2013).

Therefore, the goals set for a specific WWTP need to move beyond the protection of human health and surface waters to include minimizing the loss of scarce resources, reducing the energy, water use and waste generation, besides enabling the recycling of water and macronutrients.

Life Cycle Assessment (LCA) has already been proven as a valid methodology to assess the environmental performance of WWTPs worldwide. Using a whole-process approach and addressing all relevant environmental impacts over the WWTP's useful life, the LCA allows an assessment that goes beyond the usual trade-off between treatment efficiency and effluent quality standards (Corominas et al., 2013; Risch et al., 2014; Zang et al., 2015).

The LCA methodology is able to measure and correlate the raw materials used, chemicals consumed, the quality of treated effluent, the biological or chemical sludge generated, gaseous and particulate matter emissions to one or more indicators characteristic of specific environmental impacts such as abiotic depletion or acidification of aquatic environments. These categories of environmental impacts are selected by the researcher to answer the objectives of their studies. Corominas et al. (2013) published a critical review of the literature about the application of the LCA methodology to evaluate the environmental impacts of wastewater treatment worldwide. The authors reviewed papers published between 1996 and 2012 and did not mention any Brazilian reference. Therefore, we can conclude that LCA studies in WWTPs are very incipient and scarce in Brazil.

One of the most critical points in an LCA study is finding reliable and specific data. The lack of reliable data on the input and output flows of the processes may lead to restrictions and cause uncertainties in the result and consequently an underestimation of environmental impacts (Opher and Friedler, 2016).

The aim of this paper was to evaluate the environmental performance of a full-scale WWTP located in *Bahia* state, Brazil, applying LCA methodology for the construction and operation phases. We also present a detailed Life Cycle Inventory (LCI) and the Life Cycle Impact Assessment for this specific WWTP.

2. MATERIAL AND METHODS

The object of this study was a full-scale WWTP designed for approximately 1,000 people, located in *Lauro de Freitas* city, *Bahia* state, Brazil. It has been operating since 2008 and

consists of an Upflow Anaerobic Sludge Blanket (UASB) reactor followed by four constructed wetlands (CWL) and a disinfection step with the application of sodium hypochlorite solution (NaOCl) in a contact basin.

The UASB reactor (3.8 x 3.8 m x 5.1 m), which corresponds to a cross-section of 14.4 m², has an effective volume of 73.6 m³ and hydraulic retention time of 8.5 hours. The CWL consists of four parallel gravel-based cells, each 7.0 m × 18 m, with horizontal subsurface flow through a depth of 0.8 m. Two cells were planted with *Typha sp*. and the other two were planted with *Cyperus alternifolius sp*. The design flow rate is equal to 96 m^3 per day. A low-power electrical pump adds the sodium hypochlorite solution for disinfection.

In our work, the LCA was carried out using SimaPro® 8.0.1 PhD version. Data were collected from previous research, the construction project, operation reports of the WWTP and laboratory analyses. Pump specifications and properties of the construction materials were obtained from the websites of manufacturers and building materials suppliers. Inventory data were connected with processes of Ecoinvent® databases.

This study uses the CML 2 baseline 2000 Life Cycle Impact Assessment method that has been frequently used. Four impact categories have been chosen: abiotic depletion, global warming, acidification and eutrophication. The choice of impact categories was based on data availability and significance, i.e., these impact categories are related to the performance of the WWTP and are also those most frequently analyzed in similar studies.

The system boundary is limited to influent wastewater to the treatment plant until effluent is discharged into water bodies. The LCA focused on the construction and operation phases. Dismantling has been excluded, because the impact would be tiny compared to the construction and operation phases and this has been omitted in several LCA studies of wastewater treatment plants (Foley et al., 2010; Fuchs et al., 2011; Lopsik, 2013; Larrey-Lassale et al. 2017; Larsen, 2018).

Two system boundaries were defined. The first plan included a quantitative inventory of the WWTP (e.g. direct atmospheric emissions, effluent discharges). The second plan boundary was based on data from the Ecoinvent® database (e.g. construction materials production, chemical manufacture and electricity generation) available in SimaPro® (Figure 1), for the construction and operation phases.

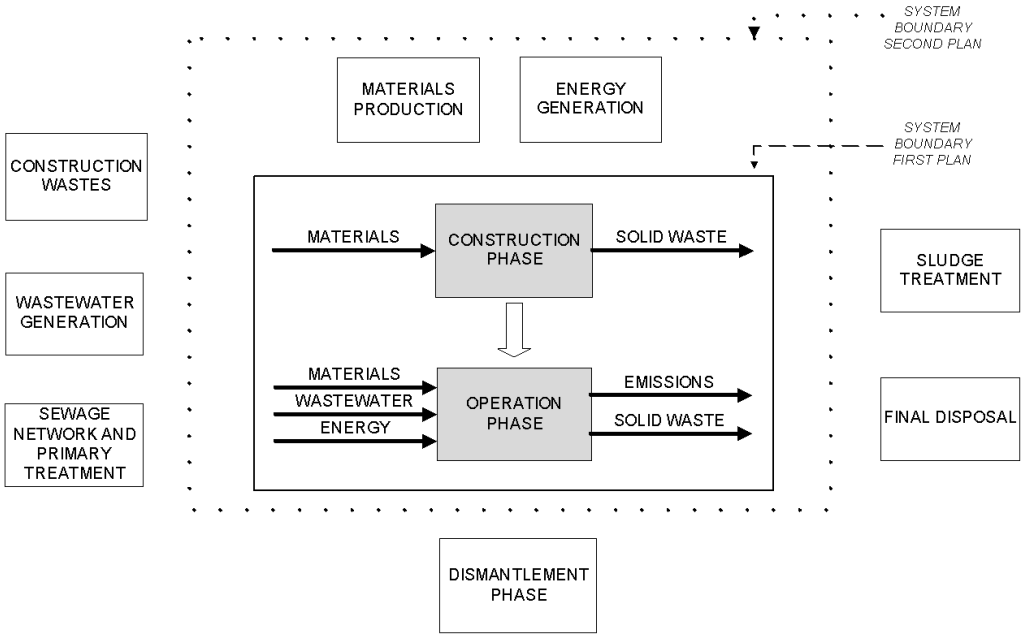

Figure 1. System boundaries of WWTP.

It is important to highlight that the process of materials production available in the Ecoinvent® database does not refer to the Brazilian reality. However, Eicker et al. (2010) evaluated the difference between the inventory of the Brazilian reality and the Ecoinvent® database, showing that it can be applied to the characterization of Brazilian processes without loss of quality of information.

The study has been carried out by including the following aspects: construction materials, energy use, chemical consumption, treated effluent discharge, gaseous emissions and the expected useful life of the WWTP equal to 20 years. The operational report of this WWTP informs that it is necessary to replace the support material (gravel) of each CWL unit every five years due to clogging. Therefore, three substitutions were considered during the life cycle of the WWTP and have been taken into account in the LCI of the operation phase. The LCA did not include the wastewater collection and transport system, land use, pre-treatment (e.g. pump station, grease and sand traps), sludge treatment and demolition or construction waste because of the lack of data.

The following aspects and criteria were considered to elaborate the LCA of the operation phase: the flow rate, the microbiological and physicochemical characteristics of the influent and effluent, the electricity and chemical consumption, atmospheric emission, equipment and process specifications. The characteristics of the influent and effluent were obtained by collecting samples and conducting laboratory analyses over a period of eight months (data not shown). The following parameters were used to characterize the wastewater: chemical oxygen demand (COD), total and volatile suspended solids (TSS and VSS), ammonia, total Kjeldahl nitrogen (TKN), nitrate, total phosphorus and residual chlorine.

The analysis of wastewater treatment goals suggests as a functional unit one cubic meter of treated wastewater. Foley et al. (2010) and Larsen (2018) agree that this is a good choice because it comes from real data. Considering the design flow rate (four cubic meter per hour) and the 20-year useful life of the WWTP, the total volume of wastewater treated in the WWTP was 700 800 m^3.

The data quality depends on the availability, source and accuracy, which should be reported to estimate the degree of the LCA uncertainty. Faced with the availability or lack of data and the study assumptions, it is important to continuously improve the information in order to ensure data quality. The inventory data (Table 1) of the construction phase were collected and calculated from the construction project and data obtained from websites of manufacturers and construction materials suppliers.

The input data for the operation phase were: loads of pollutants present in the domestic wastewater, NaOCl solution applied during the disinfection step, electricity used by the sodium hypochlorite solution pump and the gravel changed each 5 years of the CWL operation. The output data were: loads of pollutants present in the treated effluent, gaseous emissions (CH_4 from anaerobic digestion), biological sludge and the contaminated gravel that is removed from the CWL beds each five years. The quantity of the replaced gravel was calculated based on the WWTP operational reports and the operation technicians informed that there is no reuse of the contaminated gravel.

The air emissions and sludge from the UASB reactor were based on the mass balance of the fractions of COD proposed by Souza et al. (2012). Air emissions (CH_4 and N_2O) from the CWL were obtained by equations reported by the Intergovernmental Panel on Climate Change (IPCC, 2013).

Table 1. Life Cycle Inventory of construction and operation phase.

Inputs (materials)	Quantity at the end of 20 years		Correlated to functional unit	
Reinfor Reinforcing steel	38 573.5	kg	0.055	kg m^{-3}
Portland cement	54 462.7	kg	0.078	kg m^{-3}
Sand	174 143.2	kg	0.248	kg m^{-3}
Gravel, round gravel	1 036 444.8	kg	1.479	kg m^{-3}
Tap water	37 139.5	kg	0.053	kg m^{-3}
Pipes (PVC)	1 125.0	kg	0.002	kg m^{-3}
Sawnwood, Parana pine (BR)	17.70	m^3	0.001	m^3 m^{-3}
Brick	1 813.8	kg	0.003	kg m^{-3}
Glass fibre	912.9	kg	0.001	kg m^{-3}
Inputs (Pollutants in Domestic wastewater)	Quantity at the end of 20 years		Correlated to functional unit	
Chemical oxygen demand (COD)	538 102.3	kg	0.768	kg m^{-3}
Suspended solids	194 843.4	kg	0.278	kg m^{-3}
Unionized ammonia (NH_3)	26 665.4	kg	0.038	kg m^{-3}
Total Kjeldahl nitrogen	32 341.9	kg	0.046	kg m^{-3}
Total phosphorus	5 080.8	kg	0.007	kg m^{-3}
Inputs (materials)	Quantity at the end of 20 years		Correlated to functional unit	
Gravel, round gravel	648 042.8	kg	0.925	kg m^{-3}
Sodium hypochlorite solution	586 607.1	kg	0.837	kg m^{-3}
Input (electricity)	Quantity at the end of 20 years		Correlated to functional unit	
Electricity, low voltage (BR)	126 144.0	kw	0.180	kw m^{-3}
Emissions to air	Quantity at the end of 20 years		Correlated to functional unit	
Methane (CH_4)	137 545.1	kg	0.196	kg m^{-3}
Dinitrogen monoxide (N_2O)	401.5	kg	0.001	kg m^{-3}
Emissions to water (final treated effluent)	Quantity at the end of 20 years		Correlated to functional unit	
Biological oxygen demand (BOD)	14 962.1	kg	0.021	kg m^{-3}
Chemical oxygen demand (COD)	66 947.4	kg	0.096	kg m^{-3}
Suspended solids, unspecified	12 614.4	kg	0.018	kg m^{-3}
Unionized ammonia, (NH_3)	27 664.1	kg	0.039	kg m^{-3}
Total Kjeldahl nitrogen	32 061.6	kg	0.046	kg m^{-3}
Nitrate (NO_3^-)	1 226.4	kg	0.002	kg m^{-3}
Total phosphorus	5 536.3	kg	0.008	kg m^{-3}
Chlorine	546.6	kg	0.001	kg m^{-3}
Solid waste	Quantity at the end of 20 years		Correlated to functional unit	
Gravel, contaminated	648 042.8	kg	0.925	kg m^{-3}

3. RESULTS AND DISCUSSION

Analyzing the results of the Life Cycle Impact Assessment of the construction phase (Figure 2), it can be stated that the reinforcing steel and wood are the materials responsible for the most of environmental impacts in all categories chosen, followed by Portland cement and gravel. The potential impact of reinforcing steel is due to its production, mainly because of the addition of some metals like chromium, molybdenum and to a lesser extent, nickel.

Although the use of gravel had the highest correlation with the functional unit in the LCI of the construction phase, it did not show a significant environmental impact. On the other hand, the wood showed a low correlation with the functional unit, and the use of this material during construction of the WWTP results in significant environmental impacts. Therefore, these results indicate that there is no direct relation between the amount of material used and its environmental impacts. The stages of extraction or production of these materials will determine the intensity and relevance of the environmental impacts for each selected category.

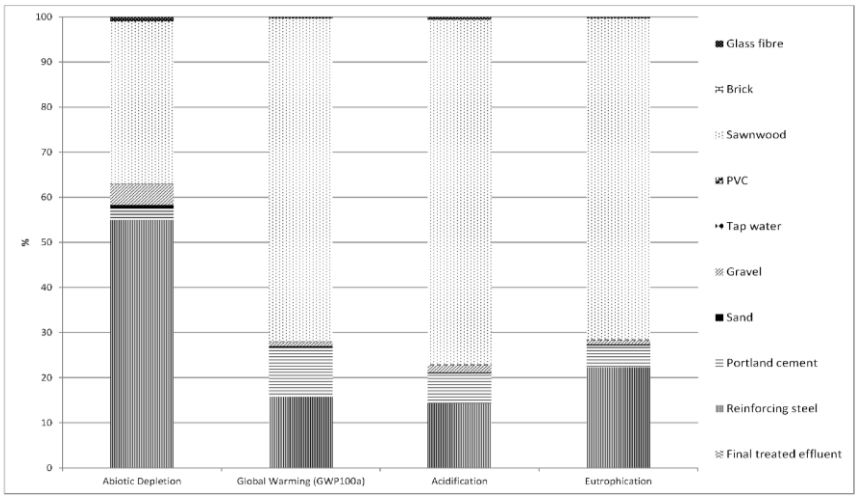

Figure 2. Assessment impact of the construction phase.

During the operation phase of the WWTP, the impacts were mainly caused by the use of the sodium hypochlorite solution in the disinfection step (Figure 3), considering the abiotic depletion and acidification categories. The methodology applied to construct the Ecoinvent® database accounts for high energy consumption in all steps of this chemical's production. Considering the global warming category, the greatest potential impact (80%) was due to methane emissions resulting from the anaerobic digestion in the UASB reactor. However, the benefits of methane generation during anaerobic digestion could be achieved with the energy recovery from the combustion of this gas.

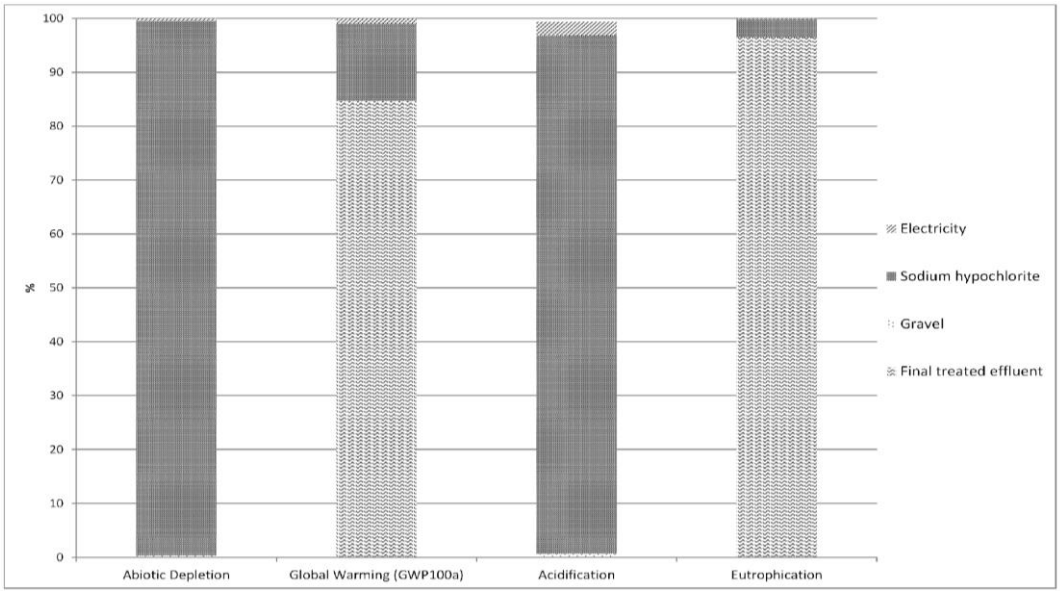

Figure 3. Assessment impact for operation phase.

Gaseous emissions (e.g. CH_4 and N_2O) have a significant impact on the global warming category. According to the IPCC (2013), CH_4 has a greenhouse effect 25 times greater than CO_2 and N_2O has 310 times more than CO_2, indicating that scientists and engineers should pay more attention to the role of greenhouse gases in the assessment of the impacts from WWTPs, especially those that apply anaerobic digestion in some of their processes. The use of the thermal energy of this gas has proven to be an excellent alternative to mitigate the environmental impacts resulting from the use of UASB reactors (Bressani-Ribeiro et al., 2017).

The wastewater treatment process was not effective in removing nitrogen and phosphorus and these pollutants present in treated effluent were responsible for the impacts (more than 90%) in the eutrophication category. Eutrophication needs to be considered as a key category in LCA studies of WWTP because the results define the trade-off between operating costs and effluent quality. It is well established that phosphorus is the limiting nutrient for occurrence of eutrophication in aquatic environments. Saeed and Sun (2017) carried out a broad review of the literature on the nutrient removal in horizontal subsurface flow constructed wetlands. These authors concluded that the removal of phosphorus were only possible with the insertion of P-adsorbing materials in the filter bed. The CWL filter beds are filled with gravel, which certainly does not allow high efficiencies of phosphorus removal during the treatment process.

The use of a sodium hypochlorite solution shows significant environmental impacts, mainly for abiotic depletion and acidification categories. Chemicals require a lot of resources and energy for their manufacture and our LCA study also considered the environmental impacts associated with the transportation logistics of these products to the WWTP site. We can conclude that the use of chemicals to remove microorganisms and improve the quality of treated effluent caused a decrease in the environmental performance of the WWTP. However, this final disinfection step is mandatory to meet the requirements of Brazilian environmental legislation, therefore, technicians and designers should investigate the effectiveness of environmentally less aggressive options for disinfection of treated effluent as sand filters or even membrane filtration, for example.

It was found from the analysis that the use of electricity for the operation phase has a lesser impact on the WWTP. These results are probably because the input data was based on the Brazilian energetic matrix, which is dominated by hydropower plants. Nevertheless, the electricity used to extract or produce construction materials such as gravel, sand and Portland cement and also sodium hypochlorite solution fabrication came from the Ecoinvent® database, which takes into account the European energy matrix based on fossil fuels. This is an important limitation of our study and should be taken into account by decision-makers. The reduction of the uncertainty of the results of the LCA study conducted in Brazil demands the construction of a Brazilian database. Although difficult and time-consuming, this task must be progressively accomplished.

Hence, a careful LCA study of the production of sodium hypochlorite solution with data obtained from Brazilian manufacturers is recommended. The production process reported in our study is more consistent with the European process, which may have overestimated the environmental impacts.

The comparative analysis between the two phases (Figure 4) confirms that the environmental impacts resulting from the WWTP operation are more significant than those of the construction for all the categories selected. Considering the acidification category, the construction phase has more than 40% of potential impact mainly because of the diesel fuel used in machines for the production of round wood according to the Ecoinvent® database.

Over the WWTP's life cycle the greatest environmental impacts contributing were as follows: the final effluent, operation and, to a lesser extent, the construction. The most relevant impact for the operation phase confirms those of other LCA studies on wastewater treatment (Lopsik, 2013; Paéz et al., 2017; Garfí et al., 2017; Sabeen et al., 2018). Some researchers have exempted the construction phase, arguing that this phase has little impact compared to the impact of the whole lifecycle WWTP (Hospido et al., 2007). The impact from the construction phase depends on the technology used in the wastewater treatment process (e.g. wetlands, UASB reactor and conventional activated sludge), so this is an assertion that needs to be assessed very carefully case by case.

Lopsik (2013) applied LCA in CWL showing that the greatest impact during the construction phase was due to the use of lightweight expanded clay aggregate as a support

material, indicating that the use of a new material can add a greater potential impact in an environmentally simple system. Studies analyzing activated sludge systems found a larger impact on the operation due to the high energy consumption (Gallego et al., 2008). Vlasopoulos et al. (2006) mentioned that the environmental impact of the construction phase may vary from 1 to 96% of the WWTP total impact. It will depend on the technology and the impact assessment method. The authors also emphasized that the comparison between different designs causes variations in the results for the categories of impact. In a general way, among a variety of technologies, anaerobic reactors and CWL have good environmental performance due to the low complexity and mechanization and low energy consumption (Sabeen et al., 2018).

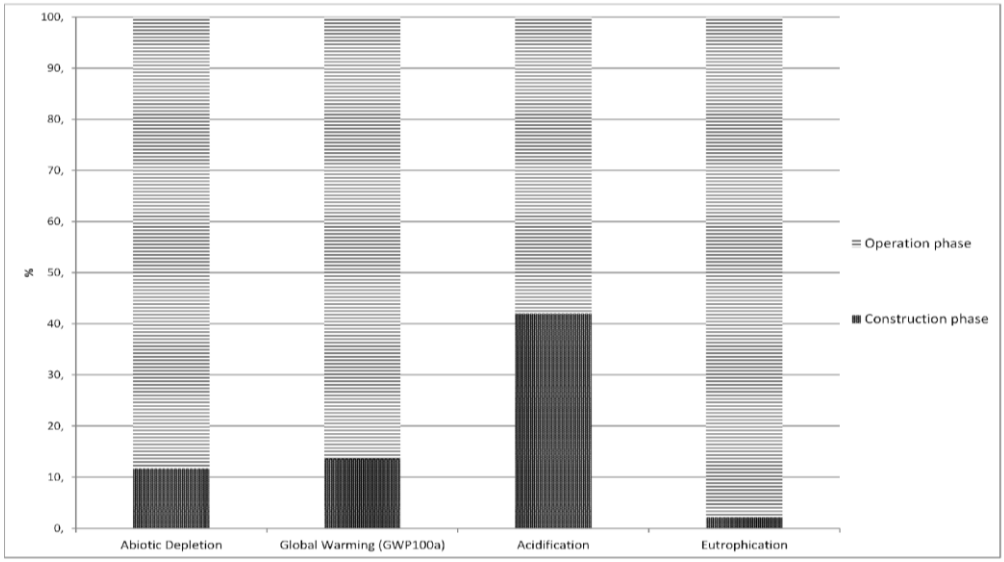

Figure 4. Construction versus operation phase.

Therefore, improving the quality of the final effluent results in a greater demand for natural resources, high energy consumption, chemical and operational complexity, in addition to the increased of the greenhouse gases emissions. It is very important to encourage rational use of water to reduce the generation of domestic wastewater, as well as to implement resource-oriented sanitation practices in order to minimize the environmental impacts of the WWTP.

4. CONCLUSION

LCA applied to a wastewater treatment plant (WWTP), a process comprised of anaerobic digestion in a UASB reactor followed by four constructed wetlands and a final effluent disinfection step, allowed concluding that:

- The use of reinforcing steel and wood during the construction of the WWTP was responsible for the most of environmental impacts in all LCA categories chosen. However, the results indicated that there is no direct relation between the amount of material used and its environmental impacts.
- Two aspects should be prioritized for the mitigation of environmental impacts during the operation of the WWTP: the reduction of methane gas emissions in the UASB reactor and the removal or recovery of the macronutrients present in the final effluent.
- The environmental impacts resulting from the WWTP operation are more significant than those of the construction for all the categories selected.
- The LCA proved to be a valid methodology for quantification of the environmental impacts associated with the domestic wastewater treatment in WWTPs.

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Previsão probabilística de enchentes para uma pequena bacia hidrográfica do Pantanal

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RESUMO

O monitoramento para a previsão de cheias de pequenas bacias hidrográficas é de grande importância tendo em vista a relação dos recursos hídricos com a sociedade, pois pode garantir o uso sustentável às comunidades urbanas de cidades lindeiras à bacia. O rio Aquidauana está inserido na planície Pantaneira sendo considerado vulnerável à inundações, no entanto, falta de um sistema eficiente para previsões de cheias e inundações. Assim, este estudo propõe um sistema de previsão probalística de enchentes para a bacia do Rio Aquidauana. Para tanto foram utilizadas as redes neurais artificiais (RNAs) do tipo *MultiLayer Perceptron* (treinamento *back-propagation)* com parâmetros otimizados pelos Algoritmos Genéticos. A RNA foi treinada e avaliada com base em dados de chuva acumulada (mm) e nível de rio (cm) à montante entre os anos de 1995 a 2014. A previsão realizada foi de 1 a 5 dias, tendo como melhor desempenho o modelo para 1 dia de previsão, com resultado de coeficiente de determinação e erro quadrático médio de 0,93 e 30 (cm), respectivamente.

Palavras-chave: monitoramento de cota, multilayer perceptron, predição, Rio Aquidauana.

Probabilistic flood forecast for a small Pantanal watershed

ABSTRACT

Monitoring for flood forecasting in small hydrographic basins is of great importance in view of the relationship of water resources with society, as it can guarantee the sustainable use of urban communities in cities bordering the basin. The Aquidauana River, classified as a small

basin, belongs to the Paraguay River basin and is an affluent of the Miranda River, forming part of the Pantanal plain, being inserted in the mapping of rivers vulnerable to flooding in the Central-West region of Brazil. This study deals with the monitoring of the river Aquidauana and uses artificial neural networks (RNAs) of the MultiLayer Perceptron type (training back-propagation) with parameters optimized by Genetic Algorithms. The RNA was trained and tested based on hydrological data between 1995 and 2014, accumulated rainfall (mm) and river level (cm) upstream. The forecast was 1 to 5 days, with the best performance of the model for 1 day of forecast, with a coefficient of determination and mean square error of 0.93 and 30 (cm), respectively.

Keywords: Aquidauana River, multilayer perceptron, prediction, quota monitoring.

1. INTRODUÇÃO

A variação de nível de rios é um processo hidrológico complexo devido à variabilidade espacial e temporal como, características de padrões de terreno, precipitação e outras variáveis associadas ao meio ambiente. Neste sentido, o uso da modelagem e a previsão precisa de eventos de alto e baixo fluxo do nível do rio auxiliam na provisão de informações necessárias para tomada de decisões estratégicas em bacias hidrográficas (Bravo et al., 2012).

Os hidrólogos vêm utilizando uma ferramenta de modelagem para gerar a cota do rio com a ajuda de dados históricos observados, fazendo projetos alternativos para comparação ou otimização, em vez de tomar decisões com base em dados observados de curto prazo. Assim, a questão da previsão de cotas por meio da precipitação tem sido uma área de pesquisa ativa ao longo da evolução da hidrologia. Diversos modelos de previsão de nível de rio, que vão de modelos empíricos a conceituais, têm sido desenvolvidos e aplicados.

Estudos recentes fizeram tentativas de mostrar que as RNAs não são puramente modelos de caixa preta, sendo assim possível esclarecer os processos hidrológicos inerentes a uma RNA, se suas características arquitetônicas forem exploradas. Jain e Prasad Indurthy (2013) investigaram a adequação de algumas técnicas determinísticas e probabilísticas, juntamente com a técnica da RNA para modelar um processo de contingente de chuva baseado em eventos observados. Os autores verificaram que os modelos de RNAs superaram as convencionais com algumas exceções e proporcionaram uma melhor representação de um processo de cota baseado em eventos.

O método de Algoritmos Genéticos (AG) pode ser usado para obter os melhores parâmetros de configuração da RNA. Neste método é utilizada uma técnica de busca e otimização inspirada no princípio de seleção natural e reprodução genética proposto por Charles Darwin, em que a seleção privilegia os indivíduos mais aptos com maior longevidade e, portanto, com maior probabilidade de reprodução. Logo, os melhores indivíduos terão mais descendentes e mais chance de perpetuarem seus códigos genéticos nas próximas gerações.

Normalmente aplicam-se algoritmos genéticos em problemas complexos de otimização: problemas com diversos parâmetros ou características que precisam ser combinadas em busca da melhor solução. Alguns autores utilizaram este processo para determinar o número de nós e camadas ocultas, a taxa de aprendizado, o *momentum* e para inicializar e otimizar os pesos de conexão de rede do BP (Yang e Honavar, 1998; Sexton et al., 1998). Heckerling et al. (2003) utilizou o AG-RNA híbrido em diversas aplicações, como na busca de arquiteturas ótimas de camada oculta, na conectividade e nos parâmetros de treinamento.

O objetivo deste estudo é desenvolver um sistema de previsão probalística de enchentes para a bacia do Rio Aquidauana, localizado na planície Pantaneira, Estado de Mato Grosso do Sul. O presente estudo categorizou um conjunto de variáveis de entrada para RNA (cota e precipitação) para previsão de cota da bacia do rio Aquidauana, sendo utilizados para tal:

Algoritmo Genético (AG) e o RNA *Multilayer Perceptron* (MLP)- Algoritmo *backpropagation* (BP). Neste trabalho, AGs foram empregados na busca dos melhores parâmetros das RNAs (taxa de aprendizado, *momentum*, função de ativação, número de camadas ocultas e número de nós).

2. APLICAÇÕES DE RNA EM RECURSOS HÍDRICOS

Na última década, os cientistas têm focado na aplicação de RNAs em campos diversos como modelagem, diagnóstico e controle de sistemas, medicina, reconhecimento de padrões e previsão de recursos hídricos. Diversos autores desenvolveram pesquisas relacionadas a recursos hídricos, como Suryanarayana et al. (2014) e Asati e Rathore (2012) que mostraram que os modelos de RLM são aplicáveis à previsão, no entanto, eles exigem uma suposição prévia sobre o tipo e a consistência da relação entre variáveis dependentes e independentes. No mundo real, as variações temporais nos dados nem sempre exibem e satisfazem regularidades simples a esta suposição. Assim, a complexidade e os problemas não-lineares tornam atrativos para tentar abordagens de RNA, na qual solucionam um ou mais problemas específicos, sendo que não pressupõem uma compreensão detalhada das características físicas de um rio e nem exigem um pré-processamento extensivo de dados.

Os conceitos de aplicação de RNA foram revisados, e a RNA mostrou ser uma ferramenta de modelagem alternativa para área de hidrologia. Apesar de vários esforços dedicados na comparação de modelos de previsão pesquisados, uma comparação conclusiva não pôde ser alcançada, pois diferentes dados de entrada foram usados para diferentes tipos de modelo, o que torna a comparação injusta.

3. ÁREA DE ESTUDOS

Neste estudo, foi selecionada a bacia do rio Aquidauana com área de 20.124 km^2. Esta bacia hidrográfica encontra-se ao sul da região Centro-Oeste do Brasil (Aquidauana) (Figura 1), fazendo parte da Bacia do Alto Paraguai (BAP) no Estado de Mato Grosso do Sul. O clima é tropical com precipitação média anual de 1537,7 mm, dos quais 80,7% da precipitação anual incidente ocorrem na estação úmida (de janeiro a abril). A característica da paisagem tem topografia plana com uma faixa de elevação de 134m-242m; o uso da terra é caracterizada por área natural (88,42%), pastagem cultivada (11,34%), área urbana (0,12%) e área agrícola (0,12%). Os principais tipos de solo segundo a classificação da EMBRAPA (2006) são: franco arenosa e franco-argiloarenosa. As principais culturas cultivadas na bacia do Aquidauana são: milho, mandioca e olerícolas. Na pecuária, conforme IBGE (2015), existem mais de 717 mil cabeças de gado bovino.

Foram usados dados pluviométricos e fluviométricos coletados a partir das estações da Agencia Nacional de Águas (ANA, 2016) entre 1995 e 2014 para teste e treinamento. A Figura 1 mostra a bacia do rio Aquidauana com três postos fluviométricos: 66945000 (Aquidauana) (~1995), 66941000 (Palmeiras) (~1965) e 66926000 (Ponte do Grego) (~1982); e quatro estações de chuvas: (01954002) Rochedo, (02055002) Palmeiras, (02055003) Fazenda Lajeado e (02054009) Santa Elisa. Nas estações fluviométricas descritas acima, as datas das instalações (mantidas em sua posição inicial) são mostradas de acordo com ANA. A estação de cota prevista é a Aquidauana (66945000), localizada dentro da cidade de Aquidauana.

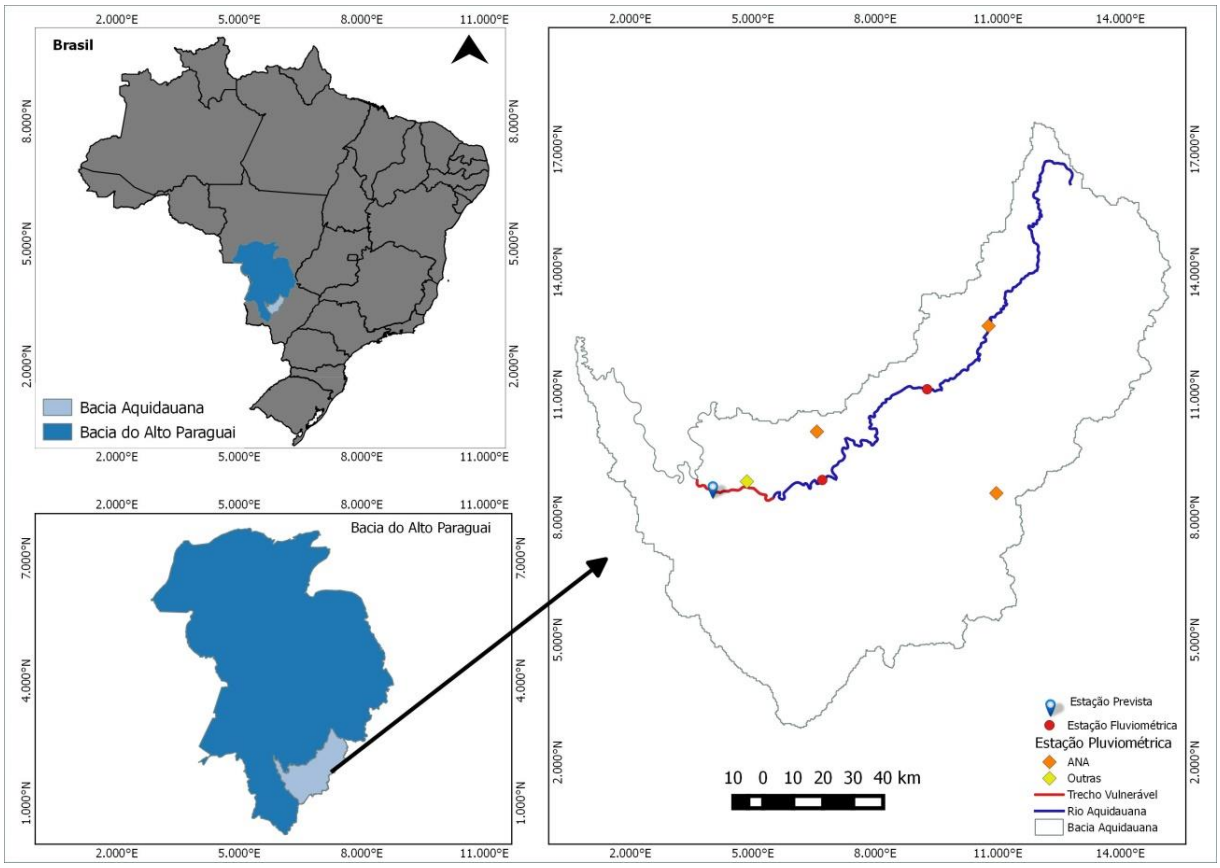

Figura 1. Mapa da bacia hidrográfica Aquidauana e das estações fluviométricas (vermelho) e pluviométricas (laranja/amarelo) do rio Aquidauana (azul). A estação de cota prevista está localizada dentro da cidade entre Aquidauana e Anastácio, local mais vulnerável à inundação.

4. MATERIAL E MÉTODOS

4.1. Pré-processamento dos dados

Para a análise dos postos pluviométricos e fluviométricos, verificou-se, primeiramente, as falhas de leitura de cotas e de precipitação em todo o período existente no banco de dados da ANA para serem usadas no treinamento e testes das RNAs. Depois de verificadas as falhas, foram extraídas do banco de dados a relação das cotas e as chuvas acumuladas diárias efetivamente medidas em ordem cronológica.

Posteriormente os dados disponíveis foram divididos em seus subconjuntos (isto é, de formação e de validação). Foi importante pré-processar os dados numa forma adequada antes de ser aplicada a RNA. O pré-processamento de dados é necessário para garantir a igualdade dos dados durante o processamento, acelerando assim o processo de aprendizagem da RNA. Existem três formas de pré-processar os dados: escalonamento de dados, normalização e transformação (Hall et al., 2009).

Assim, devido à função sigmoide utilizada na RNA, os dados hidrológicos foram normalizados no intervalo [0, 1], para evitar o problema da saturação de sinal de saída que pode, por vezes, ser encontrado em aplicações de RNA. Após o pré-processamento, a base de dados contava com 5.368 dados.

Para a avaliação inicial dos dados e de sua relação com o alagamento na bacia do rio Aquidauana, optou-se por trabalhar apenas a bacia que está dentro dos limites do município de Aquidauana.

4.2. Modelo AG-RNA

Na rede *Multilayer perceptron* (MLP) o algoritmo *backpropagation* (BP) remete a redução do erro entre a função calculada pela rede e o valor esperado, sendo o método do gradiente descendente (utilizado neste trabalho), pode ficar preso num mínimo local impossibilitando de encontrar o mínimo global.

Uma maneira de superar a restrição dos algoritmos de treinamento baseados no gradiente descendente é usar AG para executar o treinamento como uma evolução das conexões sinápticas. Assim, o AG pode ser empregado para uma busca por um conjunto ótimo de pesos globais sem calcular o gradiente descendente, evitando a estagnação precoce do processo de busca em um mínimo local.

A interpelação evolucionária de treino de uma RNA consiste nos seguintes passos:

1) Codificar cada indivíduo da geração atual, num conjunto de pesos sinápticos e construir a RNA correspondente com os pesos.

2) Avaliar cada RNA usando RMSE (*root mean square error*). A aptidão do indivíduo (cromossomo) é determinada pelo erro. Quanto maior o erro, menor sua aptidão.

3) Selecionar os pais para a recombinação de acordo com suas aptidões.

4) Aplicar operadores de recombinação e mutação gerando descendentes que formarão a próxima população.

A integração dos AGs com as RNAs (Figura 2) é vantajosa no sentido de agregar a capacidade de busca global dos AGs junto com o algoritmo de treinamento e ajuste de pesos BP.

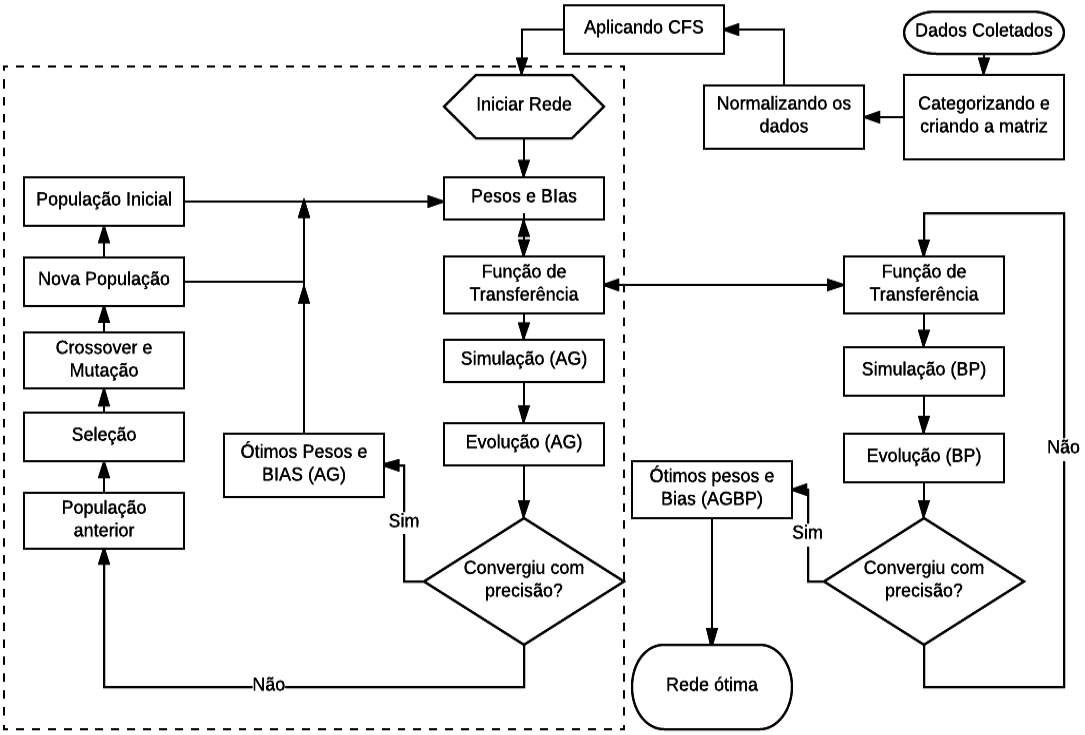

Figura 2. Fluxograma da interação do Algoritmo Genético e *backpropagation*.

O AG ajuda a resolver os mínimos locais realizando uma busca mais ampla no espaço de estados, pois ele é menos suscetível de ficar estagnado em um mínimo local, pois não depende do gradiente, em comparação com os algoritmos baseados no gradiente (Yao, 2014). Após o AG terminar seu processamento, utiliza-se o BP para uma busca local usando o conjunto de pesos pré-ajustados pelo AG. O primeiro passo do modelo híbrido consiste na formulação de

uma população de cromossomos, criados aleatoriamente (Figura 2). Nesse caso, cada gene representa um peso sináptico da RNA. Em seguida, cada cromossomo é avaliado por uma função de aptidão (função RMSE). É verificado na população, se algum candidato possui aptidão suficiente de acordo com um erro mínimo desejado. Caso não exista, o ciclo de execução do algoritmo genético é reiniciado.

Neste caso, serão escolhidos cromossomos candidatos que geram novos indivíduos, que por sua vez terão alguns genes alterados de acordo com um percentual de mutação. Em seguida esses descendentes são alocados na nova população. Esse processo repete-se até que o erro mínimo seja atingido ou um número máximo de iterações seja ultrapassado. Após a finalização do AG, o melhor cromossomo é retirado da população e uma RNA é alocada, com os pesos equivalentes aos genes desse indivíduo. Essa RNA é passada para o BP que executará um refinamento dos pesos encontrados. Desse modo pode-se entender a fase do AG, como uma etapa de atribuição inicial dos pesos da RNA.

Neste artigo foi feita a extração de regras de classificação a partir dos atributos codificados e da RNA treinada e, para isso, fez-se uso do algoritmo genético chamado SMAC (*Sequential Model-based Algorithm Configuration*). Os autores Hutter et al. (2011) comprovaram que o algoritmo mostrou um ótimo desempenho para explorar de forma automatizada os ajustes de parâmetros para vários problemas. O simulador utilizado neste trabalho é o pacote de *software* Weka (*Waikato Environment for Knowledge Analysis*), desenvolvido pela Universidade de Waikato da Nova Zelândia, na qual possui licença pública (General Public License), disponível em *World Wide Web* (www.cs.waikato.ac.nz/ml/weka).

4.3. Treinamento e avaliação do modelo

A variável *t* representa o tempo de previsão de 1 a 5 dias, sendo a janela de treinamento (1995-2013) e teste (2014), e o local previsto é dentro da cidade de Aquidauana para a estação 66945000 (Aquidauana). Os erros são analisados por 6 critérios de avaliação: R - coeficiente de correlação para dados de teste; MAE - Erro Absoluto Médio; RAE - Erro Relativo Absoluto; RMSE ─ Erro Quadrático Médio Relativo; MSRE – Erro Quadrático Relativo; NSE - Coeficiente de Eficiência Nash-Sutcliffe.

5. RESULTADOS E DISCUSSÕES

Na Tabela 1 são apresentadas as medidas de erro para os cinco modelos em que os pesos foram otimizados pelo Algoritmo Genético.

Tabela 1. Análise comparativa dos desempenhos.

t	R	RMSE (cm)	MAE (cm)	RAE (cm)	NSE
1	0,95	30	0,71	0,6328	0,93
2	0,89	45	0,66	0,4356	0,87
3	0,79	57	0,60	0,3796	0,76
4	0,69	65	0,57	0,339	0,67
5	0,56	69	0,63	0,301	0,54

R - coeficiente de correlação para dados de teste; MAE - Erro Absoluto Médio; RAE - Erro Relativo Absoluto; RMSE ─ Erro Quadrático Médio Relativo; MSRE – Erro Quadrático Relativo; NSE - Coeficiente de Eficiência Nash-Sutcliffe.

A Tabela 1 indica os parâmetros estatísticos analisados neste processo e observa-se melhores resultados no processo de teste em relação ao treinamento. Nota-se, que os índices de

erro associados às frequências seguiram a tendência de piora, em função do aumento do horizonte de previsão para os 5 dias, além de apresentar valores aceitáveis para uma previsão de nível, onde o erro variou de cerca de 30 cm para o horizonte de 1 dia e de 69 cm para o horizonte de 5 dias. Estes índices, erros associados à frequência, possibilitam um entendimento mais intuitivo e realista da incerteza do modelo de previsão, constituindo uma margem de garantia para uso do tomador de decisão em um sistema de alerta de inundações. Os dados de valores diários de NSE tendem a ser superiores aos dados de valores mensais, o que contradiz as descobertas de alguns estudos individuais (Van Liew et al., 2007). ??individuais??? se a referência é et al) Esta anomalia é potencialmente devido ao aumento de tamanhos de amostra para dados diários. Como esperado, nos NSE e R os valores da previsão foram melhores para os períodos de calibração do que os períodos de validação.

Para a bacia uma previsão ótima seria de 3 a 5 dias, pois um sistema de alerta precisa de tempo para ser acionado e tomada as providências em relação à inundação. Neste estudo, para esta bacia, os resultados são satisfatórios para a previsão de até 5 dias, observando os erros medidos pela RNA.

A Figura 3 mostra as estimativas do nível do rio fornecidas pelo modelo de predição da BP prevendo 1 a 5 dias (1D, 2D, 3D, 4D e 5D), sendo as nomenclaturas descritas no canto inferior esquerdo da Figura 3. Pode-se observar hidrogramas e gráficos de dispersão, com os valores previstos próximos dos observados, confirmando as estatísticas RMSE na Tabela 1.

Como mostra o resultado, o modelo MLP 1 apresentou as estimativas de cota (cm) mais preciso (r^2=0.95 e RMSE = 30 cm). Para a bacia hidrográfica este erro é aceitável, indicando uma boa precisão de previsão.

Nas análises verificou-se que a qualidade dos resultados depende diretamente dos dados utilizados na calibração (treinamento). Estes dados devem ser os mais abundantes possíveis e cobrir com uma densidade de frequência suficiente todo o domínio de aplicação desejada, de maneira a fornecer ao modelo a capacidade de reproduzir cenários já ocorridos. Para a bacia do Aquidauana o treinamento obtido a partir dos dados disponíveis para este trabalho indicou que o uso de redes neurais na previsão de nível é aconselhado, para o caso de estudo.

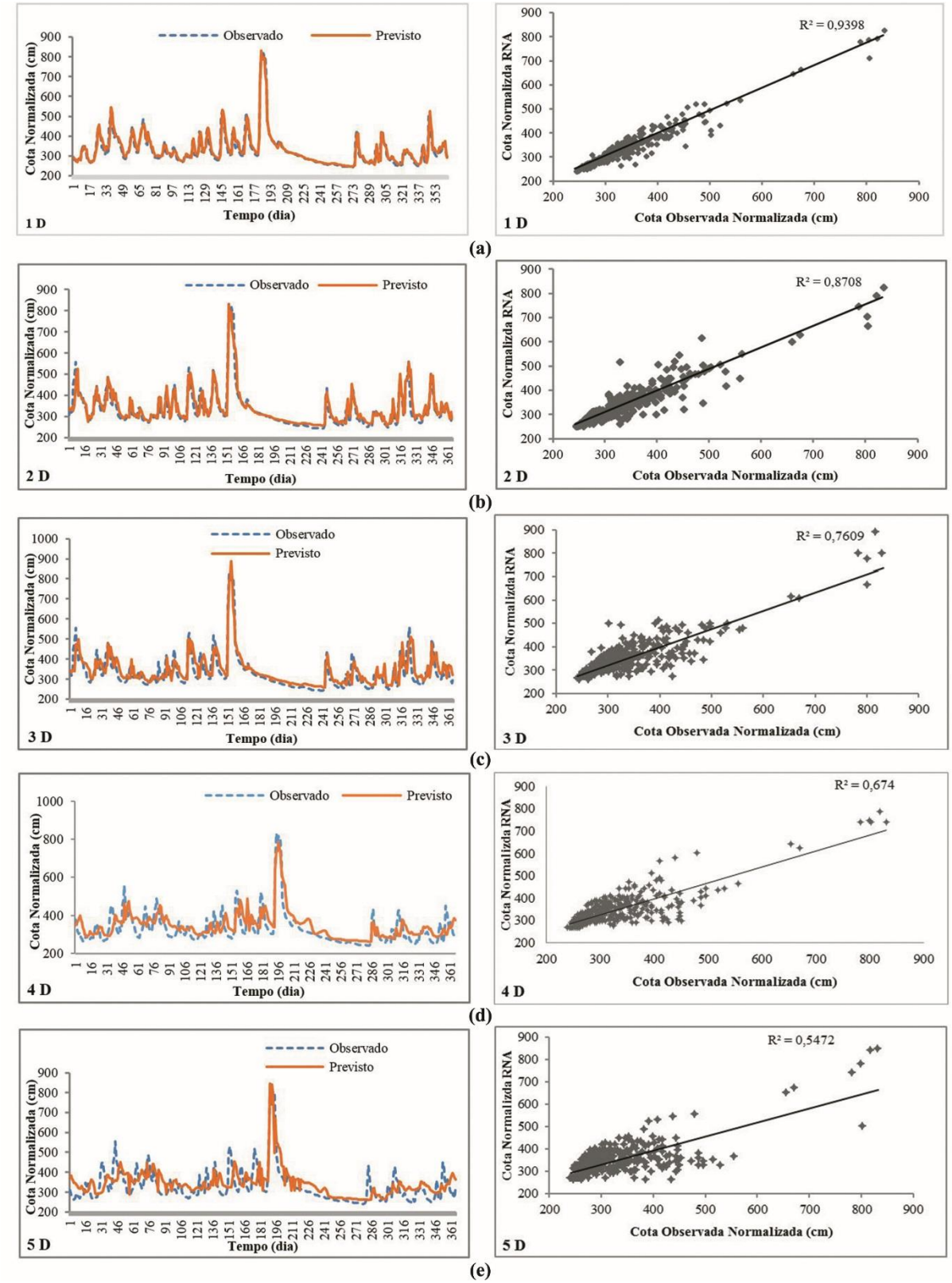

Figura 3. Evolução temporal do nível previsto para 2014 (laranja), observado (azul) e respectivos diagramas (r^2). Os dados correspondentes ao período de 1995 a 2014, obtidos das previsões 1 dia (a), 2 dias (b), 3 dias (c), 4 dias (d), 5 dias (e).

6. CONCLUSÕES

Uma vantagem no uso da modelagem chuva-cota está principalmente ligada à redução da dimensionalidade do fenômeno a duas variáveis. Nesse artigo, utilizou-se apenas a precipitação e a cota para treinamento da rede. Nessa circunstância a RNA acoplada a um AG, conseguiu realizar uma boa aproximação, sendo que no melhor modelo obteve um coeficiente de determinação R^2 0,95 em escala diária e RMSE de 30 cm na cota do rio, sendo um erro satisfatório, podendo ser utilizado como sistema de previsão de até 5 dias para essa bacia estudada

Os resultados alcançados são bons quando se analisa a baixa correlação entre as duas séries temporais chuva-cota, no caso de 0,54; quando se considera a área total da bacia hidrográfica utilizada como elemento de estudo de caso, e principalmente, por ser na prática, totalmente aceitável para um sistema de alerta de inundação.

O uso dos AG-RNA mostrou-se interessante porque permitiu um melhor desempenho da modelagem, entretanto, adiciona-se mais uma etapa de processamento para iniciar a matriz de pesos. Isso deve ser considerado principalmente quando o conjunto de dados para treinamento for muito grande, o que pode aumentar o tempo de processamento.

7. AGRADECIMENTOS

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